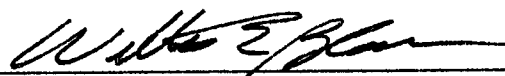


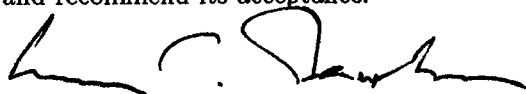
To the Graduate Council:

I am submitting herewith a dissertation written by Mark Weber entitled "Interpretation and Analysis of l -Resonance Effects upon Linear Molecules with Application to Acetylene in the $14\mu\text{m}$ Region." I have examined the final copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Physics.



William E. Blass, Major Professor

We have read this dissertation
and recommend its acceptance:



S. J. Daunt

Chia C Shih

William H. Fletcher

Accepted for the Council:



Associate Vice Chancellor
and Dean of The Graduate School

INTERPRETATION AND ANALYSIS OF ℓ -RESONANCE EFFECTS
UPON LINEAR MOLECULES
WITH APPLICATION TO ACETYLENE IN THE $14\mu\text{m}$ REGION

A Dissertation
Presented for the
Doctor of Philosophy
Degree
The University of Tennessee, Knoxville

Mark Weber
May 1992

Copyright © Mark Weber, 1991
All rights reserved

DEDICATION

This dissertation is dedicated to Helena, my parents Karl-Heinz and Christine Weber, my siblings Frank and Sabine, and all my friends on both side of the ocean who have given me invaluable support in various forms and expressions.

ACKNOWLEDGEMENTS

I would like to thank my major professor and adviser, Dr. William E. Blass, for his guidance through the course of my research. I would also like to express my gratitude to Drs. Harry C. Jacobson, Cia C. Shih, William H. Fletcher, Stephen J. Daunt, and John J. Hillman (Honorary) for serving me on my doctoral committee.

My special thanks go to Drs. William E. Blass, Stephen J. Daunt, Alvin H. Nielsen, and John J. Hillman for their assistance, valuable comments, and insight in my research area, and to Gerald McElyea and Paul Lewis for their technical assistance. I enjoyed the discussions held with John Franklin Brannon, Jr., and all people working in the Molecular Spectroscopy Laboratory at the University of Tennessee. The support of a Research Assistantship from the Department of Computational Engineering, University of Tennessee (Dr. Paul B. Crilly) during summer 1990 and 1991 and the sponsorship from the Universities Space Research Association (USRA) and NASA as a visiting scientist with Drs. John J. Hillman and William C. Maguire at the Laboratory of Extraterrestrial Physics, NASA-Goddard Space Flight Center, during summer 1991 is gratefully acknowledged by the author. Support through the Hilton A. Smith Graduate Fellowship, 1989-1991, from the University of Tennessee is gratefully acknowledged.

The acetylene FTS data whose analysis made up a major part of my research were provided by Drs. Donald E. Jennings and John J. Hillman, both from NASA-Goddard Space Flight Center, from their laboratory program at the National Solar Observatory, Kitt Peak. Dr. George W. Halsey, while a NAS/NRC Research Associate at NASA-Goddard Space Flight Center, carried out the initial reduction of the acetylene data and provided the assignment of transitions in the main and one-quantum hot bands. Dr. Sacher Nadler, NASA-GSFC, extended the assignment of the molecular bands of acetylene in the $14\mu\text{m}$ region up to the three-quantum level based upon a compilation of acetylene transitions by Dr. J. Hietanen available at the British Library, Lending Division (J. Hietanen, *Mol. Phys.*, **49**, 1029(1983)).

I would also like to express my thanks to Helena, Jackie, Hubert, Sabine, Tim, Hubertus, and Alfred who encouraged and enlightened me in difficult and good times for their friendship, love, and spiritual support.

ABSTRACT

31 absorption bands of acetylene in the $14\mu\text{m}$ bending region observed with a resolution of 0.0025cm^{-1} using FT-spectrometric (FTS) data obtained at the National Solar Observatory on Kitt Peak, Arizona, have been analyzed to obtain an improved set of molecular constants for the ν_4 and ν_5 bending modes of acetylene. The fundamental ν_5 and the seven hot bands $\nu_4 + \nu_5 \leftarrow \nu_4$ and $2\nu_5 \leftarrow \nu_5$ of the lesser isotope $^{13}\text{C}^{12}\text{CH}_2$ were observed in the natural sample up to two excited vibrational quanta. Measured transitions of the major isotope up to three excited vibrational quanta, i.e. $2\nu_4 + \nu_5$, $\nu_4 + 2\nu_5$, and $3\nu_5$, and $^{13}\text{C}^{12}\text{CH}_2$ have been fitted to an appropriate Hamiltonian of a linear molecule containing vibrational and rotational ℓ -resonances as off-diagonal matrix elements.

From the unitary transformation which diagonalizes the Hamiltonian, mixing coefficients of the perturbed levels have been used to calculate effective dipole transition moments. It is evident that ℓ -type doubling effects have a non-negligible contribution to the infrared intensities of linear molecules. Combining high-resolution Doppler limited tunable diode laser (TDL) measurements of intensities with those obtained from the FTS spectra, band intensities of the ν_5 fundamental of both isotopes and the seven strongest hotbands of the major isotope in the $14\mu\text{m}$ region have been derived. By calculating ℓ -resonance intensity factors, $W_{J,\Delta J}$, from the effective dipole transition moments, linear Herman-Wallis factors have been experimentally determined apart from the ℓ -type resonances for all seven hot bands. While band intensities retrieved from the two type of measurements (FTS and TDL) agree well, Herman-Wallis factors derived from the FTS data tend to be larger by a factor of 2-5. Possible explanations for these observed discrepancies are discussed. Nevertheless, for the first time ℓ -resonance effects on hotband intensities of the linear acetylene molecule have been quantitatively treated to obtain absolute band intensities for the strongest bands observed in the bending mode region of acetylene.

TABLE OF CONTENTS

Chapter	Page
1. OVERVIEW	
1.1 Introduction	1
1.2 Previous Work	2
1.3 Overview	4
2. THE HAMILTONIAN OF A LINEAR MOLECULE	
2.1 The Classical Hamiltonian	6
2.2 The Quantum Mechanical Hamiltonian	12
2.3 The Rovibronic Wavefunction of a Linear Molecule	15
2.4 Higher Order Hamiltonian	19
3. THE SYMMETRY OF ACETYLENE'S BENDING MODES ν_4 AND ν_5	
3.1 Introduction	33
3.2 Symmetry Groups of a Linear Molecule	33
3.3 Symmetry and Parity of the Rovibrational States	39
3.4 Nuclear Spin Statistical Weights	48
3.5 General Phase Convention for Rovibrational Eigenstates	49
3.6 Selection Rules for Electric Dipole Transitions	51
4. ROTATION-VIBRATION ANALYSIS OF ACETYLENE IN THE ν_5 REGION	
4.1 Introduction	54
4.2 Experimental Details	55
4.3 Non-Linear Least Squares Procedure	55
4.4 The Fundamental ν_5 , $\nu_4 + \nu_5 \leftarrow \nu_4$, and $2\nu_5 \leftarrow \nu_5$ of $^{12}\text{C}_2\text{H}_2$ and $^{13}\text{C}^{12}\text{CH}_2$	59
4.5 The Two Quantum Hotbands, $2\nu_4 \leftarrow 2\nu_4 + \nu_5$, $\nu_4 + \nu_5 \leftarrow \nu_4 + 2\nu_5$, and $3\nu_5 \leftarrow 2\nu_5$	69
4.6 Discussion	78

5. ABSOLUTE INFRARED INTENSITIES IN THE ν_5 REGION	
5.1 Introduction	91
5.2 Experimental Details: The TDL system	93
5.3 Terminology of Intensity Parameters	95
5.4 Methods of Intensity Retrieval (TDL Intensities)	98
5.5 Experimental Results: TDL intensities	106
5.6 Band Intensities, Electric Dipole Moment, and ℓ -Resonances	107
5.7 Data Reduction	116
5.8 Absolute FTS intensities: Part I. Intensity Retrieval	124
5.9 Absolute FTS Intensities: Part II. Experimental Results and Discussion	125
5.10 Conclusion	140
6. CONCLUSION	
6.1 Conclusion and Future Work	141
LIST OF REFERENCES	143
APPENDICES	152
A. BAND INTENSITY OF SYMMETRIC TOP MOLECULES	
A.1 Introduction	153
A.2 Transition Probability and Electric Dipole Moment Matrix Element	153
A.3 Temperature Dependence of Intensities	158
A.4 List of References	160
B. THE MOLECULAR SYMMETRY GROUP $EMS(D_{\infty h})$ AND $EMS(C_{\infty v})$	
B.1 Character Tables of the Extended Molecular Symmetry Group	161
B.2 Direct products of Symmetry Species	162
B.3 List of References	162
C. OBSERVED FREQUENCIES OF $^{12}\text{C}_2\text{H}_2$ AND $^{13}\text{C}^{12}\text{CH}_2$	163

D. LEAST SQUARES PROGRAM FOR FREQUENCY FIT	
D.1 Comments	187
D.2 References	187
D.3 Program	187
E. PERTURBED ENERGY SHIFT PLOTS OF $^{12}\text{C}_2\text{H}_2$	213
F. MIXING COEFFICIENT PLOTS FOR ACETYLENE	220
G. ℓ -RESONANCE INTENSITY FACTORS	236
H. ABSOLUTE FTS INTENSITIES OF ACETYLENE	243
VITA	254

LIST OF TABLES

Table	Page
2.1 Direction cosine matrix ($\lambda_{\alpha A}$)	8
2.2 Rotational and Vibrational ℓ -doubling matrix elements	21
2.3 Molecular parameters of a linear molecule	25
2.4 Hamiltonian of the linear acetylene molecule	26
3.1 Classification scheme of symmetry groups for rigid molecules.	38
3.2 Parity of ν_4 and ν_5 rovibrational states of acetylene	44
3.3 Nuclear statistical weights for transitions of $^{12}\text{C}_2\text{H}_2$	48
3.4 Sign of ℓ -doubling constants and parity	51
4.1 Observed transition of fundamental ν_5 and the seven strongest one quantum hotband of $^{12}\text{C}_2\text{H}_2$ and $^{13}\text{C}^{12}\text{CH}_2$	60
4.2 Reduced Hamiltonian of acetylene used in the least squares fit	61
4.3 Molecular parameter fit: groundstate, ν_5 , and $2\nu_5$ of $^{12}\text{C}_2\text{H}_2$	62
4.4 Molecular parameter fit: ν_4 and $\nu_4 + \nu_5$ of $^{12}\text{C}_2\text{H}_2$	63
4.5 Molecular parameter fit: groundstate, ν_5 , and $2\nu_5$ of $^{13}\text{C}^{12}\text{CH}_2$	64
4.6 Molecular parameter fit: ν_4 and $\nu_4 + \nu_5$ of $^{13}\text{C}^{12}\text{CH}_2$	65
4.7 Observed transition of two quantum hotbands of $^{12}\text{C}_2\text{H}_2$ in the $13.6\mu\text{m}$ region.	71
4.8 Effective Parameter fit: $2\nu_4$ and $2\nu_4 + \nu_5$ of $^{12}\text{C}_2\text{H}_2$	72
4.9 Effective Parameter fit: $\nu_4 + 2\nu_5$ of $^{12}\text{C}_2\text{H}_2$	73
4.10 Global parameter fit: groundstate, ν_5 , $2\nu_5$, and $3\nu_5$ of $^{12}\text{C}_2\text{H}_2$	77
4.11 Observed frequencies of the "forbidden" band $2\nu_4 + \nu_5^{3e} \leftarrow \nu_4^{0e}$	89
5.1 Selected individual line parameters from TDL intensity retrieval in the ν_5 fundamental of $^{12}\text{C}_2\text{H}_2$	107
5.2 Measured and calculated line intensities for $\nu_5^{1e,1f}$	108
5.3 Measured and calculated line intensities for $\nu_4 + \nu_5^{0e} \leftarrow \nu_4^{1f}$	109
5.4 Matrix elements for the two dimensional isotropic harmonic oscillator	112
5.5 Vibrational dipole matrix elements for acetylene.	113
5.6 TDL band intensities and dipole moment derivative	117
5.7 Vibrational partition sum, Q_v , of $^{12}\text{C}_2\text{H}_2$ for selected temperatures	123
5.8 FTS band intensities and square dipole moment	128
A.1 Physical constants	159

G.1 ℓ -resonance intensity factors, $W_{J,\Delta J}$: $\nu_4 + \nu_5^{0e} \leftarrow \nu_4^{1e,1f}$	237
G.2 ℓ -resonance intensity factors, $W_{J,\Delta J}$: $\nu_4 + \nu_5^{2e} \leftarrow \nu_4^{1e,1f}$	238
G.3 ℓ -resonance intensity factors, $W_{J,\Delta J}$: $\nu_4 + \nu_5^{0f} \leftarrow \nu_4^{1f,1e}$	239
G.3 ℓ -resonance intensity factors, $W_{J,\Delta J}$: $\nu_4 + \nu_5^{2f} \leftarrow \nu_4^{1f,1e}$	240
G.5 ℓ -resonance intensity factors, $W_{J,\Delta J}$: $2\nu_5^{0e} \leftarrow \nu_5^{1e,1f}$	241
G.6 ℓ -resonance intensity factors, $W_{J,\Delta J}$: $2\nu_5^{2e} \leftarrow \nu_5^{1e,1f}$	242
H.1 Absolute FTS intensities of ν_5^{1e}	244
H.2 Absolute FTS intensities of ν_5^{1e} of $^{13}\text{C}^{12}\text{CH}_2$	245
H.3 Absolute FTS intensities of $\nu_4 + \nu_5^{0e} \leftarrow \nu_4^{1e}$	246
H.4 Absolute FTS intensities of $\nu_4 + \nu_5^{2e} \leftarrow \nu_4^{1e}$	247
H.5 Absolute FTS intensities of $\nu_4 + \nu_5^{0f} \leftarrow \nu_4^{1f}$	248
H.6 Absolute FTS intensities of $\nu_4 + \nu_5^{2f} \leftarrow \nu_4^{1f}$	249
H.7 Absolute FTS intensities of $2\nu_5^{0e} \leftarrow \nu_5^{1e}$	250
H.8 Absolute FTS intensities of $2\nu_5^{2e} \leftarrow \nu_5^{1e}$	251
H.9 Absolute FTS intensities of $2\nu_5^{2f} \leftarrow \nu_5^{1f}$	252
H.10 Absolute FTS intensities of $\nu_4 + \nu_5^{0e} \leftarrow \nu_4^{1f}$	253

LIST OF FIGURES

Figure	Page
2.1 Definition of the Euler angles θ , ϕ , and χ	7
2.2 Molecule fixed axes of the isomorphic Hamiltonian	14
2.3 Schematic energy level diagram of acetylene.	32
3.1 Feasible $MS(D_{\infty h})$ group operations	35
3.2 Symmetry planes and axes of $D_{\infty h}$ point group operations	37
3.3 Transformation of the rovibrational coordinates θ , ϕ , and α_4 under MS group operations. ..	41
3.4 Transformation of the rovibrational coordinates θ , ϕ , and α_5 under MS group operations. ..	42
3.5 Rovibrational level diagram of acetylene, Part I	45
3.6 Rovibrational level diagram of acetylene, Part II	46
4.1 Section of the FTS-spectrum showing the Q -branch of the fundamental for both observed isotopomers	66
4.2 Section of the FTS-spectrum showing the acetylene Q -branch for the $\nu_4 + \nu_5^{0f} \leftarrow \nu_4^{1e}$ hotbands of both isotopes.	67
4.3 Part of the FTS-spectrum showing the acetylene Q -branch for the $2\nu_5^{0e} \leftarrow \nu_5^{1f}$ hotbands of both isotopes	68
4.4 Acetylene's Q -branches of $3\nu_5^{1e,1f} \leftarrow 2\nu_5^{2f,2e}$, $2\nu_4 + \nu_5^{1eII,1fII} \leftarrow 2\nu_4^{2f,2e}$, and $2\nu_4 + \nu_5^{1fII} \leftarrow 2\nu_4^{0e}$	74
4.5 Acetylene Q -branch of $\nu_4 + 2\nu_5^{1eII,1fII} \leftarrow \nu_4 + \nu_5^{2e,2f}$	75
4.6 Observed absorption bands of acetylene	80
4.7 Vibrational ℓ -doubling	81
4.8 Vibrational splitting of B_v	82
4.9 Perturbed energy shifts for $2\nu_4$	84
4.10 Perturbed energy shifts for $2\nu_5$	85
4.11 Perturbed energy shifts for $2\nu_4 + \nu_5$	86
4.12 Mixing of the $\Delta_g^{(e)}$ and Σ_g eigenfunctions of $2\nu_4$ and $2\nu_5$	87
4.13 Mixing of the three f states of the "unperturbed" $\nu_4 + 2\nu_5^{1fII}$ level	88
5.1 Experimental set up of the TDL spectrometer	94
5.2 Definition of equivalent width	97
5.3 Equivalent width contour plot	99
5.4 Graphical display of transmission background fit	102

5.5 Beer plot for selected ν_5 R -branch transitions for acetylene	104
5.6 Line profile fitting of ν_5 , $R(27)$ at 794.7338cm^{-1}	105
5.7 ℓ -resonance intensity perturbation factor, $W_{J,\Delta J}$: $\nu_4 + \nu_5 \leftarrow \nu_4$	114
5.8 ℓ -resonance intensity perturbation factor $W_{J,\Delta J}$: $2\nu_5 \leftarrow \nu_5$	115
5.9 Hermann-Wallis plot for ν_5^{1e} PR -transitions	118
5.10 Hermann-Wallis plot for ν_5^{1f} Q -transitions	119
5.11 Hermann-Wallis plot for $\nu_4 + \nu_5^{0e} \leftarrow \nu_5^{1f}$	120
5.12 Theoretical intensity profile of $\nu_4 + \nu_5^{0e} \leftarrow \nu_4^{1e,1f}$	121
5.13 Least squares fit of FT-spectral absorption line.	126
5.14 Hermann-Wallis plot for $^{12}\text{C}_2\text{H}_2$ ν_5^{1e} PR - transitions	130
5.15 Hermann-Wallis plot for $^{13}\text{C}^{12}\text{CH}_2$ ν_5^{1e} PR - transitions	131
5.16 Hermann-Wallis plot for $\nu_4 + \nu_5^{2e} \leftarrow \nu_4^{1e}$	132
5.17 Hermann-Wallis plot for $\nu_4 + \nu_5^{0e} \leftarrow \nu_4^{1e}$	133
5.18 Hermann-Wallis plot for $\nu_4 + \nu_5^{0f} \leftarrow \nu_4^{1f}$	134
5.19 Hermann-Wallis plot for $\nu_4 + \nu_5^{2f} \leftarrow \nu_4^{1f}$	135
5.20 Hermann-Wallis plot for $2\nu_5^{2f} \leftarrow \nu_5^{1f}$	136
5.21 Hermann-Wallis plot for $2\nu_5^{0e} \leftarrow \nu_5^{1e}$	137
5.22 Hermann-Wallis plot for $2\nu_5^{2e} \leftarrow \nu_5^{1e}$	138
5.23 Hermann-Wallis plot showing ℓ -resonance effects in $2\nu_5^{2e} \leftarrow \nu_5^{1e}$	139
E.1 Perturbed energy shifts for $2\nu_4$	214
E.2 Perturbed energy shifts for $\nu_4 + \nu_5$	215
E.3 Perturbed energy shifts for $2\nu_5$	216
E.4 Perturbed energy shifts for $2\nu_4 + \nu_5$	217
E.5 Perturbed energy shifts for $\nu_4 + 2\nu_5$	218
E.6 Perturbed energy shifts for $3\nu_5$	219
F.1 Mixing of the $\Delta_g^{(e)}$ and Σ_g eigenfunctions of $2\nu_4$ and $2\nu_5$	221
F.2 Mixing of the unperturbed eigenfunctions of $\nu_4 + \nu_5$	222
F.3 Mixing of the three e states of the "unperturbed" $2\nu_4 + \nu_5^{1eI}$ level	223
F.4 Mixing of the three e states of the "unperturbed" $2\nu_4 + \nu_5^{1eII}$ level	224
F.5 Mixing of the three e states of the "unperturbed" $2\nu_4 + \nu_5^{3e}$ level	225
F.6 Mixing of the three f states of the "unperturbed" $2\nu_4 + \nu_5^{1fI}$ level	226
F.7 Mixing of the three f states of the "unperturbed" $2\nu_4 + \nu_5^{1fII}$ level	227
F.8 Mixing of the three f states of the "unperturbed" $2\nu_4 + \nu_5^{3f}$ level	228
F.9 Mixing of the three e states of the "unperturbed" $\nu_4 + 2\nu_5^{1eI}$ level	229
F.10 Mixing of the three e states of the "unperturbed" $\nu_4 + 2\nu_5^{1eII}$ level	230

F.11 Mixing of the three e states of the "unperturbed" $\nu_4 + 2\nu_5^{3e}$ level	231
F.12 Mixing of the three f states of the "unperturbed" $\nu_4 + 2\nu_5^{1fI}$ level	232
F.13 Mixing of the three f states of the "unperturbed" $\nu_4 + 2\nu_5^{1fII}$ level	233
F.14 Mixing of the three f states of the "unperturbed" $\nu_4 + 2\nu_5^{3f}$ level	234
F.15 Mixing of the unperturbed eigenfunctions of $3\nu_5$	235

CHAPTER 1

OVERVIEW

1.1 Introduction

The linear acetylene is the simplest tetra-atomic molecule and its gas phase has been subject of numerous spectroscopic investigations over the last decades. Nevertheless, increasing resolution of astronomical observations of this molecule using for instance ultra-high resolution heterodyne observations (Kostiuk *et al.*, 1985) require refined frequency standards for acetylene's bending mode in the $14\mu\text{m}$ region. Acetylene has been detected in the atmospheres of the outer planets (Ridgway, 1974; Tokunaga *et al.*, 1976, 1979; Hanel *et al.*, 1982; Maguire *et al.*, 1984; Courtin *et al.*, 1984; Orton *et al.*, 1983; Romani and Atreya, 1988) and in circumstellar shells of red carbon stars such as IRC+10216 (Rinsland *et al.*, 1982; Kostiuk *et al.*, 1985). Since the ν_5 band is the most intense band among the five fundamentals of acetylene, it serves as a molecular probe for observations of various astronomical sources. Recently, acetylene has been discovered in interstellar molecular clouds (Lacy *et al.*, 1989) and was also observed in Earth's atmosphere (Goldman *et al.* 1981, Rinsland *et al.*, 1984). Acetylene does not possess a permanent dipole moment and, therefore, its pure rotational spectra are not observed. Best values for molecular parameters of this molecule can be only obtained through its rotation-vibration spectra as observed, for instance, in the mid-infrared bending region.

The relevance of acetylene's bending region to high-resolution astronomical observations warranted a reinvestigation of the ν_5 fundamental region using the highest available resolution and to extend the rotation-vibration analysis to higher rotational levels than in previous investigations. Using high resolution unapodized spectra obtained from the FT-spectrometer at the National Solar Observatory with a resolution of 0.0025cm^{-1} , vibrational bands in the ν_5 fundamental region have been analysed up to three excited quanta. From a complete rotation-vibration analysis using an effective Hamiltonian adapted from Amat *et al.*(1971) up to fourth order, taking into account rotational and vibrational ℓ -type resonances, an improved set of molecular constants for the bending region have been obtained for $^{12}\text{C}_2\text{H}_2$. Up to two excited vibrational quanta, the analysis included the $^{13}\text{C}^{12}\text{CH}_2$ isotope which was observed in the natural sample.

The ℓ -resonances responsible for the splitting of excited levels into parity doublets are expected to affect intensities as well. Intensity perturbation by ℓ -resonances in acetylene was qual-

itatively discussed by Moravec *et al.*(1990) and Herman *et al.*(1991), but no absolute intensity measurements which formally treat ℓ -type doubling have been reported. Infrared intensity measurements were conducted using the high resolution Doppler limited tunable diode laser spectrometer at the University of Tennessee combined with broad-band FT-spectrometric data. ℓ - resonances have been quantitatively treated for the first time in order to obtain band intensities for the fundamental and the seven strongest hotbands in the congested $14\mu\text{m}$ region. The intensity analysis was extended to the ν_5 fundamental of $^{13}\text{C}^{12}\text{CH}_2$ in order to obtain isotopic intensity ratios. This is important for the determination of astronomical isotopic $^{13}\text{C}/^{12}\text{C}$ ratio (Courtin *et al.*, 1983; Drossart *et al.*, 1985).

The aim of this project is to coherently study the influence of the vibrational and rotational ℓ -resonance observed in linear molecules on both the rovibrational energy level structure and infrared intensities for acetylene. From the results in this investigation, it is apparent that ℓ -type intensity resonances cannot be neglected for any linear polyatomic molecule.

1.2 Previous Work

The early spectroscopic studies of acetylene are referenced to in Christensen *et al.*(1956), Suzuki and Overend (1969), and Palmer *et al.*(1972). Medium resolution spectra of acetylene covering the region from $1.5\text{--}15\mu\text{m}$ were reported by Palmer *et al.*(1972) and Pliva (1972a). A comprehensive analysis of the bending mode region of acetylene to an appropriate Hamiltonian of a linear molecule is described by Pliva (1972b).

During the last two decades numerous measurements of acetylene extending from the far-infrared to the visible region have been accomplished. Far-infrared investigations of the difference band $\nu_5 \leftarrow \nu_4$ have been reported by Braund *et al.*(1973), Horneman *et al.*(1989), and Kabbadj *et al.*(1991). Combination bands in the electronic ground state involving the CH-stretch fundamentals and bending modes of ν_4 and ν_5 have been investigated in the near infrared (Baldacci *et al.*, 1973, 1977; Gershetti *et al.*1977; Ohsugi, *et al.*, 1988; Moriwaki, *et al.*1989; Herman *et al.*, 1989; Lafferty and Pine, 1990; D'Cunha *et al.*, 1991).

By means of photoacoustic intracavity spectroscopy overtone spectra have been investigated in the visible region (Sherer *et al.*, 1983; Zhan *et al.*, 1991). Conventional FT spectrometric data of acetylene in the visible reported by Smith and Winn (1988, 1991) and dispersed fluorescence spectroscopic data (Yamanouchi *et al.*, 1991) along with the other spectra observed in the visible and near infrared indicate significant Fermi and Dennison-Darling resonances between highly excited vibrational states (see also Takehisa *et al.*, 1988). Electronic spectra of acetylene reported by Watson *et al.*(1982) and Huet *et al.*(1990) involved transitions from the bending fundamental in the electronic

ground state.

Raman spectroscopy of acetylene are reported by Fast and Welsh (1972), Wang and Weber (1978), Kostyk and Welsh (1980), Finsterhölzl *et al.* (1981), and Edwards (1990).

The mid-infrared region between 500 and 800 cm^{-1} of various isotopic species of acetylene was covered by the research group at the University of Oulu, Finland, using a high-resolution FTIR (Huhanantti *et al.*, 1979; Antilla *et al.*, 1979; Hietanen *et al.*, 1979, 1981, 1986). Using a TDL spectrometer, Reddy *et al.* (1979) measured the Q -branch of $\nu_4 + \nu_5^{0e} \leftarrow \nu_4^{1f}$ for the major isotope and the singly substituted carbon-13 species. The fundamental ν_5 and $2\nu_5 - \nu_5$ were measured by Das *et al.* (1980) for all isotopic carbon species using the same spectrometer. More recently, Moravec *et al.* (1990), Hillman *et al.* (1991), and Kabbadj *et al.* (1991) reinvestigated the 14 μm region using high resolution FT-spectrometric data with a resolution better than 0.003 cm^{-1} .

Collision broadening of acetylene, using atmospheric molecules and air as perturber gas, are reported by Devi *et al.* (N_2 and air, 1985) for the $\nu_4 + \nu_5^0$ band, by Varanasi *et al.* (N_2 , 1983), Blass and Chin (H_2 , N_2 , 1987), Lambot *et al.* (N_2 , O_2 , 1989), Bouanich *et al.* (N_2 , O_2 , 1990) and Brannon (N_2 , H_2 , 1991) for the ν_5 fundamental. Temperature dependent self-broadening coefficients in the ν_5 fundamental were retrieved by Varanasi *et al.* (1983).

Only few studies on absolute intensities derived from individual line measurements have been reported. Varanasi *et al.* (1983) summarized band intensities for the ν_5 fundamental of $^{12}\text{C}_2\text{H}_2$ and $^{13}\text{C}^{12}\text{CH}_2$ and the seven associated hotbands $2\nu_5 \leftarrow \nu_5$ and $\nu_4 + \nu_5 \leftarrow \nu_4$ derived from medium resolution FTS-spectra. Weber *et al.* (1989) reported selected TDL intensities of the ν_5 fundamental and the $\nu_4 + \nu_5^{0f} \leftarrow \nu_4^{1e,1f}$ hotband. Other recent intensity measurements in the 14 μm region (Varanasi and Bangaru, 1974; Mast and King, 1976; Smit *et al.*, 1978; Kim and King, 1979; Koops *et al.*, 1984) yielded regional intensities (total intensities of a spectral region) using the Wilson-Wells-Penner-Weber method (Wilson and Wells, 1946; Penner and Weber, 1951) or Curve-of-Growth method (Kaplan and Eggers, 1956). Diode laser IR intensities are reported for the $\nu_4 + \nu_5^0$ band in the 7 μm region by Podolske *et al.* (1984) and intensities of combination bands are cited by Rinsland *et al.* (1982). The latter study applied the results to the interpretation of molecular spectra from the red carbon star IRC+10216. None of the intensity studies cited here treated the effect of vibrational and rotational ℓ -resonances on IR intensities. ℓ -type doubling of intensities for acetylene were theoretically discussed by Herman *et al.* (1991) based upon mixing of eigenstates. Moravec *et al.* (1990) qualitatively demonstrated the ℓ -resonance of intensities in form of Boltzmann plots for the $\nu_4 + \nu_5 \leftarrow \nu_4$ hotbands.

For completion of the review of acetylene, spectroscopic results with regard to the deuterated species of acetylene ranging from the microwave region to the visible and UV region can be found in Balddacci *et al.* (1976), Gherseti *et al.* (1977), Lafferty *et al.* (1977), Matsumara *et al.* (1980), Ohsugi

et al.(1988), Huet and Herman (1988), Wlodarczak *et al.*(1989), and Huet *et al.*(1991). The singly substituted deuterated species of acetylene can be observed in the microwave as opposed to the major isotope (Wlodarczak *et al.*, 1989; Matsumura *et al.*; 1980).

The theory of vibrational and rotational ℓ -resonance in the Hamiltonian of a linear molecule was first developed by Amat and Nielsen (1958a,b) and further refined by Maki and Lide (1967), Pliva (1972b), Winnewisser and Winnewisser (1972), Watson (1983), and Herman *et al.*(1991). An effective Hamiltonian more readily adapted to the spectroscopic parameters is given by Yamada *et al.*(1985). A direct analysis of the rovibrational bands to the appropriate Hamiltonian of a linear molecule was successfully demonstrated by Winnewisser and Winnewisser (1972) for HCN and by Pliva (1972b) for acetylene, for instance. In this study the twice contact transformed Hamiltonian up to fourth order of approximation as described by Amat *et al.*(1971) was adopted for the rotation-vibration analysis of acetylene's $14\mu\text{m}$ bands.

1.3 Overview

In Chapter 2 the development of the twice contact transformed Hamiltonian as described by Amat *et al.*(1971) up to fourth order of approximation is presented. Matrix elements of vibrational states up to the three quantum level of $2\nu_4 + \nu_5$, $\nu_4 + 2\nu_5$, and $3\nu_5$ including off-diagonal elements due to vibrational and rotational ℓ -resonance are summarized as needed for the energy level analysis. By reviewing the steps from the classical Hamiltonian in body-fixed coordinates to its quantum mechanical equivalent, the reader is also prepared for the symmetry consideration of the bending modes ν_4 and ν_5 in Chapter 3. The constraints given by the Eckart conditions (Eckart, 1935) specifies the molecule-fixed axis system, also called the Eckart axes. The parity of the rovibrational wave function determined from symmetry operations specifically depends on the transformation property of the rovibrational coordinates relative to the Eckart axis system (Bunker, 1979).

Using the permutation-inversion group (Longuet-Higgins, 1963; Papoušek and Aliev, 1982) and the extended molecular symmetry group (Bunker and Papoušek, 1969), the parity of the rotational, vibrational, and rovibrational symmetry species of the molecular eigenfunctions are derived. Depending on the parity of the total wavefunction, here the product of the rovibrational and nuclear spin eigen states, under nuclear permutations as required by either the Fermi or Bose statistics of identical particles, only certain combination of symmetry species of the rovibrational and nuclear spin eigenfunctions are, therefore, allowed, which lead to the observed intensity alternation of transitions within a vibrational band. In Chapter 3, general phase choices for the rovibrational eigenstates of linear molecules are discussed. Depending on the phase choices adopted, the ℓ -doubling constant, q_ℓ , changes its sign. For instance, Watson *et al.*(1982) and Herman *et al.*(1991) report positive sign,

while Plíva (1972a,b) and Hietanen *et al.* (1981,1983,1986) adopted a negative sign for the ℓ -doubling constant. One might argue that a discussion on the symmetry of the molecular levels (Chapter 3) is redundant. However, revisiting the group theoretical concepts of molecular symmetry in the special case of acetylene's bending modes illustrates the arbitrariness of assigning general phase choices which are not well related to the actual symmetry species of the vibrational and rovibrational levels from which selection rules and nuclear statistical weights are determined.

Using FT-spectrometric data obtained from the National Solar Observatory in Tucson, Arizona, at 0.0025cm^{-1} resolution, rotation-vibration bands up to three excited quanta, $2\nu_4 + \nu_5$, $\nu_4 + 2\nu_5$ and $3\nu_5$ in the $14\mu\text{m}$ region have been analyzed to retrieve improved molecular constants for the major isotope in the bending modes of acetylene. In the natural acetylene sample, the ν_5 fundamental and associated hotbands, $2\nu_5 \leftarrow \nu_5$ and $\nu_4 + \nu_5 \leftarrow \nu_4$, of the lesser isotope $^{13}\text{C}^{12}\text{CH}_2$ have been observed and analyzed. The iterative least squares fit utilizes the numerical diagonalization of the Hamiltonian and the Hellman-Feynman theorem to calculate the Jacobian matrix. The rotation-vibration analysis of acetylene's bending mode is an extension to the lower state combination difference analysis reported by Hillman *et al.* (1991). The goodness of fits for the retrieved molecular constants in this study is comparable to the nominal resolution of the spectral data.

The unitary transformation which diagonalizes the Hamiltonian also contains the mixing coefficients of the perturbed eigenfunctions causing the ℓ -resonance effects on the IR intensities. Concluding Chapter 4, energy perturbation and mixing of eigen functions in preparation for the intensity analysis are discussed. As results from mixing of states due to ℓ -type doubling, the forbidden band $2\nu_4 + \nu_5^{3e} \leftarrow \nu_4^{0e}$ has been identified.

Combining FTS-data and high resolution Doppler limited TDL intensity measurements, band intensities have been determined for the fundamental of $^{12}\text{C}_2\text{H}_2$ and $^{13}\text{C}^{12}\text{CH}_2$, and the seven hotbands, $2\nu_5 \leftarrow \nu_5$ and $\nu_4 + \nu_5 \leftarrow \nu_4$ of the major isotope. By introducing ℓ -resonance intensity factors calculated in the transformed basis set of perturbed eigen functions, the Herman-Wallis effect can be separately determined apart from ℓ -type doubling. It is shown that the reported intensities are primarily caused by the non-vanishing dipole moment derivative with respect to the antisymmetric ν_5 bend. This is expected, when the net change in vibrational quanta for the observed transition occurs in the ν_5 quantum number. Correcting for the natural abundances of the isotopic species, the intensity of the $^{13}\text{C}^{12}\text{CH}_2$ ν_5 fundamental is only slightly lower, but still within the experimental uncertainties, than the fundamental of the major isotope. Discrepancies exist between Herman-Wallis factor retrieved from the FTS data and TDL measurements. Possible explanations for the observed discrepancies are discussed.

CHAPTER 2

THE HAMILTONIAN OF A LINEAR MOLECULE

2.1 The Classical Hamiltonian

A molecule can be considered a collection of nuclei and electrons, which are held together by certain forces and undergo several types of motion. In the zeroth order Hamiltonian the following types of motion are represented:

- a.) translation of the molecule as a whole.
- b.) rotation of the nuclear framework.
- c.) internal vibrations of the nuclei.
- d.) motions of the electrons within the nuclear framework.

In absence of external fields acting on the molecule and neglecting all interactions involving the electronic and nuclear spins and the various electric and magnetic momenta associated with the molecule, the molecular Hamiltonian H in laboratory-fixed axes is given by

$$2H = \sum_i \frac{\vec{P}_i^2}{M_i} + \sum_j \frac{\vec{P}_j^2}{m} + 2V \quad (2.1)$$

where $\vec{P}_i$ and $\vec{P}_j$ are the canonical momenta conjugate with the vector position $\vec{R}_i$ and $\vec{R}_j$ of the i -th nucleus and j -th electron; M_i is the mass of the i -th nucleus and m that of the electron. The quantum mechanical Hamiltonian may be derived from the classical Hamiltonian, i.e. Eq. (2.1), transformed to the molecule fixed coordinate frame (Nielsen, 1959; Howard and Moss, 1970).

Since the translational kinetic energy can be separated off completely, the origin of the space fixed axes can be first moved to the center of mass of the molecule. After transforming the classical Hamiltonian to the molecule fixed axes, the Hamiltonian can be further split into a rotational, a vibrational and a rotation-vibration interaction term, the latter depending on both rotational and vibronic coordinates. This produces a remarkable simplification, yet the separation of the rotational and vibrational coordinates is not fully achieved (Bunker, 1979; Howard and Moss, 1970).

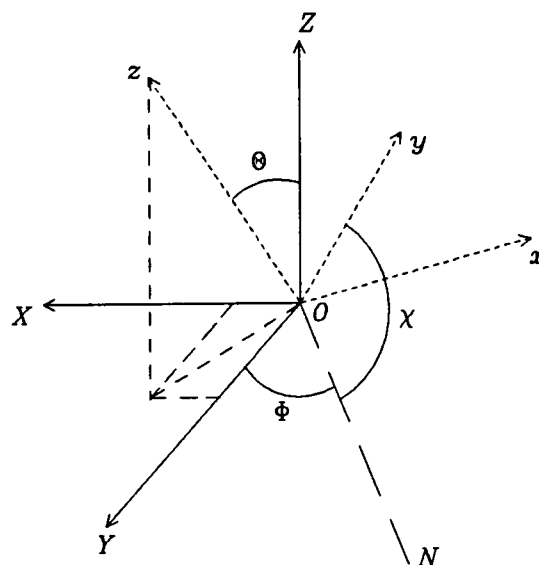


Figure 2.1. Definition of the Euler angles θ , ϕ , and χ : ($\pi \geq \theta \geq 0$, $2\pi \geq \phi \geq 0$, $2\pi \geq \chi \geq 0$).

The orientation of the space fixed axes XYZ with the origin at the center of mass to the molecule fixed axes can be defined by the three Euler angles θ, ϕ , and χ as shown in Fig. 2.1. The Euler angles are the new dynamic variables of the rotating molecule with respect to the space fixed XYZ axes. The xyz coordinates are obtained from the XYZ coordinates by successive rotations about the space fixed axes in the following way

$$(\lambda_{\alpha A}) = \mathbf{R}_Z(\chi)\mathbf{R}_Y(\theta)\mathbf{R}_Z(\phi) \quad (2.2)$$

(Brink and Satchler, 1962). $\mathbf{R}$ represents a three dimensional rotation matrix, where the subscript denotes the rotation axis and the argument indicates the rotation angle. The matrix elements $\lambda_{\alpha A}$ given in Eq. (2.2) are called the direction cosines, and are summarized in Table 2.1 (Wilson *et al.*, 1963; Nielsen, 1959). Since $(\lambda_{\alpha A})$ is an orthogonal matrix, Table 2.1 can be read down and across the columns and rows respectively.

Before summarizing the classical kinetic energy of a rotating-vibrating molecule with respect to the molecular axes, some remarks should be made concerning the Eckart conditions with regard to the distinction of linear molecules from the class of nonlinear molecules (Eckart, 1935). By transforming the classical Hamiltonian to the molecule fixed axes, certain physically reasonable

Table 2.1. Direction cosine matrix ($\lambda_{\alpha A}$): ($\alpha = x, y, z$; $A = X, Y, Z$).

$\lambda_{\alpha A}$	X	Y	Z
x	$\cos\phi\cos\theta\cos\chi - \sin\phi\sin\chi$	$\sin\phi\cos\theta\cos\chi - \cos\phi\sin\chi$	$-\sin\theta\cos\phi$
y	$-\cos\phi\cos\theta\sin\chi - \sin\phi\cos\chi$	$-\sin\phi\cos\theta\sin\chi + \cos\phi\cos\chi$	$\sin\theta\sin\phi$
z	$\sin\theta\cos\phi$	$\sin\theta\sin\phi$	$\cos\theta$

conditions are imposed on the nuclear coordinates in order to simplify the model. Two important conditions known as the Eckart conditions can be written as (Papoušek and Aliev, 1982)

$$\sum_i M_i \delta \vec{r}_i = 0 \quad (2.3)$$

and

$$\sum_i M_i \left(\vec{r}_i^{(e)} \times \delta \vec{r}_i \right) = 0 \quad (2.4)$$

or in derivative form as

$$\sum_i M_i \dot{\delta \vec{r}_i} = 0 \quad (2.5)$$

and

$$\sum_i M_i \left(\vec{r}_i^{(e)} \times \dot{\delta \vec{r}_i} \right) = 0 \quad (2.6)$$

The nuclear coordinates here are written as $\vec{r}_i = \vec{r}_i^{(e)} + \delta \vec{r}_i$ where $\delta \vec{r}_i$ is the cartesian displacement of the i -th nucleus from the equilibrium or reference configuration at $\vec{r}_i^{(e)}$.

By requiring $\sum_i M_i \vec{r}_i^{(e)} = 0$ the translational motion is separated from rotation-vibration. At this point the Hamiltonian is simplified when the molecular center of mass is identified with the center of mass of the nuclei neglecting the electron masses (Nielsen, 1959; Papoušek and Aliev, 1982). The first Eckart condition, Eqs. (2.3) and (2.5), incorporates a constraint in H , that the center of mass of the vibrational displacements be coincident with the origin of the molecule fixed axes. The second condition (2.6) guarantees that the internal angular momentum of the nuclei with respect to

the moving axis system xyz is minimized (Bunker, 1979). In another respect, the rotational Eckart conditions introduce the necessary constraints to define the three Euler angles θ , ϕ , and χ (Bunker, 1979, Papoušek and Aliev, 1982).

If the z -axis is chosen to coincide with the molecular axis of the linear molecule, the $x_i^{(e)}$ and $y_i^{(e)}$ components of the nuclei in their reference configuration are zero which reduces the two Eckart conditions from three scalar equations each to two. Thus only two Euler angles can be determined uniquely, by convention the two angles θ and ϕ corresponding to the two degrees of freedom to specify the direction of the z -axis of a linear molecule. At this point the third Euler angle χ enters as an arbitrary choice to define the orientation of the molecule fixed x and y axes.

Following the above prescription, by introducing the constraints given by the Eckart conditions and transforming the Hamiltonian from the space-fixed to the body-fixed coordinates, the classical kinetic energy of a rotating-vibrating molecule with N nuclei and n electrons can be summarized as follows (Nielsen, 1959; Papoušek and Aliev, 1982)

$$2T = \sum_{\alpha, \beta} I'_{\alpha\beta} \omega_\alpha \omega_\beta + \sum_{k=1}^{3N-6} \left(\dot{Q}_k + \sum_{\alpha, \ell} \omega_\alpha \zeta_{k, \ell}^{(\alpha)} Q_\ell \right)^2 + m \sum_{j=1}^n \sum_{\alpha} (\dot{\alpha}_j + \omega_\beta \gamma_j - \omega_\gamma \beta_j)^2 \quad (2.7)$$

with:

$\alpha, \beta, \gamma = x, y, z$ in cyclic order.

Q_k : normal coordinates, related to the cartesian displacement coordinates $\delta \vec{r}_i$ by $\sqrt{M_i} \delta \alpha_i = \sum_k \ell_{ik}^{(\alpha)} Q_k$, where $\ell_{ik}^{(\alpha)}$ is an element of the orthogonal ℓ -transformation matrix (Nielsen, 1959).

$I'_{\alpha\beta}$: matrix element of the effective inertia tensor, which depends partly on the normal coordinates as follows:

$$I'_{\alpha\beta} = I_{\alpha\beta} - \sum_{k, \ell, m} \zeta_{km}^{(\alpha)} \zeta_{\ell m}^{(\beta)} Q_k Q_\ell \quad (2.8)$$

$I_{\alpha\alpha}$ is the moment of inertia and $I_{\alpha\beta}$ is the product of inertia, i.e.

$$I_{\alpha\alpha} = \sum_i^N M_i (\beta_i^2 + \gamma_i^2), \quad (2.9)$$

and

$$I_{\alpha\beta} = - \sum_i^N M_i \alpha_i \beta_i. \quad (2.10)$$

- $\zeta_{k\ell}^{(\alpha)}$: Coriolis interaction parameter, related to the ℓ -matrix by $\zeta_{k\ell}^{(\alpha)} = \sum_i \left(\ell_{ik}^{(\beta)} \ell_{i\ell}^{(\gamma)} - \ell_{ik}^{(\gamma)} \ell_{i\ell}^{(\beta)} \right)$.
- α_i : component of the position vector $\vec{r}_i$ of the i -th nucleus with respect to the molecule-fixed axes.
- α_j : component of the position vector $\vec{r}_j$ of the j -th electron with respect to the molecule-fixed axes.
- $\vec{\omega}$ = $(\omega_x, \omega_y, \omega_z)$ the angular velocity of the xyz axis system with respect to the space-fixed XYZ coordinate system.

The kinetic energy expression Eq.(2.7) is arranged such that the effective inertia tensor $I'_{\alpha\beta}$ does not depend on the electronic coordinates. The translational motion of the center of mass is of no spectroscopic interest and, therefore, was omitted in the kinetic energy. For the transformation from the classical to the quantum mechanical Hamiltonian it is advantageous to express the kinetic energy in terms of momenta instead of velocities. By calculating $p_k = \partial T / \partial \dot{Q}_k$, the linear vibrational momentum of the k -th normal mode, $p_{\alpha_j} = \partial T / \partial \dot{\alpha}_j$, the linear electronic momentum component of the j -th electron, and $J_\alpha = \partial T / \partial \omega_\alpha$, the total rotational angular momentum, the conjugate momenta of the molecular coordinates can be introduced using the Lagrangian formalism. With the following definitions

$$p_\alpha = \sum_{k,\ell} \zeta_{k,\ell}^{(\alpha)} Q_k p_\ell, \quad (2.11)$$

called the vibrational angular momentum, and

$$\Pi_\alpha = m \sum_j \left(\dot{\beta}_j \gamma_j - \dot{\gamma}_j \beta_j \right), \quad (2.12)$$

representing the electronic angular momentum, the rotational angular momentum of the nuclear

frame, $\vec{\Omega}$, can be written as

$$\vec{\Omega} = \begin{pmatrix} J_x - p_x - \Pi_x \\ J_y - p_y - \Pi_y \\ J_z - p_z - \Pi_z \end{pmatrix} = \begin{pmatrix} I'_{xx} & I'_{xy} & I'_{xz} \\ I'_{yx} & I'_{yy} & I'_{yz} \\ I'_{zx} & I'_{zy} & I'_{zz} \end{pmatrix} \begin{pmatrix} \omega_x \\ \omega_y \\ \omega_z \end{pmatrix}. \quad (2.13)$$

To eliminate the angular velocity ω , one usually proceeds by inverting Eq. (2.13). It can be shown that in the case of linear molecules, the effective inertia tensor is singular and diagonal (Papoušek and Aliev, 1982; Moss and Howard, 1971). It can be written as

$$(I'_{\alpha\beta}) = \begin{pmatrix} I' & 0 & 0 \\ 0 & I' & 0 \\ 0 & 0 & 0 \end{pmatrix}, \quad (2.14)$$

where

$$I' = (I^o + \frac{1}{2} \sum_k a_k Q_k)^2 / I^o \quad (2.15)$$

(Watson 1970; Papoušek and Aliev 1982). From sum rules involving $\zeta_{kt}^{(\alpha)}$ and $\ell_{ik}^{(\alpha)}$, it can be shown that

$$a_k = 2 \sum_i m_i^{1/2} z_i^{(e)} \ell_{ik}^{(z)}. \quad (2.16)$$

(Watson 1970). I^o is the moment of inertia of the molecule in its equilibrium position about the x and y axes, i.e. $I^o = \sum_i m_i (z_i^{(e)})^2$.

Because of the singularity of the effective inertia matrix of a linear molecule, i.e. Eq. (2.14), the Hamiltonian must be treated differently for linear and nonlinear molecules at this point. Inserting Eq. (2.14) into Eq. (2.13), the z -component of the angular momenta, J_z is given by

$$J_z = p_z + \Pi_z; \quad (2.17)$$

Omitting the electronic angular momenta Π_α , Eq. (2.15) is known as the Sayvetz condition (Sayvetz, 1939). Inverting Eq. (2.13) to eliminate the angular velocity, the classical kinetic energy of a rotating and vibrating linear molecule is obtained as follows

$$2T = \sum_{k=1}^{3N-5} p_k^2 + \sum_{\alpha\beta} \mu_{\alpha\beta} [(J_\alpha - p_\alpha - \Pi_\alpha)(J_\beta - p_\beta - \Pi_\alpha)] + \frac{1}{m} \sum_j \sum_\alpha p_{\alpha j}^2, \quad (2.18)$$

where $\mu_{\alpha\beta} = (I')^{-1}(\delta_{\alpha\beta} - \delta_{\alpha z}\delta_{\beta z})$ and $\delta_{\alpha\beta}$ is the Kronecker symbol. The kinetic energy is now expressed in a form translatable into its quantum mechanical equivalent. The summation over the normal modes is limited to $3N - 5$ in the case of a linear molecule due to the lack of one degree of freedom. Equation (2.18) is the same for a non-linear molecule by inserting the appropriate inverse moment of inertia tensor $\mu_{\alpha\beta}$ for non-linear molecules (Watson 1968) and by summing over $3N - 6$.

By considering Eq. (2.18), two types of vibration-rotation coupling are evident: a) the centrifugal coupling, through the dependence of $\mu_{\alpha\beta}$ on the normal coordinates and b) Coriolis coupling through terms containing products of J_α and p_α . Eckart originally proposed a principal inertia axis system to minimize the centrifugal coupling (Eckart, 1934). If the vibrational amplitudes are small, this type of coupling is small, but due to the smallness of Q_k , the conjugate momenta p_k must be large from the uncertainty principle (see Eq. (2.11), Van Vleck, 1935, Aliev and Watson, 1985) and, therefore, the Coriolis coupling can become quite large. The preference of using the second Eckart condition to minimize the vibrational angular momentum in form of Eq. (2.4) over the constraints that the inverse moment of inertia is diagonal is evident. In the special case of a linear molecule, the moment of inertia matrix and its inverse are automatically diagonal by symmetry.

It should be noted that Estes (1982) and Estes and Secrest (1986) recently introduced a unified treatment of the vibration-rotation Hamiltonian. By introducing general internal coordinates, a non-singular effective inertia matrix for the linear molecule can be constructed.

2.2 The Quantum Mechanical Hamiltonian

The quantum mechanical hamiltonian of a polyatomic molecule was first derived by Wilson and Howard (1936) and in modified form by Darling and Dennison (1940). Nielsen (1951), for instance, showed that Darling-Dennison Hamiltonian is equivalent to the earlier derived Wilson-Howard Hamiltonian. The transformation of the classical Hamiltonian expressed in terms of conjugate momenta into a quantum mechanical operator form was, for instance, demonstrated by Podolsky (1928) using the method of tensor analysis. Watson (1968, 1970) later significantly simplified the Hamiltonian of non-linear and linear polyatomic molecules. Howard, Moss, and Perry (Howard and Moss, 1970a, 1970b; Moss and Perry, 1972) derived a complete Hamiltonian of a rotating, vibrating molecule in presence of a constant electromagnetic field not considered here.

As mentioned the third Euler angle χ is not a dynamic variable and causes complication in transforming the classical Hamiltonian into quantum mechanical form. Watson developed a rigorous treatment of the quantum mechanical Hamiltonian of a linear molecule, in which he chose the third Euler angle as an arbitrary function of the two other Euler angles (Watson, 1970). The correct

quantum mechanical Hamiltonian H of a linear molecule becomes

$$2H = \mu \left[\left(J_x - p_x + \frac{1}{2}i\hbar\zeta_x \right) \left(J_x - p_x - \frac{1}{2}i\hbar\zeta_x \right) + \left(J_y - p_y + \frac{1}{2}i\hbar\zeta_y \right) \left(J_y - p_y - \frac{1}{2}i\hbar\zeta_y \right) \right] + \sum_k p_k^2 + 2V, \quad (2.19)$$

where ζ_x and ζ_y are functions of the three Euler angles (Watson, 1970; Papoušek and Aliev, 1982). Electronic terms are neglected in Eq. (2.19), which is allowable if pure rotation-vibration transitions in the electronic ground state are considered.

By a similarity transformation Watson (1970) further simplified the Hamiltonian yielding an isomorphic Hamiltonian

$$2H_{\text{iso}} = \mu \left[(J'_x - p_x)^2 + (J'_y - p_y)^2 \right] + \sum_k p_k^2 + 2V \quad (2.20)$$

(Watson, 1970). The unitary transformation is described by $U = \exp(ip_z(\chi' - \chi)/\hbar)$, which corresponds to an effective rotation about the independent variable χ' instead of χ . In other words if the arbitrary angle χ describes the molecular fixed axis system xyz of the true Hamiltonian, the alternate Euler angle χ' describes the orientation of the rotated molecule-fixed axis system $x'y'z'$ of the isomorphic Hamiltonian (Fig 2.2, Watson 1970))

The isomorphic Hamiltonian has one more degree of freedom and more eigenvalues and wavefunctions than the true Hamiltonian (Hougen 1962a). While the angular momentum operators J_x , J_y and J_z in Eq. (2.19) follow complicated commutator relations, the J'_α components given in the expression of the isomorphic Hamiltonian are identical to the J_α components for nonlinear molecules with the usual commutator relationships for angular momenta (Watson, 1970; Howard and Moss, 1970b). By imposing the Sayvetz condition, i.e. Eq. (2.15), the isomorphic Hamiltonian is limited to the true eigenvalues of Eq. (2.19).

Introducing the isomorphic Hamiltonian, identical commutator relationships involving the various momenta and direction cosines exist for both linear and non-linear molecules and, the isomorphic Hamiltonian can be treated in much the same way as the Hamiltonian of a nonlinear molecule. Furthermore, quantities such as the dipole moment of a linear molecule, which determines the probability of a transition between two molecular energy states, can be calculated in a way similar to that for nonlinear molecules. The direction cosines remain the same as given in Table 2.1. One has merely to keep in mind that the interpretation of the third Euler angle χ differs in the case of linear and nonlinear molecules.

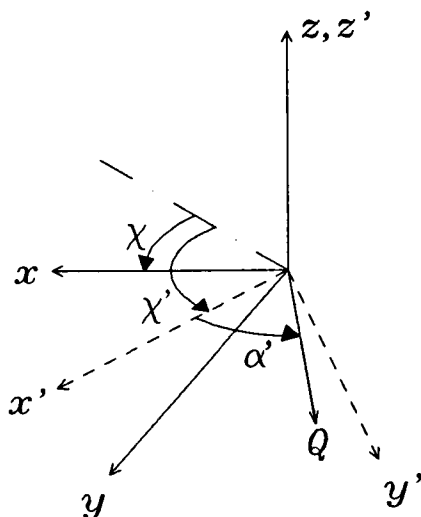


Figure 2.2. Molecule fixed axes of the isomorphic Hamiltonian. The xyz axes with arbitrary Euler angle χ is used in the correct Hamiltonian (Eq. 2.19) and the $x'y'z'$ in the isomorphic Hamiltonian (Hougen 1962b, Watson 1970). The bending vibration described by the amplitude Q has a vibrational angle $\alpha_2 = (\chi' - \chi) + \alpha'$ in the normal Hamiltonian and α' in the isomorphic hamiltonain.

In making the Born–Oppenheimer approximation (Bunker, 1979) the Hamiltonian can be separated into a rotational and vibrational part. The motions of the electrons are considered to be unaffected by the motions of the nuclei and, on the periodic time scale of their motions, only depend on the nuclear positions parametrically. Therefore, the Hamiltonian can be separated into two sets of differential equations, one for the electronic states in a specific configuration of the nuclei and the other for the rotation–vibration states in a certain electronic state. The latter equation may then be further approximated to yield the rigid–rotor, harmonic–oscillator Hamiltonian of a rotating, vibrating molecule, which is given by

$$H_{vr}^o = H_r^o + H_v^o = \frac{1}{2I^o} (J^2 - J_z'^2) + \frac{1}{2} \sum_k^{3N-5} (p_k^2 + \lambda_k Q_k^2) \quad (2.21)$$

(Allen and Cross, 1963), where $J^2 = \sum_{\alpha} J_{\alpha}'^2$ is the square of the total angular momentum. If the nuclei do not depart too far from their reference configuration, the potential V can be developed in a Taylor series in the normal coordinates, where all the higher anharmonicity terms are omitted in the last term of Eq. (2.21), and the dependence of the effective inertia tensor on the normal coordinates

as well as the vibrational angular momenta p_α (no degenerate normal modes are assumed) are neglected resulting in a complete separation of rotation and vibration in the zeroth order Hamiltonian, Eq. (2.21).

The rigid-rotor, harmonic-oscillator model for the molecular Hamiltonian is of course too limited an approximation in order to analyze rotation-vibration transitions. Anharmonic potential terms, Coriolis interaction, centrifugal distortion, and possible resonances between excited states have to be taken in account in order to correctly interpret high-resolution spectra. In a basic approach, higher order terms of the Hamiltonian can be treated by perturbation theory or by applying variational methods.

In either case, the zero order wavefunction serves as a basis set. In the variational approach the matrix representation of the rovibronic Hamiltonian is formed usually in the basis set of the rigid-rotor, harmonic-oscillator wavefunctions. Rovibronic energy levels are then, for instance, obtained by a numerical diagonalization procedure, where the new set of wavefunctions is formed by linear combinations of the former (Amat *et al.*, 1971; Aliev and Watson, 1985; Papoušek and Aliev, 1982). For later symmetry consideration of molecular eigenstates the parities can still be derived from the rigid-rotor, harmonic-oscillator wavefunctions, which are a product of an electronic wavefunction, $\Psi_e^0(\vec{r}_j)$, depending parametrically on the nuclear coordinates, a rotational part $\Psi_r^0(\theta, \phi, \chi)$ and a vibrational harmonic oscillator wavefunction $\Psi_v^0(Q_1, \dots, Q_{3N-5})$:

$$\Psi_{evr}^0 = \Psi_e^0 \Psi_v^0 \Psi_r^0. \quad (2.22)$$

Ψ_{evr}^0 is usually called the rovibronic wave function and the energy of the rotating, vibrating molecule is given by the sum of the electronic, vibrational, and rotational energy (listed here in order of their magnitude).

2.3 The Rovibronic Wavefunction of a Linear Molecule

The solution of the zeroth order Hamiltonian (2.21) given as the product of the rotational, vibrational, and electronic wavefunctions will be briefly reviewed.

a) the vibrational wavefunction Ψ_v^0 :

The last term in Eq. (2.21) represents the sum of $3N-5$ one dimensional harmonic oscillators with well-known solutions. (Nielsen, 1959; Bunker, 1979). If two modes have the same λ_k , i.e. $\lambda_r = \lambda_s$, the two modes are said to be doubly degenerate sharing the same fundamental frequency. The two harmonic oscillators with normal coordinates Q_r and Q_s can be combined to yield a two-

dimensional isotropic harmonic oscillator, where by coordinate change the solution depends on the new polar coordinates, the amplitude Q and the vibrational angle α' . The new coordinates are related to the former by

$$Q^2 = Q_r^2 + Q_s^2 \quad (2.23)$$

and

$$\alpha' = \tan^{-1}(Q_r/Q_s). \quad (2.24)$$

If the vibrational coordinates Q_k and α'_k belong to the k -th doubly degenerate normal mode, the solution of the two-dimensional isotropic harmonic oscillator takes the following form

$$\Psi_{v_k \ell_k} = F_{v_k \ell_k}(Q_k) \exp(i \ell_k \alpha'_k), \quad (2.25)$$

where $|\ell_k|$ can take only the integral values $v_k, v_k - 2, \dots, 1$ or 0 (Bunker, 1979; Nielsen, 1959). The total vibrational wavefunction of a linear molecule then consists of the product of all non-degenerate and twofold degenerate harmonic oscillator wavefunctions, which can be written as

$$\Psi_v^o = \prod_{n=1}^{N-1} \Phi_{v_n}(Q_n) \prod_{t=1}^{N-2} F_{v_t \ell_t}(Q_t) \exp(i \ell_t \alpha'_t), \quad (2.26)$$

where Φ_{v_n} is related to the Hermite polynomial of the n -th non-degenerate mode. The isomorphic Hamiltonian commutes with the vibrational angular momentum component p_z defined by Eq. (2.11) and thus

$$p_z \Psi_v^o = \ell \hbar \Psi_v^o \quad (2.27)$$

with ℓ as the vibrational projection quantum number defined as

$$\ell = \sum_t \ell_t, \quad (2.28)$$

where the sum goes over all degenerate modes.

The zeroth order vibrational energy is then given by

$$E_v^o = \hbar \sum_s^{2N-3} \sqrt{\lambda_s} (v_s + d_s/2), \quad (2.29)$$

where d_s is one or two for non-degenerate and degenerate modes, respectively and $\lambda_s = (2\pi c\omega_s)^2$. For a N -atomic linear molecule, there are $N - 2$ doubly degenerate normal modes giving rise to the perpendicular vibrational bands and $N - 1$ non-degenerate normal modes resulting in the parallel bands usually observed in infrared absorption spectra. The absorption bands associated with the bending modes are in general lower in their frequency than the parallel bands.

b) the electronic wavefunction Ψ_e^o :

The zeroth order electronic wavefunction is constructed from the product of Molecular Orbital wavefunction (Bunker, 1979) and is of the form

$$\Psi_e^o = \Phi_{\text{elec}}(\vec{r}_j) \exp(i\Lambda\chi). \quad (2.30)$$

Since the isomorphic Hamiltonian commutes with the z component of the electronic angular momentum one obtains

$$\Pi_z \Psi_e^o = \Lambda \hbar \Psi_e^o. \quad (2.31)$$

c) the rotational wavefunction Ψ_r^o :

The rotational angular momentum components J'_x , J'_y , and J'_z of the isomorphic Hamiltonian (2.20) are identical to the corresponding angular momenta of the nonlinear molecule. The components of the angular momenta with respect to the xyz coordinates can be obtained from those in space fixed coordinates by the transformation given by the direction cosine matrix as follows

$$J_\alpha = \sum_A \lambda_{\alpha A} J_A. \quad (2.32)$$

The space fixed and molecule fixed angular momenta follow usual angular momenta algebra with following commutator relations

$$[J_A, J_B] = i\hbar \epsilon_{ABC} J_C \quad (2.33)$$

and

$$[J_\alpha, J_\beta] = -i\hbar\epsilon_{\alpha\beta\gamma}J_\gamma. \quad (2.34)$$

ϵ_{ABC} and $\epsilon_{\alpha\beta\gamma}$ are the unit antisymmetric tensors. It should be noted that the sign is reversed in the second commutator relationship. The square of the angular momentum J^2 is independent of the choosen coordinate system as expected from the orthogonality of the direction cosine matrix. Since the two sets of angular momenta are defined by different set of coordinates another important commutator exists

$$[J_\alpha, J_A] = 0. \quad (2.35)$$

The fact that the operators J_α , J_A , J^2 and the Hamiltonian commute with each other, a set of basis functions $\Phi_r^o = |J, K, M\rangle$, which are simultaneous eigenfunction of the commuting operators, can be found with the properties

$$J^2|J, K, M\rangle = \hbar^2 J(J+1)|J, K, M\rangle, \quad (2.36)$$

$$J_Z|J, K, M\rangle = \hbar M|J, K, M\rangle, \quad (2.37)$$

and

$$J_z|J, K, M\rangle = \hbar K|J, K, M\rangle. \quad (2.38)$$

K and M are the projection quantum number on the molecule fixed z axis and space fixed Z axis, respectively. The symmetric-top wavefunction $|J, K, M\rangle$ can be written as

$$|J, K, M\rangle = \sqrt{1/(2\pi)} S_{JKM}(\theta, \phi) \exp(iK\chi) \quad (2.39)$$

where $S_{JKM}(\theta, \phi)$ is related to the spherical harmonics by $S_{J0M}(\theta, \phi) = Y_{JM}(\theta, \phi)$ (Allen and Cross, 1963; Bunker, 1979). To obtain the correct rotational wavefunction of the linear molecule the Sayvetz condition (2.15) has to be imposed, which is, from Eqs. (2.28), (2.31), and (2.38), given by

$$K = \Lambda + \sum_i \ell_i. \quad (2.40)$$

Only in that case the correct Hamiltonian (2.19) and the isomorphic Hamiltonian (2.20) of the linear molecule share the same eigenvalues (Watson, 1970). In the electronic ground state ($\Lambda = 0$) the rotational wavefunction of the linear molecule finally becomes

$$\Psi_r^o = |J, \ell, M\rangle = S_{J\ell M}(\theta, \phi) \exp(i\ell\chi). \quad (2.41)$$

For future reference, a shorthand notation for the rovibrational wavefunction for the linear acetylene molecule will be used, i.e.

$$\Psi_{vr}^o = |v_4^{\ell_4}, v_5^{\ell_5}; J, \ell\rangle, \quad (2.42)$$

where the non-degenerate vibrational quantum numbers are omitted, Since only excited bending vibrations are considered, and the spatial projection quantum number plays no role due to lack of field quantization except in intensity calculation the multiplicity of $2J + 1$ has to be taken into account.

2.4 Higher Order Hamiltonian

Assuming that the vibrational amplitudes are of small magnitude, which is the case for strongly bound molecules with an unique equilibrium configuration, the potential V and the inverse moment of inertia, $\mu_{\alpha\beta}$ can be expanded in terms of the normal coordinates. The first expansion leads to anharmonicity terms depending on the electronic structure and due to the finite potential in the dissociation limit, whereas the latter is responsible for the change of moment of inertia due to the vibrational motion. The terms in the potential are made up by the products of the normal coordinates, while the expansion of the inverse moment of inertia produces in the Hamiltonian terms with mixed products of the normal coordinates and conjugate momenta, Q_k and p_k , and the total angular momentum J_α . By arranging terms of the Hamiltonian in order of their magnitude and choosing an appropriate truncation of the expansions, an effective Hamiltonian can be obtained by applying perturbation theory.

Among the various perturbative methods, the sequential contact transformation has proven to be better suited to the calculation of higher order terms beyond second order in the vibration-rotation Hamiltonian (Aliev and Watson, 1985). The application of the contact transformation to the vibration-rotation problem has been subject of numerous investigations (Shaffer *et al.*, 1939, Thomas, 1942a, 1942b, Herman and Shaffer, 1948, Aliev and Aleksanyan, 1967, Aliev and Watson,

1976, 1985, Niroomand-Rad and Parker, 1979, 1981). Expressions up to fourth order in the twice contact transformed Hamiltonian are described in a monograph by Amat *et al.* (1971), which is a summary and extension of their earlier work (Goldsmith *et al.*, 1956, Amat *et al.*, 1957, Maes and Amat, 1957, Amat and Nielsen, 1957, 1958c, 1962, Grenier-Bresson *et al.* 1962). In their treatment the expressions for a linear molecule are derived from those of an axially symmetric, non-linear molecule (Amat *et al.*, 1971).

The aim of the sequential contact transformation is to further uncouple the vibrational and rotational part of the Hamiltonian, by transforming the Hamiltonian in block diagonal form where each block refers to a given vibrational level. Modification is strongest in the rotational Hamiltonian, leading to redefined molecular constants, and by removing coupling terms to higher orders new terms are added, for instance quartic and sextic centrifugaldistortion constants. (Aliev and Watson, 1985).

In the twice contact transformed Hamiltonian up to fourth order formulated by Amat and Nielsen (Amat *et al.*, 1971), two types of off-diagonal elements in terms of ℓ_t exist in case of the linear molecule. They were originally developed by Amat and Nielsen (1958a, 1958b) and expanded by Maki and Lide (1967), and Watson (1983). These matrix elements are referred to as rotational ℓ -type doubling of the form

$$\langle v_t, \ell_t | h_2^\dagger | v_t, \ell_t \pm 2 \rangle \quad (2.43)$$

and vibrational ℓ -type doubling and resonance of the form

$$\langle v_t, \ell_t, v_{t'}, \ell_{t'} | h_2^\dagger | v_t, \ell_t \pm 2, v_{t'}, \ell_{t'} \mp 2 \rangle . \quad (2.44)$$

$h_2^\dagger$ refers to the second order term of the Hamiltonian after two consecutive contact transformation containing the leading terms (Amat *et al.*, 1971). In the case of a linear molecule ℓ -type doubling is primarily due to the Coriolis interaction and is minimized by use of the Eckart conditions (Oka 1967). The quality and high resolution of the acetylene spectra requires the consideration of additional terms connecting states within a vibrational polyad where $\Delta\ell = \pm 4$. The explicit forms of these matrix elements for the lowest lying bending vibrational states as relevant for acetylene are summarized in Table 2.2.

The primary contribution to the vibrational ℓ -doubling constant r_{45}^{eff} comes from cubic and quartic anharmonicity terms in the potential (Pliva 1972) and can be physically explained as a Coriolis force due to an interaction between different normal modes, while the rotational ℓ -doubling constant q_t^{eff} stems primarily from the interaction of the vibrational mode and its angular momentum with the total rotational angular momentum (Oka 1967; Pliva 1972), hence the distinction between

Table 2.2. Rotational and Vibrational ℓ -doubling matrix elements.

$$\begin{aligned}
 \langle \dots; v_t, \ell_t; v_{t'}, \ell_{t'}; \dots | h_2^+ | \dots; v_t, \ell_t \pm 2; v_{t'}, \ell_{t'}; \dots \rangle = \\
 = q_t^{\text{eff}} \sqrt{[M - \ell(\ell \pm 1)][M - (\ell \pm 1)(\ell \pm 2)]} (v_t \mp \ell_t)(v_t \pm \ell_t + 2) \\
 q_t^{\text{eff}} = q_t^o + q_t^J M + q_t^{JJ} M^2 + \sum_s q_{ts} v_s + \sum_i q_i^\ell (\ell \pm 1) \\
 M = J(J + 1) \\
 \ell = \sum_i \ell_i
 \end{aligned}$$

$$\begin{aligned}
 \langle \dots; 1, 1; 0, 0; \dots | h_2^+ | \dots; 1, \pm 1; 0, 0; \dots \rangle &= 2 q_t^{\text{eff}} M \\
 \langle \dots; 2, 0; 0, 0; \dots | h_2^+ | \dots; 2, \pm 2; 0, 0; \dots \rangle &= 2\sqrt{2} q_t^{\text{eff}} \sqrt{M(M-2)} \\
 \langle \dots; 1, \pm 1; 1, 1; \dots | h_2^+ | \dots; 1, \mp 1; 1, 1; \dots \rangle &= 2 q_t^{\text{eff}} \sqrt{M(M-2)} \\
 \langle \dots; 1, \pm 1; 1, -1; \dots | h_2^+ | \dots; 1, \mp 1; 1, -1; \dots \rangle &= 2 q_t^{\text{eff}} \sqrt{M(M-2)} \\
 \langle \dots; 3, \pm 1; 0, 0; \dots | h_2^+ | \dots; 3, \pm 3; 0, 0; \dots \rangle &= 2\sqrt{3} q_t^{\text{eff}} \sqrt{(M-2)(M-6)} \\
 \langle \dots; 3, \mp 1; 0, 0; \dots | h_2^+ | \dots; 3, \pm 1; 0, 0; \dots \rangle &= 4 q_t^{\text{eff}} M \\
 \langle \dots; 1, \pm 1; 2, \pm 2; \dots | h_2^+ | \dots; 1, \mp 1; 2, \pm 2; \dots \rangle &= 2 q_t^{\text{eff}} \sqrt{(M-2)(M-6)} \\
 \langle \dots; 1, \pm 1; 2, \mp 2; \dots | h_2^+ | \dots; 1, \mp 1; 2, \mp 2; \dots \rangle &= 2 q_t^{\text{eff}} \sqrt{(M-2)(M-6)} \\
 \langle \dots; 1, \pm 1; 2, 0; \dots | h_2^+ | \dots; 1, \mp 1; 2, 0; \dots \rangle &= 2 q_t^{\text{eff}} M \\
 \langle \dots; 2, \pm 2; 1, \pm 1; \dots | h_2^+ | \dots; 2, 0; 1, \pm 1; \dots \rangle &= 2\sqrt{2} q_t^{\text{eff}} \sqrt{(M-2)(M-6)} \\
 \langle \dots; 2, \pm 2; 1, \mp 1; \dots | h_2^+ | \dots; 2, 0; 1, \mp 1; \dots \rangle &= 2\sqrt{2} q_t^{\text{eff}} M
 \end{aligned}$$

$$\begin{aligned}
 \langle \dots; v_t, \ell_t; v_{t'}, \ell_{t'}; \dots | h_2^+ | \dots; v_t, \ell_t \mp 2; v_{t'}, \ell_{t'} \pm 2; \dots \rangle = \\
 = \frac{r_{tt'}^{\text{eff}}}{4} \sqrt{(v_t + \ell_t + 1 \pm 1)(v_t - \ell_t + 1 \mp 1)(v_{t'} + \ell_{t'} + 1 \mp 1)(v_{t'} - \ell_{t'} + 1 \pm 1)} \\
 r_{tt'}^{\text{eff}} = r_{tt'}^o + r_{tt'}^J M + \sum_s r_{(tt')s} v_s
 \end{aligned}$$

$$\begin{aligned}
 \langle \dots; 1, \pm 1; 1, \mp 1; \dots | h_2^+ | \dots; 1, \mp 1; 1, \pm 1; \dots \rangle &= 4 R_{\pm}^{tt'} \\
 \langle \dots; 2, \pm 2; 1, \mp 1; \dots | h_2^+ | \dots; 2, 0; 1, \pm 1; \dots \rangle &= 4\sqrt{2} R_{\pm}^{tt'}
 \end{aligned}$$

Table 2.2. (*continued*)

$$\begin{aligned} \langle \dots; v_t, \ell_t; v_{t'}, \ell_{t'} \dots | h_2^+ | \dots; v_t \ell_t \pm 4; v_{t'}, \ell_{t'} \dots \rangle = \\ = \sum_{k_t} \langle \dots; v_t, \ell_t; \dots | h_2^+ | \dots; v_t, k_t; \dots \rangle \langle \dots; v_t, k_t; \dots | h_2^+ | \dots; v_t, \ell_t \pm 4; \dots \rangle \end{aligned}$$

$$\langle \dots; 2, \pm 2; 0, 0; \dots | h_2^+ | \dots; 2, \mp 2; 0, 0; \dots \rangle = 8\rho_t^{\text{eff}} M(M-2)$$

$$\langle \dots; 3, \pm 3; 0, 0; \dots | h_2^+ | \dots; 3, \mp 1; 0, 0; \dots \rangle = 8\sqrt{3}\rho_t^{\text{eff}}, M\sqrt{(M-2)(M-6)}$$

$$\langle \dots; 2, \pm 2; 1, \pm 1; \dots | h_2^+ | \dots; 2, \mp 2; 1, \pm 1 \dots \rangle = 8\rho_t^{\text{eff}} M\sqrt{(M-2)(M-6)}$$

$$\langle \dots; 2, \pm 2; 1, \mp 1; \dots | h_2^+ | \dots; 2, \mp 2; 1, \mp 1; \dots \rangle = 8\rho_t^{\text{eff}} M\sqrt{(M-2)(M-6)}$$

$$\begin{aligned} \langle \dots; v_t, \ell_t; v_{t'}, \ell_{t'} \dots | h_2^+ | \dots; v_t, \ell_t \pm 2; v_{t'}, \ell_{t'} \pm 2; \dots \rangle = \\ = \sum_{k_t, k_{t'}} \langle \dots; v_t, \ell_t; v_{t'}, \ell_{t'} \dots | h_2^+ | \dots; v_t, k_t; v_{t'}, k_{t'}; \dots \rangle \times \\ \times \langle \dots; v_t, k_t; v_{t'}, k_{t'}; \dots | h_2^+ | \dots; v_t, \ell_t \pm 2; v_{t'}, \ell_{t'} \pm 2; \dots \rangle \end{aligned}$$

$$\langle \dots; 1, \pm 1; 1, \pm 1; \dots | h_2^+ | \dots; 1, \mp 1; 1, \mp 1; \dots \rangle = 8\rho_{tt'}^{\text{eff}} M(M-2)$$

$$\langle \dots; 2, \pm 2; 1, \pm 1; \dots | h_2^+ | \dots; 2, 0; 1, \mp 1; \dots \rangle = 8\sqrt{2}\rho_{tt'}^{\text{eff}} M\sqrt{(M-2)(M-6)}$$

rotational and vibrational doubling. In fact, both anharmonicity of the potential and total rotational angular momentum influence both types of ℓ -type resonances. The physical interpretation for both types of interaction can be considered as a Coriolis force acting on the molecule from the view point as an observer in the rotating, molecule fixed axis system, and as a variation of rotational angular momentum due to the variation of moment of inertia, caused by the vibrational displacements, and to the vibrational angular momentum, because of conservation of total angular momentum, from the view point as an external observer in the space fixed axis system (Oka, 1967).

The main contribution to the rotation-vibration energy of a linear molecule, collecting diagonal terms up to fourth order, can be written as a sum of a vibrational term $G_o(v, \ell)$ and a rotational term $F_{v\ell}(J)$, i.e.

$$E(v, \ell, J) = G_o(v, \ell) + F_{v\ell}(J), \quad (2.45)$$

where

$$\begin{aligned} G_o(v, \ell) = & \sum_s \omega_s v_s + \sum_{\substack{ss' \\ s \leq s'}} x_{ss'} v_s v_{s'} + \sum_{\substack{ss's'' \\ s \leq s' \leq s''}} y_{ss's''} v_s v_{s'} v_{s''} + \\ & + \sum_{\substack{tt' \\ t \leq t'}} g_{tt'} \ell_t \ell_{t'} + \sum_{\substack{tt't'' \\ t \leq t' \leq t''}} y_{tt't''}^{t'} v_t \ell_{t'} \ell_{t''} \end{aligned} \quad (2.46)$$

and

$$F_{v\ell}(J) = B_v [J(J+1) - \ell^2] - D_v [J(J+1) - \ell^2]^2 + H_v [J(J+1) - \ell^2]^3. \quad (2.47)$$

The rotational constants depend on the vibrational motion as follows

$$B_v = B_o - \sum_s \alpha_s v_s + \sum_{\substack{ss' \\ s \leq s'}} \gamma_{ss'} v_s v_{s'} + \sum_{\substack{ss's'' \\ s \leq s' \leq s''}} \gamma_{ss's''} v_s v_{s'} v_{s''} + \sum_{\substack{tt' \\ t \leq t'}} \gamma_{tt'}^{t'} \ell_t \ell_{t'} + \sum_{\substack{tt't'' \\ t \leq t' \leq t''}} \gamma_{tt't''}^{t'} v_t \ell_{t'} \ell_{t''}, \quad (2.48)$$

$$D_v = D_o - \sum_s \beta_s v_s + \sum_{\substack{ss' \\ s \leq s'}} \beta_{ss'} v_s v_{s'} + \sum_{\substack{tt' \\ t \leq t'}} \beta^{tt'} \ell_t \ell_{t'}, \quad (2.49)$$

and

$$H_v \simeq H_o. \quad (2.50)$$

Summation over s includes all normal modes, whereas t restricts the summation to the doubly degenerate vibrational modes. Explanation of the molecular parameters are given in Table 2.3. Eqs. (2.45–2.49) are written in a form applicable to the analysis of spectra; by relating the energy to the ground state, terms of $(v_s + d_s/2)$, where d_s indicates the degeneracy of the vibrational mode, are replaced by v_s .

By symmetry adapting the rovibrational function, Eq. (2.42), the Hamiltonian is factorized into block diagonal form within a vibrational state (Plíva 1972b, Winnewisser and Winnewisser, 1972). In Table 2.4, the factorized Hamiltonian for vibrational states up to three excited quanta of the bending modes in acetylene are shown. For a given vibrational state, the factorized Hamiltonian is divided into a $+$ and $-$ block, depending on the sign of the symmetry adapted wavefunction,

$$\Psi_{|\ell|}^{\pm} = \frac{1}{\sqrt{2}} \{ |v_4^{\ell_4}, v_5^{\ell_5}; J, \ell > \pm |v_4^{-\ell_4}, v_5^{-\ell_5}; J, -\ell > \}. \quad (2.51)$$

It is customary to assign each pair of subblocks the symmetry labels e and f , which are defined in Chapter 3, Section 3.5. By making the following phase choice under the inversion E^*

$$E^* |v_4^{\ell_4}, v_5^{\ell_5}; J, \ell > = (-1)^{(J+\ell)} |v_4^{-\ell_4}, v_5^{-\ell_5}; J, -\ell >, \quad (2.52)$$

where $\ell = \sum_i \ell_i$, the e and f states can be written as

$$|v_4^{\ell_4}, v_5^{\ell_5}; J, \ell; e > = \frac{1}{\sqrt{2}} \{ |v_4^{\ell_4}, v_5^{\ell_5}; J, \ell > + (-1)^{\ell} |v_4^{-\ell_4}, v_5^{-\ell_5}; J, -\ell > \} \quad (2.53)$$

and the f states as

$$|v_4^{\ell_4}, v_5^{\ell_5}; J, \ell; f > = \frac{1}{\sqrt{2}} \{ |v_4^{\ell_4}, v_5^{\ell_5}; J, \ell > - (-1)^{\ell} |v_4^{-\ell_4}, v_5^{-\ell_5}; J, -\ell > \}. \quad (2.54)$$

For vibrational states where $\sum_i v_i$ is even, the subblock of the factorized Hamiltonian with the plus sign is labeled e and the one with the minus sign is labeled f , and vice versa if $\sum_i v_i$ is odd. Figure 2.3 shows schematically the split levels with appropriate symmetry labels. The sign of some of the molecular parameters depend on the general phase choice as discussed in Chapter 3, Section 3.5.

By applying the contact transformation, the vibrational states were first uncoupled. Symmetry adaptation of the rovibrational wavefunction leads then to the factorization of the Hamiltonian,

Table 2.3. Molecular parameters of a linear molecule. All constants are given in units of wavenumber, i.e. cm^{-1} .

ω_s	harmonic frequency of normal mode s
$x_{ss'}, y_{ss's''}, g_{tt'}, y_t^{t't''}$	vibrational anharmonicity constants
B_o	$= \hbar/(4\pi c I^o)$, groundstate constant
$\alpha_s, \gamma_{ss'}, \gamma^{tt'}$	correction to B_o due to vibration
D_o	quartic centrifugal distortion constant
$\beta_s, \beta_{ss'}$	correction to quartic centrifugal distortion constant D_o due to vibration
H_o	sextic centrifugal distortion constant
q_t^o	Coriolis interaction or rotational ℓ -doubling constant
q_{ts}, q_{tJ}	higher order correction to Coriolis interaction parameter
$r_{tt'}^o$	vibrational ℓ -doubling constant
$r_{(tt')s}, r_t^J$	higher order correction to vibrational ℓ -doubling constant
s	summation index over all normal modes
t	summation index over all degenerate normal modes
ℓ_t	projection quantum number of internal or vibrational angular momentum of mode t
ℓ	total projection quantum number, i.e. $\sum_t \ell_t = \ell$
J	total angular momentum quantum number

Table 2.4. Hamiltonian of the linear acetylene molecule. By forming Wang basis function, i.e. $\Psi_{|\ell|}^{\pm} = \frac{1}{\sqrt{2}}\{|v_4^{\ell_4}, v_5^{\ell_5}; J, \ell > \pm|v_4^{-\ell_4}, v_5^{-\ell_5}; J, -\ell >$, the Hamiltonian is brought into block diagonal form. Listed as follows are the vibrational states $(v_4, v_5) = (0, 1), (1, 1), (0, 2), (2, 1), (0, 3)$. The Hamiltonian for $(1, 0), (2, 0), (3, 0), (1, 2)$ can be obtained by switching indices 4 and 5 of the appropriate Hamiltonian listed here. $M = J(J + 1)$.

$$v_5=1$$

$$\begin{matrix} & 0^0, 1^1 & 0^0, 1^{-1} \\ \begin{matrix} 0^0, 1^1 \\ 0^0, 1^{-1} \end{matrix} & \begin{pmatrix} E_1 & W_{11} \\ W_{11} & E_1 \end{pmatrix} \end{matrix}$$

Factorized Hamiltonian:

$$\begin{matrix} & \Psi_{|\ell|=1}^+ & \Psi_{|\ell|=1}^- \\ \begin{matrix} \Psi_{|\ell|=1}^+ \\ \Psi_{|\ell|=1}^- \end{matrix} & \begin{pmatrix} E_1 + W_{11} & 0 \\ 0 & E_1 - W_{11} \end{pmatrix} \end{matrix}$$

Matrix Elements:

$$E_1 = E(0^0, 1^{\pm 1}, J)$$

$$W_{11} = 2q_5^{\text{eff}} M$$

Table 2.4. (continued)

$$v_4=1, v_5=1$$

$$\begin{array}{c} 1^1, 1^1 \quad 1^1, 1^{-1} \quad 1^{-1}, 1^1 \quad 1^{-1}, 1^{-1} \\ \begin{pmatrix} 1^1, 1^1 & \begin{pmatrix} E_2 & W_{11}^{(5)} & W_{11}^{(4)} & W_4 \\ 1^1, 1^{-1} & \begin{pmatrix} W_{11}^{(5)} & E_0 & V & W_{11}^{(4)} \\ 1^{-1}, 1^1 & \begin{pmatrix} W_{11}^{(4)} & V & E_0 & W_{11}^{(5)} \\ 1^{-1}, 1^{-1} & \begin{pmatrix} W_4 & W_{11}^{(4)} & W_{11}^{(5)} & E_2 \end{pmatrix} \end{pmatrix} \end{pmatrix} \end{pmatrix} \end{array}$$

Factorized Hamiltonian

$$\begin{array}{c} \Psi_{|\ell|=2}^+ \quad \Psi_{|\ell|=0}^+ \quad \Psi_{|\ell|=0}^- \quad \Psi_{|\ell|=2}^- \\ \begin{pmatrix} \Psi_{|\ell|=2}^+ & \begin{pmatrix} E_2 + W_4 & W_{11}^{(5)} + W_{11}^{(4)} & 0 & 0 \\ \Psi_{|\ell|=0}^+ & \begin{pmatrix} W_{11}^{(5)} + W_{11}^{(4)} & E_2 + V & 0 & 0 \\ \Psi_{|\ell|=0}^- & \begin{pmatrix} 0 & 0 & E_2 - V & W_{11}^{(5)} - W_{11}^{(4)} \\ \Psi_{|\ell|=2}^- & \begin{pmatrix} 0 & 0 & W_{11}^{(5)} - W_{11}^{(4)} & E_2 - W_4 \end{pmatrix} \end{pmatrix} \end{pmatrix} \end{pmatrix} \end{array}$$

Diagonalized Energies:

$$\begin{array}{l} \Psi_{|\ell|=2}^+, \Psi_{|\ell|=0}^+ \quad \text{subblock:} \\ e^\pm = \frac{1}{2}(E_2 + E_0) + \frac{1}{2}(V + W_4) \pm \frac{1}{2}\sqrt{(E_2 - E_0 - (V - W_4))^2 + 4(W_{11}^{(5)} + W_{11}^{(4)})^2} \\ \Psi_{|\ell|=2}^-, \Psi_{|\ell|=0}^- \quad \text{subblock:} \\ e^\pm = \frac{1}{2}(E_2 + E_0) - \frac{1}{2}(V + W_4) \pm \frac{1}{2}\sqrt{(E_2 - E_0 + (V - W_4))^2 + 4(W_{11}^{(5)} - W_{11}^{(4)})^2} \end{array}$$

Matrix Elements:

$$\begin{array}{l} E_2 = E(1^{\pm 1}, 1^{\pm 1}, J) \\ E_0 = E(1^{\pm 1}, 1^{\mp 1}, J) \\ V = 4 r_{45}^{\text{eff}} \\ W_{11}^{(4,5)} = 2 q_{4,5}^{\text{eff}} \sqrt{M(M-2)} \\ W_4 = 8 \rho_{45}^{\text{eff}} M(M-2) \end{array}$$

Table 2.4. (continued)

$$v_5=2$$

$$\begin{array}{ccc} & 0^0, 2^2 & 0^0, 2^0 & 0^0, 2^{-2} \\ \begin{array}{l} 0^0, 2^2 \\ 0^0, 2^0 \\ 0^0, 2^{-2} \end{array} & \left(\begin{array}{ccc} E_2 & W_{20} & W_{22} \\ W_{20} & E_0 & W_{20} \\ W_{22} & W_{20} & E_2 \end{array} \right) \end{array}$$

Factorized Hamiltonian:

$$\begin{array}{ccc} & \Psi_{|\ell|=2}^+ & \Psi_{|\ell|=0} & \Psi_{|\ell|=2}^- \\ \begin{array}{l} \Psi_{|\ell|=2}^+ \\ \Psi_{|\ell|=0} \\ \Psi_{|\ell|=2}^- \end{array} & \left(\begin{array}{ccc} E_2 + W_{22} & \sqrt{2}W_{20} & 0 \\ \sqrt{2}W_{22} & E_0 & 0 \\ 0 & 0 & E_2 - W_{22} \end{array} \right) \end{array}$$

Diagonalized Energies:

$$\begin{array}{l} \Psi_{|\ell|=2}^+, \Psi_{|\ell|=0}^+ \text{ subblock:} \\ e^\pm = \frac{1}{2}(E_2 + E_0 + W_{22}) \pm \frac{1}{2}\sqrt{(E_2 - E_0 + W_{22})^2 + 8W_{20}^2} \\ \Psi_{|\ell|=2}^- : \\ e = E_2 - W_{22} \end{array}$$

Matrix Elements:

$$\begin{array}{l} E_0 = E(0^0, 2^0, J) \\ E_2 = E(0^0, 2^{\pm 2}, J) \\ W_{20} = 2\sqrt{2}q_5^{\text{eff}}\sqrt{M(M-2)} \\ W_{22} = 8\rho_5^{\text{eff}}M(M-2) \end{array}$$

Table 2.4. (continued)

$$v_4=2, v_5=1:$$

$$\begin{array}{c} 2^2, 1^1 \\ 2^2, 1^{-1} \\ 2^0, 1^1 \\ 2^0, 1^{-1} \\ 2^{-2}, 1^1 \\ 2^{-2}, 1^{-1} \end{array} \begin{pmatrix} 2^2, 1^1 & 2^2, 1^{-1} & 2^0, 1^1 & 2^0, 1^{-1} & 2^{-2}, 1^1 & 2^{-2}, 1^{-1} \\ E_3 & a & c & e & f & 0 \\ a & E_2 & R & d & 0 & f \\ c & R & E_1 & b & d & e \\ e & d & b & E_1 & R & c \\ f & 0 & d & R & E_2 & a \\ 0 & f & e & c & a & E_3 \end{pmatrix}$$

Factorized Hamiltonian:

$$\begin{array}{c} \Psi_{|\ell|=3}^+ \\ \Psi_{|\ell|=1(2)}^+ \\ \Psi_{|\ell|=1(0)}^+ \\ \Psi_{|\ell|=1(0)}^- \\ \Psi_{|\ell|=1(2)}^- \\ \Psi_{|\ell|=3}^- \end{array} \begin{pmatrix} \Psi_{|\ell|=3}^+ & \Psi_{|\ell|=1(2)}^+ & \Psi_{|\ell|=1(0)}^+ & \Psi_{|\ell|=1(0)}^- & \Psi_{|\ell|=1(2)}^- & \Psi_{|\ell|=3}^- \\ E_3 & a+f & c+e & 0 & 0 & 0 \\ a+f & E_2 & R+d & 0 & 0 & 0 \\ c+e & R+d & E_1+b & 0 & 0 & 0 \\ 0 & 0 & 0 & E_1-b & R-d & c-e \\ 0 & 0 & 0 & R-d & E_2 & a-f \\ 0 & 0 & 0 & c-e & a-f & E_3 \end{pmatrix}$$

Matrix Elements:

$$E_3 = E(2^{\pm 2}, 1^{\pm 1}, J)$$

$$E_2 = E(2^{\pm 1}, 1^{\mp 1}, J)$$

$$E_1 = E(2^0, 1^{\pm 1}, J)$$

$$R = 4\sqrt{2} r_{45}^{\text{eff}}$$

$$a = 2q_5^{\text{eff}} \sqrt{(M-2)(M-6)}$$

$$b = 2q_5^{\text{eff}} M$$

$$c = 2\sqrt{2} q_4^{\text{eff}} \sqrt{(M-2)(M-6)}$$

$$d = 2\sqrt{2} q_4^{\text{eff}} M$$

$$e = 8\sqrt{2} \rho_{45}^{\text{eff}} M \sqrt{(M-2)(M-6)}$$

$$f = 8\rho_4^{\text{eff}} M \sqrt{(M-2)(M-6)}$$

Table 2.4. (continued)

$v_5=3$:

$$\begin{array}{c} 0^0, 3^3 \quad 0^0, 3^1 \quad 0^0, 3^{-1} \quad 0^0, 3^{-3} \\ \begin{pmatrix} E_3 & W_{31} & W_4 & 0 \\ W_{31} & E_1 & W_{11} & W_4 \\ W_4 & W_{11} & E_1 & W_{31} \\ 0 & W_4 & W_{31} & E_3 \end{pmatrix} \end{array}$$

Factorized Hamiltonian:

$$\begin{array}{c} \Psi_{|\ell|=3}^+ \quad \Psi_{|\ell|=1}^+ \quad \Psi_{|\ell|=1}^- \quad \Psi_{|\ell|=3}^- \\ \begin{pmatrix} E_3 & W_{31} + W_4 & 0 & 0 \\ W_{31} + W_4 & E_1 + W_{11} & 0 & 0 \\ 0 & 0 & E_1 - W_{11} & W_{31} - W_4 \\ 0 & 0 & W_{31} - W_4 & E_3 \end{pmatrix} \end{array}$$

Diagonalized Energies:

$$\begin{array}{l} \Psi_{|\ell|=3}^+, \Psi_{|\ell|=1}^+ \quad \text{subblock:} \\ e^\pm = \frac{1}{2}(E_3 + E_1) + \frac{1}{2}W_{11} \pm \frac{1}{2}\sqrt{(E_3 - E_1 - W_{11})^2 + 4(W_{31} + W_4)^2} \\ \Psi_{|\ell|=3}^-, \Psi_{|\ell|=1}^- \quad \text{subblock:} \\ e^\pm = \frac{1}{2}(E_3 + E_1) - \frac{1}{2}W_{11} \pm \frac{1}{2}\sqrt{(E_3 - E_1 + W_{11})^2 + 4(W_{31} - W_4)^2} \end{array}$$

Matrix Elements:

$$\begin{aligned} E_3 &= E(0^0, 3^{\pm 3}, J) \\ E_1 &= E(0^0, 3^{\pm 1}, J) \\ W_{11} &= 4q_5^{\text{eff}} M \\ W_{31} &= 2\sqrt{3}q_5^{\text{eff}} \sqrt{(M-2)(M-6)} \\ W_4 &= 8\sqrt{3}\rho_5^{\text{eff}} M \sqrt{(M-2)(M-6)} \end{aligned}$$

where the excited vibrational states split into parity doublets, where one component belongs to the $+$ subblock and the other to the $-$ subblock in the factorized Hamiltonian. The final diagonal energies can be calculated by solving the secular equation, as it is done for the lower lying states (see Table 2.4). It is quite cumbersome, to obtain analytical expression for the higher excited bending modes, and in these cases it is preferable to obtain energies by numerical diagonalization.

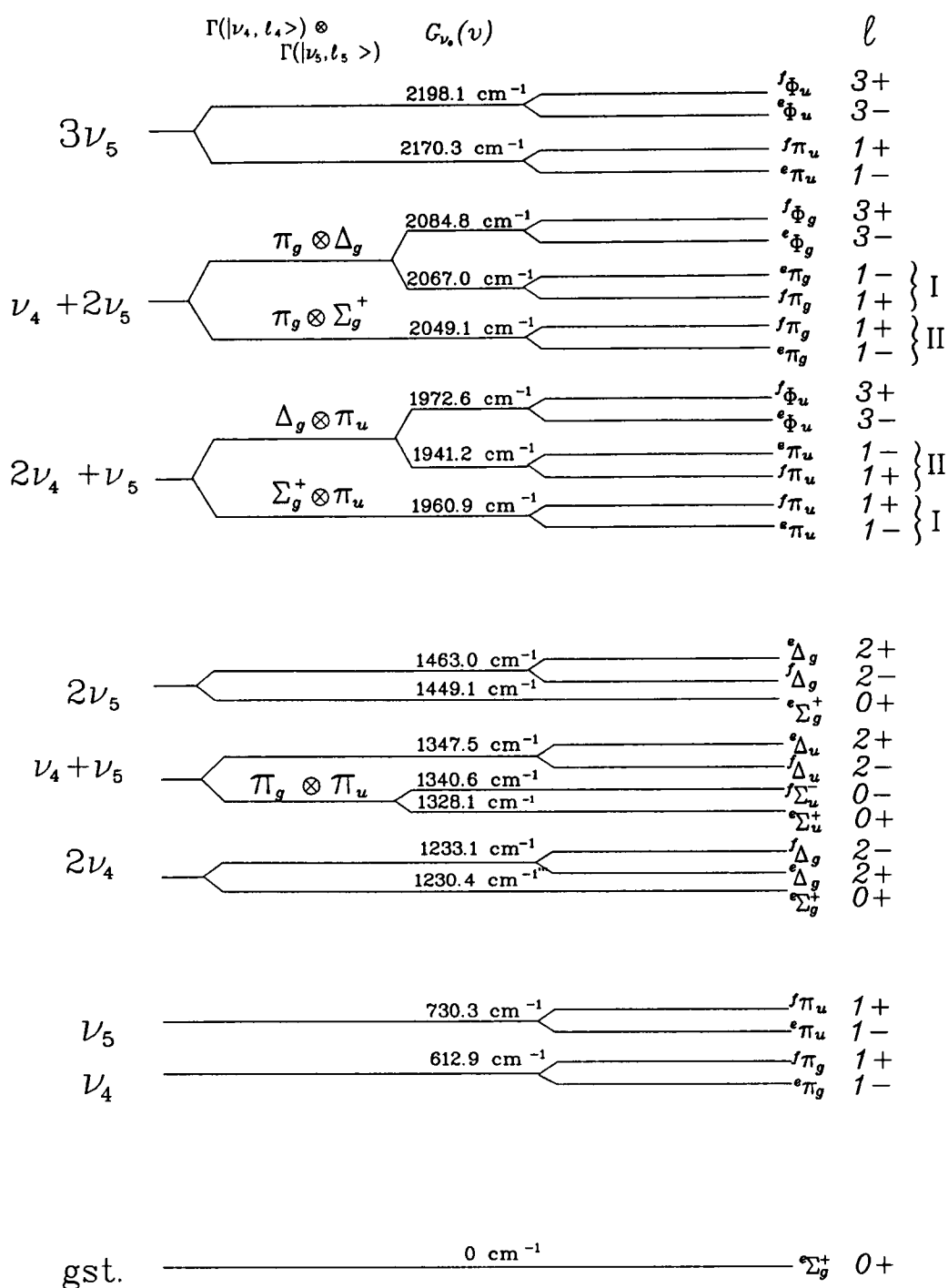


Figure 2.3. Schematic energy level diagram of acetylene. Shown are the splitting due to vibrational and rotational ℓ -type doubling. The vibrational species are obtained by the direct product of the symmetry species of $n\nu_4$ and $n\nu_5$. To the right the parity doublets are depicted which are usually distinguished by the labels e and f .

