

ABSTRACT

Off-axis Cavity Ring Down Spectroscopy with Exponential and Phase Shift
Detection: Absorption Spectra of Weak Transitions at Low Temperatures

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In this dissertation the ability of the off-axis laser injection in cavity ring down experiments is shown. Modulated continuous wave and pulsed lasers are used to obtain the absorption spectra of weak transitions at low temperatures. The absorption spectra of the red atmospheric bands of O₂ (A-band and γ -band), the overtone ($\Delta\nu=4$) band of HD and the C-H ($\Delta\nu=4, 5$ and 6) overtone spectra of polyatomic molecules (C₂H₆, CH₂D₂, CHD₃, C₃H₄, C₆H₁₀ and C₅SiH₁₀) are presented. The integrated absorption of each band was calculated as a function of the density of the gas samples and used to obtain the band strength of these weak transitions. In addition, the Fourier-transform (IR and NIR) spectra between 2500 and 13000 cm⁻¹ are presented for CH₃D, CHD₃, C₆H₁₀ and C₅SiH₁₀. The local mode harmonic frequency and anharmonicity were obtained. The harmonically coupled anharmonic oscillator (HCAO) model was used to calculate energy levels and assign the absorption bands to particular transitions of CH₃D, C₆H₁₀ and C₅SiH₁₀. Also, overtone intensities of CHD₃ were calculated using *ab initio* quantum mechanical methods and compared with the experimental data. Spectral simulations were performed in order to confirm the transitions and the temperature of

the molecules in the cell. Lastly, photolysis of ethyl acetate via high vibrational overtone absorption is proposed.

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by

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DEDICATION

A Dios, la virgen Maria y mi Familia

CHAPTER ONE

Introduction

Absorption spectroscopy of atoms and molecules in the gas phase, yielding both quantitative absolute concentrations as well as absolute frequency-dependent cross-sections, is a very powerful tool in analytical chemistry and physical chemistry. In addition to its use in purely theoretical spectroscopic investigations, gas-phase absorption spectrometric measurements are also of interest in a variety of applications ranging from pollution monitoring to process control. Although traditional absorption spectrometry has been used in these cases, its insufficient sensitivity in challenging situations, as trace detection, has been found to be its primary disadvantage. Thus, various alternative techniques have been developed in an attempt to improve the detection of gaseous species. Some of these alternative techniques are photoacoustic spectroscopy (PA), thermal lensing measurements, (2+2) resonance-enhanced multiphoton ionization (REMPI). Intracavity laser absorption spectroscopy (ICLAS) and cavity ring down (CRD)spectroscopy. Among these various absorption techniques, the CRD technique has proven to be a valuable addition, since it combines good sensitivity with a rather simple and straightforward experimental set-up.^{1,2} The advantage of CRD spectroscopy over traditional absorption spectroscopy are the intrinsic insensitivity to light source intensity fluctuation and the extremely long effective path lengths (many kilometers) within small physical spaces.

As precursors to the CRD technique can be considered the work reported by Herbelin *et al.*³ and Anderson *et al.*⁴. Herbelin *et al.*³ developed a method to determine

the reflectivity of a surface based upon the time that the light spends within an optical cavity by measuring the phase shift that light experiences when passing through an optical resonator. In 1984, Anderson *et al.*⁴ demonstrated that the reflectivity of the mirrors could be measured even better by abruptly switching off the CW light source when the intracavity field exceeded a certain threshold value and then calculate the mirrors reflectivity from the exponential decay obtained.

In 1988, O’Keefe and Deacon using a modified pulsed cavity loss spectrometer performed the first spectroscopy using a cavity ring down. They demonstrated its sensitivity by recording the absorption spectrum of the weak $b^1\Sigma_g^+(\nu = 1,2) \leftarrow X^3\Sigma_g^-(\nu = 0)$ bands of molecular oxygen. Thus, they developed a new technique which allowed an increase of several orders of magnitude in sensitivity over a wide spectral region accessible with tunable pulsed lasers.⁵

Although most CRD experiments are performed with pulsed lasers, several schemes have been developed in order to perform CRD spectroscopy with continuous wave (CW) lasers. In 1996, Engeln *et al.*⁶ reported phase-shift cavity ring-down (PS-CRD) spectroscopy in which the absorption spectrum is extracted from a measurement of the magnitude of the phase shift that an intensity modulated CW light beam experiences upon passage through an optical cavity. Later, Romanini *et al.*⁷ used the other approach; the resonant cavity mode is swept over the CW laser line; then, when sufficient light is coupled into the cavity, the laser is switched off; subsequently, the CRD transient is recorded.² Moreover, cavity ring down has been used with some variations of the technique such as Fourier Transform detection^{8-10,11}, low cost continuous wave diode laser system¹²⁻¹⁴, broadband¹⁵⁻¹⁷ and evanescent wave.¹⁸ While

CRD spectroscopy has mostly been applied to gas phase samples, there are some examples where solid samples of C_{60} ¹⁹ and liquids²⁰⁻²² have been studied using CRD.

CRD has been applied to many different types of environments such as plasma chemistry and supersonic expansions. Plasma chemistry during carbon deposition²³, microwave plasma studies of C_2 ²⁴, plasma expansion of argon and acetylene¹⁹ and free radicals within plasmas^{25, 26} have been studied. Jet-cooled metal clusters^{27, 28}, CH_3I clusters²⁹, formic acid dimers³⁰, NO and CH_4 have been published.³¹ Other studies using CRD include detection of absolute concentration in reactive flows such as flames³²⁻³⁶ and hot filament reactors.³⁷⁻³⁹

Kinetics of radicals has also been studied with CRD spectroscopy.⁴⁰⁻⁴² Other more recent studies have shown kinetic properties for the reactions of benzyl radicals,⁴³ CH radicals,⁴⁴ nitrate radicals,⁴⁵ and the reaction of Cl with various molecules found in the atmosphere.⁴⁶

CRD spectroscopy is also used for a variety of analytical purposes such as trace detection of NO_3 ^{47, 48}, NO_2 ⁴⁹, water in phosphine⁵⁰, aerosol pollutants^{51, 52} and volatile organic compounds (VOC's).⁵³⁻⁵⁵

In weak absorption studies such as high vibrational overtones, CRD has also been applied. Overtone bands of HCN⁵⁶, benzene⁵⁷, CHF_3 ⁵⁸, HNO_3 , H_2O_2 ⁵⁹, $HCCH$ ^{60, 61}, N_2O ^{13, 62}, H_2O ⁶³ and various hydrocarbons^{64, 65} have been studied with this technique. Recent studies have shown the vibrational spectrum of the 4-0 band of HD and some hydrocarbons using PS-CRD at low temperatures.⁶⁶⁻⁶⁹

Cavity Ring Down Spectroscopy

Cavity ring-down (CRD) spectroscopy is a direct absorption technique, which can be performed with pulsed or continuous light sources and has a significantly higher sensitivity than obtainable in conventional absorption spectroscopy due to its extremely long effective path lengths (many kilometers) within a small physical space.

CRD spectroscopy consists of a laser source, an optical cavity, and a detector to measure the exiting light from the optical cavity. Figure 1 shows a characteristic pulsed cavity ring down diagram.

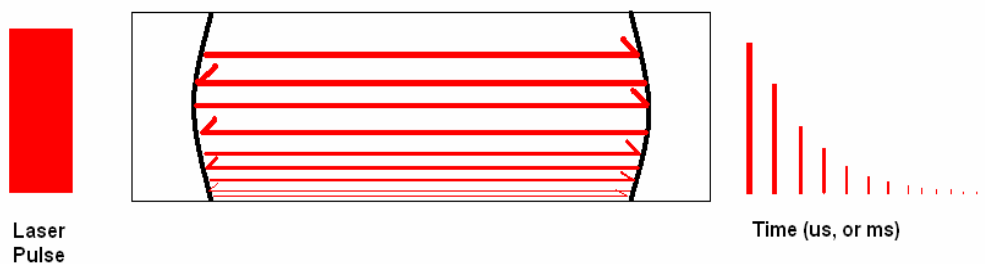


Figure 1. Pulsed Cavity Ring Down Diagram⁶⁶

In a typical ring down experiment the laser light is injected into a cavity formed by two highly reflective mirrors (reflectivity greater than 99.99 %). Aligning the mirrors in perfectly parallel configuration causes the incoming beam bounces back and forth between the mirrors or what is termed “Ringing Down”. The beam becomes trapped inside the cavity for a certain amount of time causing the long optical path length.

Due to the finite reflectivity of the mirrors, a small amount of light leaks out of the cavity. Then, the photo-sensitive detector placed behind the output mirror records the intensity of the small amount of light transmitted through it. The light intensity is

reduced by a given percentage on each round trip. The detector sees an exponential decay of light intensity. If short laser pulses are used, a very fast detector will see a train of pulses within an exponential decay envelope, but the time response of detection electronics usually means the pulses are smoothed into a single exponential curve. This is shown in Figure 2.

