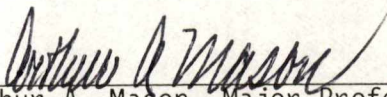
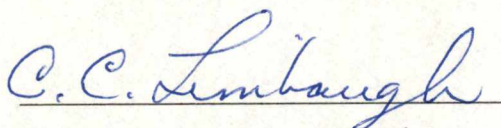


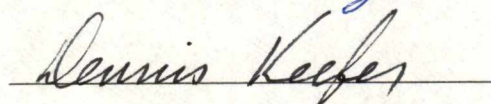
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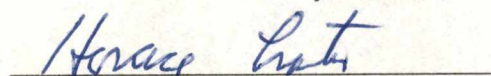
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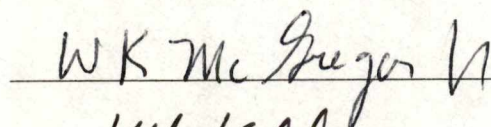

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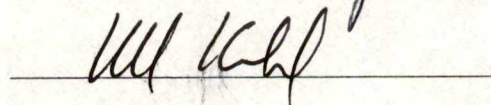
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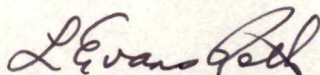

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Graduate Studies and Research

HIGH RESOLUTION TUNABLE DIODE LASER SPECTROSCOPY OF
CARBON MONOXIDE IN GAS MIXTURES AND FLAMES

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

Heard Sidney Lowry, III
March 1982

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ABSTRACT

Line strengths and widths of the P(2), P(3), P(7), P(18), and P(22) lines in the fundamental band of carbon monoxide broadened by nitrogen have been measured at temperatures in the range 300 to 600 K using a high resolution infrared (IR) tunable diode laser spectrometer. Half-widths of the P(2), P(3), P(7), and P(12) lines broadened by carbon dioxide, and the P(2), P(3), and P(7) lines broadened by water vapor were measured in the same temperature range. Broadening theory was applied to the nitrogen and carbon dioxide broadening cases and compared to the experimental values. In addition, temperature and concentration determinations have been made in the combustion gases of a flat flame burner operating at temperatures in the range 1,800 to 1,900 K using tunable diode laser spectroscopic data.

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CHAPTER I

INTRODUCTION

A current area of interest to the combustion technology community is the determination of exhaust gas species concentrations. This task has traditionally been accomplished by means of probe extraction techniques in conjunction with conventional analysis. Recently, however, there have been several studies indicating that probe extraction may chemically alter the combustor exhaust under certain conditions and thus yield erroneous results [1-4].¹ Alternate non-interference methods of measurement have been developed to overcome this problem. Non-interference optical techniques include molecular and atomic absorption and emission spectroscopy [5-9] and a number of scattering techniques including laser-induced fluorescence spectroscopy [10], Raman spectroscopy [10], and coherent anti-Stokes Raman spectroscopy (CARS) [10]. This study documents the development of high resolution IR tunable diode laser absorption spectroscopy as a combustion diagnostic technique.

In absorption spectroscopy, species concentration is related to the absorption of energy from incident radiation. This absorption is related to the number of absorbing molecules in the path of the beam, the dependence of the absorption on wavenumber (the line shape), and the temperature. Molecular collisions involving the absorbing molecules affect the line shape; thus, for a gas mixture,

¹Numbers in brackets refer to similarly numbered references in the Bibliography.

absorption is a function of the partial pressures of the diluent gases as well as the partial pressure of the absorbing gas. Each species of colliding molecule in the mixture has a characteristic effect on the absorption line shape.

The true absorption line shape is normally distorted by the spectroscopic instrumentation used to acquire the spectrum. If the instrument function is approximately an order of magnitude narrower than the width of the absorption line, the spectrum can be analyzed to yield the true line shape. In this study, instrumentation capable of producing distortionless spectra, such as the tunable diode laser spectrometer, is denoted as very high resolution instrumentation. A very high resolution spectrum combined with the knowledge of the temperature and certain molecular parameters provides the basis for a powerful non-interference technique for species determinations in the effluent streams of combustion systems.

Absorption measurements of carbon monoxide (CO) can provide information concerning combustion efficiency since CO is a product of the incomplete combustion of hydrocarbon fuels. A non-interference CO concentration monitoring system would be a useful diagnostic tool for studying techniques for improving the efficiency of experimental prototype combustors, investigating various combustion processes, and possibly providing in-flight warning of engine degradation. It could also be useful in studying CO as a pollutant, both in the stratosphere and at ground level.

Previous investigators have examined the room temperature-broadening effects of several gases on the half-widths of lines in

the fundamental infrared band of CO. Some data relating to the temperature dependence of these half-widths exist in the literature, but none exist for water vapor broadening, and very little exist at temperatures characteristic of a flame. More data are needed to determine properly the behavior of the half-widths of CO lines at elevated temperatures. A major barrier to the acquisition of these data is the construction of a gas sample cell capable of withstanding such high temperatures. Thus, some relationship between half-width and temperature must be found which will permit the extrapolation of low-temperature results to high temperatures.

The principal objective of the research reported here was the experimental determination of CO-diluent spectral line broadening parameters at elevated temperatures to determine whether this information could be used to make predictions of half-widths at flame temperatures. To accomplish this, cell measurements were made in the fundamental infrared (IR) band of CO at approximately 4.7 microns ($2,100\text{ cm}^{-1}$) in the temperature range 300 to 600 K. Nitrogen, carbon dioxide, and water vapor, which are typical products of hydrocarbon combustion, were studied as diluents.

In addition, several minor objectives were achieved:

1. Collisional broadening theory was examined to determine if the broadening parameters could be calculated successfully as a function of temperature, collisional species, and rotational quantum number.
2. The fundamental (1-0) band strength was determined from individual CO rotational line strengths.

3. A temperature measurement was obtained from the spectral analysis of CO in a heated cell and in the effluent of a flat flame burner via the two-line technique described by Hanson and Falcone [11].
4. Concentrations were deduced from the line strengths obtained in the flat flame burner measurements.

CHAPTER II

THEORETICAL DEVELOPMENT

II.1. Line Strengths

The transmission of a sample as a function of wavenumber ($\tau(\nu)$) is defined by the relationship:

$$\tau(\nu) = I(\nu)/I_0(\nu) , \quad (1)$$

where $I_0(\nu)$ is the radiation intensity incident on the sample, and $I(\nu)$ is the intensity transmitted by the sample. The monochromatic absorption coefficient ($k(\nu)$) for an optically thin gas is defined by Beer's Law [12]:

$$k(\nu) = [-1/\ell] \cdot \ln(\tau(\nu)) , \quad (2)$$

where ℓ is the thickness of a homogeneous layer of sample. If a transmission measurement is made at very high resolution, the variation of transmission with frequency will be an accurate representation of the true line shape.

The integrated absorption coefficient, or line strength, S , for an isolated absorption line is defined by the relationship [12,13]:

$$S = \int_{-\infty}^{\infty} k(\nu) d\nu . \quad (3)$$

The line strength of a given transition in a CO vibrational band can

be calculated by the approximate Herman-Wallis [14] formula as used by Hanson [15]:

$$S(m) = S^0(273.15/T)(\nu/\nu_0) \exp[-E(m)/kT] \\ [1 - \exp[-hc\nu/kT]] |m|(v''+1)/Q(T), \quad (4)$$

where S^0 is the band strength evaluated at 273.15 K and 1.0 atmosphere in units of $\text{cm}^{-2} \text{ atm}^{-1}$; ν_0 is a band center wavenumber [16]; $E(m)$ is the transition ground state energy; $Q(T)$ is the partition function for the rotation,

$$Q(T) = \sum_J (2J+1) \exp[-E(m)/kT],$$

m is the rotational index¹ defined as: $m = J+1$ for the R branch, and $m = -J$ for the P branch; v'' is the lower state vibrational quantum number; T is the temperature; and h , c , and k are Planck's constant, the speed of light, and Boltzmann's constant, respectively. For a given line (m), the line strength at a temperature, T_1 can be related to the line strength at a reference temperature T_0 by [17]:

$$S(T_1) = S(T_0) \exp \left[-E(m)/k \left[\frac{1}{T_1} - \frac{1}{T_0} \right] \right] \frac{Q(T_0)(1 - \exp(-hc\nu/kT_1))}{Q(T_1)(1 - \exp(-hc\nu/kT_0))}. \quad (5)$$

This relationship is useful for adjusting both theoretically

¹Not to be confused with the projection of the angular momentum along the axis.

calculated and experimentally determined line strengths to a common reference temperature.

At this point, a brief description of diatomic infrared molecular spectroscopy nomenclature is in order. An individual molecule such as CO, which in the ground electronic state possesses no electronic orbital or spin angular momentum, ($^1\Sigma$), can have a specific vibration-rotation quantum state which can be characterized by two non-negative integers, the vibrational quantum number v and the rotational quantum number J . Infrared absorption lines are observed when radiation is absorbed by molecules which are excited from a lower vibrational state to a higher one as a result of the absorption. The energy of the photons of the radiation corresponds to the energy separation of the two states involved. A not-to-scale partial energy level diagram with some typical transitions indicated is shown in Fig. 1. With regard to J , two types of transitions are normally observed: J is either increased or decreased by one unit. The former case is known as an "R" transition, the latter, a "P" transition. A single absorption line is identified by the symbol $\nu_u - \nu_l X(J_l)$, where ν_u and ν_l are, respectively, the upper and lower state vibrational quantum number; X is the rotational transition type letter, P or R; and J_l is the lower state rotational quantum number. The collection of lines corresponding to all the transitions between two particular vibrational states is termed a band.

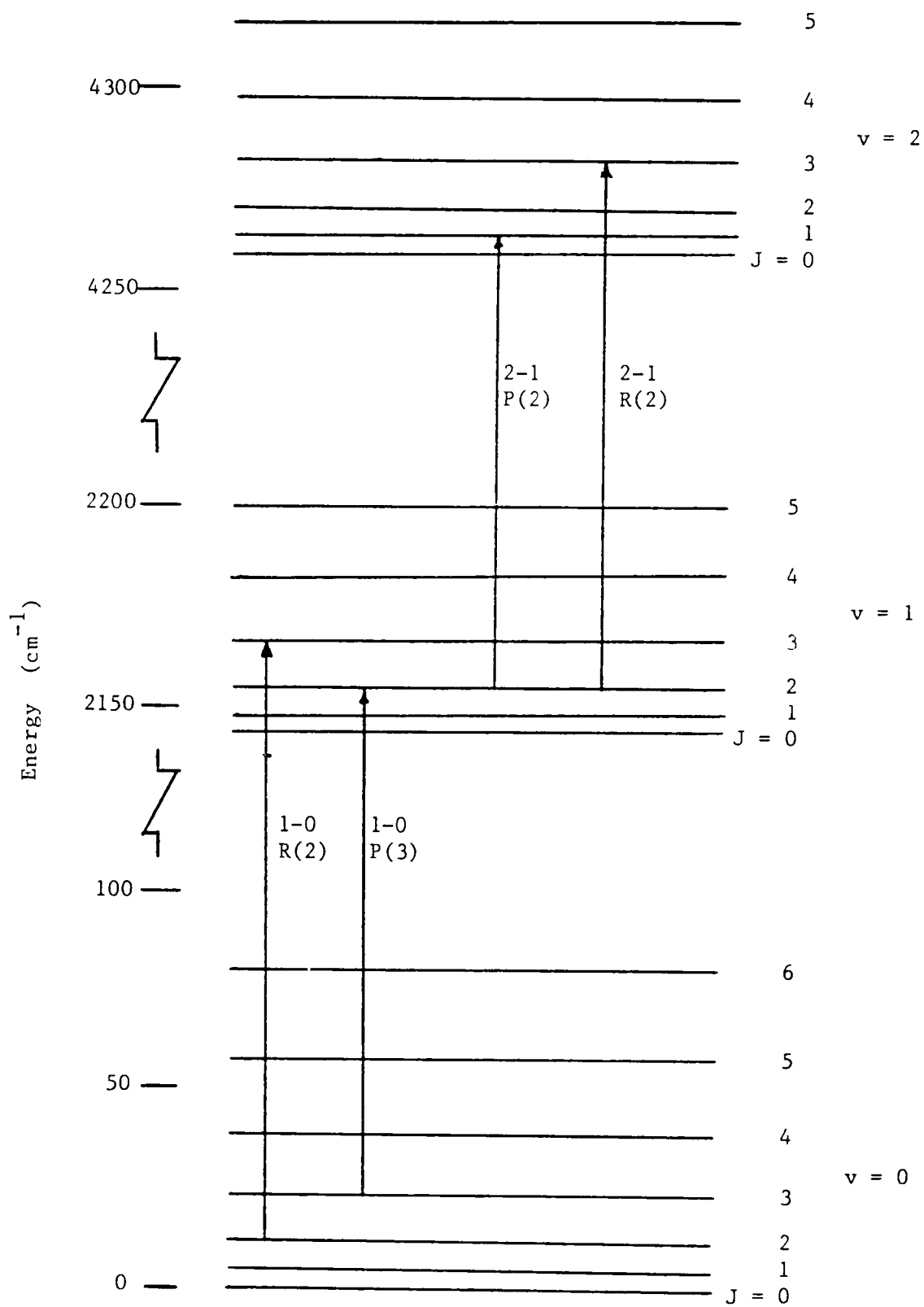


Figure 1. Typical 1Σ vibration-rotation energy level diagram.

II.2. Line Shape

In addition to the line strength, the line shape as a function of wavelength is required to specify the absorption coefficient. The key parameter of this relationship, the half-width, is defined as half of the width of the absorption coefficient $k(\nu)$ at half-height. In the limiting case of no collisional broadening (low density, high temperature), the line shape is due mainly to shifts in frequency caused by the motion of the molecules, and is given by the Doppler function [13]:

$$k(\nu) = \left[\frac{(\ln 2)}{\pi} \right]^{1/2} \frac{S}{\gamma_D} \exp \left(- \frac{(\nu - \nu_0)^2 \ln 2}{\gamma_D^2} \right), \quad (6)$$

where ν_0 is the line center wavenumber, and γ_D is the Doppler half-width:

$$\gamma_D = (2kT \ln 2 / mc^2)^{1/2} \nu_0, \quad (7)$$

and m is the mass of the absorbing molecule. In the limiting case of collisional dominance, the line shape is described by the Lorentzian function [13]:

$$k(\nu) = \frac{S}{\pi} \frac{\gamma_L}{(\nu - \nu_0)^2 + \gamma_L^2}, \quad (8)$$

where γ_L is the Lorentz half-width, for which an analytical form will be developed later. A general form, which includes both

regimes, known as the Voigt line shape, is a convolution of the two functions, and is given by Ref. [16]:

$$k(\nu) = \frac{S \sqrt{\ln 2/\pi}}{\gamma_D} \frac{a}{\pi} \int_{-\infty}^{\infty} \frac{\exp(-y^2)}{a^2 + (x-y)^2} dy, \quad (9)$$

where,

$$x = \frac{(\nu - \nu_0)}{\gamma_D} \sqrt{\ln 2}, \quad (10)$$

and

$$a = \sqrt{\ln 2} \gamma_L / \gamma_D. \quad (11)$$

Each diluent broadening gas is characterized by a Lorentz broadening parameter $\gamma_L^0 (\text{cm}^{-1} \text{ atm}^{-1})$. This parameter is defined as the collisional, or Lorentz, half-width due to the broadening of the CO lines by the diluent at one atmosphere pressure. Due to the binary nature of the collisions, the net Lorentz half-width (γ_L) of a mixture of gases can be calculated by means of the expression [18]:

$$\gamma_L = \sum_i \gamma_{L_i}^0 p_i, \quad (12)$$

where $\gamma_{L_i}^0$ is the Lorentz broadening parameter due to collisions with the i^{th} component of the mixture, and p_i is the partial pressure of that component.

II.3. Line Widths

A theoretical collisional half-width, γ_L , can be calculated by means of the theory of Anderson [19], as expanded by Tsao and

Curnutte [20].² This is a unified treatment of the statistical theory of Kuhn [21] and Margenau [22], and the impact theory of Lorentz [23], Weiskopf [24], and Lenz [25]. The statistical theory considers the idealized physical situation in which all the molecules around the radiating one are at rest and cause a static but random perturbation in the energy levels of the radiating molecule. The impact theory considers the incoherency in the emitted radiation caused by molecular collisions during the radiating process.

The ATC theory has previously been applied to broadening phenomena by Birnbaum [26], Benedict and Herman [27], and Varnasi and Tejwani [28]. This theory relates γ_L to a quantum mechanically calculated rate of change in phase of the absorbed radiation due to collisions. It includes both the adiabatic case, where neither molecule involved in the collision suffers a change in internal quantum numbers governing its unperturbed energy, and the non-adiabatic case, where these quantum numbers do change for one or both of the molecules. Although this is treated quantum mechanically, the translation of the molecules is treated classically. It is also assumed that the duration of collisions is small compared to the time between collisions (the impact approximation) so that the effects of the different collisions do not interfere with each other, the collisions are binary so that the half-widths will be proportional to the pressure, and the spectral lines are well resolved

²This will be henceforth referred to as the ATC theory.

so that the line shape can be measured directly. A very brief sketch of the theory is outlined below.

Time-dependent perturbation theory is used to develop an equation for the probability of a change from state A to state B of the unperturbed eigenstates. Switching to the interaction picture and using radiation theory, this transition probability is transformed into a constant rate of absorption:

$$W = 2\gamma \operatorname{Re} \int_0^{\infty} \exp(i\omega_k \tau) \operatorname{Tr} [\rho_0 \mu_z U_m^{-1}(\tau) \mu_z U_m(\tau)]_{av} d\tau, \quad (13)$$

where,

$$\gamma = 2\pi \omega_k / \hbar c \text{ [sec/gm cm}^3 \text{]},$$

ρ_0 is the density matrix, and μ_z is the z-component of the electric dipole. The function $U_m(\tau)$ is the time-development operator of the system³

$$U_m(\tau) = \exp \left[(-i/\hbar) \int_0^{\infty} H_m(t') dt' \right], \quad (14)$$

where,

$$H_m(t) = H_1 + H_2 + H_c(t) \quad (15)$$

³This is strictly true only if the $H(t)$ at any two instants of time commute with each other. However, in Ref. [10] it is stated that Anderson in his dissertation shows that the non-commuting terms involved can be neglected. Thus, the second-order terms which contribute to the line width (and are most sensitive to this problem) are still valid, and a time-ordered product is not necessary.

is the sum of the Hamiltonians of molecules 1 and 2, containing only the internal coordinates, and the collision interaction. The average is taken over all collisions. This rate of absorption is a function of wavelength and contains the information needed to characterize the effects of the collision process on the line shape. This is basically the point where Anderson began in Ref. [19].

By transforming to another interaction picture⁴ with an operator named T, considering the rotational states of the molecules, $|j_i m_i j_2 m_2\rangle$, and mathematically manipulating the equation for the constant rate of absorption, an equation is obtained which is written in correlation function form:

$$W = 2\gamma \sum_{j_i, j_f} \frac{\rho_{j_i j_i}}{2j_i + 1} \operatorname{Re} \int_0^{\infty} \exp(-i(\omega - \omega_{fi})\tau) \Phi(\tau) d\tau, \quad (16)$$

where,

$$\rho_{j_i j_i} = \frac{(2j_i + 1) \exp(-E_{j_i}/kT)}{\sum_n (2j_n + 1) \exp(-E_n/kT)}, \quad (17)$$

⁴The first interaction picture expresses the rate of absorption in terms of $U_m(\tau)$, while the second interaction picture uses the time-development operator for the unperturbed field only in order to simplify the remaining development.

and

$$\Phi(\tau) = \sum_{j_2} \frac{\rho_{j_i j_i}}{(2j_2+1)} \sum_{j_2'} \sum_{\substack{m_i m_i' \\ m_f m_f' \\ m_2 m_2'}} < j_i m_i | \mu_z | j_f m_f > < j_f m_f j_2 m_2 | T^{-1}(\tau) | j_f m_f' j_2' m_2' > \\ * < j_f m_f' | \mu_z | j_i m_i' > < j_i m_i' j_2' m_2' | T(\tau) | j_i m_i j_2 m_2 >_{av} . \quad (18)$$

Due to the fact that collisions may be expected to occur isotropically, relations can be written of the form:

$$< j_f m_f j_2 m_2 | T^{-1}(\tau) \mu_z T(\tau) | j_i m_i j_2' m_2' >_{av} \\ = < j_f m_f | \mu_z | j_i m_i > \delta_{j_2 j_2'} \delta_{m_2 m_2'} F(\tau) , \quad (19)$$

which yield further simplifications of Eq. (18). The function $F(\tau)$ is then determined to be:

$$F(\tau) = \exp(-n\bar{v}\sigma\tau) , \quad (20)$$

where n is the number of colliding molecules per unit volume and $\bar{v}$ is the mean collision velocity. The parameter σ is interpreted as a collision cross section and is given by:

$$\sigma = \sum_{j_2} \rho_{j_2 j_2} \sigma_{j_2} , \quad (21)$$

where,

$$\sigma_{j_2} = \int_0^{\infty} (2\pi b) \left[1 - \sum_{\substack{m_i m_i' \\ m_f m_f' \\ m_2 m_2' \\ M}} \frac{\langle j_f m_f M | j_i m_i \rangle \langle j_i m_f' M | j_i m_i' \rangle}{(2j_i+1)(2j_2+1)} \right. \\ \left. * \langle j_f m_f j_2 m_2 | T^{-1}(b) | j_f m_f' j_2' m_2' \rangle \langle j_i m_i' j_2' m_2' | T(b) | j_i m_i j_2 m_2 \rangle \right], \quad (22)$$

where b is the impact parameter. Considering σ to be complex,

$$\sigma = \sigma_r + i\sigma_i; \quad (23)$$

Eq. (16) now becomes:

$$W = 2\gamma \sum_{j_i j_f} \frac{\rho_{j_i j_i}}{(2j_i+1)} \sum_{m_i m_f} |\langle j_i m_i | \mu_z | j_f m_f \rangle|^2 \frac{n\bar{v}\sigma_r}{(\omega - \omega_{if} + n\bar{v}\sigma_i)^2 + (n\bar{v}\sigma_r)^2}. \quad (24)$$

This is basically the Lorentz line shape function with line shift:

$$\Delta\omega = (n\bar{v}/2\pi c) \sigma_i \quad (\text{cm}^{-1}), \quad (25)$$

and half-width:

$$\gamma = (n\bar{v}/2\pi c) \sigma_r \quad (\text{cm}^{-1}). \quad (26)$$

Retaining the formulation of the classical impact parameter approach,

$$\sigma = \int_0^{\infty} 2\pi b S(b) db, \quad (27)$$

where $S(b)$ is the total transition rate function, and b is the impact parameter. The function $S(b)$ is considered as a weight factor which indicates the effectiveness of a collision in disturbing the molecular radiation, and can vary from zero, for no interaction, to one, which represents total disruption of the wavetrain. A calculation to the first order of approximation in the interaction operator T yields an imaginary term, $S_1(b)$, which contributes to the frequency shift, but not to the line half-width. The function $S_2(b)$, representing a second-order approximation, is real and does contribute to the line half-width.

The interaction potential is generally expanded into a series of multipoles of differing polarity, strength, and range. The four terms of longest range are the dipole-dipole, the dipole-quadrupole, the quadrupole-dipole, and the quadrupole-quadrupole. These terms, and an isotropic hard-sphere repulsive potential entering in at a distance of closest approach, b_0 , are the only forces considered in this study. This model ignores the explicit details of shorter-range interactions, but to some extent these effects are taken into account by the value of b_0 .

From the expressions for $S_2(b)$ given in the article by Tsao and Curnutte [20] for the different interactions under consideration, one can write:

$$S(b) = S_2(b) = \sum_{\ell} c_{\ell} b^{-n_{\ell}} \left[\sum_{\ell} g_{\ell j} r_{\ell}(k) \right], \quad (28)$$

where C_ℓ , n_ℓ , and $r_\ell(k)$ are given in Table 1; $g_{\ell j}$ is a transition factor; and k is a resonance parameter defined by:

$$k = b w_{\ell j} / \hbar \bar{v} , \quad (29)$$

where $w_{\ell j}$ is the energy change of the collision process. The parameters $g_{\ell j}$ and $w_{\ell j}$ will be developed in detail in Appendix A.

Anderson assumed that the radiation is completely interrupted for very small impact parameters, which requires the evaluation of the limit, b_0 , for which

$$S_2(b < b_0) = 1 . \quad (30)$$

This is taken either as the solution of the equation:

$$S_2(b) = 1 , \quad (31)$$

or the repulsive minimum collision diameter, $b_{\min}$, given by kinetic theory, whichever is greater.

A partial cross section, σ_{v,m,j_2} , is calculated for each possible rotational state of the colliding molecules, ρ_{j_2} , in that state and summed over all states to yield the total cross section:

$$\sigma_{\text{tot}}^{(v,m)} = \sum_{j_2} \rho_{j_2} \sigma_{v,m,j_2} \quad (32)$$

for a particular radiative transition labeled by the vibrational quantum number v and rotational quantum number m . A partial collision diameter (b_{v,m,j_2}) is defined by:

Table 1. Interaction Parameters

ℓ	Type of Interaction	n_ℓ	$\Delta j_{i,f}$	Δj_2	C_ℓ	$r_\ell(k)^a$	$R_\ell(k)^a$
1	Dip-Dip	4	± 1	± 1	$4\mu_1\mu_2/9\hbar v$	$f_1(k)$	$F_1(k)$
2	Dip-Quad	6	± 1	$\pm 2,0$	$16\mu_1Q_2/45\hbar v$	$f_2(k)$	$F_2(k)$
3	Quad-Dip	6	$\pm 2,0$	± 1	$16Q_1\mu_2/45\hbar v$	$f_2(k)$	$F_2(k)$
4	Quad-Quad	8	$\pm 2,0$	$\pm 2,0$	$16Q_1Q_2/25\hbar v$	$f_3(k)$	$F_3(k)$

^aThe $f_i(k)$'s and the $F_i(k)$'s are those tabulated in Tsao and Curnutte [20]; these are reproduced in Table A.1, Appendix A.

$$\sigma_{v,m,j_2} = \pi b_{v,m,j_2}^2, \quad (33)$$

and thus the total cross section is given by:

$$\sigma_{\text{tot}}^{(v,m)} = \pi \sum_{j_2} \rho_{j_2} b_{v,m,j_2}^2. \quad (34)$$

The collision half-width for a particular transition (v,m) as a function of temperature, $\gamma_L^{v,m}(T)$, is then derived from the total cross section by the relation [29]:

$$\gamma_L^{v,m}(T) = (n\bar{v}/2\pi c) \sigma_{\text{tot}}^{(v,m)}, \quad (35)$$

where $\bar{v}$ is defined:

$$\bar{v} = (8kT/\pi M)^{1/2}, \quad (36)$$

where M is the reduced mass of the colliding system. Finally,

$$\gamma_c^{(v,m)}(T) = (n\bar{v}/2c) \sum_{j_2} \rho_{j_2} b_{v,m,j_2}^2. \quad (37)$$

The parameter b_{v,m,j_2} includes the combined quantum mechanical effects of all the intermolecular forces which induce a non-radiative transition in the colliding system. This quantity can be written [28]:

$$b_{v,m,j_2}^2 = b_o^2 \left[1 + \sum_{\ell} c_{\ell} b_o^{-n_{\ell}} \sum_j g_{\ell j} R_{\ell}(k(b_o)) \right], \quad (38)$$

where the $R_\ell(k)$ are given in Table 1. Thus, a form has been derived that can be used to calculate the half-widths from known molecular parameters.

On the basis of this theory, an approximate analytical form for the temperature dependence of γ_L for a particular intermolecular interaction has been developed by Birnbaum [26]:

$$\gamma_L \propto T^{-(j+4)/2j} = T^{-n}, \quad (39)$$

where j is an integer defined for each specific interaction, and n is defined as the temperature dependence exponent. For a process in which quadrupole-quadrupole interactions dominate, as is the case with CO broadened by CO₂ and N₂ [28,30], $j = 8$, and a temperature dependence of $T^{-3/4}$ is predicted. A hard-sphere analysis yields a temperature dependence of $T^{-1/2}$. Equation (39) has been used by various authors [31-34] to give the approximate temperature dependence of γ_L , but has also been shown to be in error [35-37] for some molecules. The temperature dependence of the foreign gas-broadened half-widths measured in this effort has been analyzed assuming a T^{-n} functional form. Agreement within experimental error was found in all cases (see Chapter IV, Sections IV.1 and IV.2).