CHAPTER 3

THE SYMMETRY OF ACETYLENE'S BENDING MODES ν_4 AND ν_5

3.1 Introduction

Group theoretical concepts used in the analysis of vibration-rotation spectral analysis can yield valuable information on the molecular energy level structure based on the structural symmetry given by the molecule. From the parity of the molecular wave function under permissible symmetry operation, selection rules for allowed electric dipole transition and nuclear statistical weights, the latter responsible for observed intensity alternation of rotational transition within a vibronic band, can be unambiguously assigned. The most powerful symmetry group is the permutation-inversion group developed by Longuet-Higgins (1963) and Hougen (1962b, 1963), which permits the separate symmetry classification of rotational, vibronic, and rovibronic energy level. The concept of nuclear permutation as a true symmetry operation is not widely used as compared to the molecular point group.

The permutation-inversion group will be here applied here to describe the parity of the ℓ -doublets and splittings of a linear molecule. From symmetry considerations of fundamentals and overtones, an appropriate general phase choice for the rovibrational wave function describing states of multiple excited vibrational modes is proposed. The consequence of possible phase choices on the sign of molecular parameters describing the molecular energy levels of a polyatomic linear molecule is discussed.

3.2 Symmetry Groups of a Linear Molecule

A symmetry operation is defined as an operation leaving the Hamiltonian invariant (Weyl, 1950; Tinkham, 1964). According to the irreducibility theorem of quantum mechanics, the set of eigenfunctions of the molecular Hamiltonian transform like the matrix of its irreducible representation (Jansen and Boon, 1967). The theorem, thus, allows the assignments of the species of the irreducible representation of the possible symmetry operation to molecular levels (Jansen and Boon, 1967). All possible symmetry operations also automatically form a group, which is called the Complete Symmetry group. In most cases it is sufficient only to consider a particular subgroup to classify molecular

eigenstates (Longuet-Higgins, 1963; Hougen, 1962b; Hougen, 1963; Dalton, 1966).

One of the most important subgroups is the Molecular Symmetry (MS) group (Bunker and Papoušek, 1969; Bunker 1975, 1979), also termed the Permutation-Inversion (PI) group (Papoušek and Aliev, 1982) or Longuet-Higgins group (Longuet-Higgins, 1963). It consists of the following group elements:

- a) all feasible permutation p of the position and spin of identical nuclei in a molecule,
- b) all feasible permutation-inversion operations p^* , where $p^* = p \cdot E^*$ and E^* is the inversion of the positions of all nuclei and electrons in the center of mass of the molecule

(Papoušek and Aliev, 1982). The MS group of linear molecules belonging to the class of centrosymmetric linear molecules always contains the following elements

$$MS(D_{\infty h}) = \{E, E^*, p, p^*\}, \quad (3.1)$$

where E is the identity element, E^* the inversion operation as defined above, and p denotes here the simultaneous exchange of all pairs of identical nuclei. If the two hydrogen nuclei of acetylene are labeled 1 and 2; the two carbon nuclei 3 and 4, p can be written as the product of two transpositions (12)(34). All feasible MS operations given by Eq. (3.1) are schematically shown in Fig. 3.1. The small arrows attached to the nuclei in Fig. 3.1 represent the cartesian displacement coordinates of the nuclei. Above the molecular axis an electron is drawn to demonstrate the effect of the MS group on the electronic coordinates.

As can be seen from Fig. 3.1, the nuclear configurations can be obtained from each other by a rotation of the nuclear framework. An exchange of the hydrogen nuclei leaving the carbon atoms in the same positions is an infeasible operation not included in Eq. (3.1), because it corresponds to a tunneling through an insuperable potential barrier in the center of mass (Bunker, 1979). For a rigid molecule infeasible operations are those, which lead to nuclear equilibrium configurations not obtainable by a simple rotation from the former (Bunker, 1979).

The power of the MS group lies in the fact that its concept can be extended to nonrigid molecules, which have large vibrational amplitudes and internal rotators, for instance, and do not possess an unique equilibrium nuclear configuration. A prominent example of a non-rigid molecule is the pyramidal Ammonia, where a finite barrier separating two potential minima in an electronic configuration permits an inversion tunneling of the nitrogen nucleus through the base formed by the hydrogen nuclei. Depending on the physical condition, e.g. high resolution of the spectrometer, the MS group of the rigid molecule, in case of Ammonia $MS(C_{3v})$, has to be extended to

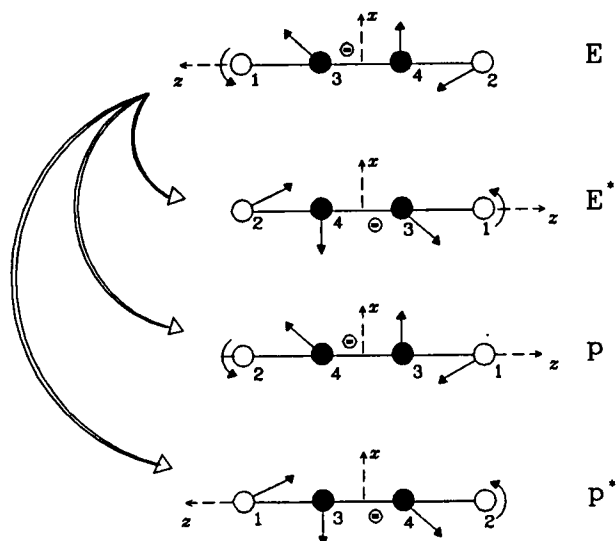


Figure 3.1. Feasible $MS(D_{\infty h})$ group operations. The small arrows attached to the nuclei show schematically the vibrational displacement vector. Circular arrows indicate motion due to the vibrational angular momentum.

a group of higher symmetry ($MS(D_{3h})$) in order to fully determine the symmetry of the resolved, nearly degenerate energy levels. The extended group then includes previously labelled infeasible operations corresponding to a change between nuclear configuration by potential barrier tunneling (Papoušek and Aliev, 1982). Other examples of non-rigid molecules are di-methylacetylene, with two methyl group as internal rotator or torsion elements (Hougen, 1964,1965; Bunker and Hougen, 1967; Longuet-Higgins, 1964; Bunker, 1967, 1968; Kirtmann, 1964; Papoušek, 1968) and the quasi-linear molecules of X_2Y_2 , such as acetylene in the excited electronic states (Yamada *et al.*, 1974, Watson *et al.*, 1982).

From the previous comments it follows immediately, that for linear molecules the MS group contains the four elements as given by Eq. (3.1), if centrosymmetric such as $^{12}C_2H_2$, or only the two elements E and E^* for the isotope $^{13}C^{12}CH_2$, whose MS group is called $MS(C_{\infty v})$.

Another symmetry group of a linear molecule is the Molecular point group (Herzberg, 1945; Bunker, 1979), which is the $D_{\infty h}$ -point group for centrosymmetric molecules and $C_{\infty v}$ -point group otherwise. The point group operations reflect and rotate the vibronic (vibrational and electronic) variables of the molecular eigenfunction, but leaves the three Euler angles unchanged in contrast

to the associated MS group, whose operations transform the vibronic variables as well as the Euler angles. Thus the MS group and the point group can be equally well used to determine the symmetry species of the vibronic wavefunction. Fig. 3.2 shows the symmetry planes and axes of the $D_{\infty h}$ -point group.

Since the overall rotational angular momentum J_α is unaffected by a point group operation, but not the electronic and vibrational angular momenta, Π_α and p_α , the Hamiltonian is not invariant under a point group operation due to different Coriolis coupling energy terms in the two configurations before and after the point group operation. Therefore, the point group cannot be used to classify the rovibronic species of the molecular levels. The MS group instead is well suited to determine the symmetry species of the rovibronic, and also separately rotational and vibrational eigenstates (Bunker, 1979).

Since the molecule fixed axes, x and y , are arbitrarily defined for a linear molecule in its reference configuration, the orientation of the x and y axes after a MS operation is not well defined; thus, the irreducible species of the rotational and the vibronic wavefunction cannot be determined by the MS group separately (Bunker, 1975, 1979; Bunker and Papoušek, 1969). For non-linear molecules it can be shown that the permutation-inversion group is isomorphic to the associated point group, if the molecule is rigid. This isomorphism is not given in the case of a linear molecule and, therefore, Bunker and Papoušek (1969) introduced the Extended Molecular Symmetry (EMS) group for linear molecules, which permits the determination of the rotational, vibrational and rovibronic species of molecular eigenstates of a linear molecule as well as the MS group does for nonlinear molecules. The elements of the EMS group of $D_{\infty h}$ point group symmetry are defined as

$$\text{EMS}(D_{\infty h}) = \{E, E_\epsilon, E_\epsilon^*, p_\epsilon, p_\epsilon^*\}, \quad (3.2)$$

where the various ϵ can assume any value (mod 2π) on the range $0 \leq \epsilon \leq 2\pi$ independently of each other.

If O_ϵ is a general element of the EMS group, the EMS group operations are defined as follows: a.) the effect of O_ϵ on the spatial coordinates of the nuclei and electrons in a molecule are the same as that of the element O in the MS group, b.) the effect of O_ϵ on the two Euler angles θ and ϕ is the same as the effect of O in the MS group, and c.) the Euler angle χ is defined by the value of ϵ according to the values

$$E_\epsilon \chi = \chi - \epsilon, \quad (3.3)$$

Table 3.1. Classification scheme of symmetry groups for rigid molecules.

	Symmetry Group		
Type of molecule	MS Group	Point Group	EMS Group
non-linear	rovibronic vibronic rotational	vibronic	—
linear	rovibronic	vibronic	rovibronic vibronic rotational

$$p_{\epsilon}\chi = 2\pi - \chi - \epsilon, \quad (3.4)$$

$$E_{\epsilon}^*\chi = \pi - \chi - \epsilon, \quad (3.5)$$

and

$$p_{\epsilon}^*\chi = \pi + \chi - \epsilon \quad (3.6)$$

(Bunker and Papoušek , 1969). The definition c) enables the EMS group to determine the symmetry of the vibronic levels in the same way as the corresponding point group does. The latter can be also stated as a consequence of the isomorphism between the extended MS group of the linear molecule and its corresponding point group (Bunker and Papoušek , 1969). In Table 3.1 the capabilities of the three here mentioned symmetry groups in classifying molecular energy levels are summarized.

This study concentrates on rotation-vibration infrared spectra with no electronic transitions and the bending modes ν_4 and ν_5 of acetylene are considered in the electronic groundstate. Under these circumstances, the MS group can be used to symmetry label the rovibrational states. In the electronic ground state ($\Lambda = 0$), the electronic wavefunction is totally symmetric and, therefore, has no bearing on the overall symmetry of the rovibrational level. The parities can be derived from the transformation properties of the rovibrational coordinates.

Four symmetry species of rovibrational levels of a centro-symmetric linear molecule are defined by the parity under MS group operation. Those are $s\Sigma_g^+$, $s\Sigma_u^-$, $a\Sigma_g^-$, or $a\Sigma_u^+$, where

the labels *g* (*gerade*), *u* (*ungerade*) stands for the parity under p^* , the labels *s* (*symmetric*), *a* (*antisymmetric*) for parity under the permutation p , and the labels + and – for the parity of the molecular eigenstates under E^* (Bunker, 1979). Due to the Sayvets condition (Sayvets 1939), $J_z - p_z = 0$, the rovibrational species can only be that of an one dimensional irreducible representation.

For linear molecules belonging to the $C_{\infty v}$ molecular symmetry group only two rovibrational species, Σ^+ and Σ^- , as defined by the inversion operation E^* , are possible. Since p and p^* are not true symmetry operations in this case, the *s, a* and *g, u* labels are dropped. Keeping this in mind, the symmetry consideration can be coherently treated for both molecular symmetries of linear molecules.

3.3 Symmetry and Parity of the Rovibrational States

Acetylene has four nuclei and exhibits five normal vibrational modes. The three non-degenerate modes by convention called ν_1 and ν_2 , both of vibrational symmetry species Σ_g^+ located at 3373cm^{-1} and 1974cm^{-1} , respectively, and $\nu_3(\Sigma_u^+)$ at 3295cm^{-1} . The two doubly degenerate modes are the symmetric bend $\nu_4(\Pi_g)$ and the antisymmetric bend $\nu_5(\Pi_u)$ at 613cm^{-1} and 730cm^{-1} , respectively. The normal modes can be determined, for instance, by group theoretical considerations as described by Shensted, 1976. Assuming that acetylene is in its electronic groundstate and all non-degenerate modes are in their totally symmetric ground state, only the transformation properties of the two dimensional harmonic oscillator times the rotational wavefunction has to be considered as it is the case for the observed fundamental and hotbands in the 730cm^{-1} region considered in this study.

The transformation property of the following wavefunction of a linear molecule will be considered:

$$\Psi_{rv}^o = \sqrt{1/(2\pi)} S_{JLM}(\theta, \phi) \exp(-\ell\chi) F_{v_5, \ell_5}(Q_5) F_{v_4, \ell_4}(Q_4) \exp(-\ell_5\alpha'_5) \exp(-\ell_4\alpha'_4), \quad (3.7)$$

where $\ell = \ell_4 + \ell_5$ according to Eq. (2.28). First, the parity will be determined for the case of singly excited vibrational quanta, i.e. $\ell = \ell_4$ and $\ell = \ell_5$. The Euler angle χ in Eq. (3.7) is the same as the independent variable χ' used in the isomorphic Hamiltonian assuming the $\chi = 0$ convention (see Fig. 2.2). The prime of the third angle has been omitted and the molecule fixed axes are identified as those of the isomorphic Hamiltonian where the primes on the axes will be omitted from here on.

Since the the third Euler angle χ as well as the x and y axes are arbitrary, the MS group can not be used to determine the transformation property of χ , α'_4 , and α'_5 , therefore, inhibiting the use of the MS group to determine the rotational and vibrational symmetry species, separately. On the other hand the transformation on the polar angle $\alpha_5 = \alpha'_5 + \chi$ is indeed well defined independent of the choice of the molecule fixed xy axes as seen in Fig. 3.3 (Bunker and Papoušek 1969; Bunker

1975, 1979). From Fig. 3.3 for ν_4 and Fig. (3.4) for ν_5 , the transformation properties of all rotation-vibration coordinates can be derived. After each MS group operation the molecule fixed axes have to be reoriented in order to preserve the Eckart conditions, Eqs. (2.3)–(2.6).

At the molecule's reference configuration there are six different ways to set the molecule fixed axes including possible left-handed and right-handed coordinate systems (Hainer *et al.*, 1949). Here the z -axis is chosen to lie on the molecular axis with the lowest principal moment of inertia. By defining the z -axis pointing towards the acetylene nuclei labelled 1 and 3, after each symmetry operation the z -axis has to lie on the same nuclei, which corresponds to the choice that the hydrogen and carbon nuclei labelled 1 and 3 respectively have positive z coordinates in the Hamiltonian. The arbitrary x -axis of the linear molecule remains fixed during the symmetry operation while the y -axis is defined by the conservation of a right-handed coordinate system.

Since the ν_4 (*trans*-bend) mode is symmetric and the ν_5 (*cis*-bend) normal mode is antisymmetric, the polar angles α_4 and α_5 exhibit different transformation behavior under the MS group operation as shown in Figs. 3.3 and 3.4. Fig. 3.3 shows that the vector Q_4 has the same orientation with respect to the space fixed axes after each symmetry operation, because the cartesian displacement coordinates are transformed into each other in contrast to those of the ν_5 vibrational mode. The absolute magnitude of the vibrational amplitudes Q_4 and Q_5 remain unaffected by any symmetry operation.

From Figs. 3.3 and 3.4, the transformation properties of the set of rovibrational coordinates can be summarized as follows

$$E^*(Q_4, Q_5, \alpha_4, \alpha_5, \theta, \phi) = (Q_4, Q_5, -\alpha_4, \pi - \alpha_5, \pi - \theta, \pi + \phi), \quad (3.8)$$

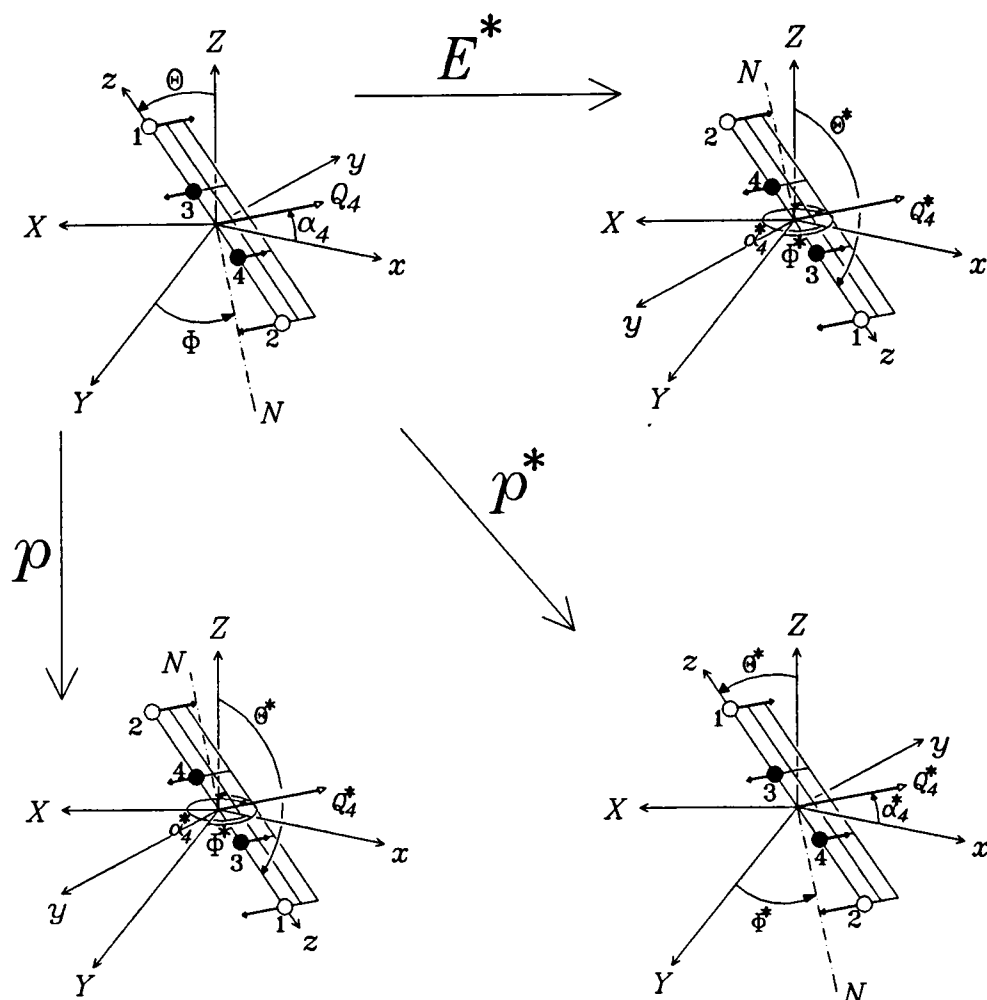
$$p(Q_4, Q_5, \alpha_4, \alpha_5, \theta, \phi) = (Q_4, Q_5, -\alpha_4, -\alpha_5, \pi - \theta, \pi + \phi), \quad (3.9)$$

and

$$p^*(Q_4, Q_5, \alpha_4, \alpha_5, \theta, \phi) = (Q_4, Q_5, \alpha_4, \pi + \alpha_5, \theta, \phi), \quad (3.10)$$

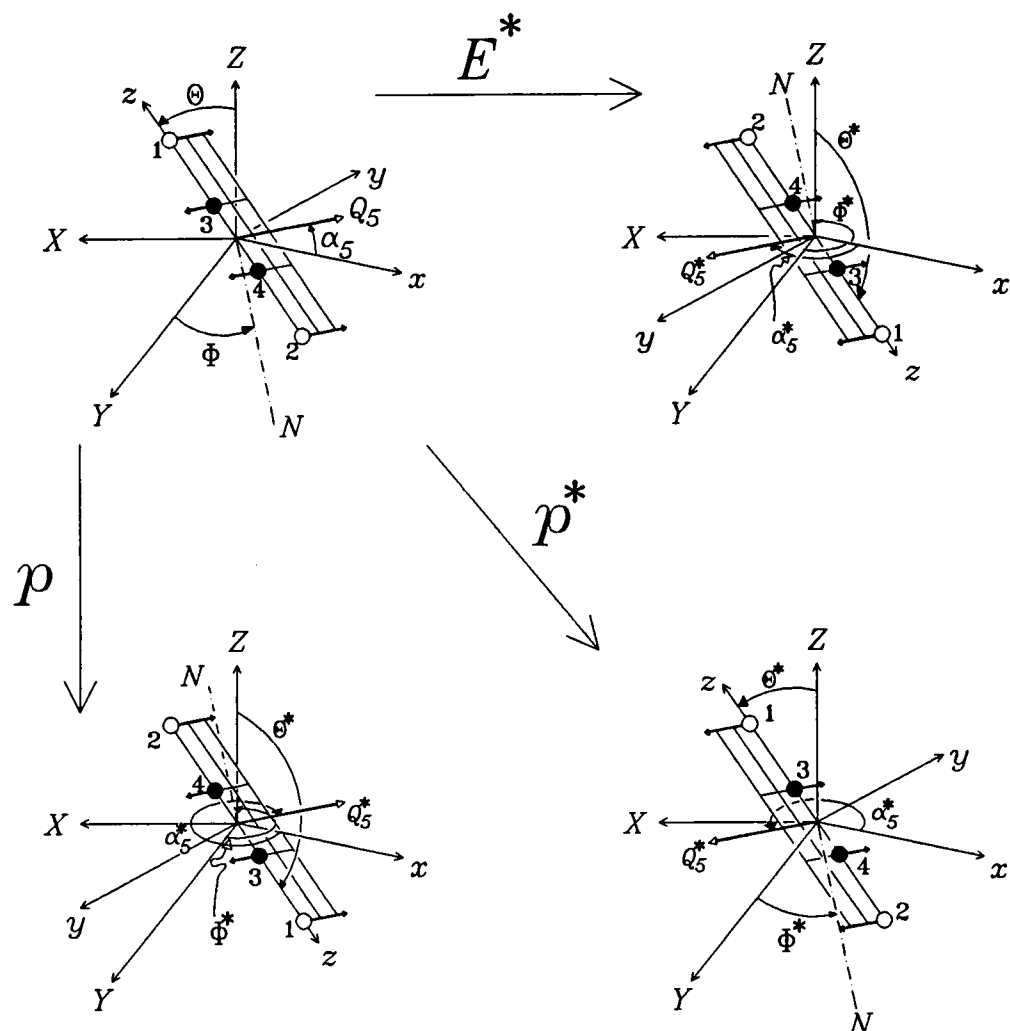
Using Eq. (3.8) the following rovibrational wavefunction of the singly excited ν_5 mode is obtained after inversion,

$$E^* \psi_{rve} = \sqrt{1/(2\pi)} S_{JLM}(\pi - \theta, \pi + \phi) F_{\nu_4, \ell_4}(Q_4) F_{\nu_5, \ell_5}(Q_5) \exp(-\ell\pi) \exp(-\ell\alpha_5) \quad (3.11)$$



Rovibrational Coordinates	MS-Group operation		
	E^*	p	p^*
θ	$\pi - \theta$	$\pi - \theta$	θ
ϕ	$\pi + \phi$	$\pi + \phi$	ϕ
α_4	$-\alpha_4$	$-\alpha_4$	α_4
Q_4	Q_4	Q_4	Q_4

Figure 3.3. Transformation of the rovibrational coordinates θ , ϕ , and α_4 under MS group operations. The transformation properties shown are valid for any bending, singly excited, and symmetric vibrational mode of a linear molecules such as ν_4 of acetylene.



Rovibrational Coordinates	MS-Group operation		
	E^*	p	p^*
θ	$\pi - \theta$	$\pi - \theta$	θ
ϕ	$\pi + \phi$	$\pi + \phi$	ϕ
α_5	$\pi - \alpha_5$	$-\alpha_5$	$\pi + \alpha_5$
Q_5	Q_5	Q_5	Q_5

Figure 3.4. Transformation of the rovibrational coordinates θ , ϕ , and α_5 under MS group operations. The transformation properties shown are valid for any bending, singly excited, and *antisymmetric* vibrational mode of a linear molecules such as ν_5 of acetylene.

If we denote with R_α^π a rotation of π about an axis in the xy plane which makes an angle α with the x axis, it can be shown that for a function f depending on the three Euler angles the following transformation is given,

$$R_\alpha^\pi f(\theta, \phi, \chi) = f(\pi - \theta, \pi + \phi, 2\pi - 2\alpha - \chi), \quad (3.12)$$

and from the behavior of the rotational symmetric top function under the same rotation it can be shown that

$$R_\alpha^\pi |JKM\rangle = (-1)^J \exp(-2K\alpha) |J - KM\rangle. \quad (3.13)$$

(Bunker 1979). By choosing $\alpha = 0$ and it immediately follows from Eqs. (3.12) and (3.13)

$$S_{J\ell M}(\pi - \theta, \pi + \phi) = (-1)^J S_{J\ell M}(\theta, \phi). \quad (3.14)$$

Inspection of Figs. 3.3 and 3.4 shows that the transformation of the Euler angle and the vibrational angle by the permutation operation p and inversion operation E^* can be described by an equivalent rotation about the molecule fixed x axis by π , which justifies the choice of R_0^π . With aid of Eq. (3.14), the effect of the inversion operation given by Eq. (3.11) can be now stated as

$$E^* \psi_{rve} = (-1)^{J+\ell} \sqrt{1/(2\pi)} S_{J\ell M}(\theta, \pi) F_{v_4 \ell_4}(Q_4) F_{v_5 \ell_5}(Q_5) \exp(-\ell\alpha_5). \quad (3.15)$$

Thus the parity of the ν_5 (as well as ν_4) rovibronic eigenstates are $(-1)^J$ for $\ell = \ell_5 = 0$ ($\ell = \ell_4 = 0$) under inversion. For $|\ell| > 0$ the rovibronic wavefunction has to be symmetry adapted in order that it transforms irreducibly, i.e.

$$\Psi_{rve}^\pm = \frac{1}{\sqrt{2}} \left\{ |v_4^{\ell_4}, v_5^{\ell_5}; J, \ell, M\rangle \pm |v_5^{-\ell_5}, v_4^{-\ell_4}; J, -\ell, M\rangle \right\}, \quad (3.16)$$

where the notation is selfexplanatory. Ψ_{rve}^+ has parity $(-1)^{J+\ell}$ and Ψ_{rve}^- parity $(-1)^{J+\ell+1}$ for ν_5 and $(-1)^J$ and $(-1)^{J+1}$, respectively, for ν_4 under inversion. The two linear combinations (3.15) form the pair of eigenstates describing the parity doublets due to rotational ℓ -type doubling in excited vibronic states of the bending modes in linear molecules. For a specific J the doublet contains species of opposite parity, which as later shown are given e and f labels.

Table 3.2. Parity of ν_4 and ν_5 rovibrational states of acetylene. + and - at the ℓ quantum number refer to the sign of the symmetry adapted wavefunction in Eq. (3.16).

Vibrational Mode	Parity		
	$E^* (\pm)$	$p (s,a)$	$p^* (g,u)$
$\nu_4, \ell+$	$(-1)^J$	+	$(-1)^J$
$\nu_4, \ell-$	$(-1)^{J+1}$	+	$(-1)^{J+1}$
$\nu_5, \ell+$	$(-1)^{J+\ell_5}$	$(-1)^{\ell_5}$	$(-1)^J$
$\nu_5, \ell-$	$(-1)^{J+\ell_5+1}$	$(-1)^{\ell_5+1}$	$(-1)^{J+1}$

With aid of Fig. 3.3 the parity under all MS group operation can be similarly determined. The parity of the ν_4 as well as of the ν_5 states are summarized in Table 3.2; Figs 3.5 and 3.6 indicate schematically the energy level structure for the lowest lying states of the bending modes. As observable in Figs. 3.5 and 3.6, for each doublet one component is + and the other -, and for each sublevel + and - alternate with ascending J values.

The EMS group can now be used to determine the species of the rotational and vibrational wavefunction separately. First the rotational part will be considered which is given by Eq. (2.39). With aid of the definition (3.5) for the arbitrary Euler angle χ , it follows

$$E_\epsilon^* |J \pm \ell M \rangle = (-1)^\ell \exp(\pm i\ell\epsilon) |J \mp \ell M \rangle. \quad (3.17)$$

The transformation behavior of the pair of functions ($|J \ell M \rangle, |J - \ell M \rangle$) can be written in matrix representation as follows

$$E_\epsilon^* \begin{pmatrix} |J \ell M \rangle \\ |J - \ell M \rangle \end{pmatrix} = \begin{pmatrix} 0 & (-1)^{J+\ell} \exp(-i\ell\epsilon) \\ (-1)^{J+\ell} \exp(i\ell\epsilon) & 0 \end{pmatrix} \begin{pmatrix} |J \ell M \rangle \\ |J - \ell M \rangle \end{pmatrix} \quad (3.18)$$

with the trace and character, $\chi(E_\epsilon^*) = 0$. Similarly with help of Eqs. (3.4)-(3.7) and the parity of the symmetric top wavefunction, Eq. (3.14), the following characters are obtained for all EMS group operation: $\chi(E_\epsilon) = 2 \cos(\ell\epsilon)$, $\chi(p_\epsilon) = 0$, and $\chi(p_\epsilon^*) = (-1)^\ell \cos(\ell\epsilon)$. Since an isomorphism exists between the EMS group and its associated point group, both groups share the same character Table (Bunker, 1979; Papousek and Aliev, 1982). From the character table of the $D_{\infty h}$ point group

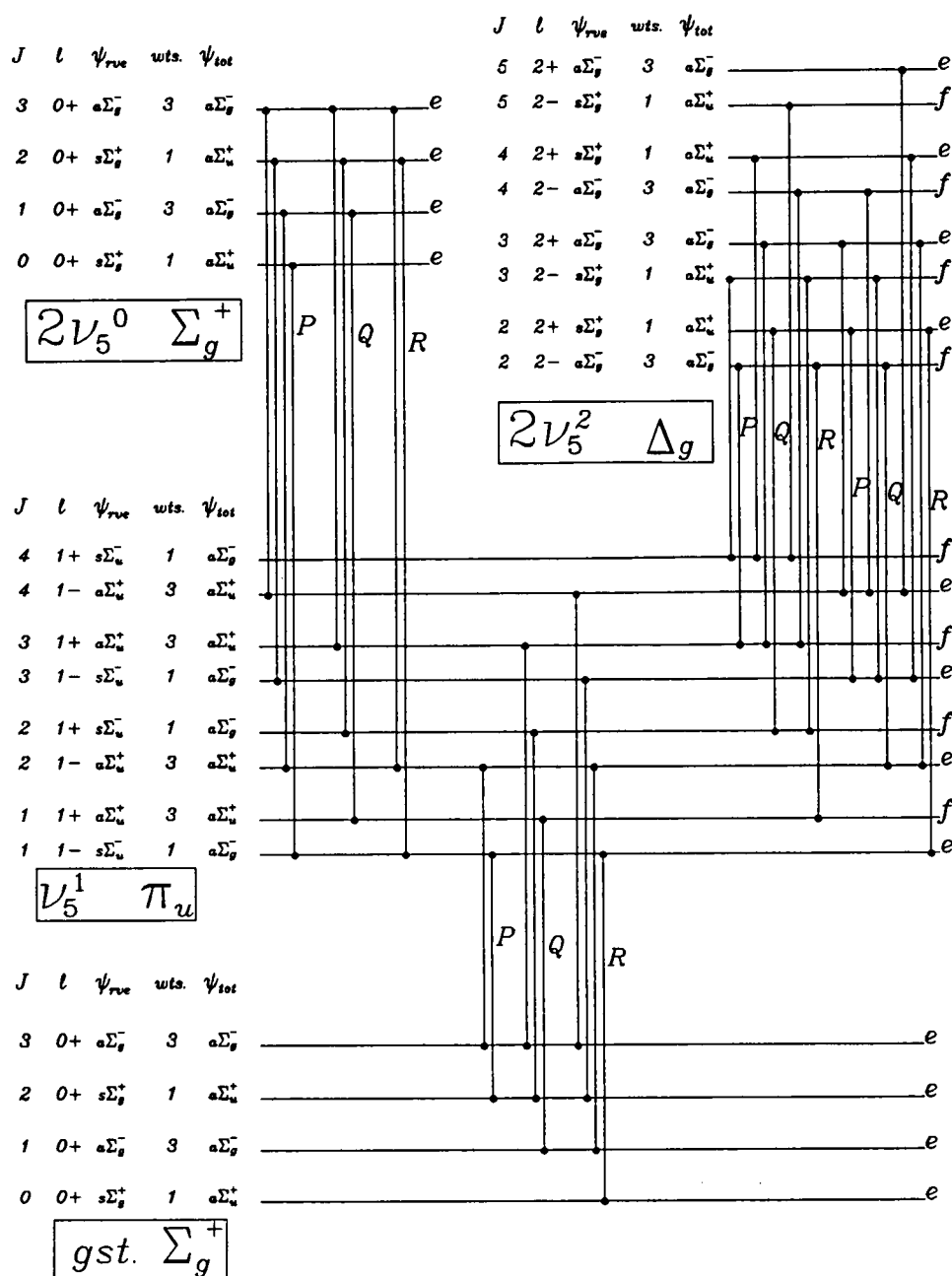


Figure 3.5. Rovibrational level diagram of acetylene, Part I. Shown are the ground state, ν_5 , and $2\nu_5$ states indicating symmetry species, nuclear statistical weights, and allowed electric dipole transitions.

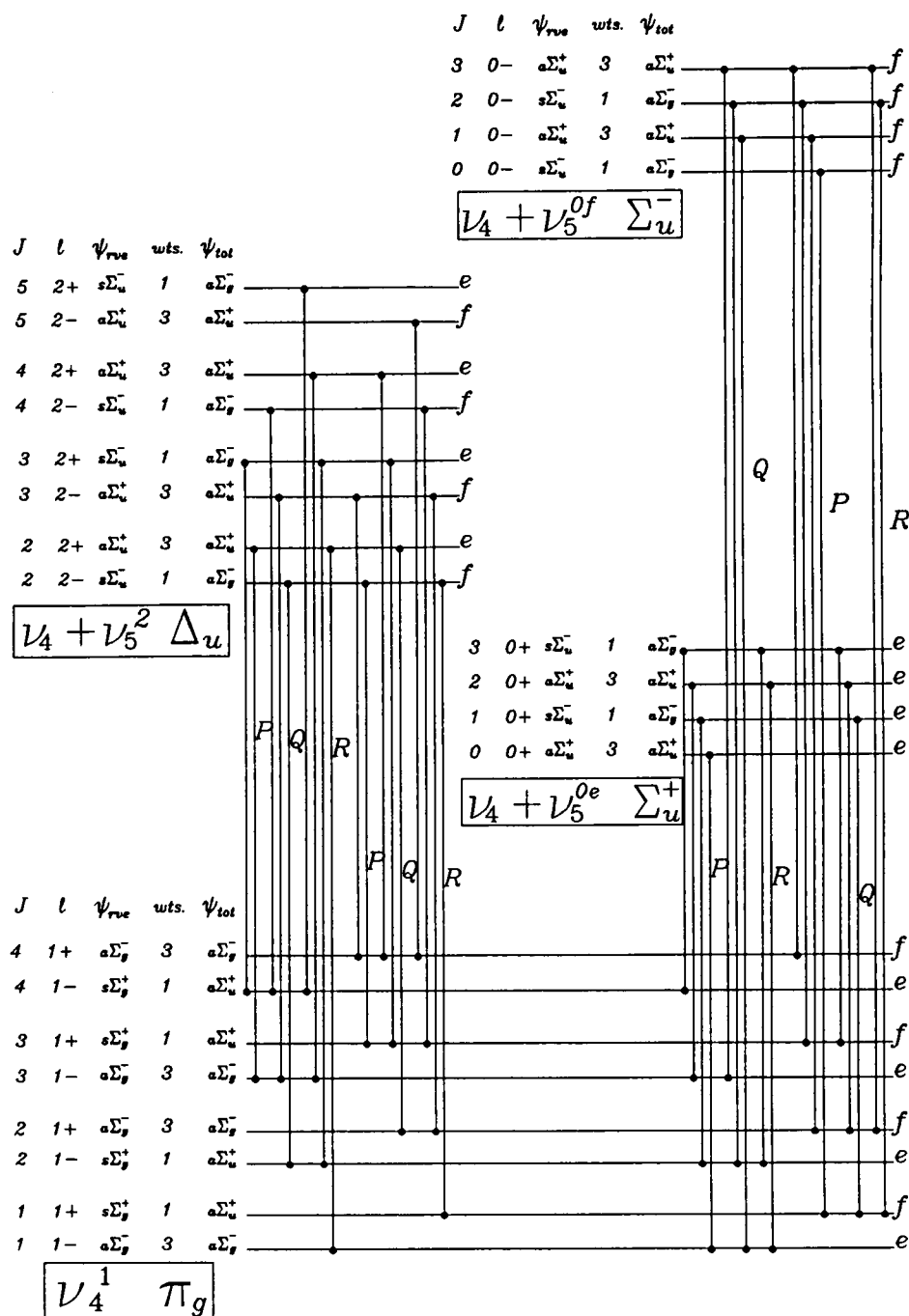


Figure 3.6. Rovibrational level diagram of acetylene, Part II. Shown are the ν_4 and $\nu_4 + \nu_5$ states including symmetry species, nuclear statistical weights, and allowed electric dipole transitions.

(Appendix B) can be deduced that the rotational states transform like the irreducible species of the ℓ dimensional irreducible representation Σ_g^+ , Σ_g^- , Π_g , Δ_g , Φ_g etc. for $\ell = 0$ (J even, J odd), 1, 2, 3, ..., respectively.

Since the transformation for the third Euler angle is defined under the EMS group, the ambiguity of the transformation of the vibrational angle is removed. Using Eqs. (3.8–3.10) for the polar angles α_4 and α_5 , and Eqs (3.3–3.6), the transformation of the vibronic angle $\alpha'_4 = \alpha_4 - \chi$ and $\alpha'_5 = \alpha_5 - \chi$ can be summarized as follows

$$E_\epsilon(\alpha'_4, \alpha'_5) = (\alpha'_4 + \epsilon, \alpha'_5 + \epsilon), \quad (3.19)$$

$$E_\epsilon^*(\alpha'_4, \alpha'_5) = (-\alpha'_4 - \pi + \epsilon, -\alpha'_5 + \epsilon), \quad (3.20)$$

$$p_\epsilon(\alpha'_4, \alpha'_5) = (-\alpha'_4 + \epsilon, -\alpha'_5 + \epsilon), \quad (3.21)$$

and

$$p_\epsilon^*(\alpha'_4, \alpha'_5) = (\alpha'_4 - \pi + \epsilon, \alpha'_5 + \epsilon). \quad (3.22)$$

Characters of the transformation of the pairs $(|v_4, \ell_4\rangle, |v_4, -\ell_4\rangle)$ and $(|v_5, \ell_5\rangle, |v_5, -\ell_5\rangle)$ can be similarly obtained as for the rotational wave function. By comparison with the character table given in Appendix B, the vibrational species for the symmetric bend ν_4 are Σ_g^+ , π_g , Δ_g , Φ_g etc. and for the antisymmetric bend ν_5 Σ_g^+ , π_u , Δ_g , Φ_u etc. for $\ell = 0, \pm 1, \pm 2, \pm 3, \dots$, respectively. The same results are obtained by applying the symmetry operation of the corresponding point groups

In Figs. 3.3 and 3.4, the Eckart axes are reoriented after a MS group operation by keeping the molecular x axis fixed and switching the y axis in order to preserve a right-handed axis system after a MS-group operation. It is also conceivable to keep the y axis fixed and switch the x axis instead. In the latter case, it can be shown that the transformation property of the polar angles α_4 , α'_4 , α_5 , and α'_5 differ from the results given in Eqs. (3.8–3.10, 3.19–3.22). However, by applying the phase convention of the symmetric top function, Eq. (3.12), for a rotation angle $\alpha = \pi$ corresponding to an equivalent rotation of π about the y axis, the parity of the rovibrational species as stated in Table 3.2 remain unaltered. The new set of vibrational angles obtained lead to the same irreducible species, and thus the reorientation of the Eckart axes by keeping the x axis fixed or by keeping the y axis fixed are equivalent.

Table 3.3. Nuclear statistical weights for transitions of $^{12}\text{C}_2\text{H}_2$. Depending on the rovibrational symmetry of the level and the nuclear statistics, the statistical weight for intensities is either 1 or 3. *e* and *f* symmetry labels are explained in Section 3.5.

Lower Level Symmetry	<i>J</i>	Symmetry Label	nucl. stat. wts.
<i>g</i>	even/odd	<i>e</i>	1/3
	even/odd	<i>f</i>	3/1
<i>u</i>	even/odd	<i>e</i>	3/1
	even/odd	<i>f</i>	1/3

3.4 Nuclear Spin Statistical Weights

From nuclear statistical weights, the proper ratio of intensity alternation of rotational lines within a vibrational band can be derived, which is necessary to compute band intensities. The statistical weights depend on the nuclear spin statistics and the symmetry of the overall wavefunction including the spin functions (Herzberg, 1945, Wilson, 1935). Half integral spin particles follow Fermi-Dirac statistics for indistinguishable particles in agreement with the Pauli exclusion principle. If there is an even number of pairs of identical nuclei with half integral spin, the permutation operation *p* will leave the overall wavefunction unaltered, according to the Bose statistics, while for those molecules with an odd number of pairs of half integral spins, the sign of the overall wavefunction will be reversed under *p*.

Since the two carbon-12 nuclei possess no nuclear spin and the hydrogen nuclei are spin 1/2 particles, the overall wavefunction must contain the species $\alpha\Sigma$ according to the Fermi-Dirac statistics, which means the direct product of the rovibronic species and spin species must contain the correct species of the overall wavefunction, i.e. $\alpha\Sigma$. The two hydrogen spins can couple to a total spin of $S = 0$ and $S = 1$. There are three symmetric spin function for $S = 1$ and one antisymmetric spin combination for $S = 0$. From the definition of the *p* and *p*^{*} operations of the MS group, the symmetric spin functions are of species $s\Sigma_g^+$ and the antisymmetric spin function of species $\alpha\Sigma_u^+$. Spatial operations such as the inversion operation *E*^{*} do not effect the nuclear spin functions.

From the required symmetry of the overall wavefunction immediately follows that rovibrational species of even parity (under the MS group operation *p*) can only combine with the antisymmetric spin function and those of odd parity only with the symmetric spin functions. Consequently the statistical weight ratio, antisymmetric to symmetric rovibronic states, are three to one, leading to the observable alternation in intensities with the same ratio observed in all fundamentals and hot-

bands of acetylene. Statistical weights for acetylene's rotation-vibration bands are given in Table 3.4. To each rovibrational level in Figs. 3.5 and 3.6 nuclear statistical weights are assigned.

The inhibition of permutation operation in case of non-symmetric linear molecules of $C_{\infty v}$ symmetry drops the restriction of the overall wavefunction to obey the Fermi or Bose statistics. The nuclear statistical weights are set to one in this case which is in accordance with the lack of observed intensity alternation in the infrared spectra of these molecules. By omitting the last two columns describing the statistical weight and the overall symmetry species in Figs 3.4 and 3.5 as well as dropping all s, a and g, u labels in the level diagram, the same diagram can be used to describe the level structure of a $C_{\infty v}$ molecule.

3.5 General Phase Convention for Rovibrational Eigenstates

Preceding a discussion on a general phase choice for the molecular eigenstates of multiple excited bending vibrations, it is useful first to introduce e and f labels which distinguish the two sublevels of opposite symmetry within an ℓ -parity doublet. According to Brown *et al.* (1975), the sublevels of a parity doublet which irreducibly transform like the rovibrational states belonging to a Σ^+ vibrational species are labelled e and those which transform like the rovibrational states of a Σ^- vibrational state are labelled f . In other words, *the sublevels with rovibrational species Σ^+ for even J are e levels* (positive parity under E^* operation), *and the sublevel with rovibrational species Σ^- for even J are f labels* (negative parity under E^*). Due to the parity alternation within a sublevel with ascending J , the opposite statement is true for odd J (Watson, 1991). The assignment of these labels are shown in Figs. 2.4, 3.5 and 3.6.

The e, f labelling supersedes the earlier c and d labelling scheme, which are used inconsistently throughout the literature. Mulliken (1931) assigned c and d labels according to the symmetry species of the lowest lying rovibrational states within a doublet. Σ^+ and Σ^- species lead in that case to the labels c and d , respectively. Using Mulliken's definition c and d labels are e and f if ℓ is even, and vice versa, if ℓ odd (Mulliken 1931). Herzberg's c, d labels introduced for electronic singlets in diatomic molecules are compatible with the e and f labels (Herzberg 1950).

The $+$ and $-$ subblock of the factorized Hamiltonian (Table 2.4) can be identified with the e and f labels. One component of the ℓ -parity doublet belongs to one subblock of the factorized Hamiltonian and the other component to the second subblock, such that each subblock belongs either to the e or f states within a vibrational multiplet. The correct assignment depends on the general phase choice of the rovibrational wave function under the inversion E^* . For acetylene, various phase conventions are reported (Plíva, 1972b; Hietanen, 1983; Watson *et al.*, 1982; Herman *et al.* 1991).

The phase conventions, commonly used, can be summarized as follows

$$E^* |v_4^{\ell_4}, v_5^{\ell_5}; J, \ell > + (-1)^{J+n(\ell, \ell_t)} |v_4^{-\ell_4}, v_5^{-\ell_5}; J, -\ell > . \quad (3.23)$$

The e and f eigen states are then characterized by

$$|v_4^{\ell_4}, v_5^{\ell_5}; J, \ell; e > = \frac{1}{\sqrt{2}} \{ |v_4^{\ell_4}, v_5^{\ell_5}; J, \ell > + (-1)^{n(\ell, \ell_t)} |v_4^{-\ell_4}, v_5^{-\ell_5}; J, -\ell > \} \quad (3.24)$$

and

$$|v_4^{\ell_4}, v_5^{\ell_5}; J, \ell; f > = \frac{1}{\sqrt{2}} \{ |v_4^{\ell_4}, v_5^{\ell_5}; J, \ell > - (-1)^{n(\ell, \ell_t)} |v_4^{-\ell_4}, v_5^{-\ell_5}; J, -\ell > \}. \quad (3.25)$$

Plíva, Hietanen, and Kauppinen chose $n(\ell, \ell_t) = 0$ and in this case the $+$ block in the factorized Hamiltonian describes the e energy levels, and the $-$ block the f energy levels. Defining $n(\ell, \ell_t) = \ell$, the reverse is true for all odd total vibrational quantum states, for instance ν_4 , $2\nu_4 + \nu_5$, $3\nu_5$ etc. This phase choice was introduced by Watson, Herman and co-workers (Watson *et al.* 1982; Herman *et al.*, 1991). As a consequence of the different phase choices, opposite signs for the interaction parameter q_t were reported. The first phase choice leads to negative values and the latter to positive values assuming the f level in the split doublet energetically lies above the e level as it is the case for ν_4 and ν_5 of acetylene. The lowest vibrational state with vibrational ℓ -resonance is $\nu_4 + \nu_5$, for which both phase choices lead to the same assignment of e and f blocks. Thus the vibrational ℓ -doubling constant has the same sign in both phase conventions.

By combining the parity of both bending modes ν_4 and ν_5 (Table 3.2) in sense of the direct product of the two vibrational symmetry species, a phase choice of

$$n(\ell, \ell_t) = \sum_t \ell_{t_a}, \quad (3.26)$$

where the summation goes over the projection quantum number ℓ_t of all antisymmetric bending modes, seems appropriate. However, as Amat and Nielsen (1958a) pointed out, ℓ_t is not a good quantum number since the potential in the Hamiltonian also depends on the difference of the two vibrational polar angles of the bending modes.

Yamada (1983) discussed general phase choices for linear molecules based on the phase choice of the matrix elements of the rotational and vibrational lowering and raising operators. From

Table 3.4. Sign of ℓ -doubling constants and parity. The effect on the sign of ℓ -doubling constant is given here for the case that the e level of the parity doublet lies above the f energy level. The + and - signs refer to the sign of the symmetry adapted basis function; g and u are the symmetry labels of the vibrational mode. If the f level is above the e level energy, all signs have to be reversed.

Vibrational State	$n(\ell, \ell_i) = 0$	$n(\ell, \ell_i) = \ell$	$n(\ell, \ell_i) = \sum_i \ell_{i_a}$
$v_t = 1$ e upper level f lower level	+ $q_t > 0$ -	- $q_t < 0$ +	$+(g), -(u)$ $-(g), +(u)$ $(g) q_t > 0; (u) q_t < 0$
$v_t = 1; v_{t'} = 1$ e upper level f lower level	+ $r_{tt'} > 0$ -	- $r_{tt'} > 0$ +	$+(g), -(u)$ $-(g), +(u)$ $(g) r_{tt'} > 0; (u) r_{tt'} < 0$

the harmonic approximation for the ℓ -doubling constant, it is apparent that q_t is independent of the phase choice (Yamada, 1983). It can be shown, that in case of acetylene q_4 and q_5 is positive, and by adding a phase to this constant, these constants can be made either both positive or negative. For this reason, the $n(\ell, \ell_i) = \ell$ phase choice was adopted in this study. This arbitrary phase choice is in conflict with the results for $v_4 = 1$ (Table 3.2) derived from geometrical considerations. The same is true for $n(\ell, \ell_i) = 0$ and the results in Table 3.2 for $v_5 = 1$. The phase choice adopted in this study leads to positive ℓ -type doubling constants if in the $v_4 = 1$ and $v_5 = 1$ states the f -level lies above the e -level as is the case for acetylene. This phase choice also agrees with the convention set forth by Cartwright and Mill (1970). For the isotopic $^{13}\text{C}^{12}\text{CH}_2$ species for which no true center of mass symmetry exists, the phase choice of the major isotope was used. The influence of the phase choices discussed here on the sign of the ℓ -doubling parameters are summarized in Table 3.4.

3.6 Selection Rules for Electric Dipole Transitions

In a quantum mechanical sense the intensity of an individual transition is a measure of the probability to undergo a transition between two molecular states. This probability is essentially proportional to the electric dipole moment matrix element, involving the product of the molecular wavefunction of the lower and upper states and the dipole moment operator. As an observer in the space-fixed axis and by recognizing that in the presence of no external fields, the space is isotropic, the discussion can be restricted to the dipole moment operator along the space fixed Z -axis. In order to evaluate

the transition moment, the dipole moment operator needs to be expressed in terms of body-fixed coordinates, i.e.

$$\mu_Z = \lambda_{xZ}\mu_x + \lambda_{yZ}\mu_y + \lambda_{zZ}\mu_z \quad (3.27)$$

It can be shown that μ_z transforms like a translation along the z -axis, i.e. T_z and λ_{zZ} , which depends on the Euler angles, like the rotation about the z axis, i.e. R_z (Hougen 1962b). The x and y components of Eq. (3.21), together, can be shown to transform the same way. The irreducible species of translation and rotation are usually given in character tables of the point group (Appendix B), and as a general rule the transition moment due to a electric dipole moment is non-vanishing, if the direct product of the species of translation and rotation is contained in the direct product of the species of the initial and final state, or

$$\Gamma(R_z) \times \Gamma(T_z) \subset \Gamma(\psi''_{rv}) \times \Gamma(\psi'_{rv}) \quad (3.28)$$

(Hougen 1962b), where the double and single prime indicate the originating and final state, respectively. It follows that the electric dipole moment operator is of species $s\Sigma_u^-$ and thus the following transitions are allowed

$$s\Sigma_g^+ \leftrightarrow s\Sigma_u^- \quad (3.29)$$

and

$$a\Sigma_u^+ \leftrightarrow a\Sigma_g^- \quad (3.30)$$

(Herzberg, 1945; Bunker, 1979). For the vibrational and rotational parts of the transition considered separately, the selection rules are

$$\Delta\ell = 0; \quad \Delta J = \pm 1 \quad (\mu_z \neq 0; \mu_x = \mu_y = 0) \quad (3.31)$$

for parallel bands and

$$\Delta\ell = \pm 1; \quad \Delta J = 0, \pm 1 \quad (\mu_z = 0; \mu_x \neq 0; \mu_y \neq 0) \quad (3.32)$$

for perpendicular bands. (Papoušek and Aliev, 1982; Allen and Cross, 1963). The selection rules can be conveniently expressed using the e and f label as follows

$$e \leftrightarrow e, \quad f \leftrightarrow f \quad (3.33)$$

for P and R branch transitions ($\Delta J = \pm 1$) and

$$e \leftrightarrow f \quad (3.34)$$

for Q branch transitions ($\Delta J = 0$). In Figs. 3.5 and 3.6 allowed infrared transition between groundstate, ν_5 , ν_4 , $\nu_4 + \nu_5$, and $2\nu_5$ are indicated for acetylene. The ν_4 fundamental is not infrared active but can be observed in Raman spectra, for instance.

CHAPTER 4

ROTATION-VIBRATION ANALYSIS OF ACETYLENE IN THE ν_5 REGION

4.1 Introduction

A total of 23 infrared active bands in the bending mode region of acetylene near $13.6\mu\text{m}$ have been analyzed. Vibrational states involved in the observed transitions range from the ground state up to three excited quanta, i.e. $2\nu_4 + \nu_5$, $\nu_4 + 2\nu_5$, and $3\nu_5$. The line position analysis of acetylene's absorption bands is based upon FT-spectrometric data obtained at the McMath Solar Telescope Facility on Kitt Peak, Arizona.

The study reported here is an extension to the recent LSCD (Lower State Combination Difference) determination of molecular parameters involving the fundamental ν_5 and the seven strongest one quantum hotbands (Hillmann *et al.* 1991). Since the rotation-vibration Hamiltonian (see Table 2.3) contains non-linear off-diagonal matrix elements due to vibrational and rotational ℓ -type doubling, a non-linear least squares fitting routine was developed to fit observed frequency directly to the energy level differences. The structure of the least squares fitting program, which utilizes the numerical diagonalization of the Hamiltonian and uses Singular Value Decomposition (SVD) to obtain improved molecular parameters in iterative steps, is described and discussed in some detail. The unitary transformation, which diagonalizes the Hamiltonian, contains the mixing coefficient for the perturbed eigenfunctions. This allows the determination of the intensity perturbation due to the mixing of eigenstates as a result of ℓ -type doubling (Chapter 5).

The energy level fit is divided into two parts. First the results of fitting the ν_5 fundamental and its seven strongest hotbands $\nu_4 + \nu_5 \leftarrow \nu_4$ and $2\nu_5 \leftarrow \nu_5$ are reported for the major isotope $^{12}\text{C}_2\text{H}_2$ and for the isotopomer $^{13}\text{C}^{12}\text{CH}_2$. Secondly, the results of the fit of the two quantum hotbands of the major isotopomer terminating in $2\nu_4 + \nu_5$, $\nu_4 + 2\nu_5$, and $3\nu_5$ are presented followed by a discussion of the results obtained in this study.

Emphasis is here put in the effect of vibrational and rotational ℓ -doubling on the mixing of the molecular eigenfunctions, which leads to some important consequences for the intensity perturbation of acetylene's absorption bands. A detailed intensity analysis, based on results obtained in this chapter, will follow in Chapter 5.

4.2 Experimental Details

The acetylene spectrum was recorded with the 1 m Fourier transform spectrometer operated at the McMath Telescope at the National Solar Observatory, National Optical Astronomy Observations, Tucson, Arizona as described by Hillman *et al.* (1991). By using a double pass configuration a nominal spectral resolution of 0.0025 cm^{-1} was achieved (Jennings *et al.* 1985). In the double pass configuration, catseye reflectors in two arms of the FT spectrometer can be moved on slides, which effectively doubles the maximum allowable path difference compared to conventional FT spectrometers with one movable mirror arm. Doubling the maximum allowable path difference in a FT spectrometer improves the spectral resolution by a factor of two (Jennings *et al.* 1985).

Details of the operation and set-up of the FT-spectrometer are described elsewhere (Hillman *et al.* 1991; Jennings *et al.* 1985). Unapodized spectra were accumulated in the optical density range of 0.1 Torr-cm to 1200 Torr-cm. The range of optical densities available permitted the assignments of hot and hot-hotband transitions. Lines of $^{13}\text{C}^{12}\text{CH}_2$ were visible in the spectra from the abundance of this species in a natural acetylene sample. The intensities of its fundamental and one quantum hotbands are on the order of the intensities of the one and two quantum hotbands of the major isotopomer, respectively. Most spectra were recorded at ambient temperature. Even at room temperature, the presence of acetylene's hotbands is quite strong.

Calibration of data used NH_3 lines of ν_2 at 850cm^{-1} . The resulting calibration was checked with H_2O background features at the low frequency end at about 600cm^{-1} . The high linearity of the wave number scale of Kitt Peak FTS data lead to a highly accurate determination of ground state parameters, $\nu_4 = 1$, and $\nu_5 = 1$ parameters by using lower state combination differences (LSCD) as reported by Hillman *et al.* (1991).

4.3 Non-Linear Least Squares Procedure

Fitting observed frequencies from spectroscopic measurements to a quantum mechanical model, i.e. the appropriate Hamiltonian, involves at least two states, the lower and upper states where the transitions originate and terminate. If one fits the observed transitions directly, differences in vibrational states are determined rather than the eigenstates themselves. As a consequence high correlations between molecular parameters may result from the fitting. On the other hand, using linear combination differences to single out individual vibrational states possess the disadvantage that information on one of the participating states, in most cases the upper state, is wasted. By including several vibrational states in a direct transition frequency fit, it is possible to derive sufficient information to model the spectrum with a global physically meaningful Hamiltonian. By limiting a transition frequency fit to one or even a few absorption bands, the data is in many cases not

sufficient to retrieve molecular parameters uniquely. From such a fit only effective parameters in terms of rotation-vibration constants of the appropriate Hamiltonian can be derived. These fits are in this context defined as effective parameter fits as opposed to global fits, which involve several vibrational states and molecular bands simultaneously.

Due to off-diagonal matrix elements, non-linear in the rotational quantum number J , in the Hamiltonian of a linear molecule, an iterative non-linear least squares procedure has to be applied. If N observed transitions are fit to a M parameter model Hamiltonian, the following normal equations can be used,

$$\nu_i^{(\text{obs})} - \nu_i^{(\text{cal})} = \sum_{j=1}^M \frac{\partial \nu_i^{(\text{cal})}}{\partial a_j^{(n)}} \delta a_j^{(n)}; \quad i = 1, N, \quad (4.1)$$

where $\nu_i^{(\text{obs})}$ and $\nu_i^{(\text{cal})}$ are the i th observed and theoretical (calculated) line positions, $a_j^{(n)}$ is the best estimate for the j th molecular parameter after n iteration, and $\delta a_j^{(n)}$ the correction to the parameter for which the normal equations are solved to obtain an improved estimate, i.e.

$$a_j^{(n+1)} = a_j^{(n)} + \delta a_j^{(n)}. \quad (4.2)$$

Calculated frequencies are obtained from the eigenvalues after diagonalization of the Hamiltonian. If we describe the diagonal Hamiltonian with $\mathbf{h}$, and the off-diagonal Hamiltonian with $\mathbf{H}$, the frequencies are calculated as follows

$$\nu_i^{(\text{cal})} = h'_{kk} - h''_{\ell\ell}, \quad (4.3)$$

where the primes indicate the upper and lower state Hamiltonians, respectively, and k and ℓ are indices indicating the proper position of the diagonal element. $\mathbf{h}'$ and $\mathbf{h}''$ are obtained by an unitary transformation, i.e. $\mathbf{h} = \mathbf{U}^T \mathbf{H} \mathbf{U}$. Employing the Hellmann-Feynman theorem (Hellmann 1937, Feynman 1939, Musher 1966) in the form cast by Castellano and Bothner-By (1964), the derivatives can be easily determined, i.e.

$$\frac{\partial \nu_i^{(\text{cal})}}{\partial a_j} = \left((\mathbf{U}')^T \frac{\partial \mathbf{H}'}{\partial a_j} \mathbf{U}' \right)_{kk} - \left((\mathbf{U}'')^T \frac{\partial \mathbf{H}''}{\partial a_j} \mathbf{U}'' \right)_{\ell\ell}, \quad (4.4)$$

using the same transformation which diagonalizes the Hamiltonian. The Hellmann-Feynman theorem was first applied to the rotation-vibration problem of molecules by Rowe and Wilson (1975).

The unitary transformation here effectively serves a threefold purpose, *i*) to obtain the eigenvectors and level energies, *ii*) to calculate the first derivatives necessary in the iterative least squares procedure, and *iii*) to calculate the effective transition dipole moment from the mixing coefficients of the eigenstates.

The normal equations in form of Eq. (4.1) are in matrix form and the solution can be obtained by inverting the derivative matrix $\mathbf{D}$, whose elements are defined by Eq. (4.3). A stable inversion procedure is to apply Singular Value Decomposition (Wilkinson and Reinsch 1971; Press *et al.* 1986), which factorizes the matrix into three factor matrices, the column-orthogonal $N \times M$ matrix $\mathbf{X}$, the $M \times M$ diagonal singular value matrix $\mathbf{W}$, and the $M \times M$ orthonormal square matrix $\mathbf{V}$, in the following way

$$\mathbf{D} = \mathbf{X}\mathbf{W}\mathbf{V}^T \longleftrightarrow \mathbf{D}^{-1} = \mathbf{V}\mathbf{W}^{-1}\mathbf{X}^T \quad (4.5)$$

If one or more singular values in $\mathbf{W}$ are small compared to the maximum singular value (for instance compared to machine precision, i.e. a factor of 10^{-12}), an indication is given that the matrix is nearly singular and a solution may not be possible. This is the case if, for instance, two or more parameters are linearly dependent. Press *et al.* (1986) propose a simple recipe to overcome the problem by setting the inverse of the very small singular values to zero and calculating the inverse of the reduced matrix according to Eq. (4.5). It can be shown in that case that the "solution" of the normal equation still yields the geometrical closest estimate for the parameter correction vector (Press *et al.* 1986). This is advantageous in a situation where the parameters vary by several orders of magnitude or if high correlations exist between parameters.

It is common to cast the normal equation Eq. (4.1) in a more compact and symmetric form by multiplying it with the transpose of the Jacobian matrix, $\mathbf{D}^T$. Round-off problems may occur (Brodersen 1990; Wilkinson and Reinsch, 1971) and did not permit the determination of the sextic constants H_v . Therefore, the compact form was avoided. Brodersen (1990) applied an alternative SVD procedure to the vibrational problem by using a scaling scheme to overcome the problem of ill-conditioned matrices and round-off errors.

Eq. (4.1) is equivalent to a linearization of the least squares problem and the typical statistics for multivariate linear regression can be applied (Bevington 1969; Draper and Smith, 1980). The correlation matrix $\mathbf{C}$ from which standard deviations and correlation coefficients can be read is approximately given by

$$\mathbf{C} \approx \mathbf{V}\mathbf{W}^{-2}\mathbf{V}^T \sigma^2, \quad (4.6)$$

where σ is the overall standard deviation defined as

$$\sigma = \sqrt{\sum_{i=1}^N \frac{(\nu_i^{(\text{obs})} - \nu_i^{(\text{cal})})^2}{N - M}} \quad (4.7)$$

In case of near singularity of the Jacobian matrix, the column in the orthonormal matrix $\mathbf{V}$ corresponding to the small singular value usually indicates the linear combination of the highly correlated parameters. The correlation matrix as well as the column of the $\mathbf{V}$ -matrix, can be therefore a good indicator for the proper choice of parameters to be fitted. To avoid the problem of near singularity, it is necessary to use effective parameters to reduce the problem, otherwise the value obtained for a highly correlated parameter is physically meaningless.

The fit considerably improves if a weighting scheme is applied and for most bands, bi-weights were employed (Beaton and Tukey, 1974; Daunt *et al.* 1984), which are defined as follows

$$w_i = \begin{cases} \sqrt{1 - \left(\frac{\nu_i^{(\text{obs})} - \nu_i^{(\text{cal})}}{m\sigma}\right)^2}; & |\nu_i^{(\text{obs})} - \nu_i^{(\text{cal})}| < m\sigma \\ 0; & |\nu_i^{(\text{obs})} - \nu_i^{(\text{cal})}| \geq m\sigma \end{cases} \quad (4.8)$$

An alternative weighting scheme uses a sharp cut-off, i.e.

$$w_i = \begin{cases} 1; & |\nu_i^{(\text{obs})} - \nu_i^{(\text{cal})}| < m\sigma \\ 0; & |\nu_i^{(\text{obs})} - \nu_i^{(\text{cal})}| \geq m\sigma \end{cases} \quad (4.9)$$

In most fits a bi-weighting scheme was preferred. Although Eq. (4.8) drops rapidly to zero near the limit; nevertheless, the continuity has some advantages over a sharp cut-off. Using weights for the observed frequencies in the least squares fit serves two purposes, first, to improve the convergence of the iterative process and, secondly, misassigned transitions or transition frequencies of lines, which are blended with other absorption features, are excluded from the fit if their standard deviation is too high.

If the initial guess for the molecular parameters to be fitted is close to the final answer, the least squares procedure usually converges in a few iterations. During the first two iteration no weighting is employed. Every second iteration, thereafter, weights are modified based on the most recent weighted standard deviation. Common values for the allowable deviation for non-zero weighted frequencies were chosen to be between 4.5–5 standard deviations. Iteration stops when,

either the improvement of the overall sum square error, Eq. (4.7), becomes negligible or the F -test for significance of regression in the linearized fit decreases below a preset value (Draper and Smith 1980).

It should be noted that from the F -number in this fit, only the significance of the regression for the fit to the corrections of the parameters but not the parameter itself can be concluded. It should be noted, that two standard deviations are calculated during each iteration, the sum square error of the observed frequency as given by Eq. (4.7) and the standard deviation of the linearized fit. The correlation matrix for the linearized fit is exactly given by Eq. (4.6) if the σ of the linearized fit is used instead of Eq. (4.7).

In the case of the two quantum hotbands, particularly the combination bands, convergence proved to be slow or impossible due to the high correlation between the vibrational parameters. In order to improve the iterative process, the fitting scheme was altered as follows. Starting with a weighting factor limit of 7 or higher in terms of the weighted standard deviation, the factor is reduced by 0.5, whenever no further improvement is possible. The weights are then readjusted and the fitting continues down to a chosen lower limit, usually 4–5 standard deviations. The altered iterative scheme also worked well for the lower quantum hotbands and was adopted for all fits.

The non-linear least squares program was written in FORTRAN and a sample program can be found in Appendix D.

4.4 The Fundamental ν_5 , $\nu_4 + \nu_5 \leftarrow \nu_4$, and $2\nu_5 \leftarrow \nu_5$ of $^{12}\text{C}_2\text{H}_2$ and $^{13}\text{C}^{12}\text{CH}_2$

A total of 876 observed transitions of the major isotope and 595 transitions of the singly substituted carbon-13 isotopomer were subjected to a global and effective least squares fit. The range of observed J values in each band is detailed in Table 4.1 and ranged up to 40 to 50 for normal acetylene and 30 to 40 for the ^{13}C species. The reduced Hamiltonian used in the analysis is given in Table 4.1. A common factor of 2 in q_i^{eff} and a factor of 8 in ρ_t and $\rho_{tt'}$ were omitted as compared to Table 2.2. The ℓ -doubling constant, q_t , differ in their magnitude by a factor of two compared with Herman *et al.* (1991), Hietanen and Kauppinen (1981), and Hietanen (1983).

As a result of the global fit encompassing the ν_5 fundamental and the seven hotbands $\nu_4 + \nu_5 \leftarrow \nu_4$, and $2\nu_5 \leftarrow \nu_5$, a set of 29 molecular constants were determined. The molecular constants retrieved from the fit along with the standard deviation from the least squares fit are summarized in the first column in Tables 4.2 and 4.3 for $^{12}\text{C}_2\text{H}_2$ and in Tables 4.4 and 4.5 for $^{13}\text{C}^{12}\text{CH}_2$, respectively. The quality of the spectrum can be seen in Fig. 4.1–4.3, where assignments are given for some Q -branches of fundamentals and hotbands for both isotopomers. Some of the molecular parameters in the global fit are effective rotation–vibration constants, since the ν_4 fundamental

Table 4.1. Observed transitions of fundamental ν_5 and the seven strongest one quantum hotband of $^{12}\text{C}_2\text{H}_2$ and $^{13}\text{C}^{12}\text{CH}_2$.

Band	$^{12}\text{C}_2\text{H}_2$				$^{13}\text{C}^{12}\text{CH}_2$			
	P	$J_{\max}$ Q	R	No. of Transitions	P	$J_{\max}$ Q	R	No. of Transitions
$\nu_5^{1e,1f}$	47	47	51	141	42	35	44	111
$\nu_4 + \nu_5^{0e} \leftarrow \nu_4^{1e,1f}$	41	38	45	113	34	32	36	88
$\nu_4 + \nu_5^{0f} \leftarrow \nu_4^{1e,1f}$	40	40	42	113	32	15	32	75
$\nu_4 + \nu_5^{2e} \leftarrow \nu_4^{1e,1f}$	37	26	41	90	30	—	33	56
$\nu_4 + \nu_5^{2f} \leftarrow \nu_4^{1e,1f}$	42	42	44	119	32	—	34	61
$2\nu_5^{0e} \leftarrow \nu_5^{1e,1f}$	42	32	46	108	34	29	34	84
$2\nu_5^{2e} \leftarrow \nu_5^{1e,1f}$	35	—	40	73	27	—	30	52
$2\nu_5^{2f} \leftarrow \nu_5^{1e,1f}$	41	40	45	119	30	12	36	68

cannot be observed in conventional infrared spectroscopy. The set of 29 parameters are considered sufficient to reproduce the high precision data.

A second fit to effective molecular constants was undertaken for the combination bands and the excited states $\nu_5 = 0, 1, 2$, separately. The results of this fitting are summarized for comparison in the second column of Tables 4.3–4.6. Although the standard deviations from all fits are on the order of tenths of a milli-wavenumber, differences were noticed in some of the molecular parameters, in particular q_4^J , q_5^J , ρ_5 , and ρ_{45} . The values of these parameters clearly depend on the choice of the parameter set, either global or effective constants. It was observed that the fit to effective parameters yielded slightly better results, i.e. the fraction of rejected transitions is lower at comparable standard deviations. It is also evident that some correlation among the parameters exist and that by choosing a different model the correlation pattern will be altered.

The molecular parameters, as derived from two separate least squares fits, are considered to be the best estimates. A good check for the quality of the fits are residual plots as a function of the rotational quantum number J for each hotband. Although the standard deviations might be satisfactorily low, residual correlation might still exist. For instance, by introducing β^{55} , an

Table 4.2. Reduced Hamiltonian of acetylene used in the least squares fit. By forming Wang basis function, i.e. $\Psi_\ell^\pm = \frac{1}{\sqrt{2}}\{|v_4^{\ell_4}, v_5^{\ell_5}; J, \ell > \pm|v_4^{-\ell_4}, v_5^{-\ell_5}; J, -\ell >\}$ the Hamiltonian is brought into block-diagonal form, each sub-block either labelled e or f (see Section 2.4). The levels $(v_4, v_5) = (1, 0), (2, 0), (3, 0), (1, 2)$ can be obtained by exchanging the indices 4 and 5 in the appropriate Hamiltonian. Here $M = J(J+1)$.

$$\begin{array}{c}
 \psi_{0e} \\
 \psi_{0e} \quad ([0^0, J])
 \end{array}$$

$$\begin{array}{c}
 \psi_{1e}^- \quad \psi_{1f}^+ \\
 \psi_{1e}^- \quad \psi_{1f}^+ \left(\begin{array}{cc} [1^1, J] - q_t^{\text{eff}} M & 0 \\ 0 & [1^1, J] + q_t^{\text{eff}} M \end{array} \right)
 \end{array}$$

$$\begin{array}{c}
 \psi_{2e}^+ \quad \psi_{0e} \quad \psi_{2f}^- \\
 \psi_{2e}^+ \quad \psi_{0e} \quad \psi_{2f}^- \left(\begin{array}{ccc} [2^2, J] + \rho_t M(M-2) & 2q_t^{\text{eff}} \sqrt{M(M-2)} & 0 \\ 2q_t^{\text{eff}} \sqrt{M(M-2)} & [2^0, J] & 0 \\ 0 & 0 & [2^2, J] - \rho_t M(M-2) \end{array} \right)
 \end{array}$$

$$\begin{array}{c}
 \psi_{2e}^+/\psi_{2f}^- \quad \psi_{0e}^+/\psi_{0f}^- \\
 \psi_{2e}^+/\psi_{2f}^- \quad \psi_{0e}^+/\psi_{0f}^- \left(\begin{array}{cc} [1^1 1^1, J] \pm \rho_{45} M(M-2) & (q_5^{\text{eff}} \pm q_4^{\text{eff}}) \sqrt{M(M-2)} \\ (q_5^{\text{eff}} \pm q_4^{\text{eff}}) \sqrt{M(M-2)} & [1^1 1^{-1}, J] \pm r_{45}^{\text{eff}} \end{array} \right)
 \end{array}$$

$$\begin{array}{c}
 \psi_{3e}^-/\psi_{3f}^+ \\
 \psi_{3e}^-/\psi_{3f}^+ \quad \psi_{1e}^-/\psi_{1f}^+ \left(\begin{array}{cc} [3^3, J] & \sqrt{3}(q_t^{\text{eff}} \mp \rho_t M) \sqrt{(M-2)(M-6)} \\ \sqrt{3}(q_t^{\text{eff}} \mp \rho_t M) \sqrt{(M-2)(M-6)} & [3^1, J] \mp 2q_t M \end{array} \right)
 \end{array}$$

$$\begin{array}{c}
 \psi_{3e}^-/\psi_{3f}^+ \quad \psi_{1e}^-/\psi_{1f}^+ \quad \psi_{1e}^-/\psi_{1f}^+ \\
 \psi_{3e}^-/\psi_{3f}^+ \quad \psi_{1e}^-/\psi_{1f}^+ \quad \psi_{1e}^-/\psi_{1f}^+ \left(\begin{array}{ccc} [2^2 1^1, J] & [2^2 1^{-1}, J] & [2^0 1^1, J] \mp q_5^{\text{eff}} M \\ (q_5^{\text{eff}} \mp \rho_4 M) \sqrt{(M-2)(M-6)} & \sqrt{2}(r_{45}^{\text{eff}} \mp q_4^{\text{eff}} M) & \\ \sqrt{2}(q_4^{\text{eff}} \mp \rho_{45} M) \sqrt{(M-2)(M-6)} & & \end{array} \right)
 \end{array}$$

Table 4.3. Molecular parameter fit: groundstate, ν_5 , and $2\nu_5$ of $^{12}\text{C}_2\text{H}_2$. All parameters are in units of cm^{-1} . Molecular constants marked with a † are calculated from parameters appearing in the same column. NZW is the number of transitions surviving the fit; wstd is the weighted standard deviation.

Molecular Parameters				
$^{12}\text{C}_2\text{H}_2$	Ground State/ ν_5 / $2\nu_5$			
	Global Parameter Fit	Effective Parameter Fit	Hillman <i>et al.</i> 1991	Hietanen and Kauppinen 1981
$E_{\nu_5=1}$	730.332 937(21)	730.332 945(16)	730.332 959(25) e	730.334 1(1)
$E_{\nu_5=2}$	1449.112 56(3)	1449.112 55(3)	–	1449.114 1(1)
$g_{55} + 2y_{55}^{55}$	3.476 049 1(82)	3.476 053 5(64)	–	3.475 95(3)
B_o	1.176 646 67(50)	1.176 646 37(40)	1.176 646 86(27)	1.176 640 6(21)
$\alpha_5 \times 10^3$	–2.232 982(90)	–	–	–2.245(7) a
$\gamma_{55} \times 10^5$	1.790 7(36)	–	–	1.24(20) a
$\gamma^{55} \times 10^4$	–1.097 48(28)	–1.097 72(22)	–	–1.095(2)
B_5	1.178 897 6†	1.178 897 21(41)	–	–
B_{55}	1.181 184 3†	1.181 183 97(41)	–	1.181 180 1(6)
$B_5 + \gamma^{55}$	1.178 787 1†	1.178 787 4†	1.178 787 44(48)	1.178 782(2) c
$q_5^o \times 10^3 \ddagger$	2.330 451(34)	2.330 378(27)	–	–2.311(2) a,b
$q_{55} \times 10^5 \ddagger$	1.872 9(25)	1.875 4(20)	–	–1.88(16) a,b
$q_5^f \times 10^8 \ddagger$	–1.916 2(16)	–1.912 4(12)	1.909 7(34)	1.99(4) a,b
$q_5^o + q_{55} \times 10^3 \ddagger$	2.349 180†	2.349 132†	–2.349 071(39)	–2.349 8(2) b
$D_o \times 10^6$	1.627 11(41)	1.626 72(35)	1.627 54(10)	1.622 1(8)
$\beta_5 \times 10^8$	–2.544 1(44)	–	–	–2.49(2) a
$\beta_{55} \times 10^{10}$	–7.45(19)	–	–	0
$D_5 \times 10^6$	1.651 8†	1.651 36(35)	1.651 75(23)	1.650 5(25) d
$D_{55} \times 10^6$	1.675 0†	1.674 58(35)	–	1.672 0(3)
$H_o \times 10^{12}$	1.52(11) f	1.403(93) f	1.674(41)	0
$H_5 \times 10^{12}$	1.52(11) f	1.403(93) f	1.65(12)	0
$H_{55} \times 10^{12}$	1.52(11) f	1.403(93) f	–	0
$\rho_5 \times 10^9$	–3.419(23)	–3.446(19)	–	–3.3(3) b
wstd. $\times 10^4$	1.26	0.95		
NZW/data	833/876	420/441		
bi-wts.	5 σ	5 σ		

a) Values taken from Hietanen 1983.

f) $H_o = H_5 = H_{55}$

b) This value is half of the number reported in cited reference.

c) was calculated as $(B_5^e + B_5^f)/2$ in cited reference.

d) was calculated as $(D_5^e + D_5^f)/2$ in cited reference.

e) from transition frequency fit of fundamental in cited reference.

‡ Sign of constant depends on adopted phase convention (see Section 3.5).

Table 4.4. Molecular parameter fit: ν_4 and $\nu_4 + \nu_5$ of $^{12}\text{C}_2\text{H}_2$. All parameters are in units of cm^{-1} . Molecular constants marked with a † are calculated from parameters appearing in the same column. NZW is the number of transitions surviving the fit; wstd is the weighted standard deviation.

Molecular Parameters $^{12}\text{C}_2\text{H}_2 \quad \nu_4 / \nu_4 + \nu_5$				
	Global Parameter Fit	Effective Parameter Fit	Hillman <i>et al.</i> 1991	Hietanen and Kauppinen 1981
$E_{\nu_4+\nu_5} - E_{\nu_4}$	728.045 225(13)	728.045 196(13)	—	728.045 8(1)
$g_{45} + y_5^{45} + y_4^{45}$	6.604 661(13)	6.604 632(13)	—	6.604 67(4)
$\alpha_4 - \gamma_{44} - \gamma^{44} \times 10^3$	-1.288 31(53)	—	—	—
$\gamma_{45} \times 10^5$	-2.441 5(73)	—	—	2.4(3) d
$\gamma^{45} \times 10^4$	-2.255 67(46)	-2.254 25(43)	—	2.256(3) d
B_4	1.177 935 0†	1.177 935 79(63)	1.177 935 9(15)	1.177 431(5) b
B_{45}	1.180 051 7†	1.180 052 74(63)	—	1.180 047 5(1)
$r_{45}^o + r_{(45)4}^{(45)} + r_{(45)5}^{(45)}$	-6.238 652(18)	-6.238 712(19)	—	-6.238 63(4)
$r_{45}^J \times 10^4$	1.948 27(67)	1.956 68(82)	—	1.962(2)
$q_4^o + q_{44} \times 10^3 \dagger$	2.615 396(31)	2.615 102(32)	-2.615 113(94)	—
$q_{54} \times 10^5 \dagger$	5.358(11)	—	—	-5.022(2) a,d
$q_{45} \times 10^5 \dagger$	3.998 5(87)	3.878 1(94)	—	-5.022(2) a,d
$q_4^J \times 10^8 \dagger$	-1.952 1(26)	-1.926 9(27)	1.929 7(78)	1.655(60) a
$q_5^J \times 10^8 \dagger$	-1.916 2†	-2.095 2(81)	—	1.91(4) a
$q_4^o + q_{44} + q_{45} \times 10^3 \dagger$	2.655 38†	2.653 88†	—	2.653 5(10) a
$q_5^o + q_{55} + q_{54} \times 10^3 \dagger$	2.402 76†	2.406 910(24)	—	2.402(1) a
$\beta_4 - \beta_{44} \times 10^8$	-3.239(24)	—	—	—
$\beta_{45} \times 10^{10}$	-5.41(42)	—	—	—
$D_4 \times 10^6$	1.659 5†	1.660 85(68)	1.660 71(75)	1.656(4) c
$D_{45} \times 10^6$	1.684 7†	1.685 18(69)	—	1.679 0(2)
$H_4 \times 10^{12}$	1.52† c	2.07(23) c	2.05(39)	0
$H_{45} \times 10^{12}$	1.52† c	2.07(23) c	—	0
$\rho_{45} \times 10^9$	-4.392(48)	-5.023(57)	—	-2.0(8)
$wstd. \times 10^4$	1.26	1.30		
$NZW/data$	833/876	415/435		
bi-wts.	5 σ	5 σ		

a) This value is half of the number reported in cited reference.

b) was calculated as $(B_5^e + B_5^f)/2$ in cited reference.

c) was calculated as $(D_5^e + D_5^f)/2$ in cited reference.

d) from Hietanen 1983.

e) $H_o = H_4 = H_{45}$

† Sign of constant depends on adopted phase convention (see Section 3.5).

Table 4.5. Molecular parameter fit: groundstate, ν_5 , and $2\nu_5$ of $^{13}\text{C}^{12}\text{CH}_2$. All parameters are in units of cm^{-1} . Molecular constants marked with a † are calculated from parameters appearing in the same column.

Molecular Parameters				
$^{13}\text{C}^{12}\text{CH}_2$	Ground State/ ν_5 / $2\nu_5$			
	Global Parameter Fit	Effective Parameter Fit	Hillman <i>et al.</i> 1991	Hietanen <i>et al.</i> 1986
$E_{\nu_5=1}$	729.378 399(37)	729.378 400(38)	729.378 449(56) b	729.378 38(2)
$E_{\nu_5=2}$	1447.257 95(7)	1447.257 95(7)	—	—
$g_{55} + 2y_5^{55}$	3.461 055(17)	3.461 054(17)	—	3.461 14(1)
B_0	1.148 459 5(10)	1.148 459 4(11)	1.148 461 07(51)	1.148 458 3(7)
$\alpha_5 \times 10^3$	-2.085 02(24)	—	—	—
$\gamma_{55} \times 10^5$	1.684(10)	—	—	—
$\gamma^{55} \times 10^4$	-1.057 78(84)	-1.057 68(85)	—	-1.063 3(7)
B_5	1.150 561 4†	1.150 561 3(11)	—	—
B_{55}	1.152 696 9†	1.152 696 8(11)	—	1.152 696 4(9)
$B_5 + \gamma^{55}$	1.150 455 6†	1.150 455 5†	1.150 454 1(13)	1.150 434 3(8)
$q_5^0 \times 10^3 \dagger$	2.223 29(14)	2.223 29(14)	—	—
$q_{55} \times 10^5 \dagger$	1.784(12)	1.782(12)	—	—
$q_5^J \times 10^8 \dagger$	-1.774(10)	-1.77(11)	1.713(25)	1.762(10)
$q_5^0 + q_{55} \times 10^3 \dagger$	2.241 3†	2.241 11†	-2.240 85(17)	-2.240 975(5) a
$D_0 \times 10^6$	1.556 5(11)	1.556 4(13)	1.557 62(23)	1.553 9(4)
$\beta_5 \times 10^8$	-2.312(20)	—	—	—
$\beta_{55} \times 10^{10}$	-5.63(94)	—	—	—
$D_5 \times 10^6$	1.579 0†	1.579 0(13)	1.576 17(98)	1.576 3(4)
$D_{55} \times 10^6$	1.600 4†	1.600 4(12)	—	1.596 7(6)
$H_0 \times 10^{12}$	1.20(38) d	1.19(42) d	1.52(11)	0
$H_5 \times 10^{12}$	1.20(38) d	1.19(42) d	0	0
$H_{55} \times 10^{12}$	1.20(38) d	1.19(42) d	—	0
$\rho_5 \times 10^9$	-3.26(11)	-3.26(11)	—	-3.8(2) a
$wstd. \times 10^4$	1.86	1.79		
$NZW/data$	546/595	291/315		
bi-wts.	5 σ	5 σ		

a) This value is half of the number reported in cited reference.

b) from transition frequency fit of fundamental in cited reference.

c) kept fixed in fit.

d) $H_0 = H_5 = H_{55}$

† Sign of constant depends on adopted phase convention (see Section 3.5).

Table 4.6. Molecular parameter fit: ν_4 and $\nu_4 + \nu_5$ of $^{13}\text{C}^{12}\text{CH}_2$. All parameters are in units of cm^{-1} . Molecular constants marked with a † are calculated from parameters appearing in the same column.

Molecular Parameters $^{13}\text{C}^{12}\text{CH}_2 \quad \nu_4 / \nu_4 + \nu_5$				
	Global Parameter Fit	Effective Parameter Fit	Hillman <i>et al.</i> 1991	Hietanen <i>et al.</i> 1986
$E_{\nu_4+\nu_5} - E_{\nu_4}$	727.139 333(26)	727.139 347(34)	—	727.139 18(2)
$g_{45} + y_5^{45} + y_4^{45}$	6.603 680(25)	6.603 683(33)	—	6.603 76(2)
$\alpha_4 - \gamma_{44} - \gamma^{44} \times 10^3$	-1.123 6(12)	—	—	—
$\gamma_{45} \times 10^5$	-2.353(20)	—	—	—
$\gamma^{45} \times 10^4$	-2.196 0(13)	-2.196 5(19)	—	-2.204(1)
B_4	1.149 583 1†	1.149 583 2(19)	1.149 582 9(16)	1.149 578 6(8)
B_{45}	1.151 555 7†	1.151 555 8(19)	—	1.151 551 8(9)
$r_{45}^o + r_{(45)4} + r_{(45)5}$	-6.201 545(33)	-6.201 536(47)	—	-6.201 57(3)
$r_{45}^J \times 10^4$	1.883 5(18)	1.884 4(36)	—	1.884(2)
$q_4^o + q_{44} \times 10^3 \dagger$	2.510 748(90)	2.510 69(15)	-2.510 81(18)	-2.510 1(1) a
$q_{45} \times 10^5 \dagger$	3.886(49)	3.889(66)	—	-4.36(7) a
$q_{54} \times 10^5 \dagger$	5.036(57)	—	—	—
$q_4^J \times 10^8 \dagger$	-1.853(12)	-1.909(54)	1.873(22)	1.72(2)
$q_5^J \times 10^8 \dagger$	-1.774†	-1.822(73)	—	1.765 5 a,b
$q_5^o + q_{55} + q_{54} \times 10^3 \dagger$	2.230 11†	2.292 2(16)	—	-2.287(1) a
$\beta_4 - \beta_{44} \times 10^8$	-2.913(78)	—	—	—
$\beta_{45} \times 10^{10}$	-3.3(19)	—	—	—
$D_4 \times 10^6$	1.585 6†	1.586 3(31)	1.584 4(12)	1.576 5(10)
$D_{45} \times 10^6$	1.608 5†	1.608 5(31)	—	1.600 3(12)
$H_4 \times 10^{12}$	1.19(35)† c	1.2(15) c	0	0
$H_{45} \times 10^{12}$	1.19(35)† c	1.2(15) c	0	0
$\rho_{45} \times 10^9$	-3.63(20)	-3.72(38)	—	-2.6(3)
$wstd. \times 10^4$	1.86	2.47		
$NZW/data$	546/595	264/280		
bi-wts.	5 σ	5 σ		

a) This value is half of the number reported in cited reference.

b) kept at fixed value.

c) $H_o = H_4 = H_{45}$

† Sign of constant depends on adopted phase convention (see Section 3.5).

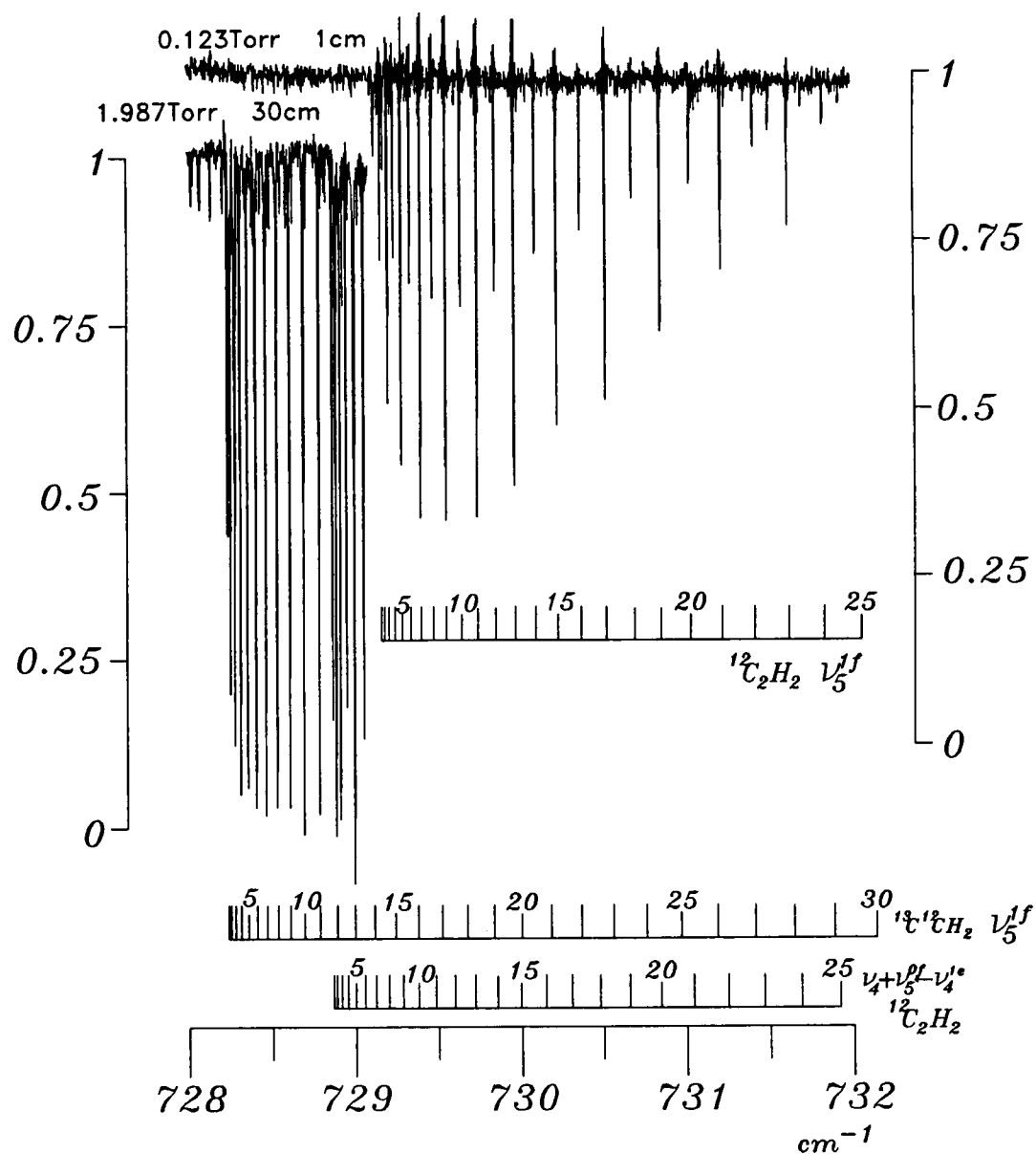


Figure 4.1. Section of the FTS-spectrum showing the Q -branch of the fundamental for both observed isotopomers. Near the band center of the fundamentals, the $\nu_4 + \nu_5^{0f} \leftarrow \nu_4^{1e}$ Q -branch commences.

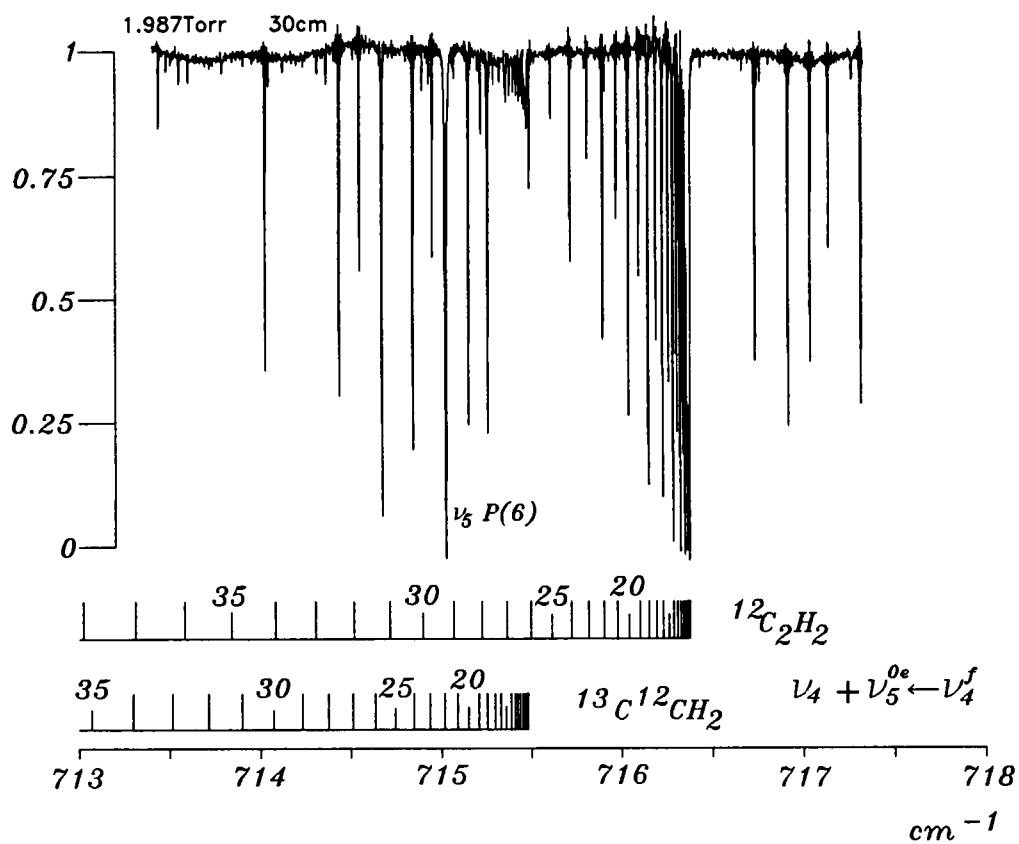


Figure 4.2. Section of the FTS-spectrum showing the acetylene Q -branch for the $\nu_4 + \nu_5^{0f} \leftarrow \nu_4^{1e}$ hotbands of both isotopes.

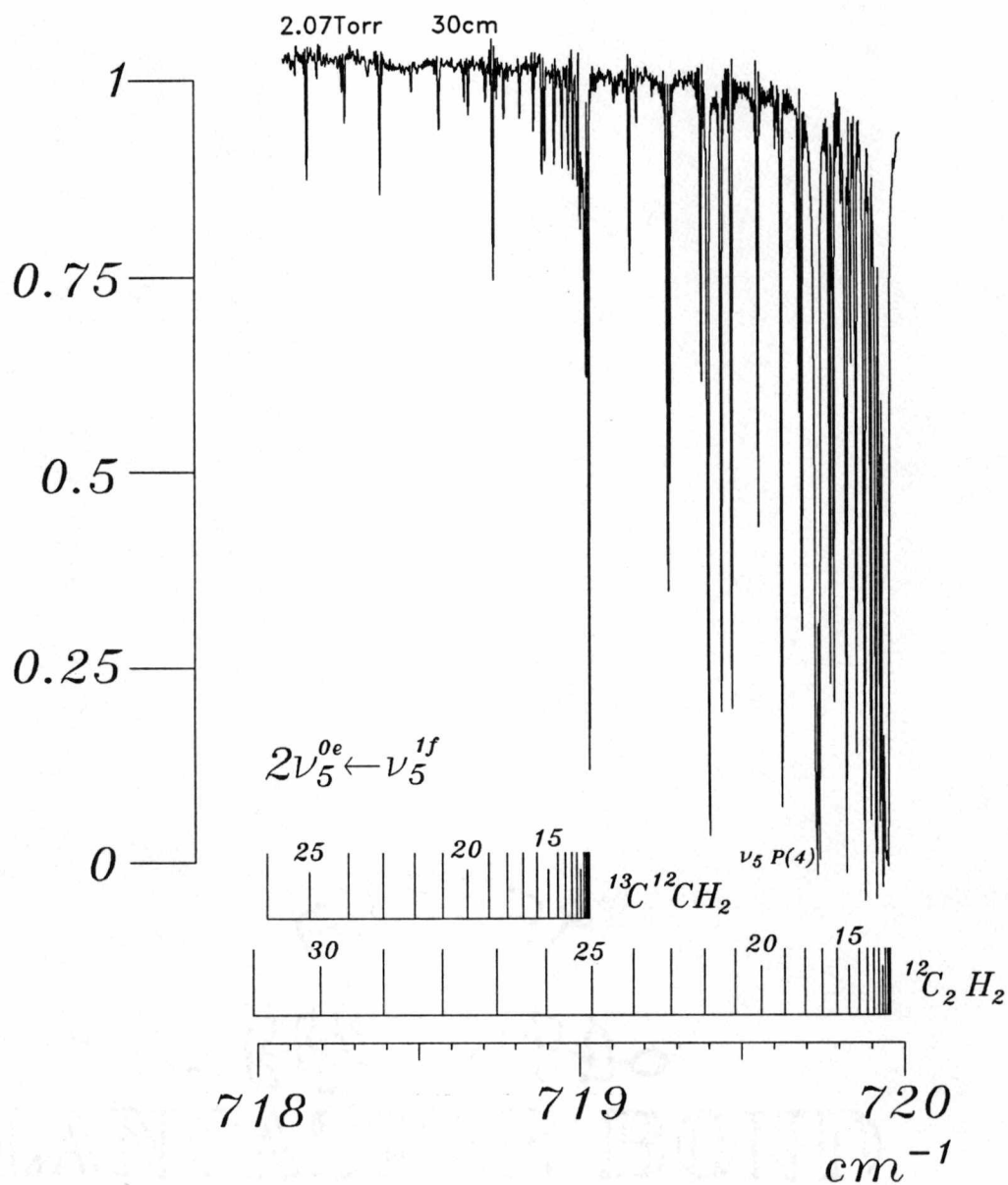


Figure 4.3. Part of the FTS-spectrum showing the acetylene Q -branch for the $2\nu_5^{0e} \leftarrow \nu_5^{1f}$ hotbands of both isotopes.

additional expansion term in the centrifugal distortion constant, D_v , the effective parameter fit of the ν_5 stack eliminated the residual correlation significantly and the standard deviation of the fit reduced by nearly one half. On the other hand, no improvement in the global fit was achieved by the introduction of the same expansion parameter. In the latter fit, the higher order Coriolis resonance parameter, ρ_5 , became unreasonably large. For this reason β^{55} was not included in both fits.

A similar correlation is observed between H_v and ρ_{45} . It can be seen that the larger ρ_{45} value in the effective parameter is related to the increase of H_v as compared to the overall fit. The sextic centrifugal constant H_v was assumed to be identical for all levels within their standard deviation for the global fit. From these observations, it is evident that the higher order parameters are strongly correlated during the least squares fit and, therefore, great care must be exercised in the selection of proper parameters in the modelling of the rotation-vibration problem. Herman *et al.*(1991) introduced q_i^{JJ} as a high order expansion term in the rotational ℓ -doubling matrix element. Although some non-vanishing contribution could be found by including such terms, no improvement was observed in the fits. Unusual values for small parameters are generally a result of particular residual correlation, whose source might be of rather systematic nature.

Nevertheless, both global and effective fit improved the precision of the molecular parameters describing the two bending vibrations by an order of magnitude compared to the most recent published study of the same bands by Hietanen and Kauppinen (1981) and Hietanen (1983) for the major isotope and to Hietanen *et al.*(1986) for $^{13}\text{C}^{12}\text{CH}_2$. As expected the fit to effective parameters is consistent with the results from the LSCD analysis as reported by Hillman *et al.*(1991). For comparison, the molecular constants retrieved in this study are compared to Hillmann *et al.*(1991) and Hietanen *et al.*(1981, 1983, 1986) in the third and fourth column of Table 4.3–4.6, respectively.

In Appendix C all transitions observed and the deviation from the calculated values are listed. Transitions marked with (i) are due to $^{13}\text{C}^{12}\text{CH}_2$; asterisks (*) indicate transitions excluded from the fit.