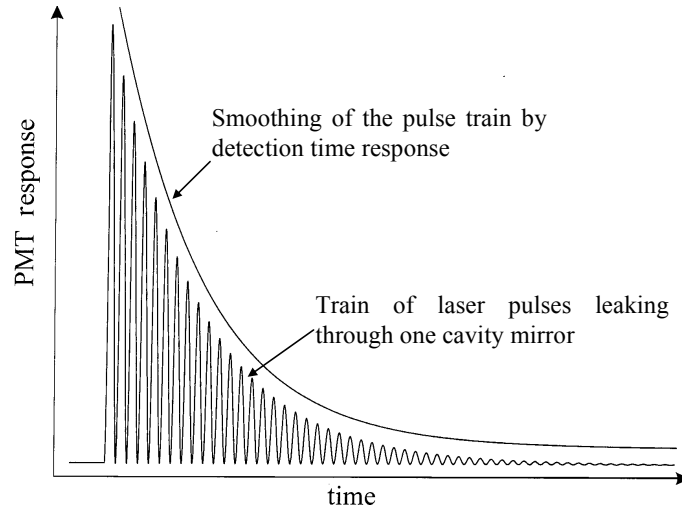


Figure 2. Exponential decay of laser light within the ring-down cavity⁷⁰

The intensity of the light transmitted (I) out of the cavity decreases as a function of time (t) and can be characterized as:

$$I(t) = I_0 e^{-(t/\tau)} \quad (1)$$

where I_0 is the initial light intensity detected and τ is the decay constant. This decay constant (τ) is commonly referred to as the ringdown time. This value can be from $1\mu\text{s}$ to $100\mu\text{s}$ or more depending upon mirror reflectivity.

The most common detection methods in cavity ring down spectroscopy are the exponential method and the phase shift method. Both methods can be used to obtain τ . The exponential CRD detection method uses an exponential fitting of the output signal

from cavity to measure the decay time. An exponential fitting program is used to obtain τ . Figure 1 shows a typical system where this detection method is used. The PS-CRD method measures the phase-shift of a modulated beam from the output beam of the cavity with respect to the modulated beam, or reference beam, before entering the cavity. The phase shift angle is related to the ring down time by the equation

$$\tan \theta = 2\pi f\tau \quad (2)$$

where θ is the phase shift angle and f is the frequency of modulation.

In Figure 3, a CW tunable laser source has been modulated, and is incident upon the optical cavity. An electro-optic modulator is used to create a square modulation frequency shape. Modulating the CW laser output produces an on/off pattern which translates into a filling/emptying of the cavity.^{66, 69}

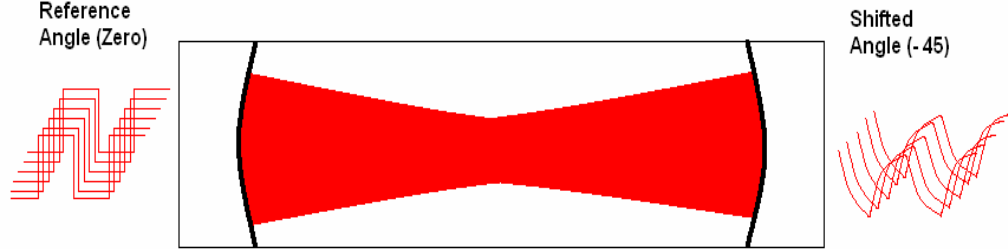


Figure 3. Phase shift cavity ring down diagram⁶⁶

The output signal from the cavity in Figure 3 resembles a shark fin. This can be described as light building up in the cavity on the positive slope side and light leaking out of the cavity on the negative slope side. The phase shift angle is monitored on the negative slope of the exiting wave. A better picture of this signal is shown in Figure 4. This figure illustrates the original signal (or reference signal) going into the cavity (bottom) and the phase shift signal detected after the beam traverses the cavity (top).

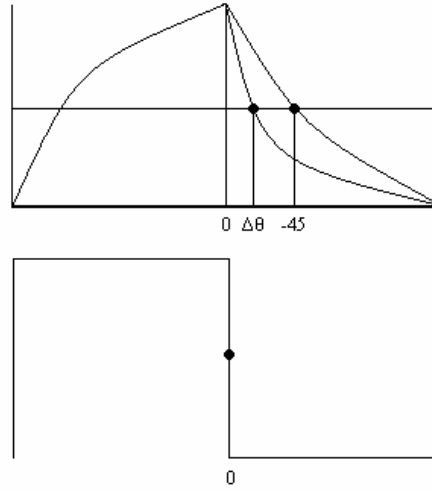


Figure 4. PS-CRD signal (top), Reference signal (bottom)

The PS-CRD signal is aligned to result in an empty cavity angle of -45. This is given by the $\tan(\theta)$ function shape. Figure 5 shows a graph of the $\tan(\theta)$ versus angle θ , where the boxed area shows to be fairly linear from -45 to 0 degrees. Angles greater than 45 are avoided because of the non-linear response of the PS-CRD system. The optical path length inside the cavity is the product (τc) where c is the speed of light.

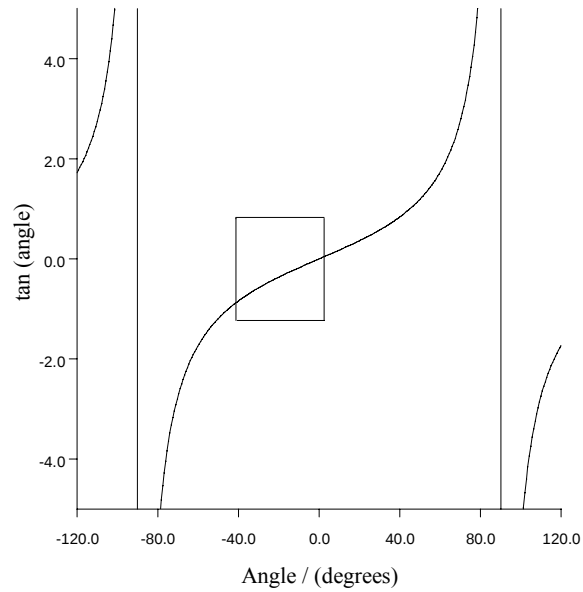


Figure 5. $\tan(\theta)$ versus θ graph

Absorption Spectroscopy

The absorption of light by a sample is described by the Beer-Lambert law which gives a quantitative relationship between the intensity of a spectral feature and the frequency-dependent absorption properties of the sample:

$$I = I_0 \exp(-\sigma C l) \quad (3)$$

where I is the transmitted intensity, I_0 is the incident intensity, σ is the absorption cross section of the sample at the wavelength of the measurement, C is the concentration of the absorber and l is the sample pathlength. The product of C and σ is the absorption coefficient, α , and the absorbance is defined as $\sigma C l$. From this equation, it can be seen that if the pathlength is long enough, very small concentration of sample or very weak absorption cross section can be detected.^{2, 70} Hence, CRD provides that long pathlength to make direct absorption measurements of either trace amount or weak absorptions.

The empty cavity ringdown time τ , is related to the distance between the mirrors and the reflectivity of the mirrors by the equation below:

$$\tau = \frac{L}{c(1-R)} \quad (4)$$

where L is the distance between the two mirrors, c is the speed of light, and R is the reflectivity of the mirrors. Thus, τ is a direct measure of the mirror reflectivity (R) because both c and L are known.

The presence of absorbing species in the cavity gives an additional mechanism for loss of light from the cavity by sample absorption speeds up the decay of the trapped light intensity. If the absorption follows Beer- Lambert law, the light intensity will still decay exponentially, with time dependence given by:⁵⁶

$$I(t) = I_0 \exp\left\{-\frac{t}{\tau} - \alpha ct\right\} \quad (5)$$

where α is the molecular absorption coefficient with respect to the wavelength, with dimensions of cm^{-1} , and c is the speed of light. The product of c and τ is the pathlength over which the absorption is measured. The decay rate is now given by

$$\frac{1}{\tau'} = \frac{1}{\tau} + c\alpha \quad (6)$$

Thus, the ring down time for a cavity filled by a absorbing gas, τ' , where the Beer-Lambert law is valid is described as:

$$\tau' = \frac{L}{c[(1-R) + \alpha(\nu)L]} \quad (7)$$

During a scan of the tunable laser in the absorption region of the sample, the ring down time (τ), is detected with the exponential fitting or the phase shift angle of the light that leaks out of the cavity. The decay time is determined as function of the wavenumber of the laser.

The decay time from the cavity filled with an absorbing gas is a combination of the sample plus the background (see equation 8), the inverse of the decay time of the empty cavity or background ($1/\tau_0$) is subtracted from the inverse of the decay time of the cavity filled ($1/\tau'$) in order to obtain the absorption of the sample

$$\alpha(\nu) = \frac{1}{c} \left(\left(\frac{1}{\tau'(\nu)} \right) - \left(\frac{1}{\tau(\nu)} \right) \right) \quad (8)$$

The calculated absorption ($\alpha(\nu)$ in cm^{-1} units) is plotted as a function of the wavenumber (cm^{-1}) to show the spectrum of the sample.

Conditions for CRD Signal

Some conditions are required to observe CRD signal. The Beer-Lambert behavior for a single pass of the light through the cavity has to be followed and the interference effects between the longitudinal and transverse modes of the cavity have to be minimized.