II.4. Molecular Parameters

The parameters used in the initial computer modeling studies of CO lines broadened by CO, N₂, CO₂, and H₂, are listed in Table 2. The dipole and quadrupole moments are those recommended by Stogryn and Stogryn [38], and the values given for $b_{\min}$ are the kinetic

Table 2. Literature Molecular Parameters

	CO	N ₂	CO ₂	H ₂
B ₀ (cm ⁻¹)	1.9225	1.99	0.3902	59.322
D x 10 ⁶ (cm ⁻¹)	6.1	5.8	0.13	4.7 x 10 ⁴
μ x 10 ¹⁸ (esu cm)	0.112	0	0	0
Q x 10 ²⁶ (esu cm ²)	5.0	3.04	8.6	1.324
b _{min} x 10 ⁸ (cm)	3.76	3.70	4.10	2.87

theory collision diameters [39]. The quadrupole moments for the broadening gases and the $b_{\min}$ were adjusted from these starting points in order to better fit the data. The molecular rotational constants B_0 and D must be known in order to calculate E_{j_i} of Eq. (17). All values are obtained from Ref. [40] unless otherwise noted.

II.5. Two-Line Temperature Determination

A simple and direct temperature measurement technique employing the tunable diode laser spectrometer for systems containing CO has been developed by Hanson and Falcone [11]. If two absorption lines are recorded nearly simultaneously in a homogeneous system, the temperature of the system can be determined from a comparison of the ratio of the experimental line strengths to the ratio of the two line strengths as obtained from Eq. (4). The sensitivity of this technique increases as the energy separation of the two lower states of the pair of lines increases. In the case of CO, there are several pairs of lines originating from different vibrational states in the $2,100\text{-cm}^{-1}$ region which can be recorded in a single scan of the diode laser. These pairs are ideally suited for the two-line technique, providing that they do not significantly overlap each other or other absorption lines. If it can be assumed that the half-widths of the two lines are equal, then the ratio of the peak absorption coefficients can be used in the place of the line strengths for low resolution applications.

II.6. Implementation of the Theory

Several computer codes were written to facilitate data analysis:

Program A was developed to analyze, using a computer graphics terminal, the raw absorption data as recorded on magnetic tape. This program performs a best-fit Voigt evaluation of the experimental line shape. This can be achieved due to the extremely high resolution of the optical system which records very nearly the true shape of the line. The line strength and the line half-width, the two adjustable parameters of the Voigt line shape, are returned from the program. The data and fit are then displayed and a hard copy is made as a permanent record. It is important to note that the line strength obtained from this procedure is a parametric best fit to the Voigt profile and not the actual integration of the absorption coefficient over the limits of the spectral line. Thus, wing measurements and corrections are completely unnecessary to the computational procedure.

Program B calculates the temperature dependence of the line strengths and widths. The strengths are calculated using Eq. (5). The widths are calculated according to the most commonly used approximation:

$$\gamma_L(T) = \gamma_L(T_0) (T/T_0)^{-0.75}, \quad (40)$$

where T_0 is a reference temperature. The program was used primarily

to adjust literature and experimental line strengths and widths to a common reference temperature for comparison purposes.

Program C was written to calculate half-widths according to the ATC theory of collisional broadening, as has been previously discussed in Section II.3. This computer program was developed only for linear perturbing and absorbing molecules. The theory has also been used to describe collision line broadening of water vapor molecules which are asymmetric top molecules [35-37], but due to the limited scope of this study and the computational difficulties involved, the program was not expanded to include the water vapor broadening of CO. A listing for this program is given in Appendix B.

Program D was developed to perform a statistical analysis on the half-width and line strength experimental data, and to fit the experimentally determined line width temperature dependence to the form of Eq. (39).

CHAPTER III

EXPERIMENTAL APPARATUS

III.1. The Optical System

The spectra were recorded using a Laser Analytics LS-3 tunable diode laser spectrometer with a manufacturer's quoted resolution of approximately $3 \times 10^{-4} \text{ cm}^{-1}$. The instrument consists of two diode lasers mounted in a temperature-controlled cold head, an f/1 collimating lens, a reference etalon, a tuning fork chopper, a monochromator assembly, and a detector module. The laser injection current is controlled by a precision power supply. Optics external to the spectrometer housing were added to allow measurements to be made through the heated cell and the flat flame burner exhaust. A schematic of the optical system is shown in Fig. 2, and the complete optical system is shown in Fig. 3.

A typical diode laser can be scanned over 50 to 150 cm^{-1} in the infrared and can be modulated at speeds from 0.0001 to $600 \text{ cm}^{-1}/\text{sec}$. The diodes employed in this study emitted radiation at or near $2,100 \text{ cm}^{-1}$.

The diode lasers are manufactured from single crystalline Pb-salt alloy semi-conductors. A laser is tuned through its range by varying the operating temperature between 15 and 100 K. Typically, a 1 K change in temperature corresponds to a 4 cm^{-1} change in wavenumber. Laser emission consists of several spectral modes characterized by line widths of the order of $3 \times 10^{-4} \text{ cm}^{-1}$ and spacings of approximately one wavenumber. Individual modes can be tuned over

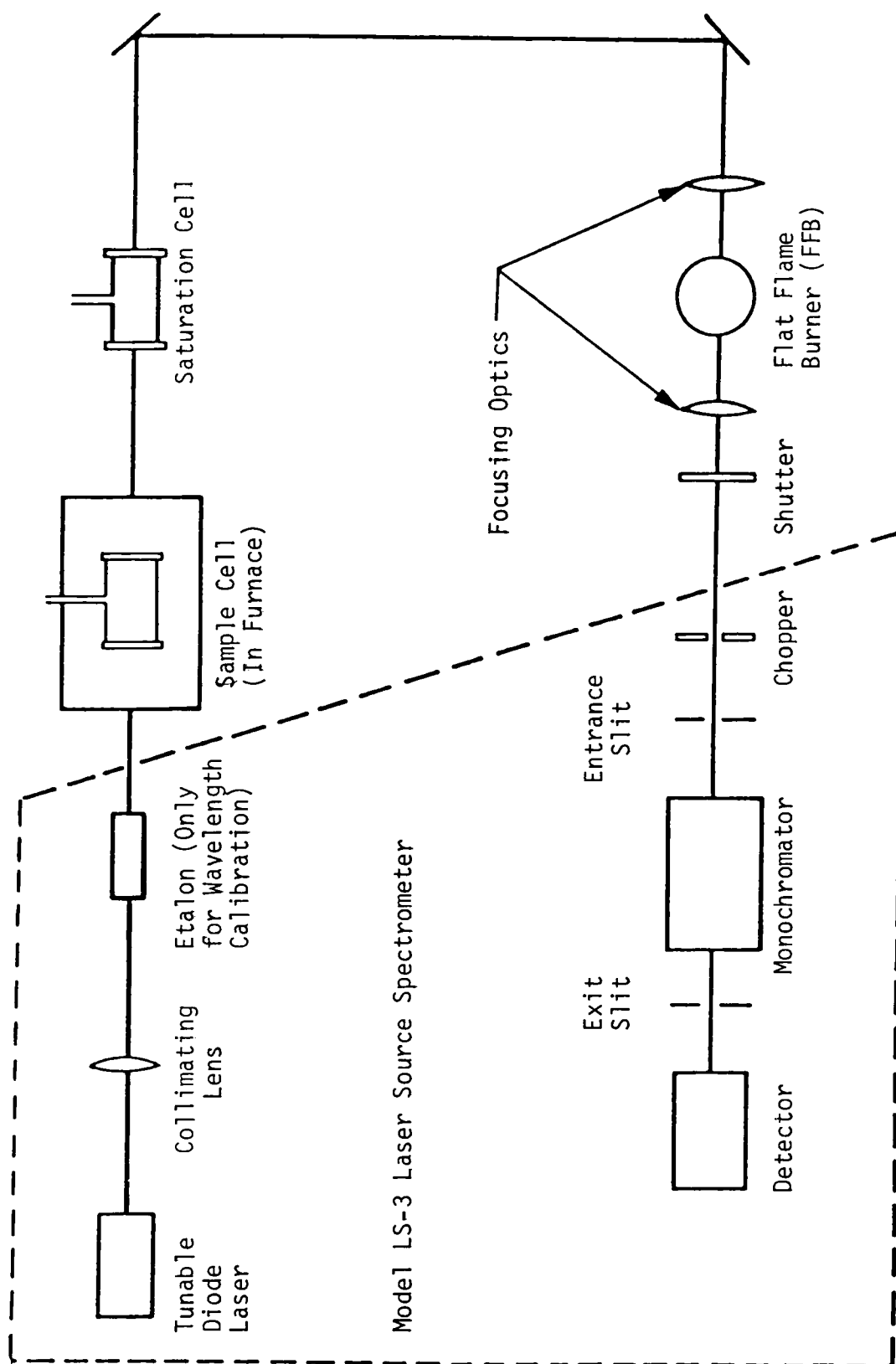


Figure 2. Schematic of laboratory optical system.

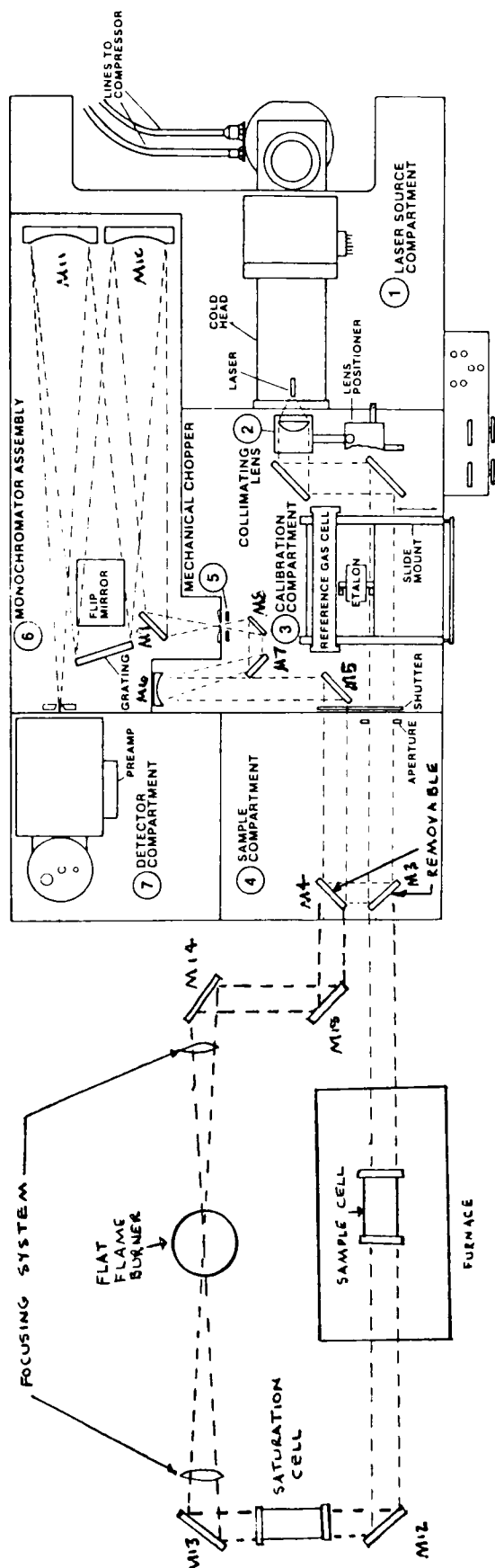


Figure 3. Diagram of laboratory optical system.

approximately a one-wavenumber range by changing the laser injection current, and are separated from the adjacent modes by the use of a grating monochromator. The monochromator also provides a coarse (0.5 cm^{-1}) absolute wavelength calibration.

A slide was used to introduce an etalon and a calibration gas cell into the optical path. The etalons used were 1- and 3-inch germanium blocks which produce fringes spaced 0.0471 and 0.0163 cm^{-1} apart at $2,115\text{ cm}^{-1}$. The etalon fringe pattern was used to relate the diode injection current to the output wavenumber. In general, there was a linear relationship between the current and the output wavenumber at a cold head temperature set point. The etalon calibration provides the information needed to determine the width of a measured spectral line. The calibration cell, when filled with a small amount of pure CO, was helpful in locating a mode suitable for spectral measurements of the line of interest.

The external optics were used to direct the collimated beam through the sample cell which was located in a three-element, 2,000-watt furnace. The sample cells were made of copper with CaF_2 windows attached with silicone rubber sealant. To avoid thermal shock damage to the CaF_2 windows, a programmable temperature controller was used to slowly heat the system to the desired temperature.

A flat flame burner with a focusing-collimating optical system was placed in the path of the external beam when required. The flat flame burner is a porous 7.62-cm-diameter copper burner. Buffer gas (N_2) flowing in a concentric outer ring was used to

isolate the flame from the ambient atmosphere, and a screen mounted above the burner surface was used to stabilize the flame.

Mirrors M12 to M15 (Fig. 3) returned the signal to the LS-3 spectrometer housing through a cell which was periodically filled with pure CO to a pressure sufficient to saturate (absorb completely in the center of) the absorption line of interest. This saturation provides an excellent test of spectral purity of the selected mode. Radiation intensity at the saturated wavelengths above the mechanically blocked beam signal intensity was attributed to radiation from nearby modes which had not been filtered sufficiently from the system. To account for this radiation, the signal level at the center of the saturated line was taken to be the true spectral zero in the analysis of the absorption spectra. A nitrogen purge system was used to flush out the saturation cell so that the residual CO did not influence subsequent measurements.

Once the beam was returned to the LS-3 housing, M6 (Fig. 3) was used to focus the collimated beam onto the f/11 Czerny-Turner monochromator entrance slits. A 400-Hz tuning fork chopper placed immediately before the entrance slit was used in the synchronous detection recording mode.

The detector used in the system was a liquid nitrogen-cooled, mercury-cadmium-telluride (HgCdTe) infrared detector with a peak wavelength response at about 10 microns ($1,000\text{ cm}^{-1}$). The detector assembly contained adjustable optics to focus radiation onto the 1-mm^2 detector. An impedance-matched, low-noise amplifier delivered the detector signal to an oscilloscope and a lock-in amplifier.

From the lock-in amplifier the signal was fed into an x-y recorder, a strip chart recorder, and the computerized data acquisition system. Figure 4 shows the laboratory optical system as previously described.

III.2. The Gas Handling System

The gas handling system used in this study consisted of two major subsystems: the sample cell fill system and the flat flame burner supply system.

The sample cell fill system consisted of valves, pressure measuring devices, and a vacuum pump in a configuration which facilitated the filling of the sample and saturation cells from bottles of calibration gases. Calibration gases of 3,080 ppm, 8,000 ppm, 2.03%, 4.89% CO in N₂, and pure CO and CO₂, were obtained from a commercial source. To obtain water vapor in the desired quantities, liquid water was heated to the temperature corresponding to the desired vapor pressure. The vapor was supplied to the sample cell through previously evacuated heated transfer lines and valves which were maintained at 400 K to prevent recondensation. The pressure was also monitored by means of a heated pressure transducer.

The flat flame burner supply system consisted of valves, pressure measuring devices, critical flow orifices, and a pressure transducer calibration and readout system in a configuration which supplied a methane/air mixture to the center ring, and nitrogen to the buffer ring of the flat flame burner. The system provided flames for which the operating parameters and exhaust species could be well-characterized. Calibration gases of pure methane, standardized

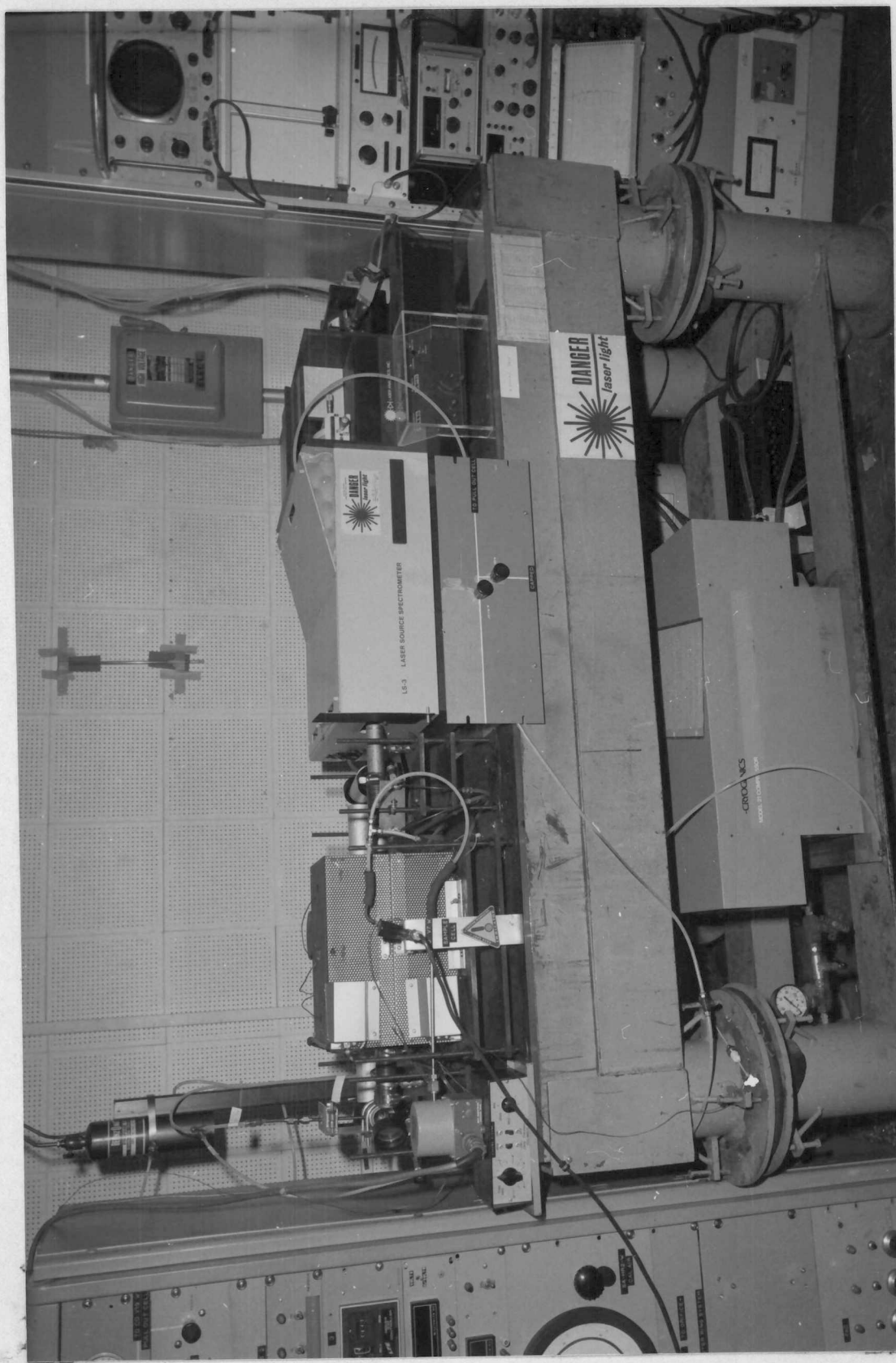


Figure 4. Photograph of laboratory optical system.

air, and pure nitrogen were commercially supplied. Figure 5 shows the gas handling and temperature control devices utilized in the laboratory system.

III.3. Data Acquisition

The primary data acquisition was accomplished using a digitized tape recording system. The system consisted of an analog signal processor, a mini-computer, and a digital tape drive system to record the data on nine-track tape. The absorption spectra were also recorded simultaneously on an x-y plotter.

The first step in taking data was to scan the region of the absorption line with the sample cell pumped out. This measured the background laser intensity without any absorption occurring. Next, sample gas of known pressure and temperature was introduced into the cell and another scan recorded. The cell was then pumped out again and a scan recorded to compare to the scan taken in the first step. These two scans provided a measure of laser scan repeatability. Next, sample gas at different conditions was introduced into the cell and a scan recorded. After a sequence of conditions had been recorded, a scan was taken with the saturation cell filled with 15 to 25 torr of pure CO to obtain the true optical zero. A scan was then recorded with the sample and saturation cells evacuated and the etalon in the beam for wavelength calibration. For pressures less than 5 psia, sample absorption traces were scanned over a region approximately 0.2-cm^{-1} -wide. The higher pressure traces were scanned over a region 0.35-cm^{-1} -wide to accommodate the broadened lines.



Figure 5. Gas-handling and thermal control systems.

Figure 6 shows the electronic control devices for the laser (left-hand equipment rack) and the data acquisition system used.

III.4. Experimental Considerations

Through the use of pure CO in the saturation cell, it was found that there could be significant adsorption of CO onto the cell walls. This cell was purged three times with nitrogen to remove as much CO as possible, and then filled with one atmosphere of nitrogen to pressure broaden any residual CO to insignificance.

To avoid changes in calibration gas concentration due to CO adsorption, the sample cell, for use in the nitrogen broadening studies, was conditioned before recording a data point by filling it with one atmosphere of calibration gas and maintaining this condition momentarily before pumping the cell down to the desired pressure. The precision and accuracy of the line strength measurements were improved upon implementation of this procedure.

For the H₂O and CO₂ broadening measurements, a knowledge of the concentration of CO was not necessary. In these cases, the sample cell was filled with low-pressure pure CO, and foreign gas was added until the desired pressure was reached.

In order to use Eqs. (1) and (2) to reduce the experimentally transmitted intensity to absorption coefficient information using a single-beam instrument, the intensity of the source in the absence



Figure 6. Data acquisition system.

of a sample ($I^0(\nu)$) must be known.¹ If $I^0(\nu)$ is a slowly varying function of wavenumber in the interval of interest, it can usually be inferred through careful interpolation of the experimental intensity ($I(\nu)$) as obtained with an absorbing sample in place. If significant variations of the source intensity with wavenumber make this determination impossible, then the absorbing sample must be removed from the optical path and an additional scan made. This was the case for the high-pressure ($p > 5$ psia) cases reported herein. Gradual drifts of $I^0(\nu)$ with time necessitated the evacuation of the sample cell after each data point. It should be noted that the need to remove the sample to establish $I^0(\nu)$ could limit the usefulness of the diode laser in a future test cell situation, especially at one atmosphere and higher pressures.

The usable portion of $I^0(\nu)$ for a particular laser injection current, cold head temperature, and monochromator position is approximately 0.35-cm^{-1} -wide. An absorption line of CO at one atmosphere and room temperature has a half-width of approximately 0.1 cm^{-1} with significant absorption occurring over approximately 0.4 cm^{-1} . Under some conditions of high pressure and low temperature, not enough absorption coefficient information can be obtained over the usable portion of $I^0(\nu)$ for an accurate determination of the line strength and half-width.

¹The ideal situation would have been to use a beam splitter and record this intensity simultaneously, but the components necessary to implement this were not readily available.

The function $I^0(\nu)$ was significantly altered by the introduction of the reference cell into the optical path. It was therefore necessary to design the optical system so that the movement of optical components was not required during the course of the experiment. It is for this reason that a fixed saturation cell, to be filled and evacuated, was employed instead of the pull-out reference cell for the determination of optical zero. The use of the etalon is an exception to the rule, because in this case, $I^0(\nu)$ is not needed.

During the initial operation of the sample cell at greater than ambient temperatures the detector output signal/noise became significantly degraded. This was determined to be due to air turbulence caused by the mixing of hot gases from the furnace with ambient air. To minimize signal degradation, water-cooled sleeves were inserted in the furnace to enclose the beam from the cell windows to the outside of the furnace. This modification smoothed the temperature gradient responsible for the turbulence.

Another problem was encountered when the sample cell was raised to the temperature of 630 K. The silicone rubber cement bonding the windows to the cell apparently outgassed large quantities of CO at these temperatures, altering significantly the absorption of the line under study. Other adhesives were investigated, but with no improvement in capability. This limited the operation of the cell to 600 K.

CHAPTER IV

HOT CELL RESULTS

Table 3 presents the conditions of measurement for the absorption data. Measurements were made at pressures ranging from 0.34 to 1.02 atmospheres for each condition shown. The uncertainty of the data due to experimental noise (3%), uncertainty in the calibration gases used (2%), pressure measurement (3%), and other uncertainties (1%), is estimated to be less than $\pm 10\%$. In addition, the 2+1 R(4) "hot line" was studied.

Figure 7 shows an example of raw data, including the 100% transmission data and etalon traces. The results of the computer analysis of that data point are shown in Fig. 8. The residual CO absorption, which was used to check laser stability, has been removed from the 100% transmission trace, and that trace subsequently smoothed by a least-squares procedure. The raw data and best-fit Voigt line are also shown in Fig. 8.

IV.1. Nitrogen Broadening

The rotational index, m (col. 1); the temperature (col. 2); the average experimental half-widths and line strengths (cols. 3 and 5); the experimental line strengths of Varanasi and Sarangi [31] (col. 7); the calculated line strengths using the band strength of Varanasi and Sarangi, where no experimental value is available (col. 8); the exponent of the temperature dependence, n (col. 10); the percentage of standard deviations (cols. 4, 6, and 11); the

Table 3. Table of CO Absorption Lines, Temperatures, and Broadeners Studied

P(m)	300 K	360 K	400 K	436 K	500 K	525 K	600 K
P(2)	N ₂	---	N ₂	---	N ₂	---	N ₂
	CO ₂	---	CO ₂	---	CO ₂	---	CO ₂
	---	---	H ₂ O	---	H ₂ O	---	H ₂ O
P(3)	N ₂	---	N ₂	---	N ₂	---	N ₂
	CO ₂	---	CO ₂	---	CO ₂	---	CO ₂
	---	---	H ₂ O	---	H ₂ O	---	H ₂ O
P(7)	N ₂	N ₂	---	N ₂	---	N ₂	N ₂
	CO ₂	---	CO ₂	---	CO ₂	---	CO ₂
	---	---	H ₂ O	---	H ₂ O	---	H ₂ O
P(12)	N ₂	---	N ₂	---	N ₂	---	N ₂
	CO ₂	---	CO ₂	---	CO ₂	---	CO ₂
P(18)	N ₂	---	---	---	---	---	---
P(22)	N ₂	---	---	---	---	---	---

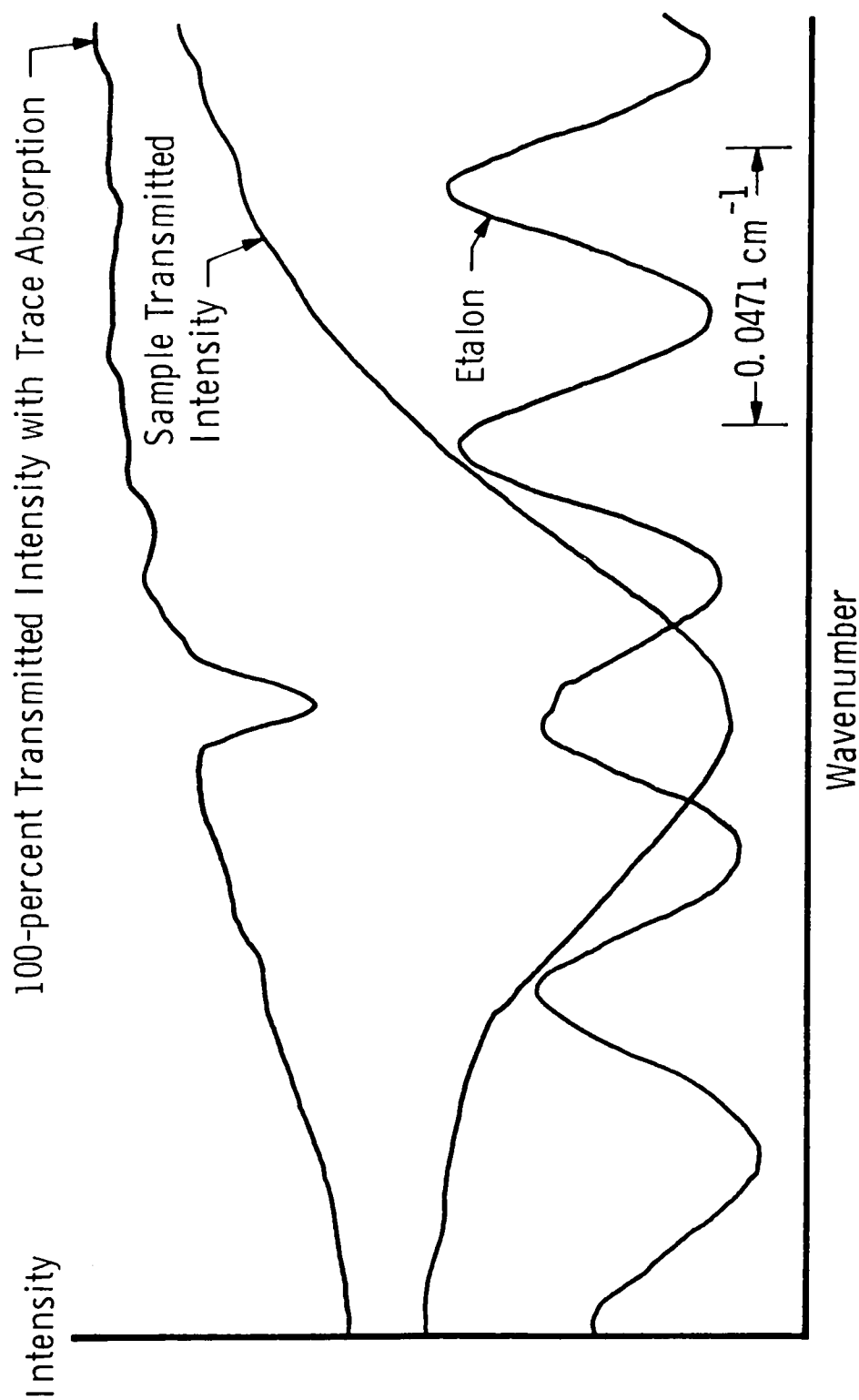


Figure 7. Example of raw data: 15 psi, 8,000-ppm carbon monoxide in nitrogen, $P(7)$ line, 601 K, with superimposed etalon.