4.5 The Two Quantum Hotbands, $2\nu_4 \leftarrow 2\nu_4 + \nu_5$, $\nu_4 + \nu_5 \leftarrow \nu_4 + 2\nu_5$, and $3\nu_5 \leftarrow 2\nu_5$

A total of 23 hotbands originating from the two quantum levels had been assigned as detailed in Table 4.7. The fit of the observed frequencies to the vibrational combination states proved quite difficult due to the vibrational ℓ -type resonance. In order to understand the problem, the vibrational

energy of $\nu_4 + 2\nu_5$ relative to the lower state are written as follows

$$\begin{aligned} G(1^{\pm 1}, 2^{\pm 2}) &= \Delta E_{455} + 4\Delta_1 + 2\Delta_2 \\ G(1^{\mp 1}, 2^{\pm 2}) &= \Delta E_{455} + 4\Delta_1 - 2\Delta_2 \\ G(1^{\pm 1}, 2^{\pm 0}) &= \Delta E_{455} \end{aligned} \quad (4.10)$$

where ΔE_{455} is the vibrational energy difference to the $\nu_4 + \nu_5$ multiplet, $\Delta_1 = g_{55} + y_4^{55} + 2y_5^{55}$ and $\Delta_2 = g_{45} + y_4^{45} + 2y_5^{45}$. In addition, a non-diagonal vibrational contribution due to ℓ -type resonance, which can be written as $r = \sqrt{2}(r_{45}^o + r_{45})_4 + 2r_{(45)5}$, has to be considered (see Table 2.3). The vibrational contribution of the off-diagonal matrix element to the vibrational energy is approximately given by

$$\begin{aligned} g(\phi_g) &= G(1^{\pm 1}, 2^{\pm 2}) \\ g(I\Pi_g) &= \frac{1}{2} [G(1^{\mp 1}, 2^{\pm 2}) + G(1^{\mp 1}, 2^0)] - r \\ g(II\Pi_g) &= \frac{1}{2} [G(1^{\mp 1}, 2^{\pm 2}) + G(1^{\mp 1}, 2^0)] + r \end{aligned} \quad (4.11)$$

By exchanging indices 4 and 5, the Roman numerals *I* and *II*, and the symmetry labels *g* and *u* in Eqs. (4.10) and (4.11), the same holds true for the $2\nu_4 + \nu_5$ states.

The two π components are strongly perturbed by vibrational ℓ resonance causing a vibrational separation of roughly $2r$ between the two states. The vibrational energy problem is to some extent underdetermined, since there are 4 vibrational parameters ($\Delta E, \Delta_1, \Delta_2, r$) to describe three vibrational term values. As a consequence, the vibrational parameters are highly correlated and convergence in the least squares fit, therefore, was more difficult to achieve. The same problem was reported by Hietanen (1983) in their investigation of the same bands. The slight vibrational indeterminacy, as stated above, is not complete since at $J = \ell$, the lowest lying rovibrational state, both, rotational and vibrational ℓ -type resonance effect the rovibrational levels and as a consequence the vibrational problem is distributed among other rotational constants. By implementing reasonable constraints on some of the rotation-vibration parameters, the least squares fit converged satisfactorily although the standard deviation in the vibrational parameters are higher than usual.

In Table 4.8 and 4.9, the effective parameter fits of the $2\nu_4$, $2\nu_4 + \nu_5$ and $\nu_4 + 2\nu_5$ vibrational states are summarized. Some assignments of Q-branch transitions of the hotbands terminating in these states are shown in Figs. 4.4 and 4.5 along with $3\nu_5 \leftarrow 2\nu_5$ Q-branch transitions.

The $\nu_4 + 2\nu_5$ state was fitted by keeping the parameters of the lower 4×4 matrix of $\nu_4 + \nu_5$ fixed to the least squares results of the previous fit. A free fit of upper state constants led to unusual

Table 4.7. Observed transitions of two quantum hotbands of $^{12}\text{C}_2\text{H}_2$ in the $13.6\mu\text{m}$ region.

$^{12}\text{C}_2\text{H}_2$				
Band	J_{max}			No. of Transitions
	P	Q	R	
$2\nu_4 + \nu_5^{1eII} \leftarrow 2\nu_4^{2e,2f}$	35	35	36	90
$2\nu_4 + \nu_5^{1fII} \leftarrow 2\nu_4^{2e,2f}$	36	33	29	84
$2\nu_4 + \nu_5^{1eI} \leftarrow 2\nu_4^{2e,2f}$	16	—	6	18
$2\nu_4 + \nu_5^{1fI} \leftarrow 2\nu_4^{2e,2f}$	21	28	21	89
$2\nu_4 + \nu_5^{3e} \leftarrow 2\nu_4^{2e,2f}$	26	39	27	65
$2\nu_4 + \nu_5^{3f} \leftarrow 2\nu_4^{2e,2f}$	33	29	30	75
$2\nu_4 + \nu_5^{1eII,1fII} \leftarrow 2\nu_4^{0e}$	16	29	23	65
$2\nu_4 + \nu_5^{1eI,1fI} \leftarrow 2\nu_4^{0e}$	31	32	29	69
$\nu_4 + 2\nu_5^{1eII,1fII} \leftarrow \nu_4 + \nu_5^{0e}$	34	33	34	92
$\nu_4 + 2\nu_5^{1eI,1fI} \leftarrow \nu_4 + \nu_5^{0e}$	24	24	26	51
$\nu_4 + 2\nu_5^{1eII,1fII} \leftarrow \nu_4 + \nu_5^{0f}$	29	31	31	58
$\nu_4 + 2\nu_5^{1eI,1fI} \leftarrow \nu_4 + \nu_5^{0f}$	35	34	37	95
$\nu_4 + 2\nu_5^{1eII} \leftarrow \nu_4 + \nu_5^{2e,2f}$	28	31	30	77
$\nu_4 + 2\nu_5^{1fII} \leftarrow \nu_4 + \nu_5^{2e,2f}$	21	28	16	53
$\nu_4 + 2\nu_5^{1eI} \leftarrow \nu_4 + \nu_5^{2e,2f}$	30	34	30	80
$\nu_4 + 2\nu_5^{1fI} \leftarrow \nu_4 + \nu_5^{2e,2f}$	33	35	35	78
$\nu_4 + 2\nu_5^{3e} \leftarrow \nu_4 + \nu_5^{2e,2f}$	32	40	36	74
$\nu_4 + 2\nu_5^{3f} \leftarrow \nu_4 + \nu_5^{2e,2f}$	33	46	33	84
$3\nu_5^{1e,1f} \leftarrow 2\nu_5^{0e}$	35	35	35	90
$3\nu_5^{1e} \leftarrow 2\nu_5^{2e,2f}$	27	33	11	54
$3\nu_5^{1f} \leftarrow 2\nu_5^{2e,2f}$	30	31	30	75
$3\nu_5^{3e} \leftarrow 2\nu_5^{2e,2f}$	33	26	33	63
$3\nu_5^{3f} \leftarrow 2\nu_5^{2e,2f}$	32	26	30	63

Table 4.8. Effective Parameter fit: $2\nu_4$ and $2\nu_4 + \nu_5$ of $^{12}\text{C}_2\text{H}_2$. All parameters are in units of cm^{-1} . NZW is the number of transitions with non-zero weights; *wstd* is the weighted standard deviation from the least squares fit.

Molecular Parameters		
$^{12}\text{C}_2\text{H}_2$	$2\nu_4/2\nu_4 + \nu_5$	
	This Work	Hietanen 1983
$E(2^0, 1^1) - E(2^0, 0^0)$	725.573 99(68)	725.570 1(18)
$g_{44} + 2y_4^{44}$	0.781 539(19)	0.780 97(6)
$g_{45} + 2y_4^{45} + y_5^{45}$	6.616 82(21)	6.615 8(5)
$y_5^{44} \times 10^2$	5.868(29)	6.01(5)
$r_{45}^o + 2r_{(45)4} + r_{(45)5}$	-6.024 05(32)	-6.026 3(7)
$r_{45}^J \times 10^4$	1.868 2(32)	1.839(8)
B_{44}	1.179 358 1(13)	1.179 358(3)
$\gamma^{44} \times 10^4$	-6.581(18)	-6.53(10)
$B_{445}(2^0, 1^{\pm 1})$	1.181 472 8(13)	-
$B_{445}(2^{\pm 2}, 1^{\pm 1})$	1.181 633 8(14)	-
$B_{445}(2^{\pm 2}, 1^{\pm 1})$	1.180 739 1(12)	-
$q_4^o + 2q_{44} \times 10^3 \ddagger$	2.606 84(13)	-2.608(4) a
$q_5^o + 2q_{54} + q_{55} \times 10^3 \ddagger$	2.475 48(31)	-2.467(1) a
$q_{45} \times 10^5 \ddagger$	3.582(18)	-3.23(6) a
$q_4^J \times 10^8 \ddagger$	-2.031(16)	2.1(5) a
$q_5^J \times 10^8 \ddagger$	-2.563(41)	2.01(5) a,b,c
$D_{44} \times 10^6$	1.693 27(85)	1.699(5)
$D_{445} \times 10^6$	1.717 59(85)	1.710(3)
$H_o \times 10^{12}$	2.07 b	0
$\rho_{45} \times 10^9$	-5.36(12)	0
$\rho_4 \times 10^9$	-1.79(29)	0
<i>wstd.</i> $\times 10^4$	3.32	
NZW/data	491/523	
bi-wts.	5 σ	

a) This value is half of the number reported in cited reference.

b) kept fixed during fit.

c) from Hietanen *et al.* 1981.

$\ddagger$ Sign of constant depends on phase convention (see Section 3.5).

Table 4.9. Effective Parameter fit: $\nu_4 + 2\nu_5$ of $^{12}\text{C}_2\text{H}_2$. All parameters are in units of cm^{-1} . NZW is the number of transitions with non-zero weights; *wstd* is the weighted standard deviation from the least squares fit. Lower state parameters of $\nu_4 + \nu_5$ were kept fixed to the (effective parameter) values in Table 4.4.

Molecular Parameters		
	$^{12}\text{C}_2\text{H}_2$	$\nu_4 + 2\nu_5$
	This Work	Hietanen 1983
$E(1^{\pm 1}, 2^0) - E_{\nu_4 + \nu_5}$	716.967 8(26)	—
$g_{55} + y_4^{55} + 2y_5^{55}$	3.399 27(99)	3.415(9)
$g_{45} + y_4^{45} + 2y_5^{45}$	6.666 10(66)	6.655(6)
$r_{45}^o + r_{(45)4} + r_{(45)5}$	-6.238 712 b	—
$r_{(45)5}^{(45)5}$	-0.095017(37)	—
$r_{45}^J \times 10^4$	2.080 53(77)	2.009(8)
B_{455}	1.182 416 3(69)	1.182 409 2(7)
$\gamma^{45} \times 10^4$	-2.319 9(17)	-2.256(3) b
$\gamma^{55} \times 10^4$	-1.094 1(24)	-1.094(5) b
$q_4^o + q_{44} + 2q_{45} \times 10^3 \ddagger$	2.701 81(13)	-2.690(1) a
$q_5^o + 2q_{54} + q_{55} \times 10^3 \ddagger$	2.421 54(27)	-2.415(3) a
$q_4^J \times 10^8 \ddagger$	-2.280(18)	2.4(2) a
$q_5^J \times 10^8 \ddagger$	-1.916 b	2.01(5) a,b,c
$D_{455} \times 10^6$	1.708 32(90)	1.705(1)
$\beta^{45} \times 10^9$	-2.07(11)	0
$H_o \times 10^{12}$	2.07 b	0
$\rho_{45} \times 10^9$	-5.42(16)	0
$\rho_5 \times 10^9$	-3.446 b	0
<i>wstd.</i> $\times 10^4$	2.11	
NZW/data	668/742	
bi-wts.	4.5 σ	

a) This value is half of the number reported in cited reference.

b) kept fixed during fit

c) from Hietanen *et al.* 1981

$\ddagger$ Sign of constant depends on phase convention (see Section 3.5).

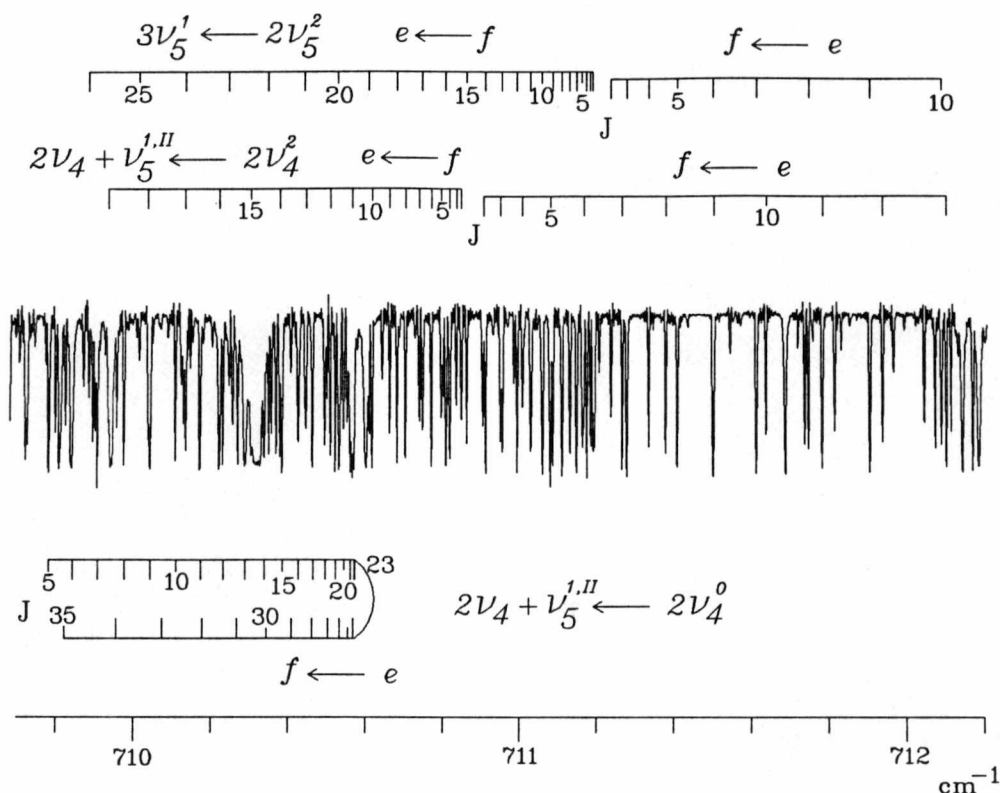


Figure 4.4. Acetylene's Q -branches of $3\nu_5^{1e,1f} \leftarrow 2\nu_5^{2f,2e}$, $2\nu_4 + \nu_5^{1eII,1fII} \leftarrow 2\nu_4^{2f,2e}$, and $2\nu_4 + \nu_5^{1fII} \leftarrow 2\nu_4^{0e}$. Assignments for five Q -branches of two-quantum hotbands are shown based on calculated frequencies. The spectrum was recorded in a White cell (White 1942) at 24m effective path length and pressure at 0.524Torr. While the four Q -branches of $3\nu_5^1 \leftarrow 2\nu_5^2$ and $2\nu_4 + \nu_5^{1II} \leftarrow 2\nu_4^2$ degrade in regular fashion into opposite directions, the Q -branch of $2\nu_4 + \nu_5^{1fII} \leftarrow 2\nu_4^{0e}$ possesses a band head at $J = 23$ (710.57437cm^{-1}), whereafter the band returns to the lower wave numbers.

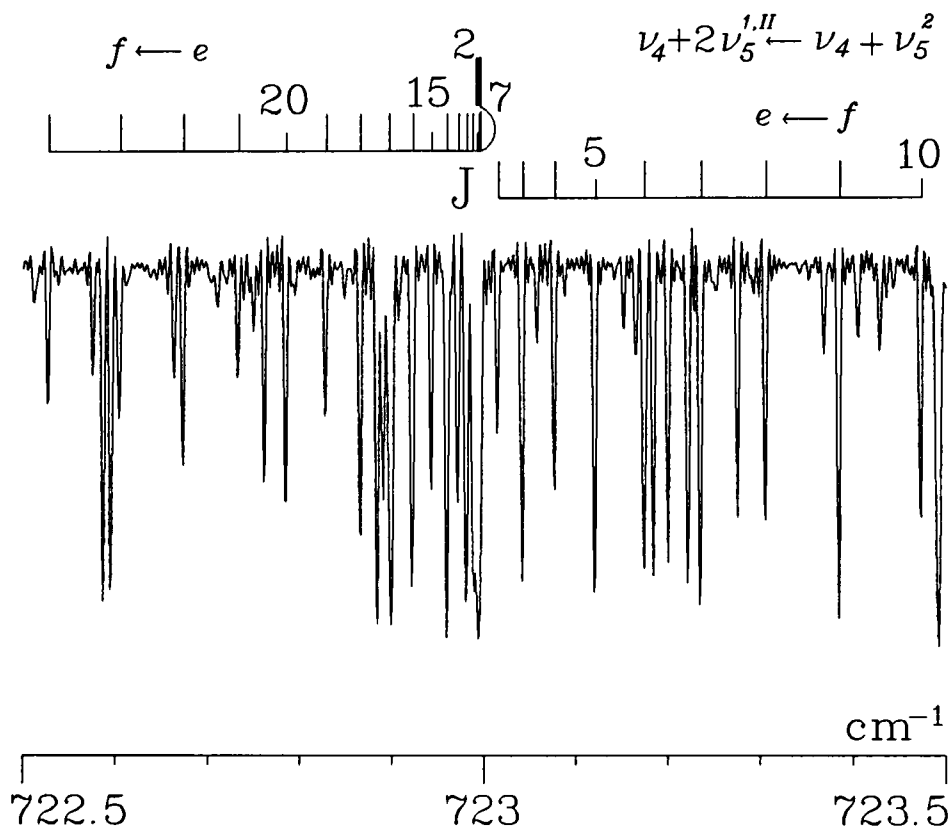


Figure 4.5. Acetylene Q-branch of $\nu_4 + 2\nu_5^{1eII,1fIII} \leftarrow \nu_4 + \nu_5^{2e,2f}$. Path length: 24m, at 0.524Torr. The $e \leftarrow f$ component proceeds towards higher wavenumbers, whereas the $f \leftarrow e$ component has a band head at $J = 7$ (722.99723cm^{-1}) and, thereafter, tends to the opposite direction.

high q_5^J , ρ_5 , and H_v values as compared to the lower state constants. By freezing ρ_5 and H_v to values known from the lower state fit, led to reasonable results for other higher order parameters. High J transitions ($J = 30 - 46$) in the Q -branch of the $\nu_4 + 2\nu_5^{3f} \leftarrow \nu_4 + \nu_5^{2e}$ branch show large deviations from the calculated values. These lines are heavily blended by the more intense lower quantum hotbands and the far wing of the ν_5 fundamental Q -branch. Their assignment is therefore considered tentative.

Since no direct transitions to $2\nu_4$ are observed in the $14\mu\text{m}$ region, both states of $2\nu_4$ and $2\nu_4 + \nu_5$ were fitted simultaneously. The unrestricted fit resulted in abnormal values for some of the high order parameters, such as q_5^J , H_v , γ_{45} and ρ_{45} . It was decided to constrain H_v and to introduce effective B -parameters in the upper state matrix for each sublevel, which drastically improved the results. The effective B -terms can be written as follows

$$\begin{aligned} B_{44}(2^{\pm 2}, 0^0) &= B_{44} + \gamma^{44} \\ B_{44}(2^0, 0^0) &= B_{44} \end{aligned} \quad (4.12)$$

for the lower state and

$$\begin{aligned} B_{455}(2^{\pm 2}, 1^{\pm 1}) &= B_{455} + 4\gamma^{44} + 2\gamma^{45} \\ B_{455}(2^{\pm 2}, 1^{\mp 1}) &= B_{455} + 4\gamma^{44} - 2\gamma^{45} \\ B_{455}(2^0, 1^{\pm 1}) &= B_{455}. \end{aligned} \quad (4.13)$$

To describe five distinct B -values in the effective parameter fit, only four parameters, B_{44} , B_{455} , γ^{44} and γ^{45} , are available. For this reason the B values of the upper state were fitted independently of each other.

The ℓ -doubling constant q_5^{eff} and, particularly, q_5^J are higher than expected. Constraining q_5^J lead to poor convergence in the iterative fit and therefore freeing the parameter is considered to be significant to the fit. A possible explanation for the abnormal value of this parameter as well as the necessity to introduce effective B -values for the upper state, may be a high order Coriolis resonance between the $\nu_2 = 1$ stretching fundamental, which lies energetically very close to the $2\nu_4 + \nu_5$ level. The perturbation between the two vibrational levels has the effect of enhancing the ℓ -resonance within the sublevels. This is also manifest in a somewhat higher value for the higher order vibrational resonance parameter r_{45}^J , indicating that the perturbation becomes stronger with increasing J .

Table 4.10. Global parameter fit: groundstate, ν_5 , $2\nu_5$, and $3\nu_5$ of $^{12}\text{C}_2\text{H}_2$. All parameters are in units of cm^{-1} . NZW is the number of transitions with non-zero weights; *wstd* is the weighted standard deviation from the least squares fit.

Molecular Parameters		
$^{12}\text{C}_2\text{H}_2$	Ground State/ ν_5 / $2\nu_5$ / $3\nu_5$	
	This Work	Hietanen 1983
ω_5	729.171 644(68)	729.173(2)
g_{55}	3.489 878(25)	3.489 9(2)
x_{55}	-2.335 641(46)	-2.336 3(16)
y_{555}	0.013 982 5(96)	1.42(3)
y_5^{55}	-0.006 918 8(86)	-6.95(8)
B_o	1.176 645 85(66)	1.176 640 6(21)
$\alpha_5 \times 10^3$	-2.229 39(16)	-2.245(7)
$\gamma_{55} \times 10^5$	1.998 3(92)	1.24(20)
$\gamma_{555} \times 10^7$	-1.12(16)	0
$\gamma_5^{55} \times 10^4$	-1.064 60(64)	-1.094(5)
$\gamma_5^{55} \times 10^6$	-1.683(18)	0
$q_5^o \times 10^3 \dagger$	2.331 92(44)	-2.311(2) a
$q_{55} \times 10^5 \dagger$	1.731 7(14)	-1.88(16) a
$q_5^J \times 10^8 \dagger$	-1.920 3(22)	1.99(4) a
$D_o \times 10^6$	1.626 49(62)	1.622 1(8)
$\beta_5 \times 10^8$	-2.625 0(68)	-2.49(2)
$\beta_{55} \times 10^{10}$	-3.19(45)	0
$\beta_5^{55} \times 10^9$	-1.249(26)	0
$H_o \times 10^{12}$	1.33(17)	0
$\rho_5 \times 10^9$	-1.812(23)	-3.3(3)
<i>wstd.</i> $\times 10^4$	2.09	
NZW/data	749/786	
bi-wts	5 σ	

a) This value is half of the number reported in cited reference.

† Sign of constant depends on phase convention (see Section 3.5).

Vibrational ℓ -doubling is absent in the $\nu_5 = 3$ state and the analysis of this state in a global fit which included the fundamental ν_5 and the three hotbands $2\nu_5 \leftarrow \nu_5$ was straightforward. Parameters such as the fundamental frequency, ω_5 , and anharmonicity constants such as x_{55} and y_{555} were determined. The results are presented in Table 4.10. Some new parameters were introduced, which were not determinable in the limited fit up to two excited quanta. These are notably vibrational corrections to the rotational constant B_v , as expressed in γ_{555} and γ_5^{55} , and to the centrifugal distortion constant D_v , i.e. β^{55} . Corrective terms such as q_5^ℓ as predicted by Watson (1983) and q_5^{JJ} , as proposed by Herman *et al.*(1991), were initially included in the fit. The extent of the vibrational states, a total of four, involved in the fit were not sufficient to determine q_5^ℓ , conclusively. The latter contribution is mainly absorbed in the lower order Coriolis interaction constants q_5^0 and q_{55} . The inclusion of q_5^{JJ} resulted in a positive sign of ρ_5 . Omitting these parameters from the fit did not alter the fit significantly except for the sign change in ρ_5 .

As observed in the analysis of the other bands, the addition of new parameters influences the outcome for other parameters. For instance the parameter γ_5^{55} reduced the value of the lower order term γ^{55} . Similarly, incorporating β^{55} has the effect of introducing an ℓ -type splitting of the effective centrifugal distortion constant within a vibrational multiplet. The lower ρ_5 value as determined from the global fit is correlated to the introduction of β^{55} .

In Table 4.8–4.10 this work is compared with the results of Hietanen (1983). It should be noted that many of his parameters were calculated from effective parameters and, therefore, show larger errors. Despite this fact, the parameters retrieved in this study form a remarkable improvement over previous published studies of roughly one order of magnitude. A complete list of all transitions up to three excited quanta as observed in this study is given in Appendix C. The list also includes the observed bands of the isotopomer of $^{13}\text{C}^{12}\text{CH}_2$.

4.6 Discussion

Figure 4.6 shows the observed rotation–vibration bands which were analyzed in this study. A total of 2486 and 595 observed frequencies of $^{12}\text{C}_2\text{H}_2$ and $^{13}\text{C}^{12}\text{CH}_2$, respectively, have been compiled in the $13.6\mu\text{m}$ region and were fitted to an appropriate Hamiltonian of a linear molecule. The spectral resolution of the data used in this study is a factor of six times higher than the recent published investigation of the major isotope by Hietanen *et al.*(1981, 1983) and almost two times higher for $^{13}\text{C}^{12}\text{CH}_2$ (Hietanen *et al.*1986).

The infrared bands of both isotopes up to two excited quanta, i.e. $\sum_i \nu_i = 2$, were simultaneously fit to global parameters. Since the $\nu_4 = 1$ fundamental is not observed in the infrared, some constants of this state remained effective parameters. The simultaneous fit favorably agreed

with the limited fit, involving in one case the overtones of ν_5 and in the other solely the combination band; results from the direct energy level fit agree with results alternatively derived from lower state combination differences (Hillmann *et al.* 1991).

Difficulties were encountered in the fit of the highly excited combination bands involving the three quantum levels of $2\nu_4 + \nu_5$ and $\nu_4 + 2\nu_5$ due to high correlation between the diagonal and non-diagonal vibrational contribution to the energy level. For this reason and the prospect of possible perturbation in the higher excited states, the $\nu_4 + 2\nu_5$ state have been fitted keeping the lower state parameters frozen. Since no transitions to the $2\nu_4$ levels are observed in this wavenumber region, the $2\nu_4 + \nu_5 \leftarrow 2\nu_4$ bands were fitted separately to effective molecular constants. In both fits to the combination states some of the higher order parameter needed to be constrained in order to obtain coherent results.

The $3\nu_5 \leftarrow 2\nu_5$ bands were fitted simultaneously with the lower overtone bands and the fundamental ν_5 . Global parameters such as ω_5 and anharmonicity constants were derived. In most fits reported here, the overall standard deviation were on the order of $2 \times 10^{-4} \text{cm}^{-1}$ or less.

Figure 4.7 demonstrates the effect of vibrational ℓ -type resonance between the two Σ components in $\nu_4 + \nu_5$ and the two π components in $2\nu_4 + \nu_5$ and $\nu_4 + 2\nu_5$. For comparison the unperturbed level energies are also indicated. In case of $2\nu_4 + \nu_5$, the $\nu_2(\Sigma_g^+)$ level (1974.3cm^{-1}) lies between the Φ_u and $I\pi_u$ component. The coincidence of both vibrational levels may explain the abnormal values obtained for q_5^{eff} and q_5^J and the need to introduce effective B -values for each of the sublevels.

Studies of highly excited overtones of acetylene in the near IR and visible spectrum (Sherer *et al.* 1982, Smith and Winn 1988, 1990, Herman *et al.*, 1989, Yamanouchi *et al.* 1991, Zhan *et al.* 1991) reveal the importance of Darling-Dennison and Fermi type resonances between highly excited vibrational levels. It is therefore expected that such perturbations play a more significant role the higher the excitation level becomes. Because of the small separation of the ν_4 and ν_5 level in the deuterated species C_2D_2 ($\Delta = 29 \text{cm}^{-1}$), resonances of the first type have been observed in the relatively low excited vibrational states such as $2\nu_4/2\nu_5$ and $2\nu_4/\nu_4 + \nu_5$ (Huet *et al.* 1991). For the major isotopic species and $^{13}\text{C}^{12}\text{CH}_2$ the separation is larger ($\Delta = 117 \text{cm}^{-1}$ and 115cm^{-1} , respectively) and, consequently, such a resonance is expected to play a less significant role in this case. The Dennison-Darling resonance connects to first order vibrational states of identical symmetry (Allen and Cross, 1963, Dennison and Darling, 1940). This might explain the weak nature of the interaction between the ν_2 and $2\nu_4 + \nu_5$ states of g and u symmetry, respectively, despite their proximity in energy.

This analysis did not require a formal treatment of vibrational resonances between distinct vibrational states. Some unusual values of molecular parameters indicate some minor perturbation, but they did not require extended perturbative treatment. In Fig 4.8 the ℓ -dependent splitting of

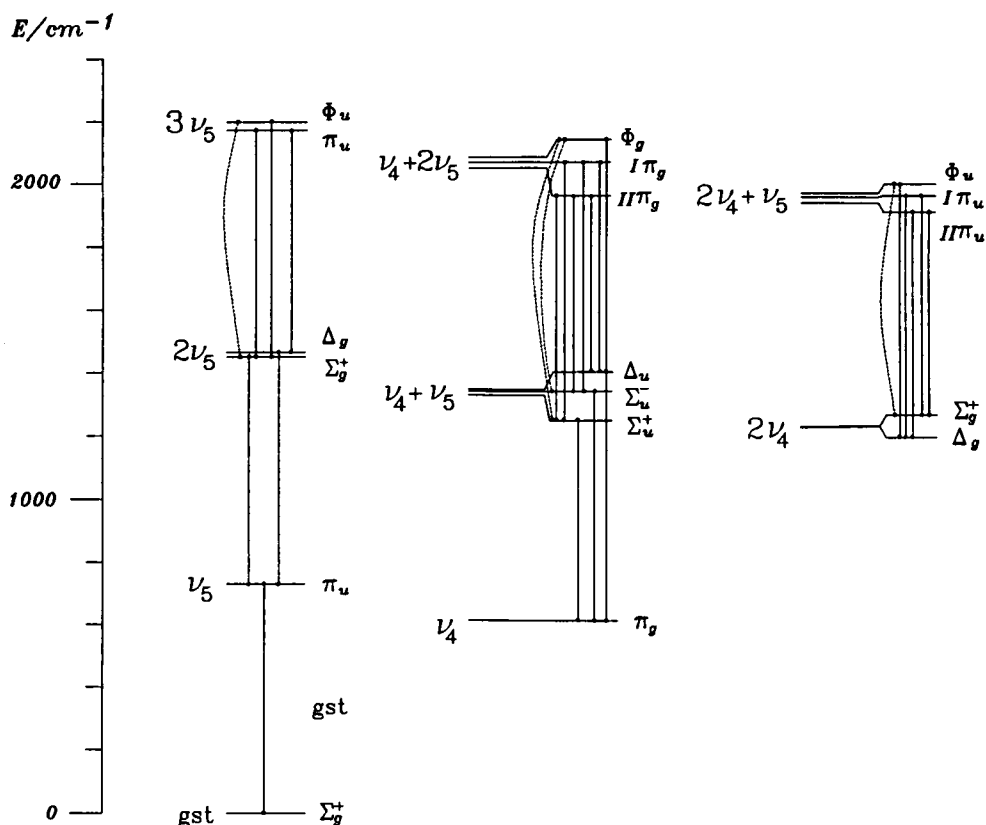


Figure 4.6. Observed absorption bands of acetylene. Transitions included in the least squares analysis are indicated by solid lines. Due to the mixing of vibrational sublevels as a result of ℓ -resonance, forbidden transitions ($\Delta\ell = 3$) are possible and shown here as curved dotted lines. The absolute energies have been estimated by using the known vibrational term values $G_v(1^{\pm 1}, 0^0) = 612.9\text{cm}^{-1}$ and $G_v(2^0, 0^0) = 1230.4\text{cm}^{-1}$ (Palmer *et al.* 1972, Hietanen *et al.* 1981, 1983). Some levels are exaggerated for clarity of presentation.

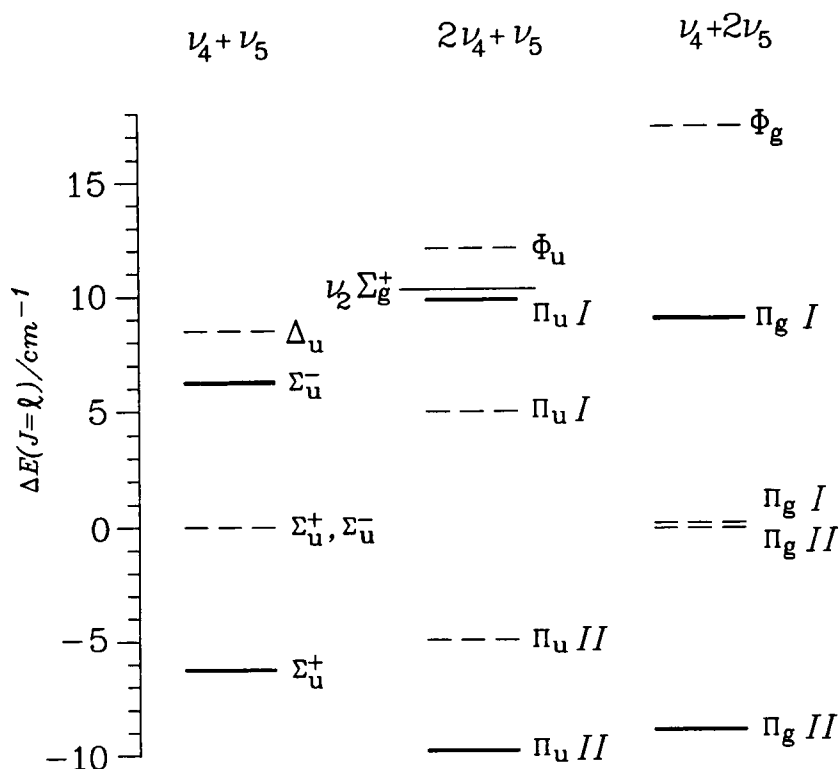


Figure 4.7. Vibrational ℓ -doubling. The ℓ -resonance is shown in symmetric arrangement. The absolute energies for the zero level indicated are 1341.39cm^{-1} for $\nu_4 + \nu_5$, 1964.04cm^{-1} for $2\nu_4 + \nu_5$, and 2097.94cm^{-1} for $\nu_4 + 2\nu_5$ (see comments in Fig. 4.6). The dashed levels are the unperturbed levels. The relative energy is also indicated for the $v_2 = 1$ non-degenerate vibrational state.

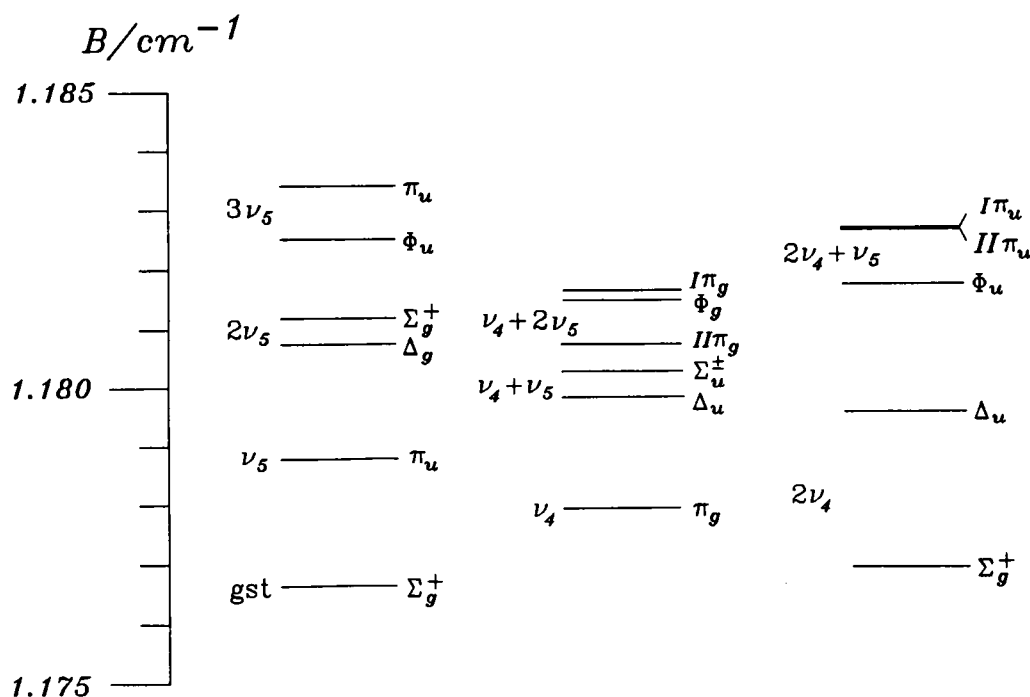


Figure 4.8. Vibrational splitting of B_v .

the B_v parameters are shown. Due to the large γ^{44} as compared to γ^{55} , the splitting is quite large for the $\ell = 2$ and $\ell = 0$ sublevels in $2\nu_4$.

Within the error limit, the results presented here agree with the unpublished results by Kabbadj *et al.*(1991). Their study covered the region from 50–1450 cm^{-1} , which included the analysis of difference bands, for instance $\nu_5 \leftarrow \nu_4$ and $2\nu_5 \leftarrow \nu_4 + \nu_5$ in the far IR, and extended to transitions up to four excited quanta (Kabbadj *et al.*1991). Differences in some of the retrieved parameters, particularly the higher order parameters, reported by Kabbadj *et al.*(1991) and in this study can be attributed to the use of a global Hamiltonian in their investigation versus an effective Hamiltonian used here. The variety of optical densities available in this study permitted to extend the rotational assignment to unprecedented high J values.

In order to emphasize the effect of ℓ -type resonances on the unperturbed energy levels of the major isotope, Fig. 4.9–4.11 show the differences between the eigenvalues, as obtained after numerical diagonalization, and the unperturbed energies, as described by the diagonal energies of the factorized Hamiltonian, for selected vibrational multiplets. Since the factorization of the Hamiltonian separates blocks of different symmetry labels, the e and f blocks do not perturb each

other within a given vibrational state.

The lowest state for which perturbation effects can be studied is the $2\nu_4$ state. Even though q_4 and q_5 are of roughly same order of magnitude, the proximity of the Σ_g^+ and Δ_g vibrational level ($\Delta = 4g_{44} \approx 3.1\text{cm}^{-1}$) is responsible for the enhancement of rotational ℓ -resonance on the unperturbed energies as compared to the two components of $2\nu_5$ ($\Delta = 4g_{55} \approx 14\text{cm}^{-1}$) (see Fig. 4.9 and 4.10). Although, the vibrational energy of $\ell = 2$ lies below the $\ell = 0$ level, the order of the corresponding rovibrational levels of $2\nu_4$ are reversed since $g_{44} < B_4$ (Hietanen 1983). In Figure 4.11 the observed energy shifts of the $2\nu_4 + \nu_5$ levels are the result of combined vibrational and rotational ℓ -resonance.

The mixing coefficients derived from the unitary transformation yield the contributions of the unperturbed eigenfunctions to each of the perturbed levels. As a consequence, absorption bands originating and terminating in different sublevels of the same vibrational state exchange intensities; usually one branch borrowing intensities to another branch and vice versa. The probability amplitudes of the unperturbed levels, i.e. the square of the mixing coefficients, are shown in Fig. 4.12 and 4.13 for the $2e$ and $0e$ component of $2\nu_4$ and $2\nu_5$ as well as for the $\nu_4 + 2\nu_5^{1fII}$ eigenstate, as an example for a three quantum level. The mixing between the Δ_g and Σ_g advances rapidly at moderate J values in case of $2\nu_4$, which is responsible for the fairly strong forbidden band $2\nu_4 + \nu_5^{3e,3f} \leftarrow 2\nu_4^{0e}$ ($\Delta\ell = 3$) observed in the spectrum. Table 4.11 lists observed and calculated transitions of the R - and P -branch of this band. Other possible "forbidden" bands in the $14\mu\text{m}$ region originating in the two quantum levels are $\nu_4 + 2\nu_5^{3e,3f} \leftarrow \nu_4 + \nu_5^{0e,0f}$ and $3\nu_5^{3e,3f} \leftarrow 2\nu_5^{0e}$, which are also drawn in the diagram of Fig. 4.6. The latter two bands are too weak to be observed in the spectra available here, since considerable mixing in the $2\nu_5$ and $\nu_4 + \nu_5$ state only occurs at higher J values ($J > 30$) in the dying wing of the rotational Boltzmann distribution at room temperature.

Among the two π_g components of $\nu_4 + 2\nu_5$, 50% mixing is instantly given due to vibrational ℓ resonance and the proximity of both unperturbed levels (Fig. 4.12, see also Fig. 4.7). One would expect the same to happen with the two Σ components of $\nu_4 + \nu_5$. By factorizing the Hamiltonian into block diagonal form, the vibrational ℓ -resonance term is removed from the off-diagonal position and added to the diagonal energy terms (see Table 2.4). The consecutive mixing of the symmetrized basis function is therefore limited to rotational effects and its magnitude is comparable to the $2\nu_5$ component.

Intensity perturbation is studied in more detail in the succeeding chapter on experimental intensities of acetylene's infrared bands. For the sake of completeness perturbed energy shifts are graphically presented in Appendix E for each vibrational state observed in this study and Appendix F contains additional depiction of square mixing coefficients for other states not mentioned here. From the preliminary remarks concerning intensity mixing, it is evident that intensity effects due to

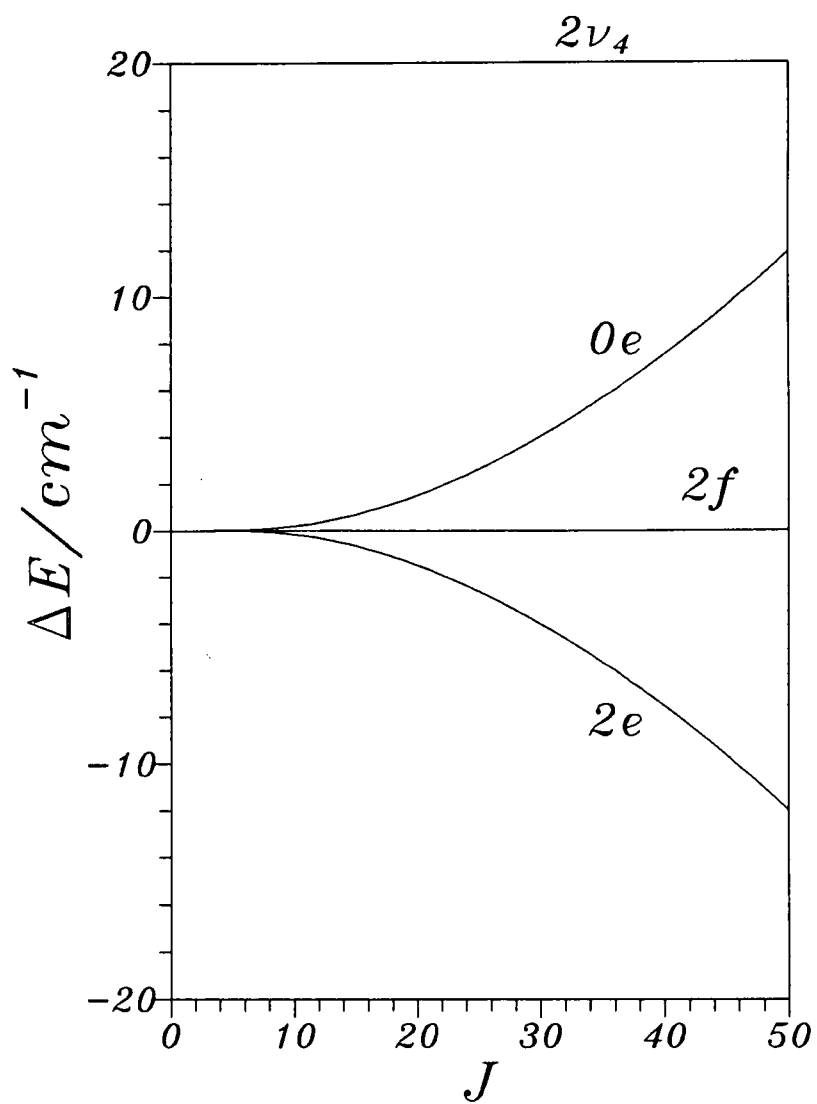


Figure 4.9. Perturbed energy shifts for $2\nu_4$.

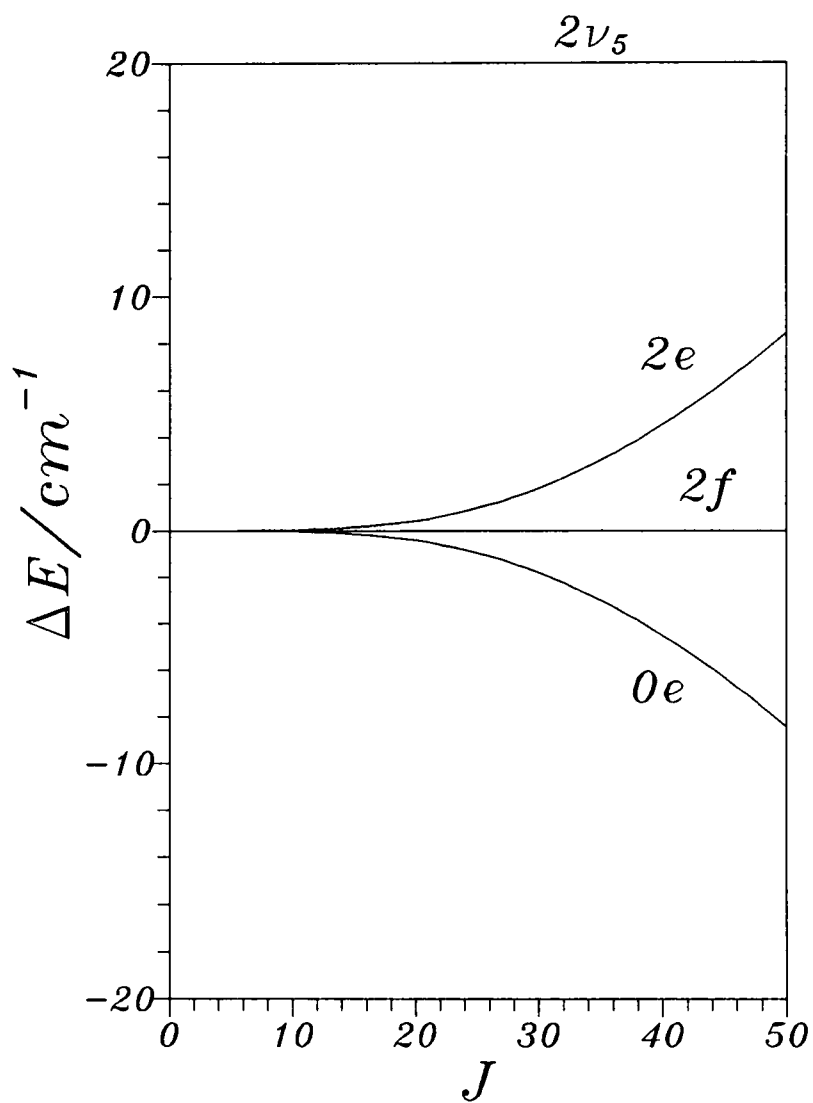


Figure 4.10. Perturbed energy shifts for $2\nu_5$.

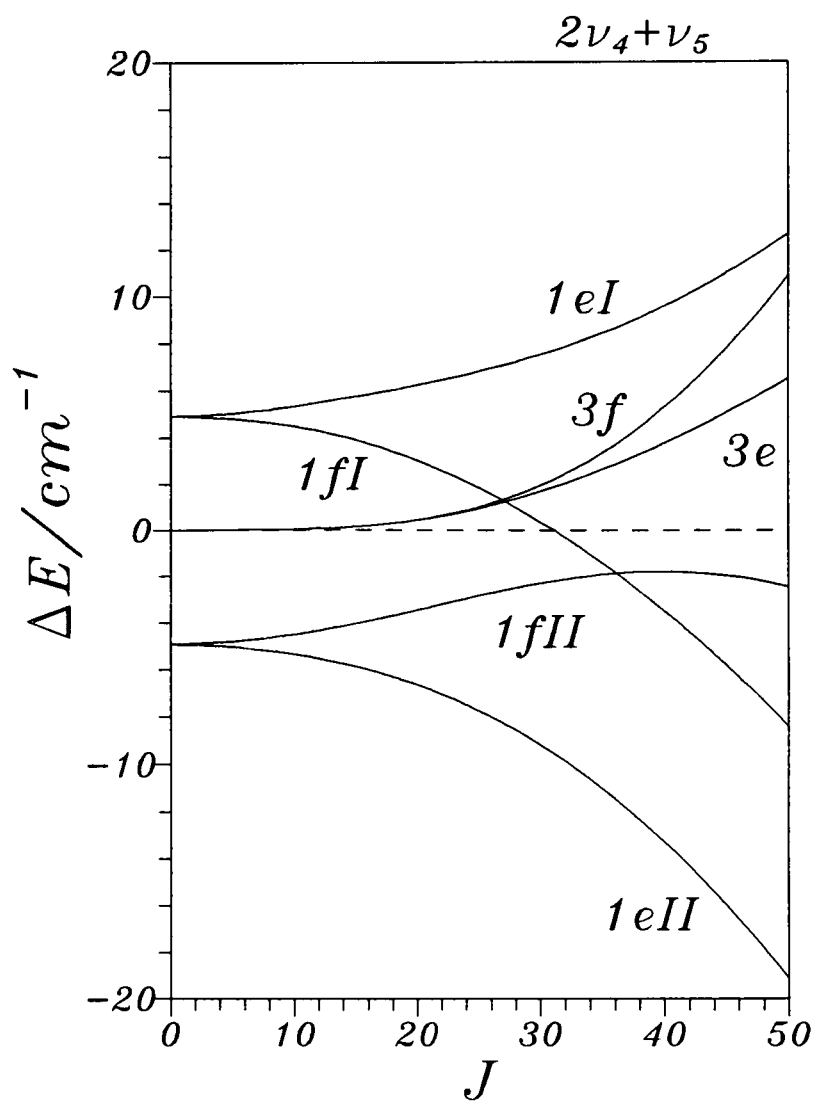


Figure 4.11. Perturbed energy shifts for $2\nu_4 + \nu_5$.

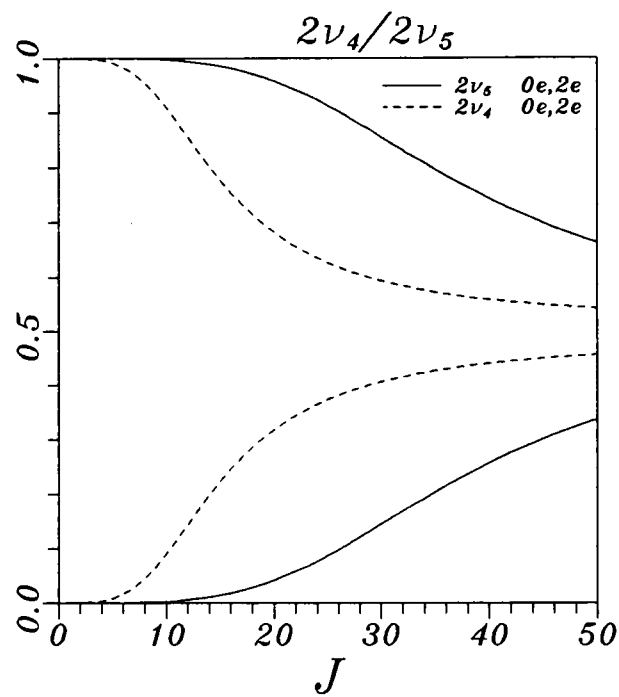


Figure 4.12. Mixing of the $\Delta_J^{(e)}$ and Σ_J eigenfunctions of $2\nu_4$ and $2\nu_5$. Shown are the squares of the mixing coefficients.

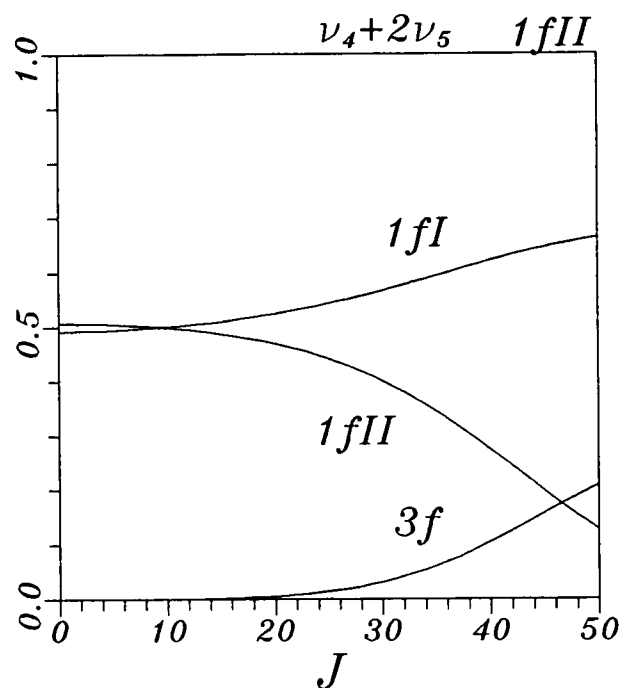


Figure 4.13. Mixing of the three f states of the "unperturbed" $\nu_4 + 2\nu_5^{1fII}$ level. Shown are the squares of the mixing coefficients. Due to vibrational ℓ resonance 50% mixing of the two π_g components are instantly given.

Table 4.11. Observed and calculated frequencies of the "forbidden" band $2\nu_4 + \nu_5^{3e} \leftarrow \nu_4^{0e}$. Observed frequencies are in cm^{-1} and observed minus calculated frequencies are given for the last digits as indicated.

<i>P</i> -branch				<i>R</i> -branch		
<i>J</i>	ν_{obs}	o-c	pk.ht.	ν_{obs}	o-c	pk.ht.
5				745.74114	-18	0.246
6				748.10809	-18	0.191
7				750.47088	-78	0.527
8				752.82984	-17	0.372
9				755.18183	-27	0.707
10				757.52711	-5	0.519
11				759.86488	0	0.791
12				762.19539	-7	0.626
13	700.74241	6	0.670	764.51943	-3	0.822
14	698.33365	-32	0.493	766.83773	3	0.665
15	695.92068	10	0.708	769.14914	-203	0.993
16	693.50368	35	0.490	771.46097	12	0.665
17	691.08333	-5	0.244	773.76798	28	0.817
18	688.66200	21	0.485	776.07292	42	0.226
19	686.23951	-5	0.720	778.37560	-49	0.873
20	683.81769	15	0.463	780.67907	17	0.614
21	681.39655	14	0.662	782.98144	10	0.796
22	678.97681	7	0.415	785.28375	-7	0.537
23	676.55901	8	0.616	787.58606	0	0.749
24	674.14336	12	0.233	789.88843	-7	0.451
25	671.72972	-13	0.532	792.19074	-18	0.668
26	669.31877	-4	0.276	784.49299	-37	0.347
27	666.90983	-31	0.430	796.79500	-56	0.558
28	664.50321	-57	0.213	799.09664	-76	0.257
29	662.09897	-69	0.329	801.39779	-93	0.419
30	659.69662	-146	0.118	803.69803	-134	0.181
31				805.99741	-175	0.293
32				808.29569	-255	0.105
33				810.59287	-269	0.203

vibrational and rotational ℓ -doubling make up the major contribution to intensity perturbation in the overtone bands of acetylene and most other polyatomic linear molecules.

CHAPTER 5

ABSOLUTE INFRARED INTENSITIES IN THE ν_5 REGION

5.1 Introduction

Numerous studies of acetylene's rotation-vibration bands in the electronic ground state and in excited electronic states have been reported. While most investigations primarily dealt with energy level structure and line positions, relatively few studies concentrated on absolute band intensities in the ν_5 region. All of the earlier work on infrared intensities in this region applied the Wilson-Wells-Penner-Weber method (Wilson and Wells, 1946; Penner and Weber, 1951) or the Curve-of-Growth method (Kaplan and Eggers, 1956) to obtain integrated intensities (Kelly *et al.* 1951; Eggers *et al.*, 1955; Wingfield and Straley, 1955; Varanasi and Bangaru, 1974). Even in times of advanced spectrometric resolution, which permits the retrieval of intensities from well isolated transitions within a vibrational band, only two studies reported individual band intensities for the strongest bands observed in the bending region. Varanasi *et al.* (1983) obtained band intensities for the ν_5 fundamental and the seven nearby strongest hotbands from medium resolution FTS spectra and Weber *et al.* 1989 reported individual line intensities from high resolution tunable diode laser measurements. Other recent intensities studies can be considered as an extension to the earlier work on integrated intensity measurements (Mast and King, 1976; Smit *et al.*, 1978; Kim and King, 1979; Koops *et al.*, 1984) to confirm *ab initio* calculations of the dipole moment function from normal mode analysis and its transferability to different isotopic species and other hydrocarbons (Galabov and Orville-Thomas, 1973; Prasad, 1978; Jona *et al.*, 1981; Smit and van Dam, 1982; Pavlushkov and Shchepkin, 1982; Nikola *et al.*, 1984).

The preliminary intensity study (Weber *et al.*, 1989) showed discrepancies of the hotband intensities retrieved from individual transitions as compared to Varanasi *et al.* (1983). Since then, the tunable diode laser (TDL) measurements conducted at the University of Tennessee have been extended to include more transitions of the fundamental and selected hotband transitions of the major isotope. In addition intensities are compared to values retrieved from FT spectrometric data obtained at the National Solar Observatory, Tucson, Arizona. From the combination of FT spectrometric data and TDL measurements, a coherent picture of the intensity distribution of fundamental and the seven one quantum hotband in the 14 μm region is established. From the discussion at the

end of Chapter 5, it is evident that perturbation due to vibrational and rotational ℓ -type resonances has to be taken into account in a meaningful intensity analysis of any linear polyatomic molecule.

For the first time experimental intensities of acetylene have been determined by properly taking care of of ℓ -resonance effect upon hotband intensities. ℓ -resonance effects on intensities have been qualitatively indicated by Moravec *et al.*(1990) and theoretically discussed by Herman *et al.*(1991) for acetylene. After correcting intensities by determining intensity factors due to ℓ -resonances, linear Herman-Wallis factor due to remaining rotation-vibration interaction can be established (Watson 1987, Herman and Wallis 1955).

Line intensities of the ν_5 fundamental and the Q -branch of $\nu_4 + \nu_5^{0e} \leftarrow \nu_4^{1f}$ have been measured using the TDL system at the University of Tennessee. Intensities of all seven one quantum hotbands of $\nu_4 + \nu_5 \leftarrow \nu_4$ and $2\nu_5 \leftarrow \nu_5$ in addition to the fundamental ν_5 of both isotopes, $^{12}\text{C}_2\text{H}_2$ and $^{13}\text{C}^{12}\text{CH}_2$, have been measured using the FT spectrometric data obtained at the National Solar Observatory at Tucson, Arizona. The zeroth order vibrational band intensities apart from resonance effects indicate that intensities of the hotbands follow the vibrational Boltzmann distribution within the error limits of the experimental data. Therefore, an unique dipole moment derivative for the ν_5 bending mode was determined.

While the retrieved vibrational band intensities from TDL and FTS measurements agree rather well, the Hermann-Wallis factors determined from the diode laser measurements are a factor of 3-5 smaller than those retrieved from the FTS measurements. Part of the problem might be related to the pressure uncertainties encountered for part of the FTS data, which were primarily taken for frequency standards (Hillman *et al.*1991, Chapter 4). Furthermore, instrumental distortion of line shape profiles in both TDL and FTS have distinct effects on the measured intensity and the method of retrieval.

To overcome problems related to correct pressures, FTS intensities have been calibrated by ratioing intensity data from the TDL measurements, for which sample temperatures and pressures were well known, with those obtained from the FTS spectrometer. While the band intensities agree with predicted values, the retrieved Herman-Wallis factors from FT spectrometric data are considered tentative. The factors determined are in the range of $A_1^{PR} = 6.0 - 13.0 \times 10^{-4}$ for all nine bands, including the fundamental of the $^{13}\text{C}^{12}\text{CH}_2$ isotopomer, and are positive in sign. In contrast, the factors derived from TDL measurements are about a factor of 2-5 times smaller and no F -factor was observed in the case of the one Q -branch measured with the TDL system.

By correcting for the natural abundance of the lesser isotopomer, it was found that its fundamental intensity is comparable in magnitude to that of the major isotope. Isotopic intensity ratio are very important for establishing isotopic abundances in the atmospheres of the outer planets. Since the singly substituted isotope was detected in Jupiter's atmosphere by Drossart *et al.*(1985),

acetylene might serve as a secondary probe to methane for stellar and planetary isotopic ratios.

5.2 Experimental Details: The TDL system

The general design and operation of the tunable diode laser (TDL) system at the University of Tennessee has been described in detail by Chin (1985) and Brannon (1991). The experimental setup and operation control are schematically shown in Fig. 5.1. Spectral resolution of this spectrometer is better than 0.0005cm^{-1} , a factor of about 3 higher than the FTS spectrometer used in this study. Intensity measurements were conducted with a Laser Analytics continuous-wave $\text{PbS}_{1-x}\text{Te}_x$ salt laser, which is mounted on a vacuum insulated cold finger and connected to a closed-cycled cryogenic Helium compressor. Coarse adjustment of the frequency output can be accomplished by adjusting the temperature control unit; scanning of the frequency in a narrow interval, typically less than 0.1cm^{-1} , is done by superimposing a 100Hz linear ramp from a Krohn-Hite wave form generator on the d.c. injection current in the LCM module. A mechanical rotating shutter synchronized with the sawtooth modulation blocks the IR beam to determine 100% absorption level at the beginning and end of each spectral scan. During a scan, the shutter is opened for transmission approximately 80-90% of the total scanning time.

The infrared beam successively passes thru the absorption cell, mechanical shutter, the monochromator assembly in Czerny-Turner configuration containing a reflecting grating with a grating constant of $d = 70\text{mm}^{-1}$, and finally to a liquid nitrogen cooled photovoltaic HgCdTe detector from Santa Barbara Research. The detected signal is amplified by a pre-amplifier and passed to a signal averager. Typical dwell time of the signal averager which adds and averages successive scans is set to $5\mu\text{s}$ per channel. At such a high rate of sweep integration with a saw tooth modulated injection current, the laser mount is prevented from reacting to the modulated heat load and adds to the temperature stability of the laser system (Jennings 1980, 1988).

For each absorption lines measured, a set of 4-5 spectra at different pressures were recorded. The acetylene sample provided by Matheson Co. had a stated purity of 99.99% and the pressure in the absorption cell was monitored by a MKS Baratron capacitance manometer equipped with a 1Torr and 1000Torr transducers (head type 315BHS1). Prior to the measurements the pressure gauges were sent to the manufacturer and a calibration check verified its nominal precision of 1% of full scale. Before each set of measurements, a scan at saturation pressure was taken to confirm the 100% absorption level as defined by the closed shutter. Frequency calibration was carried out by placing a solid Ge etalon with a free spectral range of 0.01623cm^{-1} (accurate to 1% (Chin 1985)) in the IR beam after each recorded set of spectral line measurements.

The following experimental procedures were developed to ensure optimum conditions for

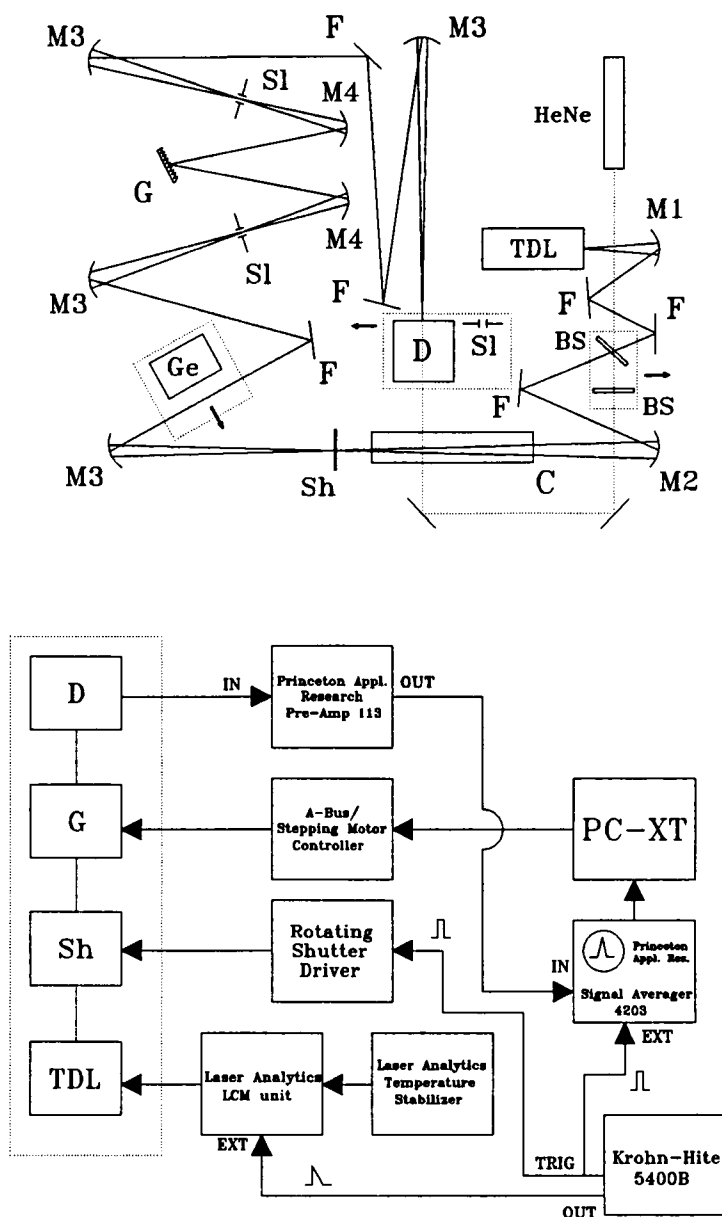


Figure 5.1. Experimental set up of the TDL spectrometer. Top: F: flat mirror, M1: $f=26.7\text{cm}$, M2: $f=121.9\text{cm}$, M3: $f=63.5\text{cm}$, M4: $f=40.6\text{cm}$, C: absorption cell, Sh: rotating shutter, Ge: solid Germanium etalon (0.01623cm^{-1}), Sl: slit, G: grating (70mm^{-1}), D: HgCdTe detector, BS: beam splitter and pellicle. Inserting a beam splitter assembly, the HeNe laser can be used to optimize and adjust the optical system in the forward and backward direction relative to the IR beam. Bottom: The various control and operation stages of the TDL spectrometer are shown. The PC-XT serves two purposes, one is to control the motion of the grating and for receiving spectral data from the microprocessor inside the signal averager.

the experiment and eliminate possible systematic errors. It was observed that the cell walls made out of stainless steel adsorb a non-negligible amount of the absorber gas, resulting in systematic low intensity readings. In order to saturate the cell walls, the cell was filled with the absorber gas overnight at slightly higher pressure than normally during the experiment. Before the recording session, the cell is evacuated for 10–15 minutes and then refilled with fresh acetylene for the intensity measurements. Equilibration time allowed for the gas before measurements were taken were on the order of 10–15 minutes.

Spurious optical fringes observed in the spectra caused by the parallel surfaces of the KBr windows attached to the cell were avoided by placing the cell at a position of convergent optical beam geometry as shown in Figure 5.1. Frequency calibration improves, if the Ge etalon is properly aligned parallel to the IR beam. This can be achieved by slowly rotating the Ge etalon and at the same time observing the shift of the etalon fringes on the display of the signal averager. By passing thru the optimum parallel position, the fringes start to shift in the opposite direction. Since the optical beam is aligned at a constant level above the optical table, vertical alignment of the etalon posed no problem.

The rapid scans thru the spectrum are averaged and stored in the 1024 memory channels of the signal averager. Each recorded spectrum consists of series of 3000–5000 averaged scans, depending on the signal-to-noise ratio of the particular laser mode observed. The higher the noise level, the more scans are averaged to produce the spectrum. A serial communication link between the PC-XT and the built-in micro processor permits the transfer of signal averager memory into the computer, where the digitized data can be further analyzed. In addition to storage of spectral data, the grating motion is controlled from a BASIC program within the PC. Using the visible fringes of the HeNe laser as a calibration source, the absolute step number of the stepping motor driving the grating assembly can be translated into the dispersed frequency permitted thru the exit slit, and vice versa.

5.3 Terminology of Intensity Parameters

An excellent review about intensity retrieval from individual measured absorptions lines is given by Smith *et al.* (1985). The important spectroscopic parameter relevant to this study will be reviewed here. One starts from the Beer–Lambert law of absorption which describes the attenuation of incoming radiation passing through a sample of gas. It is written as follows

$$I(\nu) = I_0 \exp(-\alpha(\nu)x), \quad (5.1)$$

where I_o is the intensity of the incoming monochromatic radiation and $I(\nu)$ the attenuated frequency dependent intensity due to absorption by the gas molecules (Penner 1959). The parameter $\alpha(\nu)$ is called the frequency dependent absorption coefficient; its dimension depends on the choice of units for the optical density x . Common choices for the optical density are, for instance, the products of either the absorber pressure or the number density of the absorber molecules in the sample and the radiation path length in the gas sample. For an individual absorption line the absorption coefficient can be written as

$$\alpha(\nu - \nu_o) = S\phi(\nu - \nu_o), \quad (5.2)$$

where $\phi(\nu - \nu_o)$ is the unit area line shape function centered at ν_o and S is the line strength (intensity) or integrated absorption coefficient. The dimension for the optical density in this study is $\text{cm} \cdot \text{atm}$ and the line intensity S is therefore in units of $\text{cm}^{-2} \text{atm}^{-1}$.

Neglecting radiation damping or natural line broadening (Penner 1959) and collisional narrowing effects (Varghese and Hanson, 1984), the line shape is dominated by broadening due primarily to binary collisions and due to the Doppler effect caused by the thermal motion of the particles. The resulting line shape from both broadening mechanism is described by the Voigt profile, i.e.

$$\phi(\nu - \nu_o) = \frac{Pa}{\pi} \int_{-\infty}^{\infty} dy \frac{\exp(-y^2)}{a^2 + (\xi - y)^2}, \quad (5.3)$$

where a and ξ are the reduced dimensionless Voigt parameters defined as

$$a = \sqrt{\ln 2} \frac{b_L}{b_D} \quad (5.4)$$

and

$$\xi = \sqrt{\ln 2} \frac{\nu - \nu_o}{b_d} \quad (5.5)$$

P is the normalization constant of the pure Doppler profile given by

$$P = \sqrt{\frac{\ln 2}{\pi}} / b_D. \quad (5.6)$$

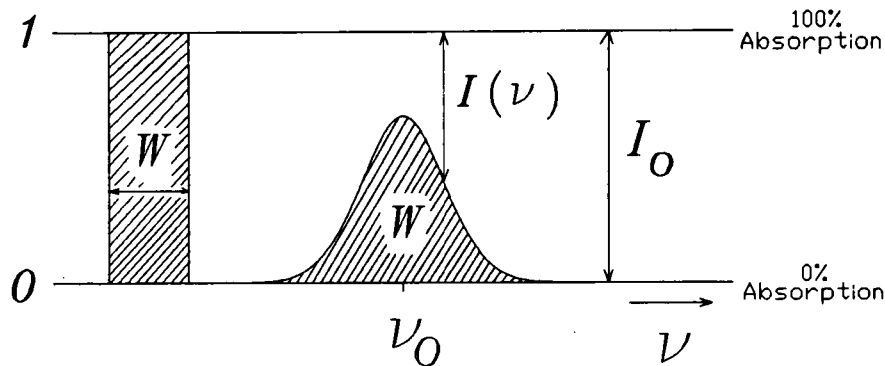


Figure 5.2. Definition of equivalent width. The equivalent width is defined as the width (and area) of a rectangle having the same value as the integrated absorption over the line profile.

The Voigt profile is the convolution of the Doppler and Lorentz profile, where b_L is the Lorentz half width of half maximum (HWHM) and b_D the Doppler half width with value

$$b_D = \nu_0 \sqrt{2 \frac{kT}{Mc^2} \ln 2}, \quad (5.7)$$

where T is the sample temperature in Kelvin, M the molecular mass, c the speed of light, and k the Boltzmann constant. In the limit $a \rightarrow 0$ and $a \rightarrow \infty$ the Voigt profile transforms into the Doppler and Lorentz profile respectively.

Another important quantity is the equivalent width, W , which is the integrated absorption of the absorption profile (see Fig. 5.2) and is defined as

$$W = \int_{-\infty}^{\infty} \frac{I_0 - I(\nu)}{I_0} d\nu = \int_{-\infty}^{\infty} [1 - \exp(-S\phi(\nu - \nu_0)x)] d\nu. \quad (5.8)$$

Fig. 5.3 shows a contour plot of the reduced equivalent width, W/b_D , as a function of the broadening parameter, a , and SPx . It can be seen from this figure that the equivalent width is a monotonic increasing function with respect to its two parameters. As a consequence SPx and in turn the line strength S can be uniquely inferred from the measured integrated absorption by an inverted search

through the reduced equivalent width table, if a is known from measurements or otherwise established. This inverted search is the prescribed method to retrieve intensities in the so called equivalent width method (Benedict *et al.* 1956, Kaplan and Eggers, 1956). In order to facilitate intensity and broadening measurements via the equivalent width, Jansson and Korb (1968) published an equivalent width table for various a and SPx covering the pure Doppler region ($a = 0$), the intermediate Voigt region, and the bordering Lorentz region up to $a = 10$.

5.4 Methods of Intensity Retrieval (TDL Intensities)

Four methods have been used in this study to aid in the retrieval of absolute intensities from individual line measurements using a TDL spectrometer. These are a) the direct method via the line center absorption, b) the equivalent width method, c) the Beer plot, and d) line profile fitting.

a) The Direct Method

The direct method works best in the Doppler region since the line intensity, S , can be directly related to the line center transmission, $\tau(\nu_o)$ at $\nu = \nu_o$. From Eqs. (5.1) and (5.2), the line center transmission for any given symmetric line shape can be stated as

$$\tau(\nu_o) = I(\nu_o)/I_o = \exp(-S\phi(0)x) \quad (5.9)$$

If $a = 0$, the Voigt shape, Eq. (5.3), becomes the Doppler profile, i.e.

$$\phi(\nu - \nu_o) = P \exp \left(-\ln 2 \left(\frac{\nu - \nu_o}{b_D} \right)^2 \right), \quad (5.10)$$

For a Doppler profile, $\phi(0) = P$ at the line center frequency, and consequently the intensity, S , can be obtained by inverting Eq. (5.9) and using Eq. (5.6), i.e.

$$S = -\frac{b_D}{x} \sqrt{\frac{\pi}{\ln 2}} \ln(\tau(\nu_o)). \quad (5.11)$$

The HWHM level of the observed line shape, where $\phi(\nu - \nu_o) = \frac{1}{2}\phi(0)$, can be shown to be the width, $\Delta\nu$, of the apparent absorption profile where the intensity of the profile reduces to

$$\tau(\nu_o + \Delta\nu) = \sqrt{I(\nu_o)I_o} \quad (5.12)$$

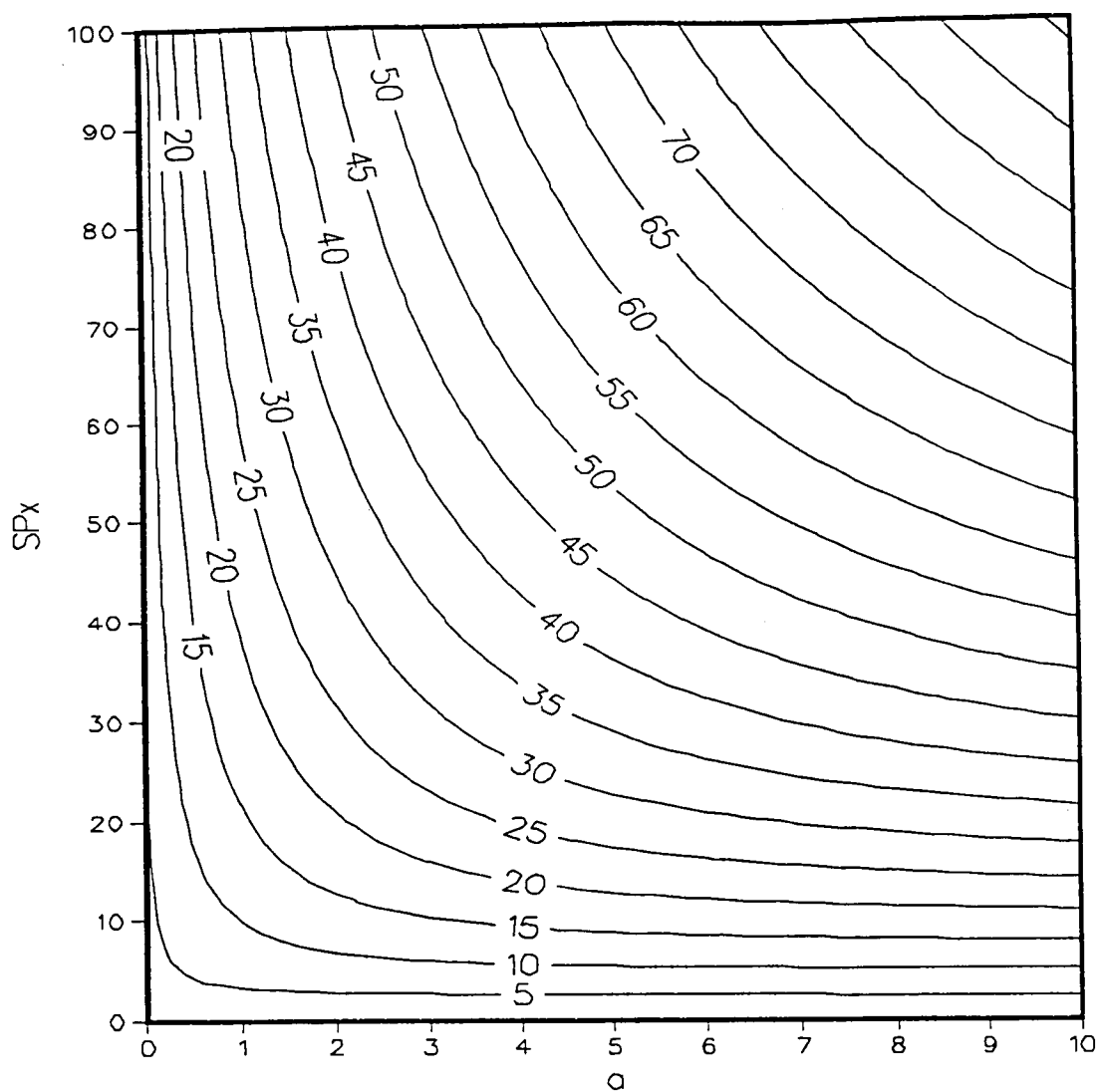


Figure 5.3. Equivalent width contour plot. The reduced equivalent width, W/b_D , is plotted as a function of the two Voigt parameters a and SPx .

(Smith *et al.*1985). If instrumental distortion of the apparent absorption profile is neglected, the observed width should equal Eq. (5.7) in the Doppler limit.

Instrumental distortion arises due to the radiation property of the diode laser, optical components, detector, and electronic amplification. Using heterodyne technique mixing a Pb-salt semiconducting diode laser output with stabilized CO₂ lasers, studies have shown that the diode laser line shape is best described by a Lorentzian line shape (Hillman *et al.*1979), with HWHM ranging from 0.07×10^{-3} to $0.7 \times 10^{-3} \text{cm}^{-1}$ (Strow 1983), which is approximately 10–80% of the Doppler width calculated for acetylene at room temperature. To correct for instrumental distortion not limited to diode laser line shape, it is common to plot correction curves for line strengths as a function of increased observed width as was done for a Lorentzian by Strow (1983) and a Gaussian response function by Strow (1983), Fridovich *et al.*(1981), and Wilkerson *et al.*(1979).

From all measurements of absorption lines reported in this study, for which the Doppler limit can be assumed ($p < 400 \text{mTorr}$), an average ratio of $b_{\text{obs}}/b_D = 1.024(27)$ was found corresponding to an average increase of 2.4% over the calculated Doppler HWHM. A previous study concerning the diode laser system used in this study found that an assumption of a Gaussian instrument function is indistinguishable from a Lorentzian line shape within the error limits (Chin 1985). As an approximate correction, the intensities in the Doppler limit were calculated by Eq. (5.11) by replacing the Doppler width by the observed width. This correction is equivalent to a correction assuming a Gaussian instrument function, where the correction to the Doppler intensity is given by $S_{\text{obs}}/S_D = b_{\text{obs}}/b_D$ (Strow 1983).

A program was designed to specifically implement the direct method using the digitized recording of an individual absorption line. In order to calibrate the spectrum, the absorption minima of the etalon fringes are fitted by a polynomial to obtain the best estimation for the location of the minima in terms of channel numbers. Since some fringes are asymmetrical in the vicinity of their absorption minima, third degree polynomials lead in general to the best estimate for fringe spacing. The absorption minima are then fitted by bi-cubic spline or a polynomial fit to obtain a conversion factor from channel numbers of the signal averager to relative frequencies as defined by the free spectral range of the Ge-etalon. In most cases only two etalon fringes were recorded and the narrow range of the recorded data proved to be nearly linear in frequency. Saturation scans are used to correct the zero transmission as defined by the shutter zero level. The determined correction factor is then automatically applied to all subsequent non saturated absorption scans of the same line. In most cases the correction was less than 2% of the unattenuated transmission intensity.

The baseline is determined by fitting the transmission background away from the line center to a n -th degree polynomial depending on the slope of the background. In most cases the background was linear, but second and third degree polynomial fits had to be applied for few lines. The user

of the program can choose between polynomial fitting, bi-cubic spline through various points of the transmission background, or a simple two-point connection. In order to avoid connecting noise spikes in the last method, the intensities are averaged in the vicinity of the chosen points. After the baseline is determined, the spectrum is normalized and the relative frequency and height of the peak are estimated by fitting a few points near the line center to a second or third degree polynomial. Using Eq. (5.12) the observed half width is determined by fitting few points near the half width level to a linear or quadratic curve on both sides of the absorption peak. The difference of frequencies determined at the half width level on each side yield the observed full width.

As output of the program the relative line center frequency, ν_o , the peak transmission, $\tau(\nu_o)$, the integrated absorption or equivalent width, W , and the observed half width, b_{obs} , are obtained. From these parameters the intensity can be then easily calculated using Eq. (5.11). The intensity retrieval program is highly interactive and during each step of the determination of saturation corrections, the baseline, the line center, the half width, and frequency calibration, the results are graphically displayed. If the user is not satisfied, each step can be repeated by varying the polynomial degree or choosing a different approximation scheme. An example of a graphic display from the program is shown in Fig. 5.4

b) The Equivalent Width Method

For this purpose a program was written to apply a two dimensional bi-cubic spline interpolation of the equivalent width table. Bi-cubic spline interpolation is frequently used for smoothing data since it improves linear interpolation by incorporating second derivatives at the tabulated points (Press *et al.*1986). In order to complete rows and columns of Jansson and Korb's equivalent width table, the same table entry as in the original paper was recalculated and complemented by modifying a program written by Atakan *et al.*(1981, 1985) for line doublets. The Voigt profile was calculated using an adapted code from Armstrong (1967). The stated accuracy of one decimal place in the sixth digit (Armstrong 1967) was more important than the increased speed of recently reported routines (Drayson 1976; Pierluissi *et al.*1977; Hui *et al.*1978; Humlíček, 1979). The revised equivalent width table is believed to be accurate to at least one decimal place in the fifth digit (Weber and Blass, 1991).

It was found that bicubic spline interpolation retrieves equivalent widths with an accuracy of 0.03 percent (Weber and Blass, 1991), a factor of about ten times higher than accomplished by bilinear interpolation of the equivalent width table (Jansson and Korb, 1968). To retrieve intensities from equivalent width measurements, an inverted search of the equivalent width table is necessary. This can be easily achieved by the method of bisection (Press *et al.*1986). The inverted search program to obtain SPx values for fixed Voigt parameter, a , using bi-cubic spline interpolation was

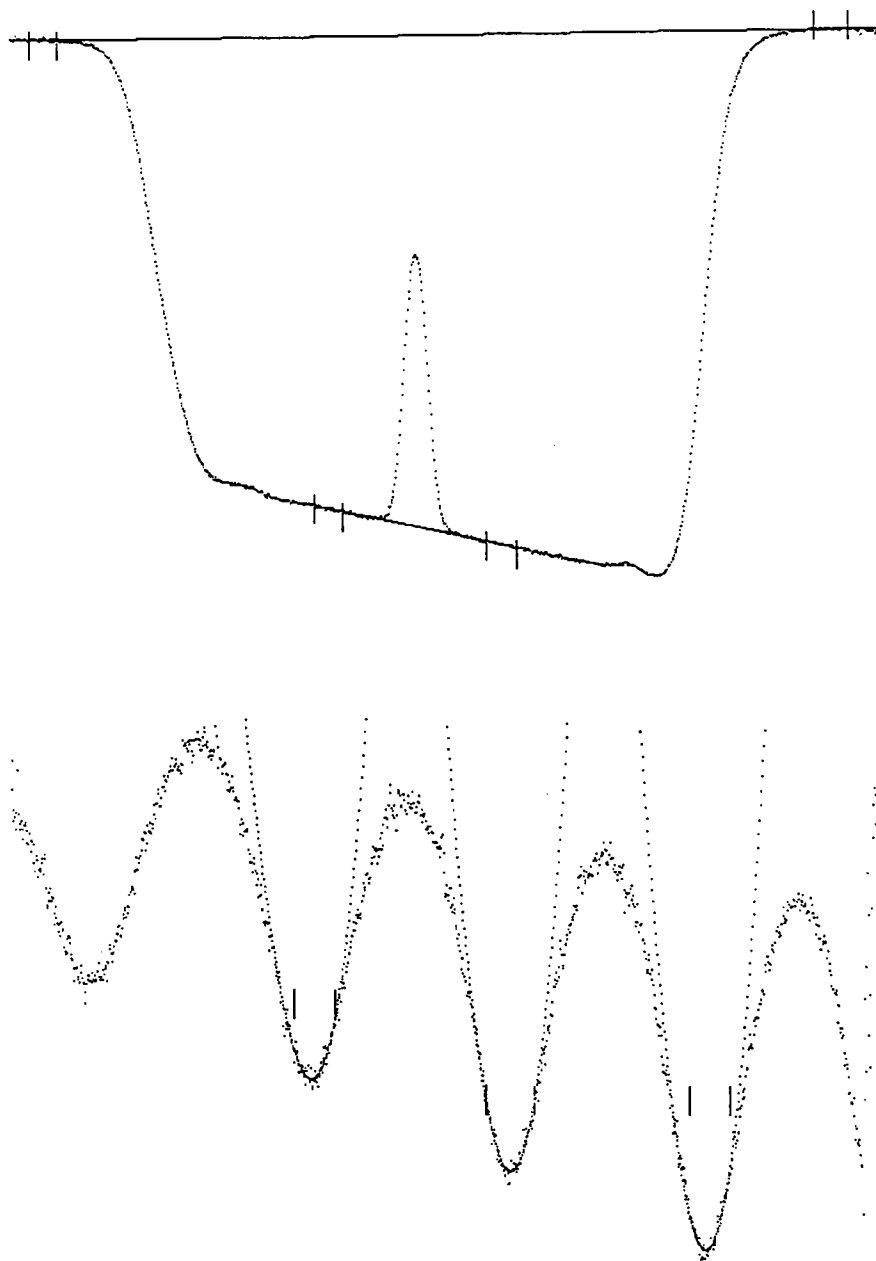


Figure 5.4. Graphical display of transmission background fit and etalon trace. Top: The transmission background as enclosed by the pair of markers is least square fitted to a straight line. Shown here is $R(19)$ of ν_5 at $p = 83.0\text{mtorr}$ and $\nu_o = 776.0810\text{cm}^{-1}$. Bottom: Etalon trace for calibration of top spectrum. Separation of absorption minima is 0.0163cm^{-1} . Each minima is fitted in its vicinity to a third degree polynomial. Each point is then subsequently fitted to determine the conversion factor of channel numbers into relative wavenumber.

shown to be nearly as fast as the direct equivalent width retrieval and about hundred times faster than by direct integration (Weber and Blass, 1991).

It has been shown that the equivalent width is independent of the instrument function (Benedict *et al.* 1956, Pugh and Rao 1976), which is important if the line shape is significantly distorted. However, the equivalent width is more sensitive to errors in the 100% transmission level (Wilkerson *et al.* 1979) and to minor frequency non-linearity in the laser tuning (Jennings 1980). For these reasons and, since the distortion of the line shape is small in this study, the direct method is preferred. Nevertheless using both methods provides a good indication for the influence of instrumental distortion on the measured line strengths.

c) Beer Plot

In the Doppler region, a linear relationship exists between the absorptivity, $-\ln(\tau)$, and the optical density, x , as can be seen from Eq. (5.11). Plotting the logarithm of the peak transmission per unit absorption length versus the pressure, p , produces a straight line if the assumption is correct that the dominant line shape of the absorption profile is a Gaussian. Errors in the 100% transmission and saturation level or pressure can result in plotted curves missing the origin. Such measurements were usually omitted from further analysis. Fig. 5.5 shows the Beer plot for selected R -branch transitions of the ν_5 fundamental.

d) Line Profile Fitting

Few absorption lines were recorded at higher pressure than 400mTorr. Those absorption profiles were fitted to a Voigt line shape in a non-linear least squares fit. The parameters fitted are the line strength, S , the line center frequency, ν_0 , and the reduced Voigt parameter, a . The evaluation of the Voigt function was accomplished by adapting a code written by Armstrong (1967). A sample fit is shown in Fig. 5.6 for the $R(27)$ line of ν_5 at $p = 835$ mTorr. The pressure was too low to confidently estimate self broadening and the value retrieved for a is rather considered as a measure for the broadening due to instrumental distortion. Some lower pressure scans were also fitted by the least squares fit and agreed well with intensity values retrieved by the direct method. A variable baseline shift was included in the least square procedure to offset errors of prior baseline removal. The determined offset was usually much smaller than 1%. Initial guesses for the line shape parameters are provided from the program described for method a).

The application of different methods in the intensity retrieval are considered complementary and were chosen to eliminate possible systematic errors as far as possible. Conflicting results reported in intensity measurements are quite common and in most cases are dependent on the chosen retrieval

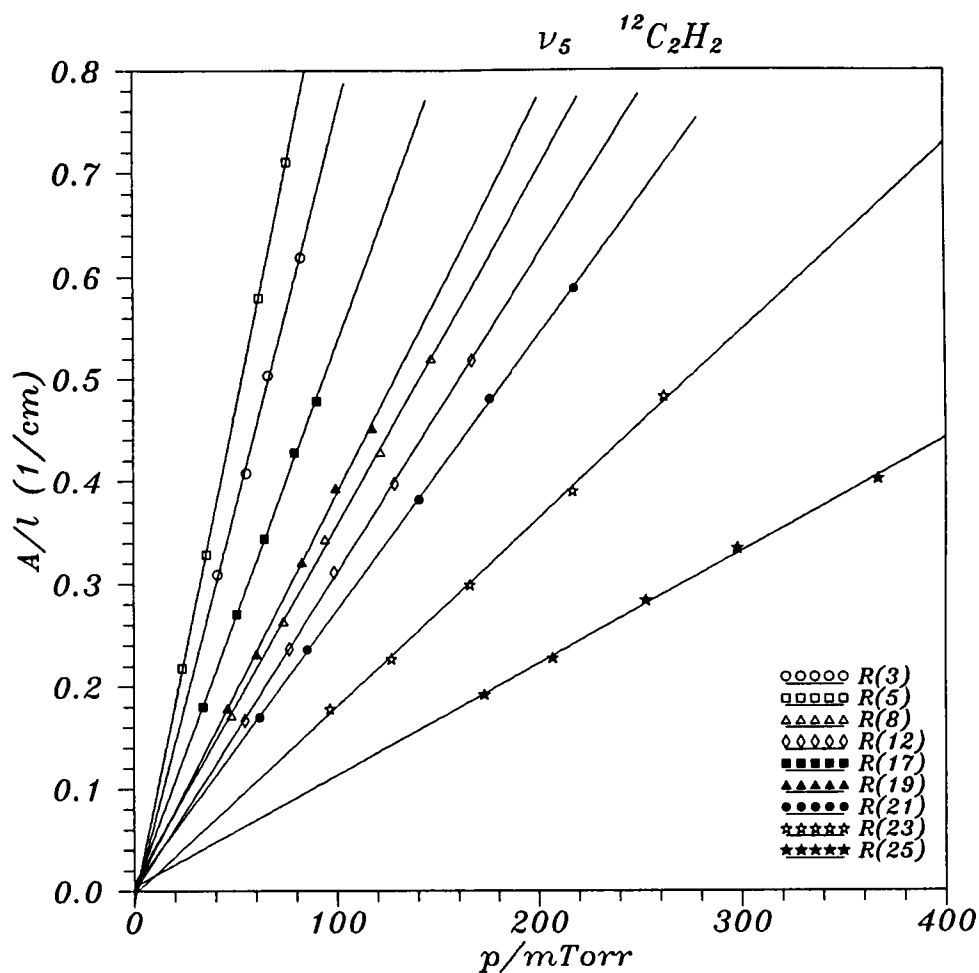


Figure 5.5. Beer plot for selected ν_5 R -branch transitions of acetylene. The absorbance per unit absorption path length is defined as $A = -\ln \tau/\ell$, where ℓ is the length of the absorption cell and τ the transmissivity of the line center peak.

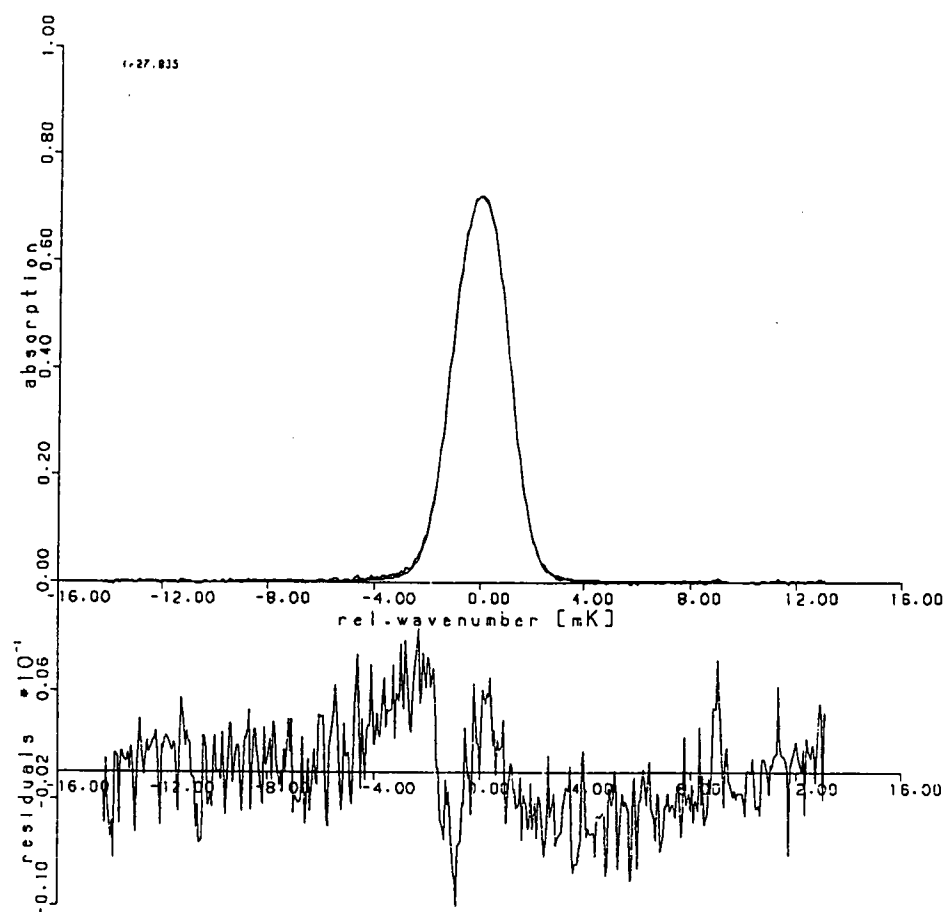


Figure 5.6. Line profile fitting of ν_5 , $R(27)$ at 794.7338cm^{-1} . Pressure was 835mTorr; and parameters retrieved are: the line strength $S = 1.016(10)\text{cm}^{-2}\text{atm}^{-1}$ and $a = 6.799(71) \times 10^{-2}$ (see text).

method. Problems in establishing accurate intensity measurements were addressed for instance by Chedin and Scott (1984) in the case of methane's ν_4 band and the consequences of errors in laboratory spectroscopic intensity measurements for the interpretation of atmospheric spectra. Potential error sources in diode laser measurements due to temperature drifts and varying stability of the operating laser modes of semiconducting lasers have been discussed by Mucha (1981), Restelli and Capellani (1985), and Jennings (1988) among others.

5.5 Experimental Results: TDL intensities

A total of 29 transitions of the fundamental ν_5 and twelve Q -branch transitions of the $\nu_4 + \nu_5^{0e} \leftarrow \nu_4^{1f}$ hot band have been measured using the TDL system. The ambient room temperature during the experiments was $298 \pm 1\text{K}$ as measured from a thermometer located near the cell. This temperature is assumed to be that of the sample in the cell. Three different cell lengths of 2.54cm, 25.4cm, and 50.8cm were used in the experiment. The majority of the measurement were taken at a pressure below 400mTorr, for which the approximation of a Doppler profile for the line shape holds. A Gaussian line profile decreases rapidly to zero and reduces the error in determining the transmission background or baseline. Even at moderately high pressure, the wing contribution to the total integrated absorption increases rapidly. The measurements were in addition limited to lines with center peak transmission varying between $\tau = 0.3 - 0.7$, to minimize error in the determination of peak center transmission. It was shown that this error is minimal if $\tau = e^{-1} = 0.37$ (Jennings, 1980). Small absorption amplitude on the other hand increases the signal-to-noise ratio, if it is defined as the ratio of line height over noise level.

Table 5.1 shows a sample of line parameters, such as observed half width, peak transmittance, pressure, and equivalent width, of some transitions observed in the ν_5 fundamental. The calculated intensities for the ν_5 fundamental using the direct method and equivalent width method are presented in Table 5.2. The standard deviations cited for each intensity are averages of the set of measurements at various pressure of the sample gas of the same transition. Eleven Q -branch transitions from $J = 11 - 22$ have been measured in the $\nu_4 + \nu_5^{0e} \leftarrow \nu_4^{1f}$ hotband, for which ℓ -resonance effects were observed. The measured and calculated hotband line intensities of this band are summarized in Table 5.3. The intensity calculations are explained in the following sections. Although the averaged intensity for each transition is satisfactorily low (1-2%), the actual standard deviation is actually higher as can be seen from the repeated measurement of $Q(23)$ of the fundamental (see Table 5.2).

Table 5.1. Selected individual line parameters from TDL intensity retrieval in the ν_5 fundamental of $^{12}\text{C}_2\text{H}_2$. Calculated Doppler widths are $b_D = 0.8383$ for $P(16)$, 0.8858 for $Q(18)$, and $0.9210 \times 10^{-3} \text{cm}^{-1}$ for $R(12)$.