Beer-Lambert behavior. Beer-Lambert behavior requires that the widths of the absorption spectral lines are greater than the linewidth of the laser light within the cavity. This condition guarantees that all of the frequencies contained within the laser are attenuated by absorption when the laser is tuned to the central frequency of the absorption line.⁷¹

Optical cavity. A stable optical and non-confocal cavity is required for a CRD experiment. An optical cavity with two mirrors is said to be stable geometrically if the light is refocused within the cavity after successive reflections from the mirrors so that the optical energy is contained or trapped within the cavity. Formation of a stable optical cavity depends upon the g-parameters of the mirrors and optical cavity.¹ Specifically:

$$0 \leq g_1 g_2 \leq 1 \quad (9)$$

where g_1 and g_2 are defined as:

$$g_1 = \left(1 - \frac{L}{r_1}\right) \quad (10)$$

$$g_2 = \left(1 - \frac{L}{r_2}\right) \quad (11)$$

where L is the distance between the two mirrors, and r_1 and r_2 are the radiuses of curvatures of the mirror surfaces.

Having a non-confocal system is introduced some mechanical flexibility so that the mirrors can move slightly, and still retain an alignment with respect to each other. If the mirrors are at each other's focal length, any mechanical disturbance can result in a loss of alignment. This approach can be defined using the following relationship

$$r < d < 2r \quad (12)$$

$$0 < d < r \quad (13)$$

where d is the distance between the mirrors and r is equal to their radius of curvature, assuming $r=r_1=r_2$. Figures 6 and 7 show two configurations for a stable optical cavity system with mirrors placed outside of the radius of curvature and with mirrors placed within radius of curvature, respectively. The mode structure of such cavity can be made very dense, especially when d/r ratio is chosen to be an irrational number.⁶

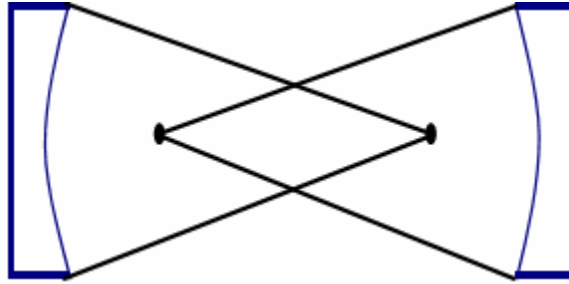


Figure 6. Stable optical cavity with mirror placed $r < d < 2r$

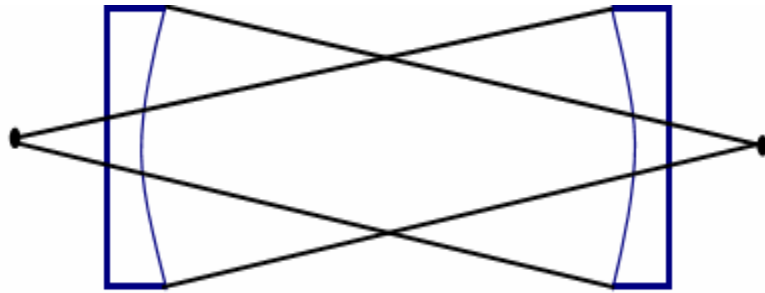


Figure 7. Stable optical cavity with mirror placed $0 < d < r$

Cavity modes. Mode structures of the cavity are another important aspect to be considered when one is working in CRD because of several problems can occur. When laser light is incident upon an optical cavity, modes of light are formed. Longitudinal and transverse modes (TEM) are possible. Transverse mode usually describe the cross sectional profile of a beam. Longitudinal (or axial) modes determine the resonant oscillation frequencies that satisfy the wavelength requirements of the cavity along a given optical path.¹

The available longitudinal mode frequencies that will be within an optical system are important considerations for a continuous scanning system like a CRD instrument. If the frequency spacing of the longitudinal modes of the cavity (the cavity free spectral range, FSR) exceeds the width of the spectral features being studied, the light of the appropriate frequency for excitation of certain spectral lines will not be injected into the cavity and the absorption features will be absent from the resultant spectrum.⁷²

Comparing the mode spacing to the line width of the laser allows for an idea of how an optical cavity will respond to a scanning CRD system. The frequency spacing ($\Delta\nu$) of longitudinal cavity modes (FSR) is defined as:

$$\Delta\nu = \frac{c}{2L} \quad (14)$$

where c is the speed of the light and L is the length of the cavity. Table 1 shows laser resolutions versus longitudinal mode spacing. As it is shown, the mode spacing is much smaller than our laser resolution giving us an overlapping multi-mode configuration. This is what makes continuous scanning possible.

Table 1. Mode Spacing Calculations

Cell length (cm)	Dye Laser Resolution (cm ⁻¹)	Ti:Sapphire Resolution (cm ⁻¹)	Longitudinal Mode Spacing (MHz)	Longitudinal Mode Spacing (cm ⁻¹)
43.5	0.07	0.17	345	0.0115

Off-Axis Alignment

For PS-CRD systems based on an on-axis alignment of the laser beam into the cavity, the coherent laser beam couples into the cavity on average only 5%⁶- 10 %⁷³ of the time. In order to increase the coupling-time efficiency, additional laser frequency dithering⁷³ and modulation of the cavity length have been applied. Also cavities with irrational number of cavity length to mirror curvature radius have been used.⁶ However, in the case of off-axis alignment of the cavity, when the laser beam has been injected into the cavity at an angle to the optical axis (off - axis), the beam may couple into the cavity continuously up to 100% of the time. This approach has been used for sensitive absorption measurements in phase-shift off-axis cavity-enhanced absorption spectroscopy (PS-OA-CEAS)⁷⁴⁻⁷⁶, off-axis cavity-enhanced absorption spectroscopy (OA-CEAS)⁷⁷⁻⁸³, wavelength modulation OA-CEAS (WM-OA-CEAS)^{77, 83, 84} and off-axis cavity ring down spectroscopy.⁸⁵

The off-axis laser beam cavity alignment decreases the cavity FSR and excites a large number of transverse cavity modes. The high number of excited cavity modes permits that cw laser radiation-cavity interaction to be considered as noncoherent on average.⁸³

Off-axis paths through optical cavities were first investigated in the mid-1960s.⁸⁶ this configuration spatially separates the multiple reflections within the cavity until the reentrant condition is fulfilled, that is the time at which the ray begins to retrace its original path through the cavity. This occurrence condition is dictated by the specific curvature and spacing of the mirrors forming the cavity.

Any stable cavity geometry can produce stable off-axis paths through the cavity, with the stability condition defined by equation (9).^{1, 80}

The previous analysis⁸⁶ demonstrates that the spot pattern on the mirrors generally lies on an ellipse. To maximize the circumference that can be fitted onto the mirror surface and thus the number of spots that can be accommodated without overlap, the elliptical form should be a circle near the edge of the mirrors, as shown in Figure 8.⁸³ The angle of a round trip rotation of the beam spot (2θ) is determined purely by the geometry of the cavity and is given by⁸⁶

$$\cos \theta = 1 - L / r \quad (15)$$

where L is the mirror spacing and r is the mirrors radius of curvature. The reentrant condition is satisfied if⁸⁶

$$2m\theta = 2n\pi \quad (16)$$

where m is the number of optical round-trip passes and n is a integer, and after every m round trips the ray starts to retrace its path.

In many respect, the properties of the cavity, including the longitudinal mode spacing ($\Delta\nu$), become similar to one that is m times longer. The longitudinal mode spacing of a cavity aligned off axis ($\Delta\nu_{\text{off-axis}}$) is

$$\Delta\nu = \frac{c}{m2L} \quad (17)$$

where c is the speed of the light, L is the length of the cavity and m is the number of optical round-trip passes. Using equations (15) and (16), m was determined only by the geometrical parameters of the cavity and not by the beam alignment. Table 2 shows m and n values obtained for two different radius of curvature, when $L = 43.5\text{cm}$, and $\Delta\nu$ for cavity aligned on-axis and off-axis.

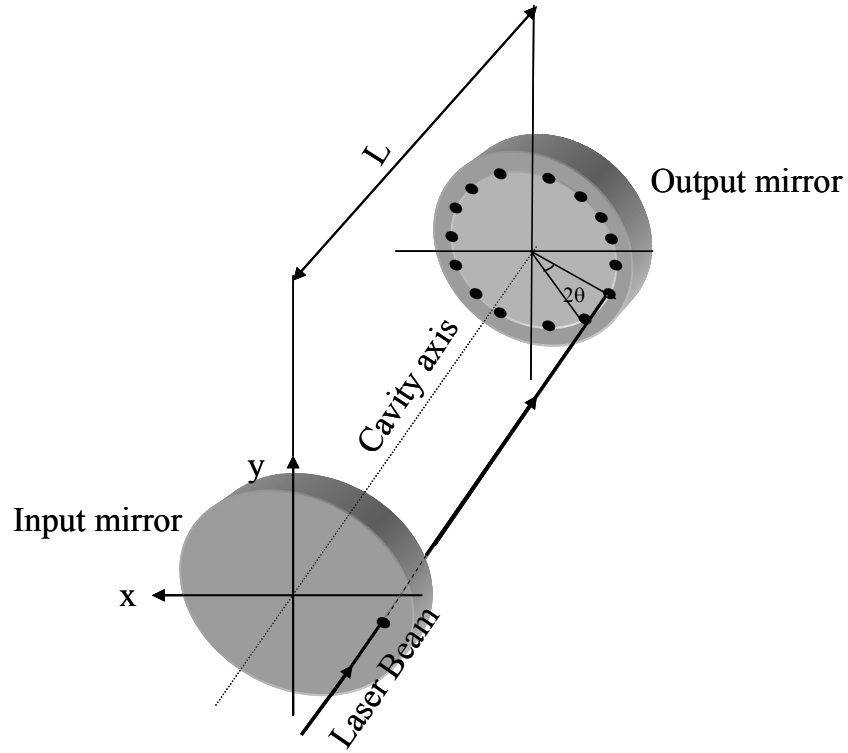


Figure 8. Off-axis beam propagation

Figure 9 shows predicted longitudinal mode spacing for a 43.5 cm cavity aligned on axis, Figure 9 (a), and off-axis, Figure 9 (b), when the reentrant condition is satisfied after 41 round trips. Off-axis alignment was used in present research to increase the time that the coherent laser beam couples into the cavity. This results in an improvement in detection sensitivity.