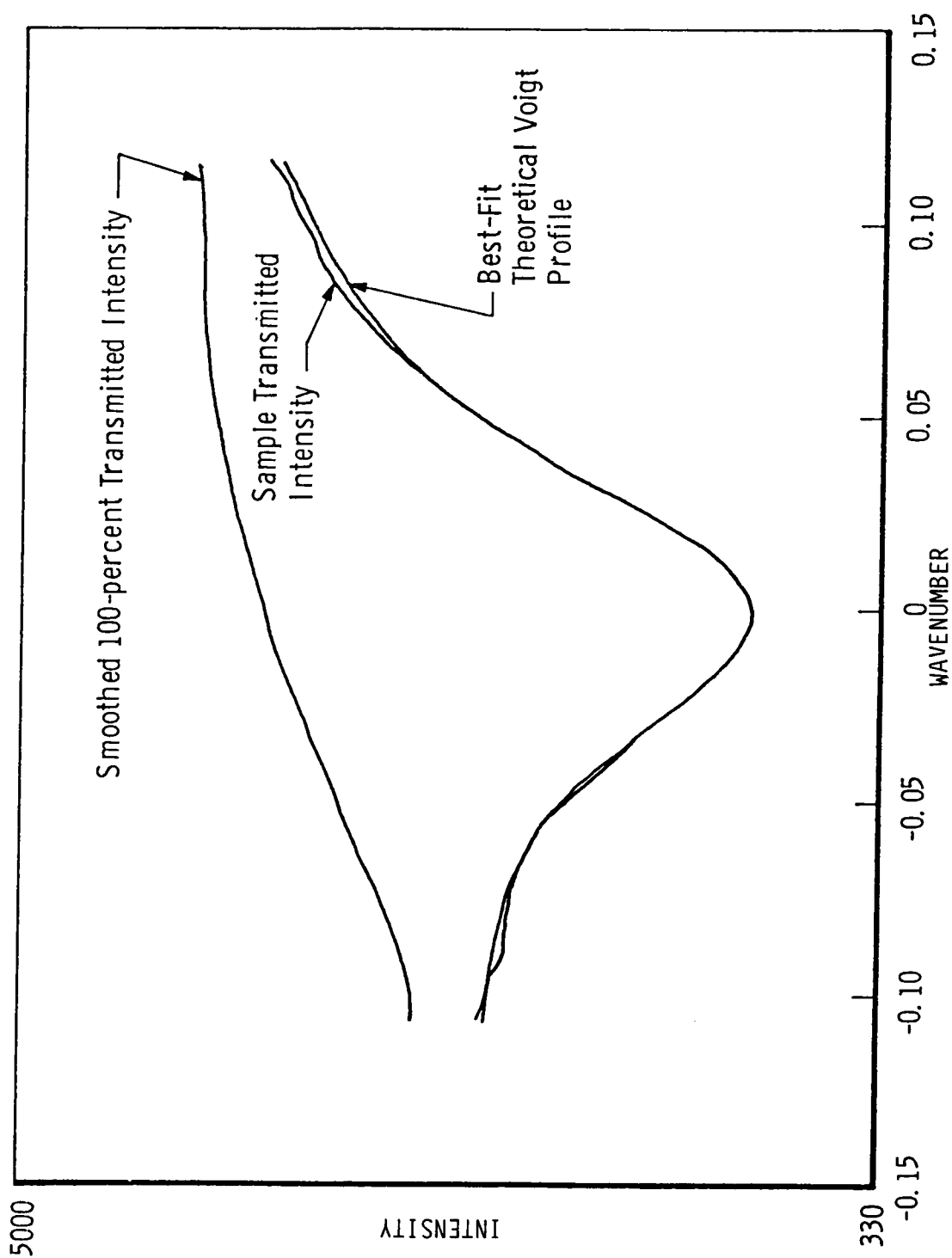


Figure 8. Example of reduced data.

percentage of deviation of the experimental line strengths around the line strength of Varanasi and Sarangi (col. 9); and the number of data points used, i_p (col. 12), are listed in Table 4. The line strengths as reported relate to 100% $C^{12}O^{16}$. It has been assumed that Varanasi and Sarangi reported results relative to 98.65% $C^{12}O^{16}$ (the normal isotopic abundance). The scattering of the broadening data is approximately $\pm 5\%$ and compares to the strengths of Varanasi and Sarangi to within $\pm 7\%$.

The fundamental band strength of $C^{12}O^{16}$ was determined from the experimental line strengths of six P-branch lines of CO broadened by nitrogen in conjunction with calculations of the rotational dependence of the line strength using the Herman-Wallis formula. Five different calibration gases were used over the temperature range 300 to 600 K, with all data subsequently normalized to standard temperature and 100% $C^{12}O^{16}$. The spectroscopic band center was used in these calculations. In Figure 9, the experimentally determined band strengths from individual rotational lines are shown on the y-axis as a function of rotational index, m . The average band strength was determined to be $250 \pm 8 \text{ cm}^{-2} \text{ atm}^{-1}$. This compares with the values of Varanasi and Sarangi: 253 ± 9 as determined by the Ladenburg-Reiche curve-of-growth method, and 257 ± 6 as determined by the Wilson-Wells-Penner-Weber method. It also compares to Varghesi and Hanson's value [41] of 256 ± 4 , which has been adjusted downward by approximately 1.2% due to a difference in definition of the band center.

Table 4. Summary of Experimental Nitrogen-Broadening Data

m	T (K)	$\gamma_{\text{avg}} \times 10^3$ ($\text{cm}^{-1} \text{atm}^{-1}$)	$\sigma_{\gamma} \times 10^2$ ($\text{cm}^2 \text{atm}^{-1}$)	$S_{\text{avg}}^{\text{exp}}$ ($\text{cm}^{-2} \text{atm}^{-1}$)	$\sigma S_{\text{exp}} \times 10^2$ ($\text{cm}^{-2} \text{atm}^{-1}$)	$S_{\text{v-s}}^{\text{exp}^a}$ ($\text{cm}^{-2} \text{atm}^{-1}$)	$S_{\text{v-s}}^{\text{cal}^a}$ ($\text{cm}^{-2} \text{atm}^{-1}$)	$\sigma S_{\text{v-s}} \times 10^2$	$n_{\text{avg}}^{\text{exp}}$	$\sigma_n^{\text{exp}} \times 10^2$	i	p
2	303	74.21	0.9	4.303	0.9	---	4.275	1.1	b	b	9	
	399	61.16	2.1	2.507	2.2	---	2.497	2.3	0.705	10.2	11	
	500	53.29	4.2	1.669	4.4	---	1.599	6.7	0.664	12.2	6	
	601	48.63	3.3	1.073	5.1	---	1.108	5.9	0.595	8.1	11	
3	300	69.55	0.6	5.857	1.1	5.912	---	1.5	b	b	5	
	400	56.00	1.6	3.362	1.9	3.417	---	2.6	0.753	7.3	6	
	500	48.69	0.9	2.153	3.3	2.217	---	3.3	0.698	2.5	7	
	601	43.08	2.4	1.500	3.5	1.545	---	3.5	0.691	5.0	8	
7	299	60.74	2.6	9.458	3.7	9.579	---	4.0	b	b	6	
	360	52.34	1.0	7.124	1.5	7.214	---	6.9	0.803	6.9	9	
	436	46.73	0.9	5.294	2.6	5.295	---	2.6	0.695	3.5	10	
	525	40.95	1.2	3.910	1.6	3.864	---	2.0	0.700	3.1	10	
12	600	37.28	2.8	2.908	3.7	3.050	---	6.1	0.701	5.7	9	
	304	56.38	3.1	6.336	1.7	6.457	---	2.7	b	b	6	
	401	46.15	1.7	5.141	1.5	5.229	---	2.3	0.724	8.0	6	
	499	40.15	1.6	4.095	1.9	4.157	---	2.5	0.687	4.6	7	
18	600	35.25	0.9	3.167	1.4	3.300	---	4.5	0.692	1.8	7	
	302	52.46	2.8	1.715	5.6	---	1.738	5.7	b	b	11	
	301	49.79	1.4	0.463	1.7	---	0.471	2.5	b	b	6	

^aAdjusted to the appropriate temperature by Eq. (5).

^bNo value for n can be calculated at the reference temperature.

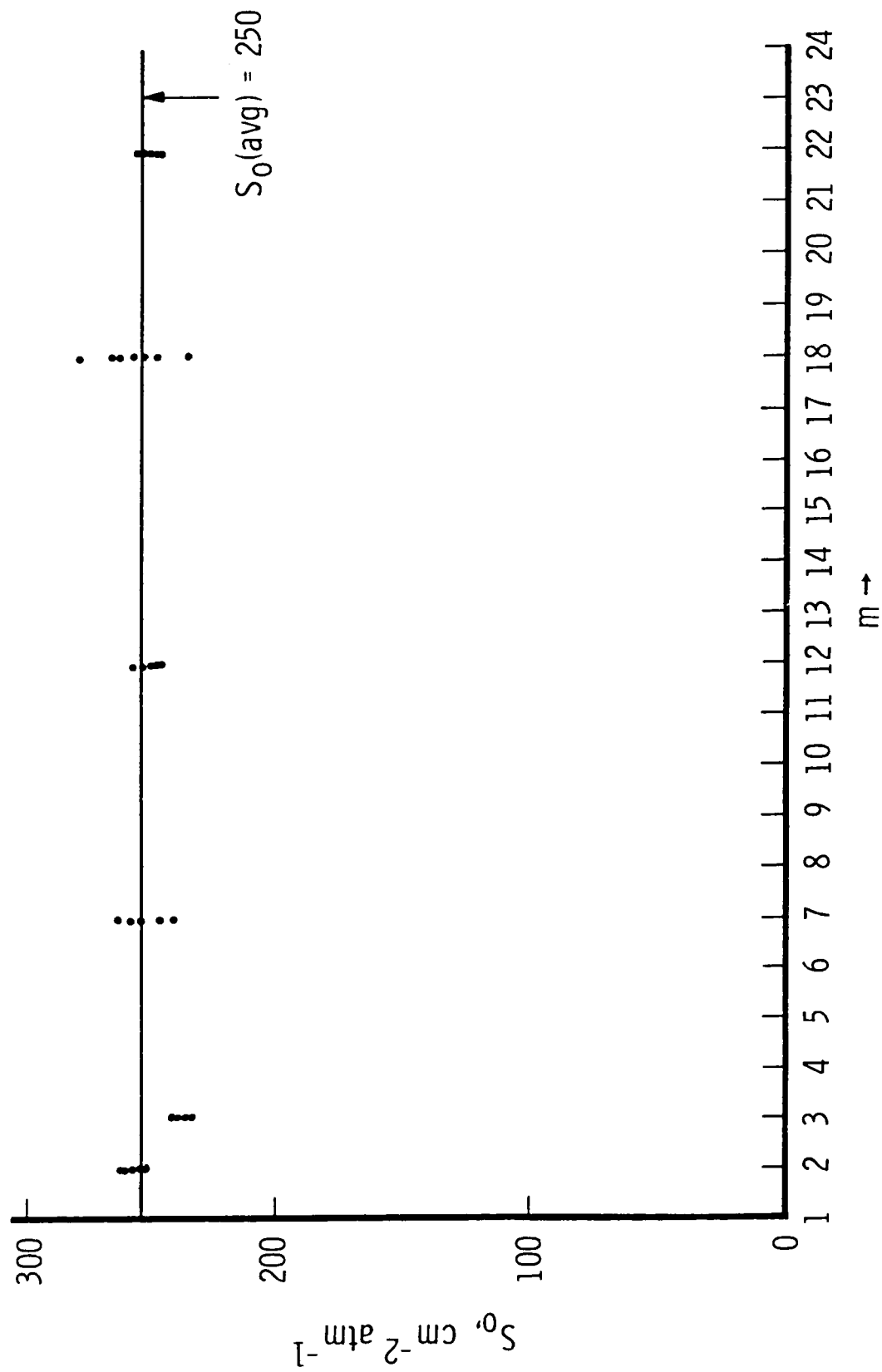


Figure 9. Band strength determination from individual experimental line strengths ($T = 298 \text{ K}$)

The experimental and calculated strengths and experimental widths corrected to the 300 K reference temperature are listed in Table 5 so that comparisons can be made between these and other room-temperature results. The values for the water vapor-broadened half-widths were extrapolated from the higher temperature data.

The relationship of the half-widths to pressure, using the experimental data from this study for three of the lines at room temperature, is shown in Fig. 10. It can be seen from these data that half-widths are proportional to pressure to a good degree of approximation (thus validating the assumption of binary collisions); therefore, measurements made at different pressures can be easily adjusted to a common pressure.

The experimental half-width data and the literature values for nitrogen broadening at 300 K are compared in Fig. 11. It can be noted that the half-widths for nitrogen broadening have a fairly strong dependence on the rotational index, m , for lower values of m , dropping 30% over the range $m = 1$ to $m = 15$. For higher values of m , the half-widths are approximately constant. Also shown in Fig. 11 is a comparison of the results of the computer model for nitrogen broadening to the experimental and literature data. Agreement is within 5% for the best fit to the experimental data, using as parameters a CO dipole moment (μ_{CO}) of 1.12×10^{-19} esu cm, a CO quadrupole moment (Q_{CO}) of 2.6×10^{-26} esu cm², an N₂ quadrupole moment (Q_{N_2}) of 3.3×10^{-26} esu cm², and a minimum collision diameter (b_{min}) of 4.17×10^{-8} cm. The value for μ_{CO} is that which is recommended by Stogryn and Stogryn [38], while the quadrupole moments

Table 5. Standardized Strengths and Line-Widths
(T = 300 K, P = 1.0 atm)

		m					
		2	3	7	12	18	22
N ₂	$\gamma^{\text{exp}} \times 10^3$ (cm ⁻¹ atm ⁻¹)	74.77	69.55	60.59	56.94	52.72	49.91
	S^{exp} (cm ⁻² atm ⁻¹)	4.388	5.857	9.410	6.384	1.728	0.467
	S^{cal} (cm ⁻² atm ⁻¹)	4.359	5.912	9.531	6.584	1.755	0.473
CO ₂	$\gamma^{\text{exp}} \times 10^3$ (cm ⁻¹ atm ⁻¹)	99.99	87.55	73.40	67.14	---	---
	$\gamma^{\text{exp}} \times 10^3$ (cm ⁻¹ atm ⁻¹)	99.16	92.14	99.56	---	---	---

^aExtrapolated values.

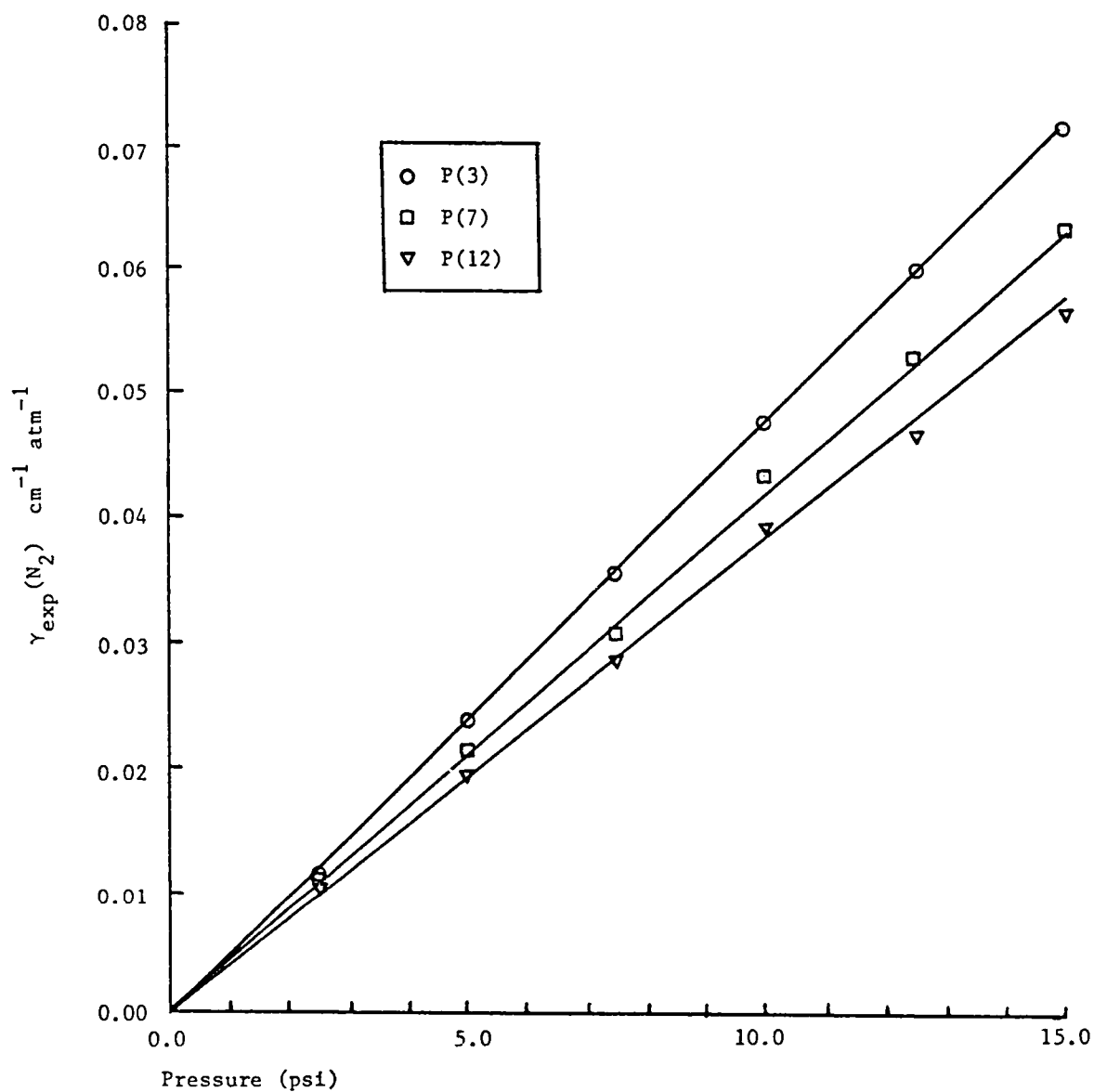


Figure 10. Nitrogen-broadened half-widths as a function of pressure for selected lines at 300 K.

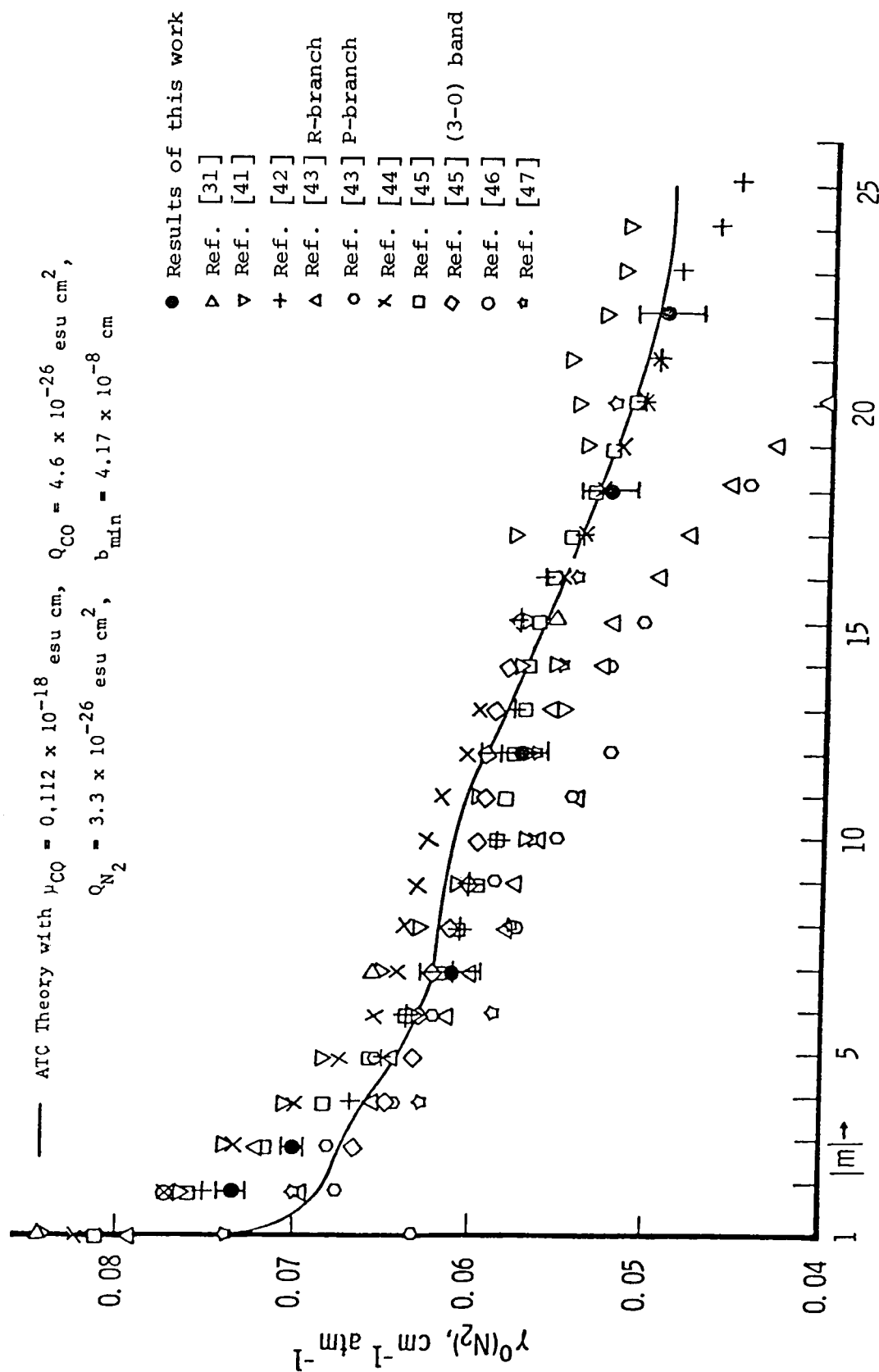


Figure 11. Nitrogen-broadened half-widths of CO compared to literature and calculated values (standardized to 1 atm and 300 K).

chosen to best fit the data are within 10% of those recommended by them. The minimum collision diameter, $b_{\min}$, was adjusted to fit the data in the high m region at 300 K.

The experimental temperature dependences of the nitrogen-broadened half-widths for the P(2), P(3), P(7), and P(12) lines determined in the present study are shown in Figs. 12 and 13. These are plotted on a log-log scale which facilitates the determination of the exponent n of Eq. (39) using the slope of the line which best fits the data. The bars indicate one standard deviation of the data, and the uncertainties shown for the temperature-dependence exponents are the statistical deviations due to experimental scatter. Also shown are the theoretical approximations using Eq. (39) for $n = 0.75$ and 0.50 , and calculations using ATC theory (see Chapter II, Section II.3) are shown for comparison to the experimental values. The measured values of n compare very well with those determined by Sell of $n = 0.75$ [33], and Sun and Griffiths of $n = 0.66$ [48].

As can be seen, the data points for different temperatures do exhibit a simple exponential temperature dependence of the form of Eq. (39). The values for the temperature-dependence exponents are somewhat different from the dominant quadrupole-quadrupole interaction ($n = 0.75$), but lie very closely to those values and to the values calculated by ATC theory. The hard-sphere approximation ($n = 0.50$) appears to be totally unacceptable.

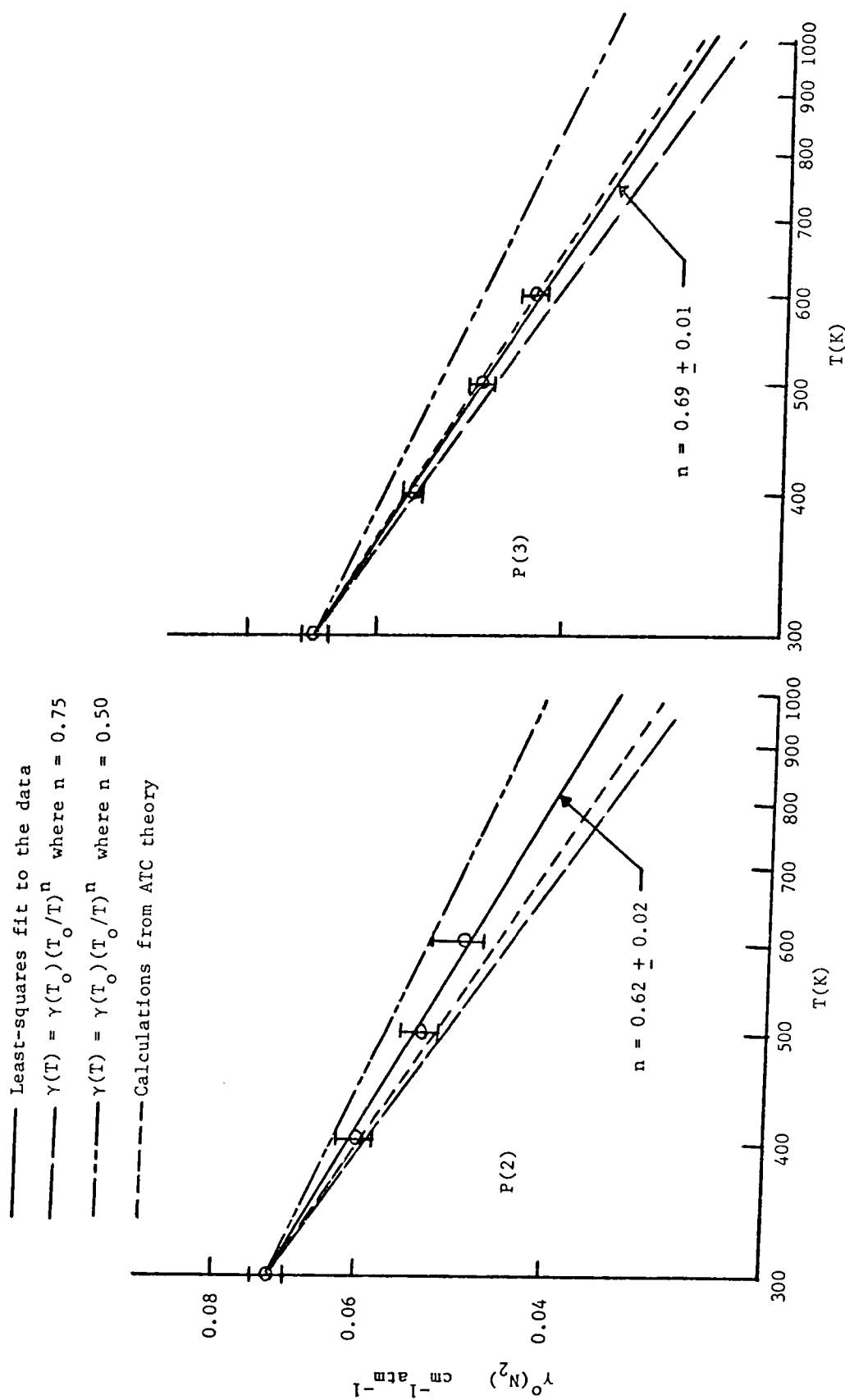


Figure 12. Temperature dependences of the P(2) and P(3) lines of CO broadened by N_2 .

