

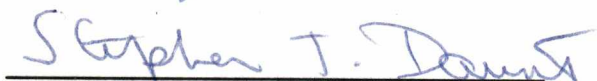
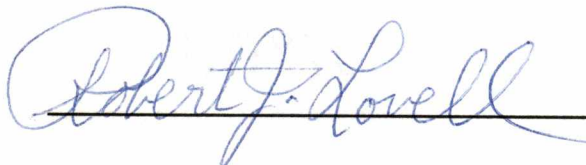
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I am submitting herewith a thesis written by Jean-Luc Salanave entitled "Acetylene Intensity Measurements Using a Tunable Laser spectrometer." I have examined the final copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Physics.



William E. Blass, Major Professor

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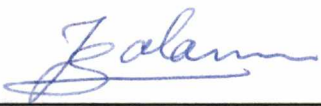


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ACETYLENE INTENSITY MEASUREMENTS
USING A TUNABLE LASER SPECTROMETER

A Thesis
presented for the
Master of Science
Degree
The University of Tennessee, Knoxville

Jean-Luc Salanave

June 1987

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ABSTRACT

High resolution knowledge of acetylene spectral features is a prerequisite for quantitative analyses in planetary atmospheres of Titan, Saturn, and Jupiter.

Line and band intensity measurements on $^{12}\text{C}_2\text{H}_2$ and $^{12}\text{C}^{13}\text{CH}_2$ around 13.7 micrometers were performed with spectral resolution of 0.0005 cm^{-1} , using a tunable diode laser spectrometer. Band intensities extracted from line intensity measurements, in units of $\text{cm}^{-2}\text{atm}^{-1}$ at 296 K, are: 565 for the ν_5 -fundamental band of $^{12}\text{C}_2\text{H}_2$, 24.6 for the $(\nu_4+\nu_5)^{0-1}$ hot band of $^{12}\text{C}_2\text{H}_2$, and 581 for the ν_5 -fundamental band of $^{12}\text{C}^{13}\text{CH}_2$.

Due to the sensitivity of the technique, pressure self-broadening of the order of 0.15 cm^{-1} per atm. for the half-width (0.0002 cm^{-1} per torr), and pressure shift of the order of -0.003 cm^{-1} at 1 torr were also observed. These latter results have to be confirmed by further measurements.

TABLE OF CONTENTS

CHAPTER	PAGE
1. INTRODUCTION.	1
2. EXPERIMENTAL SETUP AND PROCEDURE.	7
2.1 Introduction	7
2.2 Experimental setup	7
2.3 Experimental procedure	11
3. THEORY OF SPECTRAL LINES AND BAND INTENSITY MEASUREMENTS.	17
3.1 Introduction	17
3.2 Intensities.	17
3.3 Broadening	22
3.4 Extracting intensity and broadening information from experimental spectra.	23
3.5 Acetylene band designation	24
4. EXPERIMENTAL RESULTS.	26
5. DATA ANALYSIS	38
5.1 Instrumental function.	38
5.2 Line and band intensity.	39
5.3 Self-broadening and pressure shift	42
6. CONCLUSION.	45
LIST OF REFERENCES.	47
VITA.	50

LIST OF TABLES

TABLE		PAGE
4.1.	Halfwidths of acetylene spectral lines (HWHM) in units of 10^{-3} cm^{-1}	34
4.2.	Acetylene line intensity measurements S_J given in $\text{cm}^{-2} \text{ atm}^{-1}$ at 296 K.	36
5.1.	Band intensities $S_v^{(i)}$ in $\text{cm}^{-2} \text{ atm}^{-1}$ at 296K. . .	41
5.2.	Self-broadening and pressure shift (10^{-3} cm^{-1}). .	43

LIST OF FIGURES

FIGURE		PAGE
1.1.	Voyager Data Analysis Group (Goddard Space Flight Center)	2
1.2.	Acetylene spectral region from 724 to 732 cm^{-1} [13]	4
2.1.	Schematic diagram showing the radiation paths of the TDL spectrometer [4].	9
2.2.	The mechanical shutter used for the determination of 100% absorption [4]	10
2.3.	Timing diagram [4]	12
2.4.	Pressure calibration	13
2.5.	100% absorption determination. Ideal shutter "window" for an empty cell	15
2.6.	100% absorption, Saturated cell.	16
3.1.	High resolution spectra. Basic measurements.	23
4.1.	C_2H_2 - Line $Q^{(1)}(1)$ - 729.16329 cm^{-1} - Path: 5.08 cm - Temp: 296 K - Pressures (millitorr): 193.7, 47.0, 23.2, 11.6, 5.7, 2.7	27
4.2.	C_2H_2 - Line $Q^{(1)}(1)$ - 729.16329 cm^{-1} - Path: 2.535 cm - Temp: 296 K - Pressures (millitorr): 96.8, 47.0, 18.4.	27
4.3.	C_2H_2 - Lines $Q^{(1)}(3)$ - 729.20809 cm^{-1} & $Q^{(1)}(4)$ - 729.24416 cm^{-1} - Path: 2.535 cm - Temp: 296 K - Pressures (millitorr): 96.8, 58.1, 33.4, 18.4.	28
4.4.	C_2H_2 - Line $Q^{(1)}(4)$ - 729.24416 cm^{-1} - Path: 5.08 cm - Temp: 296 K - Pressures (millitorr): 195, 48.4, 23.2, 11.6, 5.8.	28

4.5.	C_2H_2 - Line $Q^{(1)}(6)$ - 729.34286 cm^{-1} - Path: 25.4 cm - Temp: 296 K - Pressures (millitorr): 18.4, 7.9, 2.5.	29
4.6.	C_2H_2 - Line $Q^{(1)}(6)$ - 729.34286 cm^{-1} - Path: 5.08 cm - Temp: 295 K - Pressures (millitorr): 195, 48.4, 23.2, 11.6, 5.8, 2.9 . . .	29
4.7.	C_2H_2 - Line $Q^{(5)}(3)$ - 728.91427 cm^{-1} - Path: 25.4 cm - Temp: 296 K - Pressures (millitorr): 469.6, 242.1, 130.7, 62.0	30
4.8.	C_2H_2 - Line $Q^{(5)}(3)$ - 728.91427 cm^{-1} - Path: 25.4 cm - Temp: 296 K - Pressures (millitorr): 484.1, 237.2, 139.4, 66.8	30
4.9.	C_2H_2 - Line $Q^{(5)}(4)$ - 728.95235 cm^{-1} - Path: 25.4 cm - Temp: 296 K - Pressures (millitorr): 944, 474.5, 275.5, 133.3, 68.0. . . .	31
4.10.	C_2H_2 - Line $Q^{(5)}(4)$ - 728.95235 cm^{-1} - Path: 25.4 cm - Temp: 296 K - Pressures (millitorr): 479.3, 273.0, 161.7, 104.6.	31
4.11.	C_2H_2 - Line $Q^{(5)}(6)$ - 729.05697 cm^{-1} - Path: 25.4 cm - Temp: 296 K - Pressures (millitorr): 968.3, 469.6, 234.8, 137.0, 62.7. . .	32
4.12.	C_2H_2 - Line $Q^{(9)}(11)$ - 728.78701 cm^{-1} - Path: 25.4 cm - Temp: 296 K - Pressures (millitorr): 581.0, 285.6, 140.4, 71.6, 34.6 . . .	32
4.13.	C_2H_2 - Line $P^{(5)}(1)$ - 726.49605 cm^{-1} - Path: 25.4 cm - Temp: 296 K - Pressures (millitorr): 978.0, 581.0, 242.1, 135.6.	33
5.1.	Self-broadening and pressure shift	44

LIST OF SYMBOLS AND ABBREVIATIONS

b_{OB}	: observed halfwidth (cm^{-1}).
b_D	: Doppler halfwidth (cm^{-1}).
b_I	: instrumental halfwidth (cm^{-1}).
HWHM	: halfwidth at half maximum.
FWHM	: fullwidth at half maximum.
S_J	: line J intensity ($\text{cm}^{-2}\text{atm}^{-1}$).
S_v^o	: vibrational intensity factor ($\text{cm}^{-2}\text{atm}^{-1}$).
$S_v^{(i)}$	: band #i integrated band intensity ($\text{cm}^{-2}\text{atm}^{-1}$).
t	: line transmittance.
p	: acetylene pressure (microns = 10^{-3} torr).
l	: path length (cm).

CHAPTER 1

INTRODUCTION

Knowledge of the positions, shapes and intensities of spectral lines and bands is a prerequisite for quantitative analyses of astrophysical observations such as the studies of planetary atmospheres.

Acetylene is of particular importance since its spectral feature at 13.7 micrometers was observed on Titan, Saturn, and Jupiter by the NASA Voyager I and II spacecraft [1: subreferences 1 to 11],[2]. Acetylene is a trace constituent formed by photodissociation of methane in these atmospheres. See Figure 1.1. Acetylene is also reported in recent observations of IRC 10216 ,a cool carbon star [3].

In low-resolution spectra, an emission or absorption feature is often seen as a wide single line. High-resolution laser heterodyne and FT-IR spectroscopy now allows detection of individual vibration-rotation lines from planetary atmospheres. Few data are available on intensities of vibration-rotation lines of acetylene. The present study should provide information needed for high-resolution astronomical analyses for the construction of planetary atmospheric models.

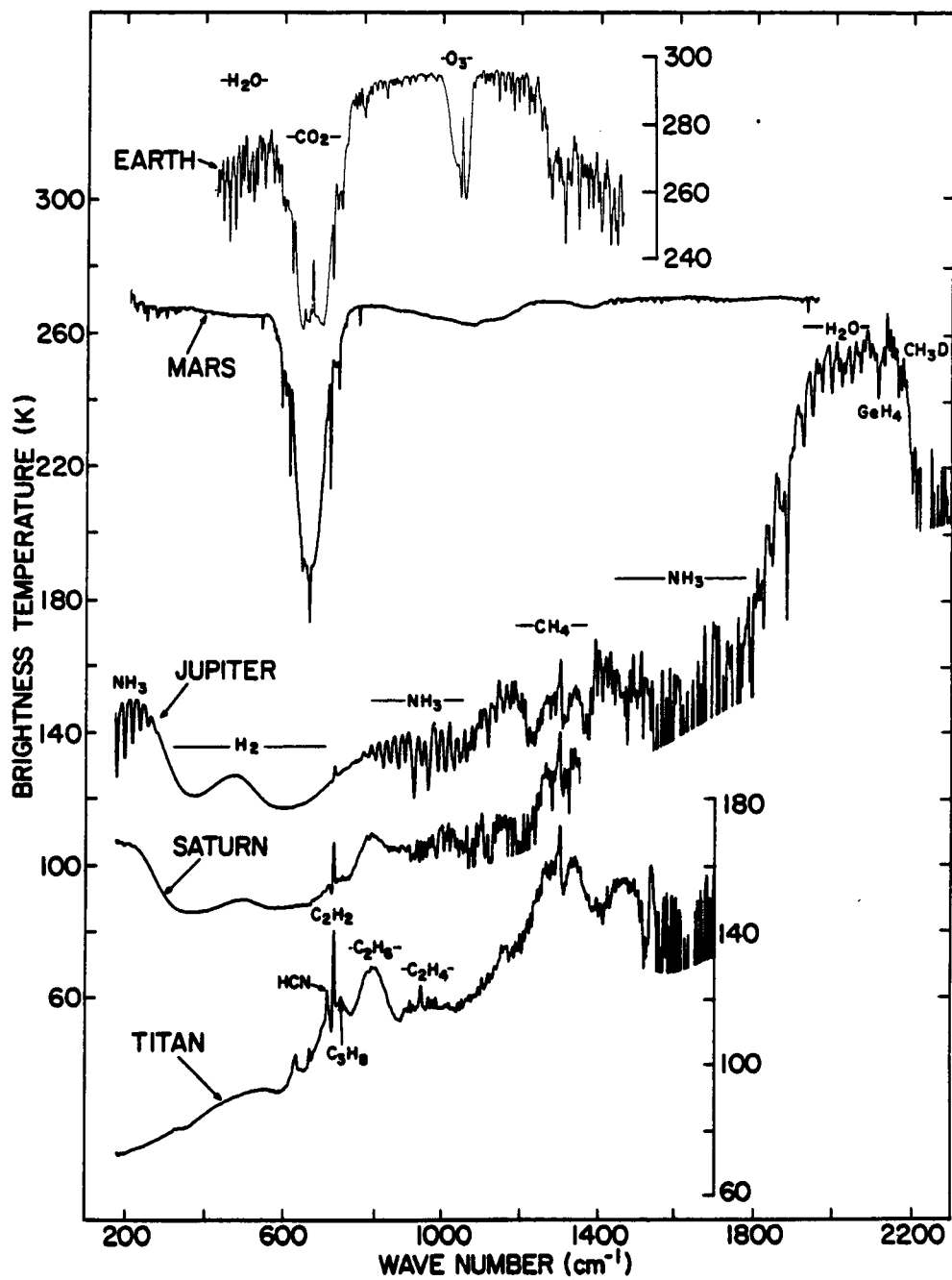


Figure 1.1: Voyager Data Analysis Group (Goddard Space Flight Center).