J	ΔJ	ℓ [cm]	T [K]	ν_o [cm^{-1}]	b_{obs} [10^{-3}cm^{-1}]	p [mTorr]	τ_o	W [cm^{-1}]
16	-1	2.54	298	691.4787	0.8617	278.	0.3038	.1531d-2
					0.8540	209.	0.4075	.1231d-2
					0.8566	158.	0.5056	.9877d-3
					0.8489	113.	0.6165	.7411d-3
					0.8489	75.5	0.7223	.5291d-3
18	0	2.54	298	730.6858	0.8905	202.	0.2534	.1730d-2
					0.8833	160.	0.3334	.1481d-2
					0.8869	127.	0.4183	.1248d-2
					0.8905	88.2	0.5394	.9543d-3
					0.8869	60.5	0.6568	.6829d-3
12	1	2.54	298	759.6952	0.9396	167.	0.2687	.1806d-2
					0.9414	129.	0.3645	.1489d-2
					0.9375	98.7	0.4542	.1239d-2
					0.9455	76.5	0.5484	.1007d-2
					0.9460	54.7	0.6553	.7458d-3

5.6 Band Intensities, Electric Dipole Moment, and ℓ -Resonances

Before the effect of vibrational and rotational ℓ -resonances on individual line intensities are discussed, it is necessary to summarize the relation between the individual line intensity, S_J , and the vibrational intensity indicative of the intensity of the particular rotation-vibration band. The index J for the line intensity is introduced to indicate the dependence of the line intensity on the rotational quantum number J as well as other rotation-vibration quantum numbers. From Appendix A, the individual line intensity is related to the vibrational intensity, S_v , as follows

$$S_J = S_v \frac{\nu_J}{\nu_o} g_J \frac{\exp(-E_r/kT)}{Q_r} \left[1 - \exp\left(-\frac{hc\nu_J}{kT}\right) \right] L_{J,\Delta J} W_{J,\Delta J} F_{J,\Delta J} \quad (5.13)$$

(see Eq. A.18). The terms defined in Eq. (5.13) are: ν_J , the transition frequency, ν_o , the band center frequency, g_J , the nuclear statistical weight, which is 1 or 3 for the major isotope and 1 for $^{13}\text{C}^{12}\text{CH}_2$ (see Table 3.3), Q_r and E_r , the rotational partition sum and energy of the lower level, respectively, $L_{J,\Delta J}$ is the square rotational transition moment or Hönl-London factor, $\Lambda_{J,\Delta J,\ell,\Delta\ell}$,

Table 5.2. Measured and calculated line intensities for $\nu_5^{1e,1f}$. Intensities are in units of $\text{cm}^{-2}\text{atm}^{-1}$ @298K and are listed in the order direct method and equivalent width. Values marked with an asterisk are results from profile fit.

ν_o	J	ΔJ	S_J	%-err.	S_J	%-err.	cal.
672.6503	24	-1	0.5251*	1.2	0.5047	1.9	0.5340
691.4787	16	-1	2.3380	0.6	2.3320	0.8	2.3147
712.6747	7	-1	9.9840	1.0	9.9700	1.1	9.8233
715.0297	6	-1	2.9570	1.6	3.0080	1.7	2.9665
722.0932	3	-1	4.1220	1.5	4.4000	0.8	4.2723
729.1811	2	0	3.5660	1.4			3.7270
729.2081	3	0	14.9540	0.4			15.1230
729.3428	6	0	7.5100	0.9	7.7620	1.1	7.8800
730.0959	14	0	7.0900	0.9	7.2620	0.7	6.7070
730.6858	18	0	3.8980	1.1	3.8880	1.0	4.0140
730.8554	19	0	10.6120	0.6	10.7200	1.0	10.2090
731.2208	21	0	7.2700	3.6	7.3100	3.4	7.0300
731.6212	23	0	4.9270	0.8	5.0300	2.2	4.5900
731.6212	23	0	4.4400	2.7	4.4100	4.5	4.5900
731.8345	24	0	1.2392	0.7	1.3200	2.8	1.2116
732.7740	28	0	0.3907	1.3	0.4056	8.4	0.4184
733.2953	30	0	0.2215	1.6	0.2407	3.4	0.2278
733.5686	31	0	0.4866	0.5	0.5002	2.6	0.4948
738.5628	3	1	10.8900	1.0	11.0080	0.4	10.9819
740.9137	4	1	4.2860	2.1	4.4800	4.2	4.2142
743.2639	5	1	14.1000	0.9	14.3100	1.1	13.9900
745.6135	6	1	4.8910	2.0	4.8500	2.7	4.9979
750.3106	8	1	5.3590	1.0	5.4420	1.5	5.3100
759.6952	12	1	4.7130	0.8	4.8200	1.2	4.6859
771.4048	17	1	8.2620	0.7	8.4700	2.1	8.2997
776.0810	19	1	6.0120	1.0	6.0190	1.2	6.0736
780.7523	21	1	4.1900	0.8	4.2050	0.6	4.2090
785.4185	23	1	2.8380	2.1	2.8760	1.7	2.7666
790.0790	25	1	1.7310	0.9	1.7240	0.9	1.7269
794.7338	27	1	1.0170*	1.6			1.0246

Table 5.3. Measured and calculated line intensities for $\nu_4 + \nu_5^{0e} \leftarrow \nu_4^{1f}$. Intensities are in units of $\text{cm}^{-2}\text{atm}^{-1}$ @298K and are listed in the order of direct method and equivalent width. Values marked with an asterisk are results from profile fit.

ν_o	J	ΔJ	S_J	%-err.	S_J	%-err.	cal.
716.3392	11	0	0.1921	1.7	0.1865	2.6	0.1879
716.3253	12	0	0.5289	0.6	0.5240	0.2	0.5249
716.3080	13	0	0.1593	0.4	0.1600	0.7	0.1598
716.2867	14	0	0.4358	0.6	0.4405	0.5	0.4297
716.2609	15	0	0.1241	3.3	0.1236	3.2	0.1261
716.2300	16	0	0.3243	1.1	0.3224	0.7	0.3271
716.1934	17	0	0.0922*	1.0			0.0927
716.1504	18	0	0.2290	0.2	0.2257	1.9	0.2326
716.1004	19	0	0.0655*	2.6			0.0638
716.0426	20	0	0.1565	0.4	0.1536	2.6	0.1548
715.9765	21	0	0.0406*	0.9			0.0411
715.9013	22	0	0.0983*	0.6			0.0967

defined as

$$\Lambda_{J,\Delta J=-1,\ell,\Delta\ell=\pm 1} = \frac{(J \mp \ell)(J \mp \ell - 1)}{2J} \quad (\text{A.9})$$

$$\Lambda_{J,\Delta J=0,\ell,\Delta\ell=\pm 1} = \frac{(2J+1)(J \pm \ell)(J \mp \ell + 1)}{2J(J+1)} \quad (\text{A.10})$$

$$\Lambda_{J,\Delta J=-1,\ell,\Delta\ell=\pm 1} = \frac{(J \pm \ell + 2)(J \pm \ell + 1)}{2(J+1)} \quad (5.14)$$

for perpendicular bands ($\Delta\ell = \pm 1$).

$F_{J,\Delta J}$ is the so called Herman-Wallis factor, which takes in case of a polyatomic linear molecule the following form:

$$F_{J,\pm 1} = [1 + A_1^{PR}m + A_2^{PR}m^2]^2 \quad (5.15)$$

for P and R -branch transitions, and

$$F_{J,0} = [1 + A_2^Q J(J+1)]^2 \quad (5.16)$$

for Q -branch transitions (Watson, 1987). Here $m = -J$ (P -branch) and $m = J+1$ (R -branch). The Herman-Wallis factor gives a measure of the break down of the zero order rigid-rotor, harmonic

oscillator model in describing the intensity. The contributions to the Herman-Wallis factor are primarily Coriolis perturbation induced between distinct vibrational levels and higher order centrifugal mixing (Watson, 1987).

A more dominant form of perturbation is caused by the ℓ -type resonance in linear molecules due to mixing of sublevels within a vibrational state, which is expressed in form of an additional factor, $W_{J,\Delta J}$, in Eq. (5.14). Expressing the band intensity, S_v , in terms of the vibrational dipole moment operator $\Gamma_{v'',v'}$, i.e.

$$S_v = \frac{8\pi^3}{3hc} \frac{L_o T_o}{p_o} \frac{a}{T} \nu_o \left[\frac{\exp(-E_v/kT)}{Q_v} \right] \Gamma_{v'',v'}^2, \quad (5.17)$$

(see Appendix A and Eq. A.12) the effective square dipole transition moment is then given by the product of the square vibrational dipole moment, the Herman-Wallis factor, and the ℓ -doubling intensity factor, i.e. $\Gamma_{v'',v'}^2 F_{J,\Delta J} W_{J,\Delta J}$. Q_v is the vibrational partition function, E_v the vibrational energy of the lower state, a the isotopic abundance, L_o is the Loschmidt number of the absorber gas at the reference condition at $T_o = 273.15\text{K}$ and $p_o = 1\text{atm}$. h and c are Planck's constant and the speed of light, respectively. In order to separate the Herman-Wallis factor from the ℓ -doubling, the product, $W_{J,\Delta J} \Gamma_{v'',v'}$ must be evaluated and factored out in the intensity analysis.

The dipole moment operator μ_v depending parametrically on the electronic configuration in the sense of the Born-Oppenheimer approximation is commonly expanded in a Taylor series in terms of normal coordinates about the nuclear equilibrium configuration as follows

$$\mu_v = \mu_v^o + \sum_a \left. \frac{\partial \mu_v}{\partial Q_a} \right|_o Q_a + \dots, \quad (5.18)$$

where the sum extends to all normal coordinates. Here the normal coordinates are those of the simple harmonic oscillator basis. For bending vibration, the two degenerate normal coordinates Q_r and Q_s are combined to form the two dimensional harmonic oscillator, by introducing polar coordinates Q and α' as defined by Eqs. (2.23) and (2.24). In terms, of the new polar coordinates the sum $Q_r + Q_s$ describing the degenerate vibration is given by

$$Q^* = Q_r + Q_s = \frac{1}{2} (Q^+ + Q^-) + \frac{1}{2i} (Q^+ - Q^-), \quad (5.19)$$

where $Q^\pm = Q e^{\pm i\alpha'}$.

Neglecting pure rotational transitions and, henceforth, the first term on the right side in Eq. (5.18), the vibrational dipole moment responsible for a rotation-vibration transition depends

to lowest order on the first dipole moment derivative. (Actually acetylene possesses no permanent dipole and is not observed in pure rotational spectra). Since transitions observed in this study only involve the two bending vibrations of ν_4 and ν_5 , all terms related to non-degenerate vibrations will be omitted. The dipole moment matrix element in the isotropic two dimensional harmonic oscillator basis set can be then written as

$$\begin{aligned}\Gamma_{v'',v'} &= \sum_{a=4,5} \mu_a \langle v_4'', \ell_4''; v_5'', \ell_5'' | Q_a^* | v_4', \ell_4'; v_5', \ell_5' \rangle = \\ &= \delta_{v_5'', v_5'} \delta_{\ell_5'', \ell_5'} \mu_4 \langle v_4'', \ell_4'' | Q_4^* | v_4', \ell_4' \rangle + \delta_{v_4'', v_4'} \delta_{\ell_4'', \ell_4'} \mu_5 \langle v_5'', \ell_5'' | Q_5^* | v_5', \ell_5' \rangle,\end{aligned}\quad (5.19)$$

in terms of the Q^* coordinates. A short-hand notation, μ_4 and μ_5 , is used for the dipole derivative matrix with respect to the degenerate normal modes and double and single primes indicate quantum numbers for lower and upper state, respectively. The transitions, observed in the $14\mu\text{m}$ region, involve transitions with a net change of $\Delta v_5 = 1$ in the set of vibrational quantum number describing the vibrational states, such that the first term in the sum of Eq. (5.19) drops out. Since there is no change in excited v_4 quanta for these transitions, it is expected that the transition moment is primarily dependent on the dipole derivative with respect to the antisymmetric bend.

Following the steps, shown in Section 2.4, the eigen bases have to be symmetry adapted, as done to obtain the factorized Hamiltonian (section 2.5) for a linear molecule. The matrix elements involving the degenerate normal coordinates can be found in textbooks (Nielsen, 1959, Shutte, 1976, Bunker, 1976) and are summarized in Table 5.4. Using Table 5.4 and Eq. (5.19), the effective dipole moment matrices connecting the various sub levels can be calculated. These matrices are given in Table 5.4 for the bands investigated in this study. An extra factor of $1/\sqrt{2}$ appears in the matrix for $\nu_4 + \nu_5 \leftarrow \nu_4$, and means that the expected intensity of these bands is half the value than expected from the vibrational Boltzmann distribution.

The dipole matrix element can be transformed using the unitary transformation, U , which diagonalizes the effective Hamiltonian. Since states with different vibrational quantum number, ℓ , are mixed, different rotational factors as expressed by the Hönl-London factor, have to be multiplied to each element of the effective dipole matrix as given in Table 5.5. Therefore, the calculation of the perturbed dipole matrix including the rotational factors separates into P -, Q - and R -branch transition moment calculation. Denoting with m_{ij} an element of the modified dipole matrix $\mathbf{M}$, it can be written as

$$m_{ij} = l_{ij} d_{ij}, \quad (5.20)$$

Table 5.4. Matrix elements for the two dimensional isotropic harmonic oscillator (Bunker, 1979). Here $Q^\pm = Qe^{\pm i\alpha} = Q_r + iQ_s$ and $|v, \ell\rangle$ the basis set for the two dimensional oscillator.

$$\begin{aligned} \langle v+1, \ell+1 | Q^+ | v, \ell \rangle &= -i\sqrt{(v+\ell+2)/2} \\ \langle v+1, \ell-1 | Q^- | v, \ell \rangle &= -i\sqrt{(v-\ell+2)/2} \\ \langle v-1, \ell+1 | Q^+ | v, \ell \rangle &= i\sqrt{(v-\ell)/2} \\ \langle v-1, \ell-1 | Q^- | v, \ell \rangle &= i\sqrt{(v+\ell)/2} \end{aligned}$$

where i and j are indices for the specific sublevel, l_{ij} the square root of the Hönl-London factor, and d_{ij} the matrix element defined in Table 5.5. The transformed dipole matrix becomes

$$\mathbf{M}' = (\mathbf{U}_J'')^T \mathbf{M} \mathbf{U}_{J+\Delta J}', \quad (5.21)$$

where J indicates the rotational level for which the mixing coefficient of the eigen states were determined. The unitary transformation for the vibrational states up to three excited quanta have been determined up to $J = 50$ as part of the numerical diagonalization procedure to determine molecular parameters for the bending levels (Chapter 4). The normalized intensity factors, $W_{J,\Delta J}$, are obtained from the matrix elements in Eq. (5.21). The normalization is achieved by dividing each square element by the appropriate Hönl-London factor of the unperturbed transition in the limit $J \rightarrow 0$. The lowest excitation levels for which effective mixing occurs are in the states $\nu_4 + \nu_5$ and $2\nu_5$ in case of acetylene. The intensity factors have been calculated for all seven hotbands reported in this study and are graphically shown in Fig. 5.7 for the $\nu_4 + \nu_5 \leftarrow \nu_4$ and in Fig. 5.8 for $2\nu_5 - \nu_5$. A detailed table of the intensity factors appears in Appendix G.

The intensity perturbation is strong for the branches going to the upper e -level in the case of $2\nu_5 - \nu_5$. At about $J = 20$, intensities are lowered or increased by 50% of the corresponding unperturbed intensity value. Since the f -levels are deperturbed after factorization of the Hamiltonian no intensity alteration should be observed for the transitions ending in the f -levels of $2\nu_5$. In the case of the combination bands the intensity perturbation is expected to be stronger for the transitions going to the two upper e -levels than those to the f -levels, due to higher mixing of the the two e -levels. For each positively perturbed branch in the sense of increasing intensities, a corresponding negative branch exist. This behavior is the typical intensity borrowing between perturbed levels.

Table 5.5. Vibrational dipole matrix elements for acetylene. Matrix elements are shown for the eight bands, ν_5 , $\nu_4 + \nu_5 \leftarrow \nu_4$, and $2\nu_5$. The vibrational sublevels of the lower state are ordered along the columns and the upper levels along the rows. It should be noted that selection rules remain in effect, which are $e \leftrightarrow f$ for Q -branch and $e \leftrightarrow e, f \leftrightarrow f$ for P - and R -branch transitions. For the combination band an extra factor of $1/\sqrt{2}$ appears reducing its intensity by half if the matrix elements are squared. The notation for the unperturbed eigen states follow those of Table 4.2.

ν_5 fundamental:

$$\begin{array}{c} \psi_{1e}^- \quad \psi_{1f}^+ \\ \psi_{0e} \begin{pmatrix} -1 & i \end{pmatrix} \mu_5 \end{array}$$

$\nu_4 + \nu_5 \leftarrow \nu_4$:

$$\begin{array}{c} \psi_{2e}^- \quad \psi_{0e}^+ \quad \psi_{0f}^- \quad \psi_{2f}^+ \\ \psi_{1e}^- \begin{pmatrix} -1 & 1 & i & i \end{pmatrix} \\ \psi_{1f}^+ \begin{pmatrix} i & i & 1 & -1 \end{pmatrix} \end{array} \frac{1}{\sqrt{2}} \mu_5$$

$2\nu_5 \leftarrow \nu_5$:

$$\begin{array}{c} \psi_{2e}^+ \quad \psi_{0e} \quad \psi_{2f}^- \\ \psi_{1e}^- \begin{pmatrix} -1 & 1 & i \end{pmatrix} \\ \psi_{1f}^+ \begin{pmatrix} i & i & -1 \end{pmatrix} \end{array} \mu_5$$

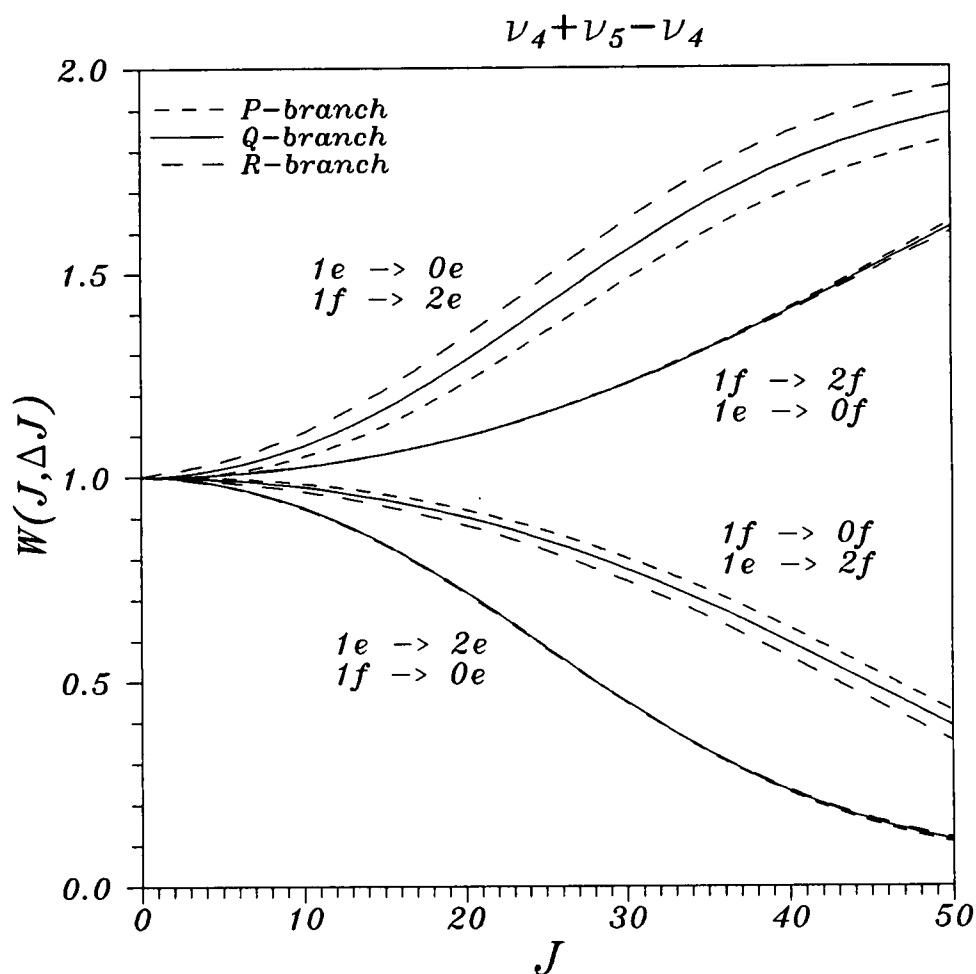


Figure 5.7. ℓ -resonance intensity perturbation factor, $W_{J,\Delta J}$: $\nu_4 + \nu_5 \leftarrow \nu_4$. The intensity factors are calculated from the effective dipole moment matrix expressed in terms of the perturbed eigenfunctions. The dipole moment operator, here, includes the rotational transition moment. Intensity factors have been normalized to one (see text).

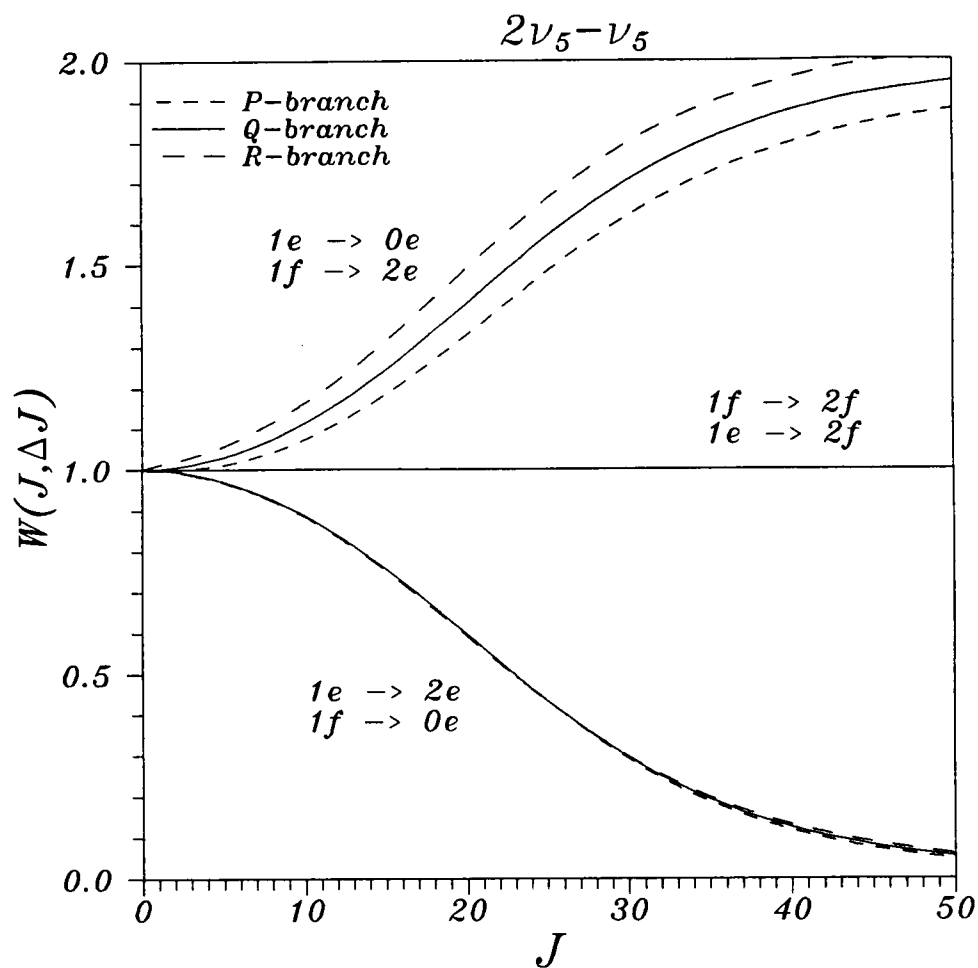


Figure 5.8. ℓ -resonance intensity perturbation factor, $W_{J,\Delta J}$: $2\nu_5 \leftarrow \nu_5$. The intensity factors are calculated from the effective dipole moment matrix expressed in terms of the perturbed eigenfunctions. The dipole moment operator, here, includes the rotational transition moment. Intensity factors have been normalized to one (see text).

Adding up all the intensities in the various band should sum approximately to the expected total intensity in absence of ℓ -resonances.

As can be seen from Figs. 5.6 and 5.7, the mixing of the eigenstates due to ℓ -resonances contribute significantly to the intensity perturbation and can not be neglected and this type of intensity perturbation can not be neglected. By introducing ℓ -resonance intensity factors, the perturbation effects are conveniently expressed as multiplicative factors to the rigid-rotor intensity expression in Eq. (5.13). By quantitatively determining the intensity factors due to ℓ -type doubling, the Herman-Wallis effect on the intensities can be separately treated.

5.7 Data Reduction

Since the intensities extended to relative low J values ($J \sim 30$), the small quadratic Hermann Wallis constant A_2^{PR} , expected to be on the order of 10^{-8} (Watson, 1987), can be neglected and a linear Herman-Wallis factor is assumed for small A_1^{PR} and A_1^Q , i.e.

$$F_{J,\pm 1} = [1 + A_1^{PR}m]^2 \approx 1 + 2A_1^{PR}m \quad (5.22)$$

A similar expression holds for the central Q -branch. The ratio of observed and calculated intensities should follow a straight curve with a slope of $2A_1^{PR}$.

First the vibrational band intensities are calculated for each transition observed by inverting Eq. (5.13) with $F_{J,\Delta J} = 1$ and an average for the band is determined. The calculated intensities are obtained by using the average band intensity to calculate intensity using Eq. (5.13). The intensity ratios $R(m) = S_{\text{obs}}/S_{\text{cal}}$ are then least squares fitted to the following model equation

$$R(m) = A + Bm = A(1 + \frac{B}{A}m), \quad (5.23)$$

where A is the multiplicative correction factor for the average band intensity obtained in the first step and $A_1^{PR} = B/(2A)$. In the least squares analysis weights were assigned to each intensity ratio according to their experimental standard deviations. The relative error for the true band intensity is then $\Delta A/A$ and approximately $\Delta B/B$ for the linear Herman-Wallis factor since $\Delta B/B$ is much larger than $\Delta A/A$.

Table 5.6 summarizes the least squares results. Herman-Wallis plots are shown for the fundamental ν_5 in Figure 5.9 (PR -branch) and Figure 5.10 (Q -branch). Figure 5.11 shows the intensity ratios for the Q -branch of $\nu_4 + \nu_5^{0e} \leftarrow \nu_4^{1f}$ for which no linear Herman-Wallis factor was

Table 5.6. TDL band intensities and square dipole moment derivative. The band center frequency is $\nu_o = 730.333\text{cm}^{-1}$ and 715.2925cm^{-1} for the fundamental and the hotband, respectively; the rotational partition function, Q_r is 352.9 and 351.5, respectively. DM: Direct method; EW: Equivalent width method.

Band		$S_v @ 298\text{K}$ $\text{cm}^{-2}\text{atm}^{-1}$	A_1^{PR} 10^{-3}	A_2^Q 10^{-4}	$\overline{S_v} @ 298\text{K}$ $\text{cm}^{-2}\text{atm}^{-1}$	$S_v @ 296\text{K}$ $\text{cm}^{-2}\text{atm}^{-1}$	μ_v^2 10^{-2}Debye^2
ν_5^{1e}	DM	561.8(20)	0.20(10)	–	564(14)	570	9.05(4)
	EW	562(10)	0.30(19)	–			
ν_5^{1f}	DM	566.3(33)	–	-0.30(34)			
	EW	577(16)	–	-0.24(31)			
$\nu_4 + \nu_5^{0e} \leftarrow \nu_4^{1f}$	DM	13.686(53)	–	0	13.68(7)	13.56	8.67(4)
	EW	13.680(73)	–	0			

observable. In order to demonstrate the effect of ℓ -resonance effects on the hotband intensities, the experimental intensities are plotted together with a theoretical intensity profile calculated with and without the intensity factors, $W_{j,\Delta j}$, in Figure 5.12.

Due to the smallness of the linear Herman–Wallis factor for the fundamental the errors are quite large $\sim 50\%$ for the PR -branch and $>100\%$ for the Q -branch. However, setting A_2^Q to zero leads to a lower band intensity ($\sim 5\%$) than the value determined from the PR -side. The Herman–Wallis factor is in good agreement with the theoretical value of $A_1^{PR} = 0.3 \times 10^{-3}$ (Maguire *et al.*1991).

The band intensity determined from the equivalent width, which is independent from the instrumental distortion of the line shape, are in excellent agreement with the data retrieved via the direct method. Only those lines for which the Doppler criterion ($p < 400\text{mTorr}$) was satisfied, were included in the separate analysis. The scatter and standard deviations for the retrieved intensities via the equivalent width method are generally larger than the corresponding direct method values. Nevertheless, statistically both methods yield results in good agreement with each other. Taking a weighted average of the independent equivalent width and direct method results, band intensity of the ν_5 fundamental is $564(14)\text{cm}^{-2}\text{atm}^{-1}$ at 298K for both PR - and Q -branches and $13.68(7)\text{cm}^{-2}\text{atm}^{-1}$ at 298K for $\nu_4 + \nu_5^{0e} \leftarrow \nu_4^{1f}$ Q -branch.

The square dipole moment, μ_v^2 , can be calculated from Eq. (5.17) and the constants given

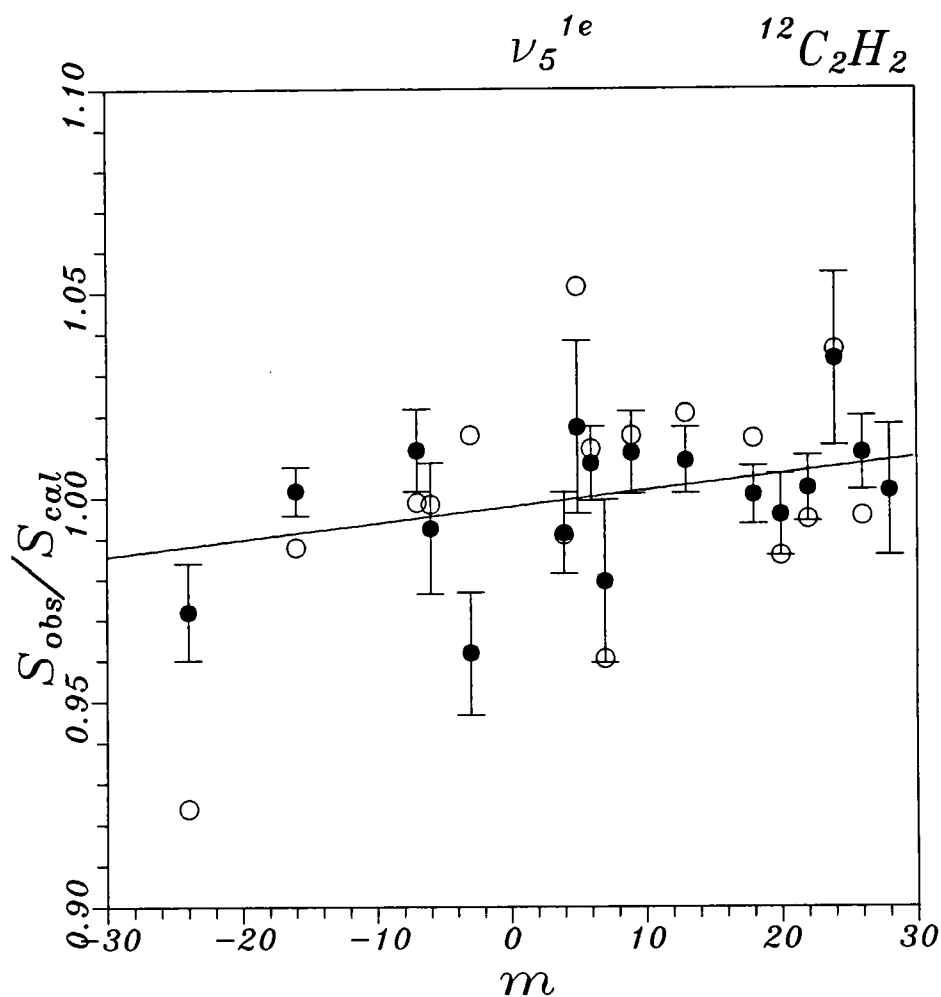


Figure 5.9. Hermann-Wallis plot for ν_5^{1e} PR -transitions. The intensity ratios are plotted as a function of m . $m = -J(P), J + 1(R)$; The solid points are the experimental values from the direct method/profile fit. Error bars are shown for these data. The light points represent the equivalent width calculation. The slope is approximately $2A_1^{PR}$ (see text).

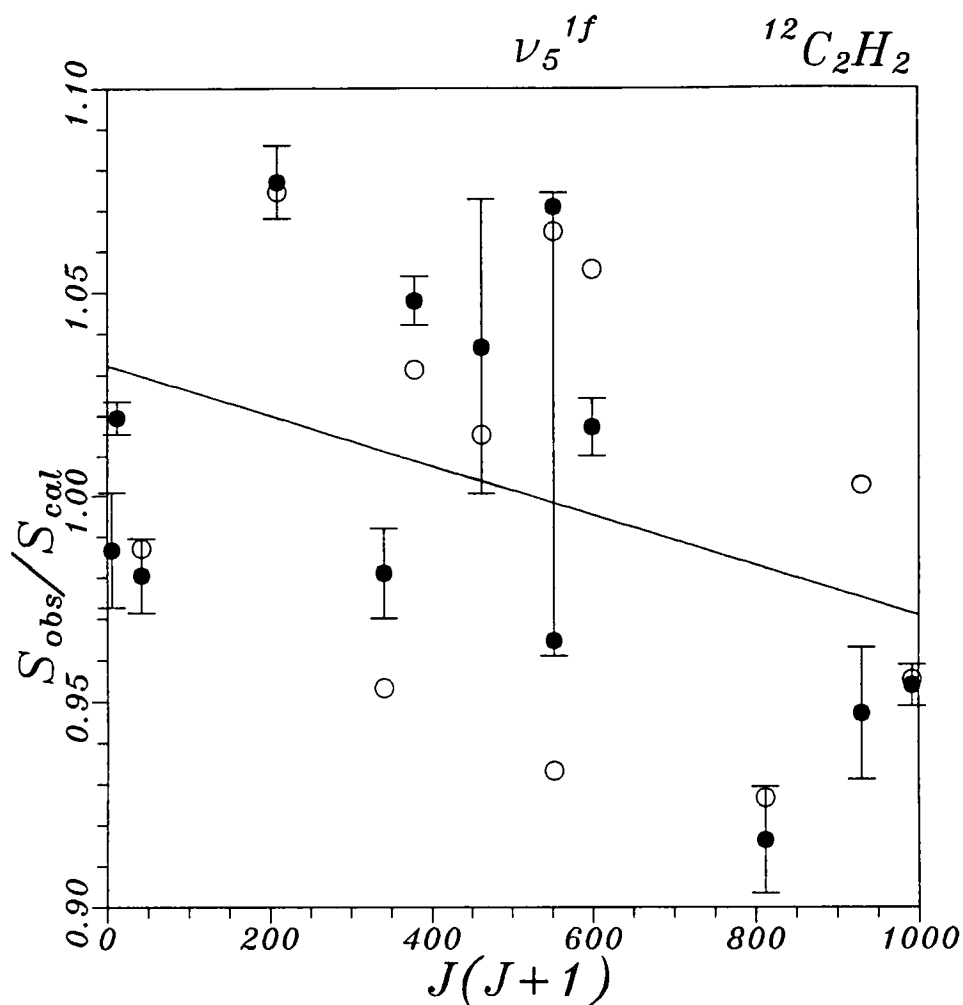


Figure 5.10. Hermann-Wallis plot for ν_5^{1f} Q-transitions. The solid points are the experimental values from the direct method/profile fit. The light points represent the equivalent width calculation. The slope is approximately $2A_2^Q$ (see text).

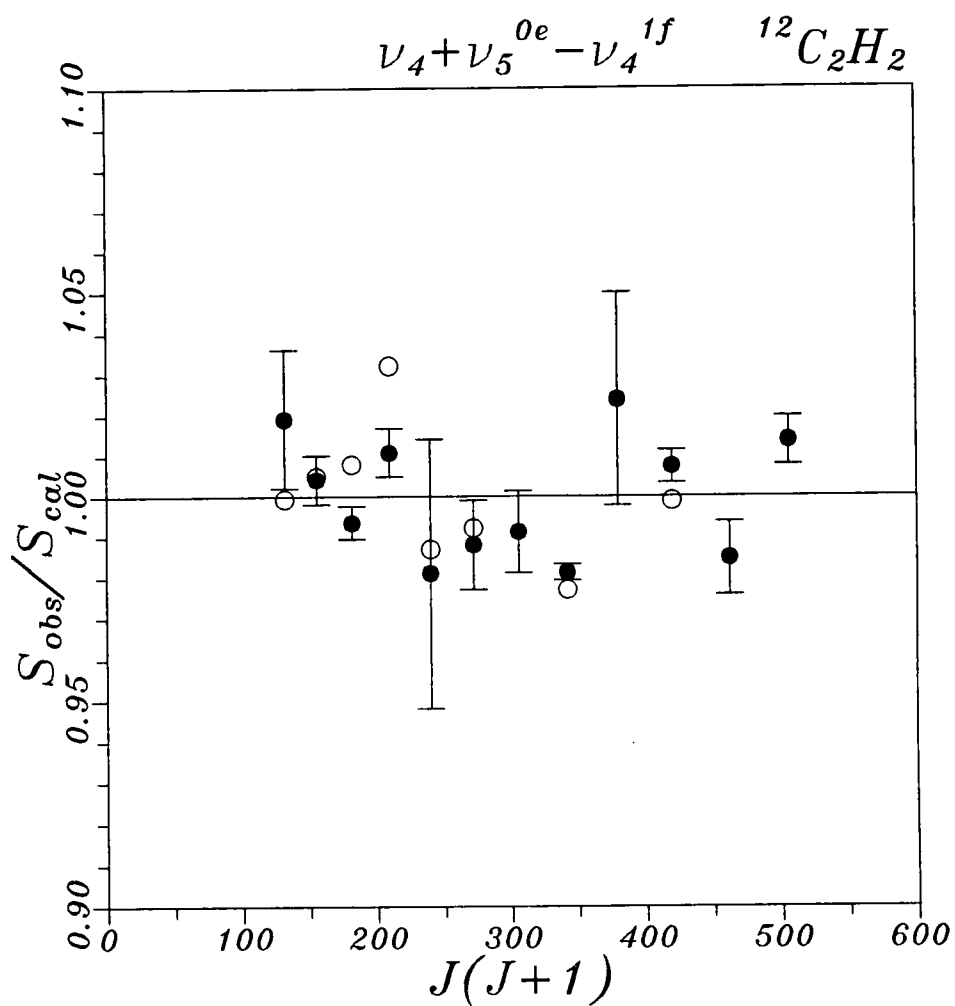


Figure 5.11. Hermann-Wallis plot for $\nu_4 + \nu_5^{0e} \leftarrow \nu_5^{1f}$. The solid points are the experimental values from the direct method/ profile fit. Error bars are shown for these data. The light points represent equivalent width measurements. The Herman-Wallis factor is not observed for this band.

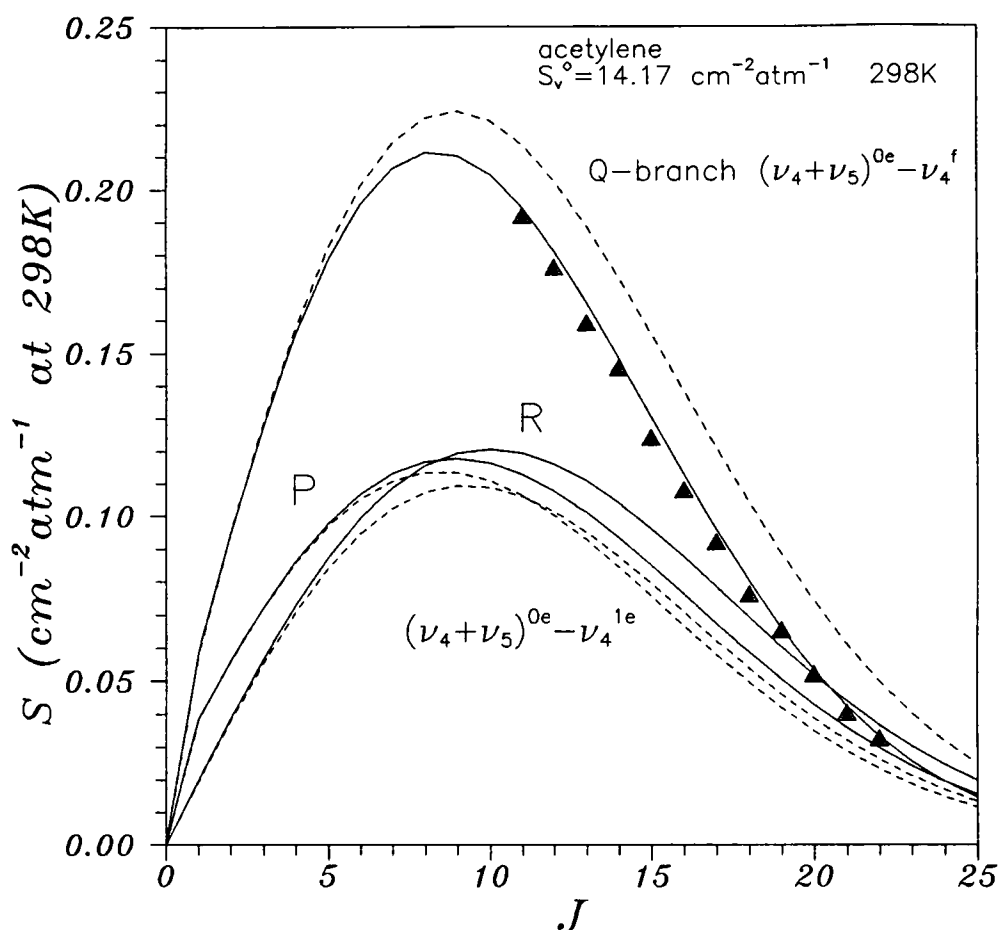


Figure 5.12. Theoretical intensity profile of $\nu_4 + \nu_5^{0e} \leftarrow \nu_4^{1e,1f}$. Calculated P, R and Q branch are shown for the hotband. The solid lines are the calculated intensities by including the ℓ -resonance intensity factors; dashed lines are the unperturbed intensities. The values were calculated for a theoretical band intensity derived from the dipole moment of the fundamental. The experimental data are shown and lie slightly below the predicted values (experimental intensity is $S_v = 13.68(7) \text{ cm}^{-2} \text{ atm}^{-1}$). For clarity of presentation the intensity alternation was removed, i.e. $g_J = 3$ for all transitions.

in Table A.1 as follows

$$\mu^2 = N_v^2 \frac{T}{3.0547 \times 10^3 \nu_o} \frac{1}{a} \frac{Q_v}{\exp(-E_v/kT)}, \quad (5.24)$$

where $N_v = 1$ for ν_5 and $2\nu_5 \leftarrow \nu_5$ and $N_v = 1/\sqrt{2}$ for $\nu_4 + \nu_5 \leftarrow \nu_4$. Here the dipole moment is in units of Debye(D). Isotopic abundances for acetylene species are calculated using the abundances of the carbon isotopes from Mathews and Rao (1976). If α_1 and α_2 are the respective atomic natural abundances of ^{13}C and ^{12}C , molecular abundances are determined by $(\alpha_1 + \alpha_2)^2$ and thus $a = 0.9778$ for $^{12}\text{C}_2\text{H}_2$ and $a = 0.0218$ for $^{13}\text{C}^{12}\text{CH}_2$. The square dipole moments as derived from the band intensity are shown in Table 5.6.

The vibrational partition function has been calculated using the vibrational energy term for the linear molecule, Eq. (2.46), limited to terms containing ω_s , x_{ss} and g_{tt} . Similarly, the rotational energy term, Eq. (2.47), including the effective B_v and centrifugal distortion constant, D_v , were used in the calculation of the rotational partition function (see Eq. A.22 and A.23, and section A.3 in Appendix A). Both, Q_v and Q_r , were calculated by numerical summation and values for Q_v at selected temperatures are summarized in Table 5.7. Temperature conversion of line intensities and band intensities from temperature T to temperature T' are governed by

$$S_v(T') = S_v(T) = \frac{T}{T'} \exp\left(-\frac{E_v}{kT} \left(\frac{1}{T'} - \frac{1}{T}\right)\right) \frac{Q_v(T)}{Q_v(T')} \quad (5.25)$$

and

$$S_J(T') = S_J(T) \frac{T}{T'} \exp\left(-\frac{E_v + E_r}{kT} \left(\frac{1}{T'} - \frac{1}{T}\right)\right) \frac{Q_v(T)Q_r(T)}{Q_v(T')Q_r(T')} \left[\frac{1 - \exp\left(-\frac{hc\nu_J}{kT'}\right)}{1 - \exp\left(-\frac{hc\nu_J}{kT}\right)} \right]. \quad (5.25)$$

(see Appendix A, Section A.3). The band intensities in Table 5.6 have been converted to the standard values for 296K.

The standard deviations for the band intensities retrieved are below 3% as calculated from the least squares fit. The actual uncertainties of the intensity parameters are considered somewhat larger. Potential error sources lie in pressure measurements, 100% and 0% transmission level determination, frequency calibration, and peak transmittance or integrated absorption retrieval. Assuming errors on the order of 1% in each of the possible error sources and, adding them up, leads to a more conservative estimate of 5% uncertainties to the retrieved S_v values.

Table 5.7. Vibrational partition sum, Q_v , of $^{12}\text{C}_2\text{H}_2$ for selected temperatures. Q_v is calculated by numerical summation. Q_v^0 is the harmonic approximation using the limit of the geometric series (see Eq. (A.28)). Molecular constants in units of cm^{-1} used for calculations are given in the bottom: (1) Finsterhölzl *et al.*, 1981, (2) Kostyk and Welsh, 1980, (3) Strey and Mills, 1976, (4) Pliva, 1972b.

$T[\text{K}]$	Q_v	Q_v^0
290	1.1639	1.1667
291	1.1659	1.1687
292	1.1679	1.1708
293	1.1700	1.1729
294	1.1721	1.1750
295	1.1741	1.1771
296	1.1762	1.1792
297	1.1783	1.1813
298	1.1805	1.1835
299	1.1826	1.1856
300	1.1847	1.1878
301	1.1869	1.1900
302	1.1891	1.1922
303	1.1913	1.1944
304	1.1935	1.1967
305	1.1957	1.1989
100	1.0003	1.0003
150	1.0074	1.0076
200	1.0355	1.0363
250	1.0937	1.0955
300	1.1847	1.1878
350	1.3092	1.3139
400	1.4677	1.4746

$$\begin{array}{lllll}
 \omega_1=3495.1^3 & \omega_2=1981.71^1 & \omega_3 = 3325.1^1 & \omega_4=609.2^4 & \omega_5=729.17 \\
 g_{44}=0.782 & g_{45}=6.528 & g_{55}=3.489 & & \\
 x_{11}=-18.57^3 & x_{12}=-13.09^3 & x_{13}=-102.39^3 & x_{14}=-15.64^2 & x_{15}=-10.84^2 \\
 x_{22}=-7.39^1 & x_{23}=-6.10^1 & x_{24}=-12.46^2 & x_{25}=-1.52^2 & x_{33}=-36.46^1 \\
 x_{34}=-6.96^1 & x_{35}=-8.69^1 & x_{44}=3.082^4 & x_{45}=-2.046^4 & x_{55}=-2.336
 \end{array}$$

5.8 Absolute FTS intensities: Part I. Intensity Retrieval

The spectral coverage of tunable diode lasers is rather limited in comparison with the broad spectral range of typical FTS-spectra. Diode laser modes usually extend to few wave numbers and gaps between adjacent modes are not uncommon. Furthermore, the stability, with regard to temperature tuning and mode hopping, and intensity of TD laser modes vary from mode to mode (Eng and Ku, 1982; McDowell, 1978). FT-spectrometers do not belong to the class of dispersive instruments and spectral information covering the entire frequency range are processed simultaneously. The spectral coverage of FT-spectrometer is usually limited, for instance, by optical filters and by the opaqueness of the beam splitter for selected wave number regions, and by the upper bound for the frequency according to the Nyquist sampling theorem (de Haseth, 1982; Bracewell, 1978; Bell, 1972). Common mid-infrared spectrometer cover spectra from 500cm^{-1} to 2000cm^{-1} . On the other hand, the spectral resolution of the best FTS-spectrometer is about a factor of 3–5 times less than that of the conventional TDL spectrometer. In terms of spectral resolution and broad band coverage, TDL and FTS-interferometers are complementary (Jennings, 1988).

The intensity measurements of intensities using TDL spectrometric data have demonstrated the considerable influence of ℓ -resonance for a selected Q -branch. In order to verify the predicted perturbation for all seven hotbands terminating in the two quantum level, i.e. the $2\nu_5$ and $\nu_4 + \nu_5$ states of acetylene, absolute intensities were measured using the broad-band FTS spectra obtained at the National Solar Observatory. In addition, FTS intensities are reported for the fundamental for both isotopic species, $^{12}\text{C}_2\text{H}_2$ and $^{13}\text{C}^{12}\text{CH}_2$. The experimental set up has been reviewed in Section 4.4 as pertinent for the line position analysis. Two spectra among the various FT-spectra used in the line position analysis (Chapter 4, Hillman *et al.*, 1991) were selected for the intensity retrieval. The first spectrum is a low pressure scan (123mTorr and 1cm absorption path length), in order to verify the fundamental ν_5 intensity of the major isotope and to test the iterative least squares fit on a low density spectrum. The same spectrum has been analyzed for the Herman-Wallis effect by Maguire *et al.* (1991), but no absolute intensities were reported. The second spectrum (1.987mTorr and 30cm) was used for the hotband analysis and measuring intensities of the $^{13}\text{C}^{12}\text{CH}_2$ ν_5 fundamental.

A non-least squares procedure was designed, which takes into account the convolution of the true profile with the appropriate instrumental profile. The latter is the known sinc type function if the spectra is unapodized as is the case for the present data. If $I_{\text{obs}}(\nu)$ is the observed intensity and $I_{\text{true}}(\nu)$ the intensity of the absorption profile following the Beer-Lambert law, i.e. Eq. (5.1), the convolution with the normalized response function $r(\nu)$ can be stated as

$$I_{\text{obs}}(\nu) = \int_{-\infty}^{\infty} I_{\text{true}}(\nu') r(\nu - \nu') d\nu', \quad (5.26)$$

where the instrument profile is given by the normalized sinc instrument function assuming a uniform filter function for the recorded interferogram.

The intensity retrieval occurs in two stages. The first program graphically displays the spectrum, such that the user can select a part of the spectrum to be fitted. Before the spectrum is entered in the least squares procedure, the selected spectral section has to be normalized by determining the transmission background. This is accomplished by piecewise averaged two point connections. Even though considerable optical fringing was observed in part of the spectrum, for narrow segments the linear approximation for the background was found sufficient. After normalizing the selected spectral range, parameters such as peak transmittance, line center frequency, observed width of the apparent profile are determined to obtain initial estimates for the least square fit. To facilitate the line parameter determination the segment can be sinc interpolated to double the point density of the spectrum.

A second program does the actual non-linear least squares fit to Eq. (5.26) and a Voigt line shape (Eq. 5.3). The non-linear least squares procedure is a modified iterative Marquardt-Levenberg routine (Press *et al.* 1986) using singular value decomposition. To improve convergence, the actual convolution is done at smaller spacing than given by the actual spectrum, and only those calculated points matching the actual spectral data are included in the least squares procedures (Johns and vander Auwera, 1990). Besides multiply doubling the point density, the convolution length for the calculation of the theoretical spectrum can be doubled or quadrupled, permitting a fit of very narrow spectral ranges in the vicinity of the line center without decreasing the accuracy of the convolution.

For both spectra the Doppler width was kept to its calculated value and fitting parameters were SPx and the line center frequency. The dimensionless broadening parameter, a , of the Voigt profile was set to zero for the low pressure spectrum (123mTorr) and calculated from the self-broadening coefficient determined by Varanasi *et al.* (1983) in the case of the high density spectrum. In addition, parameters of the response function can be subjected to a least squares estimation to allow for modification of the instrumental profile along with the other line parameters included in the fit. Varying instrumental parameters describing the sinc function in the least squares fit did not effect the outcome of the retrieved intensities. Fig. 5.13 shows an example of a least-squares approximated FTS absorption profile with residuals of the observed spectrum.

5.9 Absolute FTS Intensities: Part II. Experimental Results and Discussion

The ambient temperature was 295K and 293.3K for the low and high density spectrum, respectively. In order to reduce systematic errors in the intensity retrieval, the analysis was limited to absorption

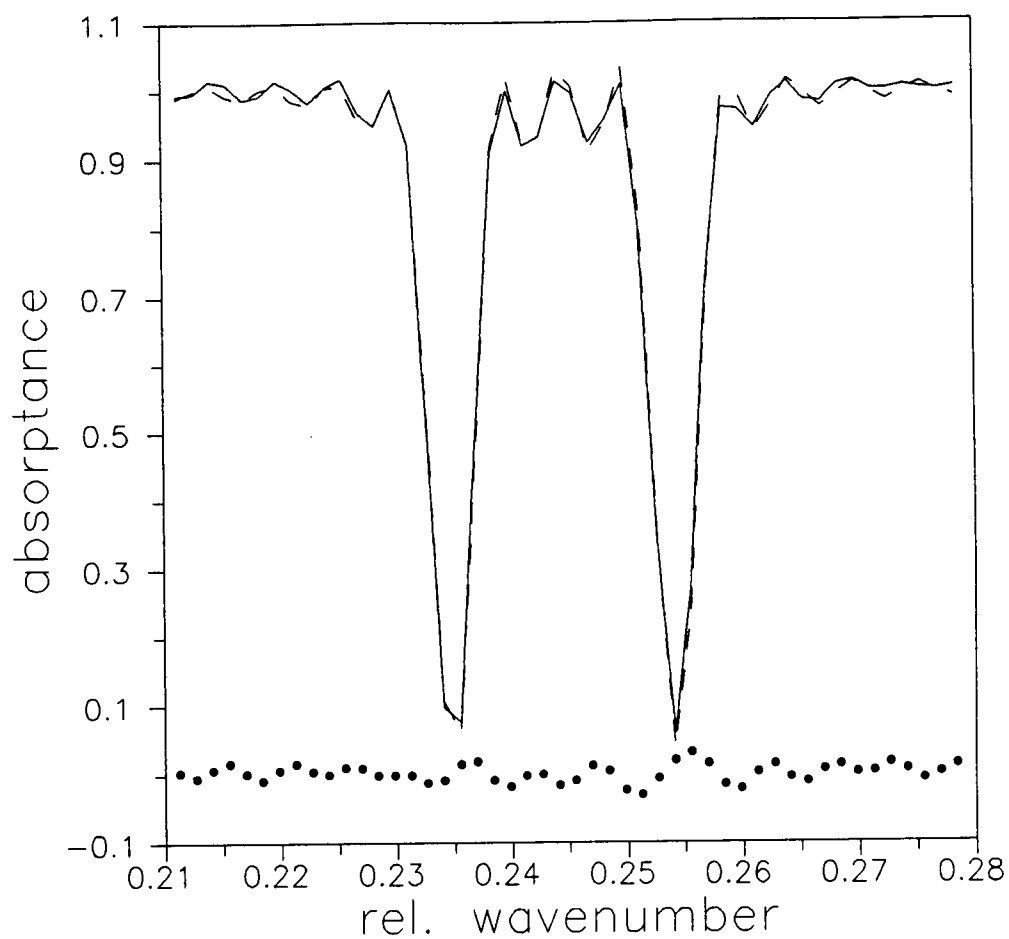


Figure 5.13. Least squares fit of FT-spectral absorption line. The dashed line show the calculated profile from the convolution of the "true" profile with the sinc-instrument function. Dots indicate residuals from the least squares fit. Depicted are $R(19)$ of the $\nu_4 + \nu_5^{0e} \leftarrow \nu_4^{1e}$ hotband and $R(6)$ of $\nu_4 + \nu_5^{0f} \leftarrow \nu_4^{1f}$. $p = 1987\text{mTorr(?)}$ and $\ell = 30\text{cm}$.

lines with a minimum peak absorption of 20%. Weak lines as well as saturated lines tend to be over estimated in their intensities. Only lines in the intermediate range of peak absorption were retained in the band intensity analysis. Most of the Q -branches were too dense to be successfully analyzed, and the analysis was limited to the PR -side of the bands. An exception was the Q -branch of $\nu_4 + \nu_5^{0e} \leftarrow \nu_4^{1f}$ for which TDL intensities are known. The band intensity analysis followed the same steps as previously outlined for the TDL intensities (Section 5.7).

The retrieved band intensities and Herman-Wallis factors for the ν_5 fundamental of both isotopes and the seven hotbands are listed in Table 5.8. For comparison purpose, the previous TDL results are also included in the Table. By comparing the Q -branch intensities of the $\nu_4 + \nu_5^{0e} \leftarrow \nu_4^{1f}$ band with the TDL intensities, it was found that the FTS-intensities of the high density spectrum were systematically low. By forming intensity ratios of identical lines measured with the different spectrometers a calibration factor of 2.245(7) was determined. The TDL intensities have been temperature corrected to match the temperature of the FTS spectrum before taking the intensity ratios. Since temperature and pressures are well known for the TDL measurements, all FTS line intensities were calibrated using this factor. The calibration is reflected in the results of Table 5.8. If the systematic low FTS intensities are due to an error in the measured absorber pressure, the corrected pressure of the high density spectrum is 0.883Torr, more than half of the indicated pressure.

Since the calibration factor was established just for 10 ten observations in dense spectral region, the actual uncertainties of retrieved intensities in Table 5.6 are assumed to be on the order of 10%. Despite this fact, the experimental hotband intensities are in good agreement with the expected intensities as calculated from the dipole moment derivative $\mu_5^2 = 0.905D$. Although the ν_4 state lies energetically below the ν_5 state, all observed $\nu_4 + \nu_5 \leftarrow \nu_4$ bands are slightly less intense than the $2\nu_5 \leftarrow \nu_5$ bands due to the normalization factor N_ν for the dipole moment. The intensity of the ν_5 fundamental of the major isotope is in excellent agreement (< 2%) with the value derived from the TDL measurements and, if corrected for the isotopic abundances, the intensity of $^{13}\text{C}^{12}\text{CH}_2$ ν_5 fundamental is about 4% lower as compared to the major isotope, which is within the uncertainties of the present measurements. All retrieved intensities of single transitions from the FTS-spectra are listed in Appendix H.

As predicted, strong ℓ -resonances were observed for all hotbands and ℓ -resonance intensity factors $W_{J,\Delta J}$ are needed to determine the Herman-Wallis effect on intensities. Fig 5.14-5.22 shows Herman-Wallis plots for the PR -branches of the seven hotbands and the two isotopic fundamental as well for the one Q -branch measured. The Herman-Wallis factors retrieved are in the range of $A_1^{PR} = 0.6-1.2 \times 10^{-3}$. Fig 5.23 shows $S_{\text{obs}}/S_{\text{cal}}$, where the ℓ -resonance intensity factor was omitted. It is evident from Fig 5.23, that the P and R side possess a discontinuity at $m = 0$. It might appear

Table 5.8. FTS band intensities and square dipole moment derivative. All intensities are cited for $T = 293.3\text{K}$, except for intensities marked with (*), $T = 295\text{K}$, and (**), $T = 298\text{K}$ or otherwise noted. $(S_v)_t$ is the expected intensity calculated from $\mu_5^2 = 0.0905\text{Debye}^2$. In the last column the intensities in square bracket are values for pure samples in order to compare intensities of the fundamental ν_5 of $^{12}\text{C}_2\text{H}_2$ and $^{13}\text{C}^{12}\text{CH}_2$.

Band	ν_o cm^{-1}	S_v $\text{cm}^{-2}\text{atm}^{-1}$	A_1^{PR}/A_2^Q 10^{-3}	μ_5^2 10^{-2}Debye^2	$(S_v)_t$ $\text{cm}^{-2}\text{atm}^{-1}$	S_v @296K $\text{cm}^{-2}\text{atm}^{-1}$
ν_5^{1e}	733.333	565.0(35)*	1.13(25)	8.96(4)	566*	562(35) [575]
$\nu_5^{1e} \text{ } ^{13}\text{C}^{12}\text{CH}_2$	729.379	12.416(53)*	0.60(14)	8.73(4)	12.87*	12.24(1) [559]
$\nu_4 + \nu_5^{2e} - \nu_4^{1e}$	734.740	15.085(85)	0.60(18)	9.52(6)	14.33	15.30(1)
$\nu_4 + \nu_5^{0e} - \nu_4^{1e}$	715.293	13.983(76)	0.69(18)	9.07(6)	13.95	14.17(1)
$\nu_4 + \nu_5^{0f} - \nu_4^{1f}$	727.770	14.968(58)	0.60(14)	9.54(6)	14.19	15.17(1)
$\nu_4 + \nu_5^{2f} - \nu_4^{1f}$	734.740	14.706(47)	0.94(11)	9.28(5)	14.33	14.91(1)
$2\nu_5^{2e} - \nu_5^{1e}$	732.684	16.375(77)	0.76(16)	9.22(5)	16.06	16.69(1)
$2\nu_5^{0e} - \nu_5^{1e}$	718.778	15.944(89)	0.59(17)	9.16(6)	15.76	16.25(1)
$2\nu_5^{2f} - \nu_5^{1f}$	732.684	16.30(13)	0.72(23)	9.18(7)	16.06	16.61(1)
$\nu_4 + \nu_5^{0e} - \nu_4^{1f}$	715.293	12.49(18)	0.115(18)	8.11(13)	13.95	12.66(18)
$\nu_5^{1e,1f}$	730.333	564(14)**	0.20(10)/ -0.030(34)	9.05(23)	-	570(14) [583]
$\nu_4 + \nu_5^{0e} - \nu_4^{1f}$	715.293	13.68(7)**	0	8.67(4)	14.28**	13.56(7)

a higher order polynomial fit is possible. An apparent choice seems to be a quadratic polynomial, but it was found to be a rather poor approximation particularly in the vicinity of $m = 0$. By taking the ℓ -resonance into account, the linear relationship for the intensity ratios is restored as is expected in the linear approximation of the Herman-Wallis effect for low rotational quantum numbers J (Fig. 5.22). This example shows that a simultaneous fit of the P and R to a polynomial in m becomes quite difficult, if the ℓ -type doubling of intensities in linear molecules are neglected in an intensity analysis. The same conclusion can be drawn from Fig 5.7 and Fig 5.8 by plotting the intensity factors $W_{J,\Delta J}$ as a function of m . For Q -branches this problem exists but is not apparent and it is possible to fit the intensity ratios to an effective Herman-Wallis factor describing the combined effect of the Herman-Wallis effect and ℓ -type doubling.

While the band intensities agree well with their predicted values, retrieved linear Herman-Wallis coefficients are higher than observed in the TDL-spectra by a factor of 3 for the ν_5 fundamental and a factor of 2-3 for the hotbands and the isotopic fundamental as compared to the fundamental observed in the TDL study. Comparing the fundamental ν_5 with the hotbands and the lesser isotope, the observed Herman-Wallis factor is about a factor of 2 higher. In case of the one Q -branch measured, a linear HW factor is observed but not in the band measured with the TDL.

Observing that for intensities retrieved from the same spectra, the F -factors are of the same order of magnitude, one might suspect these factors to be rather an indication of some kind of instrumental distortion not explained by the simple sinc-function. Since the energy level structure and molecular constants as well as the band intensities, corrected for isotopic abundances, are quite close for both isotopic species, similar F -factors might be expected for both fundamental intensities. This is not the case, rather the F -factor of the isotope matches those of the hotbands which were measured using the same spectra such that the HW-factor might be rather attributed as an instrumental artifact due to the particular experimental condition of each spectrum. Discrepancies between retrieved values from FTS and TDL data might be similarly explained by the different nature of operation in both systems. Equivalent width measurements and direct width measurements of the TDL spectra, the first independent and the latter dependent on the instrumental distortion, have shown to lead to identical results for the intensities and HW-factor, which minimizes the suspicion of skewed results due to instrumental distortion. Equivalent width measurements are difficult if not impossible for unapodized FT-spectra, since the contribution of the integrated absorption in the far wings is non-negligible due to the slowly dying wing contribution of the sinc-like response function which commonly overlaps with adjacent absorption features.

A modification of the apparent instrument function characteristic for the Fourier spectrometer have been proposed, which takes into account the field of view due to an extended radiation source (Johns and Vander Auwera, 1990; Bell, 1972) or the aperture effect (Dana and Valentin,

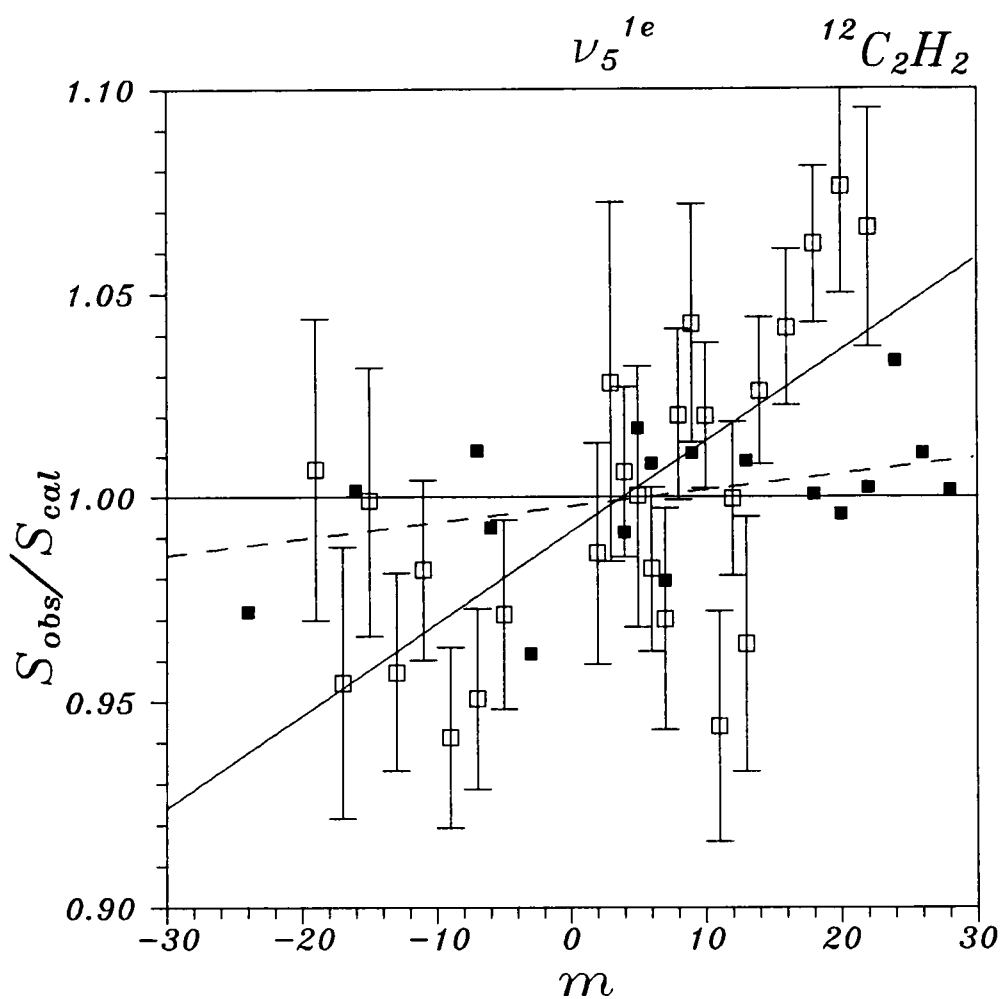


Figure 5.14. Hermann-Wallis plot for $^{12}\text{C}_2\text{H}_2$ ν_5^{1e} PR - transitions. The intensity ratios are plotted as function of m . $m = -J(P), J+1(R)$.

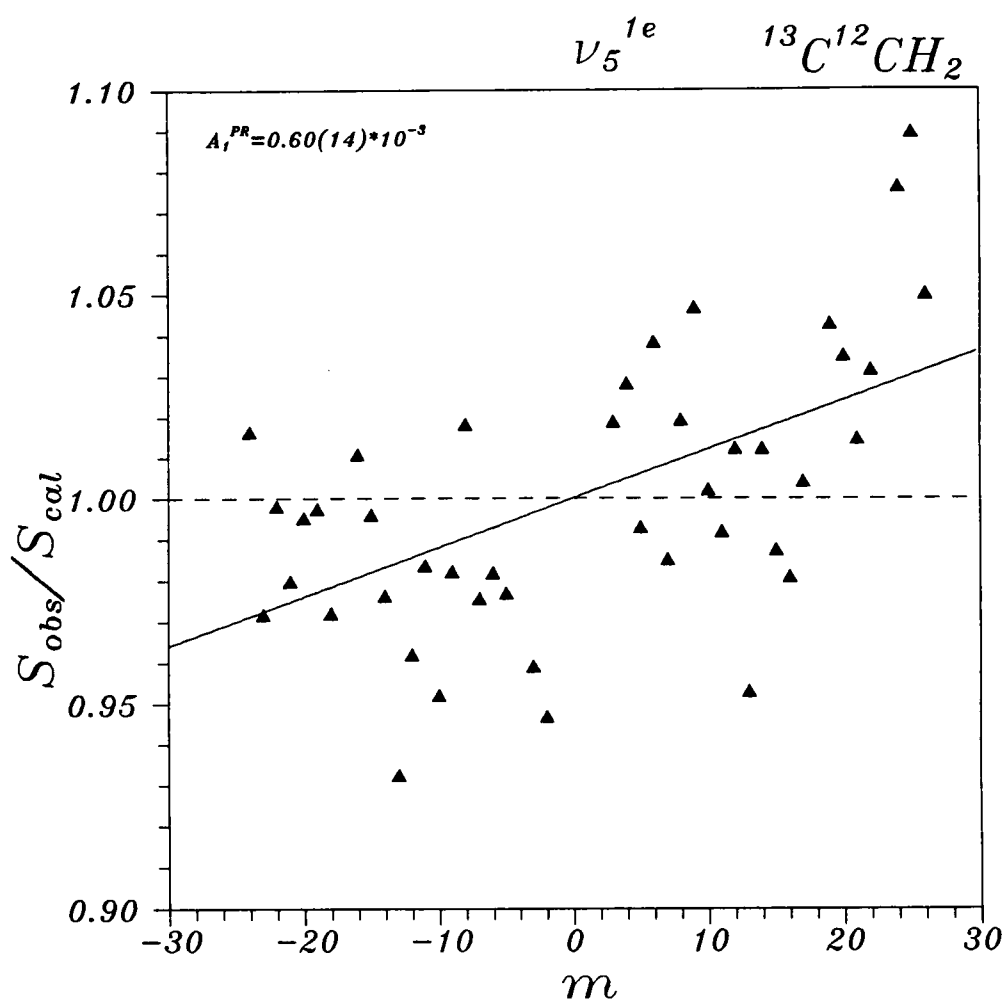


Figure 5.15. Hermann-Wallis plot for ${}^{13}\text{C}^{12}\text{CH}_2 \nu_5^{1e}$ PR - transitions. The intensity ratios are plotted as function of m . $m = -J(P), J + 1(R)$.

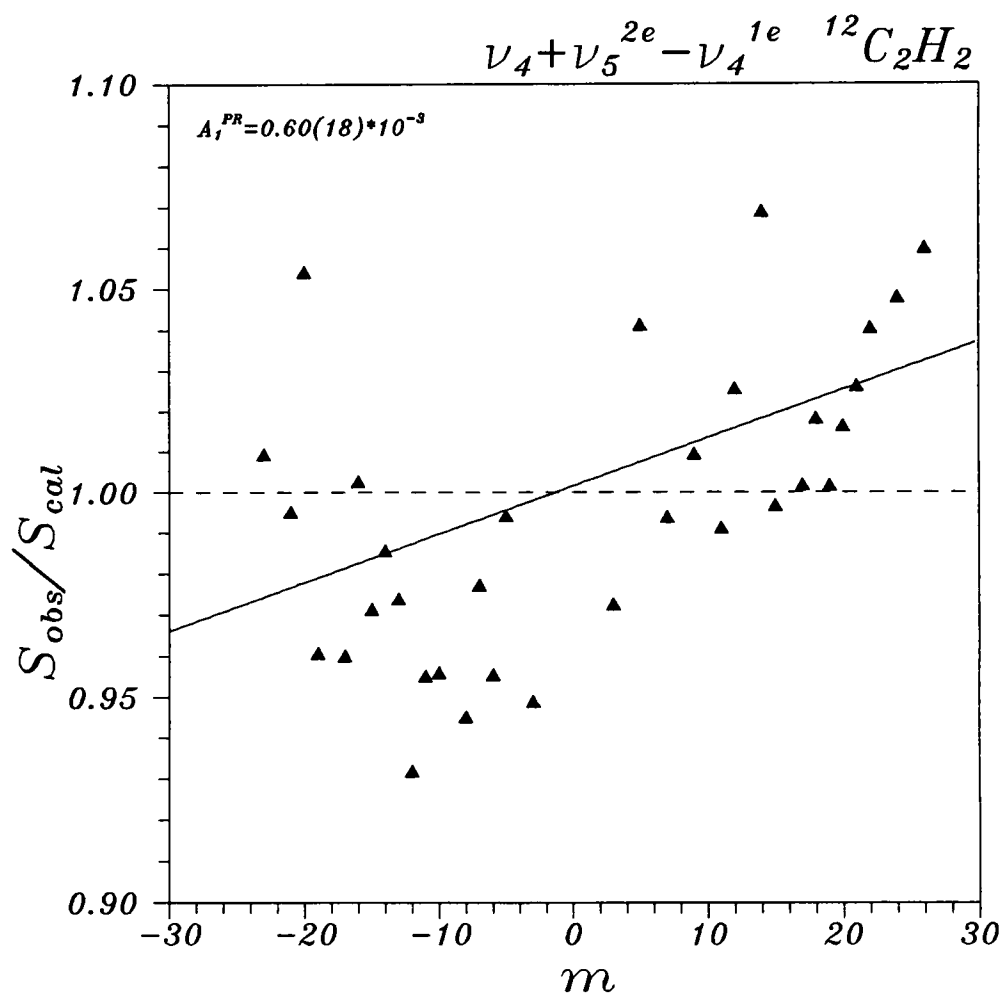


Figure 5.16. Hermann-Wallis plot for $\nu_4 + \nu_5^{2e} \leftarrow \nu_4^{1e}$. The intensity ratios are plotted as function of m . $m = -J(P), J+1(R)$.

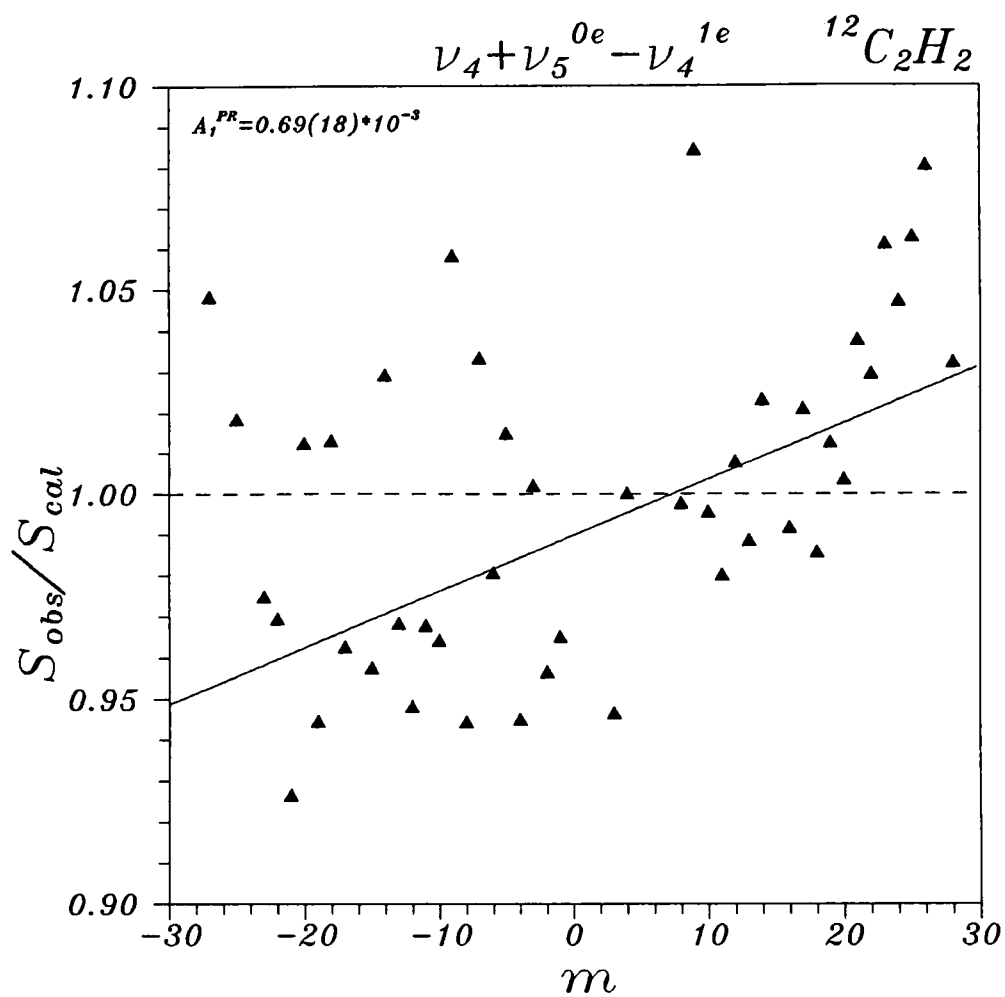


Figure 5.17. Hermann-Wallis plot for $\nu_4 + \nu_5^{0e} \leftarrow \nu_4^{1e}$. The intensity ratios are plotted as function of m . $m = -J(P), J+1(R)$.

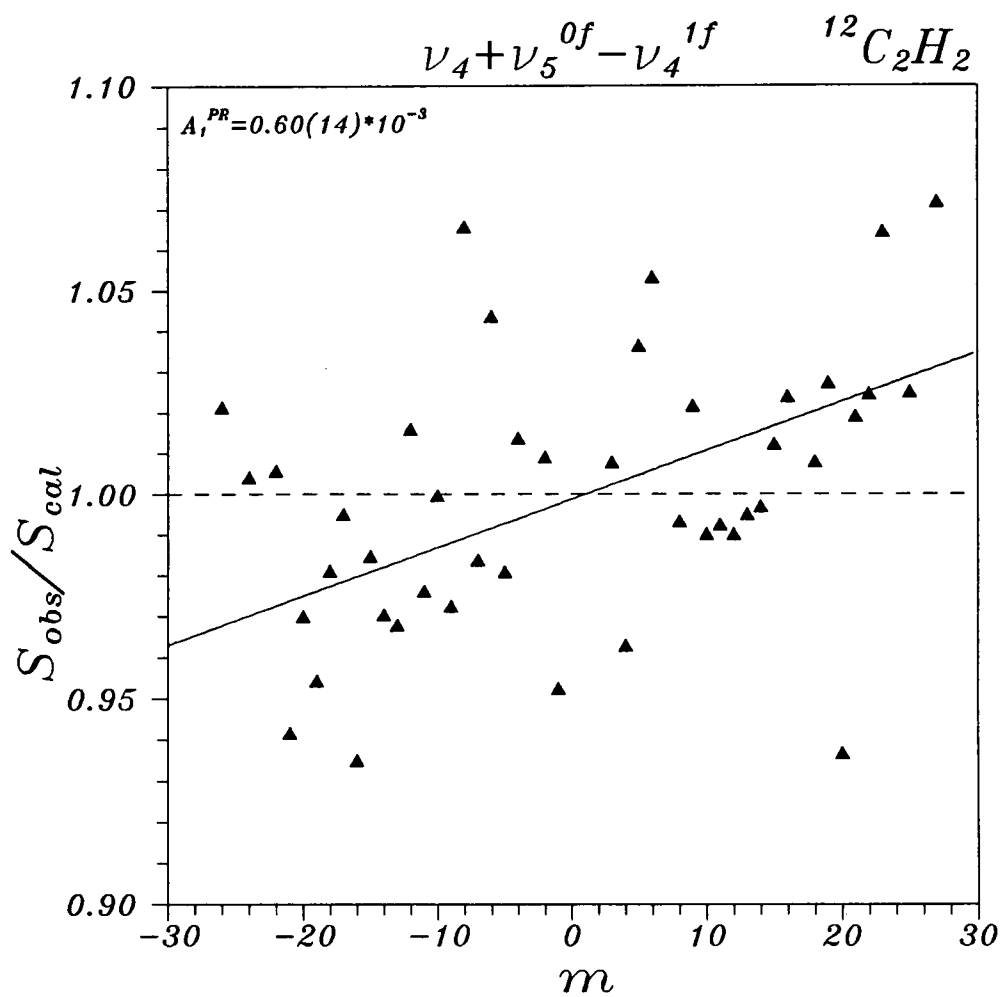


Figure 5.18. Hermann-Wallis plot for $\nu_4 + \nu_5^{0f} \leftarrow \nu_4^{1f}$. The intensity ratios are plotted as function of m . $m = -J(P), J+1(R)$.

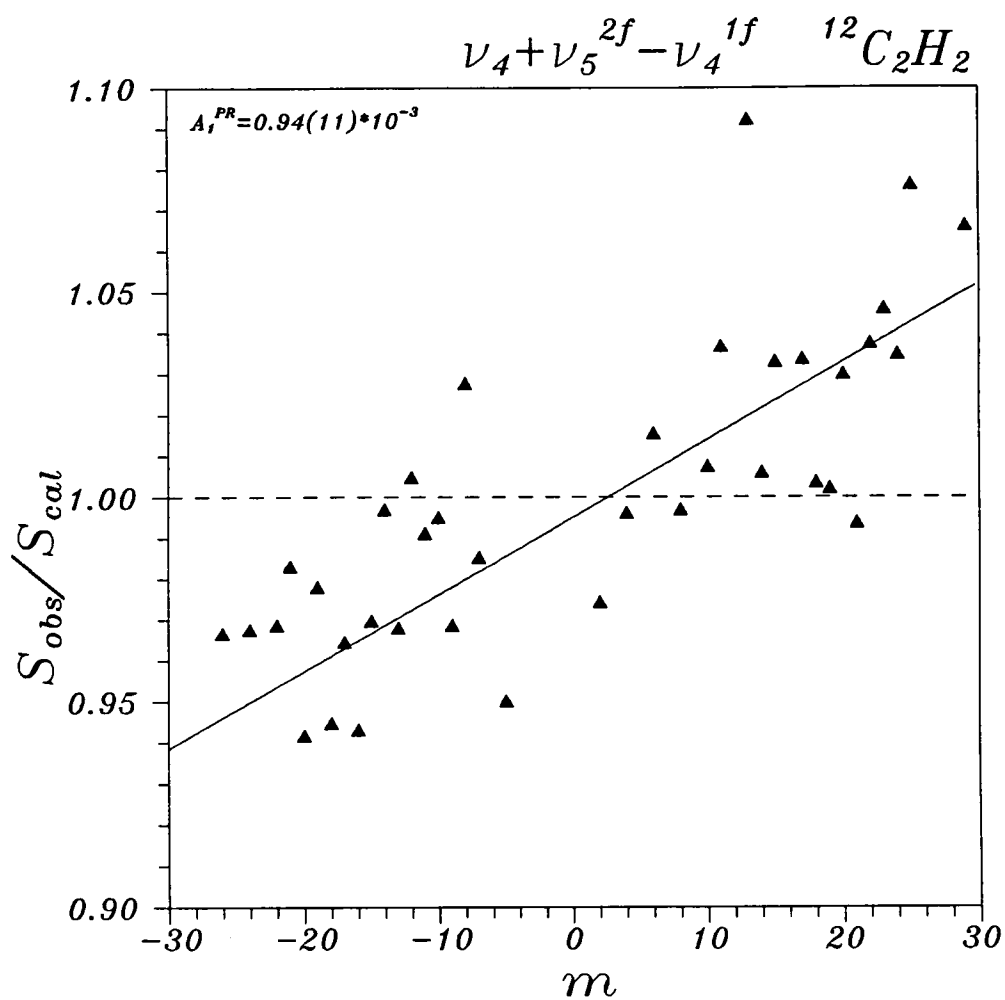


Figure 5.19. Hermann-Wallis plot for $\nu_4 + \nu_5^{2f} \leftarrow \nu_4^{1f}$. The intensity ratios are plotted as function of m . $m = -J(P), J+1(R)$.

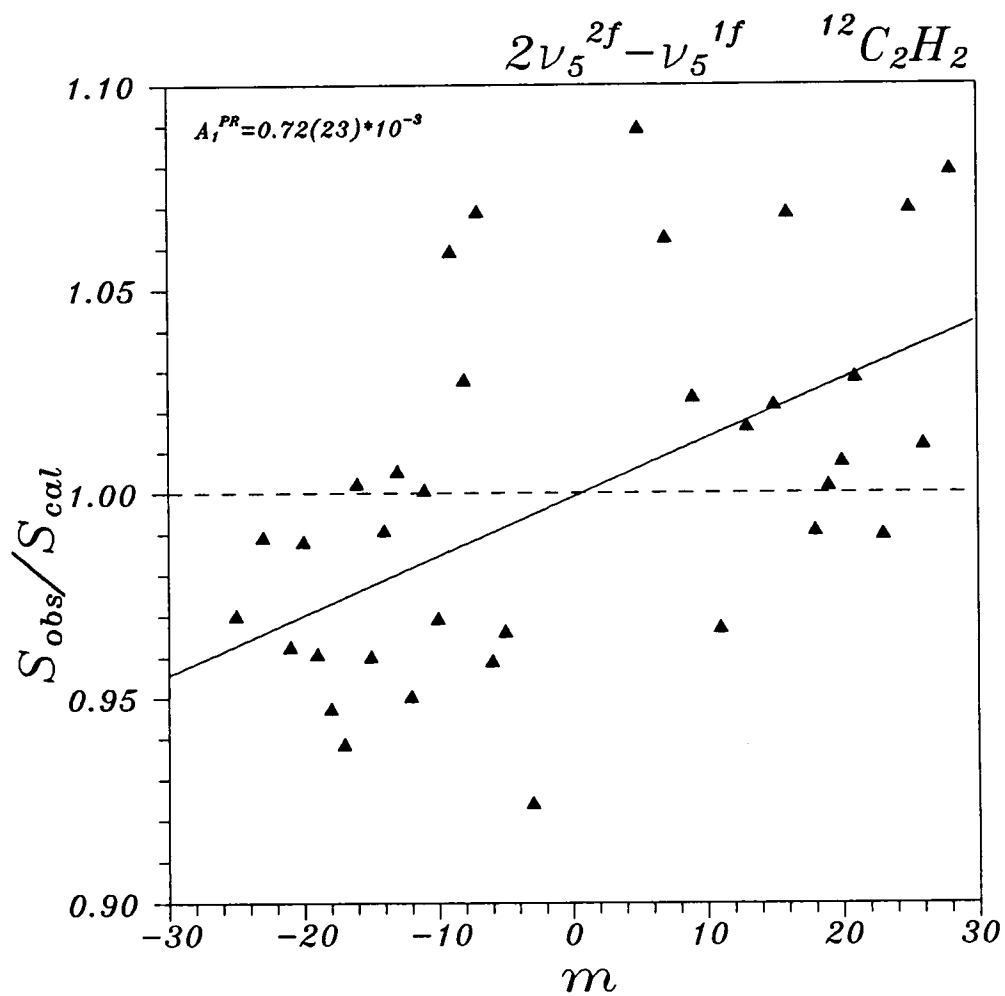


Figure 5.20. Hermann-Wallis plot for $2\nu_5^{2f} \leftarrow \nu_5^{1f}$. The intensity ratios are plotted as function of m . $m = -J(P), J+1(R)$.

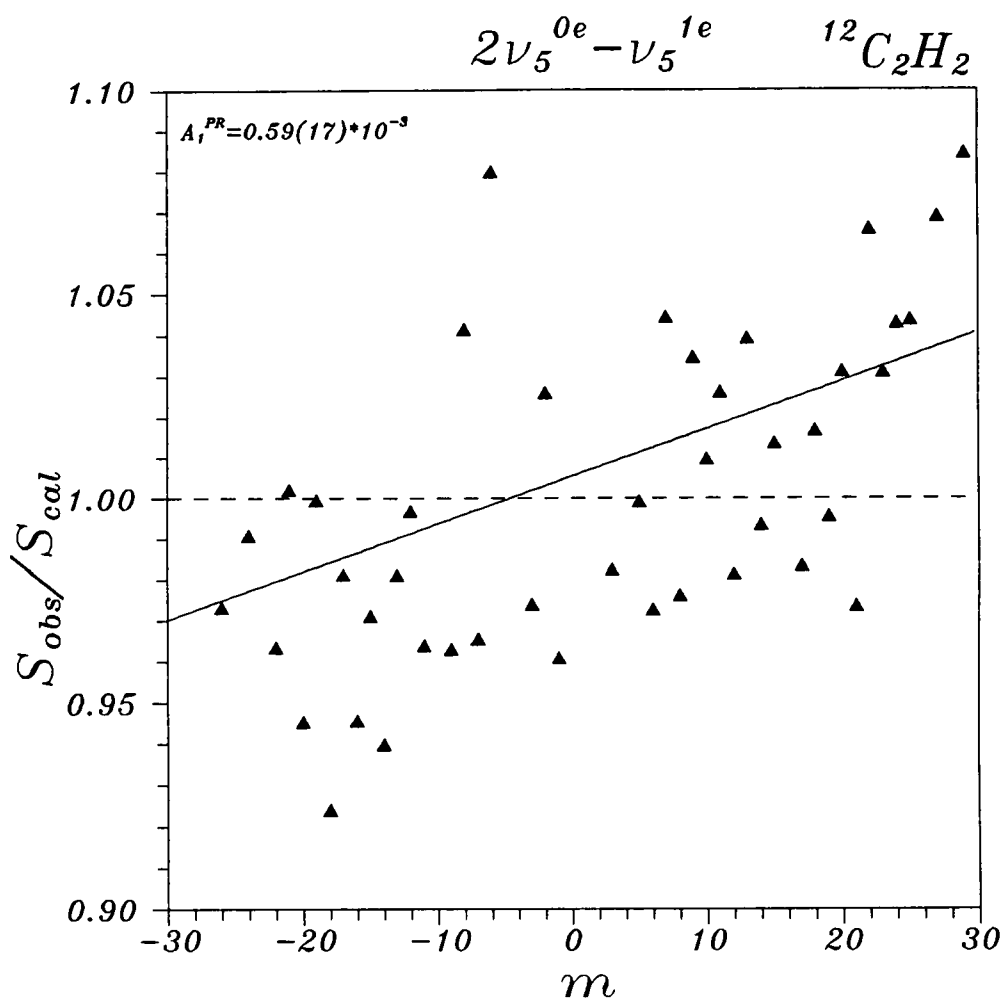


Figure 5.21. Hermann-Wallis plot for $2\nu_5^{0e} \leftarrow \nu_5^{1e}$. The intensity ratios are plotted as function of m . $m = -J(P), J+1(R)$.

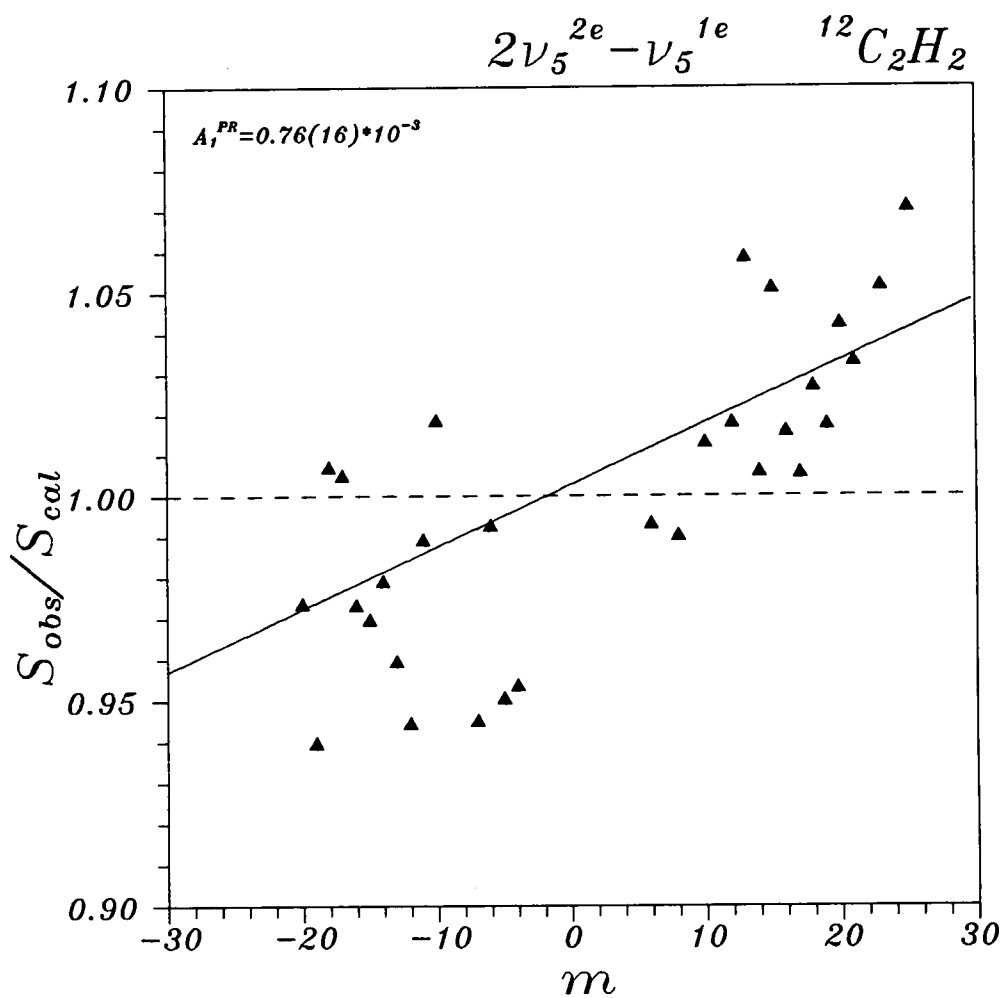


Figure 5.22. Hermann-Wallis plot for $2\nu_5^{2e} \leftarrow \nu_5^{1e}$. The intensity ratios are plotted as function of m . $m = -J(P), J+1(R)$.

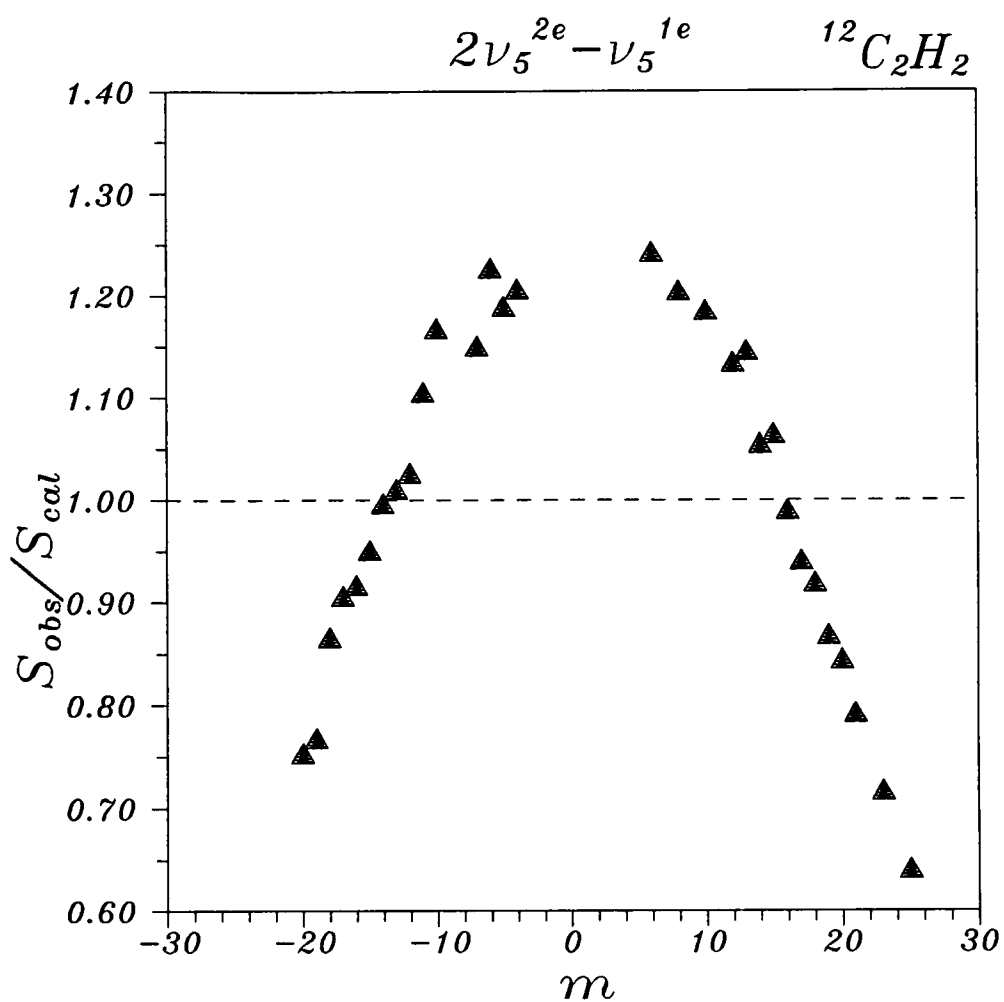


Figure 5.23. Hermann-Wallis plot showing ℓ -resonance effects in $2\nu_5^{2e} \leftarrow \nu_5^{1e}$. The intensity ratios are plotted as calculated neglecting the ℓ resonance intensity factors. ℓ -type doubling is clearly recognizable.

1988). Modification of the latter type have been attempted, but no conclusive evidence for the validity of the modified response function could be found for the two spectra by fitting selected lines to the modified response function. By further improving the signal-to-noise ratio and sampling at a somewhat higher rate might remedy the problem. By additional experiments, it is hoped to clarify the discrepancies in the observed Herman-Wallis factors. Extending TDL measurements to higher J in both P and R -branches might be helpful to reduce the uncertainties.

5.10 Conclusion

Absolute line intensities of individual transitions belonging to the ν_5 fundamental and the associated seven strongest hotbands $\nu_4 + \nu_5 \leftarrow \nu_4$ and $2\nu_5 \leftarrow \nu_5$ in the $14\mu\text{m}$ region have been measured using both tunable diode laser and Fourier transform spectrometric data. ℓ -type doubling effects have been observed for all hotbands and shown to have a large contribution to observed intensity perturbation in the excited bands. ℓ -resonance intensity factors, here called W -factor apart from the more common F -Factors have been calculated by transforming the dipole matrix elements using the same unitary transformation which numerically diagonalizes the Hamiltonian (Chapter 4). The intensities were determined by applying the rigid rotor, harmonic oscillator formula for intensities with W - and F -factors describing the effect of rotation-vibration interaction. By factoring out the calculated ℓ -resonance terms, Herman-Wallis factor could be determined for the observed bands.

Within the experimental uncertainties experimental band intensities agree well with predicted values assuming an identical square dipole moment of $\mu_5^2 = 9.05 \times 10^{-2} D^2$ for all bands. If corrected for the isotopic abundances, the intensity of the fundamental is only slightly lower than the fundamental of the major isotope, which is of importance for the retrieval of astronomical isotopic ratios (Courtin *et al.*, 1983).

Herman-Wallis factors retrieved from FT-spectra were generally higher than the one determined using the TDL-system. Possible explanations were discussed. The HW-factor as derived from the TDL measurements for the fundamental of $^{12}\text{C}_2\text{H}_2$ is in good agreement with predicted values (Maguire *et al.*, 1991). Additional experiments are needed to remove the observed discrepancies in the Herman-Wallis effects on acetylene infrared bands as derived from two distinct spectrometers.

CHAPTER 6

CONCLUSION

6.1 Conclusion and Future Work

Using FT-spectrometric data at 0.0025cm^{-1} resolution, 31 absorption bands up to three excited vibrational quanta, i.e. $2\nu_4 + \nu_5$, $\nu_4 + 2\nu_5$, and $3\nu_5$ in the $14\mu\text{m}$ region of the ν_5 fundamental of acetylene have been analyzed. Observed frequencies were fitted to an effective Hamiltonian of a linear molecule as described by Amat *et al.*(1971). Terms in the rovibrational Hamiltonian were included up to fourth order of approximation (Amat *et al.*, 1971). Molecular constants describing the bending modes of ν_4 and ν_5 have been retrieved to an accuracy reaching the experimental resolution of the spectra. Minor perturbation in the higher excited states lead to some unusual effective molecular constants, but no formal treatment apart from vibrational and rotational ℓ -type doubling was necessary. Extending the rotation-vibration analysis to even higher vibrational excitation in the electronic groundstate may necessitate the inclusion of Fermi and Dennison-Darling resonances and, in addition, the extension of the molecular Hamiltonian beyond fourth order of approximation. Eight of the absorption bands were due to the lesser isotope $^{13}\text{C}^{12}\text{CH}_2$, which was observed up to two excited vibrational quanta in the natural acetylene sample.

Transition frequencies were least mean square fitted to a numerically diagonalized Hamiltonian. The unitary transformation which diagonalizes the Hamiltonian contains in its columns the mixing coefficients of the perturbed energy levels. The mixing of eigenstates is here primarily due to the combined vibrational and rotational ℓ -type doubling observed in polyatomic linear molecules and is expected to significantly contribute to ℓ -resonance effects in the observed intensities. Combining high resolution Doppler limited TDL measurements (0.0005cm^{-1} resolution) and FTS measurements of intensities, band intensities of the fundamental of $^{12}\text{C}_2\text{H}_2$ and $^{13}\text{C}^{12}\text{CH}_2$ and the seven strong one quantum hot bands have been retrieved. In order to retrieve hot band intensities, it is necessary to quantitatively determine the effect of ℓ -type doubling. This was achieved by calculating normalized intensity factors, here called $W_{J,\Delta J}$, distinct from the known F -factors due to the Herman-Wallis effect (Watson, 1987). ℓ -resonance intensity factors were obtained by calculating the effective electric dipole transition moment in the transformed basis set as given by the mixing coefficients. The transformed transition moment must include the Hönl-London factors since mixing occurs between

levels with distinct vibrational quantum numbers ℓ . By factoring out the calculated ℓ -resonance intensity factors, band intensities and F -factors can be experimentally determined.