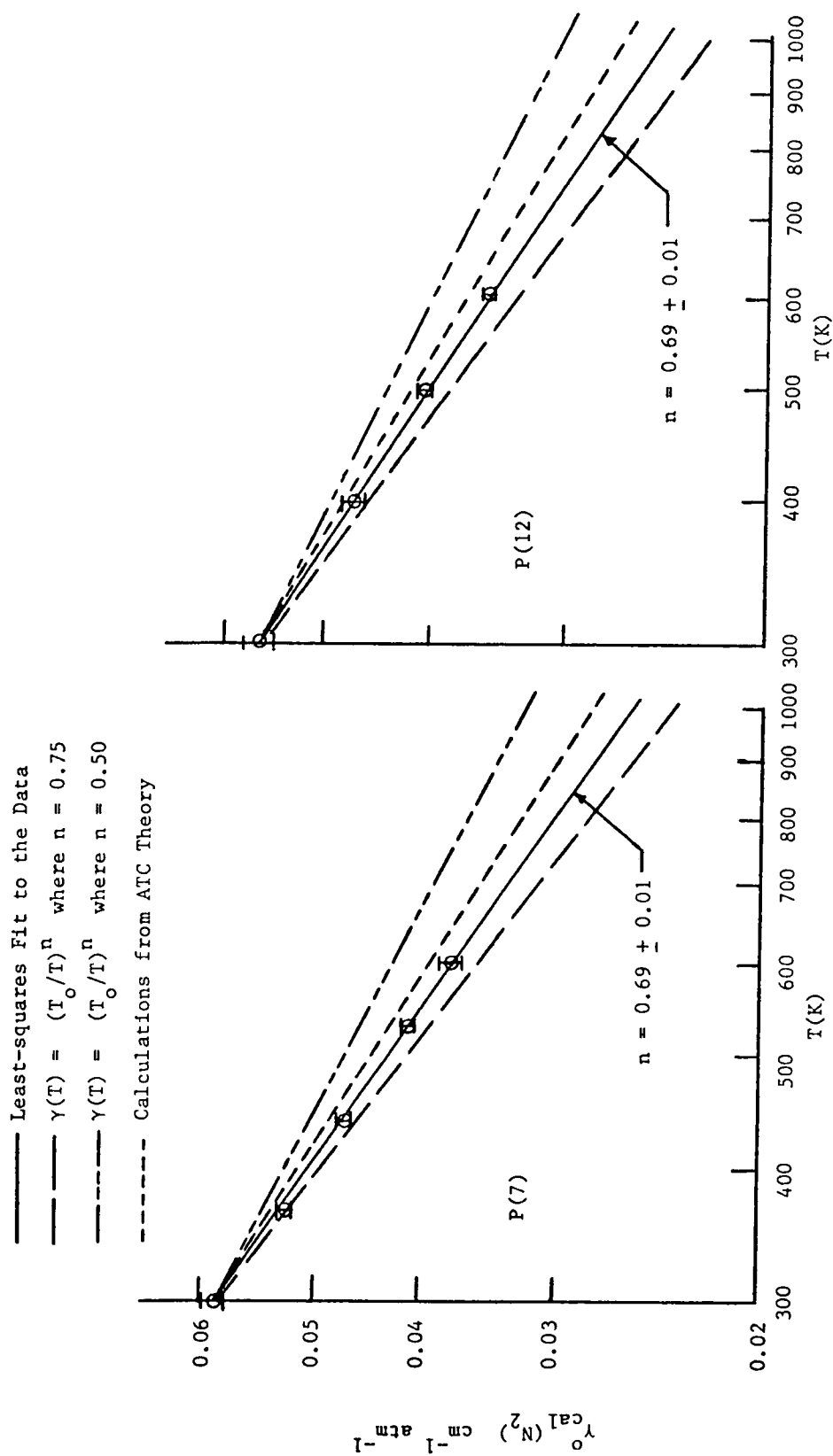


Figure 13. Temperature dependences of the P(7) and P(12) lines of CO broadened by N_2 .

IV.2. CO₂ and H₂O Broadening

The rotational index, m (col. 1); the temperature (col. 2); the measured values of the CO₂-broadened half-widths (col. 3); the exponent of the temperature dependence, n (col. 5); the percentage of standard deviation of these values (cols. 4 and 6); and the number of data points, i_p (col. 7), are presented in Table 6. The experimental values of the CO₂-broadened half-widths and some literature values at 300 K are plotted in Fig. 14. Note that the experimental values for the P(3) and P(7) lines are lower by several percent than the lowest literature values. The scatter of the data is less than 6%. It is interesting to note also that the CO₂-broadened half-widths appear to level off as a function of rotational index at a lower value of m than in nitrogen broadening for low m values, and that the CO₂-broadened half-widths are significantly higher than those for nitrogen-broadened lines. The results of ATC theory calculations for two sets of molecular parameters are also shown in Fig. 14. Both sets of molecular parameters are shown because of the differences between the experimental data and literature values. In the case of CO₂-broadening theory, the values $Q_{\text{CO}_2} = 5.9 \times 10^{-26}$ esu cm², and $b_{\text{min}} = 5.07 \times 10^{-8}$ cm were found to give the best fit to the experimental data. Agreement between the experimental data and theory (solid line) is within 6%. The molecular parameters used by Varanasi [49] were also utilized in the computer program to compare to his results and to the literature data.

Table 6. Summary of Experimental Carbon Dioxide-Broadening Data

m	T(K)	$\gamma_{\text{avg}}^{\text{exp}} (\text{cm}^{-1} \text{atm}^{-1})$	$\sigma_{\gamma} \times 10^2$	$n_{\text{avg}}^{\text{exp}}$	$\sigma_n \times 10^2$	i_p
2	302	99.49×10^{-3}	4.5	---	---	12
	400	80.94	2.4	0.735	11.3	9
	500	69.37	1.8	0.716	4.9	10
	600	60.92	3.9	0.716	7.8	10
3	299	87.77	3.3	---	---	9
	401	76.04	2.8	0.487	19.7	5
	499	64.11	1.9	0.613	6.1	9
	600	56.10	1.5	0.642	3.3	6
7	301	73.22	2.5	---	---	9
	399	60.80	3.5	0.663	18.4	8
	501	54.62	2.2	0.577	7.6	10
	599	50.76	3.2	0.534	8.6	11
12	298	67.39	2.9	---	---	9
	399	53.99	3.3	0.766	15.3	11
	502	49.39	1.4	0.596	4.7	10
	601	45.24	1.5	0.568	3.9	10

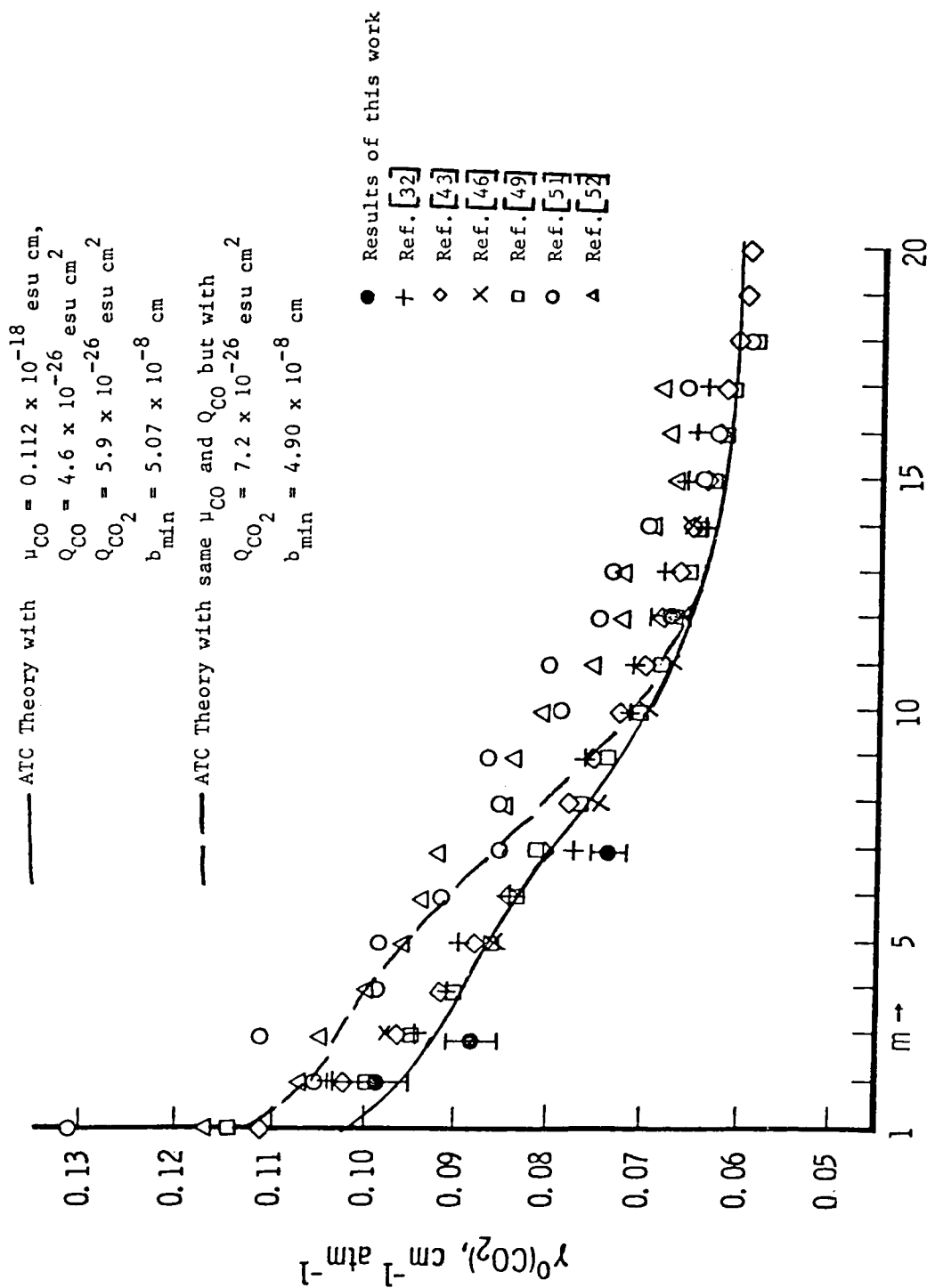


Figure 14. Carbon dioxide-broadened half-widths of CO compared to literature and calculated values (standardized to 300 K and 1.0 atm).

The H_2O -broadened half-widths are presented in Table 7 in the same manner as the CO_2 -broadened half-widths. The experimental values of the water vapor-broadened half-widths extrapolated to 300 K are plotted with the actual room-temperature data of Varghesi and Hanson [50] in Fig. 15. These are the only known literature values of CO broadened by H_2O , and the values reported here are lower by about 15%. The agreement is satisfactory, considering that Varghesi and Hanson's measurements were made at room temperature and very low pressure (approximately 25 mm), while the results of the present study were extrapolated from high-temperature data. In both methods, uncertainty in the concentration of water vapor presents a problem, and it is difficult to tell which method is the most accurate. It is interesting to note that, in contrast to CO_2 and H_2O broadening, there is very little dependence of the H_2O -broadened half-widths on rotational index.

The half-widths for CO_2 broadening standardized to 300 K are listed in Table 5, page 46. Also listed in this table are the half-widths for H_2O broadening extrapolated to 300 K. The temperature dependences of the half-widths of the P(2), P(3), P(7), and P(12) lines for CO_2 broadening are shown in Figs. 16 and 17, and the temperature dependences of the half-widths for the P(2), P(3), and P(7) lines broadened by water vapor are shown in Figs. 18 and 19 in the same manner as for the nitrogen-broadened half-widths, and with the same general type of results. Two exceptions are the P(7) and P(12) lines broadened by CO_2 . This, however, is consistent with theoretical studies which show that the value of n approaches 0.50

Table 7. Summary of Experimental Water Vapor-Broadening Data

m	T(K)	$\gamma_{\text{avg}}^{\text{exp}} (\text{cm}^{-1} \text{atm}^{-1})$	$\sigma_{\gamma} \times 10^2$	$n_{\text{avg}}^{\text{exp}}$	$\sigma_n \times 10^2$	i_p
2	400	78.89×10^{-3}	2.4	---	---	10
	501	65.51	3.4	0.822	18.7	8
	599	57.14	3.8	0.801	11.9	10
3	398	72.19	3.9	---	---	10
	501	66.74	2.9	0.333	38.5	3
	600	52.43	4.8	0.782	15.0	7
7	400	77.55	4.4	---	---	9
	513	62.98	3.4	0.839	16.1	8
	599	54.69	2.9	0.866	8.4	8

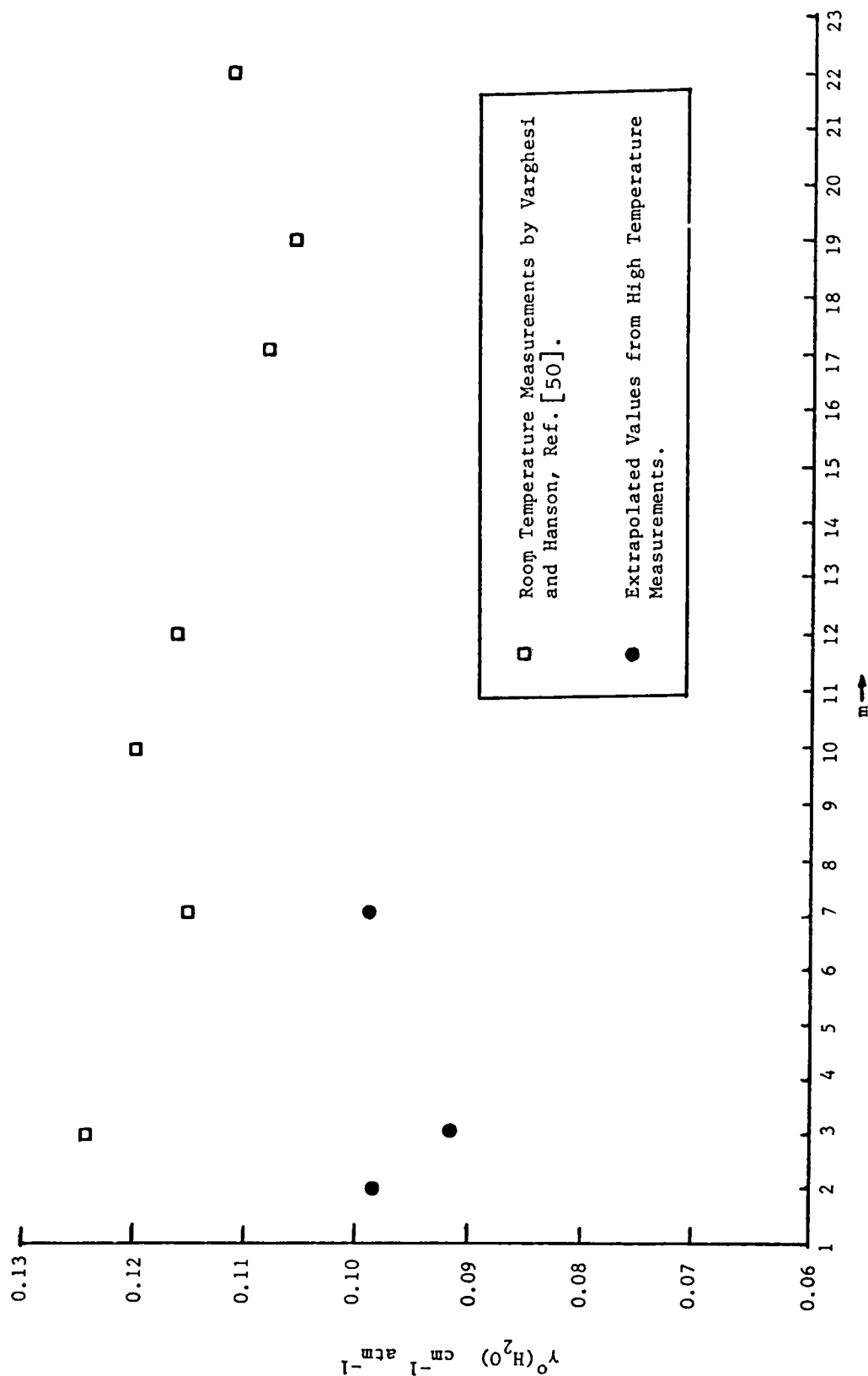


Figure 15. Comparison of water vapor-broadened CO half-widths to literature values.

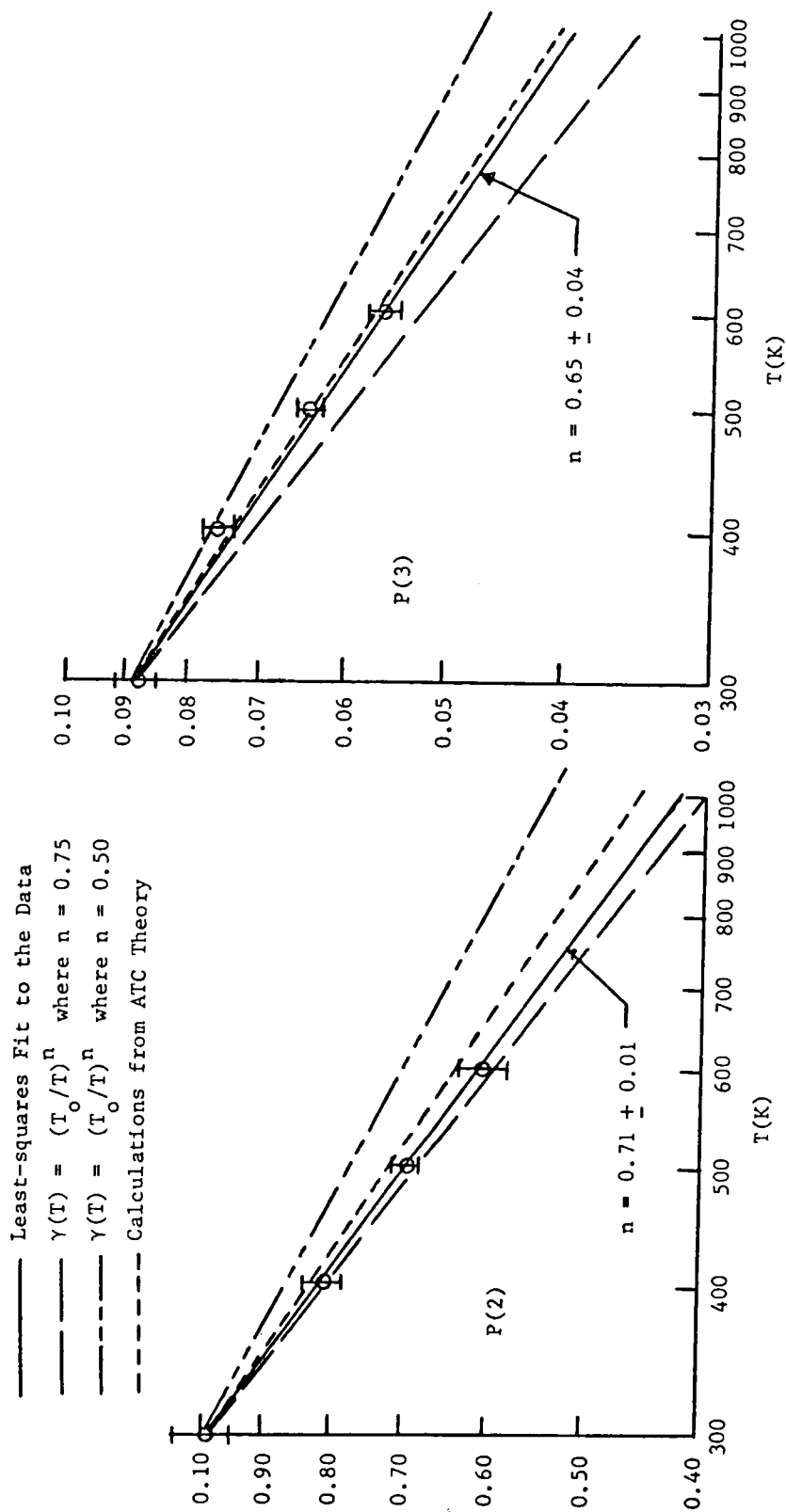


Figure 16. Temperature dependences of the P(2) and P(3) lines broadened by carbon dioxide.

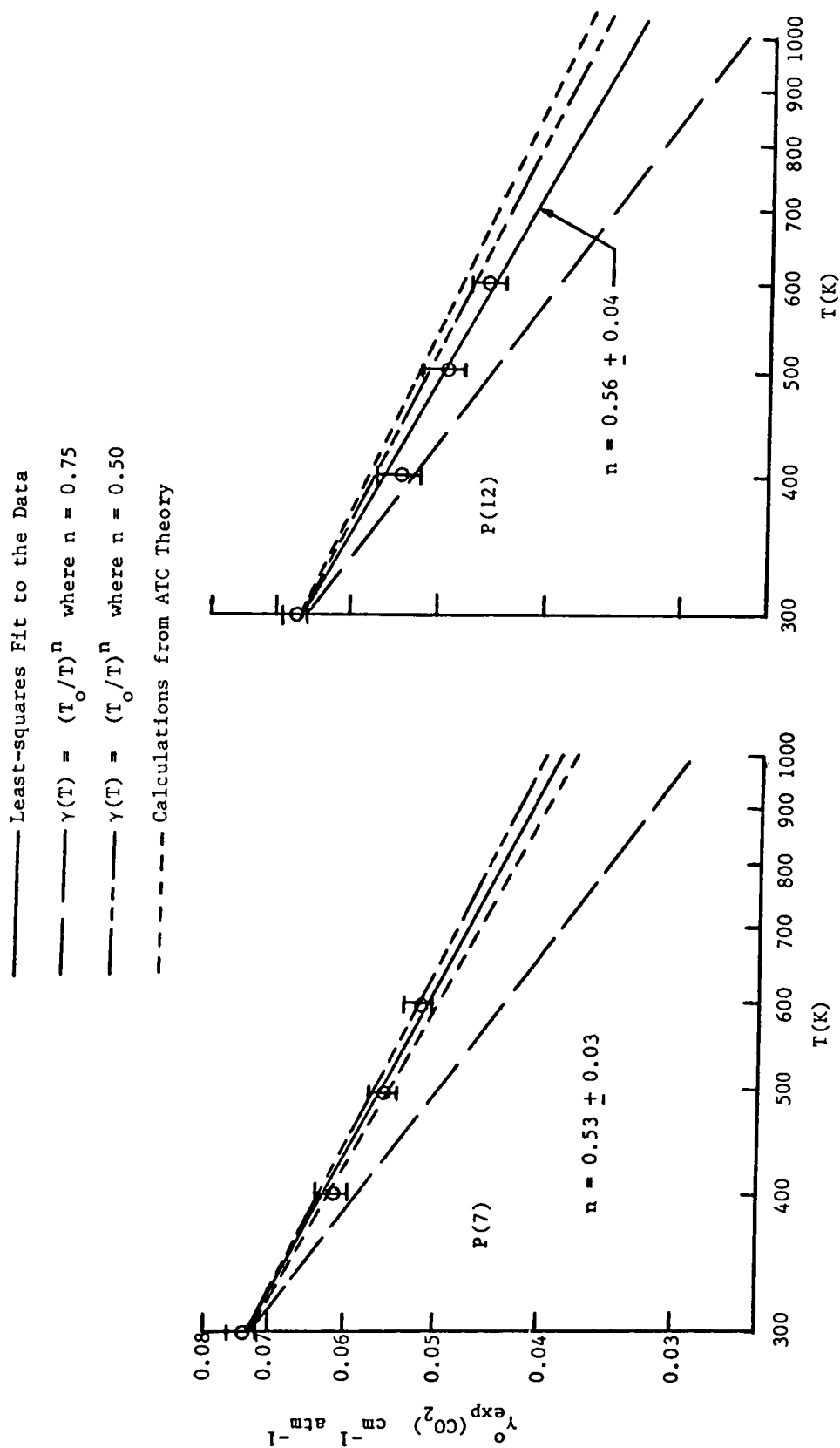


Figure 17. Temperature dependences of the P(7) and P(12) CO lines broadened by carbon dioxide.

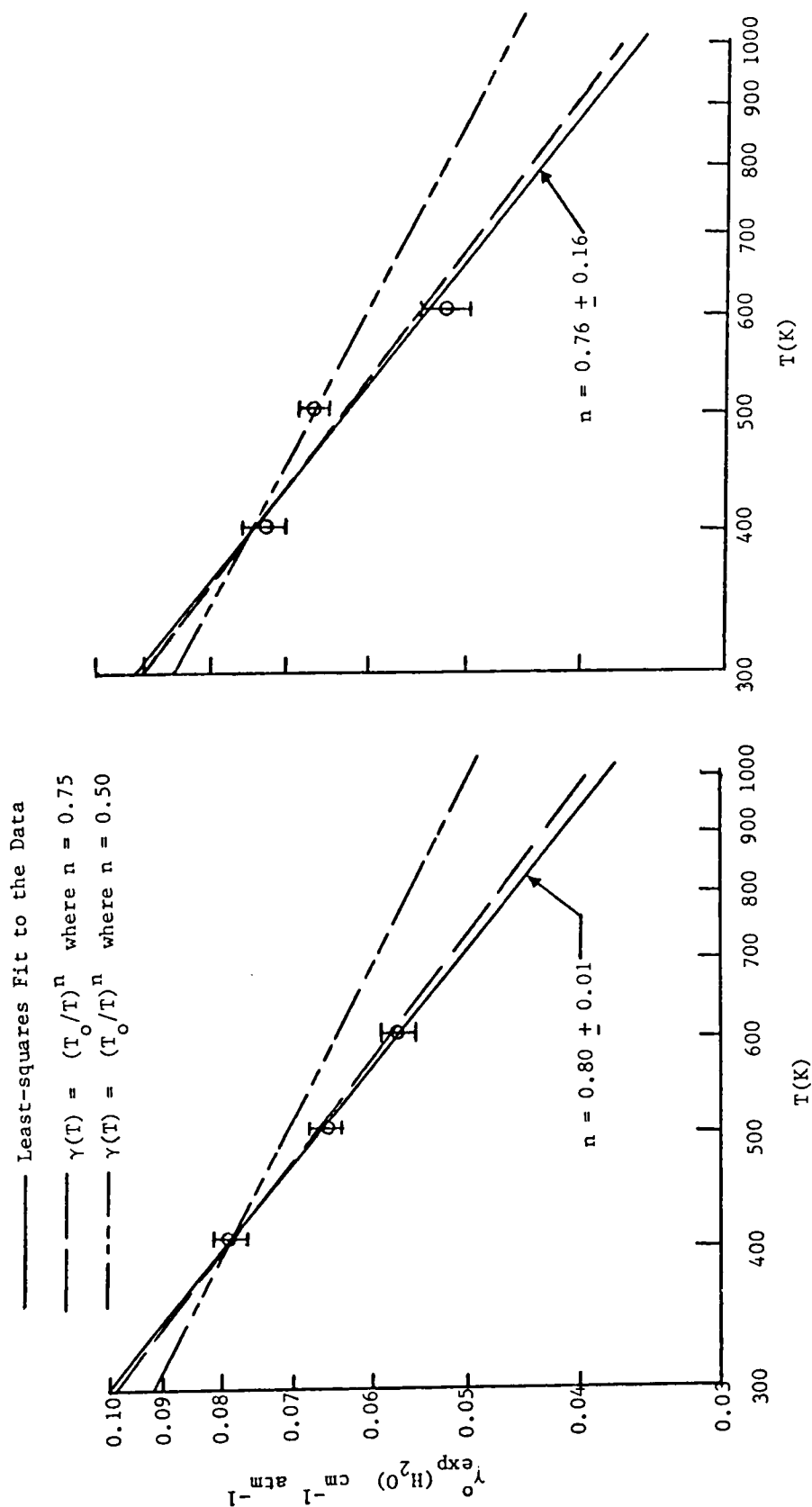


Figure 18. Temperature dependences of the P(2) and P(3) CO lines broadened by water vapor.