Our laboratory observations were taken using a swept frequency tunable diode laser (TDL) spectrometer, at the University of Tennessee Molecular Spectroscopy Laboratory (UTMSL). The same experimental system was used recently to perform acetylene collision broadening measurements by nitrogen (dominant constituent of Titan's atmosphere) and by hydrogen (dominant constituent of Jovian and Saturnian atmospheres). This TDL system is described in [4]. A summary description is presented in Chapter 2. Theory of spectral line and band intensity measurements is briefly presented in chapter 3.

Seventy-one spectral transmittance measurements are reported (See Figure 1.2). They were performed on :

- 4 Q lines in the ν_5 -fundamental band of $^{12}\text{C}_2\text{H}_2$
- 1 P line in the $(\nu_4+\nu_5)^{0-}-\nu_4^1$ band of $^{12}\text{C}_2\text{H}_2$
- 3 Q lines in the $(\nu_4+\nu_5)^{0-}-\nu_4^1$ band of $^{12}\text{C}_2\text{H}_2$
- 1 Q line in the ν_5 -fundamental band of $^{12}\text{C}^{13}\text{CH}_2$
(isotope ratio $^{13}\text{C}/^{12}\text{C} = 0.01107$).

The temperature was 296 K. We used acetylene pressures in the range 0-1000 millitorr and 3 different paths (1, 2 and 10 inches).

The spectral resolution of our TDL spectrometer is 0.0005 cm^{-1} . To our knowledge, no published data on acetylene spectra around 13.7 microns are available with a

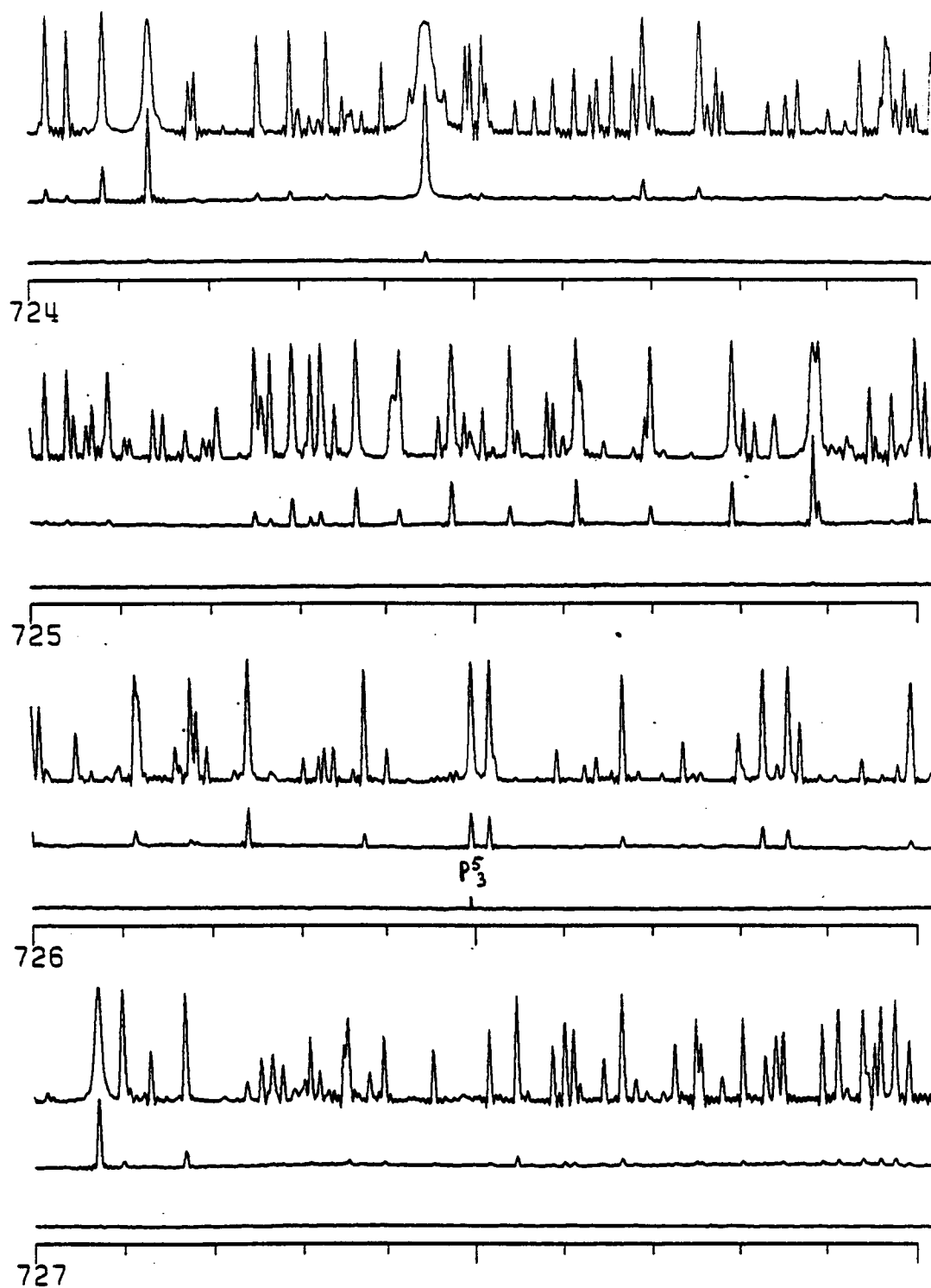
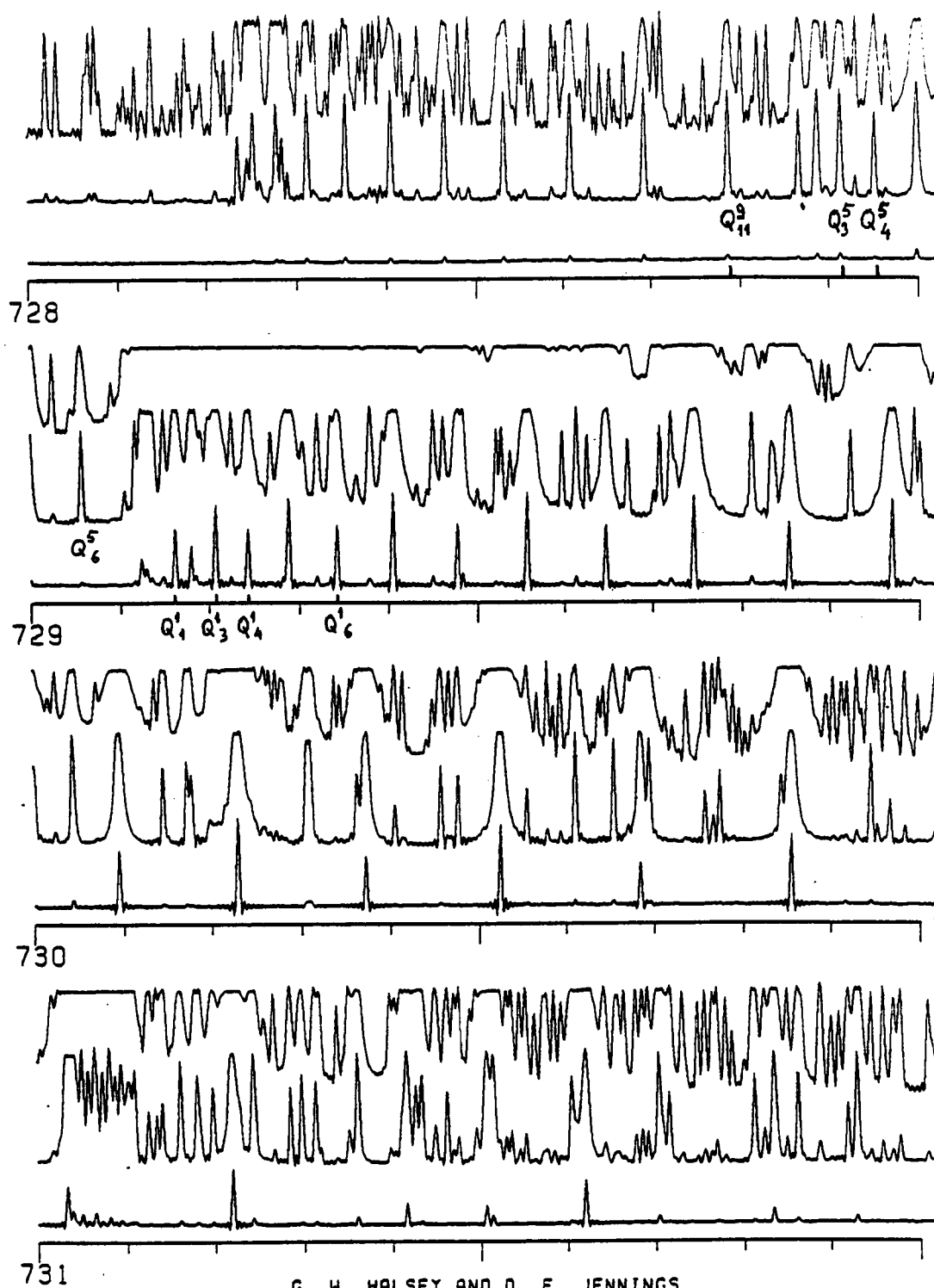


Figure 1.2: Acetylene spectral region from 724 to 732 cm^{-1}
[13]



G. W. HALSEY AND D. E. JENNINGS
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Figure 1.2 (continued)

resolution better than 0.002 cm^{-1} [5]. Computer synthesized spectra and intensity calculations on acetylene in this region, reported by Varanasi et al. [1,2], are generated from interferometric spectra with a resolution of 0.06 cm^{-1} .

Our high resolution spectrometer has allowed us to determine band intensities directly from line intensity measurements. Our results are in good agreement with Varanasi et al. In addition we have been able to measure self pressure-broadening and a pressure-dependent shift for acetylene pressures smaller than 1 torr. Our experimental data are given in chapter 4 and analysed in chapter 5.

CHAPTER 2

EXPERIMENTAL SETUP AND PROCEDURE

2.1 Introduction

Tunable diode lasers have in recent years become increasingly important for high resolution infrared spectroscopy. Their unique features include an effective linewidth of the order of 10^{-4} cm^{-1} , tunability and rapid frequency modulation. They have been used in several types of spectroscopy: absorption spectroscopy, modulation spectroscopy, heterodyne spectroscopy, opto-acoustic spectroscopy, double resonance spectroscopy [6].

2.2 Experimental setup

The observations were taken using a swept frequency tunable diode laser (TDL) spectrometer and an experimental system described in [4] and [7].

The laser is tuned through its frequency range by controlling the temperature and (or) the current injected into the diode. TDL specifications:

- Operating conditions: at 721 cm^{-1} , $I=1226 \text{ mA}$, $T=47 \text{ K}$
power $>0.1 \text{ mW}$

- Frequency range: 650 (threshold) to 750 cm^{-1} .

A schematic diagram of the experimental setup and its optical paths is given in Figure 2.1. The infrared beam passes successively through:

- the cell containing the gas to be analysed,
- a rotating shutter (see Figure 2.2) which modulates the beam at 100 Hz in order to determine the 100% absorption,
- a grating monochromator whose function is to select out an individual mode from the multimode laser emission, and whose position is given by a calibration previously stored in the memory of a computer,

before it is passed to a Hg-Td-Te detector operated at liquid nitrogen temperature.

Detection setup: the detected signal is amplified by a preamplifier before it is fed into a signal averager which displays, averages and stores the data. The signal averager is connected with a plotter and a micro-computer.