Table 2. Comparison between $\Delta\nu_{\text{off-axis}}$ and $\Delta\nu_{\text{on-axis}}$

R (cm)	m	n	$\Delta\nu_{\text{off-axis}}$		$\Delta\nu_{\text{on-axis}}$	
			$\text{cm}^{-1} \cdot 10^{-4}$	MHz	$\text{cm}^{-1} \cdot 10^{-4}$	MHz
600	41	5	2.8	8.4	115	345
100	26	8	4.4	13.3		

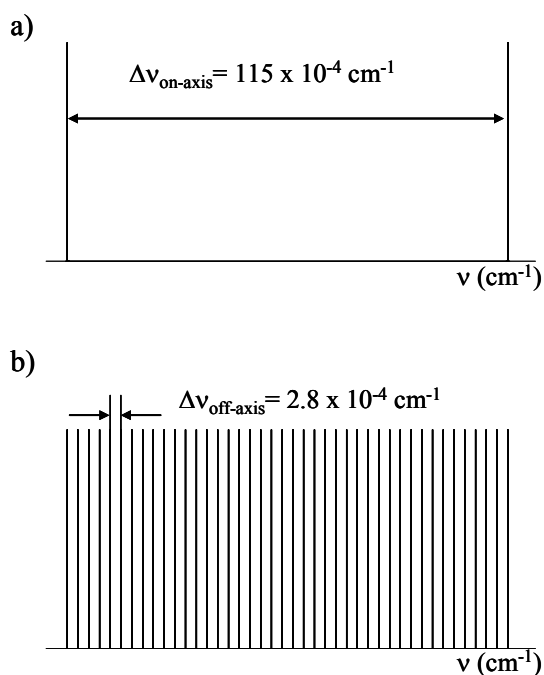


Figure 9. Predicted $\Delta\nu$ for a 43.5 cm cavity aligned (a) on axis and (b) off-axis when the reentrant condition is satisfied after 41 round

Vibrational Spectroscopy

The simplest possible assumption about the form of the vibrations in a diatomic molecule is that each atom moves toward or away from the other in simple harmonic motion. Such a motion of the two atoms can easily be reduced to the harmonic vibration of a single mass point about an equilibrium position. The potential energy in harmonic oscillator model can be approximated by a parabola, so it can be written as ⁸⁷

$$V = \frac{1}{2}k(x - x_e) \quad (18)$$

where k is the force constant of the oscillator, x_e is the equilibrium internuclear separation, and x denotes the instantaneous internuclear separation. Using this model, the permitted vibrational energy levels are defined by

$$E_v = h\nu_e \left(\nu + \frac{1}{2} \right) \quad (19)$$

where h is Plank's constant, ν_e is the fundamental frequency of a particular mode and ν is the vibrational quantum number. Harmonic oscillator selection rules only allow for transitions of $\Delta\nu = \pm 1$.

The harmonic potential is a good approximation for energies near the bottom of the well, corresponding to small displacements, but becomes poorer as the energy increases. It is, however, clear that in an actual molecule, when the atoms are at a great distance from one another, the attractive force is zero, and correspondingly, the potential energy has a constant value. Thus, the potential curve of the molecule has the form of the full curve in Figure 10.

The Morse function describes successfully the anharmonic character of atomic motion in vibrations, and it is defined as:

$$V(x) = D_e \left(1 - e^{-a(x-x_e)} \right)^2 \quad (20)$$

where D_e is the depth of the potential well, and a is an adjustable constant related to the curvature of the right-hand side of the well. The vibrational energy states for an anharmonic oscillator are defined as

$$E_v = h\nu_e \left(\nu + \frac{1}{2} \right) - h\nu_e x_e \left(\nu + \frac{1}{2} \right) \quad (21)$$

where x_e is the anharmonicity constant, defined as $x_e = h\nu_e/4D_e$ for the Morse oscillator. The anharmonicity factor makes that the selection rule $\Delta v = \pm 1$ is no longer strict, and other transitions become weakly allowed. This is the origin of overtones ($\Delta v_i = 2, 3, \dots$) and combination bands ($\Delta v_i = 1, 2, \dots; \Delta v_j = 1, 2, \dots$), appearing in the middle infrared spectrum along with fundamental transitions ($\Delta v = 1$). In general, for each increase in vibrational overtone, an approximate order of magnitude decrease in the signal size is experienced.⁸⁹

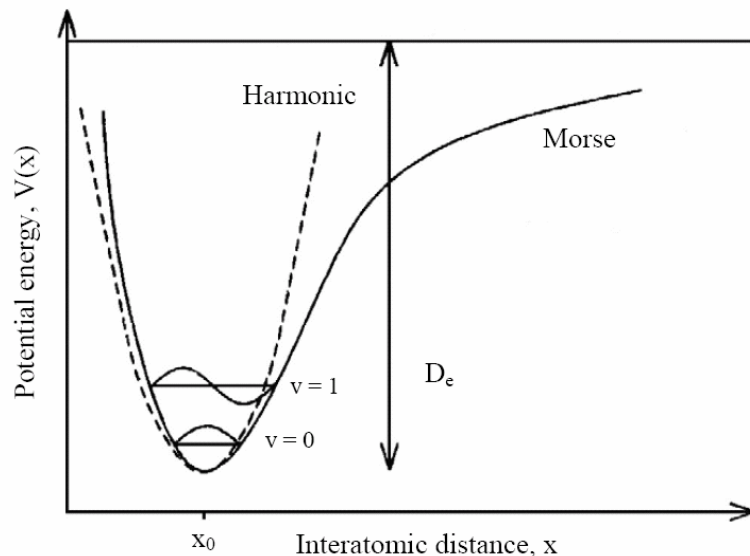


Figure 10. Approximate potential energy functions for a diatomic oscillator.⁸⁸

Local Mode Model

Conventionally, molecular vibrations are described in terms of normal modes. When a small amount of vibrational energy is placed in a molecule, the bonds behave like springs or harmonic oscillators. This behavior is the basis of the traditional normal mode model of molecular vibrations which is usually a good approach for fundamental

transitions. For example, the normal modes of water consist of a symmetric and an antisymmetric stretch and a bending mode.⁹⁰

When more and more vibrational energy is added to the molecule, the molecule will eventually dissociate, but it is unlikely to do so along one of the normal mode stretching coordinates. It is much more likely that the molecule will seek a low energy pathway for dissociation and break a single O—H bond. In other words it will dissociate along a local coordinate. As it can be observed in Figure 10, the higher the vibrational energy is, the less harmonic the vibration. The vibration becomes anharmonic, and it has been shown that in terms of a normal mode basis most of this anharmonicity is nondiagonal.⁹¹ In other words, the effect of anharmonicity is to mix the symmetric and antisymmetric stretching modes. The sum of these two is a local mode. Thus, as the vibrational energy increases and anharmonicity becomes more important, and it is expected the vibrational pattern to become more localized.⁹⁰

The local mode model of molecular vibration has been shown to successfully describe XH-stretching ($X = \text{C}, \text{N}, \text{O}$, etc) overtone spectra.^{91-94,59}

In the local mode representation the X-H bonds are considered as independent Morse oscillators with terms allowing for coupling to any equivalent bonds included as off-diagonal elements in the Hamiltonian.

Although local modes are anharmonic, the coupling of XH oscillators is well approximated by a harmonic coupling regime, and this characteristic is used in the HCAO model.⁹⁵⁻⁹⁷ The HCAO model allows straightforward calculations of state energies for XH stretching overtones and provides simple wave functions that are useful in calculations of overtone intensities. The HCAO model has been immensely useful

and has enabled spectroscopists to understand the structure of the spectra of highly excited vibrational states.⁹⁸⁻¹⁰⁵

CHAPTER TWO

Instrumental Methods and Procedures

This chapter describes instrumental setups and experimental procedures applied throughout the course of the research. The first part presents a complete description Cavity Ring Down (CRD) system. The cell design, cryostat, vacuum chamber, the two different instrumental setups (PS-CRD and exponential decay CRD) and the procedures are individually examined. Details of the instrument setup for the Fourier Transform spectrophotometer and the low temperature cryostat used for fundamental and low overtone studies are also discussed.