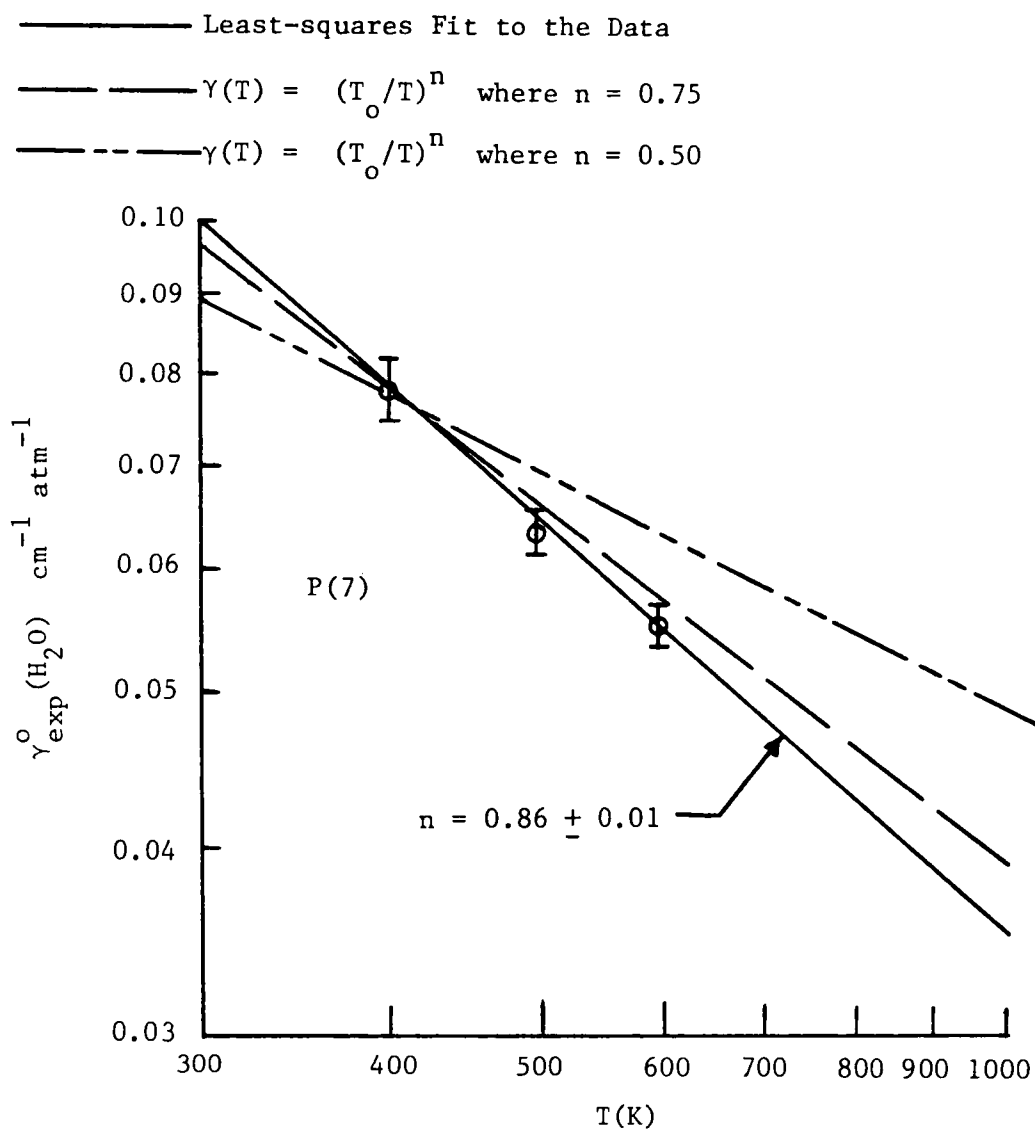


Figure 19. Temperature dependence of the P(7) CO line broadened by water vapor.

for large m for all of the broadeners considered theoretically. For CO_2 , this is achieved at approximately $m = 8$, while for N_2 this does not happen until m is approximately 16. As was stated in Chapter II, Section II.3, ATC theory calculations were not performed for the H_2O -broadened half-widths.

CHAPTER V

FLAT FLAME BURNER RESULTS

Measurements were made on the flat flame burner to make use of the two-line temperature technique and to test the proposed simple exponential temperature dependence of the half-widths.

Operation of the flat flame burner was characterized by two parameters: the equivalence ratio, Φ , and the input gas velocity standardized to 298.15 K (v_{25}) as defined by Kaskan [53]. In this study the burner was operated at four conditions: $v_{25} = 9.0, 9.5, 10.0$, and 10.5 cm/sec at a Φ of 1.2. Spectral data were taken at each condition, but only the $v_{25} = 9.5$ condition was selected for detailed analysis. Kaskan's fine-wire thermocouple-determined temperatures were assumed to be correct for these flames, but some measurements were also made using a coated fine-wire, butt-welded Pt-Pt 10% Rh thermocouple. A comparison of these values is given in Table 8. Ambient pressure during these runs was 0.966 atmosphere.

The ratio of the line strengths of the selected pair of absorption lines as obtained from the data analysis procedure indicated a temperature of $1,790 \pm 40$ K for the $v_{25} = 9.5$ flame using Hanson's technique. An example of the raw data used is shown in Fig. 20. For this method to be useful the ratio of the line strengths of these lines at a reference temperature must be known. This parameter is required to produce a temperature calibration curve. The $P(2) \ 1 \leftarrow 0$ line strength was determined experimentally, but the $R(4) \ 2 \leftarrow 1$ line strengths must be obtained by another

Table 8. Comparison of Temperatures from Thermocouple Measurements, Kaskan's Data [53], and the Two-Line Technique

v_{25}	Thermocouple Measurements	Kaskan's Data	Two-Line Method
9.0	1,845	1,816	---
9.5	1,852 ^a	1,826	1,790
10.0	1,858	1,835	---
10.5	1,901	1,843	---

^aInterpolated data.

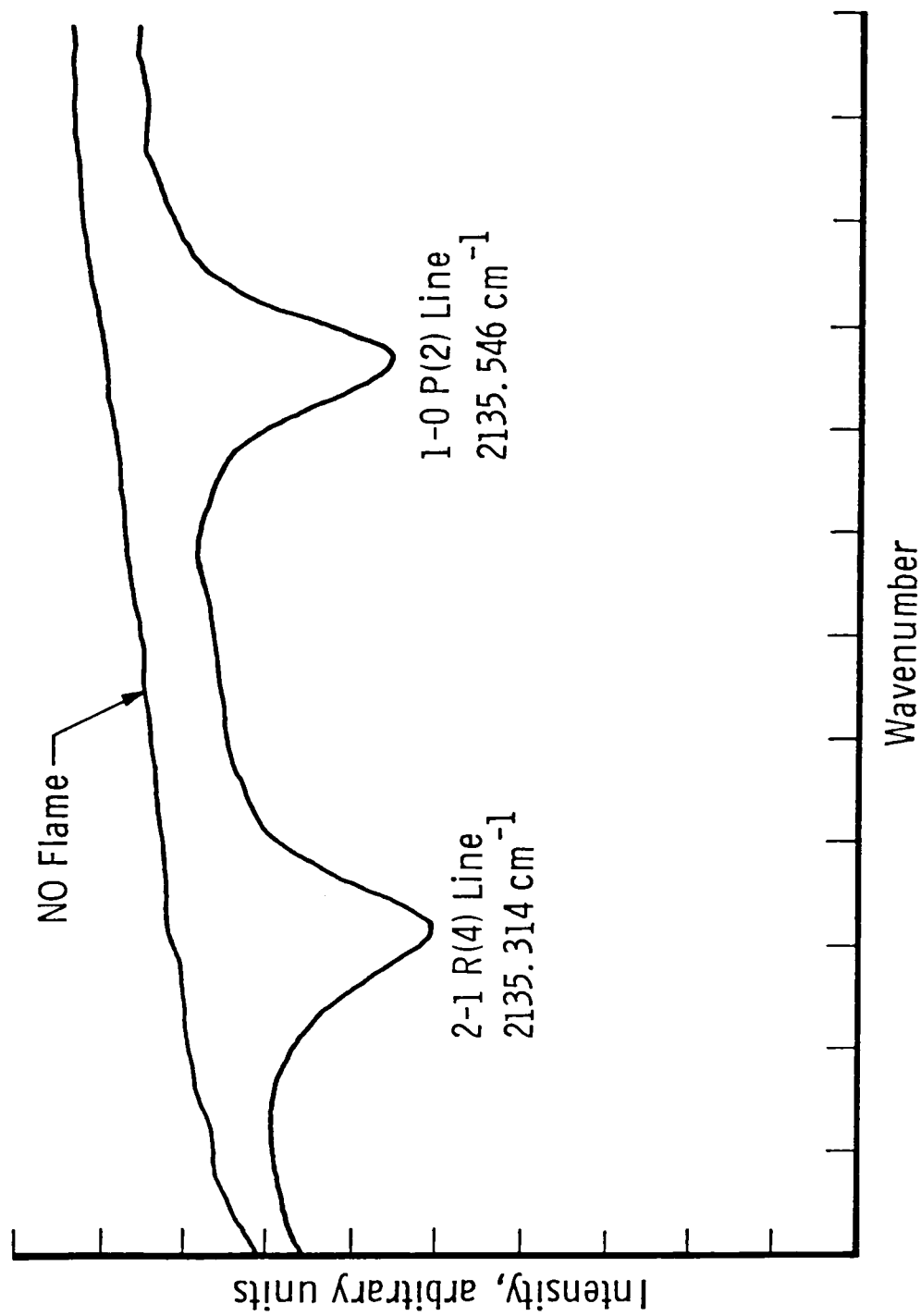


Figure 20. Example of tunable diode laser flat flame burner carbon monoxide spectra.

procedure because of the high temperature limit imposed by the present hot cell. For the purpose of this work, the $R(4) 2\leftarrow 1$ line strength was determined by using the Herman-Wallis formula (Eq. (5)) in conjunction with the $1\leftarrow 0$ band strength reported by Varanasi and Sarangi [31]. It must be stressed that the line strengths for lines in the $2\leftarrow 1$ band must be investigated experimentally if this technique is to be fully utilized.

Hanson and Falcone [11] assumed the line widths of the pair of lines under consideration to be the same. An analysis of the $2\leftarrow 1 R(4)$ and $1\leftarrow 0 P(2)$ data show the line widths for this pair of lines to be within about 1.0%. The half-width results for the two lines at the flame temperature and broadened by the combustion products are:

$$\gamma_{R(4) 2\leftarrow 1} = 0.0194 \pm 0.0005 \text{ cm}^{-1} \text{ atm}^{-1}$$

and

$$\gamma_{P(2) 1\leftarrow 0} = 0.0198 \pm 0.0005 \text{ cm}^{-1} \text{ atm}^{-1} .$$

An equilibrium calculation of the constituent mole fractions for $v_{25} = 9.5$ flame was performed based on Kaskan's temperature for the flame and input stoichiometry. The results of these calculations, along with the experimentally determined half-widths and temperature-dependence exponents, are shown in Table 9. Row 1 of this table contains the mole fractions of each of the constituents and the mixture for the flame. The half-widths of the flame constituents taken individually (cols. 1-5) and as a mixture (col. 6), normalized to 300 K and one atmosphere pressure, are shown in the

Table 9. Equilibrium Calculations of Mole Fractions for the $v_{25} = 9.5$ Flame, and Values of Half-Widths and Temperature-Dependence Exponents Used in the Flame Half-Width Calculations

	N ₂	CO ₂	CO	H ₂	H ₂ O	$\gamma^0_{\text{eff}} \times 10^3$
Mole Fraction	0.6770	0.0660	0.0416	0.0302	0.1852	1.0000
$\left[\begin{array}{l} \gamma^0 (300 \text{ K}) \times 10^3 \\ (\text{cm}^{-1} \text{ atm}^{-1}) \end{array} \right]$	74.8	100.0	81.3	74.5	99.2	81.2
P(2)						
$\left[\begin{array}{l} n_{\text{exp}} \end{array} \right]$	0.62	0.72	0.75 ^a	0.50 ^a	0.80	---
$\left[\begin{array}{l} \gamma^0 (300 \text{ K}) \times 10^3 \\ (\text{cm}^{-1} \text{ atm}^{-1}) \end{array} \right]$	60.6	73.4	69.5	71.3	99.5	69.3
P(7)						
$\left[\begin{array}{l} n_{\text{exp}} \end{array} \right]$	0.69	0.53	0.75 ^a	0.50 ^a	0.86	---

^aThis value assumed due to lack of data.

second and fourth rows. The values of the half-widths used are those determined in this study for N_2 , CO_2 , and H_2O , and those of Ref. [39] for CO and H_2 . The experimental values of the temperature-dependence exponent, n , are given in rows 3 and 5 for N_2 , CO_2 , and H_2 . Due to a lack of experimental data, the value $n = 0.75$ was assumed for CO self-broadening because of its large quadrupole moment, and $n = 0.50$ was assumed for H_2 because of its small quadrupole moment and negligible dipole moment (see Eq. (20) and subsequent discussion). Calculations were made using the ATC theory which showed that these assumptions were reasonable.

An analysis of the $P(2)$ and $P(7)$ line strengths from the flame data indicated an experimental CO mole fraction of 0.0393 and 0.0404, respectively. There are several possible reasons for the 5 to 6% difference between the measured and the calculated CO mole fractions. Uncertainties in metering the flow of the fuel and oxidizer to the burner could cause significant deviations in the experimental CO mole fractions. The possibilities also exist that the flame gases are not in equilibrium at the point of measurement, or that the input thermodynamic constants used in the calculation are in error.

In order to test the success of predicting the combustion condition line widths from the lower temperature data using the simple exponential temperature dependence of Eq. (39), the half-widths for CO in the flame were calculated using this equation and the experimentally determined values of the half-widths and temperature dependences of the major constituents of the flame. The

possibility of using the approximations $n = 0.5$ and $n = 0.75$ for the temperature-dependence exponent for all constituents was also investigated.

The calculated and experimentally determined half-widths of the P(2) line of CO at flame temperatures are listed in the first two columns of Table 10. Similarly listed are the calculated and experimentally determined half-widths of the P(7) line (cols. 3 and 4). The calculated half-widths using n_{exp} for each constituent as listed in Table 9 are given in row 1 of Table 10; similar calculations using $n_{\text{exp}} \pm 10\%$ are given in rows 2 and 3. Calculations using the temperature-dependence exponent for the dominant quadrupole-quadrupole interaction ($n = 0.75$) for all constituents are given in row 4. Calculations using the hard-sphere approximation ($n = 0.50$) for all constituents are given in row 5. It can be seen that the calculated half-widths using $n = 0.50$ for all constituents represents a very poor prediction for the experimental half-widths. The calculated values using $n = 0.75$ are a much better approximation. The more comprehensive approach using $n_{\text{exp}} \pm 10\%$ gives half-widths which are completely consistent with both the experimental data and the determination of Varghesi and Hanson [54]. The uncertainty in the experimental half-widths and the temperature-dependence exponents, however, reduces the significance of the apparent deviations of n from the approximation $n = 0.75$.¹

¹It should be noted that for low resolution equivalent width measurements, a 10% error in n results in a 15% error in line strength (and thus concentration) for $n = 0.75$.

Table 10. Results of Flame Half-Width Calculations
 Compared to Experimental Data for Two CO Lines
 (T = 1,826 K, P = 0.966 atm)

n	P(2)		P(7)	
	$\gamma_{\text{cal}}^{\text{flame}} \times 10^3$	$\gamma_{\text{exp}}^{\text{flame}} \times 10^3$	$\gamma_{\text{cal}}^{\text{flame}} \times 10^3$	$\gamma_{\text{exp}}^{\text{flame}} \times 10^3$
n_{exp}	23.6		18.5	
$n_{\text{exp}} \times 1.1$	20.9		16.3	
$n_{\text{exp}} \times 0.9$	26.7	20.4	21.2	19.8
0.75	20.2		17.3	
0.50	31.8		27.2	

The self-broadened and hydrogen-broadened half-widths used were consistent with the literature. The temperature-dependence exponents were chosen considering the nature of the molecules and the ATC theory. The values for the water vapor-broadened half-widths were extrapolated to 300 K from the experimental data taken in the range 400 to 600 K.

The ATC theory was examined in the temperature range 300 to 2,000 K for the cases of nitrogen, carbon dioxide, hydrogen, and carbon monoxide broadening to investigate the theoretical validity of Birnbaum's approximation (Eq. (39)) in the realm of flame temperatures. Table 11 presents the molecular parameters used to produce these results, which were determined as the best fit to the literature data at room temperature. These high-temperature results are shown in Figs. 21 through 24, plotted on a log-log scale. A linear dependence of half-widths on temperature using this scale indicates the simple exponential relationship of Eq. (39). The temperature dependence of all lines under consideration is reasonably consistent with this form, the higher rotational transitions being the most consistent. It is interesting to note the close agreement in the half-widths of the various lines at flame temperatures.

Table 11. Best-Fit Molecular Parameters

	CO	N ₂	CO ₂	H ₂
B ₀ (cm ⁻¹)	1.923	2.00	0.39	59.3
Dx10 ⁶ (cm ⁻¹)	6.1	5.9	0.13	4.7x10 ⁴
μx10 ¹⁸ (esu cm)	0.112	0.0	0.0	0.0
Qx10 ²⁶ (esu cm ²)	4.6	3.3	5.2	0.8
b _{min} x10 ⁸ (cm)	3.70	4.17	5.15	3.0

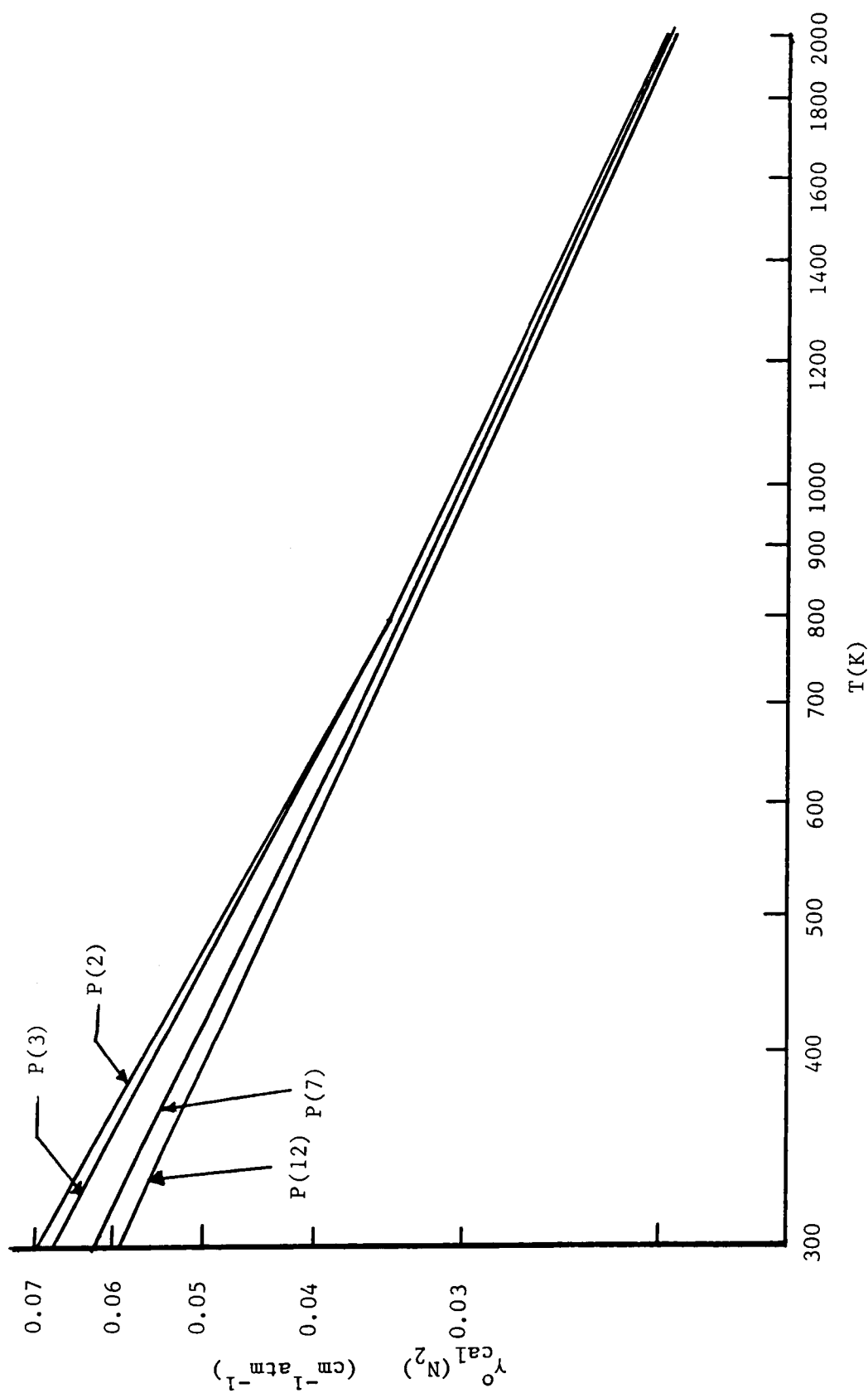


Figure 21. The ATC predictions for N_2 -broadened CO half-widths from 300 to 2,000 K.

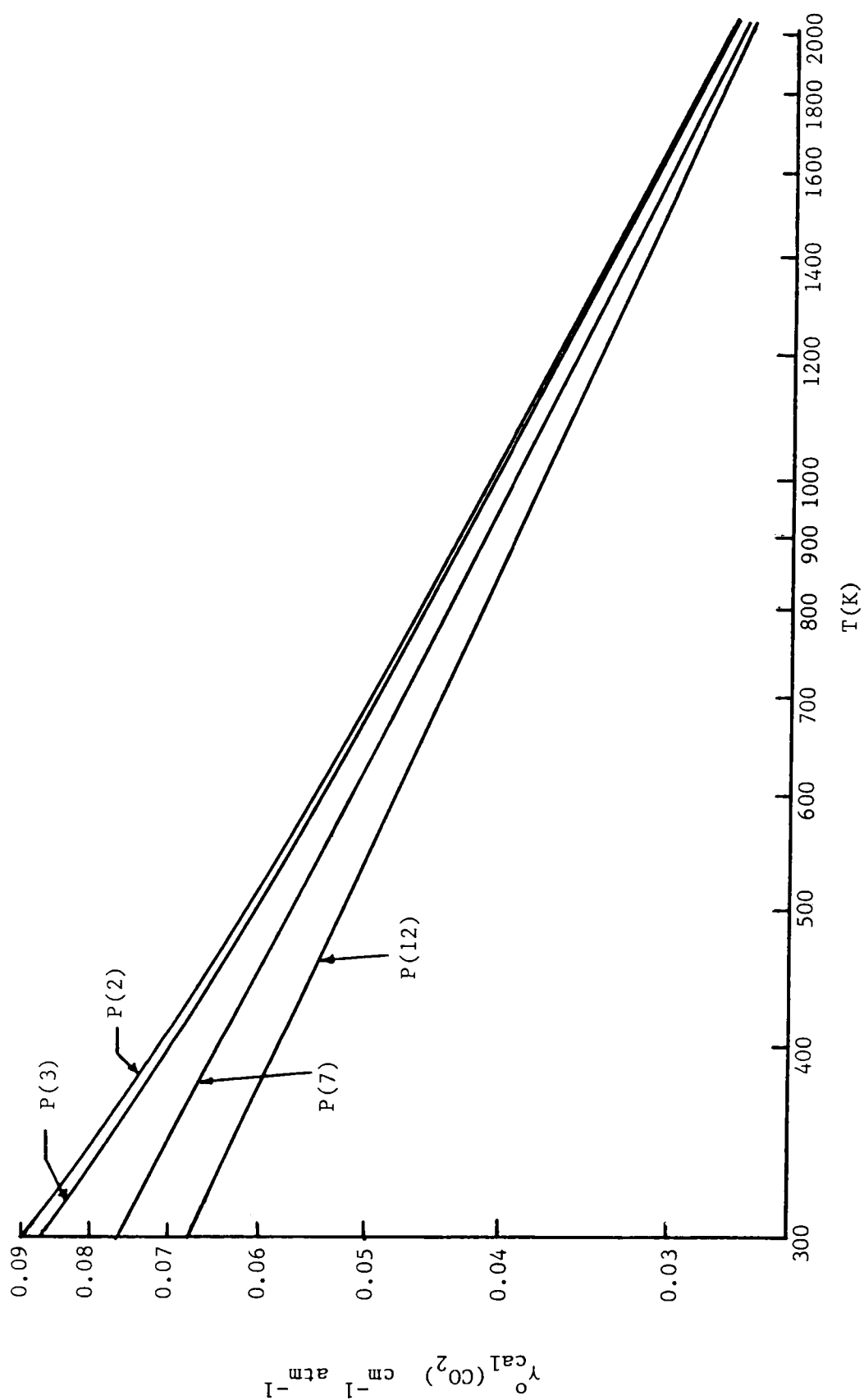


Figure 22. The ATC predictions for CO₂-broadened CO half-widths from 300 to 2,000 K.

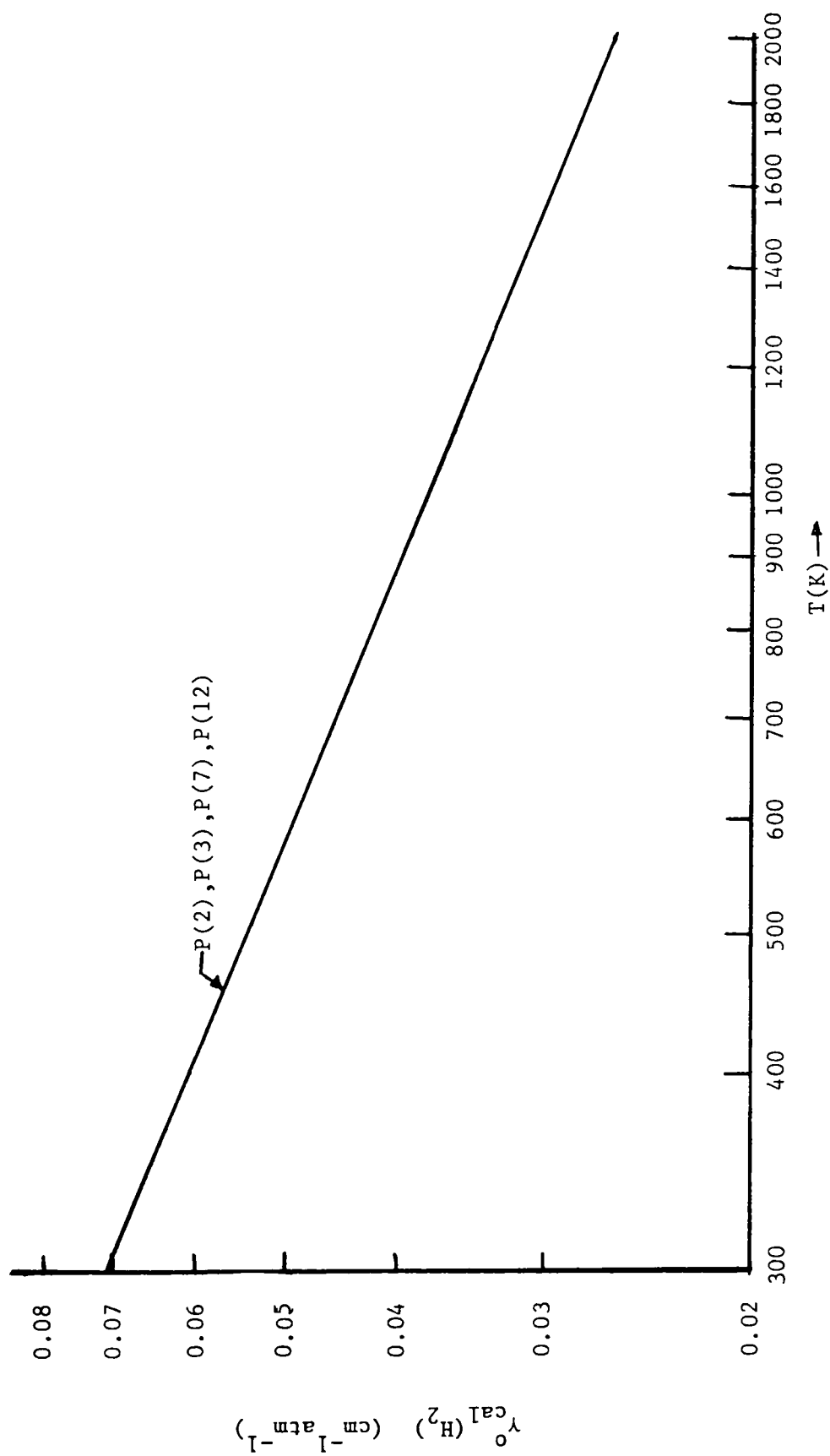


Figure 23. The ATC predictions for H₂-broadened CO half-widths from 300 to 2,000 K.