The scanning is accomplished by superimposing a sawtooth voltage ramp generated by a function generator upon the steady excitation current generated by the laser current supply. The timing diagram synchronizing ramp generator, laser sweep, signal averager scan and rotating shutter

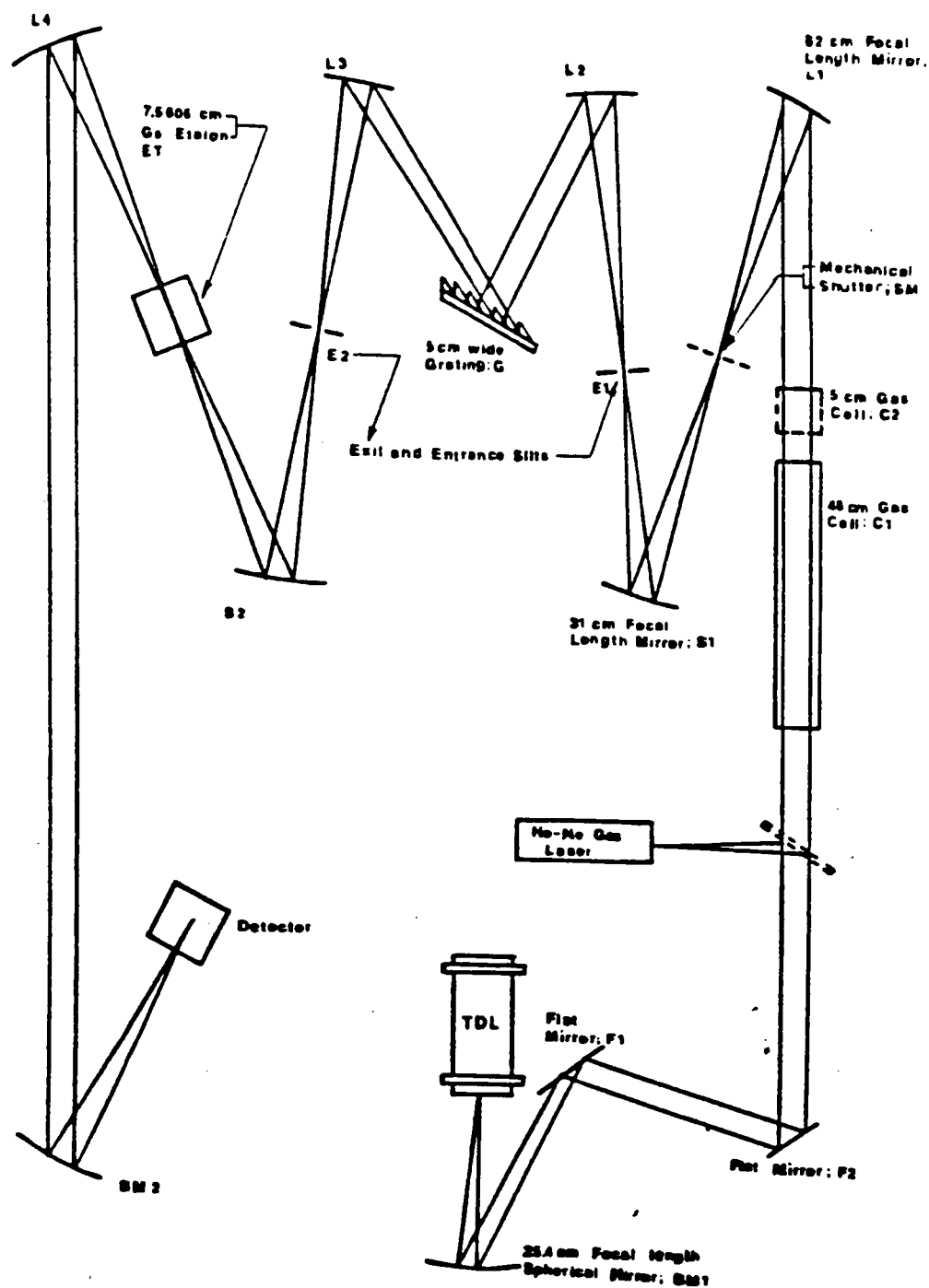


Figure 2.1: schematic diagram showing the radiation paths of the TDL spectrometer [4].

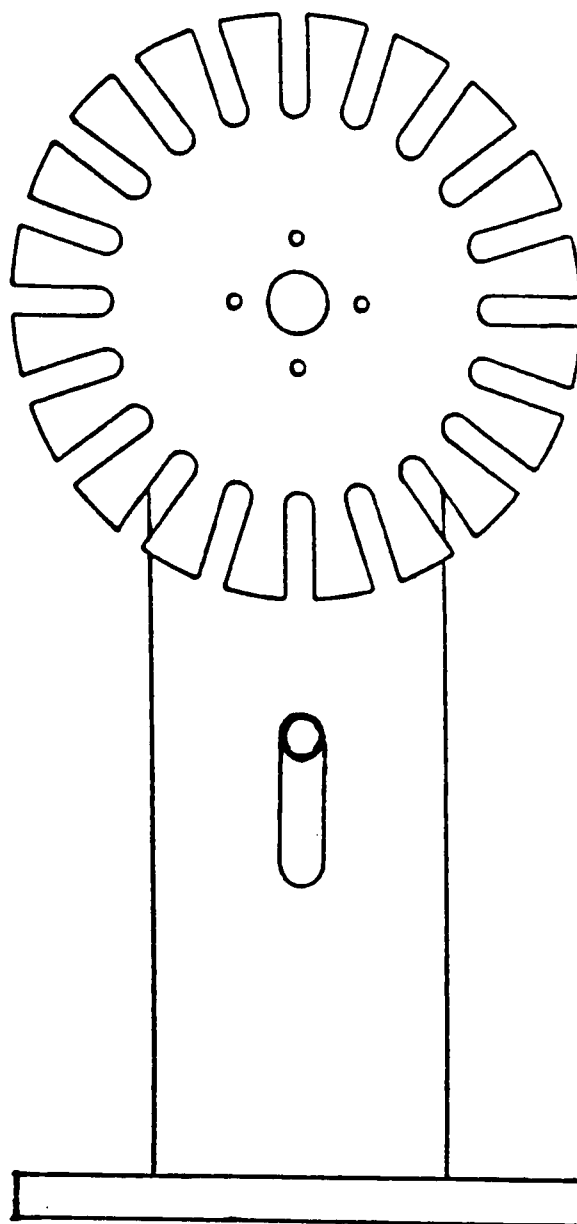


Figure 2.2: the mechanical shutter used for the determination of 100% absorption [4].

stepping motor is described in Figure 2.3. The shutter is opened for about 80% of the laser scanning time. The frequency is 100 Hz.

Gas cell: KBr window cells of 25.4, 5.08 and 2.535 cm were used. The cell is connected to a manifold equipped with a diffusion pump, acetylene supply, a 0-1 torr capacitance manometer (MKS Baratron Type 170M-6B, MKS Head Type 315BHS1), and a McLeod gauge.

2.3 Experimental procedure

The general procedure to perform the experiment and operate the system is described in [4]. Due to the complexity of this experimental setup, which is made up of many independent optical, electrical, electronic, thermal and cryogenic components, adjusting and putting together at the same time the best conditions to record a spectra is time-consuming. Investigations and adjustments are prerequisites for an eventual two-minute spectral recording.

In order to yield consistent and reliable intensity measurements, sources of systematic experimental error were detected and characterized as far as possible. Their effects on the resulting line parameters were minimized by making appropriate corrections or adjusting experimental conditions:

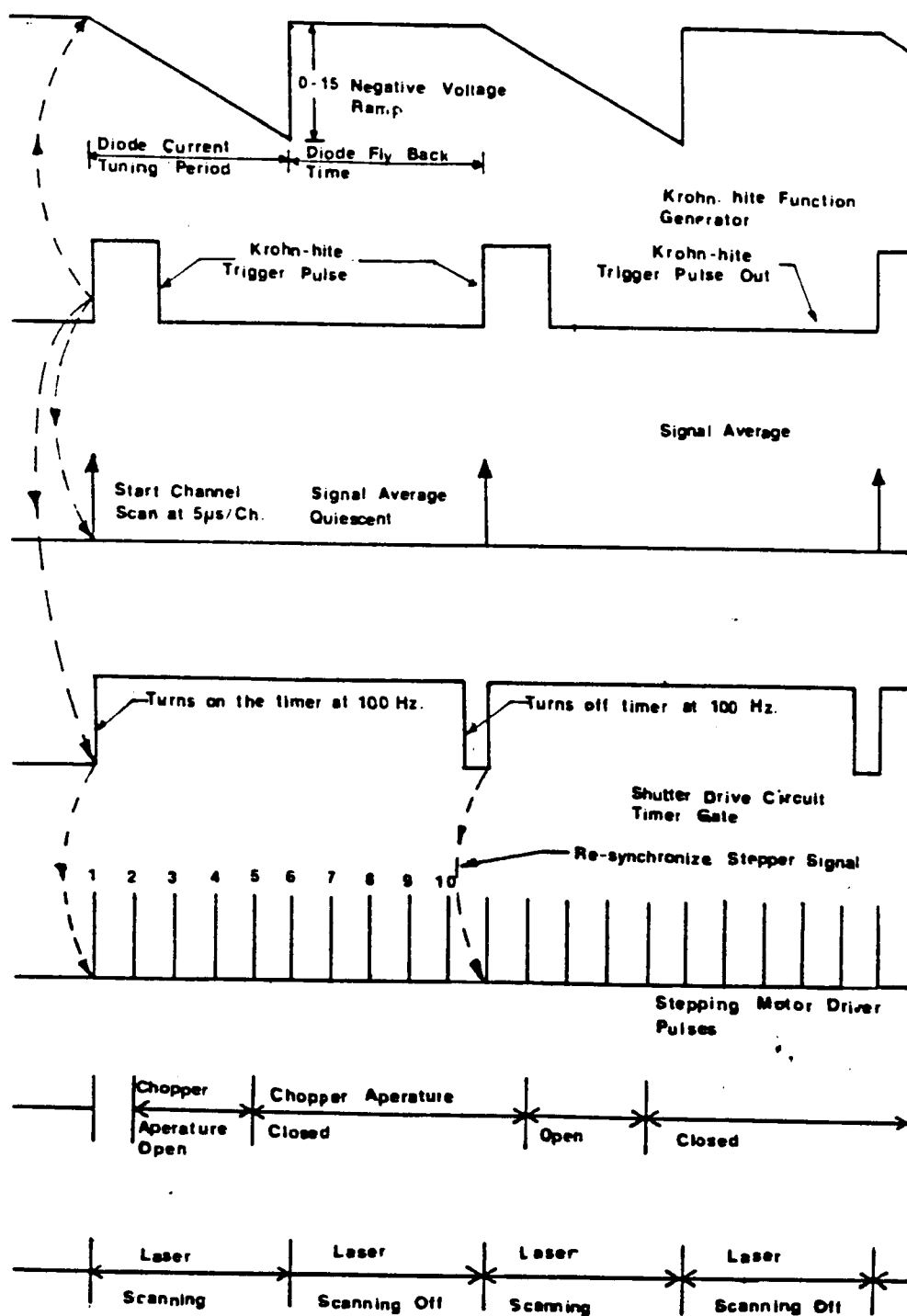


Figure 2.3: timing diagram [4].