While band intensities retrieved from both TDL and FTS intensity measurements are in good agreement, determined Herman-Wallis factors disagree between the two type of measurements. Part of the problem was identified as pressure uncertainty of the FTS spectra. The FTS intensities were calculated assuming an uniform filter function for the interferogram yielding a sinc instrumental function. Deviations from the idealized response function have not been found, which might be due to the relative low signal-to-noise ratio and nearly minimal sampling interval observed in the FT-spectra. For future work, improved signal-to-noise ratio and higher sampling rate may improve the quality of the spectra and enable the identification of a more appropriate instrument function. Furthermore, ratioing FTS spectra to an empty background scan may reduce the error in the 100% transmission level determination. Also, modest apodization of the FT-spectra should reduce the interference between adjacent absorption features due to ringing effects. The Herman-Wallis factors retrieved from the FTS data, therefore, seems to be more a result of instrumental distortion rather than inherent to the Herman-Wallis effect.

Extending the TDL intensities to a larger range of J values within a vibrational band should yield improvement in the determined Herman-Wallis factors. Nevertheless, the intensity measurements conducted in this study clearly demonstrated the non-negligible contribution of ℓ -type resonances to the absolute intensities of linear molecules. It was also shown that for the transitions observed, the dipole moment derivative is to the first order of approximation proportional to the derivative with respect to the antisymmetric bend ν_5 , as one would expect for transitions with $\Delta\nu_5 = 1$. By correcting intensities for natural abundances of isotopic species, it was shown that the intensity of the ν_5 fundamental of $^{13}\text{C}^{12}\text{CH}_2$ is only about 4% lower than that of the major isotope, which is within the experimental uncertainties. The latter result is very important for astronomical atomic isotopic ratio determinations (Drossart *et al.*, 1985).

The extension of intensity measurements to two quantum hotbands is important, since for these bands mixing of eigenstates is simultaneously given for the lower and upper state. (After factorizing the Hamiltonian, the ν_4 and ν_5 states are diagonal, such that mixing is only observed in the upper levels of the one quantum hotbands). For the one quantum hotbands, the ℓ -resonance intensity factors were calculated using the positive square root of the Hönl-London factor. The two quantum hotbands might reveal clues to the proper sign of these factors. Verification of the quantitative treatment of ℓ -resonance effects on intensities can be done by looking at the intensity perturbations of the two quantum hotbands.

LIST OF REFERENCES

- Aliev, M.R., and V.T. Aleksanyan, *Sov. Phys. (Doklady)*, **12**, 229(1967).
- Aliev, M.R., and J.K.G. Watson, *J. Mol. Spectrosc.*, **61**, 29(1976).
- Aliev, M.R., and J.K.G. Watson, Chapter 1 in *Molecular Spectroscopy: Modern Research, Vol. III*, ed. K.N. Rao, Academic Press, New York, 1985.
- Allen, H.C., Jr., and P.C. Cross, *Molecular Vib-Rotors*, Wiley and Sons, New York-London, 1963.
- Amat, G., M. Goldsmith, and H.H. Nielsen, *J. Chem. Phys.*, **27**, 838(1957).
- Amat, G., and H.H. Nielsen, *J. Mol. Spectrosc.*, **2**, 152(1958a).
- Amat, G., and H.H. Nielsen, *J. Mol. Spectrosc.*, **2**, 163(1958b).
- Amat, G., and H.H. Nielsen, *J. Chem. Phys.*, **29**, 665(1958c).
- Amat, G., and H.H. Nielsen, *J. Chem. Phys.*, **36**, 1859(1962).
- Amat, G., H.H. Nielsen, and G. Tarrago, *Rotation-Vibration of Polyatomic Molecules: Higher Order Energies and Frequencies of Spectral Transitions*, Dekker, New York, 1971.
- Antilla, R., J. Hietanen, and J. Kauppinen, *Mol. Phys.*, **37**, 925(1979).
- Armstrong, B.H., *J. Quant. Spectrosc. Rad. Transfer*, **7**, 61(1967).
- Atakan, A.K., W.E. Blass, and S.J. Daunt, NATO Grant No. 1690, Research Report II, 1981.
- Atakan, A.K., *Computer Physics Communications*, **36**, 6(1985).
- Baldacci, A., S. Ghersetti, and K.N. Rao, *J. Mol. Spectrosc.*, **48**, 600(1973).
- Baldacci, A., S. Ghersetti, and K.N. Rao, *J. Mol. Spectrosc.*, **68**, 183(1977).
- Baldacci, A., S. Ghersetti, S.C. Hurlock, and K.N. Rao, *J. Mol. Spectrosc.*, **59**, 116(1976).
- Beaton, A.E., and J.W. Tukey, in *Critical Evaluation of Chemical and Physical Structural Information*, ed. D.R. Lide and M.A. Paul, National Academy of Sciences, Washington, p. 15, 1974.
- Bell, R.J., *Introductory Fourier Transform Spectroscopy*, Academic Press, New York, 1972.
- Benedict, W.S., R. Herman, G.E. Moore, and S. Silverman, *Can. J. Phys.*, **34**, 830(1956).
- Bevington, P.R., *Data Reduction and Error Analysis for the Physical Sciences*, McGraw-Hill, New York, 1969.
- Blass, W.E., and V.W.L. Chin, *J. Quant. Spectrosc. Rad. Transfer*, **38**, 185(1987).
- Bordé, J., *J. Phys.*, **37**, 711(1976).
- Bouanich, J.P., D. Lambot, G. Blanquet, and J. Walrand, *J. Mol. Spectrosc.*, **140**, 195(1990).
- Bracewell, R.N., *The Fourier Transform and its Application*, 2nd Ed., Mc-Graw Hill, New York, 1978.
- Brannon, J.F., Jr., M.S. Thesis, University of Tennessee, 1991.
- Braund, D.B., A.R.H. Cole, and F.E. Grader, *J. Mol. Spectrosc.*, **48**, 604(1973).
- Brink, D.M., and G.R. Satchler, *Angular Momentum*, 2nd Ed., Clarendon Press, 1968.
- Brodersen, S., *J. Mol. Spectrosc.*, **142**, 122(1990).

- Brown, J.M., J.T. Hougen, K.-P. Huber, J.W.C. Johns, I. Kopp, H. Lefebvre-Brion, A.J. Merer, D.A. Ramsay, J. Rostas, and R.N. Zare, *J. Mol. Spectrosc.*, **55**, 500(1975).
- Bunker, P.R., and H.C. Longuet-Higgins, *Proc. Roy. Soc. Ser. A*, **280**, 340(1964).
- Bunker, P.R., *J. Chem. Phys.*, **47**, 718(1967).
- Bunker, P.R., and J.T. Hougen, *Can. J. Phys.*, **45**, 3867(1967).
- Bunker, P.R., *J. Chem. Phys.*, **48**, 2832(1968).
- Bunker, P.R., and D. Papoušek, *J. Mol. Spectrosc.*, **32**, 419(1969).
- Bunker, P.R., Chapter 1 in *Vibrational Spectra and Structure*, Vol. 3, ed. J. Durig, Dekker, New York, 1975.
- Bunker, P.R., *Molecular Symmetry and Spectroscopy*, Academic Press, New York-San Francisco-London, 1979.
- Cartwright, G.J., and I.M. Mills, *J. Mol. Spectrosc.*, **34**, 415(1970).
- Castellano, S., and A.A. Bothner-By, *J. Chem. Phys.*, **41**, 3863(1964).
- Chedin, A., and N.A. Scott, *J. Quant. Spectrosc. Rad. Transfer*, **32**, 453(1984).
- Chin, V.W.L., M.S. Thesis, University of Tennessee, 1985.
- Christensen, M.T., D.R. Eaton, B.A. Green, and H.W. Thompson, *Proc. Roy. Soc. (London) A.*, **238**, 15(1956).
- Courtin, R., D. Gautier, A. Marten, and V. Kunde, *Icarus*, **53**, 121(1983).
- Courtin, R., D. Gautier, A. Marten, B. Bézard, and R. Hanel, *Astrophys. J.*, **287**, 899(1984).
- Dalton, B.J., *J. Chem. Phys.*, **44**, 4406(1966).
- Dana, V., and A. Valentin, *Appl. Opt.*, **27**, 4450(1988).
- Das P.P., V.M. Devi, and K.N. Rao, *J. Mol. Spectrosc.*, **84**, 313(1980).
- Daunt, S.J., A.K. Atakan, W.E. Blass, G.W. Halsey, D.E. Jennings, D.C. Reuter, J. Susskind, and J.W. Brault, *Astrophys. J.*, **280**, 921(1984).
- D'Cunha, R., Y.A. Sarma, G. Guelachvili, R. Farrenq, Q. Kou, V.M. Devi, D.C. Benner, and K.N. Rao, *J. Mol. Spectrosc.*, **148**, 213(1991).
- Demtröder, W., *Laser Spectroscopy*, Springer-Verlag, Berlin-Heidelberg-New York, 1982.
- Devi, V.M., D.C. Benner, C.P. Rinsland, M.A.H. Smith, and B.D. Sidney, *J. Mol. Spectrosc.*, **114**, 49(1985).
- Draper, N.R., and H. Smith, *Applied Regression Analysis*, 2nd ed., John Wiley & Sons, New York, 1980.
- Drayson, S.R., *J. Quant. Spectrosc. Rad. Transfer*, **16**, 611(1976).
- Drossart, P., J. Lacy, E. Serabyn, A.T. Tokunaga, B. Bézard, and T. Encrenaz, *Astron. & Astrophys.*, **149**, L10(1985).
- Eckart, C., *Phys. Rev.*, **46**, 383(1934).

- Eckart, C., *Phys. Rev.*, **47**, 552(1935).
- Edwards, H.G.M., *Spectrochim. Acta*, **46A**, 97(1990).
- Eggers, D.F., Jr., I.C. Hisatsune, and L. van Alten, *J. Chem. Phys.*, **59**, 1124(1955).
- Eng, R.S., and R.T. Ku, *Spectrosc. Lett.*, **15**, 803(1982).
- Estes, D., Ph.D. thesis, University of Illinois, Urbana, 1982.
- Estes, D., and D. Secrest, *Mol. Phys.*, **59**, 569(1986).
- Fast, H., and H.L. Welsh, *J. Mol. Spectrosc.*, **41**, 203(1972).
- Feynman, R.P., *Phys. Rev.*, **56**, 340(1939).
- Finsterhölzl, H., H.W. Schrötter, and G. Strey, *J. Raman Spectrosc.*, **11**, 375(1981).
- Fridovich, B., V. Malathy Devi, and P.P. Das, *J. Mol. Spectrosc.*, **81**, 269(1980).
- Galabov, B., and W.J. Orville-Thomas, *J. Mol. Struct.*, **18**, 169(1973).
- Goldman, A., F.J. Murcray, R.D. Blatherwick, J.R. Gillis, F.S. Bonomo, F.H. Murcray, D.G. Murcray, and R.J. Cicerone, *J. Geophys. Res.*, **86**, 143 (1981).
- Goldman, A., M. Dang-Nhu, and J.P. Bouanich, *J. Quant. Spectrosc. Rad. Transfer*, **41**, 17(1989).
- Goldsmith, M., G. Amat, and H.H. Nielsen, *J. Chem. Phys.*, **24**, 1178(1956).
- Grenier-Bresson, M.L., G. Amat, and H.H. Nielsen, *J. Chem. Phys.*, **36**, 3454(1962).
- Hainer, R.M., P.C. Cross, and G.W. King, *J. Chem. Phys.*, **21**, 826(1949).
- Hanel, R.A., B. Conrath, F.M. Flasar, V. Kunde, W.C. Maguire, J. Pearl, J. Pirraglia, R. Samuelson, L. Herath, M. Allison, D. Cruikshank, D. Gautier, R. Gierasch, L. Horn, and C. Ponnampuruma, *Science*, **215**, 544(1982).
- de Haseth, J.A., "Fourier Transform Infrared Spectrometry" in *Fourier, Hadamard, and Hilbert Transformations in Chemistry*, ed. A.G. Marshall, Plenum Press, New York, 1982.
- Hellmann, H., *Einführung in die Quantenchemie*, Deuticke, Wien, 1937.
- Herman, M., T.R. Huet, and M. Vervloet, *Mol. Phys.*, **66**, 333(1988); M. Herman and T.R. Huet, *Mol. Phys.*, **70**, 545(1990).
- Herman, M., T.R. Huet, Y. Kabbadj, and J. Vander Auwera, *Mol. Phys.*, **72**, 75(1991).
- Herman, R.C., and W.H. Shaffer, *J. Chem. Phys.*, **16**, 453(1948).
- Herman, R., and R.F. Wallis, *J. Chem. Phys.*, **23**, 637(1955).
- Herzberg, G., *Molecular Spectra and Molecular Structure: II. Infrared and Raman Spectra of Polyatomic Molecules*, D. Van Nostrand, Princeton, N.J., 1945.
- Herzberg, G., *Molecular Spectra and Molecular Structure, I. Spectra of Diatomic Molecules*, D. Van Nostrand, Princeton, NJ-Toronto-London-New York, 1950.
- Hietanen, J., R. Antilla, and J. Kauppinen, *Mol. Phys.*, **38**, 1367(1979).
- Hietanen, J., and J. Kauppinen, *Mol. Phys.*, **42**, 411(1981).
- Hietanen, J., *Mol. Phys.*, **49**, 1029(1983).

- Hietanen, J., V.-M. Horneman, and J. Kauppinen, *Mol. Phys.*, **59**, 587(1986).
- Hillman, J.J., D.E. Jennings, and J.L. Faris, *Appl. Opt.*, **18**, 1808(1979).
- Hillman, J.J., D.E. Jennings, G.W. Halsey, S. Nadler, and W.E. Blass, *J. Mol. Spectrosc.*, **146**, 389(1991).
- Horneman, V.-M., S. Alanko, and J. Hietanen, *J. Mol. Spectrosc.*, **135**, 191(1989).
- Hougen, J.T., *J. Chem. Phys.*, **36**, 519(1962b)
- Hougen, J.T., *J. Chem. Phys.*, **37**, 1433(1962b).
- Hougen, J.T., *J. Chem. Phys.*, **39**, 358(1963).
- Hougen, J.T., *Can. J. Phys.*, **42**, 1920(1964).
- Hougen, J.T., *Can. J. Phys.*, **43**, 935(1965).
- Howard, B.J., and R.E. Moss, *Mol. Phys.*, **19**, 433(1970a).
- Howard, B.J., and R.E. Moss, *Mol. Phys.*, **20**, 147(1970b).
- Huet, T.R., and M. Herman, *J. Mol. Spectrosc.*, **132**, 361(1988).
- Huet, T.R., M. Godefroid, and M. Herman, **144**, 32(1990).
- Huet, T.R., M. Herman, and J.W.C. Johns, *J. Chem. Phys.*, **94**, 3407 (1991).
- Huhanantti, M., J. Hietanen, R. Antilla, and J. Kauppinen, *Mol. Phys.*, **37**, 905(1979).
- Hui, A.K., B.H. Armstrong, and A.A. Wray, *J. Quant. Spectrosc. Rad. Transfer*, **19**, 509(1978).
- Humlíček, J., *J. Quant. Spectrosc. Rad. Transfer*, **21**, 309(1979).
- Jansen, L., and H. Boon, *Theory of Finite Groups. Application in Physics*, North Holland, Amsterdam, 1967.
- Jansson, P.A., and C.L. Korb, *J. Quant. Spectrosc. Rad. Transfer*, **8**, 1399(1968).
- Jennings, D.E., *Appl. Opt.*, **19**, 2695(1980).
- Jennings, D.E., R. Hubbard, and J.W. Brandt, *Appl. Opt.*, **24**, 3438(1985).
- Jennings, D.E., *J. Quant. Spectrosc. Rad. Transfer*, **40**, 221(1988).
- Jona, P., M. Gussoni, and G. Zerbi, *J. Phys. Chem.*, **85**, 2210(1981).
- Johns, J.W.C., *J. Mol. Spectrosc.*, **125**, 442(1987).
- Johns, J.W.C., and J. Vander Auwera, *J. Mol. Spectrosc.*, **140**, 71(1990).
- Kabbadj, Y., M. Herman, G. Di Lonardo, L. Fusina, and J.W.C. Johns, submitted to *J. Mol. Spectrosc.*, 1991.
- Kaplan, L.D., and D.F. Eggers, Jr., *J. Chem. Phys.*, **25**, 876(1956).
- Kelly, R.L., R. Rollefson, and B.S. Shurin, *J. Chem. Phys.*, **19**, 1595(1951).
- Kim, K., and W.T. King, *J. Mol. Struct.*, **57**, 201(1979).
- Kirtmann, B., *J. Chem. Phys.*, **41**, 775(1964).
- Koops, T., W.M.A. Smit, and T. Visser, *J. Mol. Struct.*, **112**, 285(1984).
- Kostiuk, T., F. Espenak, D. Deming, M.J. Mumma, D. Zipoy, and J.J. Keady, *Bull. Am. Astr. Soc.*,

- 17, 570(1985).
- Kostyk, E., and H.L. Welsh, *Can. J. Phys.*, **58**, 534(1980).
- Lacy, J.H., N.J. Evans II, J.M. Achtermann, D.E. Bruce, J.F. Arens, and J.S. Carr, *Astrophys. J. (Letters)*, **342**, L43(1989).
- Lafferty, W.J., R.D. Suenram, and D.R. Johnson, *J. Mol. Spectrosc.*, **64**, 147(1977).
- Lafferty, W.J., and A.S. Pine, *J. Mol. Spectrosc.*, **141**, 223(1990).
- Lambot, D., G. Blanquet, and J.P. Bouanich, *J. Mol. Spectrosc.*, **136**, 86(1989).
- Longuet-Higgins, H.C., *Mol. Phys.*, **6**, 44(1963).
- Maes, S., and G. Amat, *Cah. Phys.*, **11**, 277(1957).
- Maguire, W.C., R.E. Samuelson, R.A. Hanel, and V.G. Kunde, *Bull. Am. Astr. Soc.*, **16**, 647(1984).
- Maguire, W.C., J.J. Hillman, M. Weber, W.E. Blass, *J. Geophys. Res.*, **96**, 17493(1991).
- Maki, A.G., and D.R. Lide, *J. Chem. Phys.*, **47**, 3206(1967).
- Mast, G.B., and W.T. King, *J. Phys. Chem.*, **80**, 2004(1976).
- Mathews, C.W., and K.N. Rao, Chapter 8 in *Molecular Spectroscopy: Modern Research*, ed. K.N. Rao and C.W. Weldon, Academic Press, New York, 1972.
- Matsumara, K., T. Tanaka, Y. Endo, S. Salto, E. Hirota, *J. Phys. Chem.*, **84**, 1793(1980).
- McDowell, R.S., *Advances in Infrared and Raman Spectroscopy*, Vol. 5, Heyden, London, 1978.
- McDowell, R.S., *J. Quant. Spectrosc. Rad. Transfer*, **38**, 337(1987).
- McDowell, R.S., *J. Chem. Phys.*, **88**, 356(1988).
- Moravec, A., G. Winnewisser, K.M.T. Yamada, and C.E. Blom, *Z. Naturforsch.*, **45a**, 946(1990).
- Moriwaki, N., T. Tsuchida, Y. Takehisa, N. Ohashi, *J. Mol. Spectrosc.*, **137**, 230(1989).
- Moss, R.E., and A.J. Perry, *Mol. Phys.*, **23**, 957(1972).
- Mucha, J.A., *Appl. Spectrosc.*, **36**, 141(1981).
- Mulholland, H.P., *Proc. Cambridge Phil. Soc.*, **24**, 280(1928).
- Mulliken, R.S., *Rev. Mod. Phys.*, **3**, 89(1931).
- Musher, J.I., *Am. J. Phys.*, **34**, 267(1966).
- Nielsen, H.H., *Rev. Mod. Phys.*, **23**, 90(1951).
- Nielsen, H.H., *The Vibration-Rotation and their Spectra in the Infrared*, in *Handbuch der Physik*, Band XXXVII/1, ed. S. Flügge, Springer Verlag, Berlin-Göttingen-Heidelberg, 1959.
- Nikolava, B., B. Galabov, and W.J. Orville-Thomas, *J. Mol. Struct.*, **125**, 197(1984).
- Niroomand-Rad, A., and P.M. Parker, *J. Mol. Spectrosc.*, **75**, 177(1979).
- Niroomand-Rad, A., and P.M. Parker, *J. Mol. Spectrosc.*, **85**, 40(1981).
- Ohshima, Y., Y. Matsumoto, M. Takami, and K. Kuchitsu, *Chem. Phys. Lett.*, **147**, 1(1988).
- Ohsugi, Y., A. Kitamura, N. Ohashi, *J. Mol. Spectrosc.*, **128**, 592(1988).
- Oka, T., *J. Chem. Phys.*, **47**, 5410(1967).

- Orton, G.S., A.T. Tokunaga, and J. Caldwell, *Icarus*, **56**, 147(1983).
- Palmer, K.F., M.E. Mickelson, and K.N. Rao, *J. Mol. Spectrosc.*, **44**, 131(1972).
- Papoušek, D., *J. Mol. Spectrosc.*, **28**, 161(1968).
- Papoušek, D. and M.R. Aliev, *Molecular Vibrational-Rotational Spectra*, Elsevier Scientific Publishing Company, Amsterdam-Oxford-New York, 1982.
- Pavlushkov, I.V., and D.N. Shchepkin, *Opt. Spectrosc.*, **52**, 598(1982).
- Penner, S.S., and D. Weber, *J. Chem. Phys.*, **19**, 807(1951).
- Penner, S.S., *Quantitative Molecular Spectroscopy and Gas Emissivities*, Addison-Wesley, Reading, MA, 1959.
- Pierluzzi, J.H., P.C. Vanderwood, and R.B. Gomez, *J. Quant. Spectrosc. Rad. Transfer*, **18**, 555(1977).
- Pliva, J., *J. Mol. Spectrosc.*, **44**, 145(1972a)
- Pliva, J., *J. Mol. Spectrosc.*, **44**, 165(1972b).
- Podolske, J.R., M. Loewenstein, and P. Varanasi, *J. Mol. Spectrosc.*, **107**, 241(1984).
- Podolsky, B., *Phys. Rev.*, **32**, 812(1928).
- Prasad, P.L., *J. Phys. Chem.*, **82**, 312(1978).
- Press, W.H., B.P. Flannery, S.A. Teukolsky, and W.T. Vetterling, *Numerical Recipes - The Art of Scientific Computing*, Cambridge University Press, 1986.
- Pugh, L.A. and K.N. Rao, Chapter 4 in *Molecular Spectroscopy: Modern Research, Vol.II*, ed. K.N. Rao, Academic Press, New York, 1976.
- Reddy, S.P., V.M. Devi, A. Baldacci, W. Ivancic, and K.N. Rao, *J. Mol. Spectrosc.*, **74**, 217(1979).
- Restelli, G., and F. Capellani, *J. Quant. Spectrosc. Rad. Transfer*, **33**, 465(1985).
- Ridgway, S.T., *Astrophys. J.*, **187**, L41(1974).
- Rinsland, C.P., P.A. Baldacci, and K.N. Rao, *Astrophys. J. Suppl.*, **49**, 487(1982).
- Rinsland C.P., A. Goldman, and G.M. Stokes, *Appl. Opt.*, **24**, 2044(1985).
- Robiette A.G., D.L. Gray, F.W. Birss, *Mol. Phys.*, **32**, 1591(1976).
- Romani, P.N., and S.K. Atreya, *Icarus*, **74**, 424(1988).
- Rowe, W.F., and E.B. Wilson, *J. Mol. Spectrosc.*, **56**, 163(1975).
- Sayvetz, A., *J. Chem. Phys.*, **7**, 383(1939).
- Shaffer, W.H., H.H. Nielsen, and L.H. Thomas, *Phys. Rev.*, **56**, 895(1939).
- Shensted, I.V., *A Course on the Application of Group Theory to Quantum Mechanics*, Neo Press, Peaks Island, 1976.
- Sherer, G.J., K.K. Lehmann, and W. Klemperer, *J. Chem. Phys.*, **78**, 2817(1983).
- Smit, W.M.A., A.J. van Straten, and T. Visser, *J. Mol. Struct.*, **48**, 177(1978).
- Smit, W.M.A., and T. van Dam, *J. Mol. Struct.(THEOCHEM)*, **88**, 273(1982).
- Smith, B.C., and J.S. Winn, *J. Chem. Phys.*, **89**, 4638(1988).

- Smith, B.C., and J.S. Winn, *J. Chem. Phys.*, **94**, 4120(1991).
- Shutte, C.J.H., *The Theory of Molecular Spectroscopy, Vol. 1: The Quantum Mechanics and Group Theory of Vibrating and Rotating Molecules*, North-Holland, Amsterdam, 1976.
- Smith, M.A.H., B. Fridovich, and K.N. Rao, Chapter 3 in *Molecular Spectroscopy: Modern Research, Vol.III*, ed. K.N. Rao, Academic Press, New York, 1985.
- Strey, G., and I.M. Mills, *J. Mol. Spectrosc.*, **59**, 103(1976).
- Strow, L.L., *J. Quant. Spectrosc. Rad. Transfer*, **29**, 395(1983).
- Strow, L.L., and L. Zheng, *J. Quant. Spectrosc. Rad. Transfer*, **42**, 521(1989).
- Suzuki, I., and J. Overend, *Spectrochim. Acta*, **25**, 977(1969).
- Takehisa, Y., M. Oda, and N. Ohashi, *J. Mol. Spectrosc.*, 590(1988).
- Thomas, L.H., *J. Chem. Phys.*, **10**, 532(1942).
- Thomas, L.H., *J. Chem. Phys.*, **10**, 538(1942).
- Tinkham, M., *Group Theory and Quantum Mechanics*, McGraw-Hill, New York, 1964.
- Tokunaga, A., R.F. Knacke, and T. Owen, *Astrophys. J.* **209**, 294(1976).
- Tokunaga, A., R.F. Knacke, S.T. Ridgway, and L. Wallace, *Astrophys. J.*, **232**, 603(1979).
- Toth, R. A., *Appl. Opt.*, **23**, 1825(1984).
- Van Vleck, J.H., *Phys. Rev.*, **47**, 487(1935).
- Varanasi, P., and B.R. Bangaru, *J. Quant. Spectrosc. Rad. Transfer*, **14**, 839(1974).
- Varanasi, P., L.P. Giver, and F.P.J. Valero, *J. Quant. Spectrosc. Rad. Transfer*, **30**, 497(1983); **30**, 505(1983).
- Varghese, P.L., and R.K. Hanson, *Appl. Opt.*, **23**, 2376(1984).
- Wang, I.-Y., and A. Weber, *Ind. J. of Pure and Appl. Phys.*, 358(1978).
- Watson, J.K.G., *Mol. Phys.*, **15**, 479(1968).
- Watson, J.K.G., *Mol. Phys.*, **19**, 465(1970).
- Watson, J.K.G., M. Herman, J.C. Van Craen, and R. Colin, *J. Mol. Spectrosc.*, **95**, 101(1982).
- Watson, J.K.G., *J. Mol. Spectrosc.*, **101**, 83 (1983).
- Watson, J.K.G., *J. Mol. Spectrosc.*, **125**, 428(1987).
- Watson, J.K.G., *J. Mol. Spectrosc.*, **145**, 130(1991).
- Wattson, R.R., and L.S. Rothman, *J. Mol. Spectrosc.*, **119**, 83(1986).
- Weber, M., W.E. Blass, and J.-L. Salanave, *J. Quant. Spectrosc. Rad. Transfer*, **42**, 437(1989).
- Weber, M., and W.E. Blass, manuscript in preparation, 1991.
- Weyl, H., *The Theory of Groups and Quantum Mechanics*, Dover, New York, 1950.
- White, J.U., *J. Opt. Soc. Am.*, **32**, 285 (1942).
- Wilkinson, J.H., and C. Reinsch, *Handbook for Automatic Computation, Vol. II, Linear Algebra*, Springer Verlag, New York, Heidelberg, and Berlin, 1971.

- Wilkerson, T.D., G. Schwemmer, B. Gentry, and L.P. Giver, *J. Quant. Spectrosc. Rad. Transfer*, **22**, 315(1979).
- Wlodarczak, G., J. Demaison, J. Burie, and M.C. Lasne, *Mol. Phys.*, **66**, 669(1989).
- Wilson, E.B., Jr., and A.J. Wells, *J. Chem. Phys.*, **14**, 578(1946).
- Wilson, E.B., Jr., J.C. Decius, and P.C. Cross, *Molecular Vibrations*, McGraw-Hill, 1955.
- Wingfield, E.C., and J.W. Straley, *J. Chem. Phys.*, **23**, 731(1955).
- Winnewisser, M., and B.P. Winnewisser, *J. Mol. Spectrosc.*, **41**, 143(1972).
- Yamada, K., T. Nakagawa, and K. Kuchitsu, *J. Mol. Spectrosc.*, **51**, 399(1974).
- Yamada, K., *Z. Naturforsch.*, **38a**, 821(1983).
- Yamada, K., F.W. Birss, and M.R. Aliev, *J. Mol. Spectrosc.*, **112**, 347(1985).
- Yamanouchi, K., N. Ikeda, S. Tsuchiya, D.M. Jonas, J.K. Lundberg, G.W. Adamson, R.W. Field, *J. Chem. Phys.*, **95**, 6330(1991).
- Zhan, X., O. Vahtinen, E. Kauppinen, L. Halonen, *Chem. Phys. Lett.*, **180**, 310 (1991).

APPENDICES

APPENDIX A

BAND INTENSITY OF SYMMETRIC TOP MOLECULES

A.1 Introduction

The aim of these notes is based in the attempt to clarify the confusion and ambiguity in definition and terminology of spectroscopic properties associated with band intensity retrieval from experimental line intensity of specific transitions. Those ambiguities in defining the essential spectroscopic parameters quite often make it difficult to compare intensities throughout the literature. An effort is made to outline one specific concept of band intensity retrieval in $\text{cm}^{-2}\text{atm}^{-1}$, which necessarily must not be the unique approach, but is starting, it seems, to become a standard notation as given in the review article and compilation of intensities by Smith *et al.* 1985.

Beginning with the discussion of transition probability of absorption, we will arrive at an expression, which relates individual intensities to the total rotation-vibration band intensity and the square of the transition moment (or dipole moment matrix element). Following this discussion temperature dependency of band intensities will be outlined, which enables us to convert intensities to different temperatures as it is important for application to astrophysics and atmospheric physics.

A.2 Transition Probability and Electric Dipole Moment Matrix Element

Individual line intensity merely expresses the transition probability of a molecule to undergo a transition from a lower quantum mechanical state $|A\rangle = |v''J''K''M''\rangle$ to an upper state $|B\rangle = |v'J'K'M'\rangle$ by absorption of radiation. The v, J, K , and M represent the set of quantum numbers describing the non-degenerate rotation-vibrational state. In these notes we limit ourselves to transitions in the weak-signal approximation (Demtröder 1982), where the attenuation of incoming radiation by absorption is best described by the Beer-Lambert law. In addition the statistics of level population can be assumed to be in thermal equilibrium with a balance of induced emission and absorption, and spontaneous emission as it is usually characterized by the Einstein coefficients (Penner 1959). The line intensity is then given by

$$S_{A \rightarrow B} = \frac{8\pi^3}{3hc} N a \nu_{AB} \left[\frac{\exp\left(-\frac{E_v'' + E_r''}{kT}\right)}{Q_v Q_r} \right] \left[1 - \exp\left(-\frac{hc\nu_{AB}}{kT}\right) \right] \times \\ \times \sum_{\alpha=X,Y,Z} |\langle v''J''K''M'' | \mu_\alpha | v'J'K'M' \rangle|^2, \quad (\text{A.1})$$

where $E_v'' + E_r''$ is the energy of the lower rotation-vibrational state, $Q = Q_v Q_r$ the total partition function formed by the product of rotational and vibrational Zustandssumme, ν_{AB} the transition frequency in cm^{-1} ; μ_α are the components of the dipole moment operator in the space-fixed coordinate system, XYZ (Smith *et al.* 1985, Herzberg 1950). a is the isotopic abundance of the molecule. The first term of Eq. (A.1) in brackets yields the fractional Boltzmann population of the lower rotation-vibrational state, whereas the second term in brackets is called the induced emission term. The product of these two terms times the total population N merely represents the population difference between the lower and upper state, e.g. $N' - N''$.

Eq. (A.1) is written in the form for two non-degenerate states $|A\rangle$ and $|B\rangle$. If no external field is applied to the molecule, a preferred spatial orientation is not available. In that case a rotational degeneracy in J and the nuclear spin states has to be taken in account. The line intensity can be rewritten as

$$S_{J''} = \frac{8\pi^3}{3hc} N_A \nu_{AB} \frac{\exp(-\frac{E''}{kT})}{Q_v} g_{J''} \frac{\exp(-\frac{E''}{kT})}{Q_r} \times \\ \times \left[1 - \exp(-\frac{h\nu_{AB}}{kT}) \right] \sum_{M'', M', \alpha=X,Y,Z} |\langle v'' J'' K'' M'' | \mu_\alpha | v' J' K' M' \rangle|^2 \quad (\text{A.2})$$

$g_{J''}$ is the nuclear statistical weight or multiplicity of the symmetric and/or antisymmetric nuclear spin states depending on J'' and the symmetry of the molecule (Bunker 1979, Herzberg 1945, Papoušek and Aliev 1982). In the literature the square of the transition moment as given in Eq. (A.2) is sometimes referred to as the line strength (Papoušek and Aliev 1982), which is also frequently used for line intensity.

In the same fashion as for the molecular Hamiltonian, a separation of the transition probability in a rotational and vibrational part corresponding to the zeroth order rigid rotor, harmonic oscillator Hamiltonian can be made. Intensity alteration from the zeroth order intensity distribution due to rotation-vibration interactions and resonances can be then expressed as a multiplicative factor such as the Herman-Wallis factor.

The transition moment can be separated if it is transformed to the body-fixed coordinate system and an irreducible rank 1 tensor of the dipole operator is introduced. Thus, by defining the tensor operators

$$\mu(10) = \mu_z; \quad \mu(1 \pm 1) = \mp \frac{1}{\sqrt{2}} (\mu_x \pm \mu_y) \quad (\text{A.3})$$

in the space-fixed axis system and

$$\mu'(10) = \mu_z; \quad \mu'(1 \pm 1) = \mp \frac{1}{\sqrt{2}} (\mu_x \pm \mu_y) \quad (\text{A.4})$$

in the molecular frame, the square of the transition moment can be summarized as

$$\sum_{\alpha, M'', M'} |\langle v'' J'' K'' M'' | \mu_\alpha | v' J' K' M' \rangle|^2 = \\ = \sum_{\tau, M'', M'} |\langle v'' J'' K'' M'' | \mu(1\tau) | v' J' K' M' \rangle|^2 = \\ = \sum_{\tau, \tau', M'', M'} |\langle J'' K'' M'' | D_{\tau\tau'}^{(1)} | J' K' M' \rangle|^2 |\langle v'' | \mu'(1\tau') | v' \rangle|^2 \equiv \\ \equiv \Lambda_{J, \Delta J, K, \Delta K} \Gamma_v^2, \quad (\text{A.5})$$

where $D_{\tau\tau'}^{(1)}$ is the matrix of finite rotations depending on the Euler angles and also the matrix representation of the spatial rotation group (Papoušek and Aliev 1982, Bunker 1979); xyz denote

the body-fixed axis-system. Evaluation of the sum of the D -matrix elements in Eq. (A.5) with help of the squared $3j$ symbols ultimately leads to the Hönl-London factor $\Lambda_{J,\Delta J,K,\Delta K}$ and selection rules for the allowed rotation-vibration transitions. Γ_v^2 in Eq. (A.5) represents the vibrational part of the squared dipole moment matrix element. In the last line of Eq. (A.5) the primes are omitted and the set of quantum number without primes are from now on those of the lower state. The intensity amplitudes for symmetric top molecules are given by

$$\Lambda_{J,\Delta J=-1,K,\Delta K=0} = \frac{J^2 - K^2}{J} \quad (\text{A.6})$$

$$\Lambda_{J,\Delta J=0,K,\Delta K=0} = \frac{(2J+1)K^2}{J(J+1)} \quad (\text{A.7})$$

$$\Lambda_{J,\Delta J=1,K,\Delta K=0} = \frac{(J+K+1)(J-K+1)}{J+1} \quad (\text{A.8})$$

for parallel bands ($\Delta K = 0$) and

$$\Lambda_{J,\Delta J=-1,K,\Delta K=\pm 1} = \frac{(J \mp K)(J \mp K - 1)}{2J} \quad (\text{A.9})$$

$$\Lambda_{J,\Delta J=0,K,\Delta K=\pm 1} = \frac{(2J+1)(J \pm K)(J \mp K + 1)}{2J(J+1)} \quad (\text{A.10})$$

$$\Lambda_{J,\Delta J=1,K,\Delta K=\pm 1} = \frac{(J \pm K + 2)(J \pm K + 1)}{2(J+1)} \quad (\text{A.11})$$

for perpendicular bands ($\Delta K = \pm 1$).

The vibrational band intensity can now be defined as

$$S_v = \frac{8\pi^3}{3hc} N a \nu_o \left[\frac{\exp\left(-\frac{E_v}{kT}\right)}{Q_v} \right] \Gamma_v^2, \quad (\text{A.12})$$

where ν_o is the band center frequency. Smith *et al.* 1985 define the vibrational band intensity by excluding the vibrational Boltzmann factor. Their S_v^o is related to S_v by

$$S_v = S_v^o \exp\left(-\frac{E_v}{kT}\right). \quad (\text{A.13})$$

The total band intensity of a given rotation-vibration band to another is made up by the sum of all individual transitions, e.g.

$$S_v^i = \sum_J 'S_J = \sum_{A,B} 'S_v R_{AB} F_{J,\Delta J} = S_v \sum_{A,B} 'R_{AB} F_{J,\Delta J}. \quad (\text{A.14})$$

The prime at the summation signs in Eq. (A.14) indicate the limitation of the sum to allowed transitions as defined by the selection rules. R_{AB} is the degenerate rotational factor of the transition

probability between state $|A\rangle$ and $|B\rangle$, which can be obtained by dividing Eq. (A.2) by Eq. (A.12). Hence,

$$R_{AB} = \frac{\nu_{AB}}{\nu_o} g_J \frac{\exp\left(-\frac{E_r}{kT}\right)}{Q_r} \left[1 - \exp\left(-\frac{hc\nu_{AB}}{kT}\right)\right] \Lambda_{J,\Delta J,K,\Delta K}. \quad (\text{A.15})$$

$F_{J,\Delta J}$ is the above mentioned Herman-Wallis factor. Both S_v and S_v^i are commonly called band intensity and band strength interchangeably but are not equal quantities.

Depending on the chosen units for band intensities, N appearing in Eqs. (A.1), (A.2), and (A.12) represents the number density per unit pressure ($\text{cm}^{-2}\text{atm}^{-1}$), or

$$N = 1 \quad (\text{A.16})$$

if the unit is $\text{cm}/\text{molecules}$. In the first case the number density per unit pressure can be determined by the ideal gas law $pV = nkT$, where n is the total number of molecules. Since $k = p_o/L_oT_o$ with the reference conditions $p_o = 1\text{atm}$, $T_o = 273.15\text{K}$, and with L_o equaling the Loschmidt number $2.687 \times 10^{19} \text{ molecules}/\text{cm}^3 \text{atm}$, the number density is given by

$$N = \frac{n}{pV} = \frac{T_o L_o}{p_o T}. \quad (\text{A.17})$$

(Goldman *et al.* 1989). Clearly, S_v^i and S_v in $\text{cm}^{-2}\text{atm}^{-1}$ can be interpreted as the band intensity per unit pressure and volume of the given gas sample and in $\text{cm}/\text{molecules}$ as the band intensity per total molecule number. In both cases a temperature dependence exists.

In a band intensity retrieval by least squares fit usually a normal equation is provided with S_J as an independent variable and S_v and $F_{J,\Delta J}$ as dependent variables, as follows

$$S_J = S_v R_{AB} F_{J,\Delta J} = S_v \frac{\nu_{AB}}{\nu_o} g_J \frac{\exp\left(-\frac{E_r}{kT}\right)}{Q_r} \left[1 - \exp\left(-\frac{hc\nu_{AB}}{kT}\right)\right] \Lambda_{J,\Delta J,K,\Delta K} F_{J,\Delta J} \quad (\text{A.18})$$

Frequently the line intensity is directly expressed in terms of the square of the vibrational dipole moment matrix element. With help of Eq. (A.12), Eq. (A.18) can be rewritten as

$$S_J = \frac{8\pi^3}{3hc} N a \nu_{AB} g_J \frac{\exp\left(-\frac{E_v+E_r}{kT}\right)}{Q_r Q_v} \times \left[1 - \exp\left(-\frac{hc\nu_{AB}}{kT}\right)\right] \Lambda_{J,\Delta J,K,\Delta K} \Gamma_v^2 F_{J,\Delta J}, \quad (\text{A.19})$$

where Γ_v is given in units of $\text{esu} \cdot \text{cm}$ in cgs-system. More common is the Debye unit which equals $10^{-18} \text{esu} \cdot \text{cm}$ (Conversion to MKS units: $1 \text{esu} \cdot \text{cm} = 3.336 \times 10^{-12} \text{C} \cdot \text{m}$). Eq. (A.19) holds for both rotational and vibrational transitions, while Eq. (A.18) is limited to vibrational transitions since $\nu_o = 0$ for pure rotational spectra.

Depending on the normal modes of the considered molecule, different forms of the Herman-Wallis factor have been proposed. For example Toth 1984 recommends for CO_2

$$F_{J,\Delta J} = [1 + A_1 m + A_2 J(J+1) + \dots]^2 \quad (A.20)$$

and Bordé 1976 theoretically predicted for the ν_3 fundamental of carbon dioxide

$$F_{J,\Delta J} = 1 + a_1 m + a_2 m^2 + \dots \quad (A.21)$$

with $m = J + 1$ for R-branch transitions and $m = -J$ for P-branch transition. Both forms for the Herman-Wallis factor here are equivalent. $\Gamma_v^2 F_{J,\Delta J}$ is an effective squared dipole moment since the qualitative form of the Herman-Wallis factor can be theoretically determined by a contact transformation of the zeroth order squared dipole moment operator Γ_v^2 , in the same way as done for the rigid rotor, harmonic oscillator Hamiltonian to derive the higher order terms of the energy expression due to the rotation-vibration interaction (Watson 1987, Johns 1988).

To complete the discussion of band intensity retrieval, some words should be spent on the calculation of the partition functions in Eqs. (A.18) and (A.19). The rotational partition function is given by

$$Q_r = \sum_J g_J (2J+1) \exp\left(-\frac{E_r}{kT}\right), \quad (A.22)$$

where $E_r = F_v(J, K, \dots)$ is the appropriate rotational energy expression. Q_v is defined by

$$Q_v = \sum_s \sum_{v_s=0, \dots}^{\infty, \dots} \exp\left(-\frac{E_{v_s}}{kT}\right), \quad (A.23)$$

where $E_v = G_o(v_1, v_2, \dots)$ is the appropriate vibrational energy term. The summation index s denotes the summation over all normal modes v_s and eventually other non-degenerate vibrational quantum numbers. Usually the computation of the partition function can be restricted to a finite sum.

If the vibrational band strength and, if necessary, Herman-Wallis factor are known, the total band intensity S_v^i can be readily computed by using Eq. (A.14).

The above given outline is also valid for linear molecules. From the Sayvetz condition for linear molecules (Papoušek and Aliev 1982, Amat *et al.* 1971) follows

$$K = \left| \sum_t \ell_t \right|, \quad (A.24)$$

and, therefore, K and ΔK can be replaced by ℓ and $\Delta\ell$. The summation over t extends over all perpendicular modes v_t . For parallel bands $\ell = \Delta\ell = 0$, and consequently parallel bands do not possess Q-branch transitions (see Eq.(A.7)). For spherical tops the case is more complicated, since

Eq.(A.5) for the transition moment must be expressed in linear combinations of symmetric top eigenfunctions (Robiette *et al.* 1976).

A.3 Temperature Dependence of Intensities

For atmospheric and astrophysical analysis of molecular spectra, it is necessary to convert intensities to various temperature. If the intensities at certain temperature, say T_a , are known, the line intensity at another temperature T_b can be calculated with help of Eq. (A.2) as follows

$$S_J(T_b) = S_J(T_a) \frac{N(T_b)}{N(T_a)} \exp\left(-\frac{E_v + E_r}{k}(1/T_b - 1/T_a)\right) \times \\ \times \frac{Q_v(T_a)Q_r(T_a)}{Q_v(T_b)Q_r(T_b)} \left[\frac{1 - \exp\left(-\frac{hc\nu_{AB}}{kT_b}\right)}{1 - \exp\left(-\frac{hc\nu_{AB}}{kT_a}\right)} \right]. \quad (\text{A.25})$$

A similar equation can be derived for the vibrational intensity S_v by using Eq. (A.12):

$$S_v(T_b) = S_v(T_a) \frac{N(T_b)}{N(T_a)} \frac{Q_v(T_a)}{Q_r(T_b)} \exp\left(-\frac{E_v}{k(1/T_b - 1/T_a)}\right) \quad (\text{A.26})$$

By summation over all intensities belonging to the same vibrational band, S_v^i can be obtained from Eq. (A.25). The number density ratio is given by

$$\frac{N(T_b)}{N(T_a)} = \left(\frac{T_a}{T_b}\right)^f, \quad (\text{A.27})$$

where $f = 1$ if the intensity units are in $\text{cm}^{-2}\text{atm}^{-1}$ and $f = 0$ if the units are in $\text{cm}/\text{molecules}$.

The partition functions can be simplified by using asymptotic expansions. Including solely the harmonic frequencies, the vibrational partition function can be written as

$$Q_v \approx \sum_{v_1, v_2, \dots}^{\infty} \exp\left(-\frac{hc\omega_1 v_1}{kT}\right) \exp\left(-\frac{hc\omega_2 v_2}{kT}\right) \dots = \prod_s \frac{1}{[1 - \exp(hc\omega_s/kT)]^{d_s}}, \quad (\text{A.28})$$

where d_s is the degeneracy of the harmonic frequency ω_s ,

For linear molecules the first order of the rotational partition function can be determined as

$$Q_r(T) \approx \frac{kT}{hcB}, \quad (\text{A.29})$$

when $F_v(J, \ell, \dots) = BJ(J+1)$ is assumed (Herzberg 1945, Mulholland 1928). McDowell 1988 proposed a refined and more accurate (up to second order) expression for a linear molecule, which is given by

$$Q_r(T) \approx I\sigma^{-1} \frac{\exp\left(-\frac{\beta}{3}\right)}{\beta}. \quad (\text{A.30})$$

Table A.1. Physical constants.

CONSTANTS *	
L_o	$= 2.6868 \times 10^{19} \text{ cm}^{-3} \text{ atm}^{-1}$
h	$= 6.6262 \times 10^{-27} \text{ erg sec}$
c	$= 2.9979 \times 10^{10} \text{ cm/sec}$
k	$= 1.3806 \times 10^{-16} \text{ erg/K}$
hc/k	$= 1.4388 \text{ K cm}$
$k/(hc)$	$= .69500 \text{ K}^{-1} \text{ cm}^{-1}$
$8\pi^3/3hc$	$= 4.1623 \times 10^{17} \text{ erg}^{-1} \text{ cm}^{-1}$
$T_o L_o/p_o$	$= 7.3390 \times 10^{21} \text{ cm}^{-3} \text{ atm}^{-2} \text{ K}$

* all numbers in cgs-units and atm

I is here the total nuclear spin multiplicity, e.g. $\prod_a (2I_a + 1)$; σ the classical symmetry number, and $\beta = hc B/kT$. For centro-symmetric molecules belonging to the $D_{\infty h}$ Symmetry group, $\sigma = 2$ and for $C_{\infty v}$ molecules $I = \sigma = 1$. The following asymptotic expression exists for a non-linear symmetric top

$$Q_r \approx \sqrt{\frac{\pi}{B^2 A} \left(\frac{kT}{hc} \right)^3} \quad (\text{A.31})$$

(Herzberg 1945), where $F_v(J, K, \dots) = BJ(J+1) - (A-B)K^2$. In the case of spherical molecules B is equal to A in Eq. (A.31). An improved expression for the rotational partition function of spherical tops is given by McDowell 1987.

All three approximations for the rotational partition functions, Eqs. (A.29), (A.30), and (A.31), are very good estimates except for very low temperature, e.g. in the limit $B/T \rightarrow 0$, and except for higher quantum hotbands. Up to first order the ratio of the rotational partition function at different temperatures T_a and T_b can be well approximated by

$$\frac{Q_r(T_a)}{Q_r(T_b)} = \left(\frac{T_a}{T_b} \right)^p \quad (\text{A.32})$$

with $p = 1$ for linear molecules and $p = 3/2$ for non-linear symmetric tops.

The accurate determination of the effective dipole matrix element strongly depends on precise temperature measurements even at room temperature. Especially for high J transition, temperature variations as small as 0.5K are critical for the evaluation of the Herman-Wallis factors due to the sensitivity in temperature variation of the Boltzmann factor (Johns 1988).

Conversion of intensities to other units and temperature other than those described above are summarized in the review articles of Pugh and Rao 1976 and Smith *et al.* 1985. These articles additionally contain a detailed up to date compilation of band intensities and broadening parameters of various molecules. Some physical constants used here are summarized in Table A.1.

A.4 List of References

- Amat, G., H.H. Nielsen, and G. Tarrago, *Rotation-Vibration of Polyatomic Molecules*, Marcel Dekker, Inc., New York, 1971.
- Bordé, J., *J. Phys.*, **37**, 711(1976).
- Bunker P.R., *Molecular Symmetry and Spectroscopy*, Academic Press, New York-San Francisco-London, 1979.
- Demtröder, W., *Laser Spectroscopy*, Springer-Verlag, Berlin-Heidelberg-New York, 1982.
- McDowell, R.S., *J. Chem. Phys.*, **88**, 356(1988).
- McDowell, R.S., *J. Quant. Spectrosc. Rad. Transfer*, **38**, 337(1987).
- Goldman, A., M. Dang-Nhu, and J.P. Bouanich, *J. Quant. Spectrosc. Rad. Transfer*, **41**, 17(1989).
- Herzberg, G., *Molecular Spectra and Molecular Structure, I. Spectra of Diatomic Molecules*, D. Van Nostrand Company, Inc., Princeton,NJ-Toronto-London-New York, 1950.
- Herzberg, G., *Molecular Spectra and Molecular Structure, II. Infrared and Raman Spectra of Polyatomic Molecules*, D. Van Nostrand Company, Inc., Princeton,NJ-Toronto-London-New York, 1945.
- Johns, J.W.C., *J. Mol. Spectrosc.*, **125**, 442(1987).
- Mulholland, H.P., *Proc. Cambridge Phil. Soc.*, **24**, 280(1928).
- Papoušek, D. and M.R. Aliev, *Molecular Vibrational-Rotational Spectra*, Elsevier Scientific Publishing Company, Amsterdam-Oxford-New York, 1982.
- Penner, S.S., *Quantitative Molecular Spectroscopy and Gas Emissivities*, Addison-Wesley, Reading, MA, 1959.
- Pugh, L.A. and K.N. Rao, Chapter 4 in *Molecular Spectroscopy: Modern Research, Vol.II*, ed. K.N. Rao, Academic Press, New York, 1976.
- Robiette A.G., D.L. Gray, F.W. Birss, *Mol. Phys.*, **32**, 1591(1976).
- Smith, M.A.H., B. Fridovic, and K.N. Rao, Chapter 3 in *Molecular Spectroscopy: Modern Research, Vol.III*, ed. K.N. Rao, Academic Press, New York, 1985.
- Toth, R. A., *Appl. Opt.*, **23**, 1825(1984).
- Watson, J.K.G., *J. Mol. Spectrosc.*, **125**, 428(1987).

APPENDIX B

THE MOLECULAR SYMMETRY GROUP $EMS(D_{\infty h})$ AND $EMS(C_{\infty v})$

B.1 Character Tables of the Extended Molecular Symmetry Group

$MS(C_{\infty v})$	E_o	E_ϵ	$\dots$	E_ϵ^*	
	1	2	$\dots$	∞	
$C_{\infty v}$	E	C_∞^ϵ	$\dots$	$\sigma_v^{\epsilon/2}$	
Equiv. rot.	R^o	$R_z^{-\epsilon}$	$\dots$	$R_{(\pi+\epsilon)/2}^\pi$	
Σ^+	1	1	$\dots$	1	T_z
Σ^-	1	1	$\dots$	-1	R_z
Π	2	$2\cos \epsilon$	$\dots$	0	$(T_x, T_y), (R_x, R_y)$
Δ	2	$2\cos 2\epsilon$	$\dots$	0	
Φ	2	$2\cos 3\epsilon$	$\dots$	0	
$\vdots$	$\vdots$	$\vdots$	$\dots$	$\vdots$	

$EMS(D_{\infty h})$	E_o	E_ϵ	$\dots$	E_ϵ^*	p_π^*	$p_{\pi+\epsilon}^*$	$\dots$	p_ϵ	
	1	2	$\dots$	∞	1	2	$\dots$	∞	
$D_{\infty h}$	E	C_∞^ϵ	$\dots$	$\sigma_v^{\epsilon/2}$	i	$S_{\infty+\epsilon}^\pi$	$\dots$	$C_2^{\epsilon/2}$	
Equiv. rot.	R^o	$R_z^{-\epsilon}$	$\dots$	$R_{(\pi+\epsilon)/2}^\pi$	R^o	$R_z^{-\epsilon}$	$\dots$	$R_{\epsilon/2}^\pi$	
$s\Sigma_g^+$	1	1	$\dots$	1	1	1	$\dots$	1	
$a\Sigma_g^-$	1	1	$\dots$	-1	1	1	$\dots$	-1	R_z
$a\Sigma_u^+$	1	1	$\dots$	1	-1	-1	$\dots$	-1	T_z
$s\Sigma_u^-$	1	1	$\dots$	-1	-1	-1	$\dots$	1	
Π_g	2	$2\cos \epsilon$	$\dots$	0	2	$2\cos \epsilon$	$\dots$	0	(R_x, R_y)
Π_u	2	$2\cos \epsilon$	$\dots$	0	-2	$-2\cos \epsilon$	$\dots$	0	(T_x, T_y)
Δ_g	2	$2\cos 2\epsilon$	$\dots$	0	2	$2\cos 2\epsilon$	$\dots$	0	
Δ_u	2	$2\cos 2\epsilon$	$\dots$	0	-2	$-2\cos 2\epsilon$	$\dots$	0	
Φ_g	2	$2\cos 3\epsilon$	$\dots$	0	2	$2\cos 3\epsilon$	$\dots$	0	
Φ_u	2	$2\cos 3\epsilon$	$\dots$	0	-2	$-2\cos 3\epsilon$	$\dots$	0	
$\vdots$	$\vdots$	$\vdots$	$\dots$	$\vdots$	$\vdots$	$\vdots$	$\dots$	$\vdots$	

The symmetry operation and their characters for the $EMS(C_{\infty v})$ and $EMS(D_{\infty h})$ symmetry group are listed along with their corresponding point group operations and equivalent rotations. While a point group operation transforms only vibronic variables and an equivalent rotation only

the Euler angles, the EMS group transforms all rovibronic coordinates. An isomorphism exists between a EMS group of a linear molecule and its corresponding point group (Bunker and Papoušek, 1969). Each element of the EMS group can be written as a product of a point group operation and an equivalent rotation and a nuclear spin permutation (Bunker and Papoušek, 1969). The products consist of the operations listed below the EMS group operation in each column. R_z^α is a rotation by angle α about the molecule fixed z -axis and R_α^β a rotation by β about an axis in the xy plane making an angle α with the molecule fixed x axis.

The second row in each table indicates the multiplicity of the class for which the group operation is a representative (Bunker, 1979, Tinkham, 1964). The tables are valid for molecules with integral total angular momentum (sum of electronic and rotational angular momentum).

B.2 Direct products of Symmetry Species

A table of direct products of the symmetry species of linear molecule are given, for instance, by Shutte (1976). If we use the following notation: $E_1^+ = \Sigma^+$, $E_1^- = \Sigma^-$, $E_2 = \Pi$, $E_3 = \Phi$, $E_4 = \Gamma$, etc., then the direct product can be written as

$$E_m \times E_n = E_{m+n} + E_{m+n-2} + \cdots + E_2 \quad \text{or} \quad E_1^+ + E_1^- \quad (\text{B.1})$$

for $m > 1$ and $n > 1$ and both symmetry groups. If $m = 1$, then

$$\Sigma^\pm \times E_n = E_n \quad (\text{B.2})$$

and, especially,

$$\Sigma^- \times \Sigma^- = \Sigma^+ \quad (\text{B.3})$$

and

$$\Sigma^- \times \Sigma^+ = \Sigma^- \quad (\text{B.4})$$

For $D_{\infty h}$ species, the following products are valid for g and u labels

$$g \times g = g; \quad g \times u = u; \quad u \times u = g, \quad (\text{B.5})$$

where the label of the product has to be added to each species on the right side of Eqs. (B.2–B.4).

B.3 List of References

- Bunker, P.R., and D. Papoušek, *J. Mol. Spectrosc.*, **32**, 419(1969).
 Bunker, P.R., *Molecular Symmetry and Spectroscopy*, Academic Press, New York–San Francisco–London, 1979.
 Shutte, C.J.H., *The Theory of Molecular Spectroscopy, Vol. 1: The Quantum Mechanics and Group Theory of Vibrating and Rotating Molecules*, North-Holland, Amsterdam, 1976.
 Tinkham, M., *Group Theory and Quantum Mechanics*, McGraw-Hill, New York, 1964.

APPENDIX C

OBSERVED FREQUENCIES OF $^{12}\text{C}_2\text{H}_2$ AND $^{13}\text{C}^{12}\text{CH}_2$

Observed frequencies of 2486 $^{12}\text{C}_2\text{H}_2$ and 595 $^{13}\text{C}^{12}\text{CH}_2$ transitions are listed with their quantum number assignments. Transitions marked with an asterisk (*) were excluded from the fit; transitions marked with (i) are those of $^{13}\text{C}^{12}\text{CH}_2$. Details of the absorption bands listed here are given in Table 4.1 and 4.7. The deviation from calculated frequencies in units of 10^{-5}cm^{-1} are given in the last column. Some deviations are very high which may be due to misassignments or due to strong blending with stronger absorption features.

lower level						upper level						$J \Delta J$	ν_{obs}	σ
v_4	v_5	ℓ	v_4	v_5	ℓ	v_4	v_5	ℓ	v_4	v_5	ℓ			
0	0	0	e	0	1	1	e	47	-1	618.75430	-21			
0	0	0	e	0	1	1	e	46	-1	621.08669	-8			
0	0	0	e	0	1	1	e	45	-1	623.42052	24			
0	1	1	e	0	2	0	e	42	-1	624.80252	-17			
1	0	1	e	1	1	0	e	41	-1	624.95431	1			
0	0	0	e	0	1	1	e	44	-1	625.75492	-6			
0	1	1	e	0	2	0	e	41	-1	627.08688	12			
0	0	0	e	0	1	1	e	43	-1	628.09092	7			
0	1	1	e	0	2	0	e	40	-1	629.36893	11			
1	0	1	e	1	1	0	e	39	-1	629.40311	-5			
0	0	0	e	0	1	1	e	42	-1	630.42783	-3			
1	0	1	f	1	1	2	f	42	-1	631.30455	1			
1	0	1	e	1	1	0	e	38	-1	631.62205	-8			
0	1	1	e	0	2	0	e	39	-1	631.64860	-6			
0	0	0	e	0	1	1	e	42	-1	631.78702	i	15		
2	0	2	e	2	1	1	He	35	-1	631.84617	-46			
0	1	1	f	0	2	2	f	41	-1	632.11796	-12			
2	0	2	f	2	1	1	He	36	-1	632.74882	-1170*			
0	0	0	e	0	1	1	e	41	-1	632.76603	6			
1	0	1	e	1	1	0	e	37	-1	633.83726	-14			
0	1	1	e	0	2	0	e	38	-1	633.92601	-7			
1	0	1	f	1	1	0	f	40	-1	634.01658	17			
0	0	0	e	0	1	1	e	41	-1	634.07286	i	-2		
0	1	1	f	0	2	2	f	40	-1	634.47819	-9			
0	0	0	e	0	1	1	e	40	-1	635.10515	0			
1	0	1	e	1	1	0	e	36	-1	636.04796	-103*			
1	0	1	f	1	1	2	f	40	-1	636.05797	102*			
0	1	1	e	0	2	0	e	37	-1	636.20079	-10			
1	1	2	e	1	2	1	He	28	-1	636.22893	15			
2	0	2	e	2	1	1	He	33	-1	636.25286	32			
0	0	0	e	0	1	1	e	40	-1	636.35948	i	-37		
0	2	0	e	0	3	1	e	35	-1	636.64025	34			
0	1	1	f	0	2	2	f	39	-1	636.83916	-15			
0	0	0	e	0	1	1	e	39	-1	637.44536	-1			
1	0	1	e	1	1	0	e	35	-1	638.25683	-11			
1	1	0	e	1	2	1	He	34	-1	638.32329	5			
1	0	1	f	1	1	2	f	39	-1	638.43462	14			
2	0	2	e	2	1	1	He	32	-1	638.45531	6			
0	1	1	e	0	2	0	e	36	-1	638.47277	-13			
0	0	0	e	0	1	1	e	39	-1	638.64770	i	-2		
1	0	1	f	1	1	0	f	38	-1	638.76787	11			
2	0	2	f	2	1	1	He	33	-1	639.05804	17			
0	1	1	f	0	2	2	f	38	-1	639.20098	-14			
0	0	0	e	0	1	1	e	38	-1	639.78661	2			
1	0	1	e	1	1	0	e	34	-1	640.46124	-10			
2	0	2	e	2	1	1	He	31	-1	640.65807	19			
1	1	0	e	1	2	1	He	33	-1	640.69402	21			
0	1	1	e	0	2	0	e	35	-1	640.74182	-12			
1	0	1	f	1	1	2	f	38	-1	640.81252	-26			
0	0	0	e	0	1	1	e	38	-1	640.93640	i	-7		
1	0	1	f	1	1	0	f	37	-1	641.14037	-289*			
2	0	2	f	2	1	1	He	32	-1	641.15191	-8			
0	2	0	e	0	3	1	e	33	-1	641.32409	5			
1	0	1	e	1	1	0	e	34	-1	641.34362	i	1		
1	1	2	e	1	2	1	He	26	-1	641.48107	-14			
0	1	1	f	0	2	2	f	37	-1	641.56366	0			
0	0	0	e	0	1	1	e	37	-1	642.12878	-1			
1	0	1	e	1	1	0	e	33	-1	642.66223	-10			
2	0	2	e	2	1	1	He	30	-1	642.86065	-8			
0	1	1	e	0	2	0	e	34	-1	643.00775	-11			
1	1	0	f	1	2	1	If	35	-1	643.01556	-73			
1	1	0	e	1	2	1	He	32	-1	643.06897	-2			
1	0	1	f	1	1	2	f	37	-1	643.19189	12			
0	0	0	e	0	1	1	e	37	-1	643.22607	i	0		
2	0	2	f	2	1	1	He	31	-1	643.24444	-34			
1	0	1	e	1	1	0	e	33	-1	643.49097	i	15		
1	0	1	f	1	1	0	f	36	-1	643.51861	-2			
0	2	0	e	0	3	1	e	32	-1	643.67157	-29			
0	1	1	e	0	2	0	e	34	-1	643.89252	i	7		
0	1	1	f	0	2	2	f	36	-1	643.92682	-9			
1	1	2	e	1	2	1	He	25	-1	644.07855	39			
0	2	2	e	0	3	1	e	27	-1	644.11816	-9			
1	1	0	f	1	2	1	If	29	-1	644.44336	22			
0	0	0	e	0	1	1	e	36	-1	644.47199	7			
1	0	1	e	1	1	0	e	32	-1	644.85999	-12			
2	0	2	e	2	1	1	He	29	-1	645.06427	10			
0	1	1	e	0	2	0	e	33	-1	645.27039	-11			
2	0	2	f	2	1	1	He	30	-1	645.33698	1			
1	1	0	e	1	2	1	He	31	-1	645.44879	7			
0	0	0	e	0	1	1	e	36	-1	645.51654	i	6		
1	0	1	f	1	1	2	f	36	-1	645.57154	14			
1	1	2	f	1	2	1	If	33	-1	645.60273	-9			
1	0	1	e	1	1	0	e	32	-1	645.63513	i	7		
0	2	2	f	0	3	1	f	30	-1	645.71546	-32			
1	0	1	f	1	1	0	f	35	-1	645.89386	-3			
0	2	0	e	0	3	1	e	31	-1	646.02381	5			
0	1	1	e	0	2	0	e	33	-1	646.10022	i	8		
0	1	1	f	0	2	2	f	35	-1	646.29090	9			
1	1	2	e	1	2	1	He	24	-1	646.65650	-9			
0	0	0	e	0	1	1	e	35	-1	646.81611	15			
1	0	1	e	1	1	0	e	31	-1	647.05481	-10			
2	0	2	e	2	1	1	He	28	-1	647.26868	13			
2	0	2	f	2	1	1	He	29	-1	647.42908	-27			
0	1	1	e	0	2	0	e	32	-1	647.52967	-10			
1	1	0	f	1	2	1	If	33	-1	647.66614	5			
0	2	2	f	0	3	1	f	29	-1	647.75995	-29			
1	0	1	e	1	1	0	e	31	-1	647.77662	i	2		
0	0	0	e	0	1	1	e	35	-1	647.80768	i	0		
1	1	0	e	1	2	1	He	30	-1	647.83277	-13			
1	1	2	f	1	2	1	If	32	-1	647.92628	86			
1	0	1	f	1	1	2	f	35	-1	647.95167	10			
1	0	1	f	1	1	0	f	34	-1	648.26905	1			
0	1	1	e	0	2	0	e	32	-1	648.30451	i	2		
0	2	0	e	0	3	1	e	30	-1	648.37983	-7			
1	1	0	f	1	2	1	If	27	-1	648.48591	7			
0	1	1	f	0	2	2	f	34	-1	648.65543	9			
0	0	0	e	0	1	1	e	34	-1	649.16096	9			
1	1	2	e	1	2	1	He	23	-1	649.21736	5			
1	0	1	e	1	1	0	e	30	-1	649.24686	-18			
0	2	2	e	0	3	1	e	25	-1	649.42610	-26			
2	0	2	f	2	1	1	He	27	-1	649.47431	1			
2	0	2	f	2	1	1	He	28	-1	649.52259	-12			
0	1	1	e	0	2	0	e	31	-1	649.78553	-7			
0	2	2	f	0	3	1	f	28	-1	649.80598	5			
1	0	1	e	1	1	0	e	30	-1	649.91584	i	10		
0	0	0	e	0	1	1	e	34	-1	650.09962	i	0		
1	1	0	e	1	2	1	He	29	-1	650.22145	4			
1	1	2	f	1	2	1	If	31	-1	650.24983	-8			
1	0	1	f	1	1	2	f	34	-1	650.33235	13			
0	1	1	e	0	2	0	e	31	-1	650.50538	i	-8		
0	2	0	e	0	3	1	e	29	-1	650.74031	-9			
0	1	1	f	0	2	2	f	33	-1	651.02052	6			
1	0	1	e	1	1	0	e	29	-1	651.43684	0			
0	0	0	e	0	1	1	e	33	-1	651.50667	6			

lower level										upper level																
ν_4	ν_5	ℓ	ν_4	ν_5	ℓ	J	ΔJ	ν_{obs}	O-C	ν_4	ν_5	ℓ	ν_4	ν_5	ℓ	J	ΔJ	ν_{obs}	O-C							
1	1	2	f	1	2	1	If	30	-1	652.57606			0	0	0	e	0	1	1	e	30	-1	658.54855		2	
1	1	0	e	1	2	1	He	28	-1	652.61415			1	1	2	f	1	2	1	If	21	-1	658.63052	-744*		
0	1	1	e	0	2	0	e	30	-1	652.70296	i		1	1	0	f	1	2	1	If	22	-1	658.71694		-13	
1	0	1	f	1	1	2	f	33	-1	652.71339			0	1	1	e	0	2	0	e	27	-1	658.77456		-9	
1	0	1	f	1	1	0	f	32	-1	653.01894			0	2	2	e	0	3	3	e	30	-1	658.79739		-5	
1	0	1	e	1	1	2	e	37	-1	653.07851			0	1	1	f	0	2	2	f	30	-1	658.91555	i	4	
0	2	0	e	0	3	1	e	28	-1	653.10536			1	1	2	e	1	2	3	e	31	-1	658.96279		-3	
0	1	1	f	0	2	2	f	32	-1	653.38612			0	0	0	e	0	1	1	e	30	-1	659.27462	i	40	
1	0	1	e	1	1	0	e	28	-1	653.62477			0	1	1	e	0	2	0	e	27	-1	659.27462	i	-194*	
2	0	2	f	2	1	1	If	26	-1	653.71541			1	1	2	e	1	2	1	He	19	-1	659.30001		-13	
1	0	1	f	1	1	0	f	32	-1	653.82320	i		1	1	2	e	1	2	1	He	28	-1	659.31552		-8	
0	0	0	e	0	1	1	e	32	-1	653.85323			1	1	0	f	1	2	1	If	28	-1	659.33163		7	
2	0	2	e	2	1	1	He	25	-1	653.89156			2	0	0	e	2	1	1	He	29	-1	659.37527		-32	
0	2	2	f	0	3	1	f	26	-1	653.90627			1	1	2	f	1	2	1	If	27	-1	659.56600		3	
1	0	1	e	1	1	0	e	28	-1	654.18849	i		2	0	2	f	2	1	3	f	33	-1	659.69662		-849*	
0	1	1	e	0	2	0	e	29	-1	654.28682			0	2	2	e	0	3	1	e	21	-1	659.79910		-93	
1	1	2	e	1	2	1	He	21	-1	654.28700			1	1	0	e	1	2	1	He	25	-1	659.81430		1	
2	0	0	e	2	1	1	He	31	-1	654.35207			1	0	1	f	1	1	2	f	30	-1	659.85812		-3	
0	2	2	e	0	3	1	e	23	-1	654.65126			2	0	2	f	2	1	1	If	23	-1	660.03213		-2	
1	1	0	f	1	2	1	If	30	-1	654.65901			1	0	1	f	1	1	0	f	29	-1	660.14285		2	
0	0	0	e	0	1	1	e	32	-1	654.68569	i		1	0	1	e	1	1	0	e	25	-1	660.18173		6	
1	1	2	e	1	2	1	He	30	-1	654.82009			0	2	0	e	0	3	1	e	25	-1	660.22702		-12	
1	0	1	e	1	1	2	e	36	-1	654.83724			1	0	1	e	1	1	2	e	33	-1	660.25924		5	
0	1	1	e	0	2	2	e	35	-1	654.86879			0	1	1	e	0	2	2	e	32	-1	660.31082		-2	
0	1	1	e	0	2	0	e	29	-1	654.89754	i		0	1	1	f	0	2	2	f	29	-1	660.48599		0	
1	1	2	f	1	2	1	If	29	-1	654.90487			2	0	2	e	2	1	1	He	22	-1	660.53903		-12	
1	1	0	e	1	2	1	He	27	-1	655.01058			1	0	1	e	1	1	0	e	25	-1	660.58999	i	-2	
1	0	1	f	1	1	2	f	32	-1	655.09468			1	0	1	f	1	1	2	f	30	-1	660.70627	i	15	
1	0	1	f	1	1	0	f	31	-1	655.39373			1	1	2	f	1	2	3	f	31	-1	660.73721		-14	
0	2	0	e	0	3	1	e	27	-1	655.47469			1	1	0	f	1	2	1	If	21	-1	660.79086		27	
0	1	1	f	0	2	2	f	31	-1	655.75228			1	0	1	f	1	1	0	f	29	-1	660.79096	i	567*	
1	0	1	e	1	1	0	e	27	-1	655.81112			0	0	0	e	0	1	1	e	29	-1	660.89731		3	
1	0	1	f	1	1	2	f	32	-1	656.05043	i		0	1	1	e	0	2	0	e	26	-1	661.01394		2	
2	0	2	e	2	1	1	He	24	-1	656.10390			0	2	2	e	0	3	3	e	29	-1	661.17062		0	
1	0	1	f	1	1	0	f	31	-1	656.14406	i		0	1	1	f	0	2	2	f	29	-1	661.22812	i	-15	
0	0	0	e	0	1	1	e	31	-1	656.20052			4	1	1	e	1	2	3	e	30	-1	661.31796		-9	
1	0	1	e	1	1	0	e	27	-1	656.32277	i		3	0	1	e	0	2	0	e	26	-1	661.46231	i	43	
0	2	2	e	0	3	3	e	31	-1	656.42080			0	0	0	e	0	1	1	e	29	-1	661.56936	i	-4	
1	1	2	f	1	2	3	f	33	-1	656.50771			25	1	1	0	f	1	2	1	If	27	-1	661.67087		-1
0	1	1	e	0	2	0	e	28	-1	656.53213			-24	1	1	2	e	1	2	1	He	18	-1	661.78531		7
1	1	2	e	1	2	3	e	32	-1	656.60323			-18	2	0	0	e	2	1	1	He	28	-1	661.88272		-32
1	0	1	e	1	1	2	e	35	-1	656.62026			-8	1	1	2	f	1	2	1	If	26	-1	661.89914		-16
1	1	0	f	1	2	1	If	23	-1	656.65322			-30	1	0	1	e	1	1	2	e	32	-1	662.11465		-1
0	1	1	e	0	2	2	e	34	-1	656.66030			48	2	0	2	f	2	1	1	If	22	-1	662.14798		-4
0	2	2	f	0	3	3	f	32	-1	656.72750			4	0	1	1	e	0	2	2	e	31	-1	662.16959		-124*
1	1	2	e	1	2	1	He	20	-1	656.80166			-3	0	2	2	f	0	3	1	f	22	-1	662.16959		83
2	0	0	e	2	1	1	He	30	-1	656.85201			-9	1	1	0	e	1	2	1	He	24	-1	662.22092		14
0	0	0	e	0	1	1	e	31	-1	656.97964	i		3	1	0	1	f	1	1	2	f	29	-1	662.24008		-4
1	1	0	f	1	2	1	If	29	-1	656.99441			24	0	2	2	e	0	3	1	e	20	-1	662.34647		-26
1	1	2	e	1	2	1	He	29	-1	657.06985			34	1	0	1	e	1	1	0	e	24	-1	662.36685		-2
0	1	1	e	0	2	0	e	28	-1	657.08840	i		-7	1	0	1	f	1	1	0	f	28	-1	662.51700		-16
1	1	2	f	1	2	1	If	28	-1	657.23470			38	0	2	0	e	0	3	1	e	24	-1	662.60965		-18
0	2	2	e	0	3	1	e	22	-1	657.23470			-70	1	0	1	e	1	1	0	e	24	-1	662.72403	i	2
1	1	0	e	1	2	1	He	26	-1	657.41079			1	2	0	2	e	2	1	1	He	21	-1	662.76279		-10
1	0	1	f	1	1	2	f	31	-1	657.47634			4	0	1	1	f	0	2	2	f	28	-1	662.85343		-1
1	0	1	f	1	1	0	f	30	-1	657.76830			-5	1	1	2	f	1	2	3	f	30	-1	662.87650		-111*
0	2	0	e	0	3	1	e	26	-1	657.84860			-15	0	2	2	f	0	3	3	f	29	-1	663.02335		-112*
0	2	2	f	2	1	1	If	24	-1	657.92196			1	1	0	1	f	1	1	2	f	29	-1	663.03403	i	4
1	0	1	e	1	1	0	e	26	-1	657.99679			17	1	0	1	f	1	1	0	e	28	-1	663.10538	i	7
0	2	2	f	0	3	1	f	24	-1	658.02425			24	0	0	0	e	0	1	1	e	28	-1	663.24704		-34
0	1	1	f	0	2	2	f	30	-1	658.11892			0	0	1	1	f	0	2	2	f	28	-1	663.54080	i	-51
2	0	2	e	2	1																					

lower level										upper level									
v_4	v_5	ℓ	v_4	v_5	ℓ	J	ΔJ	ν_{obs}	σ	v_4	v_5	ℓ	v_4	v_5	ℓ	J	ΔJ	ν_{obs}	σ
1	0	1e	1	1	2e	31	-1	663.99381	-3	1	1	0f	1	2	1If	24	-1	668.69963	14
1	1	0f	1	2	1If	26	-1	664.01206	2	1	1	2f	1	2	1If	23	-1	668.90898	13
0	1	1e	0	2	2e	30	-1	664.05399	14	1	0	1e	1	1	0e	21	-1	668.92979	12
1	1	2f	1	2	1If	25	-1	664.23392	-33	1	1	2f	1	2	1If	16	-1	669.13548	-135*
0	2	2f	0	3	1f	21	-1	664.25400	73	1	0	1e	1	1	0e	21	-1	669.13548	i 100
1	1	2e	1	2	1If	17	-1	664.25840	53	1	1	2e	1	2	1If	15	-1	669.16917	4
2	0	2f	2	1	1If	21	-1	664.27024	-3	1	1	0f	1	2	1If	17	-1	669.19542	-2
2	0	0e	2	1	1e	27	-1	664.38675	0	2	0	0e	2	1	1e	25	-1	669.38005	-13
1	0	1e	1	1	0e	23	-1	664.55289	4	1	0	1f	1	1	2f	26	-1	669.38640	28
1	0	1f	1	1	2f	28	-1	664.62198	-17	1	1	0e	1	2	1If	21	-1	669.45414	-3
1	1	0e	1	2	1If	23	-1	664.62998	12	2	0	2e	2	1	1If	18	-1	669.46624	27
1	0	1e	1	1	0e	23	-1	664.85910	i 9	0	2	2f	0	3	3f	26	-1	669.48893	-4
0	2	2e	0	3	1f	19	-1	664.87607	-26	1	0	1f	1	1	0f	25	-1	669.63908	-5
1	0	1f	1	1	0f	27	-1	664.89133	0	1	0	1e	1	1	2e	28	-1	669.77031	0
1	1	2f	1	2	1If	18	-1	664.90116	10	0	2	0e	0	3	1e	21	-1	669.78142	-22
1	1	0f	1	2	1If	19	-1	664.97001	14	2	0	2f	2	1	3f	28	-1	669.80882	-45
2	0	2e	2	1	1If	20	-1	664.99161	9	0	1	1e	0	2	2e	27	-1	669.84056	13
0	2	0e	0	3	1e	23	-1	664.99717	51	0	2	2e	0	3	1e	17	-1	669.88768	-22
1	1	2f	1	2	3f	29	-1	665.03342	2	0	1	1e	0	2	0e	22	-1	669.94755	7
0	2	2f	0	3	3f	28	-1	665.16233	4	0	1	1f	0	2	2f	25	-1	669.95762	-11
0	1	1f	0	2	2f	27	-1	665.22123	-1	1	0	1f	1	1	2f	26	-1	670.01683	i -11
1	0	1f	1	1	2f	28	-1	665.36185	i 6	1	0	1f	1	1	0f	25	-1	670.06407	i -16
1	0	1f	1	1	0f	27	-1	665.42533	i 0	0	1	1e	0	2	0e	22	-1	670.18254	i -3
0	1	1e	0	2	0e	24	-1	665.48466	8	0	1	1e	0	2	2e	27	-1	670.21702	i -34
0	0	0e	0	1	1e	27	-1	665.59678	4	1	0	1e	1	1	2e	28	-1	670.26237	i -8
2	0	2f	2	1	3f	30	-1	665.70096	23	0	0	0e	0	1	1e	25	-1	670.29863	5
0	1	1e	0	2	0e	24	-1	665.82542	i -8	0	1	1f	0	2	2f	25	-1	670.48186	i 14
0	1	1f	0	2	2f	27	-1	665.85557	i 98	1	1	2e	1	2	1If	23	-1	670.51207	-3
1	0	1e	1	1	2e	30	-1	665.89744	102*	0	2	2f	0	3	1f	18	-1	670.56474	29
0	2	2e	0	3	3e	27	-1	665.90629	48	0	2	2e	0	3	3e	25	-1	670.62529	-23
0	1	1e	0	2	2e	29	-1	665.96000	13	2	0	2f	2	1	1If	18	-1	670.68199	-2
1	1	2e	1	2	3e	28	-1	666.01627	-11	1	1	2e	1	2	3e	26	-1	670.69939	-19
1	1	2e	1	2	1If	25	-1	666.03837	0	2	0	0e	2	1	1If	16	-1	670.69939	283*
0	0	0e	0	1	1e	27	-1	666.16123	i -17	0	0	0e	0	1	1e	25	-1	670.75529	i -3
0	2	2f	0	3	1f	20	-1	666.34708	15	1	1	0f	1	2	1If	23	-1	671.04558	1
1	1	0f	1	2	1If	25	-1	666.35496	1	1	0	1e	1	1	0e	20	-1	671.12193	12
2	0	2f	2	1	1If	20	-1	666.39957	-3	1	1	2f	1	2	1If	22	-1	671.24834	-4
1	0	1e	1	1	2e	30	-1	666.45017	i -12	1	1	2f	1	2	1If	15	-1	671.27495	80
1	1	2f	1	2	1If	24	-1	666.57084	5	1	0	1e	1	1	0e	20	-1	671.27495	i -120*
1	1	2e	1	2	1If	16	-1	666.71891	3	1	1	0f	1	2	1If	16	-1	671.32658	-11
1	0	1e	1	1	0e	22	-1	666.74033	10	1	1	2f	1	2	3f	26	-1	671.58466	-9
2	0	0e	2	1	1e	26	-1	666.88596	-7	1	1	2e	1	2	1If	14	-1	671.60942	0
1	0	1e	1	1	0e	22	-1	666.99540	i -23	0	2	2f	0	3	3f	25	-1	671.67552	-4
1	0	1f	1	1	2f	27	-1	667.00401	-16	2	0	2e	2	1	1If	17	-1	671.71294	-18
1	1	2f	1	2	1If	17	-1	667.01267	7	1	0	1e	1	1	2e	27	-1	671.74071	-1
1	1	0e	1	2	1If	22	-1	667.04124	11	1	0	1f	1	1	2f	25	-1	671.76781	-13
1	1	0f	1	2	1If	18	-1	667.07749	85	0	1	1e	0	2	2e	26	-1	671.81474	15
1	1	2f	1	2	3f	28	-1	667.20377	2	2	0	0e	2	1	1e	24	-1	671.86846	-5
2	0	2e	2	1	1If	19	-1	667.22514	-52	1	1	0e	1	2	1If	20	-1	671.86858	6
1	0	1f	1	1	0f	26	-1	667.26530	-1	2	0	2f	2	1	3f	27	-1	671.89464	-13
0	2	2f	0	3	3f	27	-1	667.31620	-131*	1	0	1f	1	1	0f	24	-1	672.01274	2
0	2	0e	0	3	1e	22	-1	667.38767	30	0	1	1e	0	2	2e	26	-1	672.15984	i -2
0	1	1f	0	2	2f	26	-1	667.58927	-8	0	1	1e	0	2	0e	21	-1	672.17754	22
1	0	1f	1	1	2f	27	-1	667.68937	i -9	0	2	0e	0	3	1e	20	-1	672.17760	-151*
0	1	1e	0	2	0e	23	-1	667.71678	2	1	0	1e	1	1	2e	27	-1	672.19994	i -3
2	0	2f	2	1	3f	29	-1	667.74473	39	0	1	1f	0	2	2f	24	-1	672.32616	-19
1	0	1f	1	1	0f	26	-1	667.74473	i -20	1	0	1f	1	1	2f	25	-1	672.34423	i 6
1	0	1e	1	1	2e	29	-1	667.82200	-5	0	1	1e	0	2	0e	21	-1	672.35985	i -9
0	1	1e	0	2	2e	28	-1	667.88859	-19	0	2	2e	0	3	1e	16	-1	672.37157	-21
0	0	0e	0	1	1e	26	-1	667.94737	-1	1	0	1f	1	1	0f	24	-1	672.38317	i -5
0	1	1e	0	2	0e	23	-1	668.00444	i -17	0	0	0e	0	1	1e	24	-1	672.65032	2
0	1	1f	0	2	2f	26	-1	668.16801	i -6	0	2	2f	0	3	1f	17	-1	672.68975	20
0	2	2e	0	3	3e	26	-1	668.26792	31	1	1	2e	1	2	1If	22	-1	672.74822	6
1	1	2e	1	2	1If	24	-1	668.27555	-14	0	1	1f	0	2	2f	24	-1	672.79546	i -3
1	1	2e	1	2	3e	27	-1	668.35960	-17	2	0	2f	2	1	1If	17	-1	672.83629	-1
0	0	0e	0	1	1e	26	-1	668.45817	i 4	0	2	2e	0	3	3e	24	-1	672.97930	-27
2	0	2f	2	1	1If	19	-1	668.53654	-10	1	1	2e	1	2	3e	25	-1	673.03557	-51

lower level									upper level																
v_4	v_5	ℓ		v_4	v_5	ℓ	$J \Delta J$	ν_{obs}	o-c	v_4	v_5	ℓ		v_4	v_5	ℓ	$J \Delta J$	ν_{obs}	o-c						
0	0	0	e	0	1	1	e	24	-1	673.05284	i	-7	0	2	2	e	0	3	3	e	22	-1	677.67639	-20	
2	0	0	e	2	1	1	He	15	-1	673.24584		9	1	1	2	e	1	2	3	e	23	-1	677.70031	2	
1	0	1	e	1	1	0	e	19	-1	673.31743		12	1	0	1	e	1	1	0	e	17	-1	677.72119	19	
1	1	0	f	1	2	1	If	22	-1	673.39312		2	1	1	2	f	1	2	1	If	12	-1	677.76800	-6	
1	1	0	f	1	2	1	If	15	-1	673.47081		6	1	0	1	e	1	1	2	e	24	-1	677.77926	-20	
1	1	2	f	1	2	1	If	21	-1	673.58934		0	1	1	0	f	1	2	1	If	13	-1	677.79876	15	
1	0	1	e	1	1	2	e	26	-1	673.73281		5	0	1	1	e	0	2	2	e	23	-1	677.86932	64*	
1	1	2	f	1	2	3	f	25	-1	673.79332		0	0	1	1	e	0	2	2	e	23	-1	678.11120	i	31
0	1	1	e	0	2	2	e	25	-1	673.81109		14	1	0	1	e	1	1	2	e	24	-1	678.13202	i	-3
0	2	2	f	0	3	3	f	24	-1	673.87615		-8	1	1	2	f	1	2	3	f	23	-1	678.24377	2	
2	0	2	e	2	1	1	He	16	-1	673.96770		-14	2	0	2	f	2	1	3	f	24	-1	678.26672	-18	
2	0	2	f	2	1	3	f	26	-1	674.00011		5	1	1	2	f	1	2	1	If	19	-1	678.27539	7	
1	1	2	e	1	2	1	He	13	-1	674.04052		-1	2	0	0	e	2	1	1	He	13	-1	678.28930	12	
0	1	1	e	0	2	2	e	25	-1	674.12316	i	-6	0	2	2	f	0	3	3	f	22	-1	678.31579	-10	
1	0	1	f	1	1	2	f	24	-1	674.14965		8	2	0	2	e	2	1	1	He	14	-1	678.50293	2	
1	0	1	e	1	1	2	e	26	-1	674.15838	i	59	2	0	2	e	2	1	3	e	25	-1	678.68756	9	
1	1	0	e	1	2	1	He	19	-1	674.28374		0	0	1	1	e	0	2	0	e	18	-1	678.86804	13	
2	0	0	e	2	1	1	Ie	23	-1	674.35033		-1	1	1	2	e	1	2	1	He	11	-1	678.87958	148*	
1	0	1	f	1	1	0	f	23	-1	674.38610		0	0	1	1	e	0	2	0	e	18	-1	678.89465	i	0
0	1	1	e	0	2	0	e	20	-1	674.40703		14	1	0	1	f	1	1	2	f	22	-1	678.91192	-8	
0	1	1	e	0	2	0	e	20	-1	674.53728	i	-3	1	1	0	e	1	2	1	He	17	-1	679.11493	0	
0	2	0	e	0	3	1	e	19	-1	674.57909		-25	1	0	1	f	1	1	0	f	21	-1	679.13232	20	
1	0	1	f	1	1	2	f	24	-1	674.67101	i	-7	0	2	2	f	0	3	1	f	14	-1	679.13678	26	
0	1	1	f	0	2	2	f	23	-1	674.69512		-3	2	0	0	e	2	1	1	Ie	21	-1	679.29205	3	
1	0	1	f	1	1	0	f	23	-1	674.70305	i	117*	1	0	1	f	1	1	2	f	22	-1	679.32367	i	-8
0	2	2	f	0	3	1	f	16	-1	674.82653		25	1	0	1	f	1	1	0	f	21	-1	679.33850	i	35
0	2	2	e	0	3	1	e	15	-1	674.84215		-19	2	0	2	f	2	1	1	If	14	-1	679.35785	6	
1	1	2	e	1	2	1	Ie	21	-1	674.98504		55	0	2	0	e	0	3	1	e	17	-1	679.38592	-26	
2	0	2	f	2	1	1	If	16	-1	674.99938		-64	0	1	1	f	0	2	2	f	21	-1	679.43317	-1	
0	0	0	e	0	1	1	e	23	-1	675.00256		5	1	1	2	e	1	2	1	Ie	19	-1	679.46033	-7	
0	1	1	f	0	2	2	f	23	-1	675.10931	i	-4	0	0	0	e	0	1	1	e	21	-1	679.70825	-1	
0	2	2	e	0	3	3	e	23	-1	675.32934		-53	0	1	1	f	0	2	2	f	21	-1	679.73663	i	-55
0	2	0	e	0	1	1	e	23	-1	675.35094	i	5	0	2	2	e	0	3	1	e	13	-1	679.74707	-31	
1	1	2	e	1	2	3	e	24	-1	675.36956		2	1	0	1	e	1	1	2	e	23	-1	679.83289	1	
1	0	1	e	1	1	0	e	18	-1	675.51696		13	1	0	1	e	1	1	0	e	16	-1	679.88330	i	2
1	0	1	e	1	1	0	e	18	-1	675.57049	i	4	1	0	1	e	1	1	0	e	16	-1	679.93011	-34	
1	1	2	f	1	2	1	If	13	-1	675.58953		7	0	1	1	e	0	2	2	e	22	-1	679.93011	105*	
1	1	0	f	1	2	1	If	14	-1	675.62798		2	0	0	0	e	0	1	1	e	21	-1	679.94781	i	-2
1	0	1	e	1	1	2	e	25	-1	675.74535		-53	1	1	2	f	1	2	1	If	11	-1	679.96094	-4	
2	0	0	e	2	1	1	He	14	-1	675.77660		-6	1	1	0	f	1	2	1	If	12	-1	679.98303	5	
0	1	1	e	0	2	2	e	24	-1	675.82928		15	0	2	2	e	0	3	3	e	21	-1	680.01984	-13	
1	1	2	f	1	2	1	If	20	-1	675.93163		-4	1	1	2	e	1	2	3	e	22	-1	680.02869	0	
1	1	2	f	1	2	3	f	24	-1	676.01318		-11	0	1	1	e	0	2	2	e	22	-1	680.13416	i	-4
0	2	2	f	0	3	3	f	23	-1	676.08990		-9	1	0	1	e	1	1	2	e	23	-1	680.14679	i	-52
0	1	1	e	0	2	2	e	24	-1	676.10723	i	17	2	0	2	f	2	1	3	f	23	-1	680.42694	6	
2	0	2	f	2	1	3	f	25	-1	676.12444		8	1	1	0	f	1	2	1	If	19	-1	680.44348	5	
1	0	1	e	1	1	2	e	25	-1	676.13561	i	27	1	1	2	f	1	2	3	f	22	-1	680.48401	-2	
2	0	2	e	2	1	1	He	15	-1	676.23077		-9	0	2	2	f	0	3	3	f	21	-1	680.55328	19	
1	1	2	e	1	2	1	He	12	-1	676.46319		0	2	0	2	e	2	1	3	e	24	-1	680.59888	-25	
1	0	1	f	1	1	2	f	23	-1	676.53082		-12	1	1	2	f	1	2	1	If	18	-1	680.62042	18	
0	1	1	e	0	2	0	e	19	-1	676.63696		11	2	0	0	e	2	1	1	He	12	-1	680.78436	107	
1	1	0	e	1	2	1	He	18	-1	676.69940		4	2	0	2	e	2	1	1	He	13	-1	680.78479	10	
0	1	1	e	0	2	0	e	19	-1	676.71533	i	1	0	1	1	e	0	2	0	e	17	-1	681.07587	i	-11
1	0	1	f	1	1	0	f	22	-1	676.75933		9	0	1	1	e	0	2	0	e	17	-1	681.10089	8	
2	0	2	e	2	1	3	e	26	-1	676.80004		10	1	1	2	e	1	2	1	He	10	-1	681.28589	-1	
2	0	0	e	2	1	1	Ie	22	-1	676.82507		4	1	0	1	f	1	1	2	f	21	-1	681.29254	-15	
0	2	2	f	0	3	1	f	15	-1	676.97528		15	0	2	2	f	0	3	1	f	13	-1	681.31092	7	
0	2	0	e	0	3	1	e	18	-1	676.98187		1	1	0	1	f	1	1	0	f	20	-1	681.50476	4	
1	0	1	f	1	1	2	f	23	-1	676.99761	i	-2	1	1	0	e	1	2	1	He	16	-1	681.52991	-9	
1	0	1	f	1	1	0	f	22	-1	677.02020	i	0	2	0	2	f	2	1	1	If	13	-1	681.55268	-3	
0	1	1	f	0	2	2	f	22	-1	677.06420		9	2	0	2	f	2	1	1	If	21	-1	681.55274	-166	
2	0	2	f	2	1	1	If	15	-1	677.17364		-6	1	0	1	f	1	1	2	f	21	-1	681.64936	i	-3
1	1	2	e	1	2	1	Ie	20	-1	677.22168		-1	1	0	1	f	1	1	0	f	20	-1	681.65589	i	18
0	2	2	e	0	3	1	e	14	-1	677.30035		-20	1	1	2	e	1	2	1	Ie	18	-1	681.70130	7	
0	0	0	e	0	1	1	e	22	-1	677.35519		1	2	0	0	e	2	1	1	Ie	20	-1	681.75092	11	
0	1	1	f	0	2	2	f	22	-1	677.423551															

lower level										upper level										lower level										upper level									
v_4	v_5	ℓ	v_4	v_5	ℓ	J	ΔJ	ν_{obs}	O-C	v_4	v_5	ℓ	v_4	v_5	ℓ	J	ΔJ	ν_{obs}	O-C	v_4	v_5	ℓ	v_4	v_5	ℓ	J	ΔJ	ν_{obs}	O-C										
1	0	1e	1	1	2e	22	-1	681.90540	-7	0	1	1e	0	2	2e	19	-1	686.31465 i	-20	0	1	1e	1	2	1He	14	-1	686.35694	7										
0	1	1e	0	2	2e	21	-1	682.00965	-4	1	1	0e	1	2	1He	14	-1	686.39686 i	-9	1	0	1e	1	1	0e	13	-1	686.39686 i	-9										
0	1	1f	0	2	2f	20	-1	682.04944 i	-164*	2	0	2e	2	1	3e	21	-1	686.48091	5	1	0	1e	1	1	0e	13	-1	686.48091	5										
1	0	1e	1	1	0e	15	-1	682.04944 i	138*	0	1	1f	0	2	2f	18	-1	686.54066	-3	0	0	0e	0	1	1e	20	-1	686.54066	-3										
1	0	1e	1	1	0e	15	-1	682.14588	11	1	0	1e	1	1	0e	13	-1	686.59633	6	1	0	1e	1	1	0e	13	-1	686.59633	6										
1	1	2f	1	2	1He	10	-1	682.16846	1	0	2	0e	0	3	1e	14	-1	686.60477	31	1	0	1e	1	1	2e	9	-1	686.62025	-37										
1	0	1e	1	1	2e	22	-1	682.17652 i	-397*	1	1	2f	1	2	1He	8	-1	686.62800	20	0	1	1e	1	1	0e	13	-1	686.64241	24										
0	1	1e	0	2	2e	21	-1	682.17652 i	13	2	0	0e	2	1	1e	18	-1	686.64241	24	0	0	0e	0	1	1e	18	-1	686.67866 i	1										
0	0	0e	0	1	1e	20	-1	682.24665 i	-9	0	0	0e	0	1	1e	18	-1	686.76960	-5	1	1	2e	1	2	3e	19	-1	686.84523 i	0										
1	1	2e	1	2	3e	21	-1	682.35498	-12	0	0	0e	0	1	1e	18	-1	686.84523 i	0	0	0	0e	0	1	1e	18	-1	686.84523 i	0										
0	2	2e	0	3	3e	20	-1	682.36078	49	1	1	2e	1	2	3e	19	-1	687.00367	12	2	0	2e	2	1	3e	23	-1	687.00367	12										
2	0	2f	2	1	3e	22	-1	682.53455	-60	0	2	2e	0	3	3e	18	-1	687.00367	12	0	0	0e	0	1	1e	18	-1	687.00367	12										
2	0	2f	2	1	3f	22	-1	682.60358	8	0	2	2e	0	3	3e	18	-1	687.02870	18	1	1	2f	1	2	3f	19	-1	687.02870	18										
1	1	2f	1	2	3f	21	-1	682.73353	3	0	2	2e	0	3	3e	18	-1	687.03431	110*	1	1	0f	1	2	1He	18	-1	687.03431	110*										
1	1	0f	1	2	1He	18	-1	682.79615	32	0	2	2e	0	3	3e	18	-1	687.03431	110*	0	2	2f	0	3	3f	19	-1	687.25776	0										
0	2	2f	0	3	3f	20	-1	682.80164	89	0	2	2f	0	3	3f	18	-1	687.32460	1	1	1	2f	1	2	1He	17	-1	687.32460	1										
1	1	2f	1	2	1He	17	-1	682.96637	-1	1	1	0f	1	2	1He	16	-1	687.50331	-23	2	0	2e	2	1	1He	12	-1	687.50331	-23										
2	0	0e	2	1	1He	12	-1	683.07679	-2	0	1	1e	0	2	0e	14	-1	687.50331	-23	2	0	0e	2	1	1He	11	-1	683.25965	56										
2	0	0e	2	1	1He	11	-1	683.25965	56	0	1	1e	0	2	0e	14	-1	687.50331	-23	0	1	1e	0	2	0e	16	-1	683.25965 i	-33										
0	1	1e	0	2	0e	16	-1	683.33637	9	2	0	2e	2	1	1He	10	-1	687.69337	-6	0	1	1e	0	2	0e	16	-1	683.33637	9										
0	1	1e	0	2	0e	16	-1	683.33637	9	0	1	1e	0	2	0e	14	-1	687.69337	-6	0	2	2f	0	3	1f	12	-1	683.49836	-10										
0	2	2f	0	3	1f	12	-1	683.49836	-10	1	0	1f	1	1	2f	20	-1	683.67280	-14	1	0	1f	1	1	2f	20	-1	683.67280	-14										
1	0	1f	1	1	2f	20	-1	683.67280	-14	1	1	2e	1	2	1He	9	-1	683.68708	-8	1	1	2e	1	2	1He	9	-1	683.68708	-8										
1	1	2e	1	2	1He	9	-1	683.68708	-8	2	0	2f	2	1	1He	12	-1	683.75892	7	2	0	2f	2	1	1He	12	-1	683.75892	7										
2	0	2f	2	1	1He	12	-1	683.75892	7	1	1	0e	1	2	1He	24	-1	683.83997	10	1	1	0e	1	2	1He	24	-1	683.83997	10										
1	1	0e	1	2	1He	24	-1	683.83997	10	1	0	1f	1	1	0f	19	-1	683.87708	6	1	0	1f	1	1	0f	19	-1	683.87708	6										
1	0	1f	1	1	0f	19	-1	683.87708	6	2	0	2f	2	1	1He	20	-1	683.90852	-12	2	0	2f	2	1	1He	20	-1	683.90852	-12										
2	0	2f	2	1	1He	20	-1	683.90852	-12	1	1	0e	1	2	1He	15	-1	683.94501	89	1	1	0e	1	2	1He	15	-1	683.94501	89										
1	1	0e	1	2	1He	15	-1	683.94501	89	1	0	1f	1	1	0f	19	-1	683.97346 i	59	1	0	1f	1	1	0f	19	-1	683.97346 i	59										
1	0	1f	1	1	0f	19	-1	683.97346 i	59	1	0	1f	1	1	0f	19	-1	683.99634 i	2185*	1	0	1f	1	1	0f	19	-1	683.99634 i	2185*										
1	0	1f	1	1	2f	20	-1	683.99634 i	2185*	1	0	1e	1	1	2e	21	-1	683.99653	-4	1	0	1e	1	1	2e	21	-1	683.99653	-4										
1	0	1e	1	1	2e	21	-1	683.99653	-4	0	1	1e	0	2	2e	20	-1	684.10999	9	0	1	1e	0	2	2e	20	-1	684.10999	9										
0	1	1e	0	2	2e	20	-1	684.10999	9	0	1	1f	0	2	2f	19	-1	684.17145	-6	0	1	1f	0	2	2f	19	-1	684.17145	-6										
0	1	1f	0	2	2f	19	-1	684.17145	-6	1	0	1e	1	1	0e	14	-1	684.21906 i	-6	1	0	1e	1	1	0e	14	-1	684.21906 i	-6										
1	0	1e	1	1	0e	14	-1	684.21906 i	-6	1	0	1e	1	1	2e	21	-1	684.23072 i	-23	1	0	1e	1	1	2e	21	-1	684.23072 i	-23										
1	0	1e	1	1	2e	21	-1	684.23072 i	-23	0	1	1e	0	2	2e	20	-1	684.23743 i	60	0	1	1e	0	2	2e	20	-1	684.23743 i	60										
0	1	1e	0	2	2e	20	-1	684.23743 i	60	1	0	1e	1	1	0e	14	-1	684.36756	3	1	0	1e	1	1	0e	14	-1	684.36756	3										
1	1	2f	1	2	1He	9	-1	684.39106	40	1	1	0f	1	2	1He	8	-1	684.39106	40	1	1	0f	1	2	1He	8	-1	684.39106	40										
0	0	0e	0	1	1e	19	-1	684.41547	-6	1	1	2f	1	2	1He	7	-1	684.41547	-6	2	0	0e	0	1	1e	19	-1	684.41547	-6										
2	0	2e	2	1	3e	22	-1	684.49561	-8	0	1	1f	0	2	2f	17	-1	684.49561	-8	0	1	1f	0	2	2f	17	-1	684.49561	-8										
0	0	0e	0	1	1e	19	-1	684.54591 i	3	0	1	1f	0	2	2f	17	-1	684.54591 i	3	0	1	1f	0	2	2f	17	-1	684.54591 i	3										
0	2	2e	0	3	1e	11	-1	684.61036	-14	2	0	2e	2	1	1He	17	-1	689.07417	4	1	1	2e	1	2	3e	19	-1	689.12404	1										
1	1	2e	1	2	3e	20	-1	684.68018	26	0	0	0e	0	1	1e	17	-1	689.12404	1	0	0	0e	0	1	1e	17	-1	689.12404	1										
0	2	2e	0	3	3e	19	-1	684.69776	-15	0	0	0e	0	1	1e	17	-1	689.14473 i	-2	0	2	2e	2	1	3f	19	-1	689.14473 i	-2										
2	0	2f	2	1	3f	21	-1	684.79609	13	2	0	2f	2	1	3f	19	-1	689.22450	-66	1	1	2f	1	2	3f	18	-1	689.22450	-66										
1	1	2f	1	2	3f	20	-1	684.99171	12	0	2	2e	0	3	3e	17	-1	689.32637	0	1	1	2f	1	2	3f	18	-1	689.32637	0										
0	2	2f	0	3	3f	19	-1	685.05811	-4	0	2	2e	0	3	3e	17	-1	689.36653	-10	1	1	0f	1	2	1He	17	-1												