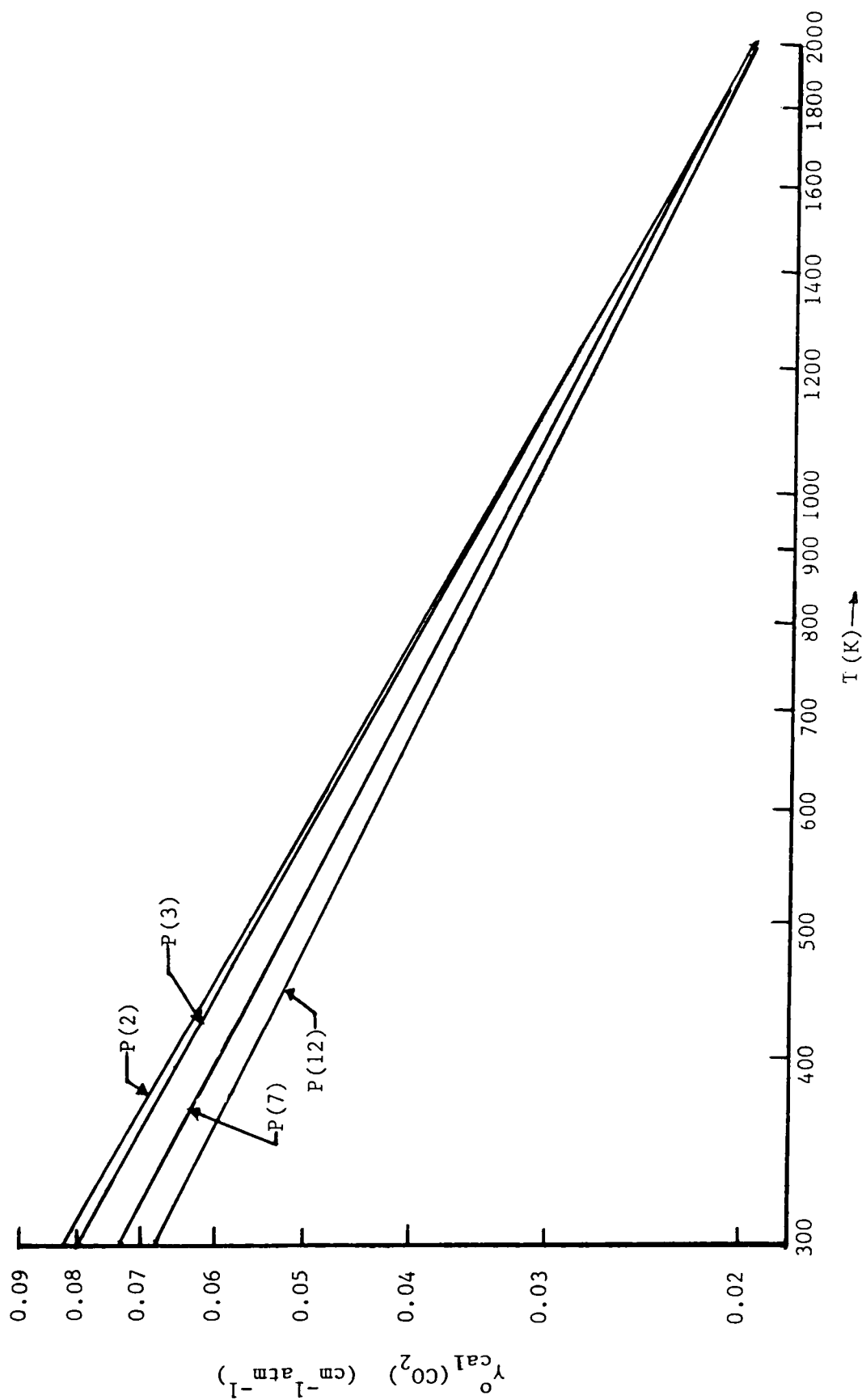


Figure 24. The ATC predictions for CO half-widths from 300 to 2,000 K.

CHAPTER VI

CONCLUSIONS

The line strengths and half-widths broadened by N_2 , CO_2 , and H_2O of several lines in the fundamental band of CO have been determined at temperatures in the range 300 to 600 K using a high resolution tunable diode laser spectrometer system. The strength of the fundamental band of CO was determined to be $250 \pm 8 \text{ cm}^{-2} \text{ atm}^{-1}$. A temperature determination was made in the effluent of a flat flame burner and found to be within 6% of the value predicted by equilibrium calculation. The diode laser has been shown to be a useful tool for analyzing the constituents of combustion processes.

Collisional broadening theory was examined for the cases of N_2 and CO_2 broadening and the results compared to experimental values of half-widths at various temperatures. The CO dipole moment, the CO, N_2 , and CO_2 quadrupole moments, and the minimum collision distances were adjusted to fit the calculated curve to the data to within $\pm 10\%$. The implementation of the computer program gave a reasonable estimate of the m-dependence of foreign gas-broadened half-widths of absorbing molecules at room temperature. Uncertainty in the values for the molecular parameters of interest, limited experimental data, and the assumptions made in the theory, however, limit the ability of the model to predict accurately the CO half-widths in the temperature regimes of combustion processes. The quantity $b_{\min}$, in particular, is little more than an adjustable parameter. A more realistic $b_{\min}$ would probably exhibit significant temperature dependence, as do the

cross sections relevant to viscosity and thermal conductivity calculations. Also, the use of a velocity distribution would be more realistic than the mean collision velocity at flame temperatures. Experimental data in the region around $m = 20$ are needed at temperatures in the range 400 to 600 K to provide a basis for further improvement of the computer model.

The experimental and calculated temperature dependences of the foreign gas-broadened lines studied indicate a simple exponential relationship between high temperature and standard temperature half-widths. The value of the temperature-dependence exponent varies for different foreign gas broadeners and rotational lines, and is generally different from the dominant quadrupole-quadrupole approximation of $n = 0.75$. This simple form has been shown to be extremely useful in determining the half-widths at flame temperatures from lower temperature trends.

Additional work is indicated for the development of a reliable technique for determining CO concentrations and flame temperatures in combustion processes using the tunable diode laser. Absorption cell measurements at higher temperatures than those reported here are required and broadening theory must be examined in greater detail in order to predict self- and foreign gas-broadened half-widths at flame temperatures. The strengths and widths of lines in the 2-1 band of carbon monoxide need to be studied in order to improve the calibration of the two-line temperature measurement technique.

In pursuit of these needs, a few improvements must be made in the experimental apparatus. An absorption cell capable of

temperatures up to 1,000 K, and an etalon which more accurately calibrates the wavenumber of the laser output are needed. In addition, refinements in the air turbulence suppression technique must be made to improve signal-to-noise ratios in the hot cell studies and in future work in turbulent test cell environments.

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APPENDICES

APPENDIX A

THEORETICAL PARAMETER DERIVATIONS

A.1. Energy Change Parameter Derivation: w_{st}

The energy change parameter w_{st} is needed in the calculation:

$$k = (2\pi(\Delta E)b / \hbar \bar{\nu}) = (2\pi w_{st}b / \hbar \bar{\nu}) , \quad (A-1)$$

and represents the change in energy occurring during the collision process. Therefore,

$$w_{st} = \Delta E = B_1 [j_i'(j_i'+1) - j_i(j_i+1) + j_f'(j_f'+1) - j_f(j_f+1)] + B_2 [j_2'(j_2'+1) - j_2(j_2+1)] , \quad (A-2)$$

where B_1 and B_2 are the rotational constants of the absorbing and colliding molecules, respectively, and the primed quantum numbers refer to the states of the molecules after undergoing the collision process. The parameter w_{st} can be written:

$$w_{st} = \Delta E_i + \Delta E_f + \Delta E_2 , \quad (A-3)$$

where,

$$\Delta E_s = B_s (j_s'(j_s'+1) - j_s(j_s+1)) ,$$

and j_s can represent j_i , j_f , or j_2 . To calculate the various w_{st} , ΔE_s is calculated for each possible transition.

For $\Delta j_s = -2$, $j_s' - j_s = -2$, and $j_s' = j_s - 2$. Then,

$$\Delta E_s = (j_s - 2)(j_s - 1) - j_s(j_s + 1) = 4j_s + 2. \quad (A-4)$$

For $\Delta j_s = -1$, $j_s' - j_s = -1$, and $j_s' = j_s - 1$. Then,

$$\Delta E_s = (j_s - 1)j_s - j_s(j_s - 1) = -2j_s. \quad (A-5)$$

For $\Delta j_s = 0$, $j_s' - j_s = 0$, and $j_s' = j_s$. Then,

$$\Delta E_s = 0. \quad (A-6)$$

For $\Delta j_s = 1$, $j_s' - j_s = 1$, and $j_s' = j_s + 1$. Then,

$$\Delta E_s = (j_s + 1)(j_s + 2) - j_s(j_s + 1) = 2j_s + 2. \quad (A-7)$$

For $j_s = 2$, $j_s' - j_s = 2$, and $j_s' = j_s + 2$. Then,

$$\Delta E_s = (j_s + 2)(j_s + 3) - j_s(j_s + 1) = 4j_s + 6. \quad (A-8)$$

Next, $\Delta J = 1$ is assumed, as in the following section. Then, $j_f = m$ and $j_i = m - 1$. Table A.1 gives the components of w_{st} for each type of Δj_s . The complete factors w_{st} are given in Table A.2 for each possible encounter. Since only the absolute value of w_{st} is used in calculating k , some values of w_{st} may be different from the corresponding values from Ref. [27] by a sign.

A.2. Transition Factor Derivation: g_{st}

From Tsao and Curnutte [20], the transition factors from Eqs. (133), (150), (161), and (163) are taken and put into a more convenient form by defining the relations:

Table A.1. Numerical Tables of the Functions $r_\ell(k)$ and $R_\ell(k)$

k	$r_1(k)$	$R_1(k)$	$r_2(k)$	$R_2(k)$	$r_4(k)$	$R_4(k)$
			$r_3(k)$	$R_3(k)$		
0.0	1.00	1.00	1.00	0.500	1.00	0.333
0.1	1.01	1.02	1.00	0.500	1.00	0.333
0.2	1.02	1.05	1.01	0.506	1.00	0.334
0.3	1.05	1.07	1.01	0.512	1.00	0.335
0.4	1.07	1.08	1.03	0.522	1.01	0.337
0.5	1.10	1.07	1.04	0.532	1.01	0.341
0.6	1.13	1.05	1.06	0.546	1.02	0.344
0.7	1.15	1.02	1.07	0.562	1.03	0.349
0.8	1.16	0.974	1.10	0.574	1.04	0.353
0.9	1.16	0.924	1.12	0.583	1.05	0.360
1.0	1.16	0.869	1.15	0.593	1.06	0.368
1.1	1.14	0.811	1.17	0.599	1.08	0.377
1.2	1.11	0.750	1.20	0.602	1.10	0.383
1.3	1.08	0.690	1.22	0.602	1.12	0.392
1.4	1.04	0.631	1.24	0.596	1.14	0.400
1.5	0.994	0.574	1.25	0.586	1.16	0.406
1.6	0.945	0.519	1.26	0.577	1.19	0.414
1.7	0.892	0.467	1.26	0.562	1.22	0.417
1.8	0.837	0.419	1.25	0.543	1.24	0.424
1.9	0.782	0.374	1.24	0.522	1.26	0.428
2.0	0.726	0.333	1.23	0.500	1.28	0.429
2.1	0.672	0.296	1.21	0.478	1.29	0.430
2.2	0.618	0.262	1.18	0.454	1.31	0.428
2.3	0.567	0.231	1.15	0.429	1.32	0.425
2.4	0.518	0.203	1.11	0.404	1.33	0.420
2.5	0.471	0.178	1.07	0.377	1.33	0.414
2.6	0.427	0.156	1.03	0.352	1.33	0.406
2.7	0.386	0.136	0.985	0.327	1.32	0.396
2.8	0.348	0.119	0.938	0.303	1.32	0.386
2.9	0.313	0.103	0.892	0.279	1.30	0.374
3.0	0.281	0.0898	0.843	0.257	1.28	0.361

Table A.1. (continued)

k	$r_1(k)$	$R_1(k)$	$r_2(k)$	$R_2(k)$	$r_4(k)$	$R_4(k)$
			$r_3(k)$	$R_3(k)$		
3.1	0.251	0.0780	0.793	0.236	1.26	0.348
3.2	0.224	0.0675	0.744	0.215	1.23	0.333
3.3	0.199	0.0584	0.698	0.196	1.20	0.318
3.4	0.177	0.0504	0.651	0.179	1.17	0.303
3.5	0.157	0.0434	0.605	0.162	1.13	0.287
3.6	0.139	0.0374	0.562	0.147	1.10	0.272
3.7	0.122	0.0322	0.519	0.132	1.06	0.257
3.8	0.108	0.0276	0.478	0.119	1.01	0.241
3.9	0.0947	0.0237	0.438	0.107	0.970	0.227
4.0	0.0832	0.0203	0.404	0.0960	0.926	0.212
4.1	0.0730	0.0174	0.374	0.0877	0.879	0.198
4.2	0.0640	0.0149	0.344	0.0793	0.836	0.184
4.3	0.0558	0.0127	0.313	0.0710	0.788	0.171
4.4	0.0487	0.0109	0.283	0.0626	0.745	0.158
4.5	0.0425	0.00927	0.253	0.0543	0.701	0.146
4.6	0.0370	0.00790	0.233	0.0493	0.658	0.135
4.7	0.0322	0.00673	0.212	0.0443	0.619	0.124
4.8	0.0279	0.00573	0.192	0.0394	0.576	0.114
4.9	0.0242	0.00487	0.171	0.0344	0.537	0.104
5.0	0.0210	0.00414	0.151	0.0294	0.502	0.0953
5.5	---	---	0.0747	0.0154	0.339	0.0593
6.0	---	---	0.0481	0.00784	0.220	0.0354
6.5	---	---	0.0258	0.00389	0.136	0.0204
7.0	---	---	0.0135	0.00190	0.0818	0.0114
7.5	---	---	0.00690	0.000907	0.0476	0.00619
8.0	---	---	0.00346	0.000429	0.0268	0.00330

Table A.2. Energy factors, w_{st} , as a
Function of Δj_i , Δj_f , and Δj_2

i	ΔJ		w_{st}
	f	2	
-1	-1		$-B_1 m$
			$-B_1 (m-1)$
	1		$B_1 (m+1)$
1			$B_1 m$
0	0		0
			0
	-2		$-B_1 (2m-1)$
-2			$-B_1 (2m-3)$
			$B_1 (2m+3)$
	2		$B_1 (2m+1)$
2		-2	$B_2 (2j_2-1)$
		-1	$-B_2 j_2$
		0	0
		1	$B_2 (j_2+1)$
		2	$B_2 (2j_2+3)$

$$D(j_s, j_s') = \langle j_s 1 k_s 0 | j_s' k_s \rangle \quad (\text{A-9})$$

$$Q(j_s, j_s') = \langle j_s 2 k_s 0 | j_s' k_s \rangle \quad (\text{A-10})$$

as is done by Benedict and Kaplan [37], where these quantities are simply the line strengths for the transitions divided by $(2j_s+1)$. In these equations, j_s may stand for the initial (j_i) or final (j_f) state of the absorbing molecule, or the state (j_2) of the colliding molecule. Equations (133), (150), (161), and (163) of Tsao and Curnutte may now be written (for linear molecules):

$$(\text{TC133}) \quad S_2(b)_{o,i} = \left(\frac{4}{9}\right) \left[\frac{\mu_1 \mu_2}{\hbar \nu} \right]^2 b^{-4} \sum_{j_i' j_2'} D(j_i, j_i') D(j_2, j_2') f_1(k) , \quad (\text{A-11})$$

$$(\text{TC150}) \quad S_2(b)_{o,i} = \left(\frac{4}{45}\right) \left[\frac{\mu_1 Q_2}{\hbar \nu} \right]^2 b^{-6} \sum_{j_i' j_2'} D(j_i, j_i') Q(j_2, j_2') f_2(k) , \quad (\text{A-12})$$

$$(\text{TC161}) \quad S_2(b)_{o,i} = \left(\frac{1}{25}\right) \left[\frac{Q_1 Q_2}{\hbar \nu} \right]^2 b^{-8} \sum_{j_i' j_2'} Q(j_i, j_i') Q(j_2, j_2') f_3(k) , \quad (\text{A-13})$$

$$\begin{aligned}
 \text{(TC163)} \quad S_2(b)_m &= (-1)^{j_i+j_f} \left(\frac{2}{25} \right) \left[\frac{Q_1 Q_2}{\hbar \nu} \right]^2 b^{-8} \\
 &\quad \left[(2j_f+1)(2j_i+1) Q(j_i, j_i) \times Q(j_f, j_f) \right]^{1/2} \\
 &\quad W(j_i j_f j_i j_f, 12) \sum_{j_2'} Q(j_2, k_2') f_3(k) . \quad \text{(A-14)}
 \end{aligned}$$

The line strengths for singlet electric dipole and quadrupole transitions ($\Lambda = 0$) are taken from Kovacs [55], normalized according to the sum rule:

$$\sum_{j''} S(j', j'') = (2j'+1) , \quad \text{(A-15)}$$

and are employed in Eqs. (A-1) and (A-2) as follows:

$$D(j_s, k_s+1) = (j_s+1)/(2j_s+1) , \quad \text{(A-16)}$$

$$D(j_s, j_s) = 0 , \quad \text{(A-17)}$$

$$D(j_s, j_s-1) = j_s/(2j_s+1) , \quad \text{(A-18)}$$

$$Q(j_s, j_s+1) = (3/2)j_s(j_s-1)/(2j_s-1)(2j_s+1) , \quad \text{(A-19)}$$

$$Q(j_s, j_s) = j_s(j_s+1)/(2j_s-1)(2j_s+3) , \quad \text{(A-20)}$$

$$Q(j_s, j_s-1) = (3/2)(j_s+1)(j_s+2)/(2j_s+3)(2j_s+1) . \quad \text{(A-21)}$$

These may now be expressed in terms of m and j_2 . To determine m , either P-branch ($\Delta J = -1$) or R-branch ($\Delta J = +1$) nomenclature may be used to obtain the set of transition factors, g_{st} , and energy

factors, w_{st} , corresponding to the possible encounters involved in the collision process. In order to follow as closely as possible the notation of Benedict and Herman [27], the R-branch nomenclature was used for this work:

$$\Delta j = j_f - j_i = 1 , \quad (A-22)$$

$$m = j_i + 1 = j_f , \quad (A-23)$$

$$j_i = m - 1 , \quad j_f = m . \quad (A-24)$$

Thus :

$$D(j_i, j_i + 1) = m / (2m - 1) , \quad (A-25)$$

$$D(j_i, j_i - 1) = (m - 1) / (2m - 1) , \quad (A-26)$$

$$D(j_f, j_f + 1) = (m + 1) / (2m + 1) , \quad (A-27)$$

$$D(j_f, j_f - 1) = m / (2m + 1) , \quad (A-28)$$

$$D(j_2, j_2 + 1) = (j_2 + 1) / (2j_2 + 1) , \quad (A-29)$$

$$D(j_2, j_2 - 1) = j_2 / (2j_2 + 1) , \quad (A-30)$$

$$Q(j_i, j_i + 2) = (3/2)m(m + 1) / (2m - 1)(2m + 1) , \quad (A-31)$$

$$Q(j_i, j_i) = (m - 1)m / (2m - 3)(2m + 1) , \quad (A-32)$$

$$Q(j_i, j_i - 2) = (3/2)(m - 1)(m - 2) / (2m - 3)(2m - 1) , \quad (A-33)$$

$$Q(j_f, j_f + 2) = (3/2)(m + 1)(m + 2) / (2m + 1)(2m + 3) , \quad (A-34)$$

$$Q(j_f, j_f) = m(m + 1) / (2m - 1)(2m + 3) , \quad (A-35)$$

$$Q(j_f, j_f - 2) = (3/2)m(m - 1) / (2m - 1)(2m + 1) , \quad (A-36)$$

$$Q(j_2, j_2 + 2) = (3/2)(j_2 + 1)(j_2 + 2) / (2j_2 + 1)(2j_2 + 3) , \quad (A-37)$$

$$Q(j_2, j_2) = j_2(j_2+1)/(2j_2-1)(2j_2+3) , \quad (A-38)$$

$$Q(j_2, j_2-2) = (3/2)(j_2-1)j_2/(2j_2+1)(2j_2-1) . \quad (A-39)$$

To obtain the quantities g_{st} as given by Benedict and Herman [27], then, each possible encounter must be listed. These are grouped according to class; i.e., dipole-dipole, dipole-quadrupole, quadrupole-dipole, and quadrupole-quadrupole. Benedict and Herman combined the dipole-quadrupole and quadrupole interactions because they dealt only with self-broadening in their study. From Eq. (2) of Ref. [27] and Eq. (4) of Ref. [37], it can be seen that g_{st} is simply the product of the transition factors for the absorbing and colliding molecules.

An important exception to this is the case of the quadrupole-quadrupole interaction where $\Delta j_i = \Delta j_f = 0$. For convenience, the contribution due to the so-called "mixed term," $S_2(b)_m$, is combined with the other terms representing $\Delta j_i = 0$ and $\Delta j_f = 0$. This can be done because of the common factor

$$\sum_{j_2'} Q(j_2, j_2') f_3(k)$$

in Eqs. (A-5) and (A-6). The transition factors under consideration, g_{45} , g_{46} , and g_{47} are derived in the following manner.

The mixed term, $S_2(b)$, can be expressed as:¹

$$S_2(b)_m = c_4 b^{-8} g_{4m} \sum_{j_2} Q(j_2, j_2') f_3(k) , \quad (A-40)$$

where,

$$g_{4m} = (-1)^{j_i + j_f} \left[(2j_i + 1)(2j_f + 1) Q(j_i, j_i) Q(j_f, j_f) \right]^{1/2} W(j_i, j_f, j_i, j_f, 12) , \quad (A-41)$$

and $W(j_i, j_f, j_i, j_f, 12)$ is a Racah coefficient [55]. The terms g_{45} , g_{46} , and g_{47} are then defined:

$$g_{45} = (g_{4m} + Q(j_i, j_i) + Q(j_f, j_f)) Q(j_2, j_2) , \quad (A-42)$$

$$g_{46} = (g_{4m} + Q(j_i, j_i) + Q(j_f, j_f)) Q(j_2, j_2 - 2) , \quad (A-43)$$

$$g_{47} = (g_{4m} + Q(j_i, j_i) + Q(j_f, j_f)) Q(j_2, j_2 + 2) . \quad (A-44)$$

As before, it is assumed that $\Delta J = 1$, which implies that $j_i = j_f + 1$ and $j_f = m$. From Ref. [56],

$$W(m-1, m, m-1, m, 12) = \left[\frac{(2m-1)(2m+2)(2m-2)(2m-3)}{4(2m+1)^2 m^2 (2m-1)^2} \right]^{1/2} , \quad (A-45)$$

¹The term $S_2(b)_m$ is zero for the dipole-dipole and dipole-quadrupole interactions of linear molecules.

Then,

$$\begin{aligned}
 g_{4m} &= (-1)^{2m+1} \left[\frac{(2m-1)(2m+1)m^2(m-1)(m+1)}{(2m-3)(2m+1)(2m+3)(2m-1)} \right]^{1/2} \\
 &\quad \left[\frac{(2m+3)(2m+2)(2m-2)(2m-3)}{4(2m+1)^2 m^2 (2m-1)^2} \right]^{1/2} \\
 &= - (m-1)(m+1)(2m+2)(2m-2)^{1/2} / (2m+1)(2m-1) \\
 &= - (2m^2-2)/(4m^2-1) . \tag{A-46}
 \end{aligned}$$

The sum $Q(j_i, j_i) + Q(j_f, j_f)$, which figures in Eqs. (A-35), (A-36), and (A-37) can be determined easily:

$$\begin{aligned}
 Q(j_i, j_i) + Q(j_f, j_f) &= m(m-1)/(2m-3)(2m+1) + m(m+1)/(2m-1)(2m+3) \\
 &= [(2m-1)(2m+3)m(m-1) + m(m+1)(2m+1)(2m-3)] \\
 &\quad / (4m^2-1)(4m^2-9) \\
 &= (8m^4-14m^2)/(4m^2-1)(4m^2-9) . \tag{A-47}
 \end{aligned}$$

Now the transition terms can be derived:

$$\begin{aligned}
 g_{45} &= \frac{(8m^4-14m^2)-(2m^2-2)(4m^2-9)}{(4m^2-1)(4m^2-9)} Q(j_2, j_2) \\
 &= [6(2m^2-3)/(4m^2-1)(4m^2-9)] Q(j_2, j_2) , \tag{A-48}
 \end{aligned}$$

$$g_{46} = [6(2m^2-3)/(4m^2-1)(4m^2-9)] Q(j_2, j_2-2) , \tag{A-49}$$

and

$$g_{47} = [6(2m^2-3)/(4m^2-1)(4m^2-9)] Q(j_2, j_2+2) . \quad (A-50)$$

The transition factors for all of the possible encounters are listed in Table A.3.

Table A.3. Transition Factors, g_{st} , and Energy Factors, w_{st} , Involved in the Possible Classes of Encounters, Δj_i , Δj_f , Δj_2

Class s	t	ΔJ		9 _{st}	w _{st}
		i	f		
<u>Dipole-Dipole Interactions</u>					
1	1		-1	1 m(j ₂ +1)/(2m+1)(2j ₂ +1)	-B ₁ ^m + B ₂ (j ₂ +1)
1	2		-1	1 (m-1)(j ₂ +1)/(2m-1)(2j ₂ +1)	-B ₁ (m-1) + B ₂ (j ₂ +1)
1	3		1	-1 (m+1)j ₂ /(2m+1)(2j ₂ +1)	B ₁ (m+1) - B ₂ j ₂
1	4		1	-1 mj ₂ /(2m-1)(2j ₂ +1)	B ₁ ^m - B ₂ j ₂
1	5		-1	-1 mj ₂ /(2m+1)(2j ₂ +1)	-B ₁ ^m - B ₂ j ₂
1	6		-1	-1 (m-1)j ₂ /(2m-1)(2j ₂ +1)	-B ₁ (m+1) + B ₂ j ₂
1	7		1	1 (m+1)(j ₂ +1)/(2m+1)(2j ₂ +1)	B ₁ (m+1) + B ₂ (j ₂ +1)
1	8		1	1 m(j ₂ +1)/(2m-1)(2j ₂ +1)	B ₁ ^m + B ₂ (j ₂ +1)

Table A.3. (continued)

Class s t	ΔJ			g_{st}	Dipole-Quadrupole Interactions	w_{st}
	i	f	2			
2 1	1	-2		$(3/2)(m+1)j_2(j_2-1)/(2m+1)(2j_2+1)(2j_2-1)$	$B_1(m+1)$	$-B_2(2j_2-1)$
2 2	1	-2		$(3/2)mj_2(j_2-1)/(2m-1)(2j_2+1)(2j_2-1)$	B_1m	$-B_2(2j_2-1)$
2 3	-1	2		$(3/2)m(j_2+1)(j_2+2)/(2m+1)(2j_2+1)(2j_2+3)$	$-B_1m$	$+B_2(2j_2+3)$
2 4	-1	2		$(3/2)(m-1)(j_2+1)(j_2+2)(2m-1)(2j_2+1)(2j_2+3)$	$-B_1(m-1)$	$+B_2(2j_2+3)$
2 5	-1	0		$mj_2(j_2+1)/(2m+1)(2j_2-1)(2j_2+3)$	$-B_1m$	
2 6	-1	0		$(m-1)j_2(j_2+1)/(2m-1)(2j_2-1)(2j_2+3)$	$-B_1(m-1)$	
2 7	1	0		$(m+1)j_2(j_2+1)/(2m+1)(2j_2-1)(2j_2+3)$	$B_1(m+1)$	
2 8	1	0		$mj_2(j_2+1)/(2m-1)(2j_2-1)(2j_2+3)$	B_1m	
2 9	-1	-2		$(3/2)mj_2(j_2-1)/(2m+1)(2j_2+1)(2j_2-1)$	$-B_1m$	$-B_2(2j_2-1)$
2 10	-1	-2		$(3/2)(m-1)j_2(j_2-1)/(2m-1)(2j_2+1)(2j_2-1)$	$-B_1(m-1)$	$-B_2(2j_2-1)$
2 11	1	2		$(3/2)(m+1)(j_2+1)(j_2+2)/(2m+1)(2j_2+1)(2j_2+3)$	$B_1(m+1)$	$+B_2(2j_2+3)$
2 12	1	2		$(3/2)m(j_2+1)(j_2+3)/(2m-1)(2j_2+1)(2j_2+3)$	B_1m	$+B_2(2j_2+3)$

Table A.3. (continued)

Class s t	ΔJ			g_{st}	Quadrupole-Dipole Interactions	w_{st}
	i	f	2			
3 1	-2	1	$(3/2)m(m-1)(j_2+1)/(2m-1)(2m+1)(2j_2+1)$		$-B_1(2m-1) + B_2(j_2 +1)$	
3 2	-2	1	$(3/2)(m-1)(m-2)j_2/(2m-3)(2m-1)(2j_2+1)$		$-B_1(2m-3) + B_2(j_2 +1)$	
3 3	2	-1	$(3/2)(m+1)(m+2)j_2/(2m+1)(2m+3)(2j_2+1)$		$B_1(2m+3) - B_2j_2$	
3 4	2	-1	$(3/2)m(m+1)j_2/(2m-1)(2m+1)(2j_2+1)$		$B_1(2m+1) - B_2j_2$	
3 5	0	-1	$m(m+1)j_2/(2m+3)(2m-1)(2j_2+1)$		$- B_2j_2$	
3 6	0	-1	$m(m-1)j_2/(2m-3)(2m+1)(2m+3)(2j_2+1)$		$- B_2j_2$	
3 7	0	1	$m(m+1)(j_2+1)/(2m-1)(2m+3)(2j_2+1)$		$B_2(j_2 +1)$	
3 8	0	1	$m(m-1)(j_2+1)/(2m-3)(2m+1)(2j_2+1)$		$B_2(j_2 +1)$	
3 9	-2	-1	$(3/2)m(m-1)j_2/(2m-1)(2m+1)(2j_2+1)$		$-B_1(2m-1) - B_2j_2$	
3 10	-2	-1	$(3/2)(m-1)(m-2)j_2/(2m-3)(2m-1)(2j_2+1)$		$-B_1(2m-3) + B_2(j_2 +1)$	
3 11	2	1	$(3/2)(m+1)(m-2)(j_2+1)/(2m+1)(2m+3)(2j_2+1)$		$B_1(2m+3) + B_2(j_2 +1)$	
3 12	2	1	$(3/2)m(m+1)(j_2+1)/(2m-1)(2m+1)(2j_2+1)$		$B_1(2m+1) + B_2(j_2 +1)$	