-pressure measurements: accuracy of experimental data is strongly dependent upon gas pressure measurements. The 0-1 torr capacitance manometer was frequently calibrated using a McLeod gauge set up on the gas cell manifold. The pressure correction curve is given in the Figure 2.4 below:

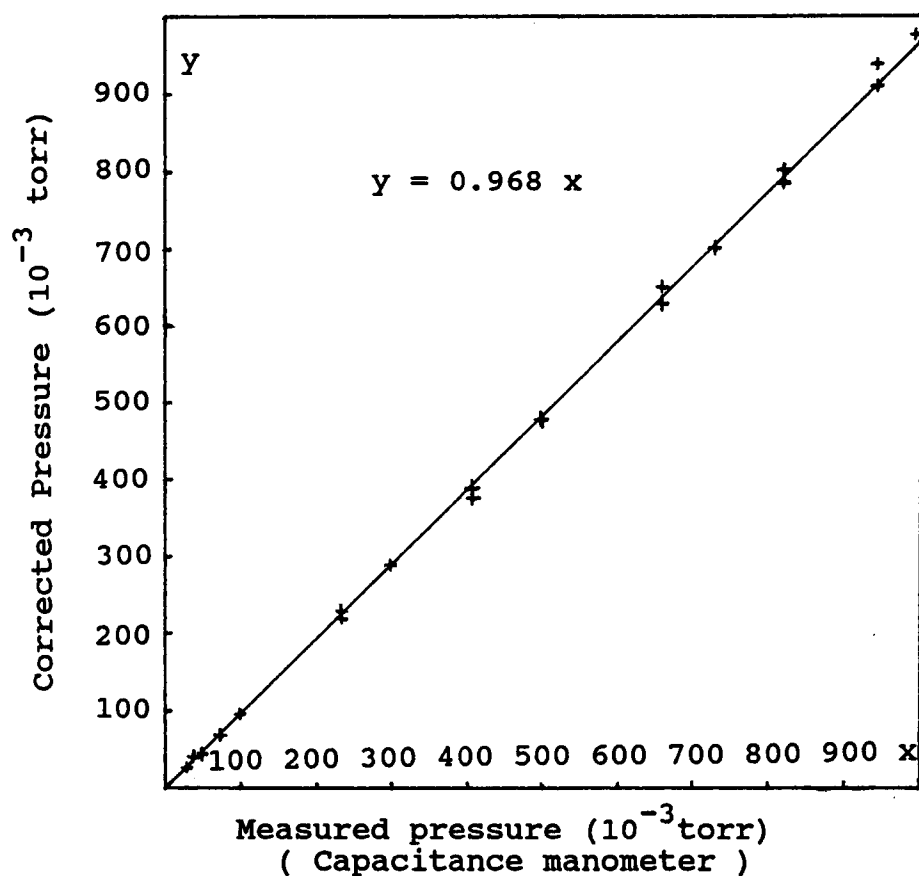


Figure 2.4: pressure calibration.

-calibration of linewidths: we used a Ge Fabry-Perot interferometer with a spectral fringe spacing of 0.01623 cm⁻¹ (accurate to 1%) to record etalon fringes immediately following each absorption spectra recording.

- Data recording period: in order to minimize perturbations due, with time, to tiny air leaks on the cell or slow fluctuations in the lasing, a set of 4 to 6 spectra was taken within a short period spanning less than 15 minutes (including acetylene pressure stabilisation, scan repetition rate of 100Hz and 3000 scans averaging for each spectra, data recording, and etalon fringes recording).
- Grounding and noise: due to the amplification factor of the detection chain, the measured signal is very noisy. This noise can be minimized by grounding systematically every electrical and electronic device, and by trying to locate and get rid of disturbing ground loops.
- The ambient temperature was 296 K and varied less than 1K.
- The tuning characteristics of the laser are complicated by mode hopping, multimode output and non-linearities. Mode hopping refers to discontinuous change in frequency during current or temperature tuning. Since weird spectral line parameters were observed near mode hopping regions, measurements in such regions are not reported in this study. In other frequency regions, where spectra were taken, experimental parameters were adjusted for each different line position in order to have maximum energy and best linearity of the signal: infrared beam path input and output mirrors, slit position, grating position,

shutter synchronization, suitable combination of laser temperature and intensity, and sawtooth scanning voltage ramp amplitude.

-100% absorption level: the laser beam is "opened and closed" at a frequency of 100Hz by the shutter which is placed ahead of the grating monochromator,. The shape of the observed signal is given by Figure 2.5:

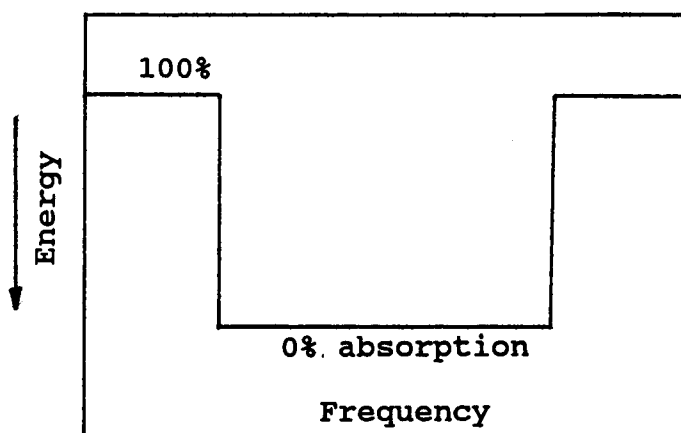


Figure 2.5: 100% absorption determination.

Ideal shutter "window" for an empty cell.

In addition the 100% absorption signal was checked with an acetylene saturation pressure for each observed transition. The mechanical shutter and the saturation cell gave the same saturated absorbance level to better than 1%, provided that the cell was placed ahead of the grating

monochromator. Two different levels, about 10% apart, are observed when the cell is placed after the grating, as showed in Figure 2.6:

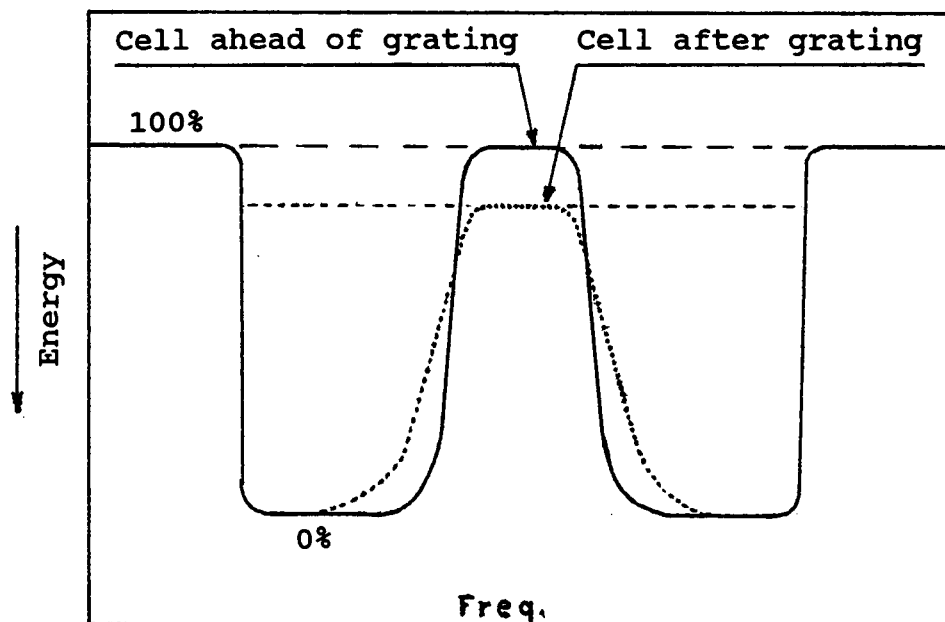


Figure 2.6: 100% absorption, saturated cell.

All recordings were taken with the cell ahead of the grating, but an explanation is still to be found for this phenomenon.

CHAPTER 3
THEORY OF
SPECTRAL LINE AND BAND INTENSITY MEASUREMENTS

3.1 Introduction

Acetylene is a linear four-atom molecule with the structural form:



It has two carbons bonded by a sigma and two pi bonds. Each carbon is bonded to a hydrogen by a sigma bond. The C $\equiv$ C bond is 1.2 Å long and the C - H bond is 1.08 Å long [4].

General molecular spectroscopy discussions about intensities and broadening theories have been given by Penner [8, chap.2 and 3] and by Smith et al. in [9]. The basic definitions used in the present work are briefly reviewed below and applied to acetylene.

3.2 Intensities

According to the Beer-Lambert law, the transmission of monochromatic radiation through a homogeneous gas sample is described by:

$$I(\nu) = I_0 e^{-k(\nu)x} \quad (1)$$

where I_0 is the unattenuated intensity of the source radiation,

$I(\nu)$ is the radiation actually detected at the frequency ν ,

$x = pl$ (p : absorber partial pressure, l : path length),

$k(\nu) = S_J f(\nu - \nu_0)$, where f is the normalised shape function,

the parameter S_J , called line intensity is defined by:

$$S_J = \int_{-\infty}^{\infty} k(\nu) d\nu = \int_{-\infty}^{\infty} (1/x) \ln(I_0/I(\nu)) d\nu. \quad (2)$$

In the present work a Doppler line shape model was justified by the low acetylene pressures (<1 torr). In that case the line intensity is given by [9, eq.(39)]:

$$S_J = (b/pl) [\pi/\ln 2]^{1/2} \ln(1/t)$$

which leads to the formula:

$$S_J = (-1617990 \ b \ \ln t) / pl \quad (3)$$

where: b is the line halfwidth (HWHM, cm^{-1})

t is the line transmittance (defined in section 3.4)

p is the pressure (10^{-3} torr)

l is the path length (cm).

The band intensity is defined as the sum of the intensities for the individual lines of the rotational structure within a band.

The intensity unit used here is: $\text{cm}^{-2}\text{atm}^{-1}$ at 296K.

Referring to the detailed discussion given by Penner [8] about Einstein coefficients, and Smith et al. [9], we can write the following relationship between the line intensity S_{AB} of a transition from lower state A to upper state B, and the dipole matrix element $\langle A|\mu|B\rangle$:

$$S_{AB} = (8\pi^3/3hc) (N/Q) \nu_{AB} e^{(-hcE_{AB}/kT)} [1 - e^{(-hc\nu_{AB}/kT)}] \langle A|\mu|B\rangle^2 \quad (4)$$

where: N = number of molecules per cm^3 per atm.

$$N = (L/p) (273.15/T)$$

L = Loschmidt's number = 2.687×10^{19} molec./ cm^3 SPT

Q = total partition function.

E_A = lower state energy.

ν_{AB} = wavenumber of the transition (cm^{-1}).

h and k are Plank's and Boltzmann's constants.

The dipole moment is given in debye.

S_{AB} has units of $\text{cm}^{-2}\text{atm}^{-1}$.

S_{AB} can be written as the product of a vibrational factor S_v^0 , a rotational factor R_{AB} , and a factor f_m . The rotational factor can be calculated using [9, eq.(14)]. For acetylene, the factor f_m is given by Varanasi [1]:

- . $m = J$ for P and Q branches,
- . $m = J+1$ for R branches,
- . in the ν_5 -fundamental band:

$f_m = (m-1)/2$	P-branch
$f_m = (2m+1)/2$	Q-branch
$f_m = (m+1)/2$	R-branch
- . in the $(\nu_4 + \nu_5)^{0-} - \nu_4^1$ band:

$f_m = (m+1)/2$	P-branch
$f_m = (2m+1)/2$	Q-branch
$f_m = (m-1)/2$	R-branch
- . in the ν_5 -fundamental of $^{12}C^{13}CH_2$:

$f_m = (m-1)$	P-branch
$f_m = (2m+1)$	Q-branch
$f_m = (m+1)$	R-branch

The resulting formula used in this study is:

$$S_v^0 = Q_R S_J / [g_J f_m \exp(-(E_v + BJ(J+1))hc/kT) (1 - \exp(-\nu_0 hc/kT))] \quad (5)$$

were the following parameters, determined by W.Blass [10] for 296 K, are used:

- for the Q-branch in the ν_5 -fundamental band:

$$Q_R = 349.560 \text{ (partition function)}, E_v = 0, B = 1.17664 \text{ cm}^{-1}, \quad (6)$$

- for the P and Q-branches in the $(\nu_4 + \nu_5)^{0-} - \nu_4^1$ band:

$$Q_R = 35.6044 \text{ (partition function)}, E_v = 612, B = 1.17664 \text{ cm}^{-1}, \quad (7)$$

- for the Q-branch in the ν_5 -fundamental of $^{12}\text{C}^{13}\text{CH}_2$:

$$Q_R = 1394.240 \text{ (partition function)}, E_v = 0, B = 1.17664 \text{ cm}^{-1}, \quad (8)$$

$$- k/hc = 0.6951 \text{ cm}^{-1}/\text{K},$$

- g_J is a nuclear statistical weight factor. In the ν_5 -fundamental band $g_J = 3$ or 1 as J is odd or even, while for band $(\nu_4 + \nu_5)^{0-} - \nu_4^1$ this factor is equal to:

3 for $^{12}\text{C}_2\text{H}_2$ lines, Q branches, J odd,

1 for $^{12}\text{C}_2\text{H}_2$ lines, Q branches, J even,

1 for $^{12}\text{C}_2\text{H}_2$ lines, PR branches, J odd,

3 for $^{12}\text{C}_2\text{H}_2$ lines, PR branches, J even,

and g_J is equal to 4 for all of the lines $^{12}\text{C}^{13}\text{CH}_2$ (Since there are 8 independent spin functions the nuclear statistical weight should be eight, but Varanasi has already included a factor 2 in the factor f_m described above).