CRD Spectroscopy at Low Temperatures

CRD Cell Design

In order to use the CRD technique at low temperatures, the experiment required the design and construction of an optical cavity attached to a low temperature cryostat. Thus, a rigid system was designed using brass and aluminum as base metals. Brass and aluminum were chosen because both materials have acceptable values of expansion coefficient and thermal conductivity for use at cryogenic temperatures. It is important because materials used must be good conductors of heat to ensure thermal equilibrium throughout the cell. The sample cell contains a central cubic cell with two arms. The central cubic cell was made of yellow brass and its dimensions are $4 \times 4 \times 4 \text{ cm}^3$. Attached to each side of central cubic cell are aluminum arms. The arms are 197.5 mm in length and 12.7mm in internal diameter. They are attached to the central cubic cell

with screw head bolts and indium O-ring seals. These are necessary because rubber O rings would freeze and crack at cryogenic temperatures. Also, indium produces a metal-metal seal that is very rigid, creating minimal flexing during cooling. A small amount of cryo-putty is also applied between the two metal pieces to ensure proper thermal conduction. The resulting cell is 435 mm in length and 12.7 mm in diameter. The cell is connected to the external gas handling system through a small section of stainless steel tubing. Figure 11 shows sample cell, the central cubic cell with two arms and details of the central cubic cell (bottom) such as dimensions, center opening, screw on top for cryostat attachment, and a side Swagelok connector for sample introduction.

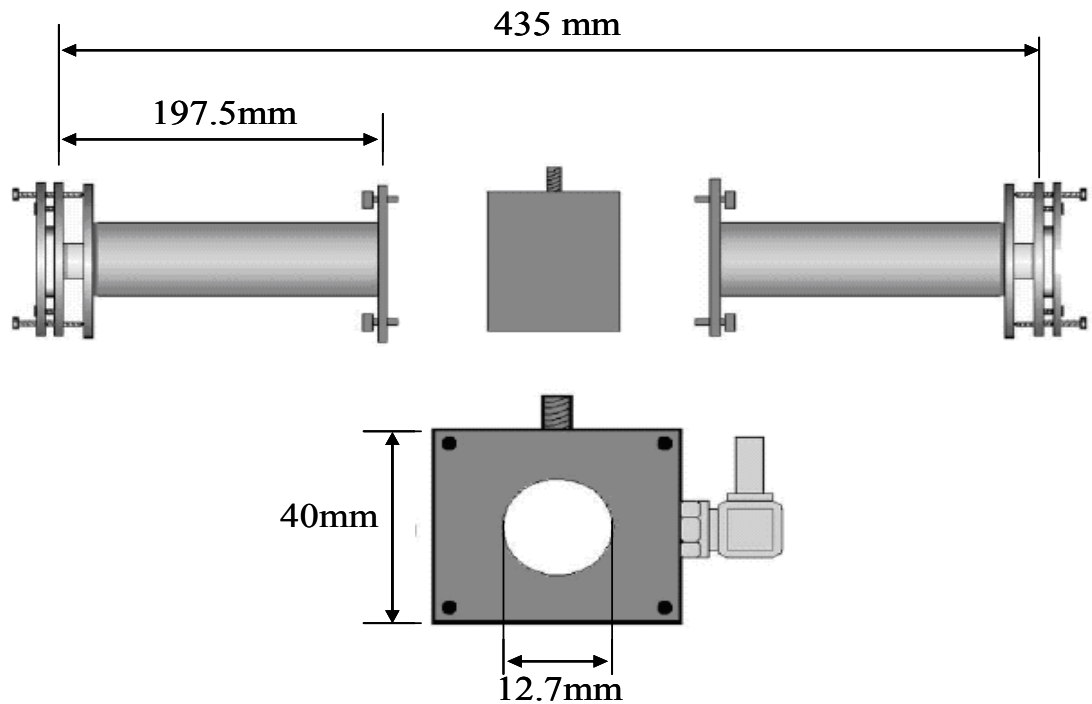


Figure 11. Schematic side view (top) of the CRD cell design. Schematic side view (bottom) of the center cubic cell

Figure 12 (top) shows a view of the right-hand side of the arm. Each arm consists of two flanges A and B that are constructed from an Aluminum solid piece. To

the left of flange A the cell diameter is 12.7 mm; between flanges A and B the cell diameter is reduced to 6 mm. Figure 12 (bottom) shows an expanded internal view with details of the right hand side of the arm. Where flange C is removable and is only used to hold one mirror of the cavity. There are four screws that are used to hold the mirror between the flanges B and C. Between the mirror and the surface of flange B a flat indium O-ring seals the cell from the vacuum that surrounds the cavity. There are four alignment screws that are threaded on flange B and stop on the surface of flange A. The system is very rigid but there is a small flexibility that allows aligning the mirrors with respect to the laser beam by rotating the alignment screws.

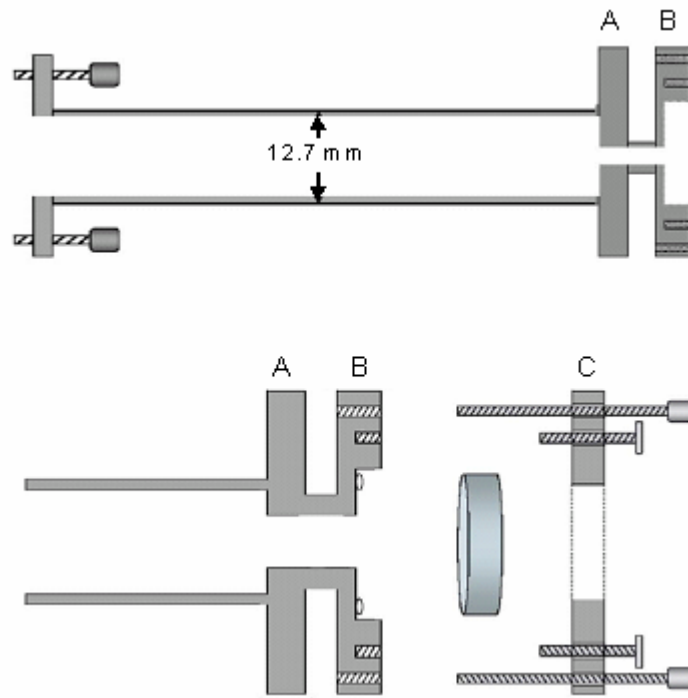


Figure 12. (Top) Schematic cross section of the right hand side arm. (Bottom) Expanded view of the right hand side of the arm, showing the indium O ring, mirror, as well as the flange and screws needed to hold the mirror.⁶⁷

After using this cell for several experiments it became apparent that it had to be modified in order to improve the CRD experiment. First, the alignment screws were

changed from 1/4" - 32 to 1/4" - 80 which meant that the number of threads per inch was increased. Using these new screws, a better alignment is possible. Second, to perform off-axis injection of the laser, the central openings of flanges A, B and C were increased to 12.7 mm. Figure 13 shows the front view from flange B with the two different central diameters. Third, the mirrors were placed in an aluminum enclosure to protect them from breakage when sealing the cell with indium o'rings (See Figure 13)

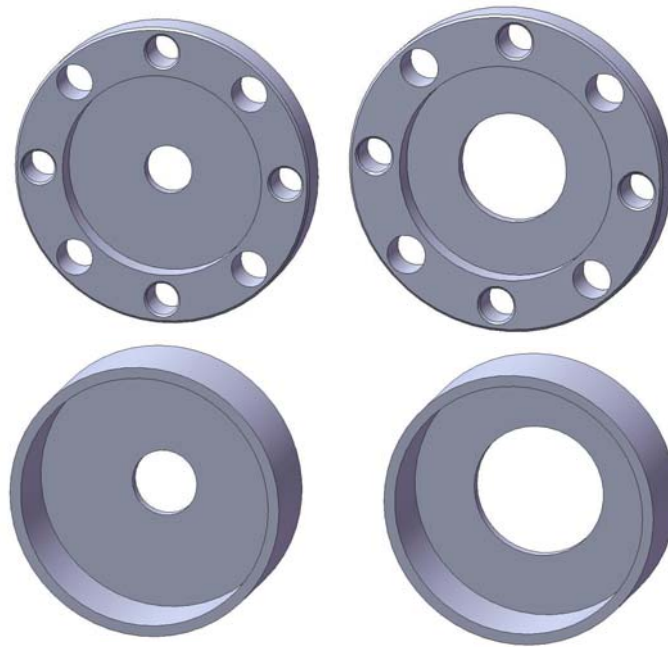


Figure 13. Top. Schematic comparison from front view of flange B. Central diameter = 6mm (left) Center diameter =12.7mm (right). Bottom. Schematic comparison from front view of aluminum enclosure used to protect the mirrors.

Three different sets of CRD mirrors were used depending on the wavelength region of interest. All of them have 20.32 mm in diameter. Table 3 summarizes bandwidth, radii of curvatures and listed reflectivity for CRD mirrors.

Table 3. Center wavelength, bandwidth and radii of curvatures for CRD mirrors

Mirror Set	Bandwidth nm	Radius of curvature m	Listed Reflectivity %
Los Gatos 760 nm	740 - 800	6	99.995
Los Gatos 722 nm	695 - 745	6	99.995
Newport 620 nm	583 - 663	1	> 99.9

CRD Cryostat and Vacuum Chamber

In order to use the CRD technique at low temperatures, the optical cavity was attached to a low temperature cryostat. The cryostat is basically a large liquid container that has a simple purpose. It supplies a continuous flow of liquid nitrogen or helium to a cold head that is attached to the CRD cell. It also contains a heater in the cold head which allows equilibrium temperatures to be obtained. The cryostat was obtained from International Cryogenics Inc. The central dewar which cools the cell can hold up to 12 L of liquid He or N₂ and is insulated by another 10 L of liquid N₂ to control boil-off. Connection of the CRD cell and cold head was achieved with a copper block, termed the "cold block", to allow for thermal contact and cooling of the cell. The complete cell (including the mirrors) is inside a vacuum chamber that thermally insulates the cell and the cold head of the cryostat from the environment. Figure 14 illustrates the cell as it looks attached to the cryostat and the vacuum jacket used.