Table A.3. (continued)

Class s t	ΔJ		g_{st}	w_{st}
	i	f		
<u>Quadrupole-Quadrupole Interactions</u>				
4 1	-2	2	$(9/4)m(m-1)(j_2+1)(j_2+2)/(2m-1)(2m+1)(2j_2+1)(2j_2+3)$	$-B_1(2m-1) + B_2(2j_2+3)$
4 2	-2	2	$(9/4)(m-1)(m-2)(j_2+1)(j_2+2)/(2m-3)(2m-1)(2j_2+1)(2j_2+3)$	$-B_1(2m-3) + B_2(2j_2+3)$
4 3	2	-2	$(9/4)(m+1)(m+2)j_2(j_2-1)/(2m+1)(2m+3)(2j_2+1)(2j_2-1)$	$B_1(2m+3) - B_2(2j_2-1)$
4 4	2	-2	$(9/4)m(m+1)j_2(j_2-1)/(2m-1)(2m+1)(2j_2+1)(2j_2-1)$	$B_1(2m+1) - B_2(2j_2-1)$
4 5	0	0	$6(2m^2-3)j_2(j_2+1)/(4m^2-1)(4m^2-9)(2j_2-1)(2j_2+3)$	0
4 6	0	-2	$9(2m^2-3)j_2(j_2-1)/(4m^2-1)(4m^2-9)(2j_2+1)(2j_2-1)$	$B_2(2j_2-1)$
4 7	0	2	$9(2m^2-3)(j_2+1)(j_2+2)/(4m^2-1)(4m^2-9)(2j_2+1)(2j_2+3)$	$B_2(2j_2+3)$
4 8	-2	0	$(3/2)m(m-1)j_2(j_2+1)/(2m-1)(2m+1)(2j_2-1)(2j_2+3)$	$-B_1(2m-1)$
4 9	-2	0	$(3/2)(m-1)(m-2)j_2(j_2+1)/(2m-3)(2m-1)(2j_2-1)(2j_2+3)$	$-B_1(2m-3)$

Table A.3. (continued)

Class	$\frac{\Delta J}{s \quad t}$	$\frac{i}{f}$	2	g_{st}	w_{st}
<u>Quadrupole-Quadrupole Interactions</u>					
4 10	2	0	$(3/2)(m+1)(m+2)(j_2+1)j_2/(2m+1)(2m+3)(2j_2-1)(2j_2+3)$	$B_1(2m+3)$	
4 11	2	0	$(3/2)m(m+1)j_2(j_2+1)/(2m-1)(2m+1)(2j_2-1)(2j_2+3)$	$B_1(2m+1)$	
4 12	-2	-2	$(9/4)m(m-1)j_2(j_2-1)/(2m-1)(2m+1)(2j_2+1)(2j_2-1)$	$-B_1(2m-1) - B_2(2j_2-1)$	
4 13	-2	-2	$(9/4)(m-1)(m-2)j_2(j_2-1)/(2m-3)(2m-1)(2j_2+1)(2j_2-1)$	$-B_1(2m-3) - B_2(2j_2-1)$	
4 14	2	2	$(9/4)(m+1)(m+2)(j_2+1)(j_2+2)/(2m+1)(2m+3)(2j_2+1)(2j_2+3)$	$B_1(2m+3) + B_2(2j_2+3)$	
4 15	2	2	$(9/4)m(m+1)(j_2+1)(j_2+2)/(2m-1)(2m+1)(2j_2+1)(2j_2+3)$	$B_1(2m+1) + B_2(2j_2+3)$	

APPENDIX B

LISTING OF COMPUTER PROGRAM

The following is a listing of the computer code used to calculate spectral half-widths according to Anderson-Tsao-Curnutte formalism.

```

COMPILER OPTIONS - NAME= MAIN,OPT=02,LINECNT=58,SIZE=0000K,
SOURCE,FRCDIC,NOLIST,NODECK,LOAD,MAP,NODEIT,IO,XREF
C*****
C
C PROGRAM C: COLLISIONAL BROADENING HALF-WIDTH CALCULATIONS.
C*****
C
C REFERENCE BENEDICT AND HERMAN, JQSRT VOL 3, P 265-278;
C AND VARANASI AND TEJWANI, JQSRT VOL 11, P 255-261.
C*****
C
C*****
C PART 1 PART 1 PART 1 PART 1 PART 1 PART 1 PART 1
C*****
C
C IMPLICIT REAL*(A-H, O-Z)
C REAL*8 K1, K2, K3, LSTRM, M, MU1, MU2, M1, M2
C REAL*8 J2,K4
C REAL*4 BOLT, BOGT
C DIMENSION HEAD(10)
C DIMENSION XG(100), YN(100)
C B0=1.00
C IW = 0
C
C READ IN THE HEADING
C
C READ (5,128) HEAD
C FORMAT (10A8)
C
C READ IN THE CONSTANTS FOR THE RADIATING MOLECULE
C
C READ (5,120) M1, B1, D1, MU1, Q1
C FORMAT (5(D10.4))
C
C READ IN THE CONSTANTS FOR THE PERTURBING MOLECULE.
C
C READ (5,120) M2, B2, D2, MU2, Q2
C
C READ IN THE MINIMUM COLLISION DIAMETER FOR THE COLLISION PROCESS.
C
C READ (5,121) BMIN
C FORMAT (D10.4)
C

```

```

C      READ IN THE START TEMPERATURE, THE STOP TEMPERATURE, AND THE
C      TEMPERATURE INCREMENT.
C
C      READ (5,122) T,TLMT, TSTEP
C      FORMAT (3(D10.4))
122
C
C      READ IN THE START M, THE STOP M, AND THE M INCREMENT.
C
C      READ (5,123) MLS, MLLM, MLSTP
C      FORMAT (3(I10))
123
C
C      JX = 1 FOR MAXIMUM PRINTOUT
C      JX = 2 FOR REDUCED PRINTOUT
C      JX = 3 FOR MINIMUM PRINTOUT
C      JX = 4 FOR BOLT AND BOGT PRINTOUT
C
C      READ (5,124) JX
C      FORMAT (I10)
124
C
C      CALCULATE THE REDUCED MASS.
C
C      M = (M1*M2)/(M1+M2)
C      HON2 = B2
C      DON2 = D2
C
C      WRITE (6,126)
C      FORMAT (10X,
125
C      1 'PROGRAM C H00827.1045')
C
C      WRITE (6,127) HEAD
C      FORMAT (10X, 10A8)
127
C      WRITE (6,116)
C      FORMAT (I13, 'M1', T23, 'M2', T33, 'M', T43, 'B1', T53, 'B2',
116
C      1 T64, 'D0')
C      WRITE (6,115) M1, M2, M, B1, B2, DON2
C      FORMAT (10X, 5(F5.2, 5X), 1P(D10.4))
115
C      WRITE (6,108)
C      WRITE (6,118)
C      FORMAT (I14, 'MU1', T29, 'MU2', T44, 'Q1', T59, 'Q2', T73, 'BMIN')
118
C      WRITE (6,117) MU1, MU2, Q1, Q2, BMIN
C      FORMAT (5X, 5(F5.2, 1P(D10.4))
117
C      WRITE (6,108)
C      FORMAT (1X,/)
109
C
C*****
C      PART 2 PART 2 PART 2 PART 2 PART 2 PART 2 PART 2
C*****

```



```

ISN 0345      WRITE (6,131) T, ML, J2, GAMMAO, YN(ML)
ISN 0346      FORMAT (10X, F10.1, 5X, I2, 5X, F5.1, 5X, I2, 5X, F10.4, 5X, F10.4)
ISN 0347      GO TO 1410
ISN 0348      CONTINUE
ISN 0349      WRITE (6,114) T, ML, J2, GAMMAO, YN(ML), BOLT, BOGT
ISN 0350      FORMAT (10X, F10.1, 5X, I2, 5X, F5.1, 5X, I2, 5X, F10.4, 5X, F10.4, 5X,
ISN 0351      1 PD10.4, 5X, I2, 5X, F10.4)
ISN 0352      1410 CONTINUE
ISN 0353      C
ISN 0354      ML = ML + MLSTP
ISN 0355      IF (ML.LE.MLLM) GO TO 1130
ISN 0356      C
ISN 0357      END THE M LOOP.
ISN 0358      C
ISN 0359      1300 CONTINUE
ISN 0360      IT = IT + 1
ISN 0361      T = T + TSTEP
ISN 0362      IF (IT.EQ.1) T = TSTRT
ISN 0363      IF (T.EQ.300.00.AND.IT.NE.0) GO TO 1500
ISN 0364      WRITE (6,129)
ISN 0365      129 FORMAT ('1')
ISN 0366      1500 CONTINUE
ISN 0367      IF (T.LE.TLMT) GO TO 1120
ISN 0368      C
ISN 0369      END TEMPERATURE LOOP.
ISN 0370      C
ISN 0371      1111 CONTINUE
ISN 0372      RETURN
ISN 0373      END

```

NMOD
NMOD

NMOD
NMOD
NMOD

NMOD
NMOD
NMOD

```

ISN 0309      * , D10.4, 10X, 'EJ2 = ', D10.4)
ISN 0310      CONTINUE
ISN 0311      J2 = J2 + 1.00
ISN 0312      TEST = RHOJ2*H2J2/RJ2RJ2
ISN 0313      TVALUE = .0001D0
ISN 0315      IF (TEST.LT.TVALUE) GO TO 1010
              GO TO 1000
C
C      END J2 LOOP.
C
ISN 0316      1010 CONTINUE
C
C*****
C      PART 5 PART 5 PART 5 PART 5 PART 5 PART 5 PART 5
C*****
C      XN = 0.010286D0*(300.00/T)**.500/M**5D0
C      GAMMA0 = XN*RJ2RJ2
C      GAMMA0 = GAMMA0*1.D16
C
C      YN(ML) = 0.00
C      IF (IT.EQ.0) XG(ML) = GAMMA0
C      IF (T.EQ.300.00) GO TO 1100
C
C      'YN' IS THE TEMPERATURE DEPENDENCE EXPONENT OF THE LINE.
C
C      YN(ML) = DLOG(GAMMA0/XG(ML))/DLOG(300.00/T)
C      YN(ML) = YN(ML)/10.00
C
C      1100 CONTINUE
C      J2 = J2 - 1.00
C      IF (ML.NE.MLS) GO TO 960
C
C      IF (JX.EQ.4) GO TO 1420
C      WRITE (6,132)
ISN 0334      132  FORMAT (T18, 'T', T26, 'ML', T35, 'J2', T45, 'GAMMA0', T65, 'N')
ISN 0335      GO TO 1430
ISN 0336      1420 CONTINUE
ISN 0337      WRITE (6,119)
ISN 0338      119  FORMAT (T18, 'T', T26, 'ML', T35, 'J2', T45, 'GAMMA0', T65, 'N',
ISN 0339      1  T76, 'BOLT', T91, 'BOGT')
ISN 0340      1430 CONTINUE
ISN 0341      960  CONTINUE
ISN 0342      HOLT = BOLT*1.008
ISN 0343      BOGT = BOGT*1.008
              IF (JX.EQ.4) GO TO 1400

```

```

ISN 0265 DO 540 JL=1,12
ISN 0266 CALL G3JL (JL,ML,J2,B1,B2,G3,W3T)
ISN 0267 K3=0.01494800*M**500*(300.000/T)**500*B0*B0*DABS(W3T)
ISN 0268 K3 = K3*1.0*08
ISN 0269 CALL F2S(K3,F3)
ISN 0270 PH003 = F3*G3
ISN 0271 IF (JX.GT.1) GO TO 565
ISN 0273 WRITE (6,113) JL,ML,J2,G3,W3T,K3,F3,PROD3
ISN 0274 CONTINUE
ISN 0275 GF3SUM = GF3SUM + PROD3
ISN 0276 CONTINUE
ISN 0277 CONTINUE
C
C
ISN 0278 IF (0.54-0.00) GO TO 750
ISN 0280 DO 560 JL=1,15
ISN 0281 CALL G4JL (JL,ML,J2,B1,B2,G4,W4T)
ISN 0282 K4 = 0.01494800*M**500*(300.00/T)**500*B0*B0*DABS(W4T)
ISN 0283 K4 = K4*1.0 08
ISN 0284 CALL F3S(K4,F4)
ISN 0285 PROD4 = F4*G4
ISN 0286 IF (JX.GT.1) GO TO 555
ISN 0288 WRITE (6,113) JL,ML,J2,G4,W4T,K4, F4,PROD4
ISN 0289 CONTINUE
ISN 0290 GF4SUM = GF4SUM + PROD4
ISN 0291 CONTINUE
ISN 0292 CONTINUE
C
C
ISN 0293 CALCULATE EJ2
EJ2 = (B0N2*J2*(J2+1.00) - DON2*J2**2.00) *1.438700/T
IF (J2.EQ.1.00) ROLT = R0
IF (J2.EQ.1.00) R0GT = R0
IF (R0.GT.R0GT) R0GT = R0
IF (R0.LT.ROLT) ROLT = R0
C
C
ISN 0294 CALCULATE R2J2, THE PARTIAL COLLISION DIAMETER.
R2J2 = ( B0**4.00 + A*GF1SUM + H*GF2SUM/B0**2.00
1 + C*GF3SUM/R0**2.00 + D*GF4SUM/R0**4.00)/B0**2.00.
RHOJ2 = (2.00*J2 +1.00)*DEXP(-EJ2)/Q
RJ2RJ2 = RJ2RJ2 + RHOJ2**2
C
ISN 0302 IF (JX.GT.2) GO TO 940
ISN 0303 WRITE (6,104) J2, RHOJ2, RJ2RJ2, EJ2
ISN 0304 FORMAT (10X, 'J2 = ',F7.2, '10X, 'RHOJ2 = ', D10.4,10X, 'RJ2RJ2 = ',
ISN 0305
ISN 0307
ISN 0308

```

800825
800825

104

```

C ***** PART 4 PART 4 PART 4 PART 4 PART 4 PART 4 PART 4 *****
C *****
C
    GF1SUM = 0.00
    GF2SUM = 0.00
    GF3SUM = 0.00
    GF4SUM = 0.00
C
    CALCULATE GF1SUM
C
    IF (A.EQ.0.000) GO TO 550
    IF (JX.GT.2) GO TO 970
    IF (J2.EQ.1.00) WRITE (6,108)
    CONTINUE
970    DO 720 JL = 1,4
        CALL G1JL (JL,ML,J2,81,H2,G1,W1T)
        K1=0.01494800**+.500*(300.000/T)**+.500*80*80*DABS(W1T)
        K1 = K1*1.0*08
        CALL F1S(K1,F1)
        PROD1 = F1*G1
        IF (JX.GT.1) GO TO 725
        WRITE (5,113) JL,ML,J2,G1,W1T,K1,F1,PROD1
725    CONTINUE
        GF1SUM = GF1SUM + PROD1
720    CONTINUE
550    CONTINUE
C
    CALCULATE GF2SUM
C
    IF (R.EQ.0.000) GO TO 570
    DO 590 JL = 1,12
        CALL G2JL (JL,ML,J2,81,H2,G2,W2T)
        K2=0.01494800**+.500*(300.000/T)**+.500*80*80*DABS(W2T)
        K2 = K2*1.0*08
        CALL F2S (K2, F2)
        PROD2 = F2*G2
        IF (JX.GT.1) GO TO 545
        WRITE (6,113) JL,ML,J2,G2,W2T,K2, F2,PROD2
545    CONTINUE
        GF2SUM = GF2SUM + PROD2
590    CONTINUE
570    CONTINUE
C
    CALCULATE GF3SUM
C
    IF (C.EQ.0.000) GO TO 730

```

```

ISN 0185      FXKLS = FXK
ISN 0186      IF (DARS(FXK).LT..01000) GO TO 640
ISN 0189      IX = IX + 1
ISN 0189      IF (XNP1.LE.0.00) GO TO 650
ISN 0191      GO TO 620
C
ISN 0192      CONTINUE
ISN 0193      IF (FXK.GT.0.00) GO TO 810
ISN 0195      IF (FXK.GT.-.100) GO TO 810
ISN 0197      XNP1 = X-.100*FXK/FXKP
ISN 0198      GO TO 810
C
ISN 0199      CONTINUE
ISN 0200      FZ = FXKLS-FXK
ISN 0201      IF (DARS(FZ).LT.0.0000100) GO TO 810
ISN 0203      XNP1 = -FXK*(XLAST-X)/(FXKLS-FXK) + X
ISN 0204      GO TO 810
C
ISN 0205      CONTINUE
ISN 0206      IM = IM + 1
C
C      REVALUE A NEGATIVE 'NEXT ESTIMATE'.
C
ISN 0207      XNP1=1.100*BMIN
ISN 0208      IF (IM.GT.1) XNP1 = 1.200*BMIN
ISN 0210      IF (IM.GT.2) XNP1 = 1.300*BMIN
ISN 0212      IF (IM.GT.3) XNP1 = .900*BMIN
ISN 0214      IF (IM.GT.4) XNP1 = .800*BMIN
C
ISN 0216      GO TO 620
C
C      HO MUST BE MORE THAN BMIN
C
ISN 0217      CONTINUE
ISN 0218      HO = BMIN
ISN 0219      GO TO 621
C
ISN 0220      CONTINUE
ISN 0221      IF (XNP1.LT.BMIN) GO TO 651
ISN 0223      CONTINUE
C
C      END HO LOOP.
C
C*****

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800826

800826

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ISN 0145 CALL FL3S (K4,FL4)
ISN 0146 PR0D4 = FL4*64
ISN 0147 IF (JX.GT.1) GO TO 535
ISN 0149 IF (IX.GT.0) GO TO 535
ISN 0151 WRITE (6,113) JL,ML,J2,G4,W4T,K4,FL4,PR0D4
ISN 0152 CONTINUE
ISN 0153 GFL4SM = GFL4SM + PR0D4
ISN 0154 CONTINUE
ISN 0155 CONTINUE

535 C
520 C CALCULATE THE FUNCTION
740 C
C
C
ISN 0156 FXK = A*GFL1SM + B*GFL2SM/H0**2.D0 + C*GFL3SM/H0**2.D0
ISN 0157 1 + D*GFL4SM/H0**4.D0 - B0**4.D0
FXK = FXK/H0**4.D0
800825
800825
800825

C
C CALCULATE THE DERIVATIVE
C
ISN 0158 FXKP = -4.D0*A*GFL1SM/H0 - 6.D0*B*GFL2SM/H0**3.D0 -
ISN 0159 1 6.D0*C*GFL3SM/H0**3.D0 - 8.D0*D*GFL4SM/H0**5.D0
FXKP = FXKP/H0**4.D0
800825
800825
800825

C
C CALCULATE THE NEXT ESTIMATE
C
C AN EMPIRICAL FUNCTION IS USED TO CALCULATE THE NEXT ESTIMATE,
C MORE QUICKLY.
C
ISN 0160 XNP1 = X-FXK/FXKP
ISN 0161 IF (DABS(FXK).GT.1.00) XNP1 = X-2.D0*FXK/FXKP
ISN 0163 IF (DABS(FXK).GT.1.001) XNP1 = X-3.D0*FXK/FXKP
ISN 0165 IF (DABS(FXK).GT.1.002) XNP1 = X-4.D0*FXK/FXKP

C
ISN 0167 IF (IX.EQ.0) GO TO A20
ISN 0169 IF (FXKLST.LT.0.000) GO TO A20
ISN 0171 IF (FXK.LT.0.000) GO TO 800
ISN 0173 CONTINUE
ISN 0174 IF (JX.GT.2) GO TO 930
ISN 0176 WRITE (6,109)
ISN 0177 FORMAT (1R, 'GLF1SM', T23, 'GFL2SM', T34, 'GFL3SM', T53, 'GFL4SM',
1 T69, 'FXK', T84, 'FXKP', T101, 'X', T115, 'XNP1')
ISN 0178 WRITE (6,101) GFL1SM, GFL2SM, GFL3SM, GFL4SM, FXK, FXKP, X, XNP1
ISN 0179 FORMAT (8(4X,D11.4))
ISN 0180 IW = IW + 1
ISN 0181 IF (IW.EQ.3000) GO TO 1111
ISN 0183 CONTINUE
ISN 0184 XLAST = X
930

```

```

ISN 0101          510      CONTINUE
C
C      CALCULATE GFL2SM
C
ISN 0102          IF (B.EQ.0.000) GO TO 530
ISN 0103          IF (B.EQ.0.) GO TO 530
ISN 0104          DO 500 JL = 1,12
ISN 0105          CALL G2JL (JL,ML,J2,B1,B2,G2,W2T)
ISN 0106          K2=0.01494800*M**500*(300.000/T)**.500*B0*80*DABS(W2T)
ISN 0107          K2 = K2*1.0*08
ISN 0108          CALL FL2S (K2, FL2)
ISN 0109          PR0D2 = FL2*G2
ISN 0110          IF (JX.GT.1) GO TO 515
ISN 0111          IF (IX.GT.0) GO TO 515
ISN 0112          WRITE (6,113) JL,ML,J2,G2,W2T,K2,FL2,PR0D2
ISN 0113          CONTINUE
ISN 0114          GFL2SM = GFL2SM + PR0D2
ISN 0115          CONTINUE
ISN 0116          500      CONTINUE
ISN 0117          530      CONTINUE
ISN 0118          C
ISN 0119          C      CALCULATE GFL3SM
ISN 0120          C
C
ISN 0121          IF (C.EQ.0.000) GO TO 710
ISN 0122          DO 580 JL = 1,12
ISN 0123          CALL G3JL (JL,ML,J2,B1,B2,G3,W3T)
ISN 0124          K3=0.01494800*M**500*(300.000/T)**.500*B0*80*DABS(W3T)
ISN 0125          K3 = K3*1.0*08
ISN 0126          CALL FL2S (K3,FL3)
ISN 0127          PR0D3 = FL3*G3
ISN 0128          IF (JX.GT.1) GO TO 525
ISN 0129          IF (IX.GT.0) GO TO 525
ISN 0130          WRITE (6,113) JL, ML, J2, G3, W3T, K3, FL3, PR0D3
ISN 0131          FORMAT (10X, I5, I5, 6(5X, 1P011.4))
ISN 0132          CONTINUE
ISN 0133          GFL3SM = GFL3SM + PR0D3
ISN 0134          CONTINUE
ISN 0135          580      CONTINUE
ISN 0136          710      CONTINUE
ISN 0137          C
ISN 0138          C      CALCULATE GFL4SM
ISN 0139          C
ISN 0139          IF (D.EQ.0.00) GO TO 740
ISN 0140          DO 520 JL=1,15
ISN 0141          CALL G4JL (JL,ML,J2,B1,B2,G4,W4T)
ISN 0142          K4 = 0.01494800*M**500*(300.00/T)**.500*B0*80*DABS(W4T)
ISN 0143          K4 = K4*1.0 08
ISN 0144

```

```

1130      CONTINUE
      RJ2RJ2=0.00
C
C      *I4* IS THE M LOOP COUNTER.
C
C      IM = 0
C
C      FIND B0
C      SOLVE THE EQUATION BY A MODIFIED NEWTON METHOD.
C
C      XNP1 = BMIN
C      J2 = 1.00
C
C      BEGIN THE J2 LOOP.
C
C      CONTINUE
C      IX = 0
C      XLAST = 1.100*BMIN
C      FXKLST = -1.000
C
C      BEGIN THE B0 LOOP.
C
C      CONTINUE
C      X = XNP1
C      GFL1SM=0.000
C      GFL2SM=0.000
C      GFL3SM=0.000
C      GFL4SM=0.000
C      B0=X
C
C      CALCULATE GFL1SM
C
C      IF (A.E0.0.000) GO TO 510
C      DO 700 JL = 1,A
C      CALL G1JL (JL,ML,J2,R1,B2,G1,W1T)
C      K1=0.01494800**4**500*(300.000/T)**.500*B0*B0*DABS(W1T)
C      K1 = K1*1.0+08
C      CALL FL1S (K1,FL1)
C      PROD1 = FL1 *G1
C      IF (JX.GT.1) GO TO 715
C      IF (IX.GT.0) GO TO 715
C      WRITE (6,113) JL,ML, J2, G1, W1T, K1, FL1, PROD1
C      CONTINUE
C      GFL1SM = GFL1SM + PROD1
C      CONTINUE
715
700

```

800826

COMPILER OPTIONS - NAME= MAIN,OPT=02,LINECNT=58,SIZE=0000K,
SOURCE,FBCDIC,NOLIST,NODECK,LOAD,MAP,NODEIT,ID,XREF

```

C
ISN 0002      SUBROUTINE PF(T,BON2, DON2, Q)
C
C      THIS SUBROUTINE CALCULATES THE PARTITION FUNCTION FOR THE
C      COLLIDING MOLECULE.
C
ISN 0003      IMPLICIT REAL*8(A-H,O-Z)
ISN 0004      REAL*8 LSTTRM, J2
ISN 0005      LSTTRM= 1.00
ISN 0006      TERM = 0.00
ISN 0007      Q = 0.00
ISN 0008      J2 = 1
ISN 0009      CONTINUE
ISN 0010      EJ2 = (BON2*J2*(J2+1.00) - DON2*J2**2.00) *1.438700/T
ISN 0011      TERM = DEXP(-EJ2)*(2.00*J2+1.00)
ISN 0012      Q=Q+TERM
ISN 0013      X = LSTTRM/Q
ISN 0014      IF(X.LT.0.000100) GO TO 420
ISN 0015      LSTTRM=TERM
ISN 0016      J2 = J2 +1
ISN 0017      GO TO 440
ISN 0018
ISN 0019      CONTINUE
ISN 0020      WRITE (6,102) T,Q
ISN 0021      FORMAT (10X,'T = ', F7.1, 10X, 'Q = ', F10.4)
ISN 0022      RETURN
ISN 0023      END