The band intensity $S_v^{(i)}$, where i refers to the band number described in section 3.5, is related to the

vibrational factor S_v^0 by the relationship:

$$S_v^{(i)} = \sum S_J = \sum S_v^0 R_{AB} f_m = S_v^0 \sum R_{AB} f_m \quad (9)$$

The resulting formula for acetylene at 296K are [10]:

- in the ν_5 -fundamental band:

$$S_v^{(i)} = 0.977436 S_v^0 \text{ cm}^{-2} \text{ atm}^{-1} \text{ for } ^{12}\text{C}_2\text{H}_2 \quad (10)$$

$$S_v^{(i)} = 0.612730 S_v^0 \text{ cm}^{-2} \text{ atm}^{-1} \text{ for } ^{12}\text{C}^{13}\text{CH}_2 \quad (11)$$

- in the $(\nu_4 + \nu_5)^{0-} - \nu_4^1$ band:

$$S_v^{(i)} = 0.915838 S_v^0 \text{ cm}^{-2} \text{ atm}^{-1} \text{ for } ^{12}\text{C}_2\text{H}_2 \quad (12)$$

3.3 Broadening

If we assume the observed spectra to be Doppler broadened, the Doppler halfwidth (HWHM) has the value:

$$b_D = 3.580 \times 10^{-7} \nu_0 (T/M)^{1/2} \quad (13)$$

where: T = temperature K

M = molecular weight (AMU)

In this experiment the observed halfwidths b_{OB} were very close to the Doppler value. But the accuracy of our spectra allows us to observe and measure pressure self-broadening, even at pressures below 1 torr. In addition, pressure-dependent shifts were observed and measured.

Penner's collision broadening formula [8, p.28] does not

take line shifts into account, but it is reported that quantum mechanical calculations indicate that collisions produce not only line broadening but also line shifts. Collision broadening and shifts are not the original purpose of our study but a brief analysis is given in section 5.3.

3.4 Extracting intensity and broadening information from experimental spectra [9],[11]

A. Basic measurements (see Figure 3.1):

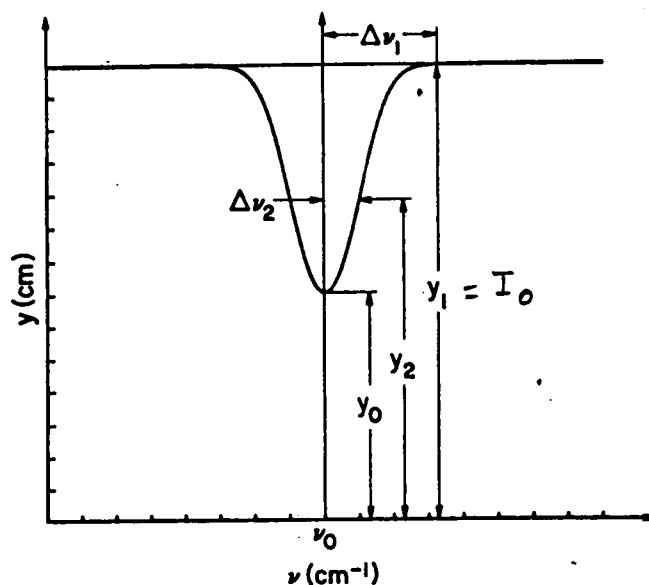


Figure 3.1: high resolution spectra.

Basic measurements.

$$\text{Line transmittance: } t = y_0/y_1 \quad (14)$$

The halfwidth at half maximum (HWHM) is measured at a height

y_2 such that

$$y_2 = \sqrt{y_0 y_1} \quad (15)$$

The integrated absorption or equivalent width is defined as:

$$W = (1/y_1)AD \quad (16)$$

where: A is the area (cm^2) between the line contour
and the 100% transmittance line,

D is the dispersion (cm^{-1}/cm).

B. Determination of HWHM and intensity: we normally used direct width measurements (see sections 4 and 5.1) and equation (3) for intensity measurements. The equivalent width method [12] was applied to a few spectra in order to check our results : the two methods are consistent to better than 4%.

3.5 Acetylene band designation

The following arbitrary band designation is used:

Band #	Transition		
1	0	to	ν_5^1
2	ν_4^1	to	$(\nu_4 + \nu_5)^2$
3	ν_4^1	to	$(\nu_4 + \nu_5)^0$
4	ν_5^1	to	$(2\nu_5)^2$
5	ν_4^1	to	$(\nu_4 + \nu_5)^0$

6	ν_5^1	to	$(2\nu_5)^0$
7	ν_4^1	to	$(\nu_4 + \nu_5)^2$
8	ν_5^1	to	$(2\nu_5)^2$

Corresponding bands of $^{12}\text{C}^{13}\text{CH}_2$ are designated by adding 8 to the band number.

The transition designation used is:

Branch^(Band number)(J),

resulting in designation such as Q⁽⁵⁾(3) for observed transition.

CHAPTER 4

EXPERIMENTAL RESULTS

Observed spectra are plotted in Figures 4. 1 to 13.

Observed half-widths b_{OB} are reported in Table 4.1, where b_D is the Doppler half-width calculated from eq. (13). The line widths are observed to be close to the Doppler width. The term $\sqrt{b_{OB}^2 - b_D^2}$ is discussed in sections 5.1 and 5.3.

Transition indicated in table 4.1 by a * were used for the determination of the instrument function (see section 5.1).

Observed transmittance t is reported in Table 4.2, together with the corresponding line intensity S_J calculated from eq. (3). $\overline{S_J}$ is the average intensity for a given line. Intensities are analysed in section 5.2.

Some spectra, either close to saturation or involving very low pressures, are not taken into account in our analysis and are not reported in the Tables.

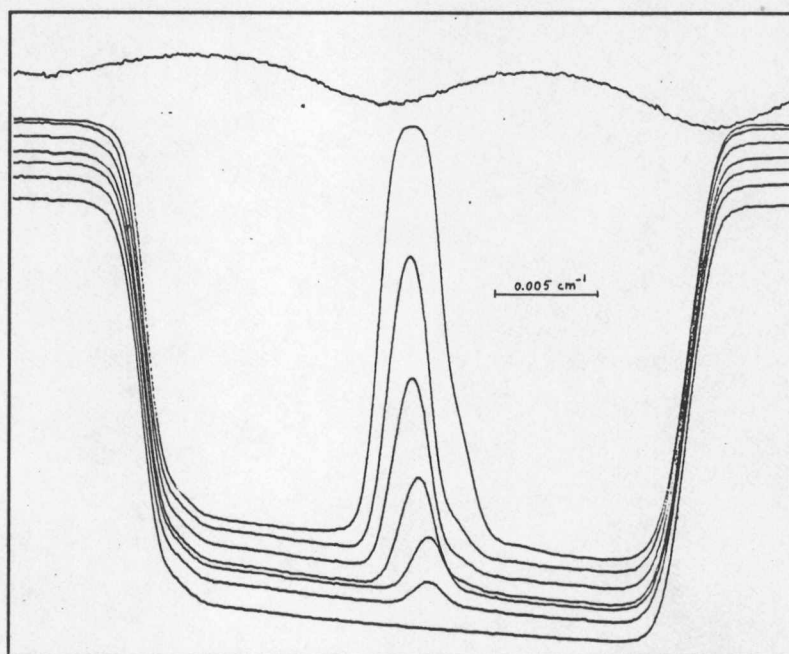


Figure 4.1:

C_2H_2 - Line $Q^{(1)}(1)$ - $729.16329 \text{ cm}^{-1}$ - Path: 5.08 cm - Temp: 296 K
 Pressures (millitorr): 193.7, 47.0, 23.2, 11.6, 5.7, 2.7

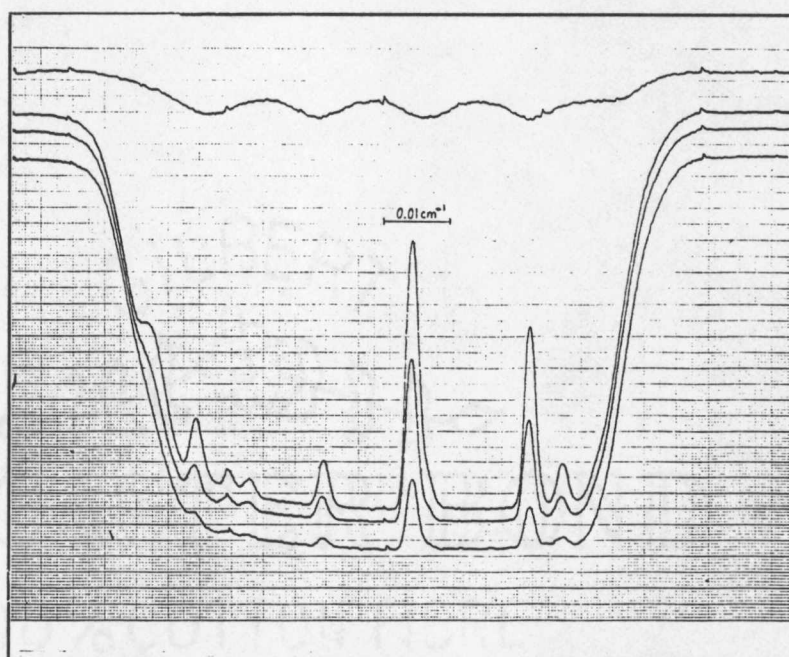


Figure 4.2:

C_2H_2 - Line $Q^{(1)}(1)$ - $729.16329 \text{ cm}^{-1}$ - Path: 2.535 cm - Temp: 296 K
 Pressures (millitorr): 96.8, 47.0, 18.4

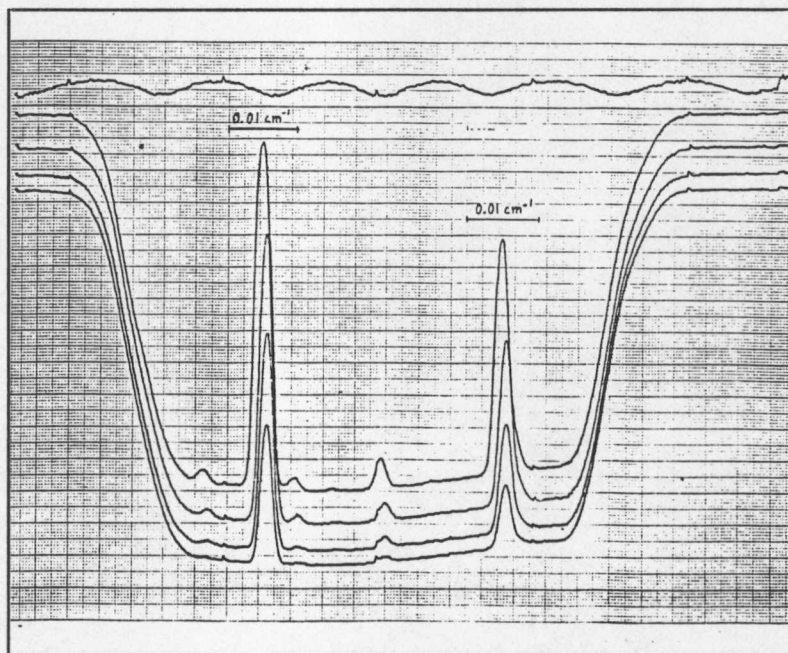


Figure 4.3:

C_2H_2 -Lines $Q^{(1)}(3)-729.20809cm^{-1}$ & $Q^{(1)}(4)-729.24416cm^{-1}$
 Path: 2.535cm- Temp: 296 K- Pressures (millitorr): 96.8, 58.1,
 33.4, 18.4