The cryostat has four vacuum ports; one is the connection from the cell to the sample system. Two ports are used to measure the vacuum pressure of the cryostat.

Other port allows access to the electrical wires for the temperature. Two thermocouples are connected to a temperature controller that measures the temperature of the cold block and the cell. The heating resistor to change the temperature of the cell is located on the cold block.

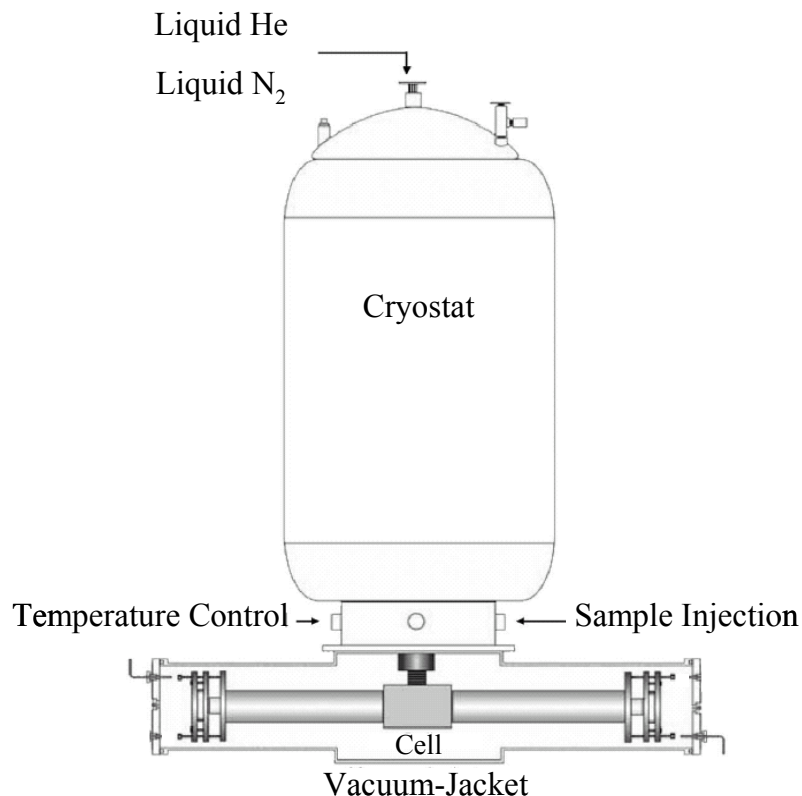


Figure 14. Schematic view of the cryostat and CRD optical cavity isolated inside a vacuum jacket.⁶⁷

The vacuum around the cell is created by using an Edwards Model 8 vacuum pump to rough the system to about 50 mTorr. A CTI cryogenic vacuum pump is then used to obtain a vacuum below 1×10^{-7} Torr.

Temperature control is achieved by balancing cooling available from cryogen flow against an electrical heater. Cryogen flow is controlled by a micrometer adjustment valve located on top of the cryostat. By opening the micrometer valve, the

liquid is allowed to flow through the cold block of the cryostat where the cell is attached. The more the valve is opened, the faster the cryogen flows through the head and the faster the system cools down.

Because of the flexing of the cell as cooling takes place, the system cannot be allowed to cool down too rapidly; otherwise alignment of the laser beam will be lost. There is also a risk of thermally shocking the mirrors which could result in cracks. Opening the micrometer valve to a setting of 35 μm allows for a cooling rate of approximately 0.40 K per minute. The temperature controller can be set to a desired temperature which is maintained by a heater attached to the cold block of the cryostat. The temperature difference between the cold block and the cell is approximately 8 K. This difference in temperature is the result of inefficient thermal energy transfer between the cold block of the cryostat and the cell at such low temperatures. It has also been found that the cryostat is very efficient, only needing cryogen filling once every other day, even when working at low temperatures.

To allow a laser beam to traverse the cell cavity and still be able to adjust the mirrors for alignment while under vacuum, manipulation devices were constructed of Plexiglas to fit on the ends of the vacuum jacket. Figure 15 shows an expanded view of the arm inside the vacuum jacket and how the alignment screws are positioned with respect to the external Allen wrenches.

A transparent Plexiglas flange (12.5 mm thickness) is held onto the ends of the vacuum jacket and sealed with Viton O rings. A sapphire window is placed at the center of the Plexiglas flange to allow for beam propagation.

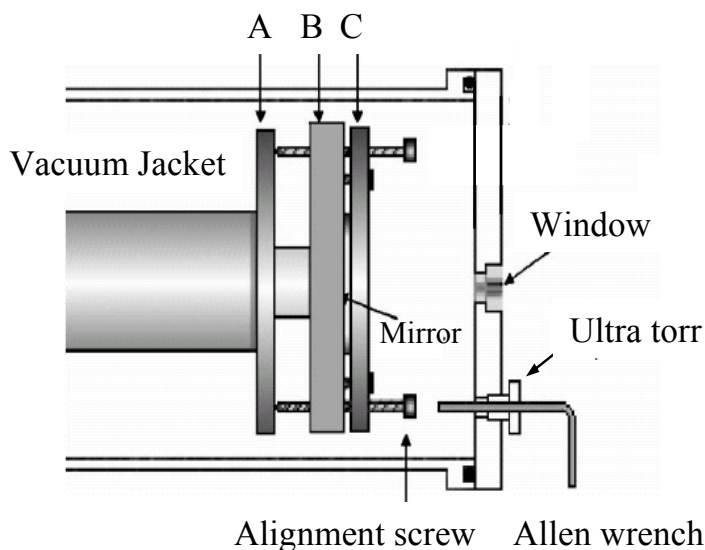


Figure 15. Schematic side view (top) of the right-hand side of the optical cavity and vacuum jacket indicating the position of the alignment screws.

The alignment of this rigid system sometimes changes slightly. In cases like this, the Allen wrench shown in Figure 5 has to be used to make a small rotation to one of the alignment screws. A vacuum tight seal is obtained around the Allen wrenches that are introduced into the vacuum jacket through ultra-torr connectors. The Allen wrench only touches an alignment screw when it is necessary to make a small correction for alignment at low temperature.

Instrumental Setup: PS-CRD Spectroscopy.

The experimental setup is shown in Figure 16. The pump laser is a solid state, frequency doubled Neodymium Yttrium Vanadium Oxide (Nd: YVO₄) laser (Coherent-Verdi) providing single wavelength (532nm) at a power of 5W. This laser is used to pump a continuous wave (Coherent 899) Ti:Sapphire ring laser with a scanning range between 700 to 800 nm or 12500-14300 cm⁻¹. Wavelength tuning of the (0.17 cm⁻¹

bandwidth) laser is accomplished with a birefringent filter driven by a stepper motor. The stepper motor is controlled with a microcomputer. The output of the Ti:Sapphire laser is passed through a Conoptics model 350-50 electro-optic modulator (EOM) to modulate the beam into a square wave of a specific frequency. The EOM is driven by a Stanford Research Systems (SRS) function generator. The beam is injected off-axis into the optical cavity and aligned by superimposing reflections of the highly reflective mirrors that create the cavity. The light that leaks out the back of the off-axis aligned cavity is focused by a lens and is detected by a Hamamatsu photomultiplier tube (PMT) powered by a high voltage power supply. The signal is sent to a Low-Noise Pre-Preamplifier (SRS) for signal conditioning. After that, it is analyzed by a Lock-In amplifier (SRS 830) where the phase angle is determined and then sent to a computer via a GPIB interface where it is processed by a LabView program written specifically for this system. The program also controls the stepper motor which drives the micrometer screw on the Ti:Sapphire laser allowing scanning to be accomplished. To obtain a reference signal, the cell can be bypassed. The whole system sits on top of a Newport 4' by 10' by 8' optical table which has vibration isolation legs to eliminate mechanical noises from the building itself.

Instrumental Setup: Exponential Decay CRD Spectroscopy.

The experimental setup is depicted in Figure 17. The second harmonic output at 532 nm of a Nd: YAG laser (Quanta-Ray DCR) is used to pump the dye-laser (Quanta-Ray, PDL-3), with a 10 Hz repetition rate. The dye laser works in the range of the DCM dye, between 600 to 680nm, with a laser pulse duration of 6ns and bandwidth of 0.07cm^{-1} . The dye laser output energy is attenuated by placing a neutral density filter at

the output. The optical density (OD) of the filter is equal to one. The output beam is shaped with the use of a simple telescope made by means of two lenses and a 100 μ m pinhole between them. The beam is injected off-axis into the optical cavity and aligned by superimposing reflections of the highly reflective mirrors that create the cavity. The size of the beam injected into the cell is controlled by using an iris.