```

COMPILER OPTIONS - NAME= MAIN,OPT=02,LINECNT=58,SIZE=0000K,
SOURCE,ERCDIC,NOLIST,NODECK,LOAD,MAP,NOEDIT,ID,XREF

```

C
ISN 0002      SUBROUTINE GLJL (JL,VL,J2, X, Y,GI,WLT)
C
ISN 0003      IMPLICIT REAL*8(A-H,O-Z)
ISN 0004      REAL*8 M, J2
ISN 0005      M = VL
ISN 0006      GO TO (1,2,3,4,5,6,7,8), JL
ISN 0007      G1 = M*(J2+1.00) / ((2.00*M+1.00) * (2.00*J2+1.00))
ISN 0008      WLT = -X*M + Y*(J2+1.00)
ISN 0009      GO TO 300
ISN 0010      G1 = (M-1.00) * (J2+1.00) / ((2.00*M-1.00) * (2.00*J2 +1.00))
ISN 0011      WLT = -X*(M-1.00) + Y*(J2+1.00)
ISN 0012      GO TO 300
ISN 0013      G1 = (M+1.00) * J2 / ((2.00*M+1.00) * (2.00*J2 +1.00))
ISN 0014      WLT = X*(M+1.00) -Y*J2
ISN 0015      GO TO 300
ISN 0016      G1 = M*J2 / ((2.00*M-1.00) * (2.00*J2+1.00))
ISN 0017      WLT = X*M-Y*J2
ISN 0018      GO TO 300
ISN 0019      G1 = M*J2 / ((2.00*M+1.00) * (2.00*J2+1.00))
ISN 0020      WLT = -X*M-Y*J2
ISN 0021      GO TO 300
ISN 0022      G1 = (M-1.00) * J2 / ((2.00*M-1.00) * (2.00*J2+1.00))
ISN 0023      WLT = -X*(M-1.00) -Y*J2
ISN 0024      GO TO 300
ISN 0025      G1 = (M+1.00) * (J2+1.00) / ((2.00*M+1.00) * (2.00*J2+1.00))
ISN 0026      WLT = X*(M+1.00) +Y*(J2+1.00)
ISN 0027      GO TO 300
ISN 0028      G1 = M*(J2+1.00) / ((2.00*M-1.00) * (2.00*J2+1.00))
ISN 0029      WLT = X*M + Y*(J2+1.00)
ISN 0030      CONTINUE
ISN 0031      RETURN
ISN 0032      END
300

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LEVEL 21.7 ( JAN 73 )                OS/360  FORTRAN H

COMPILER OPTIONS - NAME=  MAIN,OPT=02,LINECNT=58,SIZE=0000K,
                     SOURCE,EBCDIC,NOLIST,NODECK,LOAD,MAP,NODEIT,ID,XREF

C
TSN 0002      SUBROUTINE G2JL (JL,ML,J2, X, Y,G2,W2T)
C
TSN 0003      IMPLICIT REAL*8(A-H, O-Z)
TSN 0004      REAL*8 M, J2
TSN 0005      M = ML
TSN 0006      GO TO (1,2,3,4,5,6,7,8,9,10,11,12), JL
TSN 0007      G2 = 3.00*M*(M-1.00) * (J2+1.00) / (2.00*(2.00*M-1.00) * (2.00*J2+
$ 1.00) * (2.00*M+1.00))
TSN 0008      W2T = -X*(2.00*M-1.00) + Y*(J2+1.00)
TSN 0009      GO TO 100
TSN 0010      G2 = 3.00*(M-1.00) * (M-2.00) * (J2+1.00)
TSN 0011      G2 = G2/(2.00*(2.00*M-3.00) * (2.00*M-1.00) * (2.00*J2+1.00))
TSN 0012      W2T = -X*(2.00*M-3.00) + Y*(J2+1.00)
TSN 0013      GO TO 100
TSN 0014      G2 = 3.00*(M+1.00) * (M+2.00)*J2
TSN 0015      G2 = G2/(2.00*(2.00*M+1.00) * (2.00*M+3.00) * (2.00*J2+1.00))
TSN 0016      W2T = X*(2.00*M+3.00) - Y*J2
TSN 0017      GO TO 100
TSN 0018      G2 = 3.00*M*(M+1.00) *J2
TSN 0019      G2 = G2/(2.00*(2.00*M+1.00) * (2.00*M-1.00) * (2.00*J2 +1.00))
TSN 0020      W2T = X*(2.00*M+1.00) - Y*J2
TSN 0021      GO TO 100
TSN 0022      G2 = M*(M+1.00)* J2
TSN 0023      G2 = G2/(2.00*M-1) * (2.00*M+3.00) * (2.00*J2+1.00))
TSN 0024      W2T = -Y*J2
TSN 0025      GO TO 100
TSN 0026      G2 = (M-1.00)*M* J2
TSN 0027      G2 = G2/(2.00*M-3.00) * (2.00*M+1.00) * (2.00*J2+1.00))
TSN 0028      W2T = -Y*J2
TSN 0029      GO TO 100
TSN 0030      G2 = M*(M+1.00) * (J2+1.00)
TSN 0031      G2 = G2/(2.00*M-1.00) * (2.00*M+3.00) * (2.00*J2+1.00))
TSN 0032      W2T = Y*(J2+1.00)
TSN 0033      GO TO 100
TSN 0034      G2 = (M-1.00) *M*(J2+1.00)
TSN 0035      G2 = G2/(2.00*M-3.00)*(2.00*M+1.00) * (2.00*J2 +1.00))
TSN 0036      W2T = Y*(J2+1.00)
TSN 0037      GO TO 100
TSN 0038      G2 = 3.00*M*(M-1.00)* J2
TSN 0039      G2 = G2/(2.00 * (2.00*M-1.00) * (2.00*M+1.00) * (2.00*J2+1.00))
TSN 0040      W2T = -X*(2.00*M-1.00) - X*J2

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1SN 0041
1SN 0042
1SN 0043
1SN 0044
1SN 0045
1SN 0046
1SN 0047
1SN 0048
1SN 0049
1SN 0050
1SN 0051
1SN 0052
1SN 0053
1SN 0054
1SN 0055

10      GO TO 100
        G2 = 3.00* (M-1.00)* (M-2.00)* J2
        G2 = G2/(2.00* (2.00*M-3.00)* (2.00*M-1.00) * (2.00*J2+1.00))
        W2T = -X*(2.00*M-3.00) - X*J2
        GO TO 100

11      G2 = 3.00* (M+1.00)* (M+2.00) * (J2+1.00)
        G2 = G2/(2.00* (2.00*M+1.00)* (2.00*M+3.00)* (2.00*J2+1.00))
        W2T = X*(2.00*M+3.00) + Y*(J2+1.00)
        GO TO 100

12      G2 = 3.00*M* (M+1.00)* (J2+1.00)
        G2 = G2/(2.00*(2.00*M-1.00)* (2.00*M+1.00) * (2.00*J2+1.00))
        W2T = X*(2.00*M+1.00) + Y*(J2+1.00)

100     CONTINUE
        RETURN
        END

```

COMPILER OPTIONS - NAME= MAIN,OPT=02,LINECNT=58,SIZE=0000K,
SOURCE,ERCOIC,NOLIST,NODECK,LOAD,MAP,NOEDIT,ID,XREF

```

C
ISN 0002      SURROUTINE G3JL (JL,ML,J2, X,Y,G3,W3T)
C
ISN 0003      IMPLICIT REAL*8(A-H, 0-Z)
ISN 0004      REAL*8 M, J2
ISN 0005      M = ML
ISN 0006      GO TO (1,2,3,4,5,6,7,8,9,10,11,12), JL
ISN 0007      G3 = 3.00*(M+1.00)*J2*(J2-1.00)
ISN 0008      G3 = G3/(2.00*(2.00*M+1.00))* (2.00*J2-1.00) * (2.00*J2+1.00)
ISN 0009      W3T = X*(M+1.00) - Y*(2.00*J2-1.00)
ISN 0010      GO TO 100
ISN 0011      G3 = 3.00*M*J2*(J2-1.00)
ISN 0012      G3 = G3/(2.00*(2.00*M-1.00))* (2.00*J2-1.00)* (2.00*J2+1.00)
ISN 0013      W3T = X*M - Y*(2.00*J2-1.00)
ISN 0014      GO TO 100
ISN 0015      G3 = 3.00*M*(J2+1.00)*(J2+2.00)
ISN 0016      G3 = G3/(2.00*(2.00*M+1.00))* (2.00*J2+1.00) * (2.00*J2+3.00)
ISN 0017      W3T = -X*M + Y*(2.00*J2+3.00)
ISN 0018      GO TO 100
ISN 0019      G3 = 3.00*(M-1.00)* (J2+1.00)* (J2+2.00)
ISN 0020      G3 = G3/(2.00*(2.00*M-1.00))* (2.00*J2+1.00) * (2.00*J2+3.00)
ISN 0021      W3T = -X*(M-1.00) + Y*(2.00*J2+3.00)
ISN 0022      GO TO 100
ISN 0023      G3 = M*J2*(J2+1.00)
ISN 0024      G3 = G3/(2.00*M+1.00) * (2.00*J2-1.00) * (2.00*J2+3.00)
ISN 0025      W3T = -X*M
ISN 0026      GO TO 100
ISN 0027      G3 = (M-1.00)*J2*(J2+1.00)
ISN 0028      G3 = G3/(2.00*M-1.00) * (2.00*J2-1.00)* (2.00*J2+3.00)
ISN 0029      W3T = -X*(M-1.00)
ISN 0030      GO TO 100
ISN 0031      G3 = (M+1.00)*J2* (J2+1.00)
ISN 0032      G3 = G3/(2.00*M+1.00) *(2.00*J2-1.00)* (2.00*J2+3.00)
ISN 0033      W3T = X*(M+1.00)
ISN 0034      GO TO 100
ISN 0035      G3 = M*J2*(J2+1.00)
ISN 0036      G3 = G3/(2.00*M-1.00) * (2.00*J2-1.00) * (2.00*J2+3.00)
ISN 0037      W3T = X*M
ISN 0038      GO TO 100
ISN 0039      G3 = 3.00*M*J2*(J2-1.00)
ISN 0040      G3 = G3/(2.00*(2.00*M+1.00))* (2.00*J2-1.00)* (2.00*J2+1.00)

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```

ISN 0041
ISN 0042
ISN 0043
ISN 0044
ISN 0045
ISN 0046
ISN 0047
ISN 0048
ISN 0049
ISN 0050
ISN 0051
ISN 0052
ISN 0053
ISN 0054
ISN 0055
ISN 0056

10
W3T = -X*M - Y*(2.00*J2-1.00)
GO TO 100
G3 = 3.00*(M-1.00)*J2*(J2-1.00)
G3 = G3/(2.00*(2.00*M-1.00) * (2.00*J2-1.00) * (2.00*J2+1.00))
W3T = -X*(M-1.00) - Y*(2.00*J2-1.00)
GO TO 100

11
G3 = 3.00*(M+1.00)*(J2+1.00)* (J2+2.00)
G3 = G3/(2.00*(2.00*M+1.00)* (2.00*J2+1.00)*(2.00*J2+3.00))
W3T = X*(M+1.00) + Y*(2.00*J2+3.00)
GO TO 100

12
G3 = 3.00*M*(J2+1.00)* (J2+2.00)
G3 = G3/(2.00*(2.00*M-1.00)* (2.00*J2+1.00)* (2.00*J2+3.00))
W3T = X*M + Y*(2.00*J2+3.00)
GO TO 100

100
CONTINUE
RETURN
END

```

COMPILER OPTIONS - NAME= MAIN,OPT=02,LINCONT=58,SIZE=0000K,

SOURCE,EBCDIC,NOLIST,NODECK,LOAD,MAP,NOEDIT,ID,XREF

SUBROUTINE G4JL (JL,ML,J2,X,Y,G4,W4T)

C

IMPLICIT REAL*8(A-H,O-Z)

REAL*8 M,J2

M = ML

GO TO (1,2,3,4,5,6,7,8,9,10,11,12,13,14,15), JL

G4 = 9.00*M*(M-1.00)*(J2+1.00)*(J2+2.00)

G4 = G4/(4.00*(2.00*M-1.00)*(2.00*M+1.00)*(2.00*J2+1.00)*(2.00*J2

\$ *J2+3.00))

W4T = -X*(2.00*M-1.00) + Y*(2.00*J2+3.00)

GO TO 200

G4 = 9.00*(M-1.00)*(M-2.00)*(J2+1.00)*(J2+2.00)

G4 = G4/(4.00*(2.00*M-3.00)*(2.00*M-1.00)*(2.00*J2+1.00)*(2.00*J2

\$ +3.00))

W4T = -X*(2.00*M-3.00) + Y*(2.00*J2+3.00)

GO TO 200

G4 = 9.00*(M+1.00)*(M+2.00)*J2*(J2-1.00)

G4 = G4/(4.00*(2.00*M+1.00)*(2.00*J2-1.00)*(2.00*J2+1.00))

G4 = G4/(2.00*M+3.00)

W4T = X*(2.00*M+3.00) - Y*(2.00*J2-1.00)

GO TO 200

G4 = 9.00*M*(M+1.00)*J2*(J2-1.00)

G4 = G4/(4.00*(2.00*M-1.00)*(2.00*M+1.00)*(2.00*J2+1.00)

\$ *(2.00*J2-1.00))

W4T = X*(2.00*M+1.00) - Y*(2.00*J2-1.00)

GO TO 200

G4 = 6.00*(2.00*M+2.00-3.00)*J2*(J2+1.00)

G4 = G4/(4.00*M+2.00-9.00)*(2.00*J2-1.00)*(2.00*J2+3.00))

G4 = G4/(4.00*M+2.00-1.00)

W4T = 0.00

GO TO 200

G4 = 9.00*(2.00*M+2.00-3.00)*J2*(J2-1.00)

G4 = G4/(2.00*(4.00*M+2.00-1.00)*(4.00*M+2.00-9.00)*(2.00*J2-1.00)

\$ *(2.00*J2+1.00))

G4 = G4*2.

W4T = Y*(2.00*J2-1.00)

GO TO 200

G4 = 9.00*(2.00*M+2.00-3.00)*(J2+1.00)*(J2+2.00)

G4 = G4/(2.00*(4.00*M+2.00-1.00)*(4.00*M+2.00-9.00)*(2.00*J2+

\$ 3.00)*(2.00*J2+1.00))

G4 = G4*2.

```

ISN 0037      W4T = Y*(2.00*J2+3.00)
ISN 0038      GO TO 200
ISN 0039      G4 = 3.00*(M-1.00)*M*J2*(J2+1.00)
ISN 0040      G4=G4/(2.00*(2.00*M-1.00)*(2.00*M+1.00)*(2.00*J2-1.00)*
ISN 0041      $ (2.00*J2+3.00))
ISN 0042      W4T = -X*(2.00*M-1.00)
ISN 0043      GO TO 200
ISN 0044      G4 = 3.00*(M-2.00)*(M-1.00)*J2*(J2+1.00)
ISN 0045      G4=G4/(2.00*(2.00*M-3.00)*(2.00*M-1.00)*(2.00*J2-1.00)
ISN 0046      $ *(2.00*J2+3.00))
ISN 0047      W4T = -X*(2.00*M-1.00)
ISN 0048      G4 = 3.00*(M+1.00)*(M+1.00)*J2*(J2+1.00)
ISN 0049      G4 = G4/(2.00*(2.00*M+1.00)*(2.00*M+3.00)*(2.00*J2-1.00)*
ISN 0050      $ (2.00*J2+3.00))
ISN 0051      W4T = X*(2.00*M+3.00)
ISN 0052      GO TO 200
ISN 0053      G4 = 3.00*M*(M+1.00)*J2*(J2+1.00)
ISN 0054      G4 = G4/(2.00*(2.00*M-1.00)*(2.00*M+1.00)*(2.00*J2-1.00)*
ISN 0055      $ (2.00*J2+3.00))
ISN 0056      W4T = X*(2.00*M+1.00)
ISN 0057      GO TO 200
ISN 0058      G4 = 9.00*M*(M-1.00)*(J2-1.00)*J2
ISN 0059      G4 = G4/(4.00*(2.00*M-1.00)*(2.00*M+1.00)*(2.00*J2-1.00)*
ISN 0060      $ (2.00*J2+1.00))
ISN 0061      W4T = -X*(2.00*M-3.00) - Y*(2.00*J2-1.00)
ISN 0062      GO TO 200
ISN 0063      G4 = 9.00*(M+1.00)*(M+2.00)*(J2+1.00)*(J2+2.00)
ISN 0064      G4 = G4/(4.00*(2.00*M+1.00)*(2.00*M+3.00)*(2.00*J2+1.00)*
ISN 0065      $ (2.00*J2+3.00))
ISN 0066      W4T = X*(2.00*M+3.00) + Y*(2.00*J2+3.00)
ISN 0067      GO TO 200
ISN 0068      G4 = 9.00*M*(M+1.00)*(J2+1.00)*(J2+2.00)
ISN 0069      G4 = G4/(4.00*(2.00*M-1.00)*(2.00*J2+1.00)*(2.00*J2+3.00)*
ISN 0070      $ (2.00*M+1.00))
ISN 0071      W4T = X*(2.00*M+1.00) + Y*(2.00*J2+3.00)
ISN 0072      CONTINUE
          RETURN
          END

```

LEVEL 21.7 (JAN 73)

OS/360 FORTRAN H

DATE 82.049/15.14.02

COMPILER OPTIONS - NAME= MAIN,OPT=02,LINECNT=58,SIZE=0000K,
SOURCE,ERCDIC,NOLIST,NODECK,LOAD,MAP,NOEDIT,ID,XREF

```
C
TSN 0002      SURROUTINE FL1S (XK1, FL1)
C
TSN 0003      IMPLICIT REAL*8(A-H,O-Z)
TSN 0004      COMMON/TABLE/FL(51), F(51), FFL(57), FF(57), FFFL(57), FFF(57)
C
TSN 0005      IF (XK1.GE.5.00) GO TO 100
TSN 0007      K1K = IDINT(10.00*XK1) +1
TSN 0008      K1I = K1K +1
TSN 0009      FL1 = (10.00*XK1-K1K +1)*(FL(K1I)-FL(K1K)) + FL(K1K)
TSN 0010      GO TO 200
TSN 0011      CONTINUE
TSN 0012      EX=(XK1-5.00)
TSN 0013      FL1=.02100*(.25D0)**EX
TSN 0014      CONTINUE
TSN 0015      RETURN
TSN 0016      END
```

COMPILER OPTIONS - NAME= MAIN,OPT=02,LINECNT=58,SIZE=0000K,
SOURCE,EHCDCIC,NOLLIST,NODECK,LOAD,MAP,NOEDIT,ID,XREF

```

C
ISN 0002      SUBROUTINE FL2S (XK2, FL2)
C
ISN 0003      IMPLICIT REAL*(A-H, O-Z)
ISN 0004      COMMON/TABLE/FL(51), F(51), FFL(57), FFFL(57), FFF(57)
ISN 0005      IF (XK2.GE.5.D0) GO TO 100
ISN 0007      K2K = IDINT(10.D0*XK2) + 1
ISN 0008      K2I = K2K+1
ISN 0009      FL2 = (10.D0*XK2-K2K+1)*(FFL(K2I)-FFL(K2K)) + FFL(K2K)
ISN 0010      GO TO 200
ISN 0011      CONTINUE
ISN 0012      IF (XK2.GE.8.D0) GO TO 300
ISN 0014      K2K = IDINT(2.D0*(XK2-5.D0)) + 51
ISN 0015      K2I = K2K + 1
ISN 0016      FX = 2.D0*(XK2-5.D0)-K2K + 51.D0
ISN 0017      FL2 = FX*(FFL(K2I)-FFL(K2K)) + FFL(K2K)
ISN 0018      GO TO 200
ISN 0019      CONTINUE
ISN 0020      EX = (XK2-8.D0)
ISN 0021      FL2 = .0034600*(.25D0)**EX
ISN 0022      CONTINUE
ISN 0023      RETURN
ISN 0024      END
100
300
200

```

COMPILER OPTIONS - NAME= MAIN,OPT=02,INECNT=58,SIZE=0000K,
SOURCE,FBCOIC,NOLIST,NODECK,LOAD,MAP,NOEDIT,ID,XREF

```

C      SUBROUTINE EL3S (XK3, FL3)
C
      IMPLICIT REAL*8(A-H, O-Z)
      COMMON/TABLE/FL(51), F(51), FFL(57), FF(57), FFFL(57), FFF(57)
      IF(XK3.GE.5.00) GO TO 100
      K3K = I0INT(10.00*XK3) + 1
      K3I = K3K + 1
      FL3 = (10.00*XK3-K3K+1)*(FFFLL(K3I)- FFFL(K3K)) + FFFL(K3K)
      GO TO 200
100    CONTINUE
      IF(XK3.GE.9.00) GO TO 300
      K3K = I0INT(2.00*(XK3-5.00)) + 51
      K3I = K3K + 1
      FX = 2.00*(XK3-5.00)-K3K + 51.00
      FL3 = FX*(FFFLL(K3I) - FFFL(K3K)) + FFFL(K3K)
      GO TO 200
300    CONTINUE
      EX = (XK3-8.00)
      FL3 = .026800*(.2500)**EX
200    CONTINUE
      RETURN
      END

```

COMPILER OPTIONS - NAME= MAIN,OPT=02,I,INECNT=58,SIZE=0000K,
SOURCE,FHCDCIC,NOLIST,NODECK,LOAD,MAP,NOEDIT,ID,XREF

```

C
ISN 0002      SUBROUTINE F1S (XK1,F1)
C
ISN 0003      IMPLICIT REAL*8(A-H,O-Z)
ISN 0004      COMMON/TABLE/F1(51), F(51), FFL(57), FF(57), FFFL(57), FFF(57)
ISN 0005      IF(XK1.GE.5.00) GO TO 100
ISN 0007      K1K = IDINT(10.00*XK1) +1
ISN 0008      K1I = K1K +1
ISN 0009      F1 = (10.00*XK1-K1K + 1)*(F(K1I)-F(K1K)) + F(K1K)
ISN 0010      GO TO 200
ISN 0011      CONTINUE
ISN 0012      EX=(XK1-5.00)
ISN 0013      F1 = .00414D0*(.25D0)**EX
ISN 0014      CONTINUE
ISN 0015      RETURN
ISN 0016      END

```

LEVEL 21.7 (JAN 73)

OS/360 FORTRAN H

COMPILER OPTIONS - NAME= MAIN,OPT=02,LINECNT=58,SIZE=0000K,
SOURCE,FHCDIC,NOLIST,NODECK,LOAD,MAP,NODEIT,ID,XREF

```

C
ISN 0002      SUBROUTINE F2S (XK2, F2)
C
ISN 0003      IMPLICIT REAL*8(A-H, O-Z)
ISN 0004      COMMON/TAHLE/FL(51), F(51), FFL(57), FF(57), FFFL(57), FFF(57)
ISN 0005      IF(XK2.GE.5.D0) GO TO 100
ISN 0007      K2K = IDINT(10.D0*XK2) + 1
ISN 0008      K2I = K2K+1
ISN 0009      F2 = (10.D0*XK2-K2K+1)*(FF(K2I)-FF(K2K)) + FF(K2K)
ISN 0010      GO TO 200
ISN 0011      CONTINUE
ISN 0012      100
ISN 0013      IF(XK2.GE.8.D0) GO TO 300
ISN 0014      K2K = IDINT(2.D0*(XK2-5.D0)) + 51
ISN 0015      K2I = K2K + 1
ISN 0016      FX = 2.D0*(XK2-5.D0)-K2K + 51.D0
ISN 0017      F2 = FX*(FF(K2I)-FF(K2K)) + FF(K2K)
ISN 0018      GO TO 200
ISN 0019      CONTINUE
ISN 0020      300
ISN 0021      EX = (XK2-8.D0)
ISN 0022      F2 = .000429D0*(.25D0)**EX
ISN 0023      CONTINUE
ISN 0024      RETURN
ISN 0025      END

```

LEVEL 21.7 (JAN 73)

OS/360 FORTRAN H

COMPILER OPTIONS - NAME= MAIN,OPT=02,LINECNT=58,SIZE=0000K,
SOURCE,EBCDIC,NOLIST,NODECK,LOAD,MAP,NOEDIT,ID,XREF

```

C
ISN 0002      SURROUTINE F3S (XK3,F3)
C
ISN 0003      IMPLICIT REAL*8(A-H, O-Z)
ISN 0004      COMMON/TABLE/FL(51), F(51), FFL(57), FF(57), FFFL(57), FFF(57)
ISN 0005      IF(XK3.GE.5.00) GO TO 100
ISN 0007      K3K = I0INT(10.00*XK3) +1
ISN 0008      K3I = K3K +1
ISN 0009      F3 = (10.00*XK3-K3K+1)*(FFF(K3I)-FFF(K3K)) +FFF(K3K)
ISN 0010      GO TO 200
ISN 0011      CONTINUE
ISN 0012      IF(XK3.GE.8.00) GO TO 300
ISN 0014      K3K = I0INT(2.00*(XK3-5.00)) +51
ISN 0015      K3I = K3K +1
ISN 0016      FX= 2.00*(XK3-5.00)-K3K + 51.00
ISN 0017      F3 = FX*(FFF(K3I)-FFF(K3K)) + FFF(K3K)
ISN 0018      GO TO 200
ISN 0019      CONTINUE
ISN 0020      EX = (XK3-8.00)
ISN 0021      F3 = .003300*(.2500)*EX
ISN 0022      CONTINUE
ISN 0023      RETURN
ISN 0024      END

```

COMPILER OPTIONS - NAME= MAIN,OPT=02,I INECNT=58,SIZE=0000K,
SOURCE,EBCDIC,NOLIST,NOUECK,LOAD,MAP,NOEDIT,ID,XREF

ISN 0002	C	BLOCK DATA
ISN 0003	C	IMPLICIT REAL*(A-H, O-Z)
ISN 0004		COMMON/TAHLE/FL(51), F(51), FFL(57), FF(57), FFFL(57), FFF(57)
ISN 0005		DATA FL/1.000,1.0100,1.0200,1.0300,1.0400,1.0500,1.0600,1.0700,1.0800,1.0900,1.1000,1.1100,1.1200,1.1300,1.1400,1.1500,
		* 1.1600,1.1700,1.1800,1.1900,1.2000,1.2100,1.2200,1.2300,1.2400,1.2500,1.2600,1.2700,1.2800,1.2900,1.3000,1.3100,1.3200,1.3300,1.3400,1.3500,
		* .94500,.89200,.83700,.78200,.72600,.67200,.61800,.56700,
		* .51800,.47100,.42700,.38600,.34800,.31300,.28100,.25100,.22400,
		* .19900,.17700,.15700,.13900,.12200,.10800,.094700,.083200,
		* .07300,.06400,.055800,.049700,.042500,.03700,.032200,.027900,
		* .024200,.02100/
ISN 0006		DATA F/1.000,1.0200,1.0500,1.0700,1.0800,1.0700,1.0500,1.0200,
		* .97400,.92400,.86900,.81100,.7500,.6900,.63100,.57400,.51900,
		* .46700,.41900,.37400,.33300,.29600,.26200,.23100,.20300,.17800,
		* .15600,.13600,.11900,.10300,.089800,.07800,.067500,.058400,
		* .050400,.043400,.037400,.032200,.027600,.023700,.020300,
		* .017400,.014900,.012700,.010900,.0092700,.007900,.0067300,
		* .0057300,.0048700,.0041400/
ISN 0007		DATA FFL/1.000,1.000,1.0100,1.0100,1.0300,1.0400,1.0600,1.0700,
		* 1.1000,1.1200,1.1500,1.1700,1.200,1.2200,1.2400,1.2500,1.2500,
		* 1.2600,1.2500,1.2400,1.2300,1.2100,1.1800,1.1500,1.1100,1.0700,
		* 1.0300,.98500,.93800,.89200,.84300,.79300,.74400,.69800,.65100,
		* .60500,.56200,.51900,.47800,.43800,.40400,.37400,.34400,.31300,
		* .28300,.25300,.23300,.21200,.19200,.17100,.15100,.074700,
		* .048100,.025800,.013500,.006900,.0034600/
ISN 0008		DATA FF/.500,.500,.50600,.51200,.52200,.53400,.54600,.56200,
		* .57400,.58300,.59300,.59900,.60200,.60200,.59600,.58600,.57700,
		* .56200,.54300,.52200,.500,.47800,.45400,.42900,.40400,.37700,
		* .35200,.32700,.30300,.27900,.25700,.23600,.21500,.19600,.17900,
		* .16200,.14700,.13200,.11900,.10700,.09600,.087700,.079300,
		* .07100,.062600,.054300,.049300,.044300,.039400,.034400,.029400,
		* .015400,.0078400,.0038900,.001900,.00090700,.00042900/
ISN 0009		DATA FFFL/1.000,1.000,1.000,1.000,1.0100,1.0100,1.0100,1.0200,1.0300,
		* 1.0400,1.0500,1.0600,1.0800,1.1000,1.1200,1.1400,1.1600,1.1900,
		* 1.2200,1.2400,1.2600,1.2800,1.2900,1.3100,1.3200,1.3300,1.3400,
		* 1.3300,1.3200,1.3200,1.3000,1.2800,1.2600,1.2300,1.200,1.1700,
		* 1.1300,1.100,1.0600,1.0100,.97000,.92600,.87900,.83600,.78800,
		* .74500,.70100,.65800,.61900,.57600,.53700,.50200,.33900,.2200,
		* .13600,.081800,.047600,.025800/

ISN 0010

DATA FFF/.33300,.33300,.33400,.33500,.33700,.34100,.34400,.34900,
* .35300,.3600,.36800,.37700,.38300,.39200,.400,.40600,.41400,
* .41700,.42400,.42800,.42900,.4300,.42300,.42500,.4200,.41400,
* .40600,.39600,.38600,.37400,.36100,.34800,.33300,.31800,.30300,
* .28700,.27200,.25700,.24100,.22700,.21200,.19800,.18400,.17100,
* .15800,.14600,.13500,.12400,.11400,.10400,.095300,.059300,
* .035400,.020400,.011400,.0061900,.003300/
END

ISN 0011

VITA

Heard Sidney Lowry, III, was born on April 27, 1954, in Manchester, Tennessee. He received his elementary and high school education in Manchester, and graduated from Coffee County Central High School in May 1971.

In June of that same year he enrolled at David Lipscomb College in Nashville, Tennessee, where he pursued a course of study in Physics. He received the Bachelor of Arts degree in that field in June 1974. Later that month, he enrolled at The University of Tennessee Space Institute, receiving the Master of Arts degree in March 1977 and the Doctor of Philosophy degree in Physics in March 1982.

In December 1976 he began employment with ARO, Inc., at the Arnold Engineering Development Center, Arnold Air Force Station, Tennessee. In January 1981 his employment began with Calspan, Inc., at the same location.

He is interested in scouting, amateur radio, and is active in his home church. He is married to the former Brenda Gail Elam of Manchester. They have a son, Zachary Brandt, aged six months.