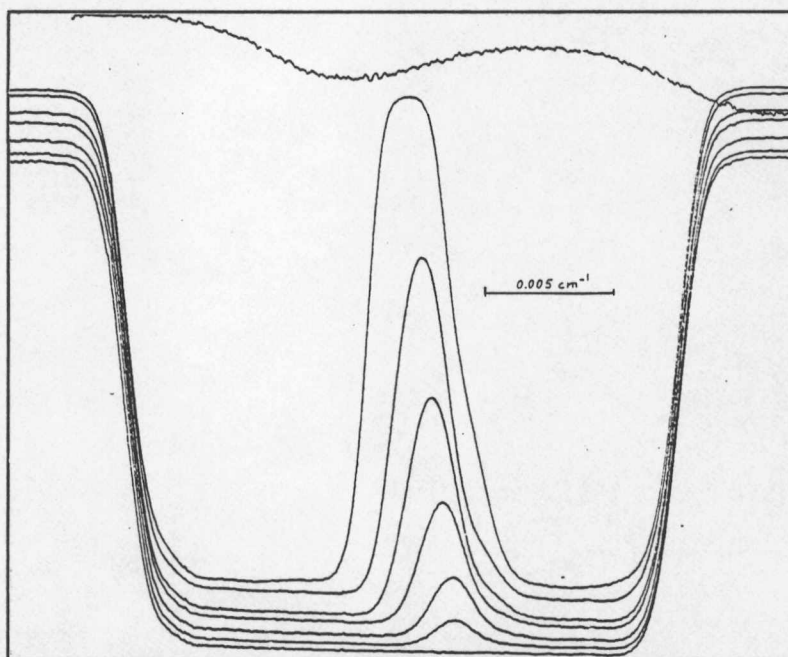


Figure 4.4:

C_2H_2 - Line $Q^{(1)}(4)-729.24416 cm^{-1}$ - Path: 5.08cm- Temp: 296 K
 Pressures (millitorr): 195, 48.4, 23.2, 11.6, 5.8

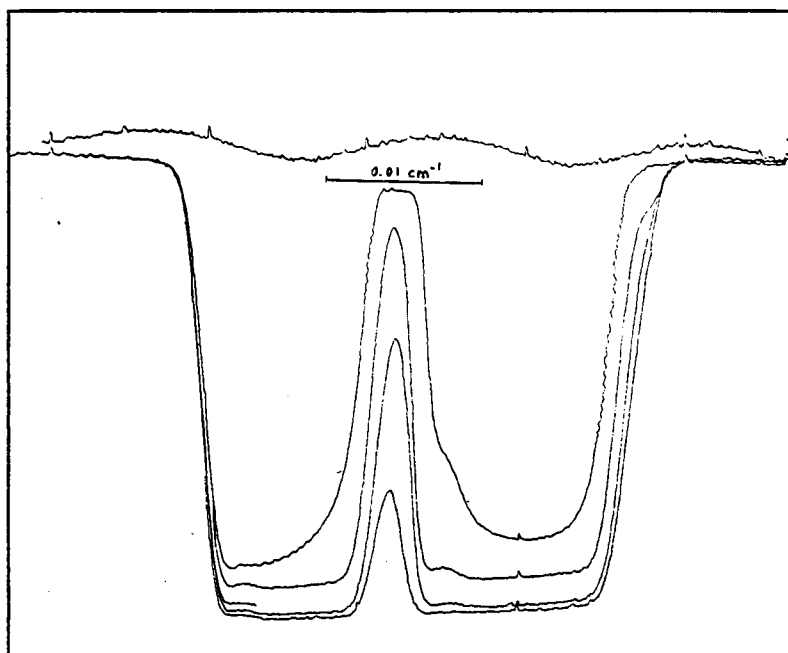


Figure 4.5:

C_2H_2 - Line $Q^{(1)}(6)$ - $729.34286 \text{ cm}^{-1}$ - Path: 25.4 cm - Temp: 296 K
 Pressures (millitorr): 18.4, 7.9, 2.5

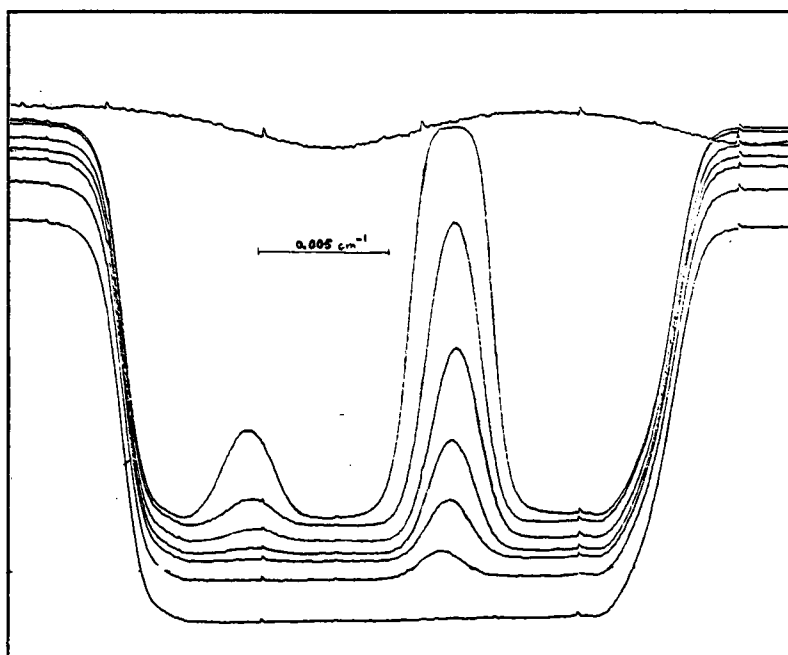


Figure 4.6:

C_2H_2 - Line $Q^{(1)}(6)$ - $729.34286 \text{ cm}^{-1}$ - Path: 5.08 cm - Temp: 295 K
 Pressures (millitorr): 195, 48.4, 23.2, 11.6, 5.8, 2.9

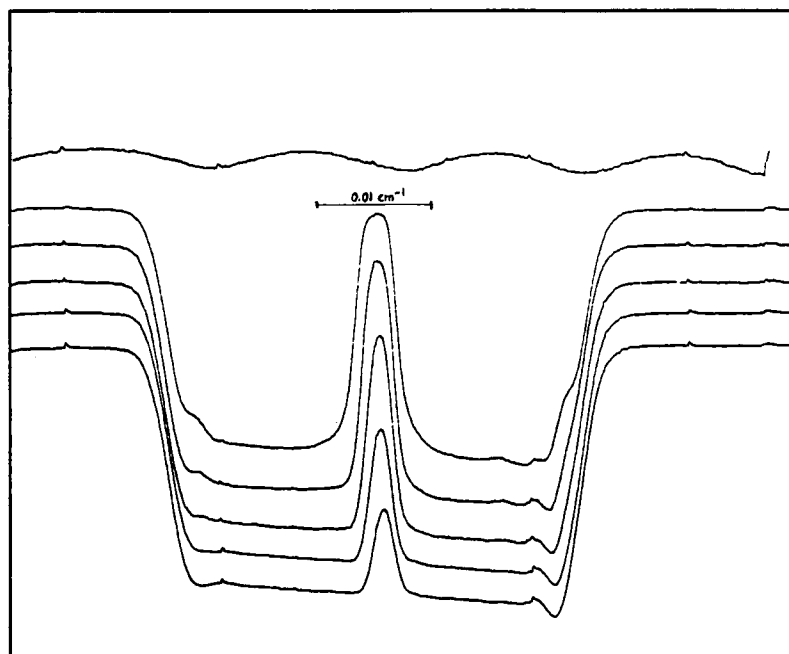


Figure 4.7:

C_2H_2 - Line $Q^{(5)}(3)$ - $728.91427 \text{ cm}^{-1}$ - Path: 25.4 cm - Temp: 296 K
 Pressures (millitorr): 469.6, 242.1, 130.7, 62.0

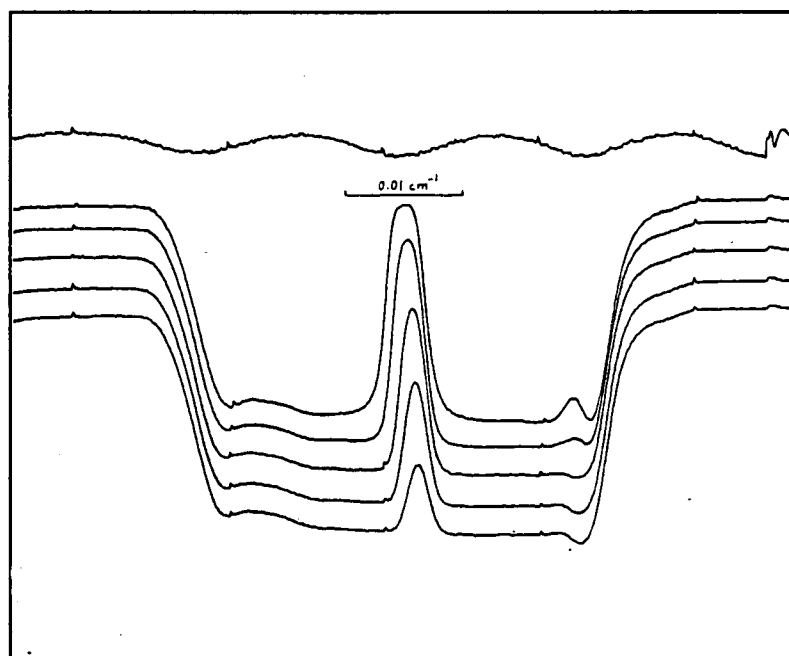


Figure 4.8:

C_2H_2 - Line $Q^{(5)}(3)$ - $728.91427 \text{ cm}^{-1}$ - Path: 25.4 cm - Temp: 296 K
 Pressures (millitorr): 484.1, 237.2, 139.4, 66.8

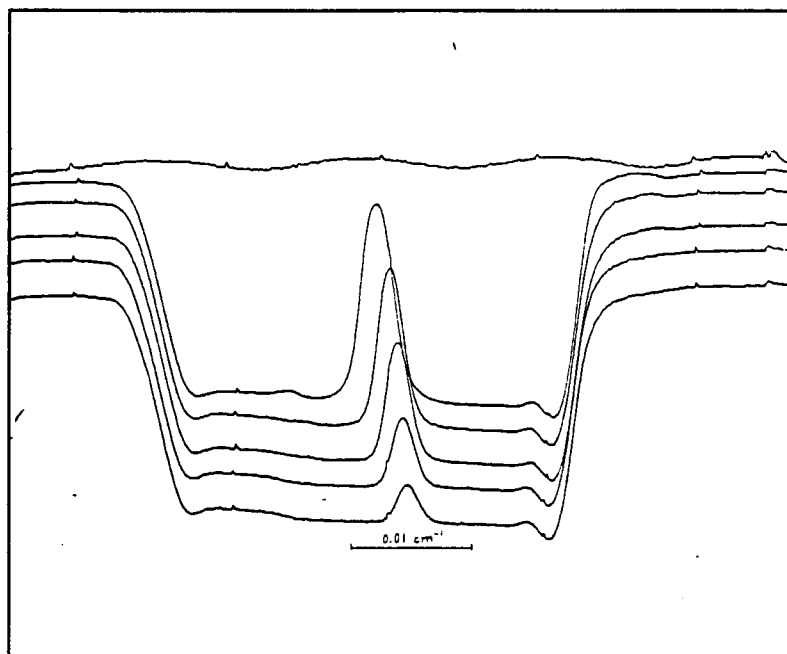


Figure 4.9:

C_2H_2 - Line $Q^{(5)}(4)$ - $728.95235 \text{ cm}^{-1}$ - Path:25.4 cm- Temp:296 K
 Pressures (millitorr): 944, 474.5, 275.5, 133.3, 68.0

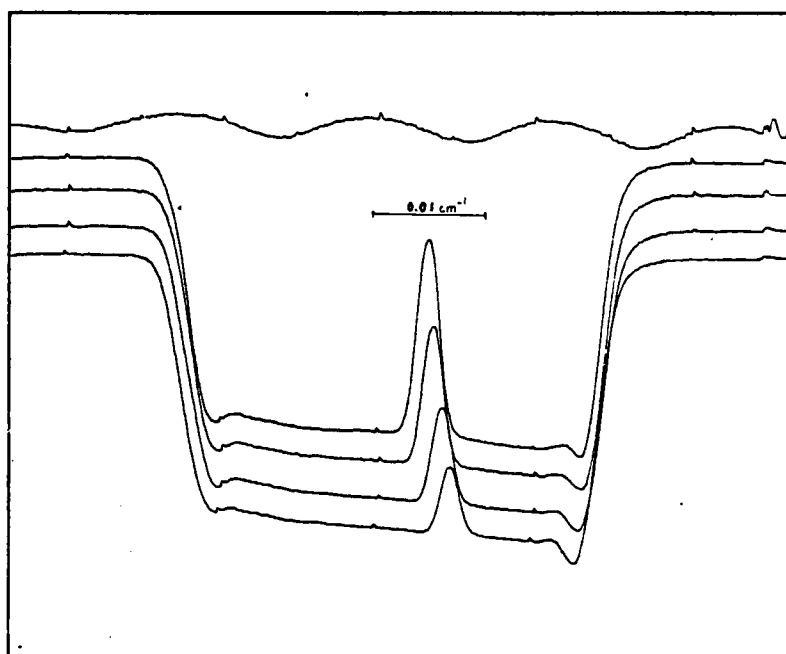


Figure 4.10:

C_2H_2 - Line $Q^{(5)}(4)$ - $728.95235 \text{ cm}^{-1}$ - Path:25.4cm- Temp:296 K
 Pressures (millitorr): 479.3, 273.0, 161.7, 104.6

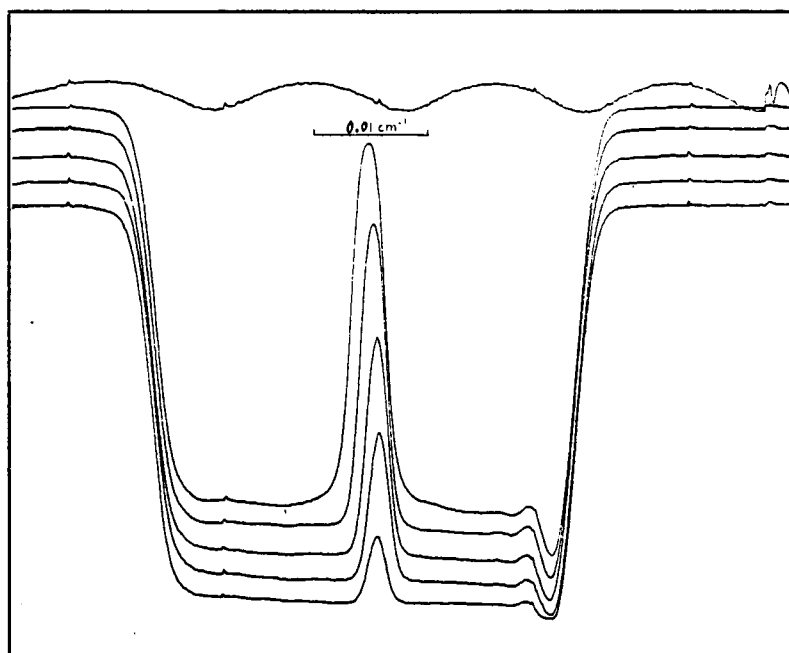


Figure 4.11:

C_2H_2 - Line $\text{Q}^{(5)}(6)$ - $729.05697 \text{ cm}^{-1}$ - Path:25.4 cm- Temp:296 K
 Pressures (millitorr): 968.3, 469.6, 234.8, 137.0, 62.7

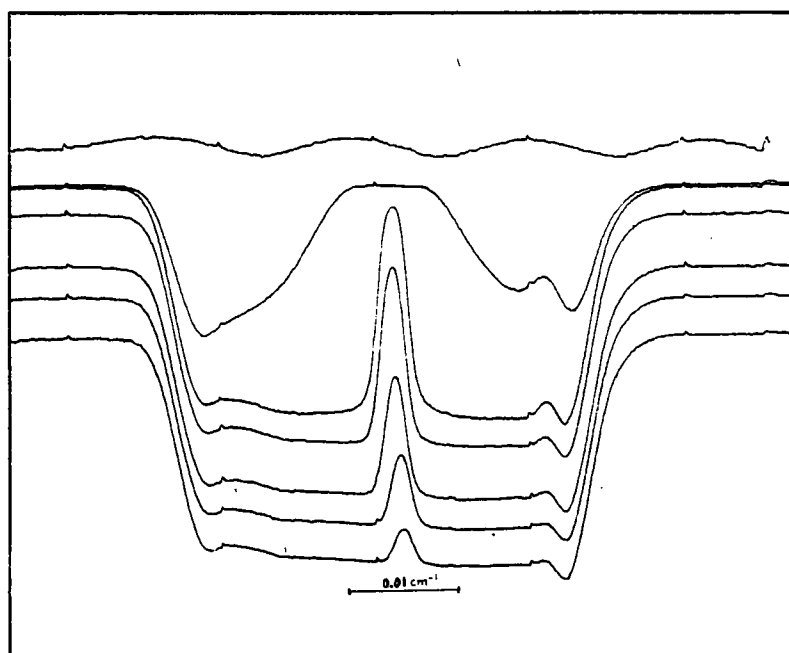


Figure 4.12:

C_2H_2 -Line $\text{Q}^{(9)}(11)$ - $728.78701 \text{ cm}^{-1}$ - Path:25.4cm- Temp:296 K
 Pressures (millitorr): 581.0, 285.6, 140.4, 71.6, 34.6

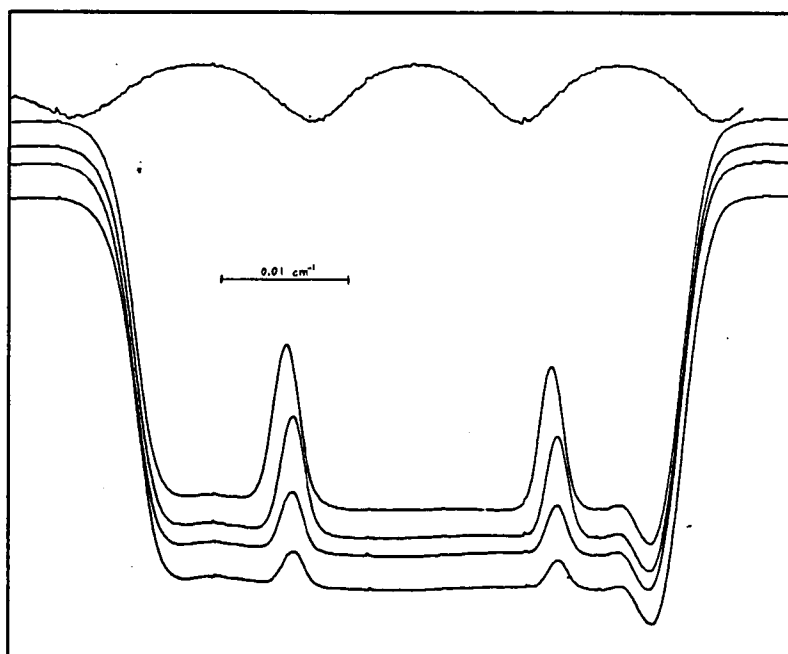


Figure 4.13:

C₂H₂ - Line P⁽⁵⁾(1) - 726.49605 cm⁻¹ - Path: 25.4 cm - Temp: 296 K
Pressures (millitorr): 978.0, 581.0, 242.1, 135.6

Table 4.1 : Halfwidths of acetylene spectral lines (HWHM)
in units of 10^{-3} cm^{-1} .

Line	Frequency cm^{-1}	Doppler b_D	Observed b_{OB}	$\sqrt{b_{OB}^2 - b_D^2}$	Pressure millitorr	Path cm
$Q^{(1)}(1)$	729.16329	0.88102	0.909	0.224*	19.4	25.4
			0.909	0.224*	7.7	
			0.912	0.236	193.7	5.08
			0.904	0.202	47.0	
			0.904	0.202	23.2	
			0.889	0.119*	11.6	
			0.889	0.119*	5.7	
			0.907	0.214*	96.8	2.535
			0.907	0.214*	47.0	
			0.907	0.214*	18.4	
$Q^{(1)}(3)$	729.20809	0.88108	0.881	0 *	96.8	2.535
			0.881	0 *	58.1	
			0.881	0 *	33.4	
			0.881	0 *	18.4	
$Q^{(1)}(4)$	729.24416	0.88112	0.939	0.325*	16.5	25.4
			0.939	0.325*	5.2	
			0.965	0.393	48.4	5.08
			0.965	0.393	23.2	
			0.940	0.327	11.6	
			0.922	0.271*	5.8	
			0.895	0.160*	96.8	2.535
			0.895	0.160*	58.1	
			0.895	0.160*	33.4	
			0.895	0.160*	18.4	
$Q^{(1)}(6)$	729.34286	0.88124	0.893	0.144*	18.4	25.4
			0.893	0.144*	7.9	
			0.902	0.191*	48.4	5.08
			0.914	0.241*	23.2	
			0.938	0.320*	11.6	
			0.932	0.302*	5.8	

* see section 5.1.

Table 4.1 (continued).

Line	Frequency cm^{-1}	Doppler b_D	Observed b_{OB}	$\sqrt{b_{OB}^2 - b_D^2}$	Pressure millitorr	Path cm
$Q^{(5)}$ (3)	728.91427	0.88073	0.967	0.399	469.6	25.4
			0.912	0.235*	242.1	
			0.912	0.235*	130.7	
			0.912	0.235*	62.0	
			0.920	0.265*	484.1	25.4
			0.920	0.265*	237.2	
			0.920	0.265*	139.4	
			0.920	0.265*	66.8	
			1.082	0.628	944	25.4
			0.990	0.451*	474.5	
$Q^{(5)}$ (4)	728.95235	0.88077	0.990	0.451*	275.5	
			0.990	0.451*	133.3	
			0.990	0.451*	68.0	
			0.907	0.217*	479.3	25.4
			0.907	0.217*	273	
			0.907	0.217*	161.7	
			0.907	0.217*	104.6	
			1.074	0.614	968.3	25.4
			0.976	0.420	469.6	
			0.948	0.351	234.8	
$Q^{(5)}$ (6)	729.05697	0.88089	0.906	0.214*	137	
			0.881	0	62.7	
			1.014	0.504	6.43	25.4
			0.942	0.334*	3.16	
			0.942	0.334*	1.55	
$^{12}\text{C}^{13}\text{C}$ (1.107%)	728.78701	0.86411	0.942	0.334*	0.79	
			0.942	0.334*	0.38	
			1.049	0.574	978	25.4
			0.986	0.450	581	
$P^{(5)}$ (1)	726.49605	0.8778	0.974	0.422	242.1	
			0.949	0.360	135.6	

* see section 5.1.

Table 4.2 : Acetylene line intensity measurements S_J given
in $\text{cm}^{-2}\text{atm}^{-1}$ at 296 K.

Line	Frequency cm^{-1}	Pressure millitorr	Path cm	Transmittance	INTENSITY S_J	avg $\overline{S_J}$
$Q^{(1)}(1)$	729.16329	19.4	25.4	0.095	7.217	7.092 $\pm .378$
		7.7		0.430	6.464	
		193.7	5.08	0.011	7.039*	
		47.0		0.305	7.512	
		23.2		0.558	7.474	
		11.6		0.748	7.429	
		5.7		0.869	7.308	
		96.8	2.535	0.319	7.029	
		47.0		0.577	6.971	
		18.4		0.819	6.477	
$Q^{(1)}(3)$	729.20809	96.8	2.535	0.070	16.312	15.316 $\pm .674$
		58.1		0.231	15.000	
		33.4		0.428	15.115	
		18.4		0.632	14.835	
$Q^{(1)}(4)$	729.24416	16.5	25.4	0.202	5.768	6.510 $\pm .454$
		5.2		0.576	6.251	
		48.4	5.08	0.321	6.976	
		23.2		0.567	7.263	
		11.6		0.760	7.042	
		5.8		0.882	6.441	
		96.8	2.535	0.348	6.486	
		58.1		0.540	6.309	
		33.4		0.699	6.378	
		18.4		0.826	6.186	
$Q^{(1)}(6)$	729.34286	18.4	25.4	0.086	7.920	8.284 $\pm .317$
		7.9		0.349	7.875	
		48.4	5.08	0.244	8.668	
		23.2		0.520	8.376	
		11.6		0.718	8.471	
		5.8		0.849	8.392	

* see section 5.2.

Table 4.2 (continued).