The light that leaks out the back of the aligned cavity is focused by a lens and is detected by a Hamamatsu photomultiplier tube powered by a high voltage power supply then sent to a SRS Low-Noise Pre-Preamplifier for signal conditioning. A digital oscilloscope (Lecroy, 9310C) is used to measure the CRD decay curves. A digital delay/ pulse generator (SRS, DG535) distributes the trigger signal to the pump laser and the digital oscilloscope. The signals were measured by averaging 21 shots and sent to the computer via a GPIB interface where it is processed by a LabView program written specifically for this system. The program also controls the stepper motor in the pulse dye laser allowing scanning to be accomplished. The whole system sits on top of two Newport 4' by 10' by 8' optical table which has vibration isolation legs to eliminate mechanical noises from the building itself.

Experimental Procedure

Off-Axis Alignment. The first stage of the experiment consists in checking the light source, making sure that it is well aligned, and at peak operating performance and power. This operation is carried out by following the optimization procedure found in each laser manual. The laser wavelength has to be adjusted to match the maximum reflective wavelength of the mirror set that will be used in the optical cavity.

Using a mirror or prism periscope assembly placed in front of the cell, the laser beam is passed through the center of the mirror-less CRD cell. After these are set they should not be moved until the on-axis alignment is complete. Next step is to place the rear mirror on the cell, it must be clean prior to use. First using an indium o-ring as a seal, make sure the reflective side is facing toward the sample cell. The mirror should be tightened to the cell to create a vacuum tight seal between the mirror, indium, and cell. Some finesse must be used here to ensure too much pressure is not put on the mirrors or they might be damaged. In order to see the back reflection of the laser beam coming from the rear mirror, a pinhole needs to be placed between the periscope assembly and the CRD cell.

Next, the back reflection must be superimposed onto the laser beam coming through the pinhole using the Allen adjustment screws on the rear mirror. After that, the front mirror is placed onto the cell just like the rear mirror. The back reflection from this is then superimposed following the same procedure for the back mirror. The above steps should get the alignment close, but more steps are needed.

To measure the CRD signal, the photo multiplier tube (PMT) is placed facing the rear mirror, the voltage is set at 900V. Using an Allen wrench small rotations of the alignment screws are made until a signal is detected on the oscilloscope. This procedure could take a little while depending on the initial alignment.

If the Phase shift method is used, once the CRD signal is obtained it is necessary to set the reference angle on the lock-in amplifier. The zero phase shift is obtained by bypassing the cavity using turning mirrors to place the beam into the side hole of the PMT. A square wave should be seen on the oscilloscope. Thus, the reference angle is

set in the lock-in amplifier by pressing the reference button located next to the phase angle display. This step is not necessary when the pulsed laser is used. With small rotations of the alignment screw, the CRD signal can be optimized. At this point the alignment of the CRD cell is on-axis. Using the periscope assembly, the incoming beam can be moved gradually off-axis of the cavity. This means that the laser beam is moving to the left or right side up to 5 or 6 mm off the center axis. Selection of the direction left or right depends only the initial alignment. In the completed process the CRD signal needs to be monitored with the oscilloscope. With small adjustments of the alignment screws in the front mirror, the CRD signal can be optimized. After that, a lens is placed between the cell and the PMT to collect the output light from the cavity. Also, an iris is placed behind the lens to decrease the beam power and scattered light.

This procedure should produce a useable CRD signal. One more step is necessary when the PS-CRD system is aligned. After the maximum obtainable angle is found, the frequency of modulation must be adjusted up or down to obtain a -45° angle. Some final adjustments will need to be made to tweak the signal, but these come from experience and practice.

Cryostat operation. Before filling the cryostat with liquid nitrogen, the vacuum jacket around the cell must be in place and the vacuum applied. While, using the cryo pump a pressure of 10^{-7} torr should be maintained within the system. At this point the CRD signal must be optimized. This signal is monitored throughout the whole process. The next step is turn on the temperature controller unit and set the temperature to room temperature. This maintains an equilibrium temperature and ensures that the cell does not cool by itself. The next stage of the experiment consists in filling the cryostat with

liquid nitrogen. Before filling the cryostat, the cooling valve on the cryostat has to be closed. The caps of the outer Dewar are taken off and the cap on the center Dewar is kept closed to avoid water condensation inside of it. The filling operation is carried out by manually pouring the cryogen into the outer Dewar using a funnel. A 10-cm copper tube supports the funnel and allows boiled-off nitrogen to escape through several vent holes. When the outer Dewar is full the caps are replaced. To fill the center Dewar the procedure above is repeated. Because the center dewar does not have an outlet, it is possible to know that the dewar is full when liquid nitrogen begins to spill out the side of the spacer. After the Dewar is full, the cap is replaced. Complete filling takes approximately three hours.

As the liquid nitrogen is added the cryostat might shift so adjusting the alignment might be necessary at this point. To reach the thermal equilibrium in the system, two hours are required.

The cool down process starts by setting the temperature controller to a lower temperature. Usually it is a good idea to set at 20 K increments to let the cell cool slowly. It can be thought of as a back-up just in case something goes wrong.

The micrometer screw on the top of the cryostat is then open to around 25 μm . This allows for the liquid nitrogen to start flowing through the cryo head and cooling of the cell to begin. After the temperature of the cell reaches 220K, it has been found that the micrometer position can be opened gradually between 25 to 75 μm to increase the rate of cooling until 0.45 K per min. If the valve is opened more than that, only icicles will form on the output, and the system does not seem to cool any faster. The time required to reach the lowest temperature with liquid nitrogen (88 K in the cell) takes

approximately 8 to 10 hours. The cooling operation is generally followed graphically using a LabView program (Temp Monitor.llb). It must be emphasized that the alignment must be monitored during the cool down process. If the alignment of this system changes slightly, the vacuum manipulator (Figure 5) can be used to adjust the alignment. Once thermal equilibrium is achieved it becomes very stable and no adjustments are required for several days. The cryostat holds liquid nitrogen very well and only needs to be filled about every two days.

Fourier Transform Spectroscopy at Low Temperatures

Spectrometer Description

To observe vibrational transitions between 2500 and 15750 cm^{-1} a Nexus 670 spectrometer from Thermo Nicolet was used. The instrument is controlled with the OMNIC software, which provides an interface to easily operate and optimize the spectrometer performance. Appropriate combination of source, beam splitter and detector allows collection of spectra in the visible and infrared. Table 4 shows the combination of parameters used in different spectral regions, chosen according to manufacturer recommendations and experimental testing.

Table 4. Combination of instrumental parameters for FTIR Spectrometer.

Spectral range (cm^{-1})	Beamsplitter	Detector	Source
2500-11000	XT-KBr	DTGS-KBr	White
8600-15750	Quartz	Si	White

Cryostat, Sample Cell and Vacuum Chamber

An APD Cryogenics Heli-tran model LT-3-110 system was used for sample cooling. The cryogen (liquid nitrogen) is forced to flow through a transfer line to the cryostat cold head by pressurized nitrogen (5 psig) and then spread out from a needle valve. Flow of liquid nitrogen (or helium) is regulated by the needle valve at the tip of the cryostat head. The cryostat is equipped with five ports: coolant exhaust, vacuum pump-out, electric feed through, BNC terminal, and a vacuum metering point. In order to avoid freezing of electrical components, a vent gas heater within the cryostat head is operating when the cryogen is flowing.¹⁰⁶⁻¹⁰⁸

The cell is a copper cylinder 35 mm in external diameter, 1.2 cm in internal diameter and 50 mm in length. Sapphire windows are mounted at each end of the cell. The windows are 2 mm thick and 20 mm in diameter. The cell windows are sealed with indium O'rings and fastened to the cell with flanges. The cell is fastened to the cryostat cold head and is connected to an external gas handling system through a small section of stainless steel tubing of 3.17 mm in diameter.

A Scientific Instruments 9650 temperature controller and indicator is used to control the cell temperature from 300 to 2 K. Silicon diode sensors in the cryostat head and the sample cell provide temperature readings displayed by the controller (SI-9650).

The vacuum chamber consists of a cylindrical aluminum unit 18.5 cm in length and 11.5 cm in external diameter with four windows. Two of them are Sapphire (2.5 cm in diameter and 0.6 cm thick) and parallel to and in line with the ones of the cell. The other two are quartz windows and parallel to each other. Flanges and screws are used to attach the windows to the chamber. O'rings (Viton) are used to make a vacuum

tight seal. Rough vacuum of the system is carried out by a mechanical pump, while high vacuum ($<10^{-6}$ Torr) is achieved with a diffusion pump. The standard cell holder is removed from the FTIR spectrometer and the low temperature cell housed in the aluminum vacuum chamber with the Sapphire windows is placed in the path of the beam. Figure 18 shows schematics of the cryostat, sample cell and vacuum chamber used in FT experiments at low temperature.