lower level										upper level										lower level										upper level									
v_4	v_5	ℓ	v_4	v_5	ℓ	J	ΔJ	ν_{obs}	O-C	v_4	v_5	ℓ	v_4	v_5	ℓ	J	ΔJ	ν_{obs}	O-C	v_4	v_5	ℓ	v_4	v_5	ℓ	J	ΔJ	ν_{obs}	O-C										
1	0	1	f	1	1	0	f	16	-1	690.92165	i	-4	1	0	1	e	1	1	2	e	16	-1	694.72000	i	1	1	0	1	e	1	1	2	e	16	-1	694.78848	i	9	
2	0	2	f	2	1	1	If	17	-1	690.96077		27	2	0	2	e	2	1	1	Ie	16	-1	694.79592		2799*	2	0	2	e	2	1	1	Ie	16	-1	694.79592		2799*	
1	0	1	f	1	1	0	f	16	-1	690.99190		0	0	1	1	e	0	2	2	e	15	-1	694.87899		-2	1	0	1	e	1	1	0	e	9	-1	694.96878		-5	
1	1	0	f	1	2	1	If	7	-1	691.11782		-9	1	0	1	e	1	1	0	e	9	-1	695.18454	i	-10	1	1	2	f	1	2	1	Ie	12	-1	695.22476		3	
1	1	2	f	1	2	1	If	6	-1	691.14736		-2	1	1	2	e	1	2	1	Ie	12	-1	695.22476		3	2	0	0	e	2	1	1	Ie	6	-1	695.38864		-4	
0	1	1	f	0	2	2	f	16	-1	691.27883		-3	1	0	1	f	1	1	0	f	14	-1	695.55178	i	0	1	0	1	f	1	1	2	f	15	-1	695.56576		-11	
0	2	0	e	0	3	1	e	12	-1	691.41543		-14	1	0	1	e	1	1	0	e	9	-1	695.59048		-5	1	1	2	e	1	2	1	Ie	4	-1	695.61227		-10	
0	0	0	e	0	1	1	e	16	-1	691.44436	i	-4	2	0	2	f	2	1	1	If	15	-1	695.65438		-16	1	1	0	f	1	2	1	If	5	-1	695.67410		-3	
2	0	2	f	2	1	3	f	18	-1	691.46059		33	1	1	0	f	1	2	1	If	4	-1	695.72940		135*	1	1	2	f	1	2	1	If	4	-1	695.72940		135*	
0	0	0	e	0	1	1	e	16	-1	691.47860		-6	1	1	2	e	1	2	1	Ie	10	-1	695.98611		-16	0	1	1	e	0	2	2	f	14	-1	696.01651		-3	
2	0	0	e	2	1	1	Ie	16	-1	691.49630		-35	1	0	1	f	1	1	0	f	14	-1	695.98611		-16	2	0	2	e	0	3	3	e	16	-1	695.96744		13	
1	1	2	e	1	2	3	e	17	-1	691.64895		14	1	0	1	f	1	1	0	f	14	-1	695.98611		-16	0	1	1	e	0	2	2	f	14	-1	696.01651		-3	
0	2	2	e	0	3	3	e	16	-1	691.69857		-5	2	0	2	f	2	1	3	f	16	-1	695.98611		-16	0	0	0	e	0	1	1	e	14	-1	696.04397	i	-1	
1	1	2	f	1	2	3	f	17	-1	691.81246		9	1	1	0	e	1	2	1	Ie	10	-1	695.98611		-16	0	1	1	f	0	2	2	f	14	-1	696.04397	i	-1	
0	2	2	e	0	3	1	e	8	-1	691.84121		-14	0	1	1	f	0	2	2	f	14	-1	696.04397	i	-1	0	0	0	e	0	1	1	e	14	-1	696.18844		-2	
0	1	1	e	0	2	0	e	12	-1	691.88210		0	0	0	0	e	0	1	1	e	14	-1	696.18844		-2	0	2	0	e	0	3	1	e	10	-1	696.22061		-24	
1	1	0	f	1	2	1	If	14	-1	692.21456		-8	1	1	2	e	1	2	3	e	15	-1	696.22061		-24	1	1	0	e	1	2	1	Ie	10	-1	696.22061		-24	
1	1	0	e	1	2	1	Ie	20	-1	692.28872		20	1	1	2	e	1	2	3	e	15	-1	696.22061		-24	0	1	1	e	0	2	0	e	12	-1	692.31844		1	
0	1	1	e	0	2	0	e	12	-1	692.31844		1	2	0	0	e	2	1	1	Ie	14	-1	696.22061		-24	2	0	2	e	2	1	1	Ie	8	-1	692.35207		-8	
2	0	2	e	2	1	1	Ie	8	-1	692.35207		-8	0	2	2	e	0	3	3	e	14	-1	696.22061		-24	1	1	2	f	1	2	1	If	13	-1	692.36208		-3	
1	1	2	f	1	2	1	If	13	-1	692.36208		-3	1	1	2	f	1	2	3	f	15	-1	696.22061		-24	0	2	2	f	0	3	1	f	8	-1	692.38729		-2	
1	0	1	e	1	1	2	e	17	-1	692.53225		8	0	2	2	f	0	3	3	f	14	-1	696.22061		-24	0	2	2	f	0	3	3	f	14	-1	696.22061		-24	
2	0	2	e	2	1	3	e	18	-1	692.58382		-26	1	1	0	e	1	2	1	Ie	18	-1	696.22061		-24	1	1	0	e	1	2	3	e	15	-1	696.22061		-24	
1	0	1	e	1	1	2	e	17	-1	692.59347	i	75	0	2	2	e	0	3	1	e	6	-1	696.22061		-24	0	2	2	e	0	3	1	e	6	-1	696.22061		-24	
0	1	1	e	0	2	2	e	16	-1	692.64724	i	0	2	0	2	e	2	1	3	e	16	-1	696.22061		-24	0	2	2	e	0	3	1	e	6	-1	696.22061		-24	
0	1	1	e	0	2	2	e	16	-1	692.69204		3	0	1	1	e	0	2	0	e	10	-1	696.22061		-24	0	1	1	e	0	2	0	e	10	-1	696.22061		-24	
2	0	2	f	2	1	1	If	8	-1	692.70205		-1	1	0	1	e	1	1	2	e	15	-1	696.22061		-24	1	0	1	e	1	1	2	e	15	-1	696.22061		-24	
1	1	2	e	1	2	1	Ie	13	-1	692.95870		7	1	0	1	e	1	1	2	e	15	-1	696.22061		-24	2	0	2	e	2	1	1	Ie	15	-1	696.22061		-24	
1	0	1	e	1	1	0	e	10	-1	692.97563	i	14	0	2	2	e	2	1	1	Ie	15	-1	696.22061		-24	0	2	2	e	2	1	1	Ie	15	-1	696.22061		-24	
2	0	0	e	2	1	1	Ie	7	-1	692.99160		-7	0	2	2	f	0	3	1	f	6	-1	696.22061		-24	0	2	2	f	0	3	1	f	6	-1	696.22061		-24	
1	0	1	f	1	1	2	f	16	-1	693.18850		-8	1	1	0	f	1	2	1	If	12	-1	696.22061		-24	1	1	0	f	1	2	1	If	12	-1	696.22061		-24	
1	1	2	e	1	2	1	Ie	5	-1	693.23684		0	0	1	1	e	0	2	2	e	14	-1	696.22061		-24	0	1	1	e	0	2	2	e	14	-1	696.22061		-24	
1	0	1	f	1	1	0	f	15	-1	693.23684	i	-16	2	0	2	e	2	1	1	Ie	6	-1	696.22061		-24	1	1	2	f	1	2	1	If	11	-1	696.22061		-24	
1	0	1	f	1	1	2	f	16	-1	693.26839	i	-8	1	1	2	f	1	2	1	If	11	-1	696.22061		-24	0	1	1	e	0	2	2	e	14	-1	696.22061		-24	
2	0	2	f	2	1	1	If	16	-1	693.30795		-14	0	1	1	e	0	2	2	e	14	-1	696.22061		-24	1	0	1	f	1	2	1	If	11	-1	696.22061		-24	
1	0	1	e	1	1	0	e	10	-1	693.32925		4	2	0	2	f	2	1	1	If	6	-1	696.22061		-24	1	0	1	e	1	1	0	e	8	-1	696.22061		-24	
1	0	1	f	1	1	0	f	15	-1	693.36282		6	1	0	1	e	1	1	0	e	8	-1	696.22061		-24	1	1	2	e	1	2	1	Ie	11	-1	696.22061		-24	
1	1	0	f	1	2	1	If	6	-1	693.38845		-15	1	1	2	e	1	2	1	Ie	11	-1	696.22061		-24	2	0	2	f	2	1	1	If	14	-1	696.22061		-24	
1	1	2	f	1	2	1	If	5	-1	693.42995		-9	2	0	0	e	2	1	1	Ie	5	-1	696.22061		-24	1	0	1	e	1	1	0	e	8	-1	696.22061		-24	
1	1	0	e	1	2	1	Ie	11	-1	693.58340		51	1	0	1	e	1	1	0	e	8	-1	696.22061		-24	1	0	1	e	1	1	0	e	8	-1	696.22061		-24	
0	1	1	f	0	2	2	f	15	-1	693.61880	i	-5	1	0	1	f	1	1	0	f	13	-1	696.22061		-24	1	0	1	f	1	1</								

lower level						upper level						J	ΔJ	ν_{obs}	O-C
ν_4	ν_5	ℓ	ν_4	ν_5	ℓ	ν_4	ν_5	ℓ	ν_4	ν_5	ℓ				
0	2	2e	0	3	1e	5	-1	699.01291	71						
2	0	2e	2	1	1e	14	-1	699.04782	876*						
1	0	1e	1	1	2e	14	-1	699.09488	4						
0	1	1e	0	2	0e	9	-1	699.11600	-11						
0	2	2f	0	3	1f	5	-1	699.20468	-24						
1	1	0f	1	2	1f	11	-1	699.28623	-9						
0	1	1e	0	2	2e	13	-1	699.29740	7						
2	0	2e	2	1	1e	5	-1	699.40097	-7						
1	1	2f	1	2	1f	10	-1	699.41934	5						
2	0	2f	2	1	1f	5	-1	699.54099	12						
1	0	1e	1	1	0e	7	-1	699.62876	i -59						
1	1	2e	1	2	1e	10	-1	699.77567	9						
1	0	1e	1	1	0e	7	-1	700.14072	-8						
2	0	0e	2	1	1e	4	-1	700.15372	107						
1	0	1f	1	1	0f	12	-1	700.17954	i -12						
1	0	1f	1	1	2f	13	-1	700.23069	i -8						
1	0	1f	1	1	2f	13	-1	700.31815	0						
2	0	2f	2	1	1f	13	-1	700.34470	-43						
1	1	2e	1	2	1e	2	-1	700.35111	3						
1	1	2f	1	2	1f	2	-1	700.37021	-9						
1	0	1f	1	1	0f	12	-1	700.47269	-1						
0	2	2f	2	1	3f	14	-1	700.51804	7						
0	1	1f	0	2	2f	12	-1	700.55674	i -5						
0	0	0e	0	1	1e	12	-1	700.64365	i -1						
0	1	1f	0	2	2f	12	-1	700.75333	-8						
1	1	0e	1	2	1e	8	-1	700.78312	0						
0	0	0e	0	1	1e	12	-1	700.89878	2						
1	1	2e	1	2	3e	13	-1	700.94242	14						
1	1	2f	1	2	3f	13	-1	700.99949	35						
0	2	0e	0	3	1e	8	-1	701.01658	11						
0	2	2e	0	3	3e	12	-1	701.02231	63						
2	0	2e	2	1	3e	14	-1	701.06016	-7						
0	2	2f	0	3	3f	12	-1	701.08103	-14						
2	0	0e	2	1	1e	12	-1	701.09000	-5						
1	0	1e	1	1	2e	13	-1	701.18058	i -12						
0	1	1e	0	2	2e	12	-1	701.29307	i 11						
1	0	1e	1	1	2e	13	-1	701.30973	3						
0	1	1e	0	2	0e	8	-1	701.39664	-8						
0	2	2f	0	3	1f	4	-1	701.50669	-23						
0	1	1e	0	2	2e	12	-1	701.52720	2						
1	1	0f	1	2	1f	10	-1	701.64445	-18						
2	0	2e	2	1	1e	4	-1	701.76005	-6						
1	1	2f	1	2	1f	9	-1	701.77335	-6						
2	0	2f	2	1	1f	4	-1	701.84629	-12						
1	0	1e	1	1	0e	6	-1	701.86521	i -21						
1	1	2e	1	2	1e	9	-1	702.06120	2						
1	0	1e	1	1	0e	6	-1	702.43021	-10						
1	0	1f	1	1	0f	11	-1	702.49265	i -5						
1	1	2f	1	2	1f	31	0	702.50010	771*						
2	0	0e	2	1	1e	3	-1	702.52354	-3						
1	0	1f	1	1	2f	12	-1	702.54960	i -12						
1	1	2f	1	2	1f	30	0	702.69260	456*						
1	0	1f	1	1	2f	12	-1	702.69279	-25						
2	0	2f	2	1	3f	13	-1	702.80753	-10						
1	0	1f	1	1	0f	11	-1	702.84165	-4						
0	1	1f	0	2	2f	11	-1	702.86881	i 6						
1	1	2f	1	2	1f	29	0	702.87553	179*						
0	0	0e	0	1	1e	11	-1	702.94346	i 1						
1	1	2f	1	2	1f	28	0	703.04972	2						
0	1	1f	0	2	2f	11	-1	703.12138	-5						
0	1	1e	0	2	0e	7	-1	703.14213	i 68						
1	1	0e	1	2	1e	7	-1	703.17594	-8						
1	1	0e	1	2	1e	15	-1	703.21684	-83						
1	1	2f	1	2	1f	27	0	703.21684	66						
0	0	0e	0	1	1e	11	-1	703.25401	0						
1	1	2f	1	2	3f	12	-1	703.31022	29						
0	2	2e	0	3	3e	11	-1	703.35368	14						
1	0	1e	1	1	2e	12	-1	703.35996	i 119*						
1	1	2f	1	2	1f	26	0	703.37327	-17						
2	0	2e	2	1	1e	12	-1	703.38468	111						
0	2	2f	0	3	3f	11	-1	703.39591	-1						
0	2	0e	0	3	1e	7	-1	703.40958	-2						
2	0	0e	2	1	1e	11	-1	703.46421	-10						
0	1	1e	0	2	2e	11	-1	703.48600	i 3						
1	1	2f	1	2	1f	25	0	703.52183	11						
1	0	1e	1	1	2e	12	-1	703.53739	14						
1	1	2f	1	2	1f	24	0	703.66166	36						
0	1	1e	0	2	0e	7	-1	703.68540	-5						
0	1	1e	0	2	2e	11	-1	703.76976	-12						
1	1	2f	1	2	1f	23	0	703.79228	-18						
0	2	2f	0	3	1f	3	-1	703.82456	78						
1	1	2f	1	2	1f	22	0	703.91539	-7						
1	1	0f	1	2	1f	9	-1	704.00334	-2						
0	1	1f	1	2	1f	21	0	704.03086	28						
1	0	1e	1	1	0e	5	-1	704.11088	i -2						
2	0	2e	2	1	1e	3	-1	704.12095	5						
1	1	2f	1	2	1f	8	-1	704.12846	14						
1	1	2f	1	2	1f	20	0	704.13822	11						
2	0	2f	2	1	1f	3	-1	704.16551	45						
1	1	2f	1	2	1f	19	0	704.23832	0						
1	1	2f	1	2	1f	18	0	704.33146	-4						
1	1	2e	1	2	1e	8	-1	704.35405	-3						
0	1	1f	1	2	1f	17	0	704.41789	-2						
2	1	2f	1	2	1f	16	0	704.49772	-10						
1	1	0f	1	2	1f	31	0	704.55363	-1449*						
1	1	2f	1	2	1f	15	0	704.57151	0						
1	1	2f	1	2	1f	14	0	704.63920	-1						
1	1	2f	1	2	1f	13	0	704.70121	2						
1	0	1e	1	1	0e	5	-1	704.72960	-12						
1	1	2f	1	2	1f	12	0	704.75792	25						
1	0	1f	1	1	0f	10	-1	704.80717	i 207*						
1	1	2f	1	2	1f	10	0	704.85508	4						
1	0	1f	1	1	2f	11	-1	704.86766	i -1						
2	0	0e	2	1	1e	2	-1	704.88890	-43						
1	1	2f	1	2	1f	9	0	704.89647	12						
1	1	2f	1	2	1f	8	0	704.93303	6						
2	1	2f	1	2	1f	7	0	704.96501	-8						
1	1	2f	1	2	1f	6	0	704.99278	-8						
1	1	2f	1	2	1f	5	0	705.01640	-1						
1	1	2f	1	2	1f	4	0	705.03526	-59						
2	0	2f	2	1	1f	11	-1	705.03526	64						
1	1	2f	1	2	1f	3	0	705.05143	15						
1	0	1f	1	1	2f	11	-1	705.06700	-3						
2	0	2f	2	1	3f	12	-1	705.10569	-11						
1	1	2e	1	2	1f	2	0	705.12028	-1						
1	1	2e	1	2	1f	3	0	705.16612	-3						
0	1	1f	0	2	2f	10	-1	705.18046	i 16						
1	0	1f	1	1	0f	10	-1	705.21013	-1						
1	1	2e	1	2	1f	4	0	705.22703	2						
0	0	0e	0	1	1e										

lower level										upper level														lower level										upper level													
v_4	v_5	ℓ	v_4	v_5	ℓ	J	ΔJ	ν_{obs}	O-C	v_4	v_5	ℓ	v_4	v_5	ℓ	J	ΔJ	ν_{obs}	O-C	v_4	v_5	ℓ	v_4	v_5	ℓ	J	ΔJ	ν_{obs}	O-C																		
0	2	2 f	0	3	3 f	10	-1	705.71599	2	1	1	2 e	1	2	1 If	21	0	708.05809	-9	2	0	0 e	2	1	1 If	9	-1	708.18566	-81																		
1	1	2 e	1	2	1 If	9	0	705.74522	7	2	0	2 f	2	1	1 If	35	0	708.25725	1318*	3	2	0	2 f	2	1	1 If	35	0	708.25725	46																	
1	0	1 e	1	1	2 e	11	-1	705.77702	-24	0	2	2 f	0	3	1 e	30	0	708.25725	-9	-19	1	1	2 e	1	2	1 If	22	0	708.28246	-158*																	
0	2	0 e	0	3	1 e	6	-1	705.79887	-73	0	1	1 e	0	2	2 e	9	-1	708.28972	98*	5	0	1	1 e	0	2	2 e	9	-1	708.28972	50																	
2	0	0 e	2	1	1 e	10	-1	705.82933	-9	0	2	2 f	0	3	1 e	29	0	708.45586	-106*	-9	1	1	2 e	1	2	1 If	23	0	708.50505	-22																	
1	1	2 e	1	2	1 If	10	0	705.88847	4	1	1	2 e	1	2	1 If	23	0	708.63048 i	79	-73	0	1	1 e	0	2	2 e	5	-1	708.64501	9																	
1	1	0 f	1	2	1 If	23	0	705.92845	-36	0	2	2 f	0	3	1 e	28	0	708.72197	-24	-9	0	2	2 f	0	3	1 e	29	0	708.82329	-1																	
0	1	1 e	0	2	0 e	6	-1	705.98259	-18	1	0	1 e	1	1	0 e	3	-1	708.96294	1	-102*	1	1	2 e	1	2	1 If	23	0	708.99346	-10																	
0	1	1 e	0	2	2 e	10	-1	706.02483	2	1	0	2 f	1	2	1 If	26	0	709.15026	-774*	2	2	0	2 f	0	3	1 e	27	0	709.27385	481*																	
1	1	2 e	1	2	1 If	11	0	706.04350	-19	1	1	2 e	1	2	1 If	26	0	709.30529	-64	-20	0	2	2 f	0	3	1 e	24	0	709.35875	-13																	
1	1	0 f	1	2	1 If	22	0	706.06053	5	1	1	2 e	1	2	1 If	26	0	709.42785 i	0	-19	1	1	2 e	1	2	1 If	26	0	709.44957	67																	
0	2	2 e	0	3	1 e	2	-1	706.13621	-14	2	0	2 f	2	1	1 If	30	0	709.50042 i	-2	3	2	0	2 f	2	1	1 If	30	0	709.54540	-1718*																	
0	2	2 f	0	3	1 f	2	-1	706.15532	-6	2	0	2 f	2	1	1 If	28	0	709.60167	222*	-20	0	2	2 f	0	3	1 e	23	0	709.62249	-3																	
1	1	0 f	1	2	1 If	21	0	706.18303	-18	1	1	2 e	1	2	1 If	28	0	709.64751	14	-14	1	0	1 f	1	1	2 f	9	-1	709.68352	-3																	
1	1	2 e	1	2	1 If	12	0	706.20988	2	2	0	2 f	2	1	1 If	28	0	709.70104	44	-18	2	0	0 e	2	1	1 If	2	0	709.71001	56																	
1	1	0 f	1	2	1 If	20	0	706.29838	-122*	1	1	2 e	1	2	1 If	28	0	709.72515	-15	2	2	0	2 f	2	1	1 If	9	-1	709.72539	62																	
1	1	0 f	1	2	1 If	8	-1	706.36369	5	1	0	1 f	1	1	0 f	8	-1	709.72991	15	-102*	1	0	1 f	1	1	0 f	8	-1	709.74962	81																	
1	1	2 e	1	2	1 If	13	0	706.38658	3	2	0	2 f	2	1	1 If	27	0	709.78472	40	3	1	0	1 f	1	1	2 f	9	-1	709.81218	6																	
1	1	0 f	1	2	1 If	19	0	706.40654	11	2	0	0 e	2	1	1 If	5	0	709.80169 i	-35	-11	2	0	2 f	2	1	1 If	27	0	709.84234 i	12																	
1	1	2 f	1	2	1 If	7	-1	706.48295	-102*	0	1	1 f	0	2	2 f	8	-1	709.84313	-214*	2	2	0	2 f	2	1	1 If	26	0	709.88799	-7																	
2	0	2 f	2	1	1 If	2	-1	706.49693	3	0	1	1 f	0	2	2 f	8	-1	709.89794 i	-21	6	2	0	2 e	2	1	3 e	10	-1	709.90569	145																	
1	1	2 e	1	2	1 If	14	0	706.57274	2	2	0	2 f	2	1	1 If	27	0	709.91106	62	6	2	0	2 e	2	1	3 e	10	-1	709.93810	-7																	
1	1	0 f	1	2	1 If	17	0	706.60069	-6	1	0	1 f	1	1	2 f	9	-1	709.94524	-3	-14	1	0	1 f	1	1	0 f	8	-1	709.96026 i	38																	
1	1	2 e	1	2	1 If	7	-1	706.65446	-14	1	0	1 f	1	1	2 f	9	-1	709.97759	-10	2	1	0	1 f	1	1	2 f	9	-1	709.97759	-10																	
1	1	0 f	1	2	1 If	16	0	706.68761	-7	2	0	0 e	2	1	1 If	26	0	710.01769	11	-14	1	1	2 e	1	2	1 If	26	0	710.04088	48																	
1	1	2 e	1	2	1 If	15	0	706.76768	15	2	0	0 e	2	1	1 If	26	0	710.04552	-128	-59	2	0	0 e	2	1	1 If	26	0	710.04552	48																	
1	1	0 f	1	2	1 If	14	0	706.84166	-59	2	0	0 e	2	1	1 If	26	0	710.11077	-9	23	2	0	2 f	2	1	1 If	26	0	710.13189 i	65																	
1	1	0 f	1	2	1 If	13	0	706.91057	23	2	0	0 e	2	1	1 If	26	0	710.13744	-30	-7	2	0	2 f	2	1	1 If	26	0	710.13744	167*																	
1	1	2 e	1	2	1 If	16	0	706.97020	23	2	0	0 e	2	1	1 If	26	0	710.17382	-9	-42	2	0	2 f	2	1	1 If	26	0	710.17382	-9																	
1	1	0 f	1	2	1 If	11	0	707.02879	-42	0	1	0 f	1	2	1 If	0	1	710.22332	-9	-15	0	1	1 f	0	2	2 f	8	-1	710.22332	-9																	
1	0	1 e	1	1	0 e	4	-1	707.03905	-15	2	0	2 f	2	1	1 If	26	0	710.22338	-70	2	2	0	2 f	2	1	1 If	26	0	710.22338	20																	
1	1	0 f	1	2	1 If	10	0	707.08037	-2	2	0	2 f	2	1	1 If	26	0	710.24828	-66	-2	2	0	2 f	2	1	1 If	26	0	710.24828	-66																	
1	0	1 f	1	1	0 f	9	-1	707.11675 i	-8	0	1	1 f	0	2	2 f	8	-1	710.25847	38	6	2	0	2 f	2	1	1 If	26	0	710.25847	38																	
1	1	0 f	1	2	1 If	9	0	707.12627	-3	0	1	1 f	0	2	2 f	8	-1	710.27148	-21	-3	2	0	2 f	2	1	1 If	26	0	710.27148	-21																	
1	1	0 f	1	2	1 If	8	0	707.16734	22	2	0	0 e	2	1	1 If	26	0	710.29082	-30	6	2	0	2 f	2	1	1 If	26	0	710.29082	-30																	
1	1	2 e	1	2	1 If	17	0	707.17906	6	0	1	1 f	0	2	2 f	8	-1	710.29149	275*	22	2	0	2 f	2	1	1 If	26	0	710.29149	275*																	
1	0	1 f	1	1	2 f	10	-1	707.18492 i	32	1	0	1 f	0	2	2 f	8	-1			32	1	0	1 f	0	2	2 f	8	-1																			
1	1	0 f	1	2	1 If	7	0	707.20299	-1	1	0	1 f	1	1	2 f	9	-1			-1	1	0	1 f	1	1	2 f	9	-1																			
1	1	0 f	1	2	1 If	6	0	707.23393	-16	0	2	2 f	0	3	1 e	20	0			-16	0	2	2 f	0	3	1 e	20	0																			
1	1	0 f	1	2	1 If	5	0	707.26042	-7	0	0	0 e	0	1	1 e	8	-1			-7	0	0	0 e	0	1	1 e	8	-1																			
1	1	0 f	1	2	1 If	3	0	707.29991	21	2	0	0 e	2	1	1 If	6	0			21	2	0	0 e	2	1	1 If	6	0																			
1	1	0 f	1	2	1 If	2	0	707.31334	69	2	0	2 f	2	1	1 If	26	0			69	2	0	2 f	2	1	1 If	26	0																			
1	1	0 f	1	2	1 If	1	0	707.32207	81	0	1	1 e	0	2	0 e	4	-1			81	0	1	1 e	0	2	0 e	4	-1																			
2	0	2 f	2	1	1 If	10	-1	707.37956	-11	2	0	2 e	2	1	3 e	10	-1			-11	2	0	2 e	2	1	3 e	10	-1																			
1	1	2 e	1	2	1 If	18	0	707.39403	50	2	0	0 e	2	1	1 If	7	0			50	2	0	0 e	2	1	1 If	7	0																			
2	0	2 f	2	1	3 f	11	-1	707.41148	-26	1	1	0 e	1	2	1 If	12	-1			-26	1	1	0 e	1	2	1 If	12	-1																			
1	0	1 f	1	1	2 f	10	-1	707.44011	4	0	2	2 f	0	3	1 e	19																															

lower level										upper level										J	ΔJ	ν_{obs}	O-C
ν_4	ν_5	ℓ	ν_4	ν_5	ℓ	ν_4	ν_5	ℓ	ν_4	ν_5	ℓ	ν_4	ν_5	ℓ	ν_4	ν_5	ℓ						
0	2	2 f	0	3	1 e	15	0	710.30706	145*	2	0	2 f	2	1	3 f	9	-1	712.04424	1				
0	0	0 e	0	1	1 e	8	-1	710.31968	2	2	0	2 f	2	1	1 If	8	-1	712.07159	-15				
1	1	0 e	1	2	1 Ife	4	-1	710.33048	73	2	0	2 e	2	1	1 If	10	0	712.08721	-15				
2	0	0 e	2	1	1 If	14	0	710.33947	-30	0	2	2 e	0	3	1 f	13	0	712.09997	13				
0	2	2 e	0	3	3 e	8	-1	710.35900	55	0	1	1 f	0	2	2 f	7	-1	712.11218 i	4				
0	2	2 f	0	3	3 f	8	-1	710.37072	-9	1	1	2 e	1	2	1 Ife	2	1	712.12975	-36				
0	2	2 f	0	3	1 e	14	0	710.38097	37	0	0	0 e	0	1	1 e	7	-1	712.14147 i	-1				
2	0	0 e	2	1	1 If	15	0	710.38720	90	2	0	2 e	2	1	3 e	9	-1	712.16784	-24				
2	0	0 e	2	1	1 If	29	0	710.40905	-35	0	1	1 e	0	2	0 e	3	-1	712.16784 i	15				
2	0	0 e	2	1	1 If	16	0	710.42852	29	1	0	1 f	1	1	2 f	8	-1	712.18316	3				
0	2	2 f	0	3	1 e	13	0	710.44781	-149*	1	1	0 e	1	2	1 Ife	11	-1	712.20013	-155*				
2	0	0 e	2	1	1 If	17	0	710.46508	-35	1	1	2 f	1	2	1 If	2	1	712.24584	62				
2	0	0 e	2	1	1 If	28	0	710.46508	320*	0	2	2 e	0	3	1 f	14	0	712.26965	21				
2	0	0 e	2	1	1 If	18	0	710.49761	-11	2	0	2 e	2	1	1 If	11	0	712.29449	0				
2	0	0 e	2	1	1 If	27	0	710.50396	56	1	0	1 f	1	1	0 f	7	-1	712.31182	-7				
0	2	2 f	0	3	1 e	12	0	710.51177	-19	0	1	1 e	0	2	2 e	7	-1	712.36682 i	8				
2	0	0 e	2	1	1 If	19	0	710.52428	-59	0	2	2 e	0	3	1 f	15	0	712.44525	17				
2	0	0 e	2	1	1 If	26	0	710.53448	-20	2	0	2 e	2	1	1 If	12	0	712.52709	21				
2	0	0 e	2	1	1 If	20	0	710.54674	20	1	0	1 e	1	1	2 e	8	-1	712.56469	3				
2	0	0 e	2	1	1 If	25	0	710.55669	21	0	1	1 f	0	2	2 f	7	-1	712.59002	11				
2	0	0 e	2	1	1 If	21	0	710.56371	137	1	1	2 f	1	2	3 f	8	-1	712.60229	98				
2	0	0 e	2	1	1 If	24	0	710.56847	-101	0	2	2 e	0	3	1 f	16	0	712.62634	80				
0	2	2 f	0	3	1 e	11	0	710.56847	-34	0	0	0 e	0	1	1 e	7	-1	712.67474	1				
0	1	1 e	0	2	2 e	8	-1	710.56890	4	0	2	2 e	0	3	3 e	7	-1	712.69757	-13				
2	0	0 e	2	1	1 If	22	0	710.57293	113	0	2	2 f	0	3	3 f	7	-1	712.70513	2				
2	0	0 e	2	1	1 If	23	0	710.57293	-144	1	1	0 e	1	2	1 Ife	3	-1	712.70538	3				
0	1	1 e	0	2	0 e	4	-1	710.60375	-14	0	2	2 e	0	3	1 f	17	0	712.80969	17				
2	0	2 f	2	1	1 Ife	19	0	710.61285	57	0	1	1 e	0	2	2 e	7	-1	712.85699	1				
0	2	2 f	0	3	1 e	10	0	710.62005	-12	2	0	0 e	2	1	1 Ife	7	-1	712.88079	3				
0	2	2 f	0	3	1 e	9	0	710.66582	-11	0	1	1 e	0	2	0 e	3	-1	712.92816	-15				
2	0	2 f	2	1	1 Ife	18	0	710.68481	1	0	2	0 e	0	3	1 e	3	-1	712.94274	-17				
0	2	2 f	0	3	1 e	8	0	710.70660	-4	0	2	2 e	0	3	1 f	18	0	712.99554	-16				
2	0	2 f	2	1	1 Ife	17	0	710.75042	-38	1	0	1 f	1	1	0 e	38	0	713.02331	-22				
0	2	2 f	0	3	1 e	6	0	710.77331	11	2	0	2 e	2	1	1 If	14	0	713.06591	-12				
2	0	2 f	2	1	1 Ife	16	0	710.81072	2	0	2	2 e	0	3	1 f	19	0	713.18310	41				
0	2	2 f	0	3	1 e	4	0	710.82091	-8	1	0	1 e	1	1	0 e	1	-1	713.18969 i	14				
2	0	2 f	2	1	1 Ife	15	0	710.86474	-12	1	0	1 f	1	1	0 e	37	0	713.31091	96*				
1	0	1 e	1	1	0 e	2	-1	710.90527 i	5	2	0	2 e	2	1	1 If	15	0	713.37054	-87				
2	0	2 f	2	1	1 Ife	14	0	710.91369	2	1	1	0 f	1	2	1 If	5	-1	713.44146	3				
2	0	2 f	2	1	1 Ife	12	0	710.99676	10	0	2	2 e	0	3	1 f	21	0	713.55413	66				
2	0	2 f	2	1	1 Ife	11	0	711.03191	41	1	0	1 f	1	1	0 e	36	0	713.58136	-2				
2	0	2 f	2	1	1 Ife	10	0	711.06231	-1	1	1	2 e	1	2	1 Ife	4	-1	713.60449	-10				
1	1	0 f	1	2	1 If	6	-1	711.08227	72	2	0	2 e	2	1	1 If	16	0	713.69928	-23				
2	0	2 f	2	1	1 Ife	9	0	711.08935	-6	1	0	1 f	1	1	0 e	32	0	713.71154 i	9				
2	0	2 f	2	1	1 Ife	8	0	711.11297	-5	0	2	2 e	0	3	1 f	22	0	713.73480	43				
2	0	2 f	2	1	1 Ife	7	0	711.13329	-10	1	0	1 f	1	1	0 e	35	0	713.83783	-1				
2	0	2 f	2	1	1 Ife	6	0	711.15063	-12	1	0	1 f	1	1	0 e	31	0	713.89795 i	7				
0	2	2 e	0	3	1 f	6	0	711.16637	-306*	0	2	2 e	0	3	1 f	23	0	713.91046	12				
2	0	2 f	2	1	1 Ife	4	0	711.17724	12	1	0	1 e	1	1	0 e	1	-1	714.02899	-16				
2	0	2 f	2	1	1 Ife	3	0	711.18652	9	2	0	2 e	2	1	1 If	17	0	714.04803	-134				
2	0	2 f	2	1	1 Ife	2	0	711.19396	64	1	0	1 f	1	1	0 f	6	-1	714.04821 i	53				
1	1	2 f	1	2	1 If	5	-1	711.19762	28	1	0	1 f	1	1	0 e	30	0	714.07255 i	175*				
2	0	2 e	2	1	1 If	2	0	711.23992	-2	1	0	1 f	1	1	0 e	34	0	714.07959	22				
2	0	2 e	2	1	1 If	3	0	711.28069	-19	0	2	2 e	0	3	1 f	24	0	714.07959	-35				
2	0	2 e	2	1	1 If	4	0	711.33678	-44	1	0	1 f	1	1	2 f	7	-1	714.12860 i	-10				
2	0	2 e	2	1	1 If	5	0	711.41033	-5	1	0	1 f	1	1	0 e	29	0	714.23022 i	-33				
0	2	2 e	0	3	1 f	9	0	711.50311	-77	0	2	2 e	0	3	1 f	25	0	714.24164	-6				
2	0	2 e	2	1	1 If	7	0	711.61401	1	1	0	1 f	1	1	0 e	33	0	714.30597	-11				
0	2	2 e	0	3	1 f	10	0	711.63853	4	2	0	0 e	2	1	1 Ife	1	1	714.31891	-4				
1	0	1 e	1	1	0 e	2	-1	711.68871	-14	2	0	2 f	2	1	3 f	8	-1	714.36950	-5				
1	0	1 f	1	1	0 f	7	-1	711.73815 i	0	1	0	1 f	1	1	0 e	28	0	714.37799 i	50				
2	0	2 e	2	1	1 If	8	0	711.74767	-28	0	2	2 e	0	3	1 f	26	0	714.39404	-18				
0	2	2 e	0	3	1 f	11	0	711.78338	7	1	0	1 e	1	1	2 e	7	-1	714.41205 i	-34				
1	0	1 f	1	1	2 f	8	-1	711.81512 i	-3	2	0	2 e	2	1	1 If	18	0	714.42059	58				
2	0	2 e	2	1	1 If	9	0	711.90539	1	2	0	2 f	2	1	1 If	7	-1	714.42059	136				
0	2	2 e	0	3	1 f	12	0	711.93755	12	0	1	1 f	0	2	2 f	6	-1	714.42059 i	-110*				
2	0	0 e	2	1	1 Ife	0	1	711.96606	23	0	0	0 e	0	1	1 e	6	-1	714.44055 i	4				

lower level					upper level					$J \Delta J$	ν_{obs}	σ
v_4	v_5	ℓ	v_4	v_5	ℓ							
2	0	2	e	2	1	3	e	8	-1	714.45013	-45	
1	1	0	e	1	2	1	Ie	10	-1	714.47516	-79	
1	1	2	e	1	2	1	IIe	3	1	714.47516	121*	
1	1	0	f	1	2	1	IIIf	2	1	714.49499	-9	
1	0	1	f	1	1	0	e	27	0	714.51153 i	-53	
1	0	1	f	1	1	0	e	32	0	714.51825	14	
0	2	2	e	0	3	1	f	27	0	714.53601	-5	
1	0	1	f	1	1	2	f	7	-1	714.55310	4	
2	0	2	e	2	1	1	Ie	7	-1	714.58423	-9	
0	1	1	e	0	2	2	e	6	-1	714.61175 i	2	
1	0	1	f	1	1	0	e	26	0	714.63464 i	-7	
1	1	2	f	1	2	1	IIIf	3	1	714.66485	-107*	
0	2	2	e	0	3	1	f	28	0	714.66485	-98	
1	0	1	f	1	1	0	f	6	-1	714.67779	-5	
1	0	1	f	1	1	0	e	31	0	714.71600	34	
1	0	1	f	1	1	0	e	25	0	714.74609 i	13	
0	2	2	e	0	3	1	f	29	0	714.78168	-50	
2	0	2	e	2	1	1	IIIf	19	0	714.81030	-15	
1	0	1	e	1	1	2	e	7	-1	714.84875	6	
0	2	2	e	0	3	1	f	30	0	714.88287	-91	
1	0	1	f	1	1	0	e	30	0	714.89917	19	
1	1	2	e	1	2	3	f	7	-1	714.93048	53	
1	1	2	f	1	2	3	f	7	-1	714.93628	116*	
1	0	1	f	1	1	0	e	23	0	714.93628 i	-18	
0	1	1	f	0	2	2	f	6	-1	714.95587	-5	
0	2	2	e	0	3	1	f	31	0	714.96875	-59	
1	0	1	f	1	1	0	e	22	0	715.01691 i	3	
0	0	0	e	0	1	1	e	6	-1	715.02966	0	
0	2	2	f	0	3	3	f	6	-1	715.04333	-37	
1	0	1	f	1	1	0	e	29	0	715.06866	28	
1	1	0	e	1	2	1	IIe	2	-1	715.07605	-13	
1	0	1	f	1	1	0	e	21	0	715.08807 i	-16	
1	0	1	f	1	1	0	e	20	0	715.15491 i	378*	
0	1	1	e	0	2	2	e	6	-1	715.15521	-1	
1	0	1	f	1	1	0	e	19	0	715.20642 i	19	
2	0	0	e	2	1	1	Ie	6	-1	715.22296	131	
1	0	1	f	1	1	0	e	18	0	715.25433 i	18	
0	1	1	e	0	2	0	e	2	-1	715.26202	-14	
1	0	1	f	1	1	0	e	17	0	715.29565 i	14	
0	2	0	e	0	3	1	e	2	-1	715.31378	-133*	
1	0	1	f	1	1	0	e	16	0	715.33105 i	12	
1	0	1	f	1	1	0	e	15	0	715.36121 i	20	
1	0	1	f	1	1	0	e	27	0	715.36670	-24	
1	0	1	f	1	1	0	e	14	0	715.38641 i	11	
1	0	1	f	1	1	0	e	13	0	715.40741 i	5	
1	0	1	f	1	1	0	e	12	0	715.42474 i	4	
1	0	1	f	1	1	0	e	11	0	715.43884 i	4	
1	0	1	f	1	1	0	e	10	0	715.45007 i	-6	
1	0	1	f	1	1	0	e	9	0	715.45923 i	13	
1	0	1	f	1	1	0	e	8	0	715.46655 i	47	
1	0	1	f	1	1	0	e	7	0	715.47253 i	111*	
1	0	1	f	1	1	0	e	26	0	715.49689	-9	
1	0	1	f	1	1	0	e	25	0	715.61499	13	
2	0	2	e	2	1	1	IIIf	21	0	715.64655	-24	
1	0	1	f	1	1	0	e	24	0	715.72119	5	
1	1	0	f	1	2	1	If	4	-1	715.80170	24	
1	0	1	f	1	1	0	e	23	0	715.81641	-1	
1	0	1	f	1	1	0	e	22	0	715.90137	4	
1	1	2	f	1	2	1	If	3	-1	715.91315	-2	
1	1	2	e	1	2	1	Ie	3	-1	715.93811	2	
1	0	1	f	1	1	0	e	21	0	715.97650	-1	
1	0	1	f	1	1	0	e	20	0	716.04266	3	
2	0	2	e	2	1	1	IIIf	22	0	716.09070	-5	
1	0	1	f	1	1	0	e	19	0	716.10040	4	
1	0	1	f	1	1	0	e	18	0	716.15045	6	
1	0	1	f	1	1	0	e	17	0	716.19342	3	
1	0	1	f	1	1	0	e	16	0	716.23004	3	
1	0	1	f	1	1	0	e	15	0	716.26093	3	
1	0	1	f	1	1	0	e	14	0	716.28668	-1	
1	0	1	f	1	1	0	e	13	0	716.30792	-5	
1	0	1	f	1	1	0	e	12	0	716.32526	-3	
1	0	1	f	1	1	0	e	11	0	716.33911	-10	
1	0	1	f	1	1	0	e	10	0	716.35022	2	
1	0	1	f	1	1	0	e	9	0	716.35889	17	
1	0	1	f	1	1	2	f	6	-1	716.44122 i	19	
2	0	2	e	2	1	1	IIIf	23	0	716.55054	-6	
2	1	0	e	2	1	1	IIe	6	-1	716.65320 i	3	
2	0	0	e	2	1	1	IIe	2	1	716.66883	9	
2	0	2	f	2	1	3	f	7	-1	716.70000	-18	
0	0	0	e	0	1	1	e	5	-1	716.73932 i	3	
2	0	2	e	2	1	3	e	7	-1	716.74994	8	
0	1	1	f	0	2	2	f	5	-1	716.74994 i	1930*	
1	1	0	e	1	2	1	Ie	9	-1	716.75879	-167*	
2	0	2	f	2	1	1	If	6	-1	716.76795	1	
1	1	2	e	1	2	1	IIe	4	1	716.81330	-7	
0	1	1	e	0	2	2	e	5	-1	716.86597 i	10	
2	0	2	e	2	1	1	Ie	6	-1	716.87854	11	
1	1	0	f	1	2	1	IIIf	3	1	716.91364	-69	
1	0	1	f	1	1	2	f	6	-1	716.92149	-36	
2	0	2	e	2	1	1	IIIf	24	0	717.02533	-4	
1	0	1	f	1	1	0	f	5	-1	717.04303	-4	
1	1	2	f	1	2	1	IIIf	4	1	717.10089	-73	
1	0	1	e	1	1	2	e	6	-1	717.14295	7	
0	1	1	f	0	2	2	f	5	-1	717.32135	-6	
0	0	0	e	0	1	1	e	5	-1	717.38440	-1	
0	1	1	e	0	2	2	e	5	-1	717.46326	6	
2	0	2	e	2	1	1	IIIf	25	0	717.51410	0	
0	1	1	f	0	2	0	e	29	0	717.55402 i	-97	
2	0	0	e	2	1	1	Ie	5	-1	717.56104	-9	
0	1	1	e	0	2	0	e	1	-1	717.60541	-11	
0	1	1	f	0	2	0	e	28	0	717.72541 i	-23	
0	1	1	f	0	2	0	e	32	0	717.76294	31	
0	1	1	f	0	2	0	e	27	0	717.88355 i	16	
0	2	2	e	0	3	1	e	2	1	717.92206	-39	
0	1	1	f	0	2	0	e	31	0	717.98560	26	
2	0	2	e	2	1	1	IIIf	26	0	718.01667	85	
0	1	1	f	0	2	0	e	26	0	718.02869 i	24	
0	2	2	f	0	3	1	f	2	1	718.03730	38	
0	1	1	f	0	2	0	e	25	0	718.16150 i	45	
1	1	0	f	1	2	1	If	3	-1	718.16156	-3	
0	1	1	f	0	2	0	e	30	0	718.19440	-1	
2	0	2	e	2	1	1	IIe	2	1	718.26117	-14	
1	1	2	f	1	2	1	If	2	-1	718.27149	-42	
1	1	2	e	1	2	1	Ie	2	-1	718.28046	22	
0	1	1	f	0	2	0	e	24	0	718.28046 i	-107*	
2	0	2	f	2	1	1	IIIf	2	1	718.35328	-3	
0	1	1	f	0	2	0	e	29	0	718.38984	1	
0	1	1	f	0	2	0	e	23	0	718.38990 i	-38	
0	1	1	f	0	2	0	e	22	0	718.48786 i	11	
2	0	2	e	2	1	1	IIIf	27	0	718.52997	41	
0	1	1	f	0	2	0	e	21	0	718.57270 i	-176*	
0	1	1	f	0	2	0	e	20	0	718.65113 i	15	
1	0	1	f	1	1	0	f	4	-1	718.66437 i	8	
0	1	1	f	0	2	0	e	19	0	718.71796 i	2	
0	1	1	f	0	2	0	e	27	0	718.73993	4	
1	0	1	f	1	1	2	f	5	-1	718.75202 i	-9	
2	0	1	f	0	2	0	e	18	0	718.77661 i	61	
0	1	1	f	0	2	0	e	17	0	718.82593 i	10	
0	1	1	f	0	2	0	e	16	0	718.86817 i	1	
0	1	1	f	0	2	0	e	26	0	718.89472	-6	
0	1	1	f	0	2	0	e	15	0	718.90357 i	-11	
1	0	1	e	1	1	2	e	5	-1	718.90357 i	29	
0	1	1	f	0	2	0	e	14	0	718.93310 i	0	
0	1	1	f	0	2	0	e	13	0	718.95710 i	-3	

lower level										upper level										J	ΔJ	ν _{obs}	O-C		
v ₄	v ₅	ℓ	v ₄	v ₅	ℓ					v ₄	v ₅	ℓ													
0	1	1	f	0	2	0	e	12	0	718.97645	i	3	2	0	2	f	2	1	1	If	3	1	720.76386	32	
0	1	1	f	0	2	0	e	11	0	718.99183	i	19	0	2	0	e	0	3	1	f	10	0	720.83082	0	
0	1	1	f	0	2	0	e	10	0	719.00336	i	-1	1	1	2	e	1	2	1	If	35	0	720.86225	-5854*	
2	0	0	e	2	1	1	If	3	1	719.01343		-83	1	1	0	e	1	2	1	If	12	0	720.92329	-1	
0	1	1	f	0	2	0	e	9	0	719.01343	i	124*	1	0	1	f	1	1	0	f	3	-1	720.97126	i	-5
0	1	1	f	0	2	0	e	8	0	719.01856	i	-7	0	2	0	e	0	3	1	f	11	0	720.99214	14	
0	1	1	f	0	2	0	e	25	0	719.03650		-2	1	0	1	f	1	1	2	f	4	-1	721.06251	i	62
2	0	2	f	2	1	3	f	6	-1	719.03650		83	1	0	1	e	1	1	0	e	1	1	721.11225	36	
0	0	0	e	0	1	1	e	4	-1	719.03736	i	-40	1	1	0	e	1	2	1	If	13	0	721.11237	-146*	
1	1	0	e	1	2	1	If	8	-1	719.05463		-13	1	0	1	e	1	1	2	e	4	-1	721.16230	i	-19
2	0	2	e	2	1	1	If	28	0	719.05463		25	0	2	0	e	0	3	1	f	12	0	721.16944	17	
2	0	2	e	2	1	3	e	6	-1	719.06367		-3	2	0	2	e	2	1	1	If	32	0	721.24098	-493*	
0	1	1	f	0	2	2	f	4	-1	719.06367	i	2471*	1	1	2	e	1	2	1	If	33	0	721.29469	-3196*	
2	0	2	f	2	1	1	If	5	-1	719.11793		-11	1	1	0	e	1	2	1	If	14	0	721.32063	46	
0	1	1	e	0	2	2	e	4	-1	719.12885	i	0	0	0	0	e	0	1	1	e	3	-1	721.33601	i	11
0	1	1	f	0	2	0	e	24	0	719.16541		1	2	0	0	e	2	1	1	If	4	1	721.35444	29	
2	0	2	e	2	1	1	If	5	-1	719.18714		-5	0	2	0	e	0	3	1	f	13	0	721.36317	23	
0	1	1	f	0	2	0	e	23	0	719.28181		1	2	0	2	f	2	1	3	f	5	-1	721.37702	142	
1	0	1	f	1	1	2	f	5	-1	719.28950		3	2	0	2	e	2	1	3	e	5	-1	721.38978	1	
1	1	0	f	1	2	1	If	4	1	719.34815		5	0	1	1	e	0	2	2	e	3	-1	721.40058	i	14
0	1	1	f	0	2	0	e	22	0	719.38618		2	2	0	2	f	2	1	1	If	4	-1	721.46919	-45	
1	0	1	f	1	1	0	f	4	-1	719.40754		-1	1	1	2	e	1	2	1	If	6	1	721.47785	12	
1	0	1	e	1	1	2	e	5	-1	719.44703		8	2	0	2	e	2	1	1	If	4	-1	721.50880	5	
0	1	1	f	0	2	0	e	21	0	719.47913		13	1	1	0	e	1	2	1	If	15	0	721.54273	22	
1	1	2	f	1	2	1	If	5	1	719.55152		-63	0	2	0	e	0	3	1	f	14	0	721.57344	10	
0	1	1	f	0	2	0	e	20	0	719.56104		13	1	0	1	f	1	1	2	f	4	-1	721.65595	8	
2	0	2	e	2	1	1	If	29	0	719.59016		83	1	0	1	e	1	1	2	e	4	-1	721.76075	9	
1	1	2	f	1	2	3	f	5	-1	719.61445		-26	1	0	1	f	1	1	0	f	3	-1	721.77113	-11	
0	1	1	f	0	2	0	e	19	0	719.63264		11	1	1	0	e	1	2	1	If	16	0	721.78096	-12	
0	1	1	f	0	2	2	f	4	-1	719.68635		2	2	0	2	e	2	1	1	If	33	0	721.80055	-1192*	
0	1	1	f	0	2	0	e	18	0	719.69459		5	0	2	0	e	0	3	1	f	15	0	721.80104	27	
0	2	2	e	0	3	3	e	4	-1	719.73225		1	1	1	2	f	1	2	3	f	4	-1	721.96003	-19	
0	2	2	f	0	3	3	f	4	-1	719.73225		-87	1	1	2	f	1	2	1	If	6	1	722.01704	-32	
0	0	0	e	0	1	1	e	4	-1	719.73890		-4	1	1	0	e	1	2	1	If	17	0	722.03608	2	
0	1	1	f	0	2	0	e	17	0	719.74781		15	0	2	0	e	0	3	1	f	16	0	722.04670	119*	
0	1	1	e	0	2	2	e	4	-1	719.78052		-5	0	1	1	f	0	2	2	f	3	-1	722.05043	-22	
0	1	1	f	0	2	0	e	16	0	719.79273		7	0	0	0	e	0	1	1	e	3	-1	722.09321	-2	
1	1	0	e	1	2	1	If	1	0	719.81696		-20	0	1	1	e	0	2	2	e	3	-1	722.10694	-14	
0	1	1	f	0	2	0	e	15	0	719.83033		4	1	1	0	e	1	2	1	If	0	1	722.15931	39	
1	1	0	e	1	2	1	If	2	0	719.84528		-10	1	1	2	e	1	2	1	If	27	0	722.23298	-107*	
0	1	1	f	0	2	0	e	14	0	719.86133		0	2	0	0	e	2	1	1	If	3	-1	722.24415	10	
0	1	1	f	0	2	0	e	13	0	719.88654		3	1	1	2	e	1	2	1	If	26	0	722.34309	5	
2	0	0	e	2	1	1	If	4	-1	719.90150		21	0	2	0	e	0	3	1	e	0	1	722.40376	167*	
0	1	1	f	0	2	0	e	12	0	719.90656		-2	1	1	2	e	1	2	1	If	25	0	722.44197	91	
0	1	1	f	0	2	0	e	11	0	719.92219		-6	1	1	2	e	1	2	1	If	24	0	722.52864	2	
0	1	1	f	0	2	0	e	10	0	719.93421		4	0	2	0	e	0	3	1	f	18	0	722.58821	39	
1	1	0	e	1	2	1	If	5	0	720.01557		26	1	1	0	e	1	2	1	If	19	0	722.59584	-14	
0	2	0	e	0	3	1	f	1	0	720.05891		11	0	2	2	e	0	3	1	e	4	1	722.60530	6	
0	2	0	e	0	3	1	f	2	0	720.08674		-7	1	1	2	e	1	2	1	If	22	0	722.67463	3	
1	1	0	e	1	2	1	If	6	0	720.10065		0	1	1	2	e	1	2	1	If	21	0	722.73426	4	
1	0	1	e	1	1	0	e	1	1	720.10072	i	-51	1	1	2	e	1	2	1	If	20	0	722.78578	4	
0	2	0	e	0	3	1	f	3	0	720.12891		1	1	1	2	e	1	2	1	If	19	0	722.82978	-4	
2	0	2	e	2	1	1	If	30	0	720.13642		292*	1	1	2	e	1	2	1	If	18	0	722.86708	-1	
0	2	0	e	0	3	1	f	4	0	720.18531		13	0	2	0	e	0	3	1	f	19	0	722.88582	12	
1	1	0	e	1	2	1	If	7	0	720.20039		-13	0	2	2	f	0	3	1	f	4	1	722.89259	49	
0	2	0	e	0	3	1	f	5	0	720.25587		7	1	1	0	e	1	2	1	If	20	0	722.90113	-6	
0	2	2	e	0	3	1	e	3	1	720.26630		-3	1	1	2	e	1	2	1	If	16	0	722.92354	-20	
1	1	0	e	1	2	1	If	8	0	720.31501		-5	1	1	2	e	1	2	1	If	15	0	722.94429	-8	
0	2	0	e	0	3	1	f	6	0	720.34119		28	1	1	2	e	1	2	1	If	14	0	722.96107	40	
0	2	2	f	0	3	1	f	3	1	720.45802		72	2	0	2	e	2	1	1	If	4	1	722.96107	-55	
1	1	0	f	1	2	1	If	2	-1	720.52216		39	1	1	2	e	1	2	1	If	13	0	722.97310	-10	
0	2	0	e	0	3	1	f	8	0	720.55567		20	1	1	2	e	1	2	1	If	12	0	722.98268	17	
1	1	0	e	1	2	1	If	10	0	720.58875		-5	1	1	2	f	1	2	1	If	2	0	723.01686	-30	
2	0	2	e	2	1	1	If	3	1	720.61170		10	1	1	2	f	1	2	1	If	3	0	723.04347	-4	
2	0	2	e	2	1	1	If	31	0	720.68556		-42	1	1	2	f	1	2	1	If	4	0	723.07863	-1	
0	2	0	e	0	3	1	f	9	0	720.68556		15	1	1	2	f	1	2	1	If	5	0	723.12275	19	
1	1	0	e	1	2	1	If	11	0	720.74842		6	1	1	2	f	1	2	1	If	6	0	723.17610	84	

lower level					upper level					J	ΔJ	ν_{obs}	O-C	
ν_4	ν_5	ℓ	ν_4	ν_5	ℓ									
2	0	2	f	2	1	1	III	f	4	1	723.18629	-17		
0	2	0	e	0	3	1	f	20	0	723.20143	-4			
1	1	0	e	1	2	1	III	f	21	0	723.22322	-14		
1	1	2	f	1	2	1	Ie	7	0	723.23683	10			
1	0	1	f	1	1	0	f	2	-1	723.27742	i	-1		
1	1	2	f	1	2	1	Ie	8	0	723.30708	9			
1	0	1	f	1	1	2	f	3	-1	723.37019	i	-14		
1	1	2	f	1	2	1	Ie	9	0	723.38600	-3			
1	1	2	f	1	2	1	Ie	10	0	723.47407	23			
1	0	1	e	1	1	0	e	2	1	723.49306	-8			
1	1	0	e	1	2	1	III	f	22	0	723.56239	-13		
1	1	2	f	1	2	1	Ie	11	0	723.57033	-9			
0	0	0	e	0	1	1	e	2	-1	723.63368	i	1		
0	1	1	e	0	2	0	e	1	1	723.64967	i	2		
1	1	0	e	1	2	1	Ie	6	-1	723.67036	-69			
1	1	2	f	1	2	1	Ie	12	0	723.67561	-16			
2	0	0	e	2	1	1	III	f	5	1	723.68666	-3		
2	0	2	f	2	1	3	f	4	-1	723.71986	23			
2	0	2	e	2	1	3	e	4	-1	723.72688	113			
1	1	2	f	1	2	1	Ie	13	0	723.78999	10			
1	1	2	e	1	2	1	III	f	7	1	723.80165	-23		
2	0	2	f	2	1	1	I	f	3	-1	723.82271	-13		
2	0	2	e	2	1	1	Ie	3	-1	723.84132	-7			
0	2	0	e	0	3	1	f	22	0	723.88661	27			
1	1	2	f	1	2	1	Ie	14	0	723.91292	15			
1	1	0	e	1	2	1	III	f	23	0	723.91896	30		
1	0	1	f	1	1	2	f	3	-1	724.02119	18			
1	1	2	f	1	2	1	Ie	15	0	724.04445	5			
1	0	1	e	1	1	2	e	3	-1	724.08394	14			
1	0	1	f	1	1	0	f	2	-1	724.13405	-6			
1	1	2	f	1	2	1	Ie	16	0	724.18532	54			
0	2	0	e	0	3	1	f	23	0	724.25502	6			
1	1	0	e	1	2	1	III	f	24	0	724.29158	-9		
2	0	0	e	2	1	1	I	f	32	0	724.30891	3800*		
1	1	2	f	1	2	1	Ie	17	0	724.33418	28			
0	0	0	e	0	1	1	e	2	-1	724.44722	1			
1	1	2	f	1	2	1	Ie	18	0	724.49116	-59			
1	1	2	f	1	2	1	III	f	7	1	724.49745	41		
1	1	0	e	1	2	1	III	f	1	1	724.50996	31		
2	0	0	e	2	1	1	Ie	2	-1	724.59096	-8			
0	2	0	e	0	3	1	f	24	0	724.64076	23			
1	1	2	f	1	2	1	Ie	19	0	724.65840	7			
1	1	0	e	1	2	1	III	f	25	0	724.68141	1		
0	1	1	e	0	2	0	e	1	1	724.69234	-16			
0	2	0	e	0	3	1	e	1	1	724.75453	31			
1	0	1	e	1	1	0	e	3	1	724.75502	i	-205*		
1	1	2	f	1	2	1	Ie	20	0	724.83363	2			
0	2	2	e	0	3	1	e	5	1	724.93861	-19			
2	0	0	e	2	1	1	I	f	30	0	725.01076	865*		
1	1	2	f	1	2	1	Ie	21	0	725.01814	56			
0	2	0	e	0	3	1	f	25	0	725.04231	-17			
1	1	0	e	1	2	1	III	f	26	0	725.08748	-10		
1	1	0	f	1	2	1	Ie	1	0	725.25044	2			
1	1	0	f	1	2	1	Ie	2	0	725.26717	15			
1	1	0	f	1	2	1	Ie	3	0	725.29189	-3			
2	0	2	e	2	1	1	III	f	5	1	725.31301	26		
1	1	0	f	1	2	1	Ie	4	0	725.32515	2			
0	2	2	f	0	3	1	f	5	1	725.34145	27			
2	0	0	e	2	1	1	I	f	29	0	725.34859	88		
1	1	0	f	1	2	1	Ie	5	0	725.36665	1			
1	1	0	f	1	2	1	Ie	6	0	725.41634	-14			
0	2	0	e	0	3	1	f	26	0	725.46010	-2			
1	1	0	f	1	2	1	Ie	7	0	725.47463	-1			
1	1	0	e	1	2	1	III	f	27	0	725.50984	-4		
1	1	0	f	1	2	1	Ie	8	0	725.54109	-5			
1	0	1	f	1	1	0	f	1	-1	725.58248	i	-12		
1	1	0	f	1	2	1	Ie	9	0	725.61598	0			
2	0	2	f	2	1	1	III	f	5	1	725.62276	90		
1	1	2	f	1	2	1	Ie	24	0	725.62294	143*			
2	0	0	e	2	1	1	I	f	28	0	725.67995	16		
1	1	0	f	1	2	1	Ie	10	0	725.69917	-1			
1	1	0	f	1	2	1	Ie	11	0	725.79079	4			
1	1	2	f	1	2	1	Ie	25	0	725.83968	-41			
1	0	1	e	1	1	0	e	3	1	725.88423	-8			
1	1	0	f	1	2	1	Ie	12	0	725.89101	31			
1	1	0	e	1	2	1	III	f	28	0	725.94783	-2		
0	1	1	e	0	2	0	e	2	1	725.97261	i	-1		
1	1	0	f	1	2	1	Ie	13	0	725.99904	0			
2	0	0	e	2	1	1	III	f	6	1	726.00972	-12		
1	1	0	f	1	2	1	Ie	14	0	726.11611	30			
1	1	2	e	1	2	1	III	f	8	1	726.12093	86		
2	0	2	f	2	1	1	I	f	2	-1	726.17751	-19		
2	0	2	e	2	1	1	Ie	2	-1	726.18434	73			
1	1	0	f	1	2	1	Ie	15	0	726.24098	-2			
1	1	2	f	1	2	1	Ie	27	0	726.30275	-25			
2	0	0	e	2	1	1	I	f	26	0	726.30275	-1		
1	1	0	f	1	2	1	Ie	16	0	726.37477	13			
1	1	0	e	1	2	1	III	f	29	0	726.40132	36		
1	0	1	f	1	1	0	f	1	-1	726.49605	-6			
1	1	0	f	1	2	1	Ie	17	0	726.51674	0			
1	1	2	f	1	2	1	Ie	28	0	726.54683	-44			
2	0	0	e	2	1	1	I	f	25	0	726.59310	-24		
3	0	1	0	f	1	2	1	Ie	18	0	726.66756	23		
1	1	0	f	1	2	1	III	f	7	1	726.73482	-12		
1	1	2	f	1	2	1	Ie	29	0	726.79866	-139*			
1	1	0	f	1	2	1	Ie	19	0	726.82643	0			
1	1	0	e	1	2	1	III	f	2	1	726.85524	4		
1	1	0	e	1	2	1	III	f	30	0	726.86879	21		
2	0	0	e	2	1	1	I	f	24	0	726.86879	-97		
1	1	2	f	1	2	1	III	f	8	1	726.99324	228*		
1	1	0	f	1	2	1	Ie	20	0	726.99373	-32			
0	1	1	e	0	2	0	e	2	1	727.07338	-10			
1	0	1	e	1	1	0	e	4	1	727.10012	i	118*		
0	2	0	e	0	3	1	e	2	1	727.10067	-50			
2	0	0	e	2	1	1	I	f	23	0	727.13173	-13		
1	1	0	f	1	2	1	Ie	21	0	727.17019	-3			
0	2	2	e	0	3	1	e	6	1	727.26656	0			
0	2	0	e	0	3	1	f	30	0	727.27816	896*			
1	1	2	f	1	2	1	Ie	31	0	727.33150	55			
1	1	0	e	1	2	1	III	f	31	0	727.34993	-3		
1	1	0	f	1	2	1	Ie	22	0	727.35482	-13			
2	0	0	e	2	1	1	I	f	22	0	727.37972	24		
1	1	0	f	1	2	1	Ie	23	0	727.54830	2			
2	1	0	f	1	2	1	I	f	0	1	727.60201	-20		
2	0	0	e	2	1	1	I	f	21	0	727.61226	-21		
2	0	2	e	2	1	1	III	f	6	1	727.66695	33		
1	1	0	f	1	2	1	Ie	24	0	727.75033	11			
0	2	0	e	0	3	1	f	31	0	727.76253	1193*			
0	2	2	f	0	3	1	f	6	1	727.80428	-5			
2	0	0	e	2	1	1	I	f	20	0	727.83065	-2		
1	0	1	e	1	1	0	f	1	0	727.89577	i	-4		
1	0	1	e	1	1	0	f	2	0	727.91353	i	-32		
1	0	1	e	1	1	0	f	3	0	727.94118	i	27		
1	1	0	f	1	2	1	Ie	25	0	727.96090	12			
1	0	1	e	1	1	0	f	4	0	727.97664	i	-34		
1	0	1	e	1	1	0	f	5	0	728.02199	i	-7		
2														

lower level						upper level						$J \Delta J$	ν_{obs}	O-C
ν_4	ν_5	ℓ	ν_4	ν_5	ℓ	ν_4	ν_5	ℓ	ν_4	ν_5	ℓ			
0 0 0 e	0 1 1 f	1	0 728.23647 i	5		0 1 1 e	0 2 2 f	10	0 729.61398	2				
0 0 0 e	0 1 1 f	2	0 728.25338 i	0		0 0 0 e	0 1 1 f	10	0 729.64791	0				
0 2 0 e	0 3 1 f	32	0 728.25582	1463*		0 2 2 e	0 3 3 f	20	0 729.66970	79				
0 0 0 e	0 1 1 f	3	0 728.27889 i	7		1 1 0 f	1 2 1 f	1e	30	0 729.67330	-497*			
1 0 1 e	1 1 0 e	4	1 728.28518	-2		0 0 0 e	0 1 1 f	18	0 729.67330 i	-13				
1 0 1 e	1 1 0 f	9	0 728.29122 i	-104*		0 2 2 e	0 3 3 f	21	0 729.70132	72				
0 0 0 e	0 1 1 f	4	0 728.31277 i	-4		0 2 2 f	0 3 3 e	16	0 729.70132	-149*				
0 1 1 e	0 2 2 f	3	0 728.31348 i	45		0 1 1 e	0 2 2 f	11	0 729.70858	-14				
1 1 0 e	1 2 1 f	4	-1 728.32229	32		1 0 1 e	1 1 0 f	13	0 729.72128	37				
2 0 0 e	2 1 1 f	7	1 728.32229	89		0 0 0 e	0 1 1 f	11	0 729.74654	0				
0 1 1 e	0 2 2 f	4	0 728.34610 i	-37		0 2 0 e	0 3 1 f	35	0 729.76772	1257*				
1 1 0 e	1 2 1 f	33	0 728.35384	319*		0 2 2 e	0 3 3 f	23	0 729.76772	515*				
0 0 0 e	0 1 1 f	5	0 728.35512 i	0		0 2 2 f	0 3 3 e	17	0 729.77926	3				
1 0 1 e	1 1 0 f	10	0 728.38277 i	56		0 2 2 e	0 3 3 f	24	0 729.79372	25				
0 1 1 e	0 2 2 f	5	0 728.38686 i	-28		0 1 1 e	0 2 2 f	12	0 729.81197	-8				
1 1 0 f	1 2 1 f	27	0 728.40591	-200*		0 2 2 e	0 3 3 f	25	0 729.82491	-4				
0 0 0 e	0 1 1 f	6	0 728.40603 i	6		0 0 0 e	0 1 1 f	12	0 729.85409	1				
1 1 2 e	1 2 1 f	9	1 728.43026	-149*		0 2 2 e	0 3 3 f	26	0 729.86349	581*				
0 1 1 e	0 2 2 f	6	0 728.43578 i	-16		0 2 2 f	0 3 3 e	18	0 729.86349	151*				
0 0 0 e	0 1 1 f	7	0 728.46535 i	7		0 1 1 e	0 2 2 f	13	0 729.92385	-9				
1 0 1 e	1 1 0 f	11	0 728.48092 i	-17		0 2 2 f	0 3 3 e	19	0 729.95193	64				
0 1 1 e	0 2 2 f	7	0 728.49274 i	-12		0 0 0 e	0 1 1 f	13	0 729.97054	2				
0 0 0 e	0 1 1 f	8	0 728.53304 i	0		1 0 1 e	1 1 0 f	15	0 729.99520	5				
0 1 1 e	0 2 2 f	8	0 728.55786 i	-3		0 0 0 e	0 1 1 f	20	0 730.00137 i	-42				
1 0 1 e	1 1 0 f	12	0 728.58895 i	6		2 0 2 e	2 1 1 f	He	7	1 730.02517	21			
0 0 0 e	0 1 1 f	9	0 728.60927 i	2		0 1 1 e	0 2 2 f	14	0 730.04452	14				
0 1 1 e	0 2 2 f	9	0 728.63110 i	8		0 2 2 f	0 3 3 e	20	0 730.04708	-35				
0 0 0 e	0 1 1 f	10	0 728.69393 i	4		1 1 2 f	1 2 1 f	If	2	1 730.07119	-95			
1 0 1 e	1 1 0 f	13	0 728.70534 i	-24		0 0 0 e	0 1 1 f	14	0 730.09591	5				
0 1 1 e	0 2 2 f	10	0 728.71240 i	14		1 1 2 e	1 2 1 f	Ie	2	1 730.12185	-48			
0 0 0 e	0 1 1 f	11	0 728.78701 i	4		1 0 1 e	1 1 0 f	16	0 730.14639	15				
0 1 1 e	0 2 2 f	11	0 728.80176 i	17		0 1 1 e	0 2 2 f	15	0 730.17367	31				
1 0 1 e	1 1 0 f	14	0 728.83108 i	-6		0 0 0 e	0 1 1 f	21	0 730.17843 i	4				
1 0 1 e	1 1 0 f	1	0 728.86666	-7		0 0 0 e	0 1 1 f	15	0 730.23007	-1				
1 1 0 f	1 2 1 f	Ie	29	0 728.88760	-222*	1 1 0 f	1 2 1 f	Ie	34	0 730.24185	-599*			
0 0 0 e	0 1 1 f	12	0 728.88760 i	-86		0 2 2 f	0 3 3 e	22	0 730.25985	-131*				
0 1 1 e	0 2 2 f	12	0 728.89915 i	16		0 2 2 f	0 3 1 f	7	1 730.28048	-86				
1 0 1 e	1 1 0 f	3	0 728.91427	-4		0 0 0 e	0 1 1 f	22	0 730.36294 i	-31				
1 0 1 e	1 1 0 f	4	0 728.95235	-1		0 0 0 e	0 1 1 f	16	0 730.37313	-2				
1 0 1 e	1 1 0 f	15	0 728.96590 i	35		0 2 2 f	0 3 3 e	23	0 730.37887	-37				
1 0 1 e	1 1 0 f	5	0 728.99941	-50		0 1 1 e	0 2 2 f	17	0 730.45675	-11				
0 0 0 e	0 1 1 f	13	0 728.99941 i	106*		1 0 1 e	1 1 0 f	18	0 730.47628	4				
1 0 1 e	1 1 0 f	6	0 729.05697	2		0 2 2 f	0 3 3 e	24	0 730.50601	92				
1 0 1 e	1 1 0 f	7	0 729.12460	113*		0 0 0 e	0 1 1 f	17	0 730.52505	-2				
0 0 0 e	0 1 1 f	1	0 729.16329	15		0 0 0 e	0 1 1 f	23	0 730.55630 i	-4				
0 1 1 e	0 2 2 f	2	0 729.16622	72*		0 1 1 e	0 2 2 f	18	0 730.61135	0				
0 0 0 e	0 1 1 f	2	0 729.18118	6		2 0 0 e	2 1 1 f	He	8	1 730.62027	108			
0 1 1 e	0 2 2 f	3	0 729.19118	-22		1 0 1 e	1 1 0 f	19	0 730.65512	4				
0 0 0 e	0 1 1 f	3	0 729.20809	2		0 0 0 e	0 1 1 f	18	0 730.68582	1				
0 1 1 e	0 2 2 f	4	0 729.22591	-1		1 0 1 e	1 1 0 f	5	1 730.69522	-33				
0 0 0 e	0 1 1 f	4	0 729.24416	15		1 1 2 e	1 2 1 f	He	10	1 730.73678	45			
0 1 1 e	0 2 2 f	5	0 729.26925	18		0 0 0 e	0 1 1 f	24	0 730.75753 i	-12				
0 0 0 e	0 1 1 f	5	0 729.28878	-14		0 1 1 e	0 2 2 f	19	0 730.77420	-11				
0 1 1 e	0 2 2 f	6	0 729.32101	18		0 2 2 f	0 3 3 e	26	0 730.78115	14				
0 0 0 e	0 1 1 f	6	0 729.34286	5		1 0 1 e	1 1 0 f	20	0 730.84298	-11				
1 0 1 e	1 1 0 f	10	0 729.37997	18		0 0 0 e	0 1 1 f	19	0 730.85531	-6				
0 0 0 e	0 1 1 f	7	0 729.40566	0		2 0 2 e	2 1 1 f	If	3	0 730.90457	45			
0 2 2 e	0 3 3 f	13	0 729.43221	3		2 0 2 e	2 1 1 f	If	4	0 730.91378	-61			
0 2 0 e	0 3 1 e	3	1 729.44277	-19		2 0 2 e	2 1 1 f	If	5	0 730.93100	106			
0 1 1 e	0 2 2 f	8	0 729.45054	34		0 1 1 e	0 2 2 f	20	0 730.94644	70*				
0 0 0 e	0 1 1 f	8	0 729.47744	-2		2 0 2 e	2 1 1 f	If	6	0 730.95388	143			
1 0 1 e	1 1 0 f	11	0 729.48428	18		0 0 0 e	0 1 1 f	25	0 730.96670 i	-45				
0 2 2 e	0 3 3 f	15	0 729.50002	-88		2 0 2 e	2 1 1 f	If	7	0 730.98416	48			
0 0 0 e	0 1 1 f	17	0 729.52163 i	-9		2 0 2 e	2 1 1 f	If	8	0 731.02584	49			
0 1 1 e	0 2 2 f	9	0 729.52755	-24		1 0 1 f	1 1 2 e	10	0 731.05026	-26				
0 0 0 e	0 1 1 f	9	0 729.55825	3		1 0 1 f	1 1 2 e	9	0 731.05764	-29				
1 0 1 e	1 1 0 f	12	0 729.59792	11		1 0 1 f	1 1 2 e	8	0 731.06527	-52				

lower level						upper level						$J \Delta J$	ν_{obs}	o-c
ν_4	ν_5	ℓ	ν_4	ν_5	ℓ	ν_4	ν_5	ℓ	ν_4	ν_5	ℓ			
1 0 1 f	1 1 2 e	7	0 731.07370	-1		1 1 2 e	1 2 3 f	20	0 731.92868	-122*				
1 0 1 f	1 1 2 e	6	0 731.08206	69*		1 0 1 e	1 1 2 f	13	0 731.93008	-3				
1 0 1 f	1 1 2 e	5	0 731.08814	-34		1 1 2 f	1 2 3 e	17	0 731.95907	3				
1 0 1 f	1 1 2 e	4	0 731.09518	40		1 1 2 e	1 2 3 f	21	0 731.97036	50				
1 0 1 f	1 1 2 e	3	0 731.10293	285*		2 0 2 e	2 1 1 If	17	0 731.97921	32				
1 0 1 f	1 1 2 e	20	0 731.10916	-37		1 1 2 e	1 2 3 f	22	0 732.01040	89				
1 0 1 f	1 1 2 e	2	0 731.10916	497*		1 1 2 f	1 2 1 If	10	1 732.02060	9				
0 1 1 e	0 2 2 f	21	0 731.12576	17		1 1 2 f	1 2 3 e	18	0 732.03518	28				
1 0 1 e	1 1 2 f	2	0 731.13559	6		0 0 0 e	0 1 1 f	25	0 732.05636	-8				
1 0 1 f	1 1 2 e	21	0 731.14193	18		1 1 2 e	1 2 3 f	24	0 732.08816	47				
2 0 2 e	2 1 1 If	10	0 731.14383	-159		1 1 2 f	1 2 3 e	19	0 732.11587	-69				
1 0 1 e	1 1 2 f	3	0 731.16269	6		1 1 2 e	1 2 3 f	25	0 732.12649	17				
1 0 1 f	1 1 2 e	22	0 731.18161	25		0 0 0 e	0 1 1 f	30	0 732.13669 i	7				
1 0 1 e	1 1 2 f	4	0 731.19849	-27		2 0 2 e	2 1 1 If	18	0 732.14535	101				
0 0 0 e	0 1 1 f	21	0 731.22079	-2		0 1 1 e	0 2 2 f	26	0 732.15042	-30				
1 0 1 e	1 1 2 f	5	0 731.24447	55		1 0 1 e	1 1 0 f	26	0 732.16208	31				
1 0 1 f	1 1 2 e	24	0 731.28537	2		1 0 1 e	1 1 2 f	15	0 732.19180	-3				
1 0 1 e	1 1 2 f	6	0 731.29824	13		1 1 2 e	1 2 3 f	27	0 732.20413	65				
0 1 1 e	0 2 2 f	22	0 731.31381	-6		1 1 2 f	1 2 3 e	20	0 732.20413	-9				
2 0 2 e	2 1 1 If	12	0 731.31912	-19		1 1 2 e	1 2 3 f	28	0 732.24283	22				
1 0 1 f	1 1 2 e	25	0 731.35159	59		0 0 0 e	0 1 1 f	26	0 732.28683	-19				
1 0 1 e	1 1 2 f	7	0 731.36142	9		1 1 2 f	1 2 3 e	21	0 732.29788	-23				
1 1 2 e	1 2 3 f	3	0 731.39859	27		1 1 2 e	1 2 3 f	30	0 732.31961	-459*				
1 1 2 f	1 2 3 e	3	0 731.39859	7		2 0 2 e	2 1 1 If	19	0 732.32077	128				
1 1 2 e	1 2 3 f	4	0 731.41122	-46		1 0 1 e	1 1 2 f	16	0 732.33621	2				
1 1 2 f	1 2 3 e	4	0 731.41122	-107*		1 1 2 e	1 2 3 f	31	0 732.35861	-922*				
0 0 0 e	0 1 1 f	22	0 731.41659	-7		0 1 1 e	0 2 2 f	27	0 732.38064	-12				
1 0 1 f	1 1 2 e	26	0 731.42678	-44		2 0 2 e	2 1 1 If	8	1 732.38931	-14				
1 0 1 e	1 1 2 f	8	0 731.43313	-24		0 0 0 e	0 1 1 f	31	0 732.39651 i	179*				
1 0 1 e	1 1 0 f	23	0 731.46194	9		1 0 1 e	1 1 0 f	27	0 732.41293	4				
1 1 2 e	1 2 3 f	7	0 731.46927	-95		1 1 2 f	1 2 1 If	3	1 732.43374	52				
1 1 2 f	1 2 3 e	7	0 731.47537	5		1 1 2 e	1 2 3 f	33	0 732.44290	-2155*				
1 1 2 e	1 2 3 f	8	0 731.49551	10		1 0 1 e	1 1 2 f	17	0 732.48953	-3				
1 1 2 f	1 2 3 e	8	0 731.50351	-39		1 1 2 e	1 2 3 f	34	0 732.48953	-2963*				
0 0 0 e	0 1 1 e	0	1 731.50705	2		1 1 2 f	1 2 3 e	23	0 732.50522	-18				
1 0 1 e	1 1 2 f	9	0 731.51468	-16		2 0 2 e	2 1 1 If	20	0 732.50522	139				
1 1 2 e	1 2 3 f	9	0 731.52255	-60		1 1 2 e	1 2 1 If	3	1 732.51626	-48				
1 1 0 e	1 2 1 If	4	1 731.53372	297*		0 0 0 e	0 1 1 f	27	0 732.52618	-5				
1 1 2 f	1 2 3 e	9	0 731.53671	26		1 1 2 e	1 2 3 f	35	0 732.53842	-4098*				
2 0 2 e	2 1 1 If	14	0 731.54635	-51		0 1 1 e	0 2 2 f	28	0 732.61893	-15				
1 1 2 e	1 2 3 f	10	0 731.55337	14		1 0 1 e	1 1 2 f	18	0 732.65195	2				
1 1 2 f	1 2 3 e	10	0 731.57241	-71		0 0 0 e	0 1 1 f	32	0 732.66092 i	10				
1 1 2 e	1 2 3 f	11	0 731.58541	-3		1 0 1 e	1 1 0 f	28	0 732.67294	10				
1 0 1 e	1 1 2 f	10	0 731.60586	73*		2 0 2 e	2 1 1 If	21	0 732.69650	-42				
0 0 0 e	0 1 1 f	23	0 731.62112	-11		1 1 2 e	1 2 3 f	38	0 732.72403	-7956*				
0 0 0 e	0 1 1 f	28	0 731.64383 i	-71		1 1 2 f	1 2 3 e	25	0 732.74008	-2				
2 0 2 e	2 1 1 If	0	1 731.66732	-22		0 2 2 f	0 3 1 f	8	1 732.77389	193*				
2 0 2 e	2 1 1 If	15	0 731.67929	-18		0 0 0 e	0 1 1 f	28	0 732.77392	-10				
1 0 1 e	1 1 0 f	24	0 731.68625	5		1 0 1 e	1 1 2 f	19	0 732.82236	-94*				
1 1 2 e	1 2 3 f	14	0 731.69247	7		0 1 1 e	0 2 2 f	29	0 732.86557	-8				
1 0 1 e	1 1 2 f	11	0 731.70474	30		0 1 1 e	0 2 2 e	1	1 732.88242 i	3				
0 1 1 e	0 2 2 f	24	0 731.71560	1		1 0 1 e	1 1 0 f	29	0 732.94199	43				
1 1 2 e	1 2 3 f	15	0 731.73068	4		1 1 2 e	1 2 3 f	41	0 732.99148	-12370*				
1 1 2 e	1 2 3 f	16	0 731.76956	-18		1 0 1 e	1 1 2 f	20	0 733.00333	-33				
0 2 0 e	0 3 1 e	4	1 731.77908	-56		1 1 2 f	1 2 3 e	27	0 733.00333	-45				
1 1 2 e	1 2 3 f	17	0 731.81094	149*		0 0 0 e	0 1 1 f	29	0 733.03027	-10				
1 0 1 e	1 1 0 e	6	1 731.81094 i	153*		1 1 2 e	1 2 1 If	11	1 733.03274	-44				
1 1 2 f	1 2 3 e	15	0 731.82419	32		1 1 2 e	1 2 3 f	42	0 733.10788	-13528*				
2 0 2 e	2 1 1 If	16	0 731.82419	48		2 0 2 e	2 1 1 If	23	0 733.10831	23				
2 0 2 e	2 1 1 If	16	0 731.82419	48		1 0 1 e	1 1 0 e	6	1 733.11514	8				
0 0 0 e	0 1 1 f	24	0 731.83450	0		0 1 1 e	0 2 2 f	30	0 733.12057	13				
1 1 2 e	1 2 3 f	18	0 731.84964	12		1 1 2 f	1 2 3 e	28	0 733.14670	-25				
0 1 1 e	0 2 0 e	4	1 731.86209	-8		2 0 2 f	2 1 3 e	4	0 733.16562	-22				
1 1 2 f	1 2 3 e	16	0 731.88766	-111*		2 0 2 e	2 1 3 f	4	0 733.17166	-29				
0 0 0 e	0 1 1 f	29	0 731.88766 i	111*		2 0 2 f	2 1 3 e	5	0 733.18350	-1				
0 2 2 e	0 3 1 e	8	1 731.90188	-54		1 0 1 e	1 1 2 f	21	0 733.19321	19				
1 0 1 e	1 1 0 f	25	0 731.91958	6		2 0 2 e	2 1 3 f	5	0 733.19833	66				

lower level									upper level														
v_4	v_5	ℓ	v_4	v_5	ℓ	J	ΔJ	ν_{obs}	O-C	v_4	v_5	ℓ	v_4	v_5	ℓ	J	ΔJ	ν_{obs}	O-C				
2	0	2	f	2	1	3	e	6	0	733.20517	-21	1	0	1	e	1	1	2	f	28	0	734.77017	4
1	0	1	e	1	1	0	f	30	0	733.21854	-44	1	1	2	f	1	2	1	If	4	1	734.79288	-169*
2	0	2	f	2	1	3	e	7	0	733.23245	62	1	0	1	f	1	1	0	f	2	1	734.79288 i	-19
2	0	2	f	2	1	3	e	8	0	733.26309	-18	0	1	1	e	0	2	2	f	36	0	734.82016	-20
2	0	2	e	2	1	3	f	7	0	733.28146	-3	2	0	2	e	2	1	3	f	17	0	734.82743	-19
0	0	0	e	0	1	1	f	30	0	733.29520	-5	1	0	1	f	1	1	2	f	1	1	734.89102 i	-6
1	1	2	f	1	2	3	e	29	0	733.29922	131*	1	0	1	e	1	1	2	e	1	1	734.90109 i	-7
2	0	2	f	2	1	3	e	9	0	733.29922	-99	1	1	2	e	1	2	1	Ie	4	1	734.91953	1
2	0	2	e	2	1	1	If	24	0	733.32571	6	1	0	1	e	1	1	2	f	29	0	735.03128	-8
2	0	2	f	2	1	3	e	10	0	733.34341	21	1	1	2	f	1	2	3	e	38	0	735.03128	214*
0	1	1	e	0	2	2	f	31	0	733.38229	-115*	0	0	0	e	0	1	1	f	36	0	735.06174	-10
1	0	1	e	1	1	2	f	22	0	733.39151	15	1	0	1	e	1	1	0	f	36	0	735.06180	-117*
1	1	2	e	1	2	3	f	44	0	733.39151	-14902*	2	0	2	e	2	1	3	f	18	0	735.10861	8
2	0	2	e	2	1	3	f	9	0	733.42386	-14	0	0	0	e	0	1	1	e	2	1	735.11563 i	0
2	0	2	f	2	1	3	e	12	0	733.44986	4	0	1	1	e	0	2	2	f	37	0	735.13242	51*
1	1	2	f	1	2	3	e	30	0	733.45828	147*	2	0	0	e	2	1	1	He	10	1	735.16525	-55
1	0	1	e	1	1	0	f	31	0	733.50510	4	0	1	1	f	0	2	2	f	2	1	735.20279 i	2662*
0	0	0	e	0	1	1	f	35	0	733.51468 i	786*	0	1	1	e	0	2	2	e	2	1	735.20279 i	-54
2	0	2	f	2	1	3	e	13	0	733.51480	0	0	2	2	f	0	3	1	f	9	1	735.27628	37
2	0	2	e	2	1	3	f	10	0	733.52231	-24	1	0	1	e	1	1	2	f	30	0	735.30185	28
2	0	2	e	2	1	1	If	25	0	733.55106	10	1	1	2	e	1	2	1	He	12	1	735.32151	-8
0	0	0	e	0	1	1	f	31	0	733.56854	-10	0	1	1	e	0	2	0	e	6	1	735.34818 i	124*
1	0	1	f	1	1	0	f	1	1	733.57620	-35	0	0	0	e	0	1	1	f	37	0	735.38541	-8
2	0	2	f	2	1	3	e	14	0	733.58841	-9	1	0	1	e	1	1	0	f	37	0	735.39951	-7
1	0	1	e	1	1	2	f	23	0	733.59866	-4	2	0	2	e	2	1	3	f	19	0	735.41422	-9
2	0	2	e	2	1	3	f	11	0	733.64139	-5	0	1	1	e	0	2	2	f	38	0	735.45145	1
0	1	1	e	0	2	2	f	32	0	733.65451	-10	2	0	2	f	2	1	1	If	9	1	735.48270	-64
2	0	2	f	2	1	3	e	15	0	733.67178	15	1	1	2	f	1	2	3	e	40	0	735.50693	-216*
1	1	2	e	1	2	3	f	46	0	733.76511	-13260*	1	0	1	e	1	1	0	e	7	1	735.54337	-3
2	0	2	f	2	1	3	e	16	0	733.76511	22	1	0	1	e	1	1	2	f	31	0	735.58078	2
2	0	2	e	2	1	3	f	12	0	733.78201	20	2	0	2	f	2	1	3	e	27	0	735.62461	4808*
2	0	2	e	2	1	1	If	26	0	733.78250	-139	0	0	0	e	0	1	1	f	38	0	735.71744	5
1	0	1	e	1	1	0	f	32	0	733.80063	90*	1	0	1	e	1	1	0	f	38	0	735.74497	61
1	1	2	f	1	2	3	e	32	0	733.80063	160*	2	0	2	e	2	1	3	f	20	0	735.74497	-42
1	0	1	e	1	1	2	f	24	0	733.81479	-23	0	1	1	e	0	2	2	f	39	0	735.77866	-24
0	0	0	e	0	1	1	e	1	1	733.85959	13	1	0	1	f	1	1	2	f	1	1	735.82645	14
0	1	1	f	0	2	2	f	1	1	733.86209	27	1	0	1	e	1	1	2	f	32	0	735.86863	-31
0	1	1	e	0	2	2	e	1	1	733.87070	-57*	1	0	1	f	1	1	0	f	2	1	735.93476	7
0	1	1	e	0	2	2	f	33	0	733.93485	94*	0	0	0	e	0	1	1	f	39	0	736.05747	-2
2	0	2	e	2	1	3	f	13	0	733.94449	5	1	0	1	e	1	1	0	f	39	0	736.09732	8
1	1	2	f	1	2	3	e	33	0	733.98441	181*	2	0	2	e	2	1	3	f	21	0	736.10300	73
2	0	2	f	2	1	3	e	18	0	733.98441	13	0	1	1	e	0	2	2	f	40	0	736.11454	27
2	0	2	e	2	1	1	If	27	0	734.02414	-22	1	0	1	e	1	1	2	f	33	0	736.16617	7
1	0	1	e	1	1	2	f	25	0	734.04013	-19	1	1	0	e	1	2	1	He	6	1	736.18570	-5
1	0	1	e	1	1	0	f	33	0	734.10251	-41	0	0	0	e	0	1	1	e	2	1	736.21140	0
0	2	0	e	0	3	1	e	5	1	734.11112	-17	0	1	1	f	0	2	2	f	2	1	736.22178	10
2	0	2	f	2	1	3	e	19	0	734.11136	-10	0	1	1	e	0	2	2	e	2	1	736.25016	0
2	0	2	e	2	1	3	f	14	0	734.12906	-86	0	2	2	e	0	3	3	e	2	1	736.26389	83
0	0	0	e	0	1	1	f	33	0	734.14066	-10	0	2	2	f	0	3	3	f	2	1	736.26389	77
1	1	2	f	1	2	3	e	34	0	734.17752	289*	0	0	0	e	0	1	1	f	40	0	736.40561	-16
1	0	1	e	1	1	0	e	7	1	734.17752 i	9	2	0	0	e	2	1	1	Ie	2	1	736.41721	-17
0	2	2	e	0	3	1	e	9	1	734.20926	3	0	2	0	e	0	3	1	e	6	1	736.43796	-8
0	1	1	e	0	2	2	f	34	0	734.22122	-11	1	0	1	e	1	1	0	f	40	0	736.45829	15
2	0	2	f	2	1	3	e	20	0	734.25125	43	1	0	1	e	1	1	2	f	34	0	736.47233	9
2	0	2	e	2	1	1	If	28	0	734.26901	-328*	2	0	2	e	2	1	3	f	22	0	736.48569	21
0	1	1	e	0	2	0	e	5	1	734.26932	4	0	2	2	e	0	3	1	e	10	1	736.50748	-15
1	0	1	e	1	1	2	f	26	0	734.27493	32	1	0	1	e	1	1	0	e	8	1	736.55344 i	-8
2	0	2	e	2	1	3	f	15	0	734.33878	9	0	1	1	e	0	2	0	e	6	1	736.68430	-8
1	0	1	e	1	1	0	f	34	0	734.41440	-17	0	0	0	e	0	1	1	f	41	0	736.76234	17
0	0	0	e	0	1	1	f	34	0	734.43930	-14	1	1	0	f	1	2	1	If	11	1	736.77579	-9
0	1	1	e	0	2	2	f	35	0	734.51773	91*	1	0	1	e	1	1	2	f	35	0	736.78739	2
1	0	1	e	1	1	2	f	27	0	734.51779	-9	2	0	2	e	2	1	3	f	23	0	736.89329	-226*
1	1	2	f	1	2	1	If	11	1	734.55533	-22	2	0	2	f	2	1	3	e	32	0	737.03196	14940*
1	1	0	f	1	2	1	If	3	1	734.68161	-2	1	1	0	f	1	2	1	If	4	1	737.04105	0
1	0	1	e	1	1	0	f	35	0	734.73447	-14	1	0	1	f	1	1	0	f	3	1	737.09299 i	6
0	0	0	e	0	1	1	f	35	0	734.74637	-11	1	1	2	f	1	2	1	If	12	1	737.10361	-6
2	0	2	e	2	1	1	He	9	1	734.76132	-23	1	0	1	e	1	1	2	f	36	0	737.11173	24