Line	Frequency cm^{-1}	Pressure millitorr	Path cm	Transmittance	INTENSITY S_J	avg $\overline{S_J}$
$Q^{(5)}(3)$	728.91427	469.6	25.4	0.067	0.3616	0.3578 ± 0.0242
		242.1		0.216	0.3761	
		130.7		0.462	0.3510	
		62.0		0.654	0.4069	
		484.1	25.4	0.064	0.3369	
		237.2		0.249	0.3485	
		139.4		0.440	0.3495	
		66.8		0.689	0.3114	
$Q^{(5)}(4)$	728.95235	944	25.4	0.118	0.1471*	0.1538 ± 0.0068
		474.5		0.304	0.1443	
		275.5		0.483	0.1567	
		133.3		0.697	0.1610	
		68.0	25.4	0.847	0.1449	
		479.3		0.287	0.1547	
		273		0.487	0.1564	
		161.7		0.643	0.1629	
$Q^{(5)}(6)$	729.05697	104.6	25.4	0.759	0.1568	0.1845 ± 0.0161
		968.3		0.093	0.1648*	
		469.6		0.238	0.1815	
		234.8		0.456	0.1988	
		137		0.626	0.2030	
$Q^{(9)}_{11}$ $^{12}_C^{13}_C$ (1.107%)	728.78701	62.7	25.4	0.832	0.1745	27.746 ± 1.704
		6.43		0.083	24.326*	
		3.16		0.228	27.315	
		1.55		0.470	28.439	
		0.79		0.685	27.960	
$P^{(5)}(1)$	726.49605	0.38	25.4	0.846	25.694	0.03670 ± 0.0030
		978		0.583	.03266	
		581		0.701	.03619	
		242.1		0.852	.03916	
		135.6		0.915	.03878	

* see section 5.2.

CHAPTER 5

DATA ANALYSIS

5.1 Instrument function

Observed lines are the convolution of the effective instrument function and the Doppler profile of the spectral lines. Assuming that the instrument function is Gaussian, the observed half-width resulting from the convolution of two Gaussian profiles is given by:

$$b_{OB}^2 = b_D^2 + b_I^2 \quad (17)$$

where:

b_{OB} is the observed half-width,
 b_D is the Doppler half-width,
 b_I is the instrumental half-width.

The line profile of the TDL-system could possibly be better represented by a Lorentzian than a Gaussian. Chin [4] checked that the resulting convolution using a Voigt profile leads to instrument widths of the same order of magnitude.

Tables 4.1 show that small collision broadening is measured at higher pressures. Due to the high expansion of our spectra, it is difficult to determine the absolute line

width with a good accuracy, but width differences between lines belonging to the same set of spectra are significant. This justifies the method described below to calculate the instrumental width, and the method used in section 5.3 to analyse the collision broadening.

Assuming that collision broadening is not significant in low pressure spectra, the quantity $\sqrt{b_{OB}^2 - b_D^2}$ marked by * in tables 4.1 is supposed to represent the instrumental width b_I . Averaging these data leads to:

$$b_I = 0.000228 \pm 0.000117 \text{ cm}^{-1}.$$

It follows that the resolution of our TDL-spectra, given by the instrumental full-width, is about 0.0005 cm^{-1} .

5.2 Line and band intensity

Line intensities, in tables 4.2, are calculated using eq. (3). According to the remark given in 5.1, related to the inaccuracy of the absolute observed width, the following correction is used for the term b of eq. (3): the average value of all the terms $\sqrt{b_{OB}^2 - b_D^2}$ in tables 4.1 (not only the terms marked by a *) is $0.0003048 \text{ cm}^{-1}$; a convolution of this value and the Doppler width is taken for b to calculate the intensity of each line:

$$b = \sqrt{b_D^2 + 0.0003048^2}$$

The line intensities S_J are presented in tables 4.2. An average S_J is given for each line.

∗: for a few lines significantly broadened an additional correction is used which takes into account the ratio between the width of the line and the mean width of the corresponding set of spectra; these intensities are marked with a ∗ in tables 4.2. In these few cases, b is given by:

$$b = [b_{OB}/(\text{mean } b_{OB})] \sqrt{b_D^2 + 0.0003048^2}$$

From S_J , the vibrational factor S_v^0 is calculated using eqs. (5), (6), (7), (8), and the band intensity $S_v^{(i)}$ using eqs. (10), (11), (12). Different lines in the same band generate consistent results for the band intensity. Results are presented in table 5.1. A comparison with published values is given in Chapter 6 (conclusion).

Table 5.1: Band intensities $S_v^{(i)}$ in $\text{cm}^{-2}\text{atm}^{-1}$ at 296K.

Line	Frequency	S_J	S_v^o	$S_v^{(i)}$	$\overline{S_v^{(i)}}$	var.	n meas.
$Q^{(1)}(1)$	729.16329	7.092	574	561			
$Q^{(1)}(3)$	729.20809	15.316	563	550	<u>565</u>	<u>± 31</u>	30
$Q^{(1)}(4)$	729.24416	6.510	584	571			
$Q^{(1)}(6)$	729.34286	8.284	583	570			
$Q^{(5)}(3)$	728.91427	0.3578	26.3	24.1			
$Q^{(5)}(4)$	728.95235	0.1538	27.6	25.3			
$Q^{(5)}(6)$	729.05697	0.1845	26.1	23.9	<u>24.6</u>	<u>± 1.7</u>	26
$P^{(5)}(1)$	726.49605	0.03670	27.3	25.0			
$Q^{(9)}(11)$	728.78701	26.746	948	581	<u>581</u>	<u>± 37</u>	5

5.3 Self broadening and pressure shift

See remarks in section 3.3.

Self broadening data can be extracted from tables 4.1, from sets of spectra showing consistent and measurable broadenings increasing with the pressure.

Pressure shift data can be measured from Figures 4.1, 4.4, 4.9, 4.10 and 4.13. In the other spectra, the shift is not significant or lateral adjustments were done on the laser parameters between successive pressures.

Self-broadening and pressure shift data are presented in Table 5.2, and plotted in Figure 5.1.

The pressure broadening is of the order of magnitude of 0.15 cm^{-1} per atm (0.0002 cm^{-1} per torr). The pressure shift seems to behave non-linearly: the line position is proportionally more shifted by the first hundredths of a torr than by higher pressures around 1 torr. The measured shift is of the order of -0.003 cm^{-1} at 1 torr.

Table 5.2: Self-broadening and pressure shift (10^{-3}cm^{-1})

Line	b_{OB}	Broadening	Shift	Pressure
$Q^{(1)}(1)$	0.912	0.023	-1.08	193.7
	0.904	0.015	-0.87	47.0
	0.904	0.015		23.2
	0.889	0	-0.51	11.6
	0.889	0	0	5.7
$Q^{(1)}(4)$	1.026		-1.41	190
	0.965	0.043	-1.05	48.4
	0.965	0.043	-0.74	23.2
	0.940	0.018	-0.32	11.6
	0.922	0	0	5.8
$Q^{(5)}(4)$	1.082		-3.43	944
	0.990		-2.11	474.5
	0.990		-1.13	275.5
	0.990		-0.53	133.3
	0.990		0	68.0
	0.907		-2.55	479.3
	0.907		-1.98	273
	0.907		-1.13	161.7
	0.907		0	104.6
$Q^{(5)}(6)$	1.074	0.193		968.3
	0.976	0.095		469.6
	0.948	0.067		234.8
	0.906	0.025		137
	0.881	0		62.7

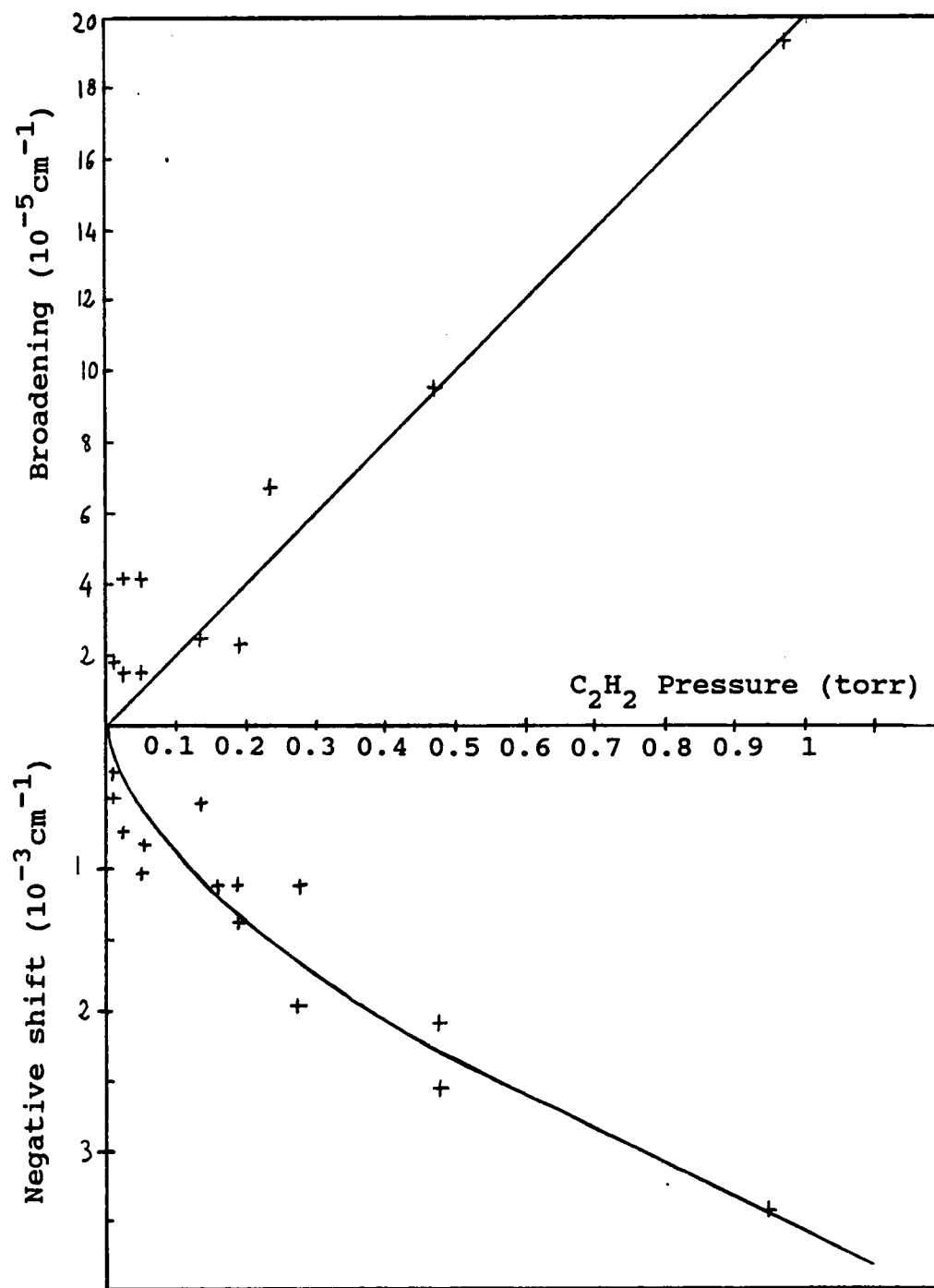


Figure 5.1: self-broadening and pressure shift.

CHAPTER 6

CONCLUSION

Either in the ν_5 -fundamental band (#1) or in the $(\nu_4+\nu_5)^{0-}-\nu_4^1$ "hot band" (#5), intensity analysis results presented in section 5.2 exhibit very good consistency and homogeneity, and demonstrate the sensibility of the TDL-spectrometer high resolution technique. Band intensities generated from different lines or from different branches in the same band lead to identical results.

Moreover, our results provide a good confirmation of the values generated from low resolution techniques published by Varanasi et al.[1]:

Transition	band freq.	Varanasi $s_v^{(i)}$	Our results $s_v^{(i)}$
ν_5 -fundamental	729.1553	596	565 ± 31
ν_5 -fund. $^{12}\text{C}^{13}\text{C}$	728.2288	$6/0.01107=542$	581 ± 37
$(\nu_4+\nu_5)^{0-}-\nu_4^1$	728.8574	19	24.6 ± 1.7

$^{12}\text{C}^{13}\text{CH}_2$ intensity measurement is interesting since

it could provide information to determine planetary atmospheric $^{13}\text{C}/^{12}\text{C}$ ratios (an abnormal value has been derived recently from Jupiter's Voyager data [1, sub-ref.31])).

In addition, our experiment yields raw measurements, for acetylene at low pressure (<1 torr), of a collision self-broadening coefficient of the order of 0.15 cm^{-1} per atm, and a pressure shift of about -0.003 cm^{-1} at 1 torr. These observations suggest further investigations.

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LIST OF REFERENCES

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After two years overseas (New Caledonia), teaching mathematics, physics and music, he was employed by the uranium enrichment company Eurodif, Pierrelatte, France. There, he gained professional experience in nuclear and chemical engineering, successively in charge of : facility start-up and testing (1977), production (1979), process improvement (1981), and quality assurance(1985).

On sabbatical leave from Eurodif, from September 1986 to July 1987, he has studied toward a Master's degree with a major in Physics, at the University of Tennessee, Knoxville.