lower level										upper level										lower level										upper level									
v_4	v_5	ℓ	v_4	v_5	ℓ	J	ΔJ	ν_{obs}	O-C	v_4	v_5	ℓ	v_4	v_5	ℓ	J	ΔJ	ν_{obs}	O-C	v_4	v_5	ℓ	v_4	v_5	ℓ	J	ΔJ	ν_{obs}	O-C										
0	0	0	e	0	1	1	f	42	0	737.12687	22	0	1	1	e	0	2	2	e	4	1	739.87034	i	-5	0	1	1	e	0	2	2	e	4	1	739.87034	i	-5		
2	0	2	e	2	1	1	He	10	1	737.14219	-11	2	0	2	e	2	1	3	f	29	0	739.95109	-200*	2	0	2	e	2	1	3	f	29	0	739.95109	-200*				
1	1	2	f	1	2	1	If	5	1	737.15604	-9	0	1	1	e	0	2	0	e	8	1	740.07853	i	-14	0	1	1	e	0	2	0	e	8	1	740.07853	i	-14		
1	0	1	f	1	1	2	f	2	1	737.19065	i	-1	1	1	0	e	1	2	1	He	0	1	740.08830	22	1	1	0	e	1	2	1	He	0	1	740.08830	22			
1	0	1	e	1	1	2	e	2	1	737.22092	i	-6	2	0	2	e	2	1	3	e	2	1	740.22654	-41	2	0	2	e	2	1	3	e	2	1	740.22654	-41			
1	1	2	e	1	2	1	He	5	1	737.33103	55	2	0	2	f	2	1	3	f	2	1	740.22654	0	2	0	2	f	2	1	3	f	2	1	740.22654	0				
0	0	0	e	0	1	1	e	3	1	737.41044	i	6	0	2	2	f	0	3	1	f	11	1	740.32261	10	0	2	2	f	0	3	1	f	11	1	740.32261	10			
2	0	0	e	2	1	1	He	11	1	737.41050	-121	2	0	2	f	2	1	1	If	3	1	740.34056	-15	2	0	2	f	2	1	1	If	3	1	740.34056	-15				
0	0	0	e	0	1	1	f	43	0	737.49967	50*	2	0	2	e	2	1	1	He	3	1	740.39762	-13	2	0	2	e	2	1	1	He	3	1	740.39762	-13				
0	1	1	f	0	2	2	f	3	1	737.49967	i	2164*	1	0	1	e	1	1	0	e	9	1	740.42497	0	1	0	1	e	1	1	0	e	9	1	740.42497	0			
0	1	1	e	0	2	2	e	3	1	737.53263	i	2	2	0	2	f	2	1	1	If	11	1	740.48155	-3	2	0	2	f	2	1	1	If	11	1	740.48155	-3			
1	1	2	e	1	2	1	He	13	1	737.60154	72	1	0	1	f	1	1	2	f	3	1	740.53825	8	1	0	1	f	1	1	2	f	3	1	740.53825	8				
1	1	0	e	1	2	1	If	14	0	737.70914	102*	1	0	1	e	1	1	2	e	3	1	740.60161	7	1	0	1	e	1	1	2	e	3	1	740.60161	7				
0	1	1	e	0	2	0	e	7	1	737.70914	i	-31	1	0	1	f	1	1	0	f	4	1	740.64769	-5	1	0	1	f	1	1	0	f	4	1	740.64769	-5			
1	1	0	e	1	2	1	If	15	0	737.71885	-51	1	1	0	e	1	2	1	He	8	1	740.82066	-8	1	1	0	e	1	2	1	He	8	1	740.82066	-8				
1	1	0	e	1	2	1	If	16	0	737.73484	-2	1	1	2	f	1	2	3	f	3	1	740.85063	4	1	1	2	f	1	2	3	f	3	1	740.85063	4				
1	1	0	e	1	2	1	If	17	0	737.75504	-21	0	0	0	e	0	1	1	e	4	1	740.91368	2	0	0	0	e	0	1	1	e	4	1	740.91368	2				
1	1	0	e	1	2	1	If	18	0	737.78117	-4	0	1	1	f	0	2	2	f	4	1	740.93870	-2	0	1	1	f	0	2	2	f	4	1	740.93870	-2				
1	0	1	e	1	1	2	f	38	0	737.78745	75*	0	2	2	e	0	3	3	e	4	1	741.01823	102	0	2	2	e	0	3	3	e	4	1	741.01823	102				
0	2	2	f	0	3	1	f	10	1	737.79307	20	0	2	2	f	0	3	3	f	4	1	741.01823	13	0	2	2	f	0	3	3	f	4	1	741.01823	13				
2	0	2	e	2	1	3	f	25	0	737.79996	138	0	1	1	e	0	2	2	e	4	1	741.03471	0	0	1	1	e	0	2	2	e	4	1	741.03471	0				
1	1	0	e	1	2	1	If	19	0	737.81309	-32	0	2	0	e	0	3	1	e	8	1	741.07707	-47	0	2	0	e	0	3	1	e	8	1	741.07707	-47				
1	1	0	e	1	2	1	If	20	0	737.85252	-5	2	0	0	e	2	1	1	He	4	1	741.18675	-38	2	0	0	e	2	1	1	He	4	1	741.18675	-38				
0	0	0	e	0	1	1	f	44	0	737.88004	36	1	0	1	e	1	1	0	e	10	1	741.32829	i	-2	1	0	1	e	1	1	0	e	10	1	741.32829	i	-2		
1	1	0	e	1	2	1	If	21	0	737.89933	-6	0	1	1	e	0	2	0	e	8	1	741.53666	-3	0	1	1	e	0	2	0	e	8	1	741.53666	-3				
1	1	0	e	1	2	1	If	22	0	737.95499	42	1	0	1	f	1	1	0	f	5	1	741.68901	i	-7	1	0	1	f	1	1	0	f	5	1	741.68901	i	-7		
2	0	2	f	2	1	1	If	2	1	737.97922	268*	1	1	0	f	1	2	1	If	6	1	741.75896	-15	1	1	0	f	1	2	1	If	6	1	741.75896	-15				
1	0	1	e	1	1	0	e	8	1	737.97990	-27	1	0	1	f	1	1	2	f	4	1	741.78496	i	-2	1	0	1	f	1	1	2	f	4	1	741.78496	i	-2		
2	0	2	e	2	1	1	He	2	1	738.00974	-21	2	0	0	e	2	1	1	He	13	1	741.84465	2	2	0	0	e	2	1	1	He	13	1	741.84465	2				
1	1	0	e	1	2	1	If	23	0	738.01939	57	1	1	0	f	1	2	1	If	13	1	741.87364	0	1	1	0	f	1	2	1	If	13	1	741.87364	0				
1	1	0	e	1	2	1	If	24	0	738.09281	1	1	1	2	f	1	2	1	If	7	1	741.87938	-40	1	1	2	f	1	2	1	If	7	1	741.87938	-40				
1	0	1	e	1	1	2	f	39	0	738.13786	7	1	0	1	e	1	1	2	e	4	1	741.88670	i	1	1	0	1	e	1	1	2	e	4	1	741.88670	i	1		
1	0	1	f	1	1	2	f	2	1	738.18308	6	2	0	2	e	2	1	1	He	12	1	741.93114	-53	2	0	2	e	2	1	1	He	12	1	741.93114	-53				
1	0	1	e	1	1	2	e	2	1	738.21464	4	0	0	0	e	0	1	1	e	5	1	741.99797	i	3	0	0	0	e	0	1	1	e	5	1	741.99797	i	3		
1	0	1	f	1	1	0	f	3	1	738.29173	-4	0	1	1	f	0	2	2	f	5	1	742.07884	i	7	0	1	1	f	0	2	2	f	5	1	742.07884	i	7		
1	1	2	f	1	2	3	f	2	1	738.47746	7	1	1	2	e	1	2	1	He	15	1	742.12852	1	1	1	2	e	1	2	1	He	15	1	742.12852	1				
1	1	0	e	1	2	1	He	7	1	738.50553	-16	1	1	2	e	1	2	1	He	7	1	742.17589	-1	1	1	2	e	1	2	1	He	7	1	742.17589	-1				
0	0	0	e	0	1	1	e	3	1	738.56278	-3	0	1	1	e	0	2	2	e	5	1	742.21696	i	5	0	1	1	e	0	2	2	e	5	1	742.21696	i	5		
0	1	1	f	0	2	2	f	3	1	738.58048	-18	0	1	1	e	0	2	0	e	9	1	742.45396	i	-14	0	1	1	e	0	2	0	e	9	1	742.45396	i	-14		
0	2	2	e	0	3	3	e	3	1	738.63798	-53	1	1	0	e	1	2	1	He	1	1	742.46446	44	1	1	0	e	1	2	1	He	1	1	742.46446	44				
0	2	2	f	0	3	3	f	3	1	738.63798	-82	2	0	2	e	2	1	3	e	3	1	742.59972	-60	2	0	2	e	2	1	3	e	3	1	742.59972	-60				
0	1	1	e	0	2	2	e	3	1	738.63810	19	2	0	2	f	2	1	3	f	3	1	742.59972	144	2	0	2	f	2	1	3	f	3	1	742.59972	144				
0	0	0	e	0	1	1	f	46	0	738.66508	58*	2	0	2	f	2	1	1	If	4	1	742.70586	-16																

lower level										upper level											
v_4	v_5	ℓ	v_4	v_5	ℓ	J	ΔJ	ν_{obs}	O-C	v_4	v_5	ℓ	v_4	v_5	ℓ	J	ΔJ	ν_{obs}	O-C		
1	1	2	e	1	2	1	IIe	16	1 744.37688	161*	1	1	2	f	1	2	1	If	10	1 748.96594	-10
0	1	1	f	0	2	2	f	6	1 744.37688 i	-69	0	1	1	f	0	2	2	f	8	1 748.97210 i	25
1	1	0	f	1	2	1	IIff	14	1 744.44066	1	2	0	2	e	2	1	1	IIe	15	1 749.18212	4
0	1	1	e	0	2	2	e	6	1 744.57238 i	-5	0	1	1	e	0	2	2	e	8	1 749.31183 i	-2
1	1	2	e	1	2	1	Ie	8	1 744.60967	-8	1	1	2	e	1	2	1	Ie	10	1 749.49768	-18
1	1	2	f	1	2	1	IIff	15	1 744.81426	-833*	0	1	1	e	0	2	0	e	12	1 749.61169 i	3
0	1	1	e	0	2	0	e	10	1 744.83507 i	-8	1	1	0	e	1	2	1	Ie	4	1 749.63696	6
1	1	0	e	1	2	1	Ie	2	1 744.84734	-9	2	0	2	f	2	1	3	f	6	1 749.73687	-14
2	0	2	f	2	1	3	f	4	1 744.97362	-13	2	0	2	e	2	1	3	e	6	1 749.76495	-10
2	0	2	e	2	1	3	e	4	1 744.97991	5	2	0	2	f	2	1	1	If	7	1 749.80639	-20
2	0	2	f	2	1	1	If	5	1 745.07103	-123	1	0	1	f	1	1	2	f	7	1 749.94262	-1
2	0	2	e	2	1	1	Ie	5	1 745.20183	-2	1	1	0	e	1	2	1	IIe	12	1 750.03497	-6
1	0	1	f	1	1	2	f	5	1 745.24376	5	1	0	1	f	1	1	0	f	8	1 750.05951	-7
1	0	1	e	1	1	0	e	11	1 745.33672	2	1	0	1	e	1	1	2	e	7	1 750.24402	3
1	0	1	f	1	1	0	f	6	1 745.35613	-2	1	0	1	e	1	1	0	e	13	1 750.27441	1
1	0	1	e	1	1	2	e	5	1 745.40349	5	0	0	0	e	0	1	1	e	8	1 750.31054	-3
1	1	0	e	1	2	1	IIe	10	1 745.43664	-7	0	1	1	f	0	2	2	f	8	1 750.36090	0
2	0	2	f	2	1	1	IIff	13	1 745.52117	57	1	1	2	e	1	2	3	e	7	1 750.37250	-31
0	0	0	e	0	1	1	e	6	1 745.61352	3	1	1	2	f	1	2	3	f	7	1 750.37805	-1
0	1	1	f	0	2	2	f	6	1 745.65191	1	0	2	2	f	0	3	1	f	15	1 750.56048	111*
0	2	0	e	0	3	1	e	10	1 745.69964	-32	0	2	2	e	0	3	3	e	8	1 750.56048	-12
0	2	2	f	0	3	3	f	6	1 745.78631	-152*	0	2	2	f	0	3	3	f	8	1 750.57318	-3
0	1	1	e	0	2	2	e	6	1 745.85650	-3	2	0	2	f	2	1	1	IIff	15	1 750.59643	-9
2	0	0	e	2	1	1	Ie	6	1 745.96416	-13	0	1	1	e	0	2	2	e	8	1 750.71820	-8
1	0	1	e	1	1	0	e	12	1 746.13024 i	1	2	0	0	e	2	1	1	Ie	8	1 750.73187	8
2	0	0	e	2	1	1	IIe	15	1 746.19695	-2	1	0	1	f	1	1	0	f	9	1 750.86578 i	-4
1	0	1	f	1	1	0	f	7	1 746.28041 i	25	1	0	1	e	1	1	0	e	14	1 750.95410 i	-104*
1	0	1	f	1	1	2	f	6	1 746.37249 i	-8	1	0	1	f	1	1	2	f	8	1 750.95410 i	91
0	1	1	e	0	2	0	e	10	1 746.41479	1	1	1	2	e	1	2	1	IIe	19	1 751.03625	-1
1	1	0	f	1	2	1	If	8	1 746.47594	0	0	0	0	e	0	1	1	e	9	1 751.16431 i	7
0	0	0	e	0	1	1	e	7	1 746.58251 i	-16	1	1	0	f	1	2	1	If	10	1 751.19128	-10
1	0	1	e	1	1	2	e	6	1 746.58715 i	-95	0	1	1	f	0	2	2	f	9	1 751.26733 i	8
1	1	2	f	1	2	1	If	9	1 746.60393	4	0	1	1	e	0	2	0	e	12	1 751.31348	1
1	1	2	e	1	2	1	IIe	17	1 746.61028	84	1	1	2	f	1	2	1	If	11	1 751.32764	-56
0	1	1	f	0	2	2	f	7	1 746.67541 i	13	1	0	1	e	1	1	2	e	8	1 751.32764 i	82
2	0	2	e	2	1	1	IIe	14	1 746.75719	0	2	0	2	e	2	1	1	IIe	16	1 751.61377	-25
0	1	1	e	0	2	2	e	7	1 746.93731 i	2	0	1	1	e	0	2	2	e	9	1 751.69660 i	5
1	1	0	f	1	2	1	IIff	15	1 747.01928	9	1	1	2	e	1	2	1	Ie	11	1 751.95123	-5
1	1	2	e	1	2	1	Ie	9	1 747.05084	30	0	1	1	e	0	2	0	e	13	1 752.00574 i	-3
0	1	1	e	0	2	0	e	11	1 747.22118 i	-4	1	1	0	e	1	2	1	Ie	5	1 752.04315	-4
1	1	0	e	1	2	1	Ie	3	1 747.23822	-14	2	0	2	f	2	1	3	f	7	1 752.12543	-9
2	0	2	f	2	1	3	f	5	1 747.35314	-8	2	0	2	f	2	1	1	If	8	1 752.17499	90
2	0	2	e	2	1	3	e	5	1 747.36718	-21	2	0	2	e	2	1	3	e	7	1 752.17499	-22
1	1	2	f	1	2	1	IIff	16	1 747.40685	-1211*	1	1	0	f	1	2	1	IIff	17	1 752.20905	1
1	0	1	f	1	1	2	f	6	1 747.59405	4	1	0	1	f	1	1	2	f	8	1 752.28949	-2
2	0	2	e	2	1	1	Ie	6	1 747.62078	-29	1	1	0	e	1	2	1	IIe	13	1 752.32794	-18
1	0	1	f	1	1	0	f	7	1 747.70849	-2	1	0	1	f	1	1	0	f	9	1 752.40930	0
1	1	0	e	1	2	1	IIe	11	1 747.73779	-18	2	0	0	e	2	1	1	IIe	18	1 752.57349	13
1	0	1	e	1	1	0	e	12	1 747.80261	2	0	2	0	e	0	3	1	e	13	1 752.60700	-2
1	0	1	e	1	1	2	e	6	1 747.81844	-33	0	0	0	e	0	1	1	e	9	1 752.65796	-3
0	0	0	e	0	1	1	e	7	1 747.96240	0	1	0	1	e	1	1	2	e	8	1 752.67963	24
1	1	2	f	1	2	3	f	6	1 747.99011	-76	0	1	1	f	0	2	2	f	9	1 752.71375	2
0	2	0	e	0	3	1	e	11	1 748.00366	-184*	1	0	1	e	1	1	0	e	14	1 752.75153	3
0	1	1	f	0	2	2	f	7	1 748.00689	-5	1	1	2	e	1	2	3	e	8	1 752.76013	-4
2	0	2	f	2	1	1	IIff	14	1 748.05407	-15	1	1	2	f	1	2	3	f	8	1 752.76904	8
0	2	2	e	0	3	3	e	7	1 748.17095	-1	0	2	2	e	0	3	3	e	9	1 752.95221	-5
0	2	2	f	0	3	3	f	7	1 748.17883	34	0	2	2	f	0	3	3	f	9	1 752.97211	-6
0	1	1	e	0	2	2	e	7	1 748.28216	-5	2	0	0	e	2	1	1	Ie	9	1 753.10541	-103
2	0	0	e	2	1	1	IIe	16	1 748.34252	-21	2	0	2	f	2	1	1	IIff	16	1 753.14655	-39
2	0	0	e	2	1	1	Ie	7	1 748.35034	-4	0	2	2	f	0	3	1	f	16	1 753.14655	85
1	0	1	e	1	1	0	e	13	1 748.54016 i	7	1	0	1	f	1	1	0	f	10	1 753.15613 i	-36
1	0	1	f	1	1	0	f	8	1 748.57366 i	-3	0	1	1	e	0	2	2	e	9	1 753.16522	1
1	0	1	f	1	1	2	f	7	1 748.66369 i	-8	1	1	2	e	1	2	1	IIe	20	1 753.22657	-41
1	1	0	f	1	2	1	If	9	1 748.83374	-11	1	0	1	f	1	1	2	f	9	1 753.24073 i	-6
0	1	1	e	0	2	0	e	11	1 748.86193	3	1	0	1	e	1	1	0	e	15	1 753.37482 i	3
0	0	0	e	0	1	1	e	8	1 748.87390 i	3	0	0	0	e	0	1	1	e	10	1 753.45380 i	5
1	0	1	e	1	1	2	e	7	1 748.95263 i	-4	1	1	0	f	1	2	1	If	11	1 753.54853	0

lower level						upper level						$J \Delta J$	ν_{obs}	O-C
v_4	v_5	ℓ	v_4	v_5	ℓ	v_4	v_5	ℓ	v_4	v_5	ℓ			
0	1	1	f	0	2	2	f	10	1	753.56116	i	-28		
1	1	2	f	1	2	1	If	12	1	753.69025		-9		
1	0	1	e	1	1	2	e	9	1	753.71082	i	-2		
0	1	1	e	0	2	0	e	13	1	753.76874		1		
2	0	2	e	2	1	1	He	17	1	754.05207		-8		
0	1	1	e	0	2	2	e	10	1	754.09192	i	6		
0	1	1	e	0	2	0	e	14	1	754.40271	i	-12		
1	1	2	e	1	2	1	Ie	12	1	754.41034		5		
1	1	0	e	1	2	1	Ie	6	1	754.45734		-4		
2	0	2	f	2	1	3	f	8	1	754.51917		-32		
2	0	2	f	2	1	1	If	9	1	754.54108		-2		
2	0	2	e	2	1	3	e	8	1	754.60004		-22		
1	1	0	e	1	2	1	He	14	1	754.61744		-8		
1	0	1	f	1	1	2	f	9	1	754.63471		7		
2	0	0	e	2	1	1	He	19	1	754.65815		3		
1	0	1	f	1	1	0	f	10	1	754.75764		0		
1	1	0	f	1	2	1	If	18	1	754.81946		14		
0	2	0	e	0	3	1	e	14	1	754.90363		-20		
0	0	0	e	0	1	1	e	10	1	755.00458		-1		
0	1	1	f	0	2	2	f	10	1	755.06537		-3		
1	0	1	e	1	1	2	e	9	1	755.12537		8		
1	1	2	e	1	2	3	e	9	1	755.14991		9		
1	1	2	f	1	2	3	f	9	1	755.16370		2		
1	0	1	e	1	1	0	e	15	1	755.23334		8		
0	2	2	e	0	3	3	e	10	1	755.34553		-5		
0	2	2	f	0	3	3	f	10	1	755.37556		-2		
1	1	2	e	1	2	1	He	21	1	755.40119		-10		
1	0	1	f	1	1	0	f	11	1	755.44562	i	-6		
2	0	0	e	2	1	1	Ie	10	1	755.47248		-8		
1	0	1	f	1	1	2	f	10	1	755.52650	i	-5		
0	1	1	e	0	2	2	e	10	1	755.62354		2		
2	0	2	f	2	1	1	If	17	1	755.70515		30		
0	0	0	e	0	1	1	e	11	1	755.74244	i	8		
0	2	2	f	0	3	1	f	17	1	755.74244		72		
1	0	1	e	1	1	0	e	16	1	755.79847	i	7		
0	1	1	f	0	2	2	f	11	1	755.85444	i	5		
1	1	0	f	1	2	1	If	12	1	755.90498		-29		
1	1	2	f	1	2	1	If	13	1	756.05238		-6		
1	0	1	e	1	1	2	e	10	1	756.10599	i	92		
0	1	1	e	0	2	0	e	14	1	756.22694		5		
0	1	1	e	0	2	2	e	11	1	756.49708	i	-122*		
0	1	1	e	0	2	0	e	15	1	756.80213	i	4		
1	1	2	e	1	2	1	Ie	13	1	756.87446		9		
1	1	0	e	1	2	1	Ie	7	1	756.88093		122*		
1	1	0	e	1	2	1	He	15	1	756.90357		7		
2	0	2	f	2	1	1	If	10	1	756.91023		207*		
2	0	2	f	2	1	3	f	9	1	756.91828		-24		
1	0	1	f	1	1	2	f	10	1	756.97798		0		
2	0	2	e	2	1	3	e	9	1	757.04243		-1		
1	0	1	f	1	1	0	f	11	1	757.10450		-3		
0	2	0	e	0	3	1	e	15	1	757.19844		-13		
0	0	0	e	0	1	1	e	11	1	757.35035		0		
0	1	1	f	0	2	2	f	11	1	757.41584		-3		
1	1	2	e	1	2	3	e	10	1	757.54151		1		
1	1	2	f	1	2	3	f	10	1	757.56208		-30		
1	0	1	e	1	1	2	e	10	1	757.58210		2		
1	0	1	e	1	1	0	e	16	1	757.71907		7		
1	0	1	f	1	1	0	f	12	1	757.73341	i	9		
0	2	2	e	0	3	3	e	11	1	757.74049		35		
0	2	2	f	0	3	3	f	11	1	757.78364		-4		
1	0	1	f	1	1	2	f	11	1	757.81037	i	-7		
2	0	0	e	2	1	1	Ie	11	1	757.82887		6		
0	0	0	e	0	1	1	e	12	1	758.03010	i	7		
0	1	1	e	0	2	2	e	11	1	758.09382		3		
0	1	1	f	0	2	2	f	12	1	758.14582	i	-22		
1	0	1	e	1	1	0	e	17	1	758.22541	i	7		
1	1	0	f	1	2	1	If	13	1	758.26149		-11		
2	0	2	f	2	1	1	If	18	1	758.26967		8		
0	2	2	f	0	3	1	f	18	1	758.34706		30		
1	1	2	f	1	2	1	If	14	1	758.41438		-8		
1	0	1	e	1	1	2	e	11	1	758.50984	i	-3		
0	1	1	e	0	2	0	e	15	1	758.68721		5		
2	0	0	e	2	1	1	He	21	1	758.76576		-15		
0	1	1	e	0	2	2	e	12	1	758.91646	i	4		
2	0	2	e	2	1	1	He	19	1	758.94362		-8		
1	1	0	e	1	2	1	He	16	1	759.18629		-10		
2	0	1	e	0	2	0	e	16	1	759.20277	i	-3		
2	0	2	f	2	1	1	If	11	1	759.27382		-18		
1	1	0	e	1	2	1	Ie	8	1	759.31080		38		
1	0	1	f	1	1	2	f	11	1	759.31978		29		
2	0	2	f	2	1	3	f	10	1	759.32387		-22		
1	1	2	e	1	2	1	Ie	14	1	759.34279		-17		
1	0	1	f	1	1	0	f	12	1	759.44990		-4		
0	2	0	e	0	3	1	e	16	1	759.49177		4		
2	0	2	e	2	1	3	e	10	1	759.50368		2		
0	0	0	e	0	1	1	e	12	1	759.69520		-2		
0	1	1	f	0	2	2	f	12	1	759.76497		-12		
1	1	2	e	1	2	3	e	11	1	759.93501		8		
1	1	2	f	1	2	3	f	11	1	759.96529		6		
1	0	1	f	1	1	0	f	13	1	760.01936	i	-1		
1	0	1	e	1	1	2	e	11	1	760.05019		6		
1	0	1	f	1	1	2	f	12	1	760.09236	i	-6		
0	2	2	e	0	3	3	e	12	1	760.13545		-7		
2	0	0	e	2	1	1	Ie	12	1	760.17421		-9		
0	2	2	f	0	3	3	f	12	1	760.19643		-33		
1	0	1	e	1	1	0	e	17	1	760.20808		7		
0	0	0	e	0	1	1	e	13	1	760.31679	i	7		
2	0	1	f	0	2	2	f	13	1	760.43636	i	-1		
0	1	1	e	0	2	2	e	12	1	760.57668		5		
1	1	0	f	1	2	1	If	14	1	760.61751		1		
1	0	1	e	1	1	0	e	18	1	760.65492	i	-2		
1	1	2	f	1	2	1	If	15	1	760.77632		-5		
2	0	0	e	2	1	1	He	22	1	760.78841		-18		
2	0	2	f	2	1	1	If	19	1	760.84065		19		
1	0	1	e	1	1	2	e	12	1	760.92556	i	-8		
0	2	2	f	0	3	1	f	19	1	760.96046		36		
0	1	1	e	0	2	0	e	16	1	761.14876		6		
0	1	1	e	0	2	2	e	13	1	761.34688	i	8		
2	0	2	e	2	1	1	He	20	1	761.39540		-11		
1	1	0	e	1	2	1	He	17	1	761.46645		-6		
0	1	1	e	0	2	0	e	17	1	761.60420	i	0		
2	0	2	f	2	1	1	If	12	1	761.63851		-4		
1	0	1	f	1	1	2	f	12	1	761.65908		-6		
2	0	2	f	2	1	3	f	11	1	761.73659		9		
1	1	0	e	1	2	1	Ie	9	1	761.74971		-11		
0	2	0	e	0	3	1	e	17	1	761.78371		-4		
1	0	1	f	1	1	0	f	13	1	761.79378		-2		
1	1	2	e	1	2	1	He	24	1	761.81557		-52		
1	1	2	e	1	2	1	Ie	15	1	761.81557		10		
2	0	2	e	2	1	3	e	11	1	761.98531		-16		
0	0	0	e	0	1	1	e	13	1	762.03941		25		
0	1	1	f	0	2	2	f	13	1	762.11299		-3		
1	0	1	f	1	1	0	f	14	1	762.30379	i	1		
1	1	2	e	1	2	3	e	12	1	762.32973		-6		
1	1	2	f	1</										

lower level										upper level										lower level										upper level									
v_4	v_5	ℓ	v_4	v_5	ℓ	J	ΔJ	ν_{obs}	O-C	v_4	v_5	ℓ	v_4	v_5	ℓ	J	ΔJ	ν_{obs}	O-C	v_4	v_5	ℓ	v_4	v_5	ℓ	J	ΔJ	ν_{obs}	O-C										
1	1	0	f	1	2	1	If	15	1	762.97280	-17	1	0	1	e	1	1	0	e	21	1	767.95258	i	-30	1	1	0	f	1	2	1	If	23	1	767.99966	-42			
0	1	1	e	0	2	2	e	13	1	763.07271	3	1	1	0	f	1	2	1	If	23	1	768.05063	120*	1	1	2	e	1	2	1	If	27	1	768.10721	4				
1	0	1	e	1	1	0	e	19	1	763.08675	i	23	1	1	2	e	1	2	1	If	27	1	768.24313	i	-12	0	1	1	e	0	2	2	e	15	1	768.29373	-8		
1	0	1	e	1	1	2	e	13	1	763.35268	i	-13	0	1	1	e	0	2	2	e	15	1	768.53299	9	2	0	2	f	2	1	1	If	20	1	768.58243	-3			
0	2	2	f	2	1	1	If	20	1	763.41671	-4	1	0	1	e	1	1	2	e	15	1	768.65713	-52	0	2	2	f	0	3	1	f	20	1	768.71811	-262*				
0	2	2	f	0	3	1	f	20	1	763.58120	27	1	1	0	e	1	2	1	If	20	1	768.80472	i	-29	0	1	1	e	0	2	0	e	19	1	768.85156	1			
0	1	1	e	0	2	0	e	17	1	763.61080	10	0	1	1	e	0	2	0	e	19	1	768.88183	20	1	0	1	e	1	1	2	e	15	1	769.02158	8				
1	1	0	e	1	2	1	If	18	1	763.74422	1	2	0	2	f	2	1	1	If	22	1	769.06503	3	0	1	1	e	1	2	1	If	12	1	769.12375	2				
0	1	1	e	0	2	2	e	14	1	763.79012	i	4	0	2	0	e	0	3	1	e	20	1	769.14877	6	0	2	0	e	0	3	1	e	20	1	769.19308	10			
2	0	2	e	2	1	1	If	21	1	763.85018	-18	1	0	1	f	1	1	2	f	15	1	769.22232	-6	1	0	1	e	1	1	2	e	15	1	769.25009	0				
1	1	2	e	1	2	1	If	25	1	763.91347	-173*	2	0	2	f	2	1	1	If	15	1	769.26620	-19	1	0	1	e	1	1	2	e	15	1	769.29966	-42				
1	0	1	f	1	1	2	f	13	1	763.99685	-5	0	1	1	e	0	2	2	e	16	1	769.32778	-22	1	0	1	e	1	1	2	e	15	1	769.34908	11				
0	1	1	e	0	2	0	e	18	1	764.00619	i	67	2	0	2	e	2	1	1	If	22	1	769.36613	-33	0	1	1	e	0	2	0	e	18	1	769.38243	i	-124*		
0	2	0	e	0	3	1	e	18	1	764.07558	46	0	1	1	e	0	2	0	e	20	1	769.4131	9	1	0	1	e	1	1	2	e	15	1	769.44131	9				
1	0	1	f	1	1	0	f	14	1	764.13607	0	1	0	1	f	1	1	0	f	16	1	769.45297	i	7	2	0	2	f	2	1	3	f	12	1	769.48891	-7			
2	0	2	f	2	1	3	f	12	1	764.15639	-1	0	2	2	f	0	3	1	f	22	1	769.49972	-4	1	0	1	e	1	1	2	e	15	1	769.51943	i	3			
1	1	0	e	1	2	1	If	16	1	764.19820	-4	2	0	2	f	2	1	3	f	14	1	769.53669	i	19	1	0	1	e	1	1	2	e	15	1	769.55843	175*			
1	1	2	e	1	2	1	If	16	1	764.29120	-6	0	0	0	e	0	1	1	e	16	1	769.58243	i	-124*	1	0	1	e	1	1	2	e	15	1	769.60392	5			
0	0	0	e	0	1	1	e	14	1	764.38210	-3	1	1	0	e	1	2	1	If	16	1	769.62241	5	1	0	1	e	1	1	2	e	15	1	769.64701	0				
0	1	1	f	0	2	2	f	14	1	764.45956	-7	0	1	1	e	0	2	2	e	16	1	769.67151	-10	1	0	1	e	1	1	2	e	15	1	769.69978	15				
2	0	2	e	2	1	3	e	12	1	764.48891	-7	1	0	1	f	1	1	2	f	17	1	769.71512	-10	1	0	1	e	1	1	2	e	15	1	769.73404	i	-7			
1	0	1	f	1	1	0	f	15	1	764.58669	i	19	1	1	2	e	1	2	1	If	18	1	769.75009	0	1	0	1	e	1	1	2	e	15	1	769.76950	-20			
1	0	1	f	1	1	2	f	14	1	764.65054	i	-2	2	0	0	e	2	1	1	If	16	1	769.79177	i	-8	1	1	0	e	1	2	1	If	19	1	769.80472	i	-29	
1	1	2	e	1	2	3	e	13	1	764.72579	4	0	0	0	e	0	1	1	e	17	1	769.82243	i	-130*	1	0	1	e	1	1	2	e	15	1	769.84183	20			
1	1	2	f	1	2	3	f	13	1	764.78420	4	1	1	2	e	1	2	3	e	15	1	769.85156	1	2	0	2	f	2	1	3	f	12	1	769.88183	20				
2	0	0	e	2	1	1	If	14	1	764.83102	0	2	0	2	e	2	1	3	e	14	1	769.90392	-53	1	0	1	e	1	1	2	e	15	1	769.92666	-10				
0	0	0	e	0	1	1	e	15	1	764.88705	i	5	0	1	1	f	0	2	2	f	17	1	769.95258	i	-30	1	0	1	e	1	1	2	e	15	1	769.97783	15		
0	2	2	e	0	3	3	e	14	1	764.92666	-10	1	1	2	f	1	2	3	f	15	1	769.99783	15	1	0	1	e	1	1	2	e	15	1	770.01290	i	0			
0	1	1	f	0	2	2	f	15	1	765.01290	i	0	0	2	2	e	0	3	3	e	16	1	770.03969	20	1	0	1	e	1	1	2	e	15	1	770.06503	3			
1	0	1	e	1	1	2	e	13	1	765.02187	0	0	2	2	f	0	3	3	f	16	1	770.08304	9	1	0	1	e	1	1	2	e	15	1	770.10721	4				
0	2	2	f	0	3	3	f	14	1	765.03921	5	1	1	0	f	1	2	1	If	18	1	770.12375	2	1	0	1	e	1	1	2	e	15	1	770.14877	6				
1	0	1	e	1	1	0	e	19	1	765.19308	10	1	0	1	e	1	1	2	e	15	1	770.16922	16	1	0	1	e	1	1	2	e	15	1	770.19308	10				
1	1	0	f	1	2	1	If	16	1	765.32778	-22	1	1	2	e	1	2	1	If	18	1	770.22232	-6	1	0	1	e	1	1	2	e	15	1	770.24313	i	-12			
1	1	0	f	1	2	1	If	22	1	765.34908	11	1	0	1	e	1	1	0	e	21	1	770.25009	0	1	0	1	e	1	1	2	e	15	1	770.26620	-19				
1	1	2	f	1	2	1	If	17	1	765.49972	-4	1	1	2	f	1	2	1	If	19	1	770.28243	i	-130*	1	0	1	e	1	1	2	e	15	1	770.29966	-42			
1	0	1	e	1	1	0	e	20	1	765.51943	i	3	1	0	1	e	1	1	0	e	22	1	770.30472	i	-29	1	0	1	e	1	1	2	e	15	1	770.32778	-22		
0	1	1	e	0	2	2	e	14	1	765.58438	175*	1	1	0	e	1	2	1	If	21	1	770.34908	11	1	0	1	e	1	1	2	e	15	1	770.36613	-33				
1	0	1	e	1	1	2	e	14	1	765.79177	i	-8	0	1	1	e	0	2	2	e	16	1	770.38243	i	-124*	1	0	1	e	1	1	2	e	15	1	770.39966	-42		
2	0	2	f	2	1	1	If	21	1	765.99783	15	1	0	1	e	1	1	2	e	16	1	770.4131	9	1	0	1	e	1	1	2	e	15	1	770.4297	i	7			
1	1	0	e	1	2	1	If	19	1	766.01974	-11	0	2	0	e	0	3	1	e	21	1	770.44131	9	1	0	1	e	1	1	2	e	15	1	770.45297	i	7			
0	1	1	e	0	2	0	e	18	1	766.07241	5	0	1	1	e	0	2	0	e	20	1	770.46613	-33	1	0	1	e	1	1	2	e	15	1	770.48243	i	-124*			
0	2	2	f	0	3	1	f	21	1	766.20864	22	1	0	1	f	1	1	2	f	16	1	770.49972	-4	1	0	1	e	1	1	2	e	15	1	770.51943	i	3			
0	1	1	e	0	2	2	e	15	1	766.24691	i	2	2	0	2	f	2	1																					

lower level										upper level										lower level										upper level									
v_4	v_5	ℓ	v_4	v_5	ℓ	J	ΔJ	ν_{obs}	o-c	v_4	v_5	ℓ	v_4	v_5	ℓ	J	ΔJ	ν_{obs}	o-c	v_4	v_5	ℓ	v_4	v_5	ℓ	J	ΔJ	ν_{obs}	o-c										
0	1	1e	0	2	2e	17		1 773.20292	8	1	0	1f	1	1	0f	21		1 778.24419	i	-11	1	0	1f	1	1	2f	20		1 778.27641	i	0								
0	2	0e	0	3	1e	22		1 773.24241	-22	0	1	1e	0	2	0e	23		1 778.34959		0	0	1	1e	0	2	0e	24		1 778.37560	i	271*								
1	1	0f	1	2	1If	25		1 773.31876	-45	0	1	1e	0	2	0e	23		1 778.34959		0	1	0	1f	1	1	2f	17		1 773.32841		-8								
1	0	1f	1	1	2f	17		1 773.32841	-8	0	1	1e	0	2	0e	24		1 778.37560	i	271*	0	1	1e	0	2	0e	24		1 778.37560	i	271*								
0	1	1e	0	2	0e	21		1 773.44773	9	0	1	1e	0	2	0e	24		1 778.37560	i	271*	0	1	1e	0	2	0e	24		1 778.37560	i	271*								
1	0	1f	1	1	0f	18		1 773.48814	-2	0	0	0e	0	1	1e	20		1 778.41720		-10	0	0	0e	0	1	1e	20		1 778.41720		-10								
0	1	1e	0	2	0e	22		1 773.59586	i	12	0	1	1f	0	2	2f	20		1 778.50908		-11	0	1	1f	0	2	2f	20		1 778.50908		-11							
2	0	2e	2	1	1He	25		1 773.68650	-8	2	0	0e	2	1	1e	20		1 778.52733		15	2	0	0e	2	1	1e	20		1 778.52733		15								
1	0	1f	1	1	0f	19		1 773.69950	i	11	0	0	0e	0	1	1e	21		1 778.57063	i	35	1	0	1f	1	1	0f	19		1 773.69950	i	11							
0	1	1e	0	2	2e	18		1 773.70560	i	55	2	0	2e	2	1	1He	27		1 778.60625		-5	2	0	2e	2	1	1He	27		1 778.60625		-5							
0	0	0e	0	1	1e	18		1 773.74351	1	1	1	0f	1	2	1If	27		1 778.65489		0	1	1	0f	1	2	1If	27		1 778.65489		0								
1	0	1f	1	1	2f	18		1 773.75968	i	1693*	0	1	1f	0	2	2f	21		1 778.70671	i	1	0	1	1f	0	2	2f	21		1 778.70671	i	1							
0	1	1f	0	2	2f	18		1 773.83195	-5	0	1	1e	0	2	2e	20		1 778.75670	i	6	0	1	1e	0	2	2e	20		1 778.75670	i	6								
2	0	2f	2	1	3f	16		1 773.92527	8	2	0	2f	2	1	3f	18		1 778.87364		20	2	0	2f	2	1	3f	18		1 778.87364		20								
2	0	0e	2	1	1e	18		1 774.00553	-29	2	0	2f	2	1	1If	26		1 778.94335		3	2	0	2f	2	1	1If	26		1 778.94335		3								
0	0	0e	0	1	1e	19		1 774.01414	i	4	1	1	0e	1	2	1e	16		1 779.10234		-4	1	1	0e	1	2	1e	16		1 779.10234		-4							
1	1	2e	1	2	1He	30		1 774.07859	-64	1	1	2e	1	2	3e	19		1 779.10234		-3	1	1	2e	1	2	3e	19		1 779.10234		-3								
1	1	0e	1	2	1e	14		1 774.09037	-4	1	1	2e	1	2	1e	22		1 779.17739		8	1	1	2e	1	2	1e	22		1 779.17739		8								
0	2	2f	0	3	1f	24		1 774.12162	34	0	2	2e	0	3	3e	20		1 779.26628		-18	0	2	2e	0	3	3e	20		1 779.26628		-18								
0	1	1f	0	2	2f	19		1 774.14835	i	-2	1	1	2f	1	2	3f	19		1 779.36650		-4	0	1	1f	0	2	2f	19		1 774.14835	i	-2							
1	1	2e	1	2	1e	20		1 774.21397	-1	0	2	2f	0	3	1f	26		1 779.41124		-2	1	1	2e	1	2	1e	20		1 774.21397		-1								
1	1	2e	1	2	3e	17		1 774.31303	19	1	1	0f	1	2	1If	22		1 779.44908		-5	1	1	2e	1	2	3e	17		1 774.31303		19								
1	1	2f	1	2	3f	17		1 774.48222	3	1	1	0e	1	2	1He	25		1 779.65129		-4	1	1	2f	1	2	3f	17		1 774.48222		3								
0	2	2e	0	3	3e	18		1 774.49644	-12	1	1	2f	1	2	1If	23		1 779.66448		0	0	2	2e	0	3	3e	18		1 774.49644		-12								
2	0	2e	2	1	3e	16		1 774.73228	15	0	2	2f	0	3	3f	20		1 779.72801		-6	2	0	2e	2	1	3e	16		1 774.73228		15								
1	1	0f	1	2	1If	20		1 774.74369	-9	2	0	2e	2	1	3e	18		1 779.99480		-3	1	1	0f	1	2	1If	20		1 774.74369		-9								
0	2	2f	0	3	3f	18		1 774.80052	-7	1	0	1e	1	1	0e	26		1 780.10558	i	-35	0	2	2f	0	3	3f	18		1 774.80052		-7								
1	1	2f	1	2	1If	21		1 774.94407	5	0	2	0e	0	3	1e	25		1 780.13005		-17	1	1	2f	1	2	1If	21		1 774.94407		5								
1	1	0e	1	2	1He	23		1 775.10990	57	1	0	1e	1	1	0e	25		1 780.15123		6	1	1	0e	1	2	1He	23		1 775.10990		57								
1	0	1e	1	1	2e	17		1 775.12223	3	1	0	1e	1	1	2e	19		1 780.25988		-1	1	0	1e	1	1	2e	17		1 775.12223		3								
1	0	1e	1	1	0e	23		1 775.17033	6	1	0	1f	1	1	2f	20		1 780.30583		-15	1	0	1e	1	1	0e	23		1 775.17033		6								
1	0	1e	1	1	0e	24		1 775.25010	i	-8	1	0	1f	1	1	0f	21		1 780.48278		-1	1	0	1e	1	1	0e	24		1 775.25010	i	-8							
0	2	0e	0	3	1e	23		1 775.53648	-41	1	0	1f	1	1	0f	22		1 780.51366	i	0	0	2	0e	0	3	1e	23		1 775.53648		-41								
1	0	1f	1	1	2f	18		1 775.65629	-9	1	0	1f	1	1	2f	21		1 780.53997	i	-8	1	0	1f	1	1	2f	18		1 775.65629		-9								
0	1	1e	0	2	2e	18		1 775.77543	5	1	0	1e	1	1	2e	20		1 780.70427	i	2	0	1	1e	0	2	2e	18		1 775.77543		5								
2	0	2f	2	1	1If	18		1 775.77549	-314*	0	0	0e	0	1	1e	21		1 780.75237		4	2	0	2f	2	1	1If	18		1 775.77549		-314*								
1	0	1f	1	1	0f	19		1 775.82170	5	0	1	1e	0	2	0e	25		1 780.75707	i	194*	1	0	1f	1	1	0f	19		1 775.82170		5								
0	1	1e	0	2	0e	22		1 775.90055	4	2	0	0e	2	1	1e	21		1 780.77242		-33	0	1	1e	0	2	0e	22		1 775.90055		4								
1	0	1f	1	1	0f	20		1 775.97282	i	-3	0	1	1e	0	2	0e	24		1 780.79436		-1	1	0	1f	1	1	0f	20		1 775.97282	i	-3							
0	1	1e	0	2	0e	23		1 775.98625	i	-2	0	1	1f	0	2	2f	21		1 780.84563		24	0	1	1e	0	2	0e	23		1 775.98625	i	-2							
1	0	1f	1	1	2f	19		1 776.01072	i	8	0	0	0e	0	1	1e	22		1 780.84563		-76	1	0	1f	1	1	2f	19		1 776.01072	i	8							
0	0	0e	0	1	1e	19		1 776.08104	3	0	1	1e	0	2	2e	20		1 780.97326		13	0	0	0e	0	1	1e	19		1 776.08104		3								
2	0	2e	2	1	1He	26		1 776.14665	-12	0	1	1f	0	2	2f	22		1 780.98351	i	14	2	0	2e	2	1	1He	26		1 776.14665		-12								
0	1	1f	0	2	2f	19		1 776.17131	-7	0	1	1e	0	2	2e	21		1 781.30801	i	-7	0	1	1f	0	2	2f	19		1 776.17131		-7								
0	1	1e	0	2	2e	19		1 776.22251	i	2	2	0	2f	2	1	3f	19		1 781.36626		11	0	1	1e	0	2	2e	19		1 776.22251	i	2							
2	0	0e	2	1	1e	19		1 776.27171	1	1	1	2e	1	2	3e	20		1 781.																					

lower level						upper level						$J \Delta J$	ν_{obs}	O-C
ν_4	ν_5	ℓ	ν_4	ν_5	ℓ	ν_4	ν_5	ℓ	ν_4	ν_5	ℓ			
0 0 0 e	0 1 1 e	23	1 783.12121 i	8		1 1 0 e	1 2 1 He	29	1 788.74256	-1				
0 1 1 e	0 2 0 e	26	1 783.13250 i	-12		0 2 2 e	0 3 3 e	24	1 788.75690	5				
0 1 1 f	0 2 2 f	22	1 783.17986	-8		1 1 0 f	1 2 1 If	26	1 788.85529	4				
0 1 1 e	0 2 0 e	25	1 783.23443	1		0 1 1 e	0 2 2 e	23	1 788.91022	11				
1 0 1 e	1 1 2 e	21	1 783.24157 i	40		2 0 2 f	2 1 3 f	22	1 788.92749	8				
0 1 1 f	0 2 2 f	23	1 783.25829 i	-5		0 1 1 e	0 2 2 e	24	1 789.07068 i	-18				
2 0 2 e	2 1 1 He	29	1 783.52148	8		1 1 2 e	1 2 1 Ie	26	1 789.08032	25				
0 1 1 e	0 2 2 e	21	1 783.59973	17		1 1 2 f	1 2 1 If	27	1 789.10102	1				
2 0 2 f	2 1 3 f	20	1 783.87255	32		1 1 2 f	1 2 3 f	23	1 789.22351	-4				
0 1 1 e	0 2 2 e	22	1 783.87866 i	136*		1 1 0 e	1 2 1 Ie	20	1 789.28107	26				
1 1 2 e	1 2 3 e	21	1 783.88446	20		1 1 0 f	1 2 1 If	31	1 789.33930	-413*				
1 1 0 f	1 2 1 If	29	1 783.99713	-205*		0 2 0 e	0 3 1 e	29	1 789.33930	3				
0 2 2 e	0 3 3 e	22	1 784.02093	-6		1 0 1 f	1 1 0 f	26	1 789.57300 i	381*				
2 0 2 f	2 1 1 If	28	1 784.12463	1		1 0 1 f	1 1 2 f	25	1 789.57300 i	14				
1 1 2 e	1 2 1 Ie	24	1 784.13458	12		1 0 1 f	1 1 2 f	24	1 789.57972	-7				
1 1 0 f	1 2 1 If	24	1 784.15289	-2		2 0 0 e	2 1 1 Ie	25	1 789.66761	4				
1 1 0 e	1 2 1 Ie	18	1 784.16418	-3		0 2 2 f	0 3 3 f	24	1 789.70453	0				
1 1 0 e	1 2 1 He	27	1 784.19506	2		1 0 1 e	1 1 0 e	30	1 789.77369 i	-119*				
1 1 2 f	1 2 3 f	21	1 784.27899	6		1 0 1 f	1 1 0 f	25	1 789.77991	-10				
1 1 2 f	1 2 1 If	25	1 784.38342	-13		0 0 0 e	0 1 1 e	26	1 789.93671 i	1				
0 2 2 f	0 3 3 f	22	1 784.69378	-8		0 2 2 f	0 3 1 f	30	1 789.98298	-65				
0 2 2 f	0 3 1 e	28	1 784.70178	-31		0 0 0 e	0 1 1 e	25	1 790.07905	1				
0 2 0 e	0 3 1 e	27	1 784.73089	-2		0 1 1 f	0 2 2 f	25	1 790.17322	-10				
1 0 1 f	1 1 2 f	22	1 784.94708	-9		0 1 1 e	0 2 0 e	29	1 790.23365 i	-7				
1 0 1 f	1 1 0 f	24	1 785.04583 i	-11		0 1 1 e	0 2 0 e	28	1 790.52277	-15				
1 0 1 f	1 1 2 f	23	1 785.06091 i	7		1 0 1 e	1 1 2 e	23	1 790.73456	8				
1 0 1 e	1 1 0 e	27	1 785.11993	-3		2 0 2 e	2 1 3 e	22	1 790.80256	-7				
1 0 1 f	1 1 0 f	23	1 785.13574	-1		2 0 2 e	2 1 1 He	32	1 790.87745	-9				
2 0 0 e	2 1 1 Ie	23	1 785.23639	0		1 0 1 e	1 1 2 e	24	1 790.95148 i	-4				
2 0 2 e	2 1 3 e	20	1 785.35211	6		1 1 0 e	1 2 1 He	30	1 791.01832	6				
0 0 0 e	0 1 1 e	24	1 785.39447 i	2		1 1 2 e	1 2 3 e	24	1 791.03443	-3				
0 0 0 e	0 1 1 e	23	1 785.41845	0		0 2 2 e	0 3 3 e	25	1 791.11689	-11				
1 0 1 e	1 1 2 e	21	1 785.46240	3		1 1 0 f	1 2 1 If	27	1 791.20594	2				
0 1 1 e	0 2 0 e	27	1 785.50464 i	-40		1 1 2 f	1 2 1 If	28	1 791.45917	11				
0 1 1 f	0 2 2 f	23	1 785.51269	-12		2 0 2 f	2 1 3 f	23	1 791.47803	8				
0 1 1 f	0 2 2 f	24	1 785.53161 i	5		1 1 2 e	1 2 1 Ie	27	1 791.54688	-12				
0 1 1 e	0 2 0 e	26	1 785.66931	-7		0 1 1 e	0 2 2 e	24	1 791.59522	17				
1 0 1 e	1 1 2 e	22	1 785.79431 i	-2		0 2 0 e	0 3 1 e	30	1 791.64668	51				
2 0 2 e	2 1 1 He	30	1 785.97601	-5		0 1 1 e	0 2 2 e	25	1 791.69599 i	7				
0 1 1 e	0 2 2 e	22	1 786.24518	11		1 1 2 f	1 2 3 f	24	1 791.70936	-10				
1 1 2 e	1 2 3 e	22	1 786.27112	-3		1 0 1 f	1 1 0 f	27	1 791.82594 i	-133*				
0 2 2 e	0 3 3 e	23	1 786.39178	35		1 0 1 f	1 1 2 f	26	1 791.82594 i	41				
1 1 0 e	1 2 1 He	28	1 786.46734	-88		1 1 0 e	1 2 1 Ie	21	1 791.86091	-34				
1 1 0 f	1 2 1 If	25	1 786.50427	2		2 0 0 e	2 1 1 Ie	26	1 791.87263	1				
1 1 2 e	1 2 1 Ie	25	1 786.60895	-7		1 0 1 f	1 1 2 f	25	1 791.89271	-13				
2 0 2 f	2 1 1 If	29	1 786.71319	78		1 0 1 f	1 1 0 f	26	1 792.09858	-13				
1 1 2 f	1 2 3 f	22	1 786.74658	-34		1 0 1 e	1 1 0 e	31	1 792.17964 i	-85				
0 2 0 e	0 3 1 e	28	1 787.03412	-2		0 0 0 e	0 1 1 e	27	1 792.20558 i	4				
0 2 2 f	0 3 3 f	23	1 787.19318	5		0 2 2 f	0 3 3 f	25	1 792.22895	-6				
1 0 1 f	1 1 2 f	23	1 787.26434	-23		0 1 1 f	0 2 2 f	27	1 792.34034 i	0				
1 0 1 f	1 1 0 f	25	1 787.30811 i	-61		0 0 0 e	0 1 1 e	26	1 792.40711	-4				
1 0 1 f	1 1 2 f	24	1 787.31799 i	4		0 1 1 f	0 2 2 f	26	1 792.50092	4				
0 2 2 f	0 3 1 f	29	1 787.34387	-80		1 0 1 e	1 1 0 e	30	1 792.54078	-14				
1 0 1 e	1 1 0 e	29	1 787.36450 i	30		0 1 1 e	0 2 0 e	30	1 792.58967 i	0				
1 0 1 f	1 1 0 f	24	1 787.45889	-11		0 1 1 e	0 2 0 e	29	1 792.94099	-14				
1 0 1 e	1 1 0 e	28	1 787.59839	0		1 1 0 e	1 2 1 He	31	1 793.29554	11				
0 0 0 e	0 1 1 e	25	1 787.66638 i	6		2 0 2 e	2 1 1 He	33	1 793.32374	12				
0 0 0 e	0 1 1 e	24	1 787.74945	-1		1 0 1 e	1 1 2 e	24	1 793.39808	1				
0 1 1 f	0 2 2 f	25	1 787.80292 i	-7		1 1 2 e	1 2 3 e	25	1 793.40998	0				
0 1 1 f	0 2 2 f	24	1 787.84387	-8		1 1 0 f	1 2 1 If	28	1 793.55647	17				
0 1 1 e	0 2 0 e	28	1 787.87207 i	-7		1 0 1 e	1 1 2 e	25	1 793.55647 i	-14				
2 0 2 e	2 1 3 e	21	1 788.06574	-5		2 0 2 e	2 1 3 e	23	1 793.56251	23				
1 0 1 e	1 1 2 e	22	1 788.08954	11		1 1 2 f	1 2 1 If	29	1 793.81660	-1				
0 1 1 e	0 2 0 e	27	1 788.09900	5		0 2 0 e	0 3 1 e	31	1 793.95478	5				
1 0 1 e	1 1 2 e	23	1 788.36408 i	-19		1 1 2 e	1 2 1 Ie	28	1 794.00911	-15				
2 0 2 e	2 1 1 He	31	1 788.42822	-2		2 0 2 f	2 1 3 f	24	1 794.04487	13				
1 1 2 e	1 2 3 e	23	1 788.65467	-3		2 0 0 e	2 1 1 Ie	27	1 794.07191	42				

lower level						upper level						$J \Delta J$	ν_{obs}	O-C
ν_4	ν_5	ℓ	ν_4	ν_5	ℓ	ν_4	ν_5	ℓ	J	ΔJ	ν_{obs}			
1	0	1	f	1	1	2	f	27	1	794.07618	i	21		
1	0	1	f	1	1	0	f	28	1	794.08351	i	60		
1	0	1	f	1	1	2	f	26	1	794.20375		6		
0	1	1	e	0	2	2	e	25	1	794.30030		10		
0	1	1	e	0	2	2	e	26	1	794.34004	i	-16		
1	0	1	f	1	1	0	f	27	1	794.41498		-7		
0	0	0	e	0	1	1	e	28	1	794.47291	i	9		
1	0	1	e	1	1	0	e	32	1	794.58070	i	0		
0	1	1	f	0	2	2	f	28	1	794.60621	i	2		
0	0	0	e	0	1	1	e	27	1	794.73372		-3		
0	2	2	f	0	3	3	f	26	1	794.76759		-3		
0	1	1	f	0	2	2	f	27	1	794.82655		-5		
0	1	1	e	0	2	0	e	31	1	794.93995	i	7		
1	0	1	e	1	1	0	e	31	1	795.00410		-12		
0	1	1	e	0	2	0	e	30	1	795.35341		-8		
1	1	0	e	1	2	1	He	32	1	795.57417		2		
2	0	2	e	2	1	1	He	34	1	795.76625		9		
1	1	2	e	1	2	3	e	26	1	795.78090		5		
0	2	2	e	0	3	3	e	27	1	795.82063		-2		
1	1	0	f	1	2	1	If	29	1	795.90645		6		
1	0	1	e	1	1	2	e	25	1	796.08076		3		
1	1	2	f	1	2	1	If	30	1	796.17281		-82		
1	0	1	e	1	1	2	e	26	1	796.18050	i	50		
2	0	0	e	2	1	1	Ie	28	1	796.26491		9		
0	2	0	e	0	3	1	e	32	1	796.26491		16		
1	0	1	f	1	1	2	f	28	1	796.32423	i	8		
1	0	1	f	1	1	0	f	29	1	796.33601	i	-2		
2	0	2	e	2	1	3	e	24	1	796.34480		41		
1	1	2	e	1	2	1	Ie	29	1	796.46626		-8		
1	0	1	f	1	1	2	f	27	1	796.51228		-5		
1	1	2	f	1	2	3	e	26	1	796.71193		0		
1	0	1	f	1	1	0	f	28	1	796.72884		-10		
0	0	0	e	0	1	1	e	29	1	796.73842	i	-5		
0	1	1	f	0	2	2	f	29	1	796.87019	i	9		
1	0	1	e	1	1	0	e	33	1	796.97524	i	3		
0	1	1	e	0	2	2	e	27	1	797.00380	i	-9		
0	1	1	e	0	2	2	e	26	1	797.02590		11		
0	0	0	e	0	1	1	e	28	1	797.05879		-1		
0	1	1	f	0	2	2	f	28	1	797.15041		-2		
0	1	1	e	0	2	0	e	32	1	797.28438	i	5		
0	2	2	f	0	3	3	f	27	1	797.32143		1		
1	0	1	e	1	1	0	e	32	1	797.46163		-12		
0	1	1	e	0	2	0	e	31	1	797.75991		-4		
1	1	0	e	1	2	1	He	33	1	797.85445		-1		
1	1	2	e	1	2	3	e	27	1	798.14669		1		
0	2	2	e	0	3	3	e	28	1	798.16390		-3		
2	0	2	e	2	1	1	He	35	1	798.20491		4		
1	1	0	f	1	2	1	If	30	1	798.25624		2		
2	0	0	e	2	1	1	Ie	29	1	798.45339		22		
1	1	2	f	1	2	1	If	31	1	798.53011		5		
1	0	1	f	1	1	2	f	29	1	798.56984	i	-22		
0	2	0	e	0	3	1	e	33	1	798.57680		76		
1	0	1	f	1	1	0	f	30	1	798.58675	i	17		
1	0	1	e	1	1	2	e	26	1	798.78261		-34		
1	0	1	f	1	1	2	f	28	1	798.81889		15		
1	1	2	e	1	2	1	Ie	30	1	798.91750		-30		
0	0	0	e	0	1	1	e	30	1	799.00246	i	-2		
1	0	1	f	1	1	0	f	29	1	799.04036		3		
0	1	1	f	0	2	2	f	30	1	799.13210	i	8		
2	0	2	e	2	1	3	e	25	1	799.14852		-6		
1	1	2	f	1	2	3	f	27	1	799.23000		-1		
0	0	0	e	0	1	1	e	29	1	799.38222		-3		
0	1	1	f	0	2	2	f	29	1	799.47231		-1		
2	0	2	f	2	1	1	If	34	1	799.58925		-29		
0	1	1	e	0	2	0	e	33	1	799.62301	i	0		
0	1	1	e	0	2	2	e	28	1	799.68709	i	-2		
1	1	0	e	1	2	1	Ie	24	1	799.69857		-7		
0	1	1	e	0	2	2	e	27	1	799.77212		15		
0	2	2	f	0	3	3	f	28	1	799.89150		-4		
1	0	1	e	1	1	0	e	33	1	799.91311		-15		
1	0	1	e	1	1	0	e	34	1	799.97524	i	61146*		
1	1	0	e	1	2	1	He	34	1	800.13644		6		
0	1	1	e	0	2	0	e	32	1	800.16036		-14		
0	2	2	e	0	3	3	e	29	1	800.50130		-14		
1	1	2	e	1	2	3	e	28	1	800.50741		28		
1	1	0	f	1	2	1	If	31	1	800.60580		0		
2	0	2	e	2	1	1	He	36	1	800.63821		-126		
1	0	1	f	1	1	2	f	30	1	800.81368	i	0		
1	0	1	f	1	1	0	f	31	1	800.83443	i	-5		
1	1	2	f	1	2	1	If	32	1	800.88778		191*		
0	2	0	e	0	3	1	e	34	1	800.88778		-58		
1	0	1	f	1	1	2	f	29	1	801.12293		2		
0	0	0	e	0	1	1	e	31	1	801.26484	i	5		
1	0	1	f	1	1	0	f	30	1	801.34908		-5		
0	1	1	f	0	2	2	f	31	1	801.39144	i	-50		
1	0	1	e	1	1	2	e	28	1	801.48324	i	-16		
1	0	1	e	1	1	2	e	27	1	801.50533		16		
0	0	0	e	0	1	1	e	30	1	801.70407		0		
1	0	1	e	1	1	0	e	35	1	801.74648	i	28		
1	1	2	f	1	2	3	f	28	1	801.76046		3		
0	1	1	f	0	2	2	f	30	1	801.79226		1		
2	0	2	f	2	1	3	f	27	1	801.84963		1		
0	1	1	e	0	2	0	e	34	1	801.95614	i	19		
2	0	2	e	2	1	3	e	26	1	801.97433		-16		
1	0	1	e	1	1	0	e	34	1	802.35836		-16		
0	1	1	e	0	2	2	e	29	1	802.39004	i	12		
0	2	2	f	0	3	3	f	29	1	802.47909		-3		
0	1	1	e	0	2	2	e	28	1	802.53891		9		
0	1	1	e	0	2	0	e	33	1	802.55502		-15		
1	1	2	e	1	2	3	e	29	1	802.86197		10		
1	1	0	f	1	2	1	If	32	1	802.95517		2		
2	0	2	e	2	1	1	He	37	1	802.96973		0		
1	0	1	f	1	1	0	f	32	1	803.07980	i	14		
0	2	0	e	0	3	1	e	35	1	803.20181		33		
1	1	2	f	1	2	1	If	33	1	803.24075		-25		
1	0	1	f	1	1	2	f	30	1	803.42489		6		
0	0	0	e	0	1	1	e	32	1	803.52542	i	6		
1	0	1	f	0	2	2	f	32	1	803.64834	i	-146*		
1	0	1	f	1	1	0	f	31	1	803.65524		-4		
0	0	0	e	0	1	1	e	31	1	804.02420		0		
0	1	1	f	0	2	2	f	31	1	804.11014		-3		
1	0	1	e	1	1	0	e	36	1	804.12228	i	-5		
1	0	1	e	1	1	2	e	29	1	804.16409	i	-7		
1	0	1	e	1	1	2	e	28	1	804.24777		-1		
2	1	2	f	1	2	3	f	29	1	804.30404		-2		
2	0	2	f	2	1	3	f	28	1	804.48837		0		
1	0	1	e	1	1	0	e	35	1	804.79721		-15		
2	0	2	e	2	1	3	e	27	1	804.82150		-22		
0	1	1	e	0	2	0	e	34	1	804.94394		-8		
1	1	0	e	1	2	1	Ie	26	1	805.00937		-27		
0	2	2	f	0	3	3	f	30	1	805.08517		-14		
0	1	1	e	0	2	2	e	30	1	805.11227	i	-5		
1	1	2	e	1	2	3	e	30	1	805.21066		1		
1	0	1	f	1	1	2	f	32	1	805.29379	i	-26		
1	1	0	f	1	2	1	If	33	1	805.30435		8		
0	1	1	e	0	2	2	e	29	1	805.32639		2		
1	0	1	f	1	1	2	f	31	1	805.72458		9		
0	0	0	e	0	1	1	e	33	1	805.78421	i	5		
1	0	1	f	1	1	0	f	32	1	805.95871		1		
0	0	0	e	0										

lower level										upper level										J	ΔJ	ν_{obs}	O-C
ν_4	ν_5	ℓ	ν_4	ν_5	ℓ					ν_4	ν_5	ℓ											
2	0	2	f	2	1	3	f	29	1	807.14646	-35	1	0	1	e	1	1	0	e	41	1	819.29763	623*
1	0	1	e	1	1	0	e	36	1	807.22953	-14	1	0	1	f	1	1	2	f	37	1	819.47460	8
0	1	1	e	0	2	0	e	35	1	807.32706	-7	0	1	1	e	0	2	2	e	34	1	819.57116	-12
1	0	1	f	1	1	2	f	33	1	807.53086	i 9	1	0	1	f	1	1	0	f	38	1	819.71765	4
1	1	2	e	1	2	3	e	31	1	807.55326	2	0	0	0	e	0	1	1	e	38	1	820.21453	5
1	1	0	f	1	2	1	If	34	1	807.65299	-18	0	1	1	f	0	2	2	f	38	1	820.27612	13
1	1	2	f	1	2	1	If	35	1	807.94901	7	1	0	1	e	1	1	2	e	34	1	821.14685	4
1	0	1	f	1	1	2	f	32	1	808.02195	7	0	1	1	e	0	2	0	e	41	1	821.51147	9
0	0	0	e	0	1	1	e	34	1	808.04117	i 4	0	0	0	e	0	1	1	e	40	1	821.54266	i 10
0	1	1	e	0	2	2	e	30	1	808.13462	6	1	0	1	e	1	1	0	e	42	1	821.68390	5
0	1	1	f	0	2	2	f	34	1	808.15891	i -29	1	0	1	f	1	1	2	f	38	1	821.75824	9
1	0	1	f	1	1	0	f	33	1	808.25925	-6	1	0	1	f	1	1	0	f	39	1	821.99963	-13
0	0	0	e	0	1	1	e	33	1	808.65928	2	0	1	1	e	0	2	2	e	35	1	822.48503	454*
0	1	1	f	0	2	2	f	33	1	808.73984	2	0	0	0	e	0	1	1	e	39	1	822.51965	3
1	1	2	f	1	2	3	f	31	1	809.43467	-3	0	1	1	f	0	2	2	f	39	1	822.57654	14
1	0	1	e	1	1	2	e	31	1	809.58530	i -3	0	0	0	e	0	1	1	e	41	1	823.78565	i -2
1	0	1	e	1	1	0	e	37	1	809.65525	-10	0	1	1	e	0	2	0	e	42	1	823.85767	21
0	1	1	e	0	2	0	e	36	1	809.70451	-9	1	0	1	e	1	1	2	e	35	1	824.03870	11
1	0	1	f	1	1	2	f	34	1	809.76511	i -6	1	0	1	f	1	1	2	f	39	1	824.03870	-79*
0	2	2	e	0	3	3	e	33	1	809.78782	-698*	1	0	1	e	1	1	0	e	43	1	824.07007	28
1	0	1	e	1	1	2	e	30	1	809.79551	4	1	0	1	f	1	1	0	f	40	1	824.27875	21
2	0	2	f	2	1	3	f	30	1	809.82548	-8	0	0	0	e	0	1	1	e	40	1	824.82270	1
1	1	2	e	1	2	3	e	32	1	809.88944	-1	0	1	1	f	0	2	2	f	40	1	824.87451	7
1	1	0	f	1	2	1	If	35	1	810.00193	8	0	1	1	e	0	2	2	e	36	1	825.40900	-26
0	0	0	e	0	1	1	e	35	1	810.29630	i 4	0	0	0	e	0	1	1	e	42	1	826.02643	i -21
1	0	1	f	1	1	2	f	33	1	810.31706	7	0	1	1	e	0	2	0	e	43	1	826.19910	39
0	1	1	f	0	2	2	f	35	1	810.41111	i 44	1	0	1	f	1	1	2	f	40	1	826.31849	-2
1	0	1	f	1	1	0	f	34	1	810.55705	0	1	0	1	e	1	1	0	e	44	1	826.44971	41
0	1	1	e	0	2	2	e	31	1	810.96330	0	1	0	1	f	1	1	0	f	41	1	826.55359	-30
0	0	0	e	0	1	1	e	34	1	810.97410	1	1	0	1	e	1	1	2	e	36	1	826.95185	-10
0	1	1	f	0	2	2	f	34	1	811.05149	1	0	0	0	e	0	1	1	e	41	1	827.12366	1
1	1	2	f	1	2	3	f	32	1	812.02311	-57	0	1	1	f	0	2	2	f	41	1	827.17011	4
1	0	1	e	1	1	0	e	38	1	812.07573	136*	0	0	0	e	0	1	1	e	43	1	828.26539	i -3
0	1	1	e	0	2	0	e	37	1	812.07573	-81*	0	1	1	e	0	2	2	e	37	1	828.35700	-30
1	1	2	e	1	2	3	e	33	1	812.21904	-11	0	1	1	e	0	2	0	e	44	1	828.53599	75*
1	0	1	e	1	1	2	e	32	1	812.32609	i -11	1	0	1	f	1	1	2	f	41	1	828.59516	-7
0	0	0	e	0	1	1	e	36	1	812.54948	i 0	1	0	1	f	1	1	0	f	42	1	828.82472	-99*
1	0	1	e	1	1	2	e	31	1	812.60099	-8	1	0	1	e	1	1	0	e	45	1	828.82472	223*
1	0	1	f	1	1	2	f	34	1	812.60991	10	0	0	0	e	0	1	1	e	42	1	829.42245	0
0	1	1	f	0	2	2	f	36	1	812.66014	i 20	0	1	1	f	0	2	2	f	42	1	829.46308	-17
1	0	1	f	1	1	0	f	35	1	812.85179	-3	1	0	1	e	1	1	2	e	37	1	829.88667	-15
0	0	0	e	0	1	1	e	35	1	813.28709	1	0	0	0	e	0	1	1	e	44	1	830.50203	i 6
0	1	1	f	0	2	2	f	35	1	813.36101	5	1	0	1	f	1	1	2	f	42	1	830.86940	-25
0	1	1	e	0	2	2	e	32	1	813.81242	-4	0	1	1	e	0	2	0	e	45	1	830.86940	224*
0	1	1	e	0	2	0	e	38	1	814.44304	-3	0	1	1	e	0	2	2	e	38	1	831.32399	-35
1	0	1	e	1	1	0	e	39	1	814.48662	-9	0	0	0	e	0	1	1	e	43	1	831.71903	-3
1	1	2	f	1	2	3	f	33	1	814.62962	-14	0	1	1	f	0	2	2	f	43	1	831.75398	4
1	1	0	f	1	2	1	If	37	1	814.69853	4	1	0	1	e	1	1	2	e	38	1	832.84303	-5
0	0	0	e	0	1	1	e	37	1	814.80083	i 7	1	0	1	f	1	1	2	f	43	1	833.14168	-7
1	0	1	f	1	1	2	f	35	1	814.90050	16	0	1	1	e	0	2	0	e	46	1	833.19515	60*
1	0	1	e	1	1	2	e	33	1	815.08757	i 11	0	0	0	e	0	1	1	e	44	1	834.01310	-31
1	0	1	f	1	1	0	f	36	1	815.14354	-2	0	1	1	f	0	2	2	f	44	1	834.04219	9
1	0	1	e	1	1	2	e	32	1	815.42809	-1	0	1	1	e	0	2	2	e	39	1	834.31020	9
0	0	0	e	0	1	1	e	36	1	815.59825	9	1	0	1	f	1	1	2	f	44	1	835.41109	-45
0	1	1	f	0	2	2	f	36	1	815.66832	9	1	0	1	e	1	1	2	e	39	1	835.82058	0
0	1	1	e	0	2	2	e	33	1	816.68181	-5	0	0	0	e	0	1	1	e	45	1	836.30546	-2
0	1	1	e	0	2	0	e	39	1	816.80431	0	0	1	1	f	0	2	2	f	45	1	836.32771	2
1	0	1	e	1	1	0	e	40	1	816.89245	8	0	1	1	e	0	2	2	e	40	1	837.31411	-21
0	0	0	e	0	1	1	e	38	1	817.04992	i -15	0	0	0	e	0	1	1	e	46	1	838.59520	-2
1	0	1	f	1	1	2	f	36	1	817.18871	13	1	0	1	e	1	1	2	e	40	1	838.81948	32
1	0	1	f	1	1	0	f	37	1	817.43224	6	0	0	0	e	0	1	1	e	47	1	840.88256	-2
0	0	0	e	0	1	1	e	37	1	817.90734	3	1	0	1	e	1	1	2	e	41	1	841.83865	5
0	1	1	f	0	2	2	f	37	1	817.97338	12	0	0	0	e	0	1	1	e	48	1	843.16729	-23
1	0	1	e	1	1	2	e	33	1	818.27660	-5	0	0	0	e	0	1	1	e	49	1	845.44989	-10
0	1	1	e	0	2	0	e	40	1	819.16039	2	0	0	0	e	0	1	1	e	50	1	847.72986	-10
1	1	2	e	1	2	3	e	36	1	819.16039	-803*	0	0	0	e	0	1	1	e	51	1	850.00745	8
0	0	0	e	0	1	1	e	39	1	819.29125	i -610*												

APPENDIX D

LEAST SQUARES PROGRAM FOR FREQUENCY FIT

D.1 Comments

The basic concept of the least squares program is described in some detail in Section 4.3. The program listed here was specifically written for the global fit of the $3\nu_5$, $2\nu_5$, and ground vibrational states and is written in FORTRAN.

Subroutine INDEX identifies the correct position of the diagonal energy corresponding to the states involved in the observed transition. All matrix elements of the Hamiltonian, as given in Table 2.4, are written in function routines. Subroutine LINFIT is a multivariate linear least squares routine, where most terms are defined, for instance, in Draper and Smith (1980).

MATDIAG does the eigenvalue calculation of the Hamilton matrix. It calls up several routines, which were adapted to double precision calculation from Press *et al.* (1986). These routines are TRED2, which reduces the matrix into tridiagonal form by a Householder transformation, and TQLI, which iteratively determines the eigenvalues and eigenvectors of the tridiagonal matrix using the QL algorithm with implicit shifts (Smith 1980, Press *et al.* 1986). SVD is the singular value decomposition routine used in the least square fit to invert the Jacobian matrix.

D.2 References

- Draper, N.R., and H. Smith, *Applied Regression Analysis*, 2nd ed., John Wiley & Sons, New York, 1980.
- Press, W.H., B.P. Flannery, S.T. Teukolsky, and W.T. Vetterling, *Numerical Recipes—The Art of Scientific Computing*, Cambridge University Press, New York, 1986.
- Smith, B.T., *et al.*, *Matrix Eigensystem Routines—EISPACK Guide*, 2nd Ed., Vol. 6 in *Lecture Notes in Computer Science*, Springer Verlag, New York, 1976.

D.3 Program

```
      IMPLICIT REAL*8 (A-H,O-Z)
      PARAMETER(NP=60,NBNDMAX=10,NMAX=3000,NEIG=12)
      PARAMETER(JMAX=52,MDIAG=370)
      DIMENSION A(NP),B(NP),C(NP),H(NBNDMAX,MDIAG),
*             HD(NP,NBNDMAX,MDIAG),V(NP,NP),W(NP),UN(NP,NP),
*             EV(NP),VAR(NP,NMAX),Y(NMAX),X(NMAX,NP),
*             EE1(NEIG,NEIG),EE2(NEIG,NEIG),
*             DB(NP),DC(NP),LISTBND(50),TEMP(NP,NP),SIGMA(NP),
*             CSIGMA(NP),COR(NP),WY(NMAX),CWY(NMAX),U(2,3,20,20)
*-----
* INITIAL GUESSES OF PARAMETER
*-----
```

```

LISTBND(1)=1
LISTBND(2)=6
LISTBND(3)=4
LISTBND(4)=8
NBAND=9
DO 10000 I=1,8
10000      LISTBND(I+4)=40+I
DO 10001 I=1,10
10001      LISTBND(12+I)=49+I
DO 10002 I=1,5
10002      LISTBND(4+I)=30+I
NTERMS=25
ALPHA=.3D0
B( 1)=    0.7291716709E+03
B( 2)=   -0.2335721965E+01
B( 3)=    0.1399995156E-01
B( 4)=   -0.6933810642E-02
B( 5)=    0.3489954894E+01
B( 6)=    0.1176647504E+01
B( 7)=   -0.2229119880E-02
B( 8)=    0.2054630242E-04
B( 9)=   -0.1069746033E-03
B(10)=   -0.1921162720E-06
B(11)=   -0.1617506818E-05
B(12)=    0.1629006177E-05
B(13)=   -0.3614762652E-07
B(14)=    0.4967559618E-08
B(15)=   -0.1660726782E-07
B(16)=    0.2456674353E-11
B(17)=    0.2331566092E-02
B(18)=    0.1755958245E-04
B(19)=   -0.1908264251E-07
B(20)=   -0.8339428727E-13
B(21)=   -0.1901312614E-04
B(22)=    0.1784174002E-07
B(23)=    0.1925616144E-07
B(24)=    0.3439516272E-12
OPEN(UNIT=13,FILE='ALLACE.DAT',STATUS='OLD')
OPEN(UNIT=16,FILE='HF1.LOG',STATUS='NEW')
OPEN(UNIT=15,FILE='FH2.DAT',STATUS='NEW')
STDEV=1.D10
LSITER=0
ITERSTOP=0
DO 5 I=1,NMAX
      WY(I)=1.D0
5      CONTINUE
      F=1000.D0
*-----
* START OF ITERATIVE LEAST SQUARE (START OF LOOP)
*-----
1      LSITER=LSITER+1
*-----

```

* DETERMINE DIAGONAL ENERGIES AND THEIR DERIVATIVES
 * ACCORDING TO HELLMAN-FEYNMAN THEOREM

```

*-----
      DO 10 J=0,JMAX
*-----
* 3V5
*          H2D(J) DIAGONAL ENERGY OF ROT.QN. J
*          H2DD(K,J) DIAGONAL DERIVATIVE WITH ROT.QN. J
*          AND WITH RESPECT TO K-TH PARAMETER
*-----
      N1=10
      N2=J*4
      UN(1,1)=E3_3(A,B,J,NP)+W3_6(A,B,J,NP)
      UN(1,2)=W3_13(A,B,J,NP)+W3_4(A,B,J,NP)
      UN(1,3)=0.D0
      UN(1,4)=0.D0
      UN(2,2)=E3_1(A,B,J,NP)+W3_11(A,B,J,NP)
      UN(2,3)=0.D0
      UN(2,4)=0.D0
      UN(3,3)=E3_1(A,B,J,NP)-W3_11(A,B,J,NP)
      UN(3,4)=W3_13(A,B,J,NP)-W3_4(A,B,J,NP)
      UN(4,4)=E3_3(A,B,J,NP)-W3_6(A,B,J,NP)
      DO 203 K=1,4
      DO 203 L=1,K
          UN(K,L)=UN(L,K)
203      CONTINUE
      CALL MATDIAG(UN,4,NP,EV)
      DO 303 K=1,4
          H(N1,N2+K)=EV(K)
303      CONTINUE
      IF(ITERSTOP.EQ.0) THEN
          DO 503 K=1,NTERMS
              DO 403 M=1,4
                  DO 403 L=1,4
                      V(M,L)=0.D0
403      CONTINUE
              BB=B(K)
              DEL=1.D0/1000.D0
              IF(DABS(BB).GT.0.D0) DEL=DABS(BB)/1000.D0
              DO 603 L=-1,1,2
                  B(K)=BB+L*DEL
                  V(1,1)=V(1,1)+L*(E3_3(A,B,J,NP)+W3_6(A,B,J,NP))
                  V(1,2)=V(1,2)+L*(W3_13(A,B,J,NP)+W3_4(A,B,J,NP))
                  V(1,3)=V(1,3)+L*0.D0
                  V(1,4)=0.D0
                  V(2,2)=V(2,2)+L*(E3_1(A,B,J,NP)+W3_11(A,B,J,NP))
                  V(2,3)=V(2,3)+L*0.D0
                  V(2,4)=0.D0
                  V(3,3)=V(3,3)+L*(E3_1(A,B,J,NP)-W3_11(A,B,J,NP))
                  V(3,4)=V(3,4)+L*(W3_13(A,B,J,NP)-W3_4(A,B,J,NP))
                  V(4,4)=V(4,4)+L*(E3_3(A,B,J,NP)-W3_6(A,B,J,NP))
603      CONTINUE

```

```

DO 703 N=1,4
DO 703 M=1,N
    V(M,N)=V(M,N)/(2.DO*DEL)
    V(N,M)=V(M,N)
703    CONTINUE
DO 803 M=1,4
DO 803 N=1,4
    TEMP(M,N)=0.DO
DO 803 L=1,4
    TEMP(M,N)=TEMP(M,N)+V(M,L)*UN(L,N)
803    CONTINUE
DO 903 M=1,4
    HD(K,N1,N2+M)=0.DO
DO 903 N=1,4
    HD(K,N1,N2+M)=HD(K,N1,N2+M)+UN(N,M)*TEMP(N,M)
903    CONTINUE
    B(K)=BB
503    CONTINUE
    ENDIF
*-----
* 2V5
*      H2D(J) DIAGONAL ENERGY OF ROT.QN. J
*      H2DD(K,J) DIAGONAL DERIVATIVE WITH ROT.QN. J
*      AND WITH RESPECT TO K-TH PARAMETER
*-----
    N1=6
    N2=3*J
    UN(1,1)=E22(A,B,J,NP)+W22(A,B,J,NP)
    UN(1,2)=DSQRT(2.DO)*W20(A,B,J,NP)
    UN(1,3)=0.DO
    UN(2,2)=E20(A,B,J,NP)
    UN(2,3)=0.DO
    UN(3,3)=UN(1,1)-2.DO*W22(A,B,J,NP)
    DO 200 K=1,3
    DO 200 L=1,K
        UN(K,L)=UN(L,K)
200    CONTINUE
    CALL MATDIAG(UN,3,NP,EV)
    DO 300 K=1,3
        H(N1,N2+K)=EV(K)
    DO 300 M=1,3
    DO 301 LL=1,2
        U(2,LL,M,K)=U(2,LL+1,M,K)
301    CONTINUE
        U(2,3,M,K)=UN(M,K)
300    CONTINUE
    IF(J.LE.5)WRITE(19,'(3(1X,I3),6(G16.8))')
    *      LSITER,N1,J,(EV(K),K=1,3)
    IF(ITERSTOP.EQ.0) THEN
    DO 500 K=1,NTERMS
    DO 400 M=1,3
    DO 400 L=1,3

```



```

      V(M,L)=0.DO
400      CONTINUE
      BB=B(K)
      DEL=1.DO/1000.DO
      IF(DABS(BB).GT.0.DO) DEL=DABS(BB)/1000.DO
      DO 600 L=-1,1,2
          B(K)=BB+L*DEL
          V(1,1)=V(1,1)+L*(E22(A,B,J,NP)+W22(A,B,J,NP))
          V(1,2)=V(1,2)+L*DSQRT(2.DO)*W20(A,B,J,NP)
          V(2,2)=V(2,2)+L*E20(A,B,J,NP)
          V(1,3)=V(1,3)+L*0.DO
          V(3,3)=V(3,3)+L*(E22(A,B,J,NP)-W22(A,B,J,NP))
          V(2,3)=V(1,3)
600      CONTINUE
      DO 700 N=1,3
      DO 700 M=1,N
          V(M,N)=V(M,N)/(2.DO*DEL)
          V(N,M)=V(M,N)
700      CONTINUE
      DO 800 M=1,3
      DO 800 N=1,3
          TEMP(M,N)=0.DO
          DO 800 L=1,3
              TEMP(M,N)=TEMP(M,N)+V(M,L)*UN(L,N)
800      CONTINUE
      DO 900 M=1,3
          HD(K,N1,N2+M)=0.DO
      DO 900 N=1,3
          HD(K,N1,N2+M)=HD(K,N1,N2+M)+UN(N,M)*TEMP(N,M)
900      CONTINUE
      B(K)=BB
500      CONTINUE
      ENDIF

*-----
* V5          H1D(J) DIAGONAL ENERGY OF ROT.QN. J
*             H1DD(K,J) DIAGONAL DERIVATIVE WITH ROT.QN. J
*             AND WITH RESPECT TO K-TH PARAMETER
*-----

      N1=3
      N2=2*J
      UN(1,1)=E1(A,B,J,NP)
      UN(1,2)=W11(A,B,J,NP)
      UN(2,2)=UN(1,1)
      DO 1200 K=1,2
      DO 1200 L=1,K
          UN(K,L)=UN(L,K)
1200      CONTINUE
      CALL MATDIAG(UN,2,NP,EV)
      DO 1300 K=1,2
          H(N1,N2+K)=EV(K)
1300      CONTINUE
      IF(J.LE.5)WRITE(19,'(3(1X,I3),6(G16.8))')

```

```

*          LSITER,N1,J,(EV(K),K=1,2)
IF(ITERSTOP.EQ.0) THEN
  DO 1500 K=1,NTERMS
    DO 1400 M=1,2
      DO 1400 L=1,2
        V(M,L)=0.D0
1400      CONTINUE
        BB=B(K)
        DEL=1.D-3
        IF(DABS(BB).GT.0.D0) DEL=DABS(BB)/1000.D0
        DO 1600 L=-1,1,2
          B(K)=BB+L*DEL
          V(1,1)=V(1,1)+L*E1(A,B,J,NP)
          V(1,2)=V(1,2)+L*W11(A,B,J,NP)
          V(2,2)=V(1,1)
1600      CONTINUE
        DO 1700 N=1,2
          DO 1700 M=1,N
            V(M,N)=V(M,N)/(2.D0*DEL)
            V(N,M)=V(M,N)
1700      CONTINUE
        DO 1800 M=1,2
          DO 1800 N=1,2
            TEMP(M,N)=0.D0
            DO 1800 L=1,2
              TEMP(M,N)=TEMP(M,N)+V(M,L)*UN(L,N)
1800      CONTINUE
        DO 1900 M=1,2
          HD(K,N1,N2+M)=0.D0
          DO 1900 N=1,2
            HD(K,N1,N2+M)=HD(K,N1,N2+M)+UN(N,M)*TEMP(N,M)
1900      CONTINUE
        B(K)=BB
1500      CONTINUE
  ENDIF

*-----
* GROUNDSTATE
*-----

N1=1
N2=J+1
H(N1,N2)=GST(A,B,J,NP)
IF(J.LE.5)WRITE(19,'(3(1X,I3),6(G16.8))')
*          LSITER,N1,J,(EV(K),K=1,1)
IF(ITERSTOP.EQ.0) THEN
  DO 1950 K=1,NTERMS
    BB=B(K)
    DEL=1.D-3
    IF(DABS(B(K)).GT.0.D0) DEL=DABS(B(K))/1000.D0
    B(K)=BB+DEL
    F2=GST(A,B,J,NP)
    B(K)=BB-DEL
    HD(K,N1,N2)=(F2-GST(A,B,J,NP))/(2.D0*DEL)

```

```

          B(K)=BB
1950      CONTINUE
          ENDIF
*-----
* GATHERING DATA AND PREPARATION OF NORMAL EQUATION
*-----
          SEOLD=SE
          NNZOLD=NNZ
          SE=0.D0
          USE=0.D0
          NNZ=0
          SUMWY=0.D0
          NDAT=1
2000      I=0
          READ(13,*,ERR=2000,END=20) LL,LU,JD,J,VF,NB
2100      I=I+1
          IF(I.GT.NBAND) GOTO 2000
          IF(NB.EQ.LISTBND(I)) GOTO 2200
          GOTO 2100
2200      CONTINUE
          IF((J.GT.60).AND.(LISTBND(I).GT.29)) GOTO 2000
          CALL INDEX(LL,J,M1,M2)
          CALL INDEX(LU,J+JD,N1,N2)
          DO 2300 I=1,NTERMS
              X(NDAT,I)=HD(I,N1,N2)-HD(I,M1,M2)
2300      CONTINUE
          Y(NDAT)=VF-(H(N1,N2)-H(M1,M2))
          IF(LSITER.EQ.1) THEN
              WRITE(15,'(1X,3(1X,I4),4(1X,G16.8))')
*          J,JD,NB,VF,H(N1,N2)-H(M1,M2),
*          Y(NDAT),WY(NDAT)*Y(NDAT)
          ENDIF
          SE=SE+(Y(NDAT)*WY(NDAT))**2
          SUMWY=SUMWY+WY(NDAT)
          USE=USE+Y(NDAT)**2
          CWY(NDAT)=WY(NDAT)
          NDAT=NDAT+1
          GOTO 2000
20      CONTINUE
          NDAT=NDAT-1
          IF(LSITER.EQ.1) NNZOLD=NDAT
          STDEV=DSQRT(SE/SUMWY)
          USTDEV=DSQRT(USE/(NDAT-NTERMS))
          IF(ITERSTOP.EQ.0) THEN
              DO 7000 I=1,NDAT
                  WY(I)=0.D0
                  DELTA=Y(I)**2/(4.D0*STDEV)**2
                  IF(MOD(LSITER,2).NE.0) THEN
                      WY(I)=CWY(I)
                      IF(WY(I).GT.0.D0) NNZ=NNZ+1
                  ELSEIF(DELTA.LT.1.D0) THEN
                      WY(I)=DSQRT(1.D0-DELTA)

```

```

        NNZ=NNZ+1
        ENDIF
7000    CONTINUE
        ENDIF

*-----
* END OF PREPARATION LOOP, STATISTICS BEFORE LEAST SQUARE FIT
*-----

        REWIND 13
        IF (LSITER.GT.1) THEN
            DO 2400 I=1,NTERMS
                SIGMA(I)=SIGMA(I)*DSQRT(SE)/DSQRT(SSE)
                DO 2400 J=1,NTERMS
                    VAR(I,J)=VAR(I,J)*SE/SSE
2400        CONTINUE
            ENDIF
            WRITE(16, '(1X,/,1X,1A,I3,1A)') 'BEFORE ',LSITER,'TH ITERATION'
            WRITE(16,*) NTERMS,' PARAMETERS'
            WRITE(16,*) NDAT,' TRANSITIONS ',NNZ,' NZWTS'
            DO 2500 I=1,NTERMS
                WRITE(16, '(1X,1A,I3,1A,G20.13,1A,G12.4,1A)')
*                'B(',I,')=' ,B(I), ' (' ,SIGMA(I),')'
2500    CONTINUE
            WRITE(16, '(5(1X,1A,G12.5,/),//)') ' SSE=' ,SE, ' MSSE=' ,
* SE/(SUMWY), ' STDEV=' ,DSQRT(SE/(SUMWY)),
* ' USE=' ,USE, ' USTDEV=' ,DSQRT(USE/(NDAT-NTERMS))
            WRITE(6,*) 'BEFORE ',LSITER,'TH ITERATION'
            WRITE(6,*) NTERMS,' PARAMETERS'
            WRITE(6,*) NDAT,' TRANSITIONS ',NNZ,' NZWTS'
            DO 2550 I=1,NTERMS
                WRITE(6, '(1X,1A,I3,1A,G20.13,1A,G12.4,1A)')
*                'B(',I,')=' ,B(I), ' (' ,SIGMA(I),')'
2550    CONTINUE
            WRITE(6, '(5(1X,1A,G12.5,/),//)') ' SSE=' ,SE, ' MSSE=' ,
* SE/SUMWY, ' STDEV=' ,DSQRT(SE/SUMWY),
* ' USE=' ,USE, ' USTDEV=' ,DSQRT(USE/(NDAT-NTERMS))
            DO 2570 I=1,NTERMS
                C(I)=B(I)
                DC(I)=SIGMA(I)
2570    CONTINUE
            CSSE=SE
            MEMITER=LSITER-1

*-----
* TERMINATION CRITERION
*-----

        IF (DABS(SE-SEOLD).LT.1.D-3*DABS(SE).OR.ITERSTOP.EQ.1)
*        GOTO 4999
        IF (F.LE.1.DO) THEN
            ITERSTOP=1
            DO 2585 I=1,NTERMS
                B(I)=C(I)
                SIGMA(I)=DC(I)
2585    CONTINUE

```

```

                DO 2590 I=1,NDAT
                    WY(I)=CWY(I)
2590            CONTINUE
                LSITER=MEMITER-1
                SE=CSSE
                GOTO 1

            ENDIF

*-----
* LINEARIZED LEAST SQUARE FIT + STATISTICS
*-----

        CALL LINFIT(Y,WY,X,DB,NDAT,NTERMS,NMAX,NP,
*           SIGMA,VAR,COR,SSRG,SSE,SSRM,SSM,R,F)
        WRITE(16,'(1X,1A)') '-----'
        WRITE(16,*) LSITER,' ITERATION ',NDAT,' TRANSITIONS ',
*           NTERMS,' PARAMETERS', NNZ,' NONZEROW.'
        WRITE(16,*) 'LEAST-SQUARE ESTIMATES OF LINEARIZED FIT:'
        DO 2600 I=1,NTERMS
2600            WRITE(16,'(1X,1A,I3,1A,G12.5,1A,2(G12.5,1A))')
*                'DB(',I,')= ',DB(I),' (',SIGMA(I),'), CORY=',COR(I)
        WRITE(16,*) 'VARIANCE MATRIX '
        DO 2700 I=1,NTERMS
        DO 2700 J=1,I
2700            WRITE(16,'(1X,2(I3,1X),1(G12.5,1X))') I,J,VAR(I,J)
        WRITE(16,'(1X,2(1A,G12.5))') 'SSE= ',SSE, ' MSS= ',SSM
        WRITE(16,'(1X,3(1A,G12.5))') 'SSRG=',SSRG, ' MSSRG=',SSRM,
*           ' F=',SSRM/SSM
        WRITE(16,'(1X,2(1A,G12.5))') 'S= ',DSQRT(SSM), ' R^2= ',R
        DO 2800 I=1,NTERMS
C                IF(DABS(SIGMA(I)).LT.DB(I)) THEN
                    B(I)=B(I)+ALPHA*DB(I)
C                ENDIF
C                IF(DABS(B(I)).LT.DABS(SIGMA(I)))THEN
                    B(I)=0.D0
C                ENDIF
2800            CONTINUE
            OPEN(1,FILE='PAR.DAT',STATUS='NEW')
            DO 9876 I=1,NTERMS
                WRITE(1,'(1X,7X,1A,I3,1A,E20.10)')
*                'B(',I,')=',B(I)
9876        CONTINUE
            CLOSE(1)
            GOTO 1

*-----
* END OF BIG LOOP OR ONE ITERATION, FINAL STATISTICS
*-----

4999        CLOSE(16)
            OPEN(UNIT=17,FILE='HF1.DAT',STATUS='NEW')
            SE=0.D0
            USE=0.D0
            NDAT=1
            SUMWY=0.D0
            NNZ=0

```

```

5000  I=0
      READ(13,*,ERR=5000,END=30) LL,LU,JD,J,VF,NB
5100  I=I+1
      IF(I.GT.NBAND) GOTO 5000
      IF(NB.EQ.LISTBND(I)) GOTO 5200
      GOTO 5100
5200  CONTINUE
      IF((J.GT.60).AND.(LISTBND(I).GT.29)) GOTO 5000
      CALL INDEX(LL,J,M1,M2)
      CALL INDEX(LU,J+JD,N1,N2)
      DV=(VF-(H(N1,N2)-H(M1,M2)))
      IF(WY(NDAT).GT.0.DO) NNZ=NNZ+1
      SE=SE+(DV*WY(NDAT))*2
      USE=USE+DV**2
      SUMWY=SUMWY+WY(NDAT)
      WRITE(17, '(1X,3(I3,1X),2(G15.8,1X),2(F15.10,1X))')
*      J,JD,NB,VF,H(N1,N2)-H(M1,M2),DV,DV*WY(NDAT)
      NDAT=NDAT+1
      GOTO 5000
30    CONTINUE
      NDAT=NDAT-1
      WRITE(17,*) LSITER,' ITERATION'
      WRITE(17,*) NTERMS,' PARAMETERS'
      WRITE(17,*) NDAT,' TRANSITIONS ', NNZ,' NONZEROWTS.'
      DO 5300 I=1,NTERMS
          WRITE(17, '(1X,1A,I3,1A,E16.9,1A,G12.5,1A)')
*          'B(',I,')=' ,B(I), ' (',SIGMA(I),')'
5300  CONTINUE
      WRITE(17, '(5(1X,1A,G12.5,/),/))' ' SSE=',SE,' MSSE=',
*      SE/SUMWY,' STDEV=',DSQRT(SE/SUMWY),
*      ' USSE=',USE,' USTDEV',DSQRT(USE/(NDAT-NTERMS))
      CLOSE(17)
8100  WRITE(6,*) 'TY #LOW,#LUP,JD,LLMIN,LUMIN'
      READ(5,*) LL,LU,JD,LLMIN,LUMIN
      IF(ABS(JD).LE.1) OPEN(1,FILE='BAND.DAT',STATUS='NEW')
      IF(JD.EQ.0) THEN
          DO 8110 J=0,50
              CALL INDEX(LL,J,M1,M2)
              CALL INDEX(LU,J,N1,N2)
              VF=(H(N1,N2)-H(M1,M2))
              IF((J.LT.LLMIN).OR.(J.LT.LUMIN))VF=0
              WRITE(1, '(1X,4(I4,1X),G16.9)') LL,LU,J,JD,VF
8110  CONTINUE
              CLOSE(1)
              GOTO 8100
          ELSEIF(ABS(JD).EQ.1) THEN
              I=1
              DO 8120 J=0,50
                  CALL INDEX(LL,J,M1,M2)
                  CALL INDEX(LU,J+I,N1,N2)
                  VF1=(H(N1,N2)-H(M1,M2))
                  IF((J.LT.LLMIN).OR.(J+I.LT.LUMIN))VF1=0.DO

```

```

      CALL INDEX(LU,J-I,N1,N2)
      VF2=(H(N1,N2)-H(M1,M2))
      IF((J.LT.LLMIN).OR.(J-I.LT.LUMIN))VF2=0.DO
      WRITE(1,'(1X,4(I4,1X),2(G16.9,1X))') LL,LU,J,I,VF2,VF1
8120      CONTINUE
      CLOSE(1)
      GOTO 8100

    ENDIF
  STOP
END

```

*

```

SUBROUTINE INDEX(LEV,J,N1,N2)
IF(LEV.EQ.0) THEN
  N1=1
  N2=J+1
ELSEIF(LEV.EQ.1) THEN
  N1=2
  N2=2*J+1
ELSEIF(LEV.EQ.2) THEN
  N1=2
  N2=2*J+2
ELSEIF(LEV.EQ.3) THEN
  N1=3
  N2=2*J+1
ELSEIF(LEV.EQ.4) THEN
  N1=3
  N2=2*J+2
ELSEIF(LEV.EQ.5) THEN
  N1=4
  N2=3*J+1
ELSEIF(LEV.EQ.6) THEN
  N1=4
  N2=3*J+3
ELSEIF(LEV.EQ.7) THEN
  N1=4
  N2=3*J+2
ELSEIF(LEV.EQ.8) THEN
  N1=5
  N2=4*J+2
ELSEIF(LEV.EQ.9) THEN
  N1=5
  N2=4*J+1
ELSEIF(LEV.EQ.10) THEN
  N1=5
  N2=4*J+4
ELSEIF(LEV.EQ.11) THEN
  N1=5
  N2=4*J+3
ELSEIF(LEV.EQ.12) THEN
  N1=6
  N2=3*J+2
ELSEIF(LEV.EQ.13) THEN

```

```

      N1=6
      N2=3*J+1
ELSEIF(LEV.EQ.14) THEN
      N1=6
      N2=3*J+3
ELSEIF(LEV.EQ.31) THEN
      N1=10
      N2=4*J+4
ELSEIF(LEV.EQ.32) THEN
      N1=10
      N2=4*J+1
ELSEIF(LEV.EQ.33) THEN
      N1=10
      N2=4*J+3
ELSEIF(LEV.EQ.34) THEN
      N1=10
      N2=4*J+2
ELSEIF(LEV.EQ.25) THEN
      N1=9
      N2=6*J+6
ELSEIF(LEV.EQ.26) THEN
      N1=9
      N2=6*J+3
ELSEIF(LEV.EQ.27) THEN
      N1=9
      N2=6*J+5
ELSEIF(LEV.EQ.28) THEN
      N1=9
      N2=6*J+2
ELSEIF(LEV.EQ.29) THEN
      N1=9
      N2=6*J+4
ELSEIF(LEV.EQ.30) THEN
      N1=9
      N2=6*J+1
ELSEIF(LEV.EQ.19) THEN
      N1=8
      N2=6*J+6
ELSEIF(LEV.EQ.20) THEN
      N1=8
      N2=6*J+3
ELSEIF(LEV.EQ.21) THEN
      N1=8
      N2=6*J+5
ELSEIF(LEV.EQ.22) THEN
      N1=8
      N2=6*J+2
ELSEIF(LEV.EQ.23) THEN
      N1=8
      N2=6*J+4
ELSEIF(LEV.EQ.24) THEN
      N1=8

```



```

        N2=6*J+1
ELSE
        PAUSE 'INVALID INDEXING'
ENDIF
RETURN
END

*
FUNCTION GST(A,B,J,NP)
IMPLICIT REAL*8 (A-H,O-Z)
DIMENSION A(NP),B(NP)
X=J*(J+1.D0)
GST=B(6)*X-B(12)*X**2+B(16)*X**3
RETURN
END

*
FUNCTION E1(A,B,J,NP)
IMPLICIT REAL*8 (A-H,O-Z)
DIMENSION A(NP),B(NP)
X=J*(J+1.D0)-1.D0
E1=0.D0
IF(J.GE.1) THEN
        E1=B(1)+B(2)+B(3)+B(4)+B(5)+
*       (B(6)-B(7)+B(8)+B(9)+B(10)+B(11))*X
        E1=E1-(B(12)-B(13)+B(14)+B(15))*X**2+
*       (B(16)-B(25))*X**3
ENDIF
RETURN
END

*
FUNCTION W11(A,B,J,NP)
IMPLICIT REAL*8 (A-H,O-Z)
DIMENSION A(NP),B(NP)
X=J*(J+1.D0)
W11=(B(17)+B(18)+B(19)*X+B(20)*X**2)*X
RETURN
END

*
FUNCTION E22(A,B,J,NP)
IMPLICIT REAL*8 (A-H,O-Z)
DIMENSION A(NP),B(NP)
X=J*(J+1.D0)-4.D0
E22=0.D0
IF(J.GE.2)
*   E22=2.D0*B(1)+4.D0*B(2)+8.D0*B(3)+8.D0*B(4)+4.D0*B(5)
*   +(B(6)-2.D0*B(7)+4.D0*B(8)
*   +4.D0*B(9)+8.D0*B(10)+8.D0*B(11))*X
*   -(B(12)-2.D0*B(13)+4.D0*B(14)+4.D0*B(15))*X**2+
*   (B(16)-2.D0*B(25))*X**3
RETURN
END

*
FUNCTION E20(A,B,J,NP)

```

```

      IMPLICIT REAL*8 (A-H,O-Z)
      DIMENSION A(NP),B(NP)
      X=J*(J+1.D0)
      E20=0.D0
      IF(J.GE.0)
*      E20=2.D0*B(1)+4.D0*B(2)+8.D0*B(3)
*      +(B(6)-2.D0*B(7)+4.D0*B(8)
*      +8.D0*B(10))*X
*      -(B(12)-2.D0*B(13)+4.D0*B(14))*X**2+
*      (B(16)-2.D0*B(25))*X**3
      RETURN
      END
*
      FUNCTION W20(A,B,J,NP)
      IMPLICIT REAL*8 (A-H,O-Z)
      DIMENSION A(NP),B(NP)
      X=J*(J+1.D0)
      IF(X.GT.2.D0)
*      W20=DSQRT(2.D0)
*      *(B(17)+2.D0*B(18)+B(19)*X+B(20)*X**2+B(21))
*      *DSQRT(X*(X-2))
      RETURN
      END
*
      FUNCTION W22(A,B,J,NP)
      IMPLICIT REAL*8 (A-H,O-Z)
      DIMENSION A(NP),B(NP)
      X=J*(J+1.D0)
      IF(X.GT.2.D0)W22=(B(22)+B(24)*X)*X*(X-2)
      RETURN
      END
*
*
      FUNCTION E3_3(A,B,J,NP)
      IMPLICIT REAL*8 (A-H,O-Z)
      DIMENSION A(NP),B(NP)
      X=J*(J+1.D0)-9.D0
      E3_3=0.D0
      IF(J.GE.3)
*      E3_3=3.D0*B(1)+9.D0*B(2)+27.D0*B(3)
*      +27.D0*B(4)+9.D0*B(5)
*      +(B(6)-3.D0*B(7)+9.D0*B(8)+9.D0*B(9)
*      +27.D0*B(10)+27.D0*B(11))*X
*      -(B(12)-3.D0*B(13)+9.D0*B(14)+9.D0*B(15))*X**2
*      +(B(16)-3.D0*B(25))*X**3
      RETURN
      END
*
      FUNCTION E3_1(A,B,J,NP)
      IMPLICIT REAL*8 (A-H,O-Z)
      DIMENSION A(NP),B(NP)
      X=J*(J+1.D0)-1.D0

```

```

      E3_1=0.D0
      IF(J.GE.1)
*      E3_1=3.D0*B(1)+9.D0*B(2)+27.D0*B(3)
*      +3.D0*B(4)+B(5)
*      +(B(6)-3.D0*B(7)+9.D0*B(8)+B(9)
*      +27.D0*B(10)+3.D0*B(11))*X
*      -(B(12)-3.D0*B(13)+9.D0*B(14)+B(15))*X**2
*      +(B(16)-3.D0*B(25))*X**3
      RETURN
      END
*
      FUNCTION W3_11(A,B,J,NP)
      IMPLICIT REAL*8 (A-H,O-Z)
      DIMENSION A(NP),B(NP)
      X=J*(J+1.D0)
      W3_11=0.D0
      IF(J.GE.1) W3_11=2.D0*(B(17)+3.D0*B(18)+B(19)*X
*      +B(20)*X**2)*X
      RETURN
      END

      FUNCTION W3_13(A,B,J,NP)
      IMPLICIT REAL*8 (A-H,O-Z)
      DIMENSION A(NP),B(NP)
      X=J*(J+1.D0)
      W3_13=0.D0
      IF(J.GE.3)
*      W3_13=DSQRT(3.D0)*(B(17)+3.D0*B(18)+B(19)*X
*      +B(20)*X**2+4.D0*B(21))
*      *DSQRT(X-2.D0)*DSQRT(X-6.D0)
      RETURN
      END

      FUNCTION W3_4(A,B,J,NP)
      IMPLICIT REAL*8 (A-H,O-Z)
      DIMENSION A(NP),B(NP)
      X=J*(J+1.D0)
      W3_4=0.D0
      IF(J.GE.3) THEN
        W3_4=DSQRT(3.D0)*
*      (B(23)+B(24)*X)*X*DSQRT(X-2.D0)*DSQRT(X-6.D0)
      ENDIF
      RETURN
      END

      FUNCTION W3_6(A,B,J,NP)
      IMPLICIT REAL*8 (A-H,O-Z)
      DIMENSION A(NP),B(NP)
      X=J*(J+1.D0)
      W3_6=0.D0
      IF(J.GE.100) THEN
        W3_6=B(50)*X*(X-2.D0)*(X-6.D0)
      ENDIF

```

```

      RETURN
      END

*
*
*
      SUBROUTINE LINFIT(Y,WY,X,B,NDATA,NTERMS,ND,NT,
*                      SIGMA,VAR,COR,SSRG,SSE,SSRM,SSM,R,F)
      IMPLICIT REAL*8 (A-H,O-Z)
      PARAMETER (NDMAX=3000,NPMAX=60)
      DIMENSION Y(1),X(ND,1),B(1),
*              VAR(NT,1),SIGMA(1),COR(1),WY(1)
      DIMENSION Z(NDMAX,NPMAX),W(NPMAX),V(NPMAX,NPMAX),
*              SUMX(NPMAX),SUMX2(NPMAX),A(NPMAX)

*
* MULTIVARIATE LINEAR LEAST SQUARE FIT
*
*      MODEL Y=X*B (MATRIX-NOTATION)
*
* 1) CALCULATION OF SOLUTION  $B=X^{-1}Y$  BY
*     USING SINGULAR VALUE DECOMPOSITION (SVD)
*
*      SVD:  $X=U*W*V^T$ 
*           THEN  $X^{-1}=V*W^{-1}*U^T$ 
*            $VAR=V*W^{-2}*V^T*(SSE/NDAT-NTERMS)$ 
*
      DO 10 K=1,NDATA
C      PRINT*, K,WY(K)
      DO 10 L=1,NTERMS
          VAR(L,K)=0.DO
          Z(K,L)=WY(K)*X(K,L)
10      CONTINUE
      CALL SVDCMP(Z,NDATA,NTERMS,NDMAX,NPMAX,W,V)
      WMAX=0.DO
      WMIN=W(1)
      DO 20 I=1,NTERMS
          IF(DABS(W(I)).GT.WMAX) WMAX=DABS(W(I))
          IF(DABS(W(I)).LT.WMAX) WMIN=DABS(W(I))
20      CONTINUE
      WM=1.D-12*WMAX
      DO 30 I=1,NTERMS
          IF(DABS(W(I)).LT.WM) THEN
              W(I)=0.DO
              WRITE(6,*) 'SINGULAR VALUE SET TO 0'
          ENDIF
30      CONTINUE
C      WRITE(6, '(1X,1A,3(G12.6))') 'WMIN,WMAX ',WMIN,WMAX,WMIN/WMAX
      DO 40 I=1,NTERMS
          DO 40 J=1,NDATA
              VAR(I,J)=0.DO
              DO 40 K=1,NTERMS
                  IF(W(K).NE.0.DO)
*                      VAR(I,J)=VAR(I,J)+V(I,K)*Z(J,K)/W(K)

```

```

40      CONTINUE
      DO 60 I=1, NTERMS
        B(I)=0.D0
        DO 60 K=1, NDATA
          B(I)=B(I)+VAR(I,K)*Y(K)*WY(K)
60      CONTINUE
      DO 11 I=1, NTERMS
        A(I)=0.D0
        DO 12 K=1, NDATA
          A(I)=A(I)+X(K,I)*Y(K)*WY(K)**2
12      CONTINUE
      DO 11 J=1, NTERMS
        VAR(I,J)=0.D0
        DO 11 K=1, NTERMS
          IF(W(K).NE.0.D0)
            *      VAR(I,J)=VAR(I,J)+V(I,K)*V(J,K)/W(K)**2
11      CONTINUE
      *
      * 2) DETERMINING RESIDUALS AND CORRELATION MATRIX
      *
      *          VAR : VARIANCE-MATRIX
      *                  DIAG.ELEMENT VARIANCES OF PARAM.
      *                  OFF-DIAG CORRELAT. COEFF.
      *          COR : CORR BETWEEN VAR AND RESPONSE
      *          SSE : SUM SQUARE ERROR
      *          SSRG : SUM SQUARE ERROR DUE TO REGRESSION
      *          MSS : MEAN SQUARE ERROR
      *          MSSR : MEAN SQUARE ERROR DYE TO REGRESSION
      *          R : CORRELATION COEFFICIENT
      *          F : F-NUMBER FOR TESTING THE NULL
      *                  HYPOTHESIS (NDATA-NTERMS VS NTERMS-1)
      *                  DEGREE OF FREEDOM)
      DO 65 I=1, NTERMS
        SUMX(I)=0.D0
        SUMX2(I)=0.D0
        COR(I)=0.D0
65      CONTINUE
      SUMY2=0.D0
      SUMY=0.D0
      SSRG=0.D0
      SSE=0.D0
      DO 70 I=1, NDATA
        SUMY2=SUMY2+Y(I)*Y(I)*WY(I)**2
        SUMY=SUMY+Y(I)*WY(I)
        DO 75 J=1, NTERMS
          SUMX(J)=SUMX(J)+X(I,J)*WY(I)
          SUMX2(J)=SUMX2(J)+X(I,J)**2*WY(I)**2
75      CONTINUE
70      CONTINUE
      DO 80 I=1, NTERMS
        SSRG=SSRG+A(I)*B(I)
80      CONTINUE

```

```

SSE=SUMY2-SSRG
SSM=SSE/(NDATA-NTERMS+0.D0)
SSRM=SSRG/NTERMS
R=(SSRG-SUMY**2/NDATA)/(SUMY2-SUMY**2/NDATA)
IF (NTERMS.NE.1) F=(SSRG-SUMY**2/NDATA)/(SSM*(NTERMS-1))
SY=SUMY2-SUMY**2/NDATA
DO 90 I=1,NTERMS
    SIGMA(I)=DSQRT(VAR(I,I))*DSQRT(SSM)
90  CONTINUE
DO 130 I=1,NTERMS
C    DO 135 K=1,NTERMS-1
C        VAR(I,K)=VAR(I,K)/(SIGMA(I)*SIGMA(K))
C        VAR(K,I)=VAR(K,I)/(SIGMA(I)*SIGMA(K))
C135  CONTINUE
    DO 130 J=1,NDATA
        COR(I)=COR(I)+(WY(J)*Y(J)-SUMY/NDATA)
        *      *(WY(J)*X(J,I)-SUMX(I)/NDATA)
130  CONTINUE
    DO 140 I=1,NTERMS
        DN=(SUMX2(I)-SUMX(I)**2/NDATA)*SY
        IF(DN.GT.0.D0) THEN
            COR(I)=COR(I)/DSQRT(DN)
        ELSE
            COR(I)=0.D0
        ENDIF
140  CONTINUE
    RETURN
    END
*
SUBROUTINE MATDIAG(A,NDIM,NP,D)
PARAMETER (M=10)
IMPLICIT REAL*8 (A-H,O-Z)
DIMENSION A(NP,NP),D(NP),E(M)
CALL TRED2(A,NDIM,NP,D,E)
CALL TQLI(D,E,NDIM,NP,A)
RETURN
END
*
SUBROUTINE TRED2(A,N,NP,D,E)
IMPLICIT REAL*8 (A-H,O-Z)
DIMENSION A(NP,NP),D(NP),E(NP)
IF(N.GT.1)THEN
    DO 18 I=N,2,-1
        L=I-1
        H=0.D0
        SCALE=0.D0
        IF(L.GT.1)THEN
            DO 11 K=1,L
                SCALE=SCALE+DABS(A(I,K))
11         CONTINUE
            IF(SCALE.EQ.0.D0)THEN
                E(I)=A(I,L)

```

```

ELSE
  DO 12 K=1,L
    A(I,K)=A(I,K)/SCALE
    H=H+A(I,K)**2
12  CONTINUE
    F=A(I,L)
    G=-DSIGN(DSQRT(H),F)
    E(I)=SCALE*G
    H=H-F*G
    A(I,L)=F-G
    F=0.D0
    DO 15 J=1,L
      A(J,I)=A(I,J)/H
      G=0.D0
      DO 13 K=1,J
        G=G+A(J,K)*A(I,K)
13      CONTINUE
      IF(L.GT.J)THEN
        DO 14 K=J+1,L
          G=G+A(K,J)*A(I,K)
14          CONTINUE
        ENDIF
        E(J)=G/H
        F=F+E(J)*A(I,J)
15      CONTINUE
      HH=F/(H+H)
      DO 17 J=1,L
        F=A(I,J)
        G=E(J)-HH*F
        E(J)=G
        DO 16 K=1,J
          A(J,K)=A(J,K)-F*E(K)-G*A(I,K)
16          CONTINUE
17          CONTINUE
        ENDIF
      ELSE
        E(I)=A(I,L)
      ENDIF
      D(I)=H
18      CONTINUE
    ENDIF
    D(1)=0.D0
    E(1)=0.D0
    DO 23 I=1,N
      L=I-1
      IF(D(I).NE.0.D0)THEN
        DO 21 J=1,L
          G=0.D0
          DO 19 K=1,L
            G=G+A(I,K)*A(K,J)
19          CONTINUE
          DO 20 K=1,L

```

```

      A(K,J)=A(K,J)-G*A(K,I)
20      CONTINUE
21      CONTINUE
      ENDIF
      D(I)=A(I,I)
      A(I,I)=1.D0
      IF(L.GE.1)THEN
        DO 22 J=1,L
          A(I,J)=0.D0
          A(J,I)=0.D0
22      CONTINUE
      ENDIF
23      CONTINUE
      RETURN
      END
*
      SUBROUTINE TQLI(D,E,N,NP,Z)
        IMPLICIT REAL*8 (A-H,O-Z)
        DIMENSION D(NP),E(NP),Z(NP,NP)
        IF (N.GT.1) THEN
          DO 11 I=2,N
            E(I-1)=E(I)
11      CONTINUE
            E(N)=0.D0
            DO 15 L=1,N
              ITER=0
1      DO 12 M=L,N-1
                DD=DABS(D(M))+DABS(D(M+1))
                IF (DABS(E(M))+DD.EQ.DD) GO TO 2
12      CONTINUE
                M=N
2      IF(M.NE.L)THEN
              IF(ITER.EQ.30)PAUSE 'TOO MANY ITERATIONS'
              ITER=ITER+1
              G=(D(L+1)-D(L))/(2.D0*E(L))
              R=DSQRT(G**2+1.D0)
              G=D(M)-D(L)+E(L)/(G+DSIGN(R,G))
              S=1.D0
              C=1.D0
              P=0.D0
              DO 14 I=M-1,L,-1
                F=S*E(I)
                B=C*E(I)
                IF(DABS(F).GE.DABS(G))THEN
                  C=G/F
                  R=DSQRT(C**2+1.D0)
                  E(I+1)=F*R
                  S=1.D0/R
                  C=C*S
                ELSE
                  S=F/G
                  R=DSQRT(S**2+1.)

```



```

        E(I+1)=G*R
        C=1.DO/R
        S=S*C
    ENDIF
    G=D(I+1)-P
    R=(D(I)-G)*S+2.DO*C*B
    P=S*R
    D(I+1)=G+P
    G=C*R-B
    DO 13 K=1,N
        F=Z(K,I+1)
        Z(K,I+1)=S*Z(K,I)+C*F
        Z(K,I)=C*Z(K,I)-S*F
13      CONTINUE
14      CONTINUE
        D(L)=D(L)-P
        E(L)=G
        E(M)=0.DO
        GO TO 1
    ENDIF
15      CONTINUE
ENDIF
RETURN
END
*
SUBROUTINE SVDcmp(A,M,N,MP,NP,W,V)
IMPLICIT REAL*8 (A-H,O-Z)
PARAMETER (NMAX=100)
DIMENSION A(MP,NP),W(NP),V(NP,NP),RV1(NMAX)
IF(M.LT.N) PAUSE 'YOU MUST AUGMENT A WITH ZERO ROWS.'
G=0.DO
SCALE=0.DO
ANORM=0.DO
DO 25 I=1,N
    L=I+1
    RV1(I)=SCALE*G
    G=0.DO
    S=0.DO
    SCALE=0.DO
    IF(I.LE.M) THEN
        DO 11 K=I,M
            SCALE=SCALE+DABS(A(K,I))
11        CONTINUE
        IF(SCALE.NE.0.DO) THEN
            DO 12 K=I,M
                A(K,I)=A(K,I)/SCALE
                S=S+A(K,I)*A(K,I)
12            CONTINUE
            F=A(I,I)
            G=-DSIGN(DSQRT(S),F)
            H=F*G-S
            A(I,I)=F-G

```

```

IF(I.NE.N) THEN
  DO 15 J=L,N
    S=0.DO
    DO 13 K=I,M
      S=S+A(K,I)*A(K,J)
13    CONTINUE
      F=S/H
      DO 14 K=I,M
        A(K,J)=A(K,J)+F*A(K,I)
14      CONTINUE
15    CONTINUE
  END IF
  DO 16 K=I,M
    A(K,I)=SCALE*A(K,I)
16  CONTINUE
  END IF
END IF
W(I)=SCALE*G
G=0.DO
S=0.DO
SCALE=0.0
IF((I.LE.M).AND.(I.NE.N)) THEN
  DO 17 K=L,N
    SCALE=SCALE+DABS(A(I,K))
17  CONTINUE
  IF(SCALE.NE.0.DO) THEN
    DO 18 K=L,N
      A(I,K)=A(I,K)/SCALE
      S=S+A(I,K)*A(I,K)
18    CONTINUE
      F=A(I,L)
      G=-DSIGN(DSQRT(S),F)
      H=F*G-S
      A(I,L)=F-G
      DO 19 K=L,N
        RV1(K)=A(I,K)/H
19      CONTINUE
      IF(I.NE.M) THEN
        DO 23 J=L,M
          S=0.DO
          DO 21 K=L,N
            S=S+A(J,K)*A(I,K)
21          CONTINUE
          DO 22 K=L,N
            A(J,K)=A(J,K)+S*RV1(K)
22          CONTINUE
23        CONTINUE
      END IF
      DO 24 K=L,N
        A(I,K)=SCALE*A(I,K)
24      CONTINUE
    END IF
  END IF

```

```

      END IF
      ANORM=DMAX1(ANORM,(DABS(W(I))+DABS(RV1(I))))
25  CONTINUE
      DO 32 I=N,1,-1
        IF (I.LT.N) THEN
          IF (G.NE.0.DO) THEN
            DO 26 J=L,N
              V(J,I)=(A(I,J)/A(I,L))/G
26          CONTINUE
            DO 29 J=L,N
              S=0.DO
              DO 27 K=L,N
                S=S+A(I,K)*V(K,J)
27          CONTINUE
              DO 28 K=L,N
                V(K,J)=V(K,J)+S*V(K,I)
28          CONTINUE
29          CONTINUE
          END IF
          DO 31 J=L,N
            V(I,J)=0.DO
            V(J,I)=0.DO
31          CONTINUE
          END IF
          V(I,I)=1.DO
          G=RV1(I)
          L=I
32         CONTINUE
          DO 39 I=N,1,-1
            L=I+1
            G=W(I)
            IF(I.LT.N) THEN
              DO 33 J=L,N
                A(I,J)=0.DO
33          CONTINUE
            END IF
            IF(G.NE.0.DO) THEN
              G=1.DO/G
              IF(I.NE.N) THEN
                DO 36 J=L,N
                  S=0.DO
                  DO 34 K=L,M
                    S=S+A(K,I)*A(K,J)
34          CONTINUE
                  F=(S/A(I,I))*G
                  DO 35 K=I,M
                    A(K,J)=A(K,J)+F*A(K,I)
35          CONTINUE
36          CONTINUE
                END IF
                DO 37 J=I,M
                  A(J,I)=A(J,I)*G

```

```

37          CONTINUE
          ELSE
              DO 38 J=I,M
                  A(J,I)=0.DO
38          CONTINUE
          END IF
          A(I,I)=A(I,I)+1.DO
39  CONTINUE
      DO 49 K=N,1,-1
      DO 48 ITS=1,30
          DO 41 L=K,1,-1
              NM=L-1
              IF((DABS(RV1(L))+ANORM).EQ.ANORM) GOTO 2
              IF((DABS(W(NM))+ANORM).EQ.ANORM) GOTO 1
41          CONTINUE
          *
          *
          *
          1      C=0.DO
              S=1.DO
              DO 43 I=L,K
                  F=S*RV1(I)
                  IF((DABS(F)+ANORM).NE.ANORM) THEN
                      G=W(I)
                      H=DSQRT(F*F+G*G)
                      W(I)=H
                      H=1.DO/H
                      C=(G*H)
                      S=-(F*H)
                      DO 42 J=1,M
                          Y=A(J,NM)
                          Z=A(J,I)
                          A(J,NM)=(Y*C)+(Z*S)
                          A(J,I)=-(Y*S)+(Z*C)
42                      CONTINUE
                      END IF
43          CONTINUE
          *
          *
          *
          2      Z=W(K)
              IF(L.EQ.K) THEN
                  IF (Z.LT.0.DO) THEN
                      W(K)=-Z
                      DO 44 J=1,N
                          V(J,K)=-V(J,K)
44                      CONTINUE
                  END IF
                  GOTO 3
              ENDIF
          IF (ITS.EQ.30) PAUSE 'NO CONVERGENCE IN 30 ITERATIONS'
          X=W(L)

```

```

NM=K-1
Y=W(NM)
G=RV1(NM)
H=RV1(K)
F=((Y-Z)*(Y+Z)+(G-H)*(G+H))/(2.DO*H*Y)
G=DSQRT(F*F+1.DO)
F=((X-Z)*(X+Z)+H*((Y/(F+DSIGN(G,F)))-H))/X
C=1.DO
S=1.DO
DO 47 J=L,NM
    I=J+1
    G=RV1(I)
    Y=W(I)
    H=S*G
    G=C*G
    Z=DSQRT(F*F+H*H)
    RV1(J)=Z
    C=F/Z
    S=H/Z
    F=(X*C)+(G*S)
    G=-(X*S)+(G*C)
    H=Y*S
    Y=Y*C
DO 45 JJ=1,N
    X=V(JJ,J)
    Z=V(JJ,I)
    V(JJ,J)=(X*C)+(Z*S)
    V(JJ,I)=-(X*S)+(Z*C)
45    CONTINUE
    Z=DSQRT(F*F+H*H)
    W(J)=Z
    IF(Z.NE.0.DO) THEN
        Z=1.DO/Z
        C=F*Z
        S=H*Z
    END IF
    F=(C*G)+(S*Y)
    X=-(S*G)+(C*Y)
DO 46 JJ=1,M
    Y=A(JJ,J)
    Z=A(JJ,I)
    A(JJ,J)=(Y*C)+(Z*S)
    A(JJ,I)=-(Y*S)+(Z*C)
46    CONTINUE
47    CONTINUE
    RV1(L)=0.DO
    RV1(K)=F
    W(K)=X
48    CONTINUE
3    CONTINUE
49    CONTINUE
RETURN

```

END

APPENDIX E

PERTURBED ENERGY SHIFT PLOTS OF $^{12}\text{C}_2\text{H}_2$

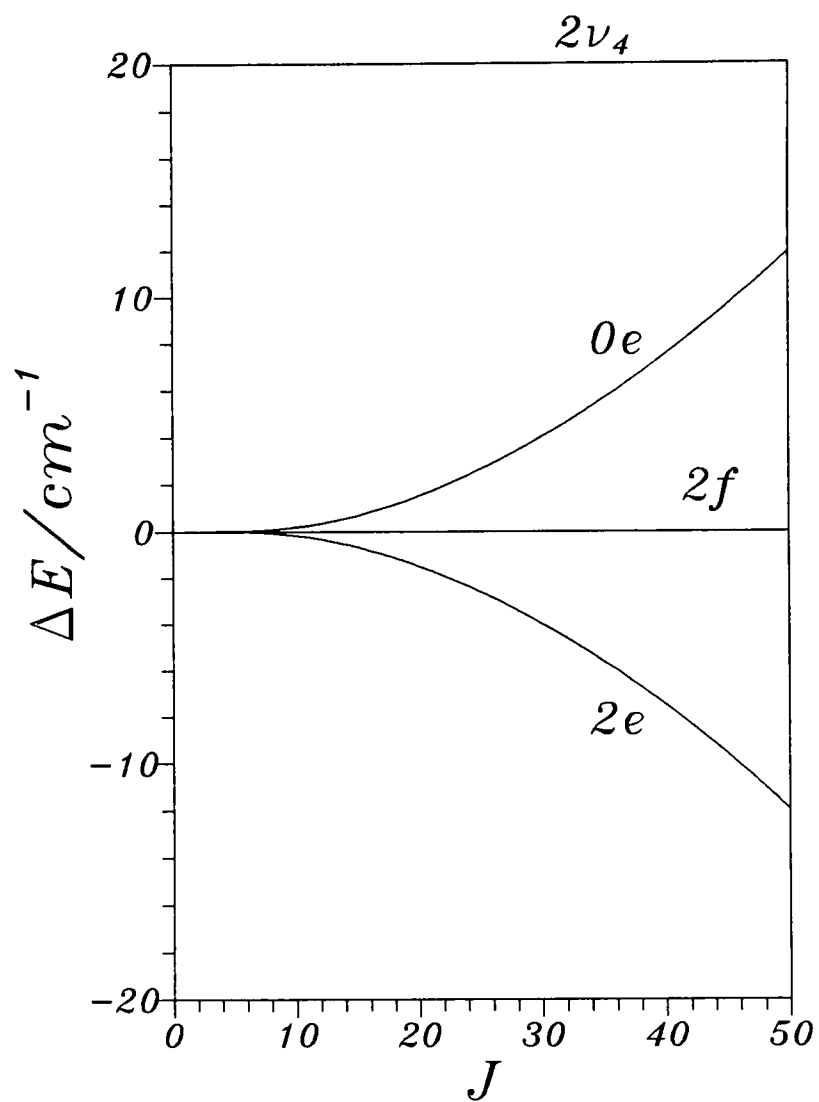


Figure E.1. Perturbed energy shifts for $2\nu_4$.

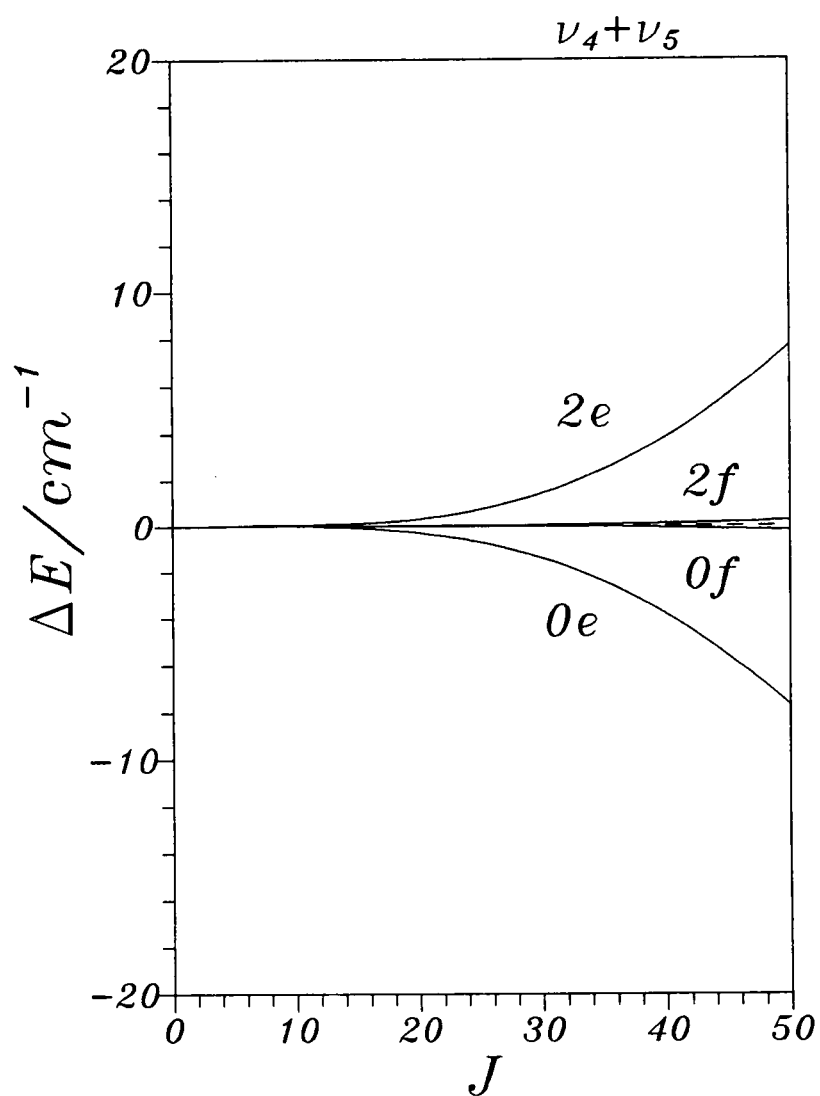


Figure E.2. Perturbed energy shifts for $\nu_4 + \nu_5$.

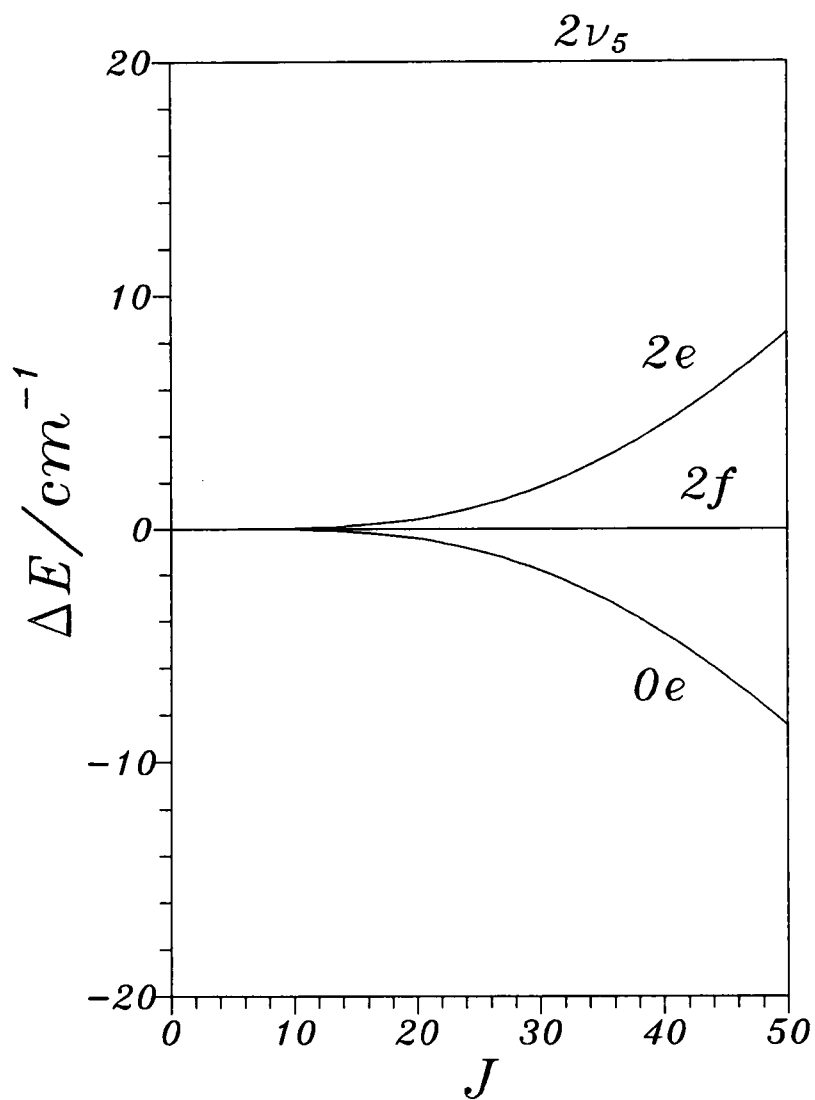


Figure E.3. Perturbed energy shifts for $2\nu_5$.

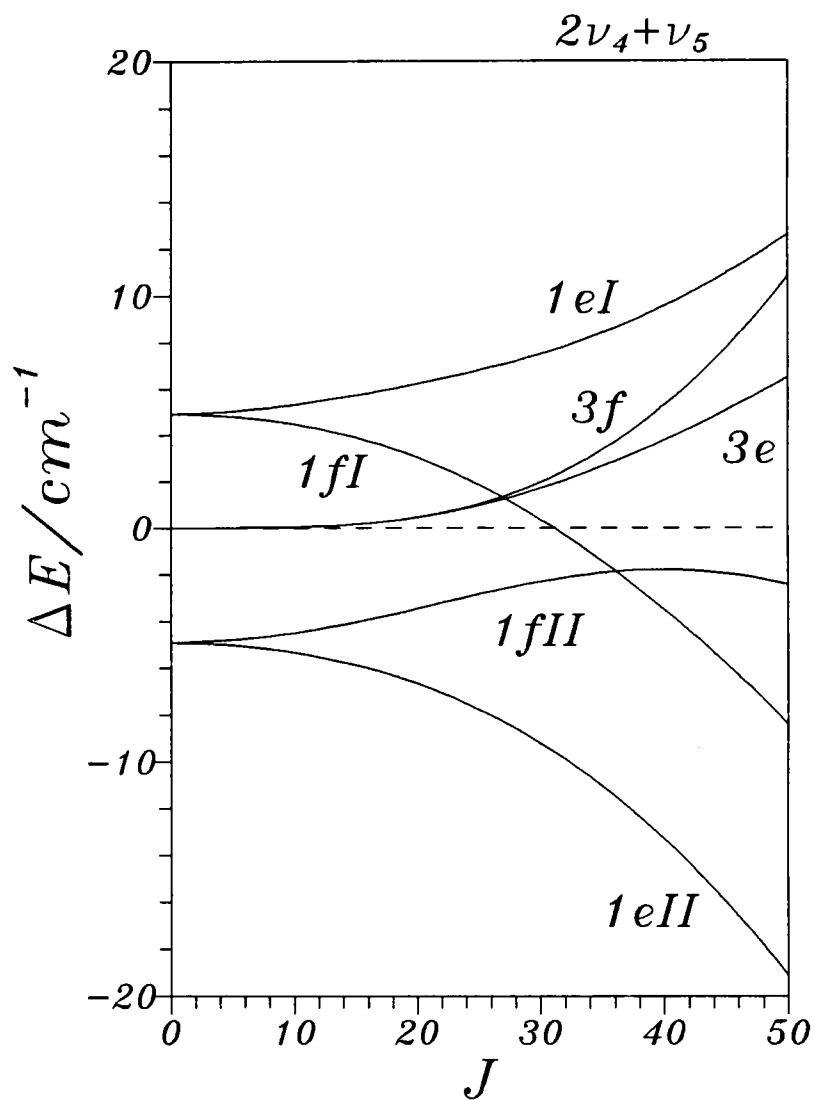


Figure E.4. Perturbed energy shifts for $2\nu_4 + \nu_5$.

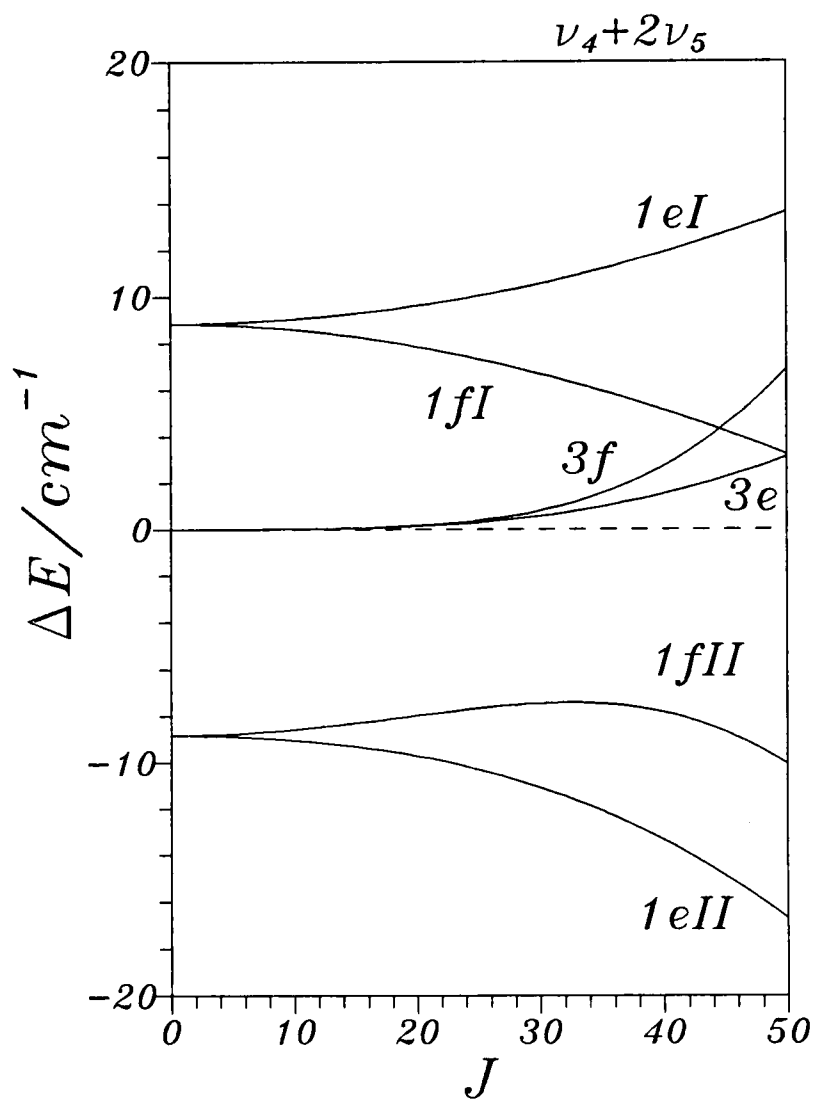


Figure E.5. Perturbed energy shifts for $\nu_4 + 2\nu_5$.

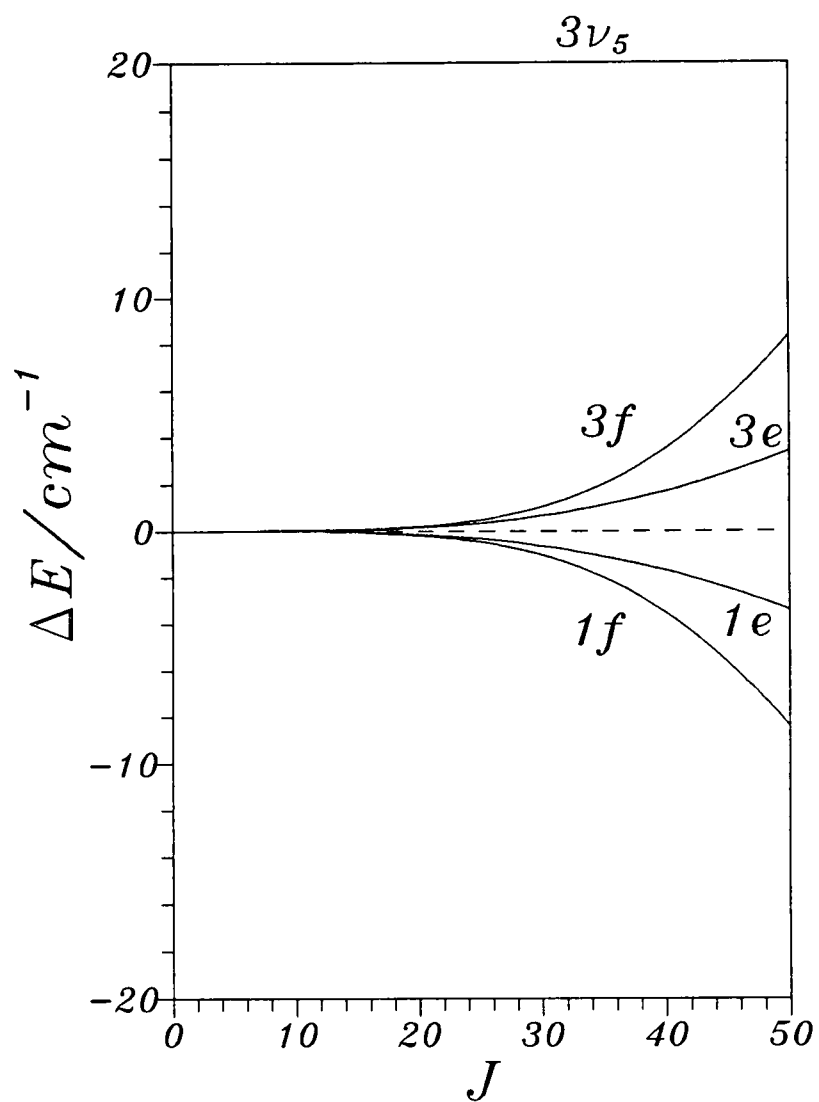


Figure E.6. Perturbed energy shifts for $3\nu_5$.

APPENDIX F

MIXING COEFFICIENT PLOTS FOR ACETYLENE

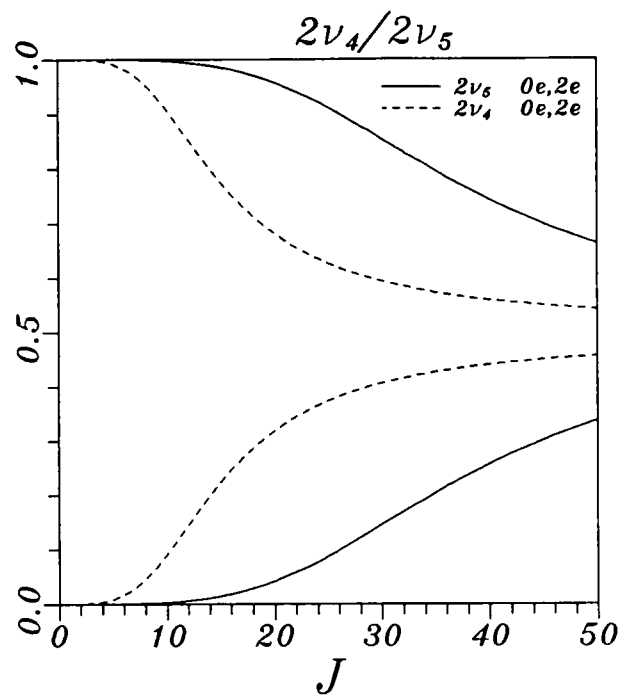


Figure F.1. Mixing of the $\Delta_j^{(e)}$ and Σ_j eigenfunctions of $2\nu_4$ and $2\nu_5$. Shown are the squares of the mixing coefficients.

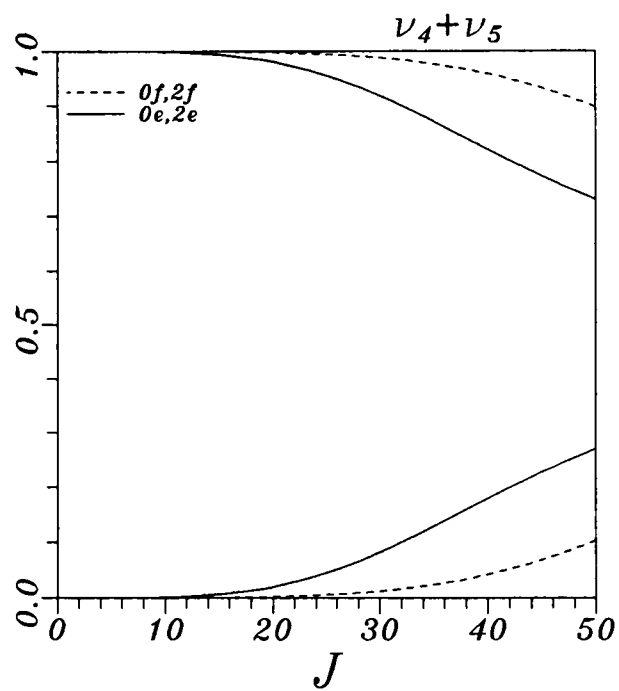


Figure F.2. Mixing of the unperturbed eigenfunctions of $\nu_4 + \nu_5$. Shown are the squares of the mixing coefficients.

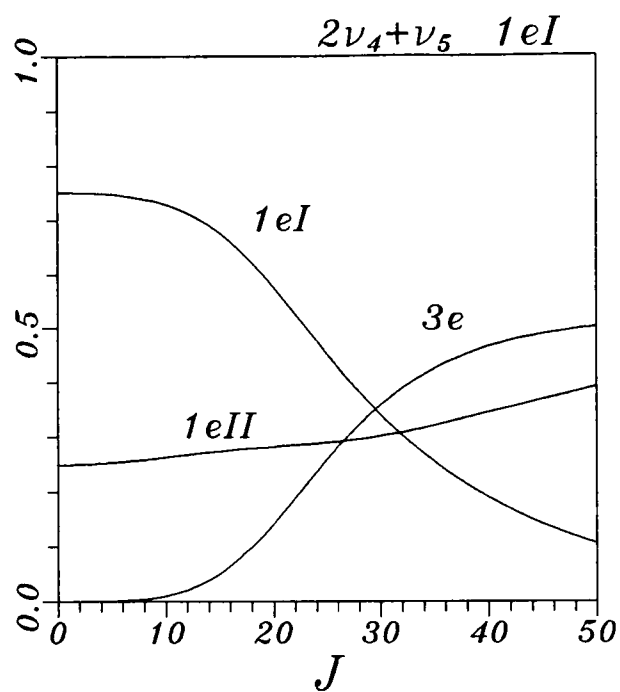


Figure F.3. Mixing of the three e states of the "unperturbed" $2\nu_4 + \nu_5^{1eI}$ level. Shown are the squares of the mixing coefficients.

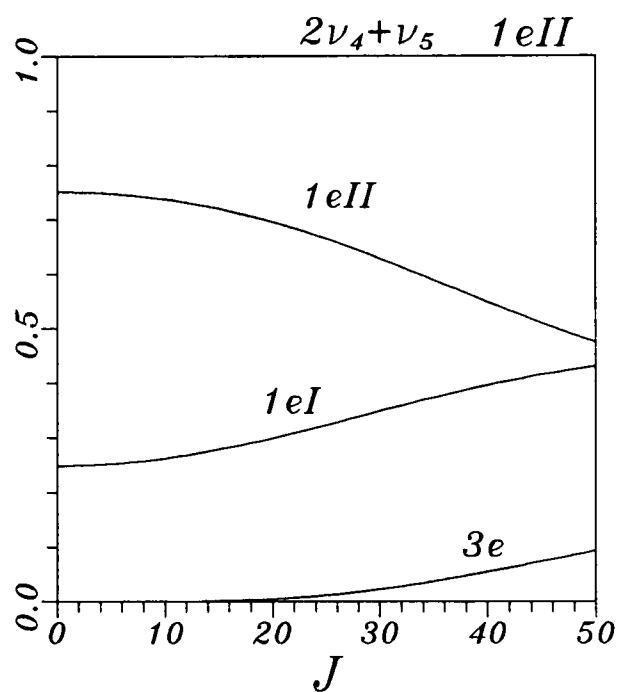


Figure F.4. Mixing of the three e states of the "unperturbed" $2\nu_4 + \nu_5^{1eII}$ level. Shown are the squares of the mixing coefficients.

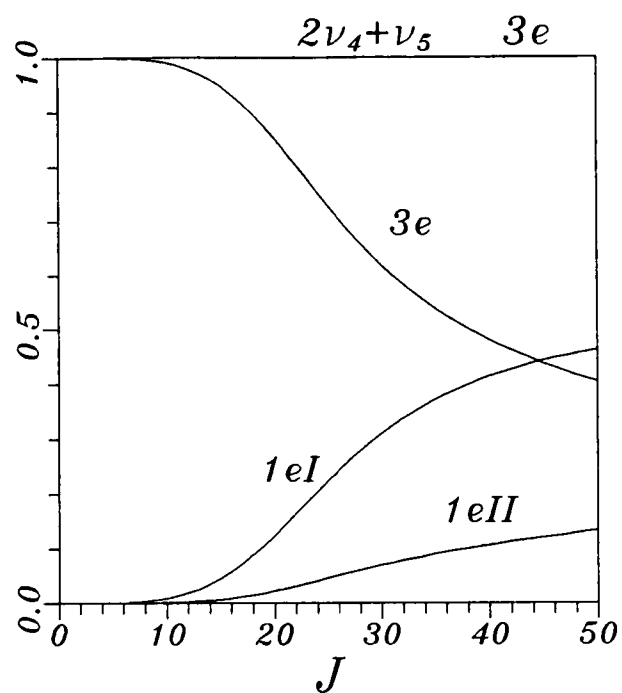


Figure F.5. Mixing of the three e states of the "unperturbed" $2\nu_4 + \nu_5^{3e}$ level. Shown are the squares of the mixing coefficients.

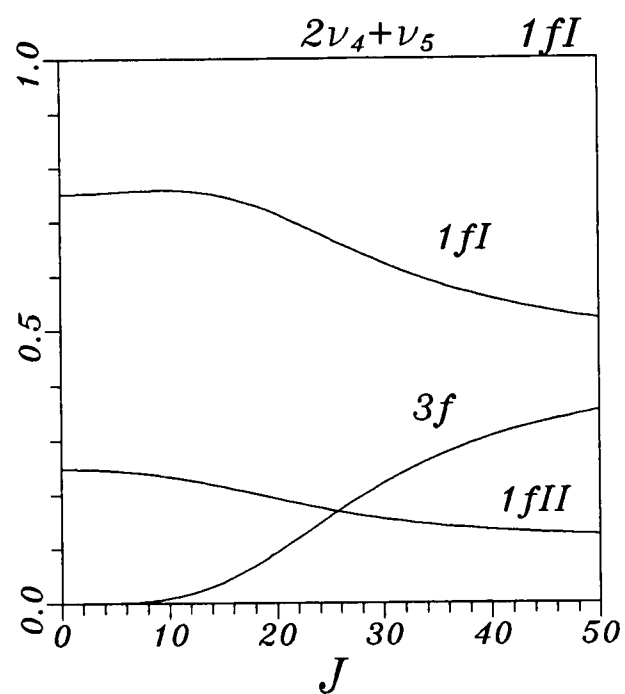


Figure F.6. Mixing of the three f states of the "unperturbed" $2\nu_4 + \nu_5^{1fI}$ level. Shown are the squares of the mixing coefficients.

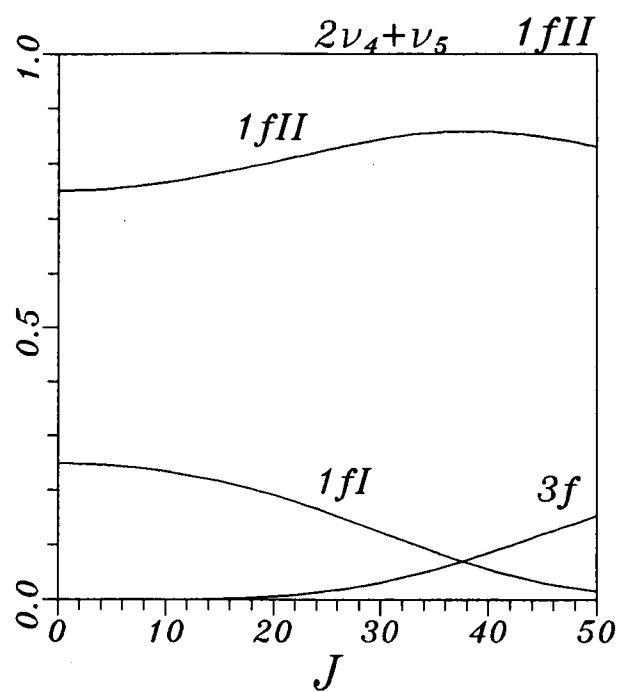


Figure F.7. Mixing of the three f states of the "unperturbed" $2\nu_4 + \nu_5^{1fII}$ level. Shown are the squares of the mixing coefficients.

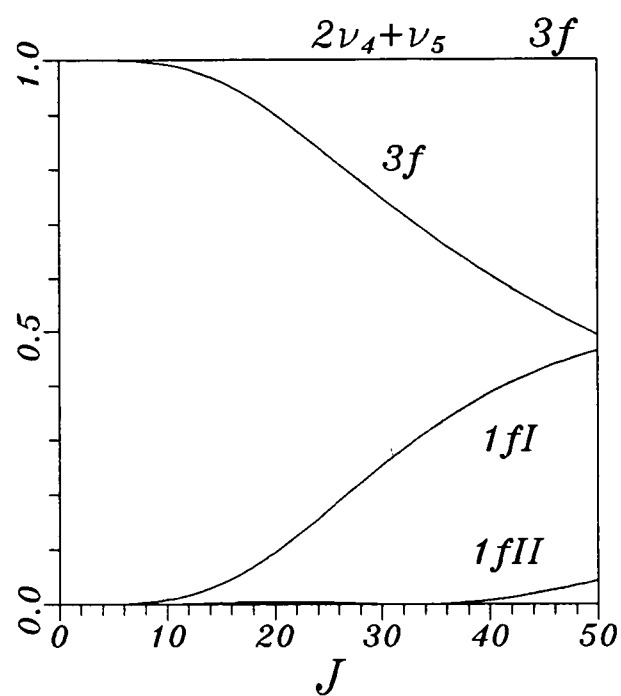


Figure F.8. Mixing of the three f states of the "unperturbed" $2\nu_4 + \nu_5^{3f}$ level. Shown are the squares of the mixing coefficients.

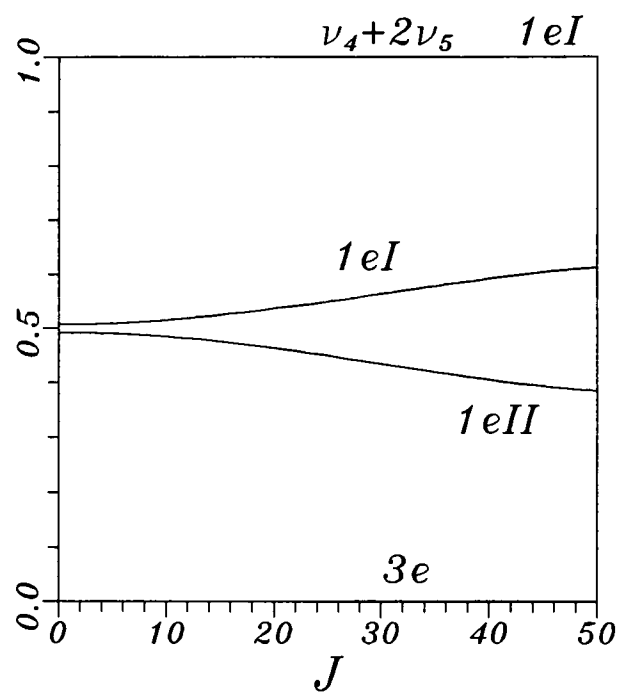


Figure F.9. Mixing of the three e states of the "unperturbed" $\nu_4 + 2\nu_5^{1eI}$ level. Shown are the squares of the mixing coefficients.

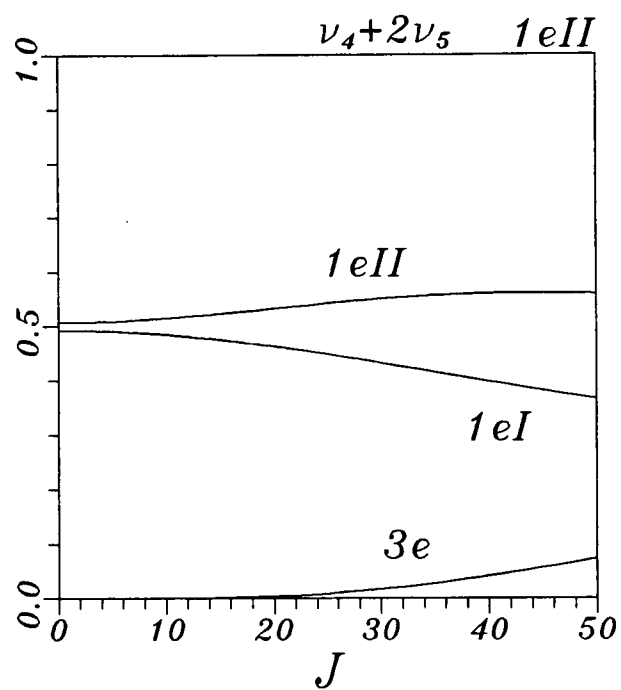


Figure F.10. Mixing of the three e states of the "unperturbed" $\nu_4 + 2\nu_5^{1eII}$ level. Shown are the squares of the mixing coefficients.

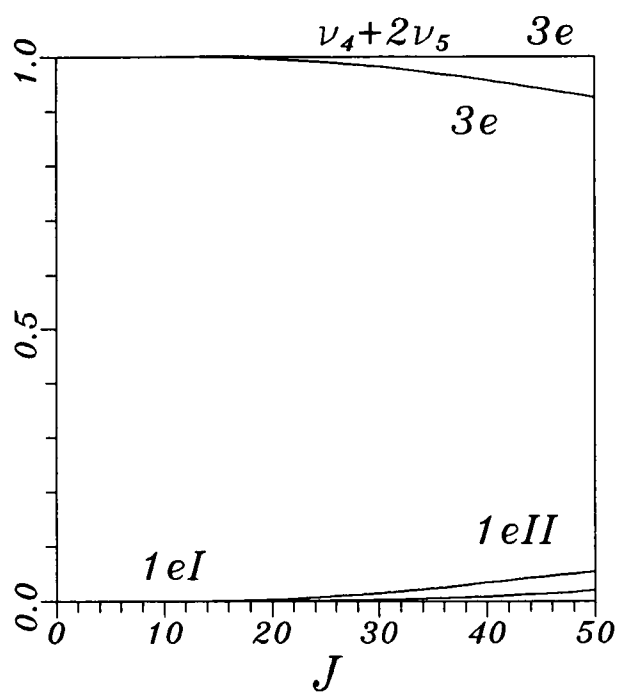


Figure F.11. Mixing of the three e states of the "unperturbed" $\nu_4 + 2\nu_5^{3e}$ level. Shown are the squares of the mixing coefficients.

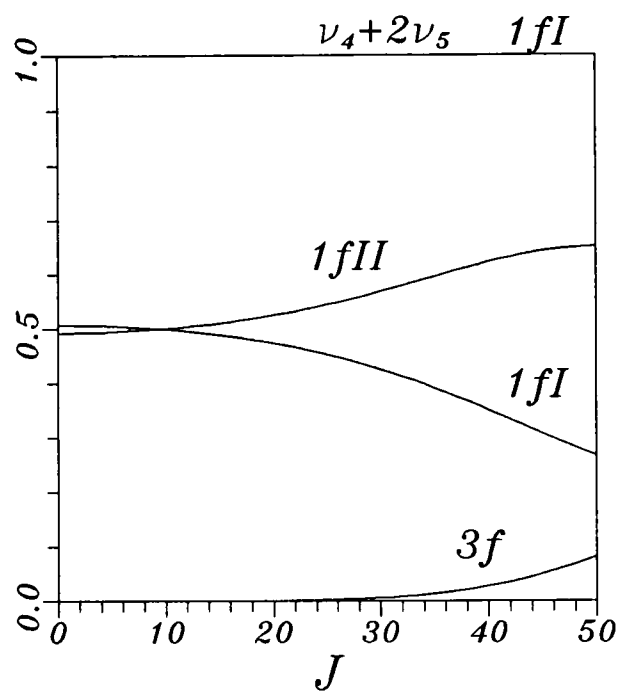


Figure F.12. Mixing of the three f states of the "unperturbed" $\nu_4 + 2\nu_5^{1fI}$ level. Shown are the squares of the mixing coefficients.

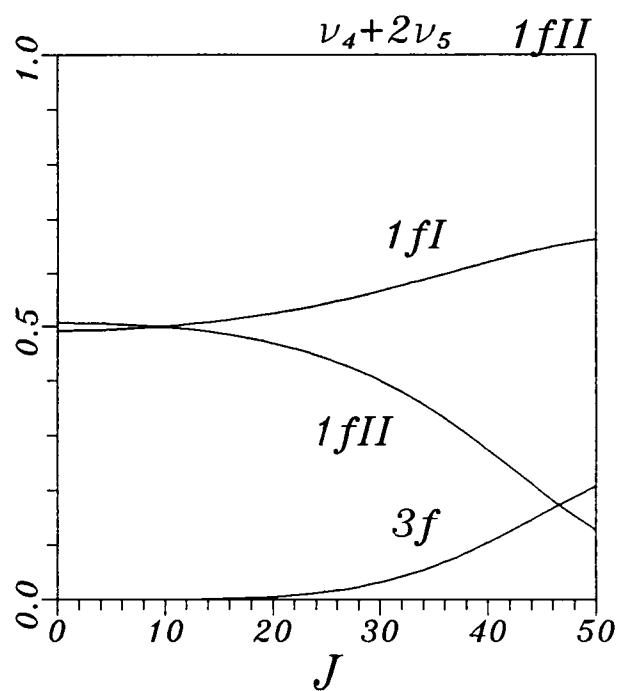


Figure F.13. Mixing of the three f states of the "unperturbed" $\nu_4 + 2\nu_5^{1fII}$ level. Shown are the squares of the mixing coefficients.

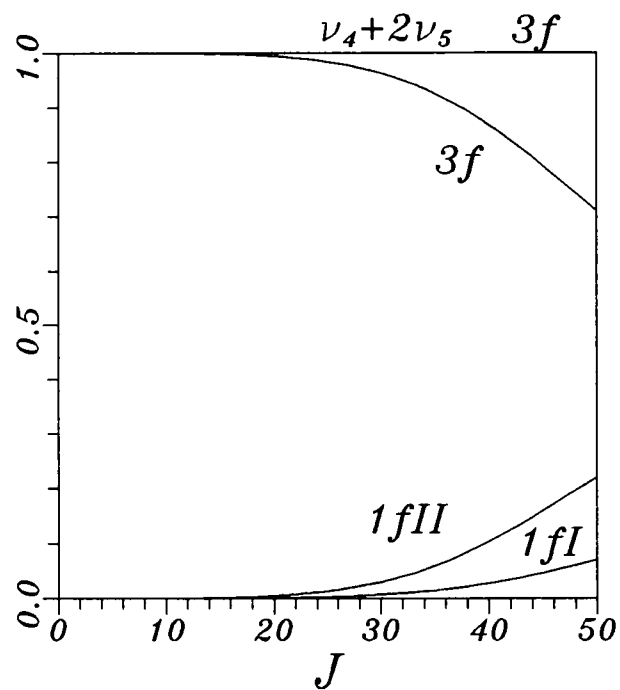


Figure F.14. Mixing of the three f states of the "unperturbed" $\nu_4 + 2\nu_5^{3f}$ level. Shown are the squares of the mixing coefficients.

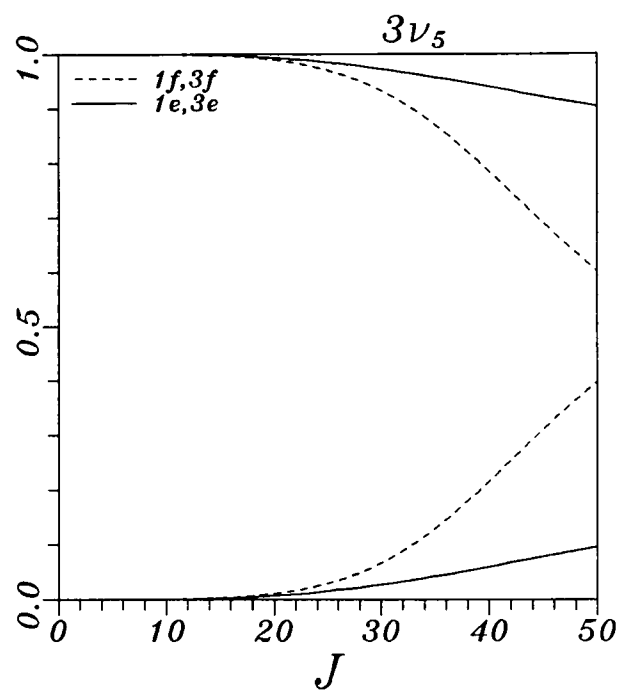


Figure F.15. Mixing of the unperturbed eigenfunctions of $3\nu_5$. Shown are the squares of the mixing coefficients.

APPENDIX G

ℓ -RESONANCE INTENSITY FACTORS

Table G.1. ℓ -resonance intensity factors, $W_{J,\Delta J}$: $\nu_4 + \nu_5^{0e} \leftarrow \nu_4^{1e,1f}$.

J	$\Delta J = -1$ (P)	$\Delta J = 0$ (Q)	$\Delta J = 1$ (R)
0	1.0000	1.0000	1.0000
1	1.0000	1.0000	1.0083
2	1.0000	0.9973	1.0138
3	1.0014	0.9931	1.0207
4	1.0041	0.9876	1.0290
5	1.0082	0.9807	1.0387
6	1.0137	0.9725	1.0498
7	1.0206	0.9628	1.0623
8	1.0288	0.9518	1.0762
9	1.0383	0.9394	1.0915
10	1.0492	0.9257	1.1082
11	1.0615	0.9106	1.1262
12	1.0751	0.8941	1.1455
13	1.0899	0.8764	1.1661
14	1.1061	0.8574	1.1880
15	1.1235	0.8372	1.2111
16	1.1421	0.8158	1.2353
17	1.1618	0.7933	1.2605
18	1.1827	0.7697	1.2867
19	1.2045	0.7453	1.3138
20	1.2273	0.7200	1.3415
21	1.2509	0.6939	1.3698
22	1.2753	0.6673	1.3986
23	1.3002	0.6402	1.4277
24	1.3257	0.6127	1.4570
25	1.3515	0.5851	1.4862
26	1.3775	0.5575	1.5153
27	1.4035	0.5299	1.5441
28	1.4296	0.5026	1.5724
29	1.4554	0.4757	1.6001
30	1.4809	0.4493	1.6271
31	1.5059	0.4236	1.6533
32	1.5304	0.3985	1.6785
33	1.5542	0.3744	1.7028
34	1.5773	0.3511	1.7259
35	1.5996	0.3288	1.7480
36	1.6209	0.3075	1.7690
37	1.6414	0.2872	1.7888
38	1.6609	0.2680	1.8075
39	1.6795	0.2498	1.8250
40	1.6970	0.2327	1.8415
41	1.7137	0.2166	1.8569
42	1.7293	0.2015	1.8712
43	1.7441	0.1874	1.8845
44	1.7579	0.1742	1.8969
45	1.7709	0.1619	1.9084

Table G.2. ℓ -resonance intensity factors, $W_{J,\Delta J}$: $\nu_4 + \nu_5^{2e} \leftarrow \nu_4^{1e,1f}$.

J	$\Delta J = -1 (P)$	$\Delta J = 0 (Q)$	$\Delta J = 1 (R)$
0	1.0000	1.0000	1.0000
1	1.0000	1.0000	0.9986
2	1.0000	1.0041	0.9959
3	0.9918	1.0083	0.9917
4	0.9863	1.0138	0.9862
5	0.9794	1.0206	0.9793
6	0.9712	1.0289	0.9709
7	0.9616	1.0386	0.9612
8	0.9507	1.0496	0.9501
9	0.9384	1.0620	0.9376
10	0.9248	1.0757	0.9237
11	0.9098	1.0901	0.9085
12	0.8936	1.1073	0.8919
13	0.8760	1.1250	0.8740
14	0.8572	1.1440	0.8548
15	0.8372	1.1642	0.8344
16	0.8160	1.1856	0.8129
17	0.7936	1.2081	0.7902
18	0.7703	1.2316	0.7665
19	0.7460	1.2561	0.7419
20	0.7208	1.2814	0.7165
21	0.6949	1.3074	0.6905
22	0.6684	1.3340	0.6638
23	0.6413	1.3611	0.6368
24	0.6138	1.3886	0.6094
25	0.5862	1.4162	0.5819
26	0.5584	1.4438	0.5545
27	0.5306	1.4713	0.5272
28	0.5031	1.4986	0.5002
29	0.4759	1.5255	0.4737
30	0.4492	1.5519	0.4477
31	0.4231	1.5776	0.4224
32	0.3977	1.6026	0.3979
33	0.3731	1.6268	0.3742
34	0.3494	1.6500	0.3515
35	0.3267	1.6723	0.3296
36	0.3050	1.6936	0.3088
37	0.2843	1.7138	0.2891
38	0.2647	1.7330	0.2703
39	0.2461	1.7511	0.2526
40	0.2287	1.7682	0.2359
41	0.2122	1.7843	0.2201
42	0.1968	1.7994	0.2054
43	0.1825	1.8135	0.1915
44	0.1690	1.8267	0.1786
45	0.1565	1.8390	0.1665

Table G.3. ℓ -resonance intensity factors, $W_{J,\Delta J}: \nu_4 + \nu_5^{0f} \leftarrow \nu_4^{1f,1e}$.

J	$\Delta J = -1 (P)$	$\Delta J = 0 (Q)$	$\Delta J = 1 (R)$
0	1.0000	1.0000	1.0000
1	1.0000	1.0000	0.9973
2	1.0000	1.0009	0.9955
3	0.9996	1.0022	0.9933
4	0.9987	1.0040	0.9906
5	0.9973	1.0063	0.9874
6	0.9955	1.0090	0.9838
7	0.9933	1.0121	0.9798
8	0.9905	1.0158	0.9752
9	0.9874	1.0199	0.9702
10	0.9837	1.0244	0.9647
11	0.9796	1.0295	0.9588
12	0.9750	1.0350	0.9523
13	0.9699	1.0410	0.9454
14	0.9644	1.0475	0.9379
15	0.9583	1.0545	0.9300
16	0.9517	1.0620	0.9215
17	0.9446	1.0701	0.9125
18	0.9370	1.0786	0.9030
19	0.9289	1.0877	0.8929
20	0.9203	1.0973	0.8823
21	0.9111	1.1075	0.8712
22	0.9013	1.1182	0.8595
23	0.8910	1.1295	0.8473
24	0.8802	1.1413	0.8345
25	0.8688	1.1537	0.8211
26	0.8568	1.1667	0.8072
27	0.8442	1.1802	0.7927
28	0.8311	1.1943	0.7777
29	0.8174	1.2090	0.7621
30	0.8031	1.2242	0.7460
31	0.7883	1.2399	0.7294
32	0.7728	1.2562	0.7123
33	0.7569	1.2731	0.6946
34	0.7404	1.2904	0.6765
35	0.7233	1.3082	0.6579
36	0.7058	1.3266	0.6389
37	0.6877	1.3453	0.6196
38	0.6692	1.3645	0.5998
39	0.6503	1.3840	0.5798
40	0.6310	1.4039	0.5595
41	0.6113	1.4241	0.5389
42	0.5913	1.4445	0.5182
43	0.5710	1.4651	0.4974
44	0.5505	1.4859	0.4765
45	0.5298	1.5067	0.4556

Table G.4. ℓ -resonance intensity factors, $W_{J,\Delta J}: \nu_4 + \nu_5^{2f} \leftarrow \nu_4^{1f,1e}$.

J	$\Delta J = -1 (P)$	$\Delta J = 0 (Q)$	$\Delta J = 1 (R)$
0	1.0000	1.0000	1.0000
1	1.0000	1.0000	1.0004
2	1.0000	0.9987	1.0013
3	1.0027	0.9973	1.0027
4	1.0045	0.9955	1.0045
5	1.0067	0.9933	1.0067
6	1.0094	0.9906	1.0094
7	1.0126	0.9874	1.0126
8	1.0162	0.9838	1.0162
9	1.0203	0.9797	1.0203
10	1.0249	0.9751	1.0249
11	1.0299	0.9701	1.0299
12	1.0354	0.9646	1.0354
13	1.0415	0.9586	1.0414
14	1.0480	0.9521	1.0479
15	1.0550	0.9450	1.0549
16	1.0625	0.9375	1.0624
17	1.0706	0.9295	1.0705
18	1.0792	0.9209	1.0790
19	1.0883	0.9118	1.0881
20	1.0979	0.9022	1.0977
21	1.1081	0.8920	1.1078
22	1.1189	0.8813	1.1185
23	1.1302	0.8700	1.1297
24	1.1421	0.8582	1.1415
25	1.1545	0.8458	1.1538
26	1.1676	0.8328	1.1667
27	1.1812	0.8193	1.1801
28	1.1954	0.8052	1.1941
29	1.2102	0.7906	1.2086
30	1.2255	0.7754	1.2237
31	1.2414	0.7596	1.2393
32	1.2579	0.7433	1.2553
33	1.2750	0.7265	1.2719
34	1.2926	0.7091	1.2890
35	1.3107	0.6913	1.3066
36	1.3293	0.6730	1.3245
37	1.3484	0.6542	1.3429
38	1.3680	0.6350	1.3616
39	1.3880	0.6155	1.3807
40	1.4084	0.5956	1.4001
41	1.4291	0.5754	1.4197
42	1.4501	0.5550	1.4395
43	1.4714	0.5344	1.4594
44	1.4929	0.5136	1.4794
45	1.5145	0.4928	1.4995

Table G.5. ℓ -resonance intensity factors, $W_{J,\Delta J}: 2\nu_5^{0e} \leftarrow \nu_5^{1e,1f}$.

J	$\Delta J = -1 (P)$	$\Delta J = 0 (Q)$	$\Delta J = 1 (R)$
0	1.0000	1.0000	1.0000
1	1.0000	1.0000	1.0124
2	1.0000	0.9959	1.0207
3	1.0020	0.9897	1.0310
4	1.0061	0.9814	1.0435
5	1.0123	0.9711	1.0581
6	1.0205	0.9587	1.0748
7	1.0307	0.9443	1.0936
8	1.0429	0.9278	1.1144
9	1.0572	0.9093	1.1372
10	1.0734	0.8888	1.1620
11	1.0916	0.8664	1.1887
12	1.1116	0.8422	1.2172
13	1.1334	0.8162	1.2474
14	1.1569	0.7886	1.2790
15	1.1821	0.7595	1.3120
16	1.2087	0.7291	1.3460
17	1.2365	0.6976	1.3809
18	1.2655	0.6652	1.4165
19	1.2955	0.6322	1.4523
20	1.3260	0.5987	1.4883
21	1.3571	0.5652	1.5239
22	1.3883	0.5317	1.5591
23	1.4195	0.4987	1.5935
24	1.4503	0.4663	1.6269
25	1.4807	0.4348	1.6591
26	1.5103	0.4043	1.6899
27	1.5390	0.3751	1.7191
28	1.5666	0.3472	1.7468
29	1.5931	0.3207	1.7728
30	1.6182	0.2958	1.7971
31	1.6420	0.2724	1.8196
32	1.6644	0.2505	1.8406
33	1.6855	0.2302	1.8598
34	1.7051	0.2113	1.8775
35	1.7234	0.1939	1.8938
36	1.7404	0.1778	1.9086
37	1.7562	0.1631	1.9221
38	1.7707	0.1495	1.9343
39	1.7842	0.1371	1.9455
40	1.7966	0.1257	1.9556
41	1.8081	0.1153	1.9647
42	1.8186	0.1059	1.9729
43	1.8283	0.0972	1.9804
44	1.8373	0.0893	1.9871
45	1.8455	0.0821	1.9931

Table G.6. ℓ -resonance intensity factors, $W_{J,\Delta J}$: $2\nu_5^{2e} \leftarrow \nu_5^{1e,1f}$.

J	$\Delta J = -1 (P)$	$\Delta J = 0 (Q)$	$\Delta J = 1 (R)$
0	1.0000	1.0000	1.0000
1	1.0000	1.0000	0.99793
2	1.0000	1.0061	0.99378
3	0.98765	1.0123	0.98756
4	0.97944	1.0206	0.97924
5	0.96919	1.0309	0.96883
6	0.95691	1.0433	0.95633
7	0.94260	1.0578	0.94175
8	0.92630	1.0742	0.92509
9	0.90801	1.0927	0.90639
10	0.88778	1.1132	0.88570
11	0.86566	1.1356	0.86307
12	0.84170	1.1598	0.83860
13	0.81601	1.1858	0.81238
14	0.78869	1.2134	0.78456
15	0.75986	1.2424	0.75529
16	0.72968	1.2728	0.72477
17	0.69835	1.3043	0.69320
18	0.66605	1.3367	0.66083
19	0.63304	1.3697	0.62791
20	0.59954	1.4031	0.59469
21	0.56582	1.4367	0.56145
22	0.53214	1.4701	0.52845
23	0.49877	1.5031	0.49595
24	0.46595	1.5354	0.46416
25	0.43392	1.5669	0.43330
26	0.40290	1.5973	0.40355
27	0.37305	1.6265	0.37505
28	0.34453	1.6544	0.34791
29	0.31745	1.6808	0.32221
30	0.29189	1.7057	0.29799
31	0.26790	1.7291	0.27527
32	0.24549	1.7509	0.25405
33	0.22465	1.7712	0.23430
34	0.20536	1.7900	0.21597
35	0.18756	1.8074	0.19901
36	0.17118	1.8234	0.18335
37	0.15616	1.8381	0.16892
38	0.14241	1.8516	0.15564
39	0.12985	1.8640	0.14344
40	0.11840	1.8753	0.13223
41	0.10796	1.8856	0.12196
42	0.09847	1.8951	0.11253
43	0.08983	1.9037	0.10390
44	0.08198	1.9116	0.09598
45	0.07485	1.9188	0.08873

APPENDIX H

ABSOLUTE FTS INTENSITIES OF ACETYLENE

Table H.1. Absolute FTS intensities of ν_5^{1e} .

ν_o [cm ⁻¹]	J	ΔJ	S_J [cm ⁻² atm ⁻¹ @ 295K]	%	cal.
684.4155	19	-1	4.5390	3.7	4.2776
689.1240	17	-1	5.8910	3.3	5.8825
693.8335	15	-1	7.9340	3.3	7.6064
698.5436	13	-1	9.1550	2.4	9.2028
703.2540	11	-1	10.5040	2.2	10.3394
707.9645	9	-1	10.3240	2.2	10.6513
712.6747	7	-1	9.5740	2.2	9.8251
717.3844	5	-1	7.6250	2.3	7.6943
733.8595	1	1	6.9920	2.7	7.0597
736.2114	2	1	3.1770	4.4	3.0843
738.5628	3	1	11.3050	2.1	11.2393
740.9137	4	1	4.3090	3.2	4.3189
743.2639	5	1	14.0360	2.0	14.3554
745.6135	6	1	4.9460	2.7	5.1342
747.9624	7	1	16.2570	2.1	16.0824
750.3106	8	1	5.6330	2.9	5.4651
752.6580	9	1	16.4590	1.8	16.3585
755.0046	10	1	4.9560	2.8	5.3340
757.3504	11	1	15.0860	1.9	15.3670
759.6952	12	1	4.5670	3.1	4.8342
762.0392	13	1	13.5060	1.8	13.4615
766.7241	15	1	11.2190	1.9	11.0631
771.4048	17	1	8.8150	1.9	8.5642
776.0810	19	1	6.5030	2.6	6.2625
780.7523	21	1	4.4400	2.9	4.3346

Table H.2. Absolute FTS intensities of ν_5^{1e} of $^{13}\text{C}^{12}\text{CH}_2$.

ν_o [cm ⁻¹]	J	ΔJ	S_J [cm ⁻² atm ⁻¹ @ 293.3K]	%	cal.
723.6337	2	-1	0.0308	3.8	0.0324
721.3359	3	-1	0.0601	5.6	0.0624
716.7393	5	-1	0.1098	4.7	0.1117
714.4405	6	-1	0.1285	4.2	0.1299
712.1415	7	-1	0.1411	4.0	0.1434
709.8422	8	-1	0.1564	4.3	0.1521
707.5428	9	-1	0.1553	3.9	0.1564
705.2432	10	-1	0.1508	6.3	0.1564
702.9435	11	-1	0.1523	3.8	0.1528
700.6437	12	-1	0.1427	3.9	0.1461
698.3438	13	-1	0.1298	4.9	0.1371
696.0440	14	-1	0.1253	6.3	0.1262
693.7442	15	-1	0.1159	3.7	0.1142
691.4444	16	-1	0.1049	3.9	0.1017
686.8452	18	-1	0.0765	3.8	0.0770
684.5459	19	-1	0.0669	3.2	0.0655
682.2427	20	-1	0.0560	4.4	0.0549
679.9478	21	-1	0.0457	6.9	0.0454
677.6492	22	-1	0.0380	4.1	0.0371
675.3509	23	-1	0.0298	3.4	0.0298
673.0529	24	-1	0.0248	3.5	0.0237
735.1156	2	1	0.1348	4.0	0.1328
737.4104	3	1	0.1649	4.0	0.1612
739.7045	4	1	0.1834	3.8	0.1858
741.9979	5	1	0.2122	4.0	0.2058
744.2907	6	1	0.2158	4.2	0.2209
746.5827	7	1	0.2329	6.5	0.2307
748.8739	8	1	0.2437	8.0	0.2353
751.1642	9	1	0.2327	4.3	0.2350
753.4538	10	1	0.2252	3.8	0.2301
755.7424	11	1	0.2207	4.3	0.2212
758.0300	12	1	0.1962	3.8	0.2091
760.3167	13	1	0.1935	3.7	0.1944
762.6024	14	1	0.1726	5.1	0.1779
764.8870	15	1	0.1544	3.8	0.1604
767.1705	16	1	0.1402	4.0	0.1425
771.7341	18	1	0.1098	4.1	0.1077
774.0141	19	1	0.0927	3.6	0.0917
776.2928	20	1	0.0763	3.2	0.0771
778.5703	21	1	0.0642	3.3	0.0639
783.1211	23	1	0.0442	3.4	0.0422
785.3945	24	1	0.0356	3.6	0.0337
787.6663	25	1	0.0270	3.2	0.0265

Table H.3. Absolute FTS intensities of $\nu_4 + \nu_5^{0e} \leftarrow \nu_4^{1e}$.

ν_o [cm ⁻¹]	J	ΔJ	S_J [cm ⁻² atm ⁻¹ @ 293.3K]	%	cal.
714.0291	1	-1	0.1132	4.0	0.1159
711.6888	2	-1	0.0546	2.3	0.0564
709.3589	3	-1	0.2205	4.2	0.2170
707.0392	4	-1	0.0826	0.3	0.0861
704.7297	5	-1	0.3017	4.5	0.2925
702.4303	6	-1	0.1060	4.0	0.1062
700.1408	7	-1	0.3542	5.3	0.3364
697.8610	8	-1	0.1112	4.3	0.1154
695.5905	9	-1	0.3762	5.5	0.3481
693.3292	10	-1	0.1127	6.8	0.1143
691.0767	11	-1	0.3287	5.3	0.3317
688.8325	12	-1	0.1022	4.2	0.1051
686.5963	13	-1	0.2930	5.5	0.2948
684.3675	14	-1	0.0956	4.7	0.0904
682.1458	15	-1	0.2423	4.7	0.2460
677.7210	17	-1	0.1922	4.7	0.1935
675.5168	18	-1	0.0586	3.1	0.0560
673.3173	19	-1	0.1406	3.8	0.1440
671.1218	20	-1	0.0425	3.3	0.0406
668.9297	21	-1	0.0974	7.2	0.1014
666.7402	22	-1	0.0280	3.7	0.0278
664.5529	23	-1	0.0686	3.6	0.0678
660.1817	25	-1	0.0455	3.7	0.0429
655.8112	27	-1	0.0282	3.6	0.0258
723.4931	2	1	0.0372	3.1	0.0390
725.8843	3	1	0.1726	5.1	0.1716
735.5434	7	1	0.3290	4.4	0.3295
737.9802	8	1	0.1262	5.2	0.1165
740.4250	9	1	0.3589	3.9	0.3610
742.8773	10	1	0.1188	4.5	0.1215
745.3367	11	1	0.3620	3.1	0.3606
747.8026	12	1	0.1148	8.0	0.1167
750.2744	13	1	0.3393	0.7	0.3337
755.2333	15	1	0.2840	4.7	0.2888
757.7190	16	1	0.0884	4.1	0.0875
760.2080	17	1	0.2291	5.1	0.2349
762.6996	18	1	0.0691	3.0	0.0691
765.1930	19	1	0.1784	3.4	0.1802
767.6875	20	1	0.0527	4.7	0.0515
770.1823	21	1	0.1323	2.9	0.1306
772.6768	22	1	0.0378	2.7	0.0363
775.1703	23	1	0.0920	3.4	0.0895
777.6619	24	1	0.0252	6.1	0.0242
780.1512	25	1	0.0615	3.2	0.0581
785.1200	27	1	0.0360	4.3	0.0357

Table H.4. Absolute FTS intensities of $\nu_4 + \nu_5^{2e} \leftarrow \nu_4^{1e}$.

ν_o [cm ⁻¹]	J	ΔJ	S_J [cm ⁻² atm ⁻¹]	% [293.3K]	cal.
724.0838	3	-1	0.0366	3.5	0.0385
719.4470	5	-1	0.1220	6.3	0.1221
717.1429	6	-1	0.0500	3.1	0.0521
714.8487	7	-1	0.1796	4.1	0.1825
712.5647	8	-1	0.0637	4.9	0.0668
708.0284	10	-1	0.0685	4.9	0.0709
705.7770	11	-1	0.2014	4.6	0.2084
703.5373	12	-1	0.0625	3.4	0.0662
701.3097	13	-1	0.1825	4.2	0.1848
699.0948	14	-1	0.0560	6.8	0.0560
696.8932	15	-1	0.1476	4.3	0.1495
694.7055	16	-1	0.0443	0.6	0.0435
692.5321	17	-1	0.1091	3.9	0.1115
688.2315	19	-1	0.0758	2.7	0.0773
686.1055	20	-1	0.0225	4.4	0.0209
683.9966	21	-1	0.0508	3.8	0.0499
679.8329	23	-1	0.0312	3.1	0.0301
738.2146	2	1	0.1328	3.9	0.1372
742.9978	4	1	0.1647	7.4	0.1594
747.8188	6	1	0.1681	8.2	0.1708
752.6794	8	1	0.1681	5.2	0.1686
755.1253	9	1	0.5328	3.5	0.4881
757.5821	10	1	0.1505	3.1	0.1541
760.0501	11	1	0.4343	3.7	0.4303
765.0219	13	1	0.3713	4.2	0.3538
767.5265	14	1	0.1019	3.1	0.1043
772.5761	16	1	0.0761	3.0	0.0776
775.1222	17	1	0.1951	3.6	0.1961
777.6832	18	1	0.0530	3.8	0.0542
780.2599	19	1	0.1314	3.3	0.1326
782.8527	20	1	0.0355	4.2	0.0355
785.4624	21	1	0.0853	3.2	0.0843
790.7345	23	1	0.0512	3.2	0.0504
796.0807	25	1	0.0291	3.5	0.0283

Table H.5. Absolute FTS intensities of $\nu_4 + \nu_5^{0f} \leftarrow \nu_4^{1f}$.

ν_o [cm ⁻¹]	J	ΔJ	S_J [cm ⁻² atm ⁻¹ @ 293.3K]	%	cal.
726.4961	1	-1	0.0398	3.2	0.0417
724.1341	2	-1	0.1847	4.1	0.1824
719.4075	4	-1	0.2828	0.7	0.2773
717.0431	5	-1	0.1028	3.1	0.1041
714.6778	6	-1	0.3553	4.4	0.3376
712.3119	7	-1	0.1170	3.5	0.1178
709.9453	8	-1	0.3875	4.5	0.3597
707.5780	9	-1	0.1172	3.8	0.1191
705.2101	10	-1	0.3517	0.8	0.3471
702.8417	11	-1	0.1091	3.5	0.1102
700.4727	12	-1	0.3186	4.7	0.3087
698.1032	13	-1	0.0929	0.3	0.0944
695.7332	14	-1	0.2525	4.9	0.2554
693.3628	15	-1	0.0758	7.7	0.0755
690.9912	16	-1	0.1888	2.1	0.1978
688.6206	17	-1	0.0576	3.5	0.0567
686.2490	18	-1	0.1445	5.0	0.1439
683.8770	19	-1	0.0391	3.5	0.0400
681.5047	20	-1	0.0981	3.4	0.0986
679.1321	21	-1	0.0257	7.5	0.0267
676.7592	22	-1	0.0659	4.1	0.0637
672.0127	24	-1	0.0403	3.5	0.0390
667.2653	26	-1	0.0238	3.8	0.0225
735.9347	2	1	0.1247	3.4	0.1240
738.2918	3	1	0.0576	2.9	0.0600
740.6477	4	1	0.2369	4.2	0.2297
743.0025	5	1	0.0947	7.4	0.0905
747.7085	7	1	0.1076	3.8	0.1092
750.0596	8	1	0.3454	0.7	0.3413
752.4093	9	1	0.1130	3.4	0.1153
754.7576	10	1	0.3355	3.8	0.3420
757.1045	11	1	0.1078	3.3	0.1103
759.4499	12	1	0.3076	3.9	0.3135
761.7938	13	1	0.0954	3.8	0.0972
764.1361	14	1	0.2651	4.1	0.2662
766.4767	15	1	0.0801	3.1	0.0796
771.1528	17	1	0.0603	2.9	0.0611
773.4882	18	1	0.1575	3.0	0.1566
775.8217	19	1	0.0403	5.6	0.0440
778.1532	20	1	0.1089	2.9	0.1094
780.4828	21	1	0.0298	3.1	0.0298
782.8103	22	1	0.0747	2.9	0.0720
787.4590	24	1	0.0446	3.1	0.0448
792.0987	26	1	0.0273	3.3	0.0263

Table H.6. Absolute FTS intensities of $\nu_4 + \nu_5^{2f} \leftarrow \nu_4^{1f}$.

ν_o [cm ⁻¹]	J	ΔJ	S_J [cm ⁻² atm ⁻¹ @ 293.3K]	%	cal.
719.2895	5	-1	0.0394	3.3	0.0409
714.5531	7	-1	0.0627	3.2	0.0625
712.1831	8	-1	0.2192	6.3	0.2090
709.8121	9	-1	0.0736	0.4	0.0743
707.4401	10	-1	0.2340	4.7	0.2296
705.0670	11	-1	0.0779	4.3	0.0765
702.6930	12	-1	0.2313	4.0	0.2239
700.3181	13	-1	0.0710	0.3	0.0712
697.9424	14	-1	0.2052	3.9	0.1994
695.5659	15	-1	0.0611	5.2	0.0609
693.1886	16	-1	0.1609	4.1	0.1646
690.8106	17	-1	0.0487	3.0	0.0486
688.4319	18	-1	0.1249	4.3	0.1271
686.0527	19	-1	0.0371	3.3	0.0364
683.6729	20	-1	0.0907	3.7	0.0922
681.2927	21	-1	0.0263	5.8	0.0256
678.9120	22	-1	0.0641	7.0	0.0631
674.1496	24	-1	0.0417	3.9	0.0409
669.3861	26	-1	0.0257	44.7	0.0251
735.8263	1	1	0.1211	7.6	0.1241
740.5382	3	1	0.1474	3.4	0.1483
745.2437	5	1	0.1703	4.0	0.1688
749.9426	7	1	0.1757	4.0	0.1780
754.6346	9	1	0.1737	4.7	0.1748
756.9780	10	1	0.5173	3.8	0.5068
761.6591	12	1	0.4842	3.8	0.4519
763.9969	13	1	0.1370	3.4	0.1391
766.3328	14	1	0.3834	4.0	0.3798
770.9986	16	1	0.3038	8.9	0.3018
773.3285	17	1	0.0857	3.1	0.0879
775.6564	18	1	0.2210	3.8	0.2272
777.9822	19	1	0.0643	2.6	0.0644
780.3060	20	1	0.1559	3.5	0.1623
782.6276	21	1	0.0449	4.0	0.0448
784.9472	22	1	0.1109	3.2	0.1101
787.2646	23	1	0.0295	3.0	0.0297
789.5798	24	1	0.0734	2.7	0.0711
798.8187	28	1	0.0259	3.8	0.0255

Table H.7. Absolute FTS intensities of $2\nu_5^{0e} \leftarrow \nu_5^{1e}$.

ν_o [cm ⁻¹]	J	ΔJ	S_J [cm ⁻² atm ⁻¹ •293.3K]	%	cal.
717.6055	1	-1	0.0425	3.1	0.0444
715.2622	2	-1	0.1987	5.1	0.1942
712.9283	3	-1	0.0808	0.5	0.0831
710.6039	4	-1	0.3285	11.6	0.2974
705.9827	6	-1	0.3985	0.8	0.3683
703.6854	7	-1	0.1260	4.3	0.1300
701.3967	8	-1	0.4214	4.1	0.4029
699.1161	9	-1	0.1314	5.7	0.1357
696.8432	10	-1	0.3620	3.6	0.4030
694.5775	11	-1	0.1269	5.9	0.1306
692.3184	12	-1	0.3767	5.3	0.3743
690.0654	13	-1	0.1163	3.7	0.1173
687.8179	14	-1	0.3098	4.4	0.3258
685.5751	15	-1	0.0974	3.9	0.0990
683.3363	16	-1	0.2561	4.7	0.2670
681.1008	17	-1	0.0785	3.2	0.0788
678.8679	18	-1	0.1940	6.1	0.2064
676.6368	19	-1	0.0603	3.2	0.0592
674.4069	20	-1	0.1454	5.6	0.1509
672.1773	21	-1	0.0430	3.5	0.0421
669.9475	22	-1	0.1026	5.5	0.1042
665.4846	24	-1	0.0691	0.4	0.0681
661.0139	26	-1	0.0421	3.6	0.0421
727.0735	2	1	0.1319	3.9	0.1353
731.8622	4	1	0.2547	7.0	0.2577
734.2693	5	1	0.0992	9.1	0.1032
736.6844	6	1	0.3647	3.7	0.3539
739.1070	7	1	0.1249	3.2	0.1298
741.5367	8	1	0.4230	3.7	0.4152
743.9728	9	1	0.1429	3.9	0.1439
746.4148	10	1	0.4421	3.7	0.4386
748.8619	11	1	0.1402	7.9	0.1456
751.3135	12	1	0.4345	3.6	0.4266
753.7687	13	1	0.1328	3.6	0.1365
756.2269	14	1	0.3830	3.9	0.3864
761.1487	16	1	0.3146	3.6	0.3278
763.6107	17	1	0.0975	3.5	0.0983
766.0724	18	1	0.2534	4.0	0.2615
768.5329	19	1	0.0763	2.9	0.0761
770.9916	20	1	0.1856	8.7	0.1963
773.4476	21	1	0.0573	3.6	0.0555
775.9005	22	1	0.1388	1.6	0.1390
778.3496	23	1	0.0385	7.6	0.0381
780.7944	24	1	0.0936	3.4	0.0928
785.6694	26	1	0.0603	3.2	0.0585
790.5229	28	1	0.0363	2.5	0.0348

Table H.8. Absolute FTS intensities of $2\nu_5^{2e} \leftarrow \nu_5^{1e}$.

ν_o [cm ⁻¹]	J	ΔJ	S_J [cm ⁻² atm ⁻¹ @ 293.3K]	%	cal.
719.7806	4	-1	0.0848	8.8	0.0886
717.4632	5	-1	0.0419	2.4	0.0439
715.1552	6	-1	0.1676	4.2	0.1678
712.8570	7	-1	0.0619	4.4	0.0650
706.0248	10	-1	0.2294	0.8	0.2225
703.7699	11	-1	0.0722	4.4	0.0720
701.5272	12	-1	0.1955	4.6	0.2038
699.2973	13	-1	0.0609	4.4	0.0625
697.0810	14	-1	0.1678	5.1	0.1683
694.8790	15	-1	0.0487	3.0	0.0492
692.6920	16	-1	0.1262	5.9	0.1269
690.5208	17	-1	0.0366	4.1	0.0356
688.3662	18	-1	0.0910	3.7	0.0881
686.2290	19	-1	0.0229	10.8	0.0238
684.1099	20	-1	0.0567	3.6	0.0567
743.4408	5	1	0.1773	4.3	0.1807
748.2822	7	1	0.1795	3.9	0.1840
753.1652	9	1	0.1716	3.5	0.1725
758.0938	11	1	0.1491	3.5	0.1496
760.5766	12	1	0.4207	3.6	0.4065
763.0727	13	1	0.1183	3.4	0.1205
765.5826	14	1	0.3235	4.0	0.3158
768.1072	15	1	0.0893	3.3	0.0903
770.6470	16	1	0.2234	4.0	0.2286
773.2028	17	1	0.0629	3.0	0.0632
775.7754	18	1	0.1523	3.1	0.1545
778.3653	19	1	0.0416	7.0	0.0413
780.9731	20	1	0.0974	3.2	0.0976
786.2451	22	1	0.0585	3.3	0.0577
791.5950	24	1	0.0329	2.7	0.0321

Table H.9. Absolute FTS intensities of $2\nu_5^{2f} \leftarrow \nu_5^{1f}$.

ν_o [cm ⁻¹]	J	ΔJ	S_J [cm ⁻² atm ⁻¹ @ 293.3K]	%	cal.
722.0507	3	-1	0.0389	5.3	0.0419
719.6863	4	-1	0.0268	9.2	0.0299
717.3214	5	-1	0.1312	3.6	0.1346
714.9559	6	-1	0.0560	3.5	0.0579
712.5899	7	-1	0.2214	4.9	0.2048
710.2234	8	-1	0.0790	5.7	0.0759
707.8565	9	-1	0.2599	5.2	0.2419
705.4891	10	-1	0.0815	3.3	0.0827
703.1214	11	-1	0.2516	4.7	0.2471
700.7534	12	-1	0.0774	3.2	0.0800
698.3851	13	-1	0.2333	5.1	0.2275
696.0165	14	-1	0.0713	6.9	0.0705
693.6478	15	-1	0.1892	4.4	0.1926
691.2789	16	-1	0.0590	3.4	0.0574
688.9098	17	-1	0.1460	3.7	0.1516
686.5407	18	-1	0.0426	3.5	0.0437
684.1715	19	-1	0.1105	4.1	0.1117
681.8023	20	-1	0.0318	5.5	0.0312
679.4332	21	-1	0.0770	3.2	0.0774
674.6952	23	-1	0.0519	3.9	0.0507
669.9577	25	-1	0.0316	9.3	0.0313
740.9387	4	1	0.1895	5.9	0.1750
745.6519	6	1	0.2007	4.8	0.1906
750.3609	8	1	0.1946	6.7	0.1924
755.0654	10	1	0.1726	4.7	0.1811
759.7651	12	1	0.1595	3.9	0.1597
762.1130	13	1	0.4934	4.5	0.4399
764.4596	14	1	0.1328	3.7	0.1326
766.8049	15	1	0.3708	4.3	0.3547
769.1487	16	1	0.0905	4.5	0.1039
771.4911	17	1	0.2612	4.6	0.2702
773.8320	18	1	0.0752	3.0	0.0770
776.1714	19	1	0.1910	3.7	0.1948
778.5092	20	1	0.0540	3.5	0.0540
783.1799	22	1	0.0345	3.6	0.0360
787.8440	24	1	0.0235	3.1	0.0228
790.1733	25	1	0.0520	5.2	0.0532
794.8266	27	1	0.0324	2.8	0.0312

Table H.10. Absolute FTS intensities of $\nu_4 + \nu_5^{0e} \leftarrow \nu_4^{1f}$.

ν_o [cm ⁻¹]	J	ΔJ	S_J [cm ⁻² atm ⁻¹ @ 293.3K]	%	cal.
716.2609	15	0	0.1199	3.0	0.1209
716.2300	16	0	0.316	3.5	0.3150
716.1934	17	0	0.0896	1.5	0.0897
716.1504	18	0	0.2219	1.7	0.2259
716.1004	19	0	0.0632	1.6	0.0622
716.0426	20	0	0.1505	4.0	0.1518
715.9765	21	0	0.0416	3.4	0.0405
715.9013	22	0	0.0945	5.5	0.0957
715.8164	23	0	0.0248	4.5	0.0248
715.7211	24	0	0.0566	3.3	0.0567
715.4970	26	0	0.0313	3.5	0.0317

VITA

Mark Weber was born in Trier, F.R. Germany, on April 4, 1961. He attended Max Planck Gymnasium in Trier and graduated in 1981. After a year as a social work trainee in a home for mentally retarded adults in Trier, he entered the University of Bonn. In 1984 he passed the examination for his first diplom (Vordiplom), whereupon he started the graduate program at the same university.

In fall 1986 he came to the University of Tennessee, Knoxville, U.S.A., as an exchange student. From 1987 till December 1991 he worked on his Ph.D. degree in physics at the University of Tennessee.

The author is a member of the Deutsche Physikalische Gesellschaft and the Coblenz Society. Honors include a Hilton A. Smith Graduate Scholarship from the University of Tennessee (1989–1991) and a Coblenz Society Student Award (1988). He published and co-authored five papers in scientific journals and participated in four presentations at professional scientific meetings.

In 1990 he married Helena Vasques de Carvalho from Vila Nova de Gaia, Portugal.

Publications:

"Tunable Diode Laser Measurements of the $14\mu\text{m}$ Line Strengths in C_2H_2 ", M. Weber, W.E. Blass, and Jean-Luc Salanave, *Journal of Quantitative Spectroscopy and Radiation Transfer*, **42**, 437 (1989).

"Laboratory Studies, Analysis, and Interpretation of the Spectra of Hydrocarbons present in Planetary Atmospheres Including Cyanoacetylene, Acetylene, Propane, and Ethane", W.E. Blass, S.J. Daunt, A.V. Peters and M. Weber, in *Proceedings of the First International Conference on Laboratory Research for Planetary Atmospheres, 1990*, NASA Conference Publication 3077, p.54–63.

"Herman–Wallis Factors in the C_2H_2 ν_5 Infrared Fundamental Region", W.C. Maguire, J.J. Hillman, M. Weber, and W.E. Blass, *Journal of Geophysical Research*, **96**, 17493 (1991).

"Adaptive Noise Filtering Using an Error-Backpropagation Neural Network", M. Weber, P.B. Crilly and W.E. Blass, *IEEE Transaction on Instrumentation and Measurement*, 40, 820 (1991).

"Line Positions and IR Intensities of Acetylene: ℓ -Resonance Effects in the ν_5 , $2\nu_5 \leftarrow \nu_5$, and $\nu_4 + \nu_5 \leftarrow \nu_4$ Bands near 13.7μ ", M. Weber, W.E. Blass, G.W. Halsey, J.J. Hillman, and W.C. Maguire, submitted to *Spectrochimica Acta*, 1991.