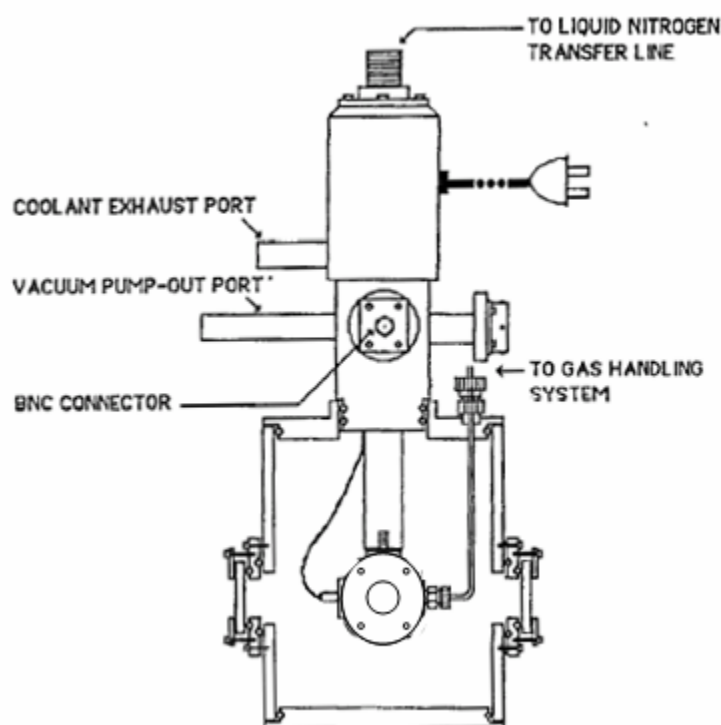


Figure 18. Schematics of the cryostat, sample cell and vacuum chamber used in FT experiments at low temperature.¹⁰⁷

Experimental Procedure

Cryostat Operation. The first stage of the experiment consists in filling a 100 liter Dewar with liquid nitrogen. This operation is made by flowing liquid nitrogen through the Dewar until it is full. This Dewar can hold up to 52 L of liquid He or N₂.

The transfer line bayonet is introduced inside the Dewar and securely fastened with a rubber sleeve and hose clamps. The Pressurization necessary to push cryogen through the transfer line is provided by an appropriate connection to the laboratory nitrogen line. The pressure is then adjusted about to 5 psig. The adjustment knob (needle valve) on the cryostat head and both flowmeters must be open to allow liquid nitrogen to flow. The cryogen starts to flow through the transfer line to the cryostat cold head within 20 minutes. At this point, the vent gas heater must be plugged in to avoid freeze damage of electrical components. The SI-9650 controller can be turned on, providing a 25-V setting for the heater output voltage. Complete cool down process, time required to reach the lowest temperature with liquid nitrogen (84 K in the cell) takes approximately 30 minutes. Upon stabilization, the adjustment knob on the cryostat head should be closed almost completely to save cryogen. Accurate control of liquid nitrogen flow is able with the flowmeter. A setting of 15 to 20 mm on the flowmeter provides a suitable amount of cryogen for operation at all temperatures. Wait 30 minutes for temperature stabilization before acquiring any spectra. Using the SI-9650 a new temperature can be set and controlled.

CHAPTER THREE

High Vibrational Overtone ($\Delta\nu = 5$) Spectra of Ethylene and Dideuteromethane. C-H Spectra ($\Delta\nu = 1-4$) of CH_3D

The chapter is divided in two different sections. The first section presents measurements of the ($\Delta\nu = 5$) C-H stretching overtone spectra of ethylene (C_2H_4) and dideuteromethane (CH_2D_2) using Phase Shift Cavity Ring Down (PS-CRD) spectroscopy at 295K and 140K between 13300 to 14300 cm^{-1} . The path length used in these experiments was 2 Km. In order to show the effectiveness of the PS-CRD system, the integrated absorption bands of high vibrational overtones were measured. The band strength values were calculated and compared with values found in the literature using other techniques.

The second section shows the spectra of CH_3D around the C-H fundamental and overtone transitions. Measurements were made using a White cell having a path length of 7.2 m and a commercial Fourier Transform (FT) spectrophotometer. The local mode parameters, the harmonic frequency (ω), the anharmonicity (ωx) and the interbond coupling parameter (λ) were obtained from the experimental data and were used with the Harmonically Coupled Anharmonic Oscillator (HCAO) model to calculate frequencies and assign absorption bands.

Ethylene (C_2H_4): C-H ($\Delta\nu = 5$) Vibrational Overtone Absorption

The fourth vibrational overtone of the C-H stretch in C_2H_4 was used to test the PS-CRD measurements because its absorption spectrum and band strength values are well known.^{109,64,110} The ($\nu=0\rightarrow5$) high vibrational overtone of C_2H_4 shows a single

absorption band corresponding to the symmetric stretch of the C-H bonds. Figure 19 shows the pressure series of six separate measurements ranging from 66 Torr to 20 Torr of Ethylene taken at 295K. The figure shows the reproducibility and sensitivity of the PS-CRD measurements. Table 5 presents the band maximum, the band absorption, and the full width at half maximum (FWHM) of each pressure.

Table 5. ($\Delta v=5$) C_2H_4 at 295 K, Pressure, Band Maximum, Band Absorption, and FWHM.

Pressure (torr)	Band Maximum (cm^{-1})	Band Absorption ($10^{-6} cm^{-1}$)	FWHM (cm^{-1})
66	14079.4	4.46	102.2
56	14078.5	3.76	102.6
36	14079.0	2.69	102.8
30	14078.4	2.24	103.2
26	14078.8	1.88	102.0
20	14079.7	1.43	103.0
Avg.	14078.9 ± 0.5		102.6 ± 0.4

The average band maximum was at $(14078.9 \pm 0.5) cm^{-1}$ and the FWHM average was $(102.6 \pm 0.4) cm^{-1}$. Band absorption intensities decrease linearly with decreasing pressure as expected.

In order to obtain the band strength values (S_0), the integrated absorption (S) has to be obtained. The integrated absorption, in cm^{-2} , is represented as

$$S = \int \alpha(\nu) d\nu \quad (22)$$

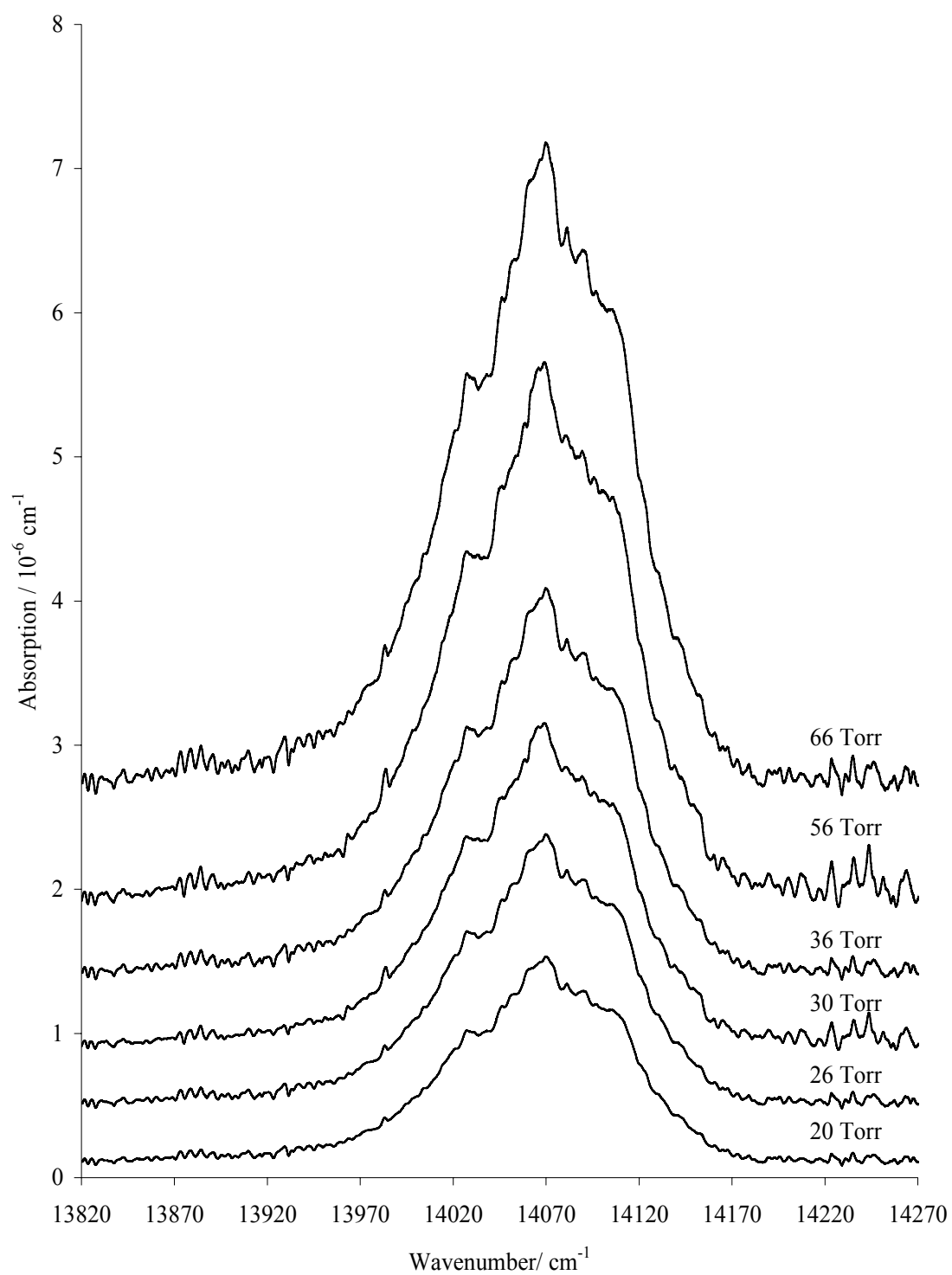


Figure 19. ($\Delta v = 5$) C_2H_4 Absorption Pressure Series at 295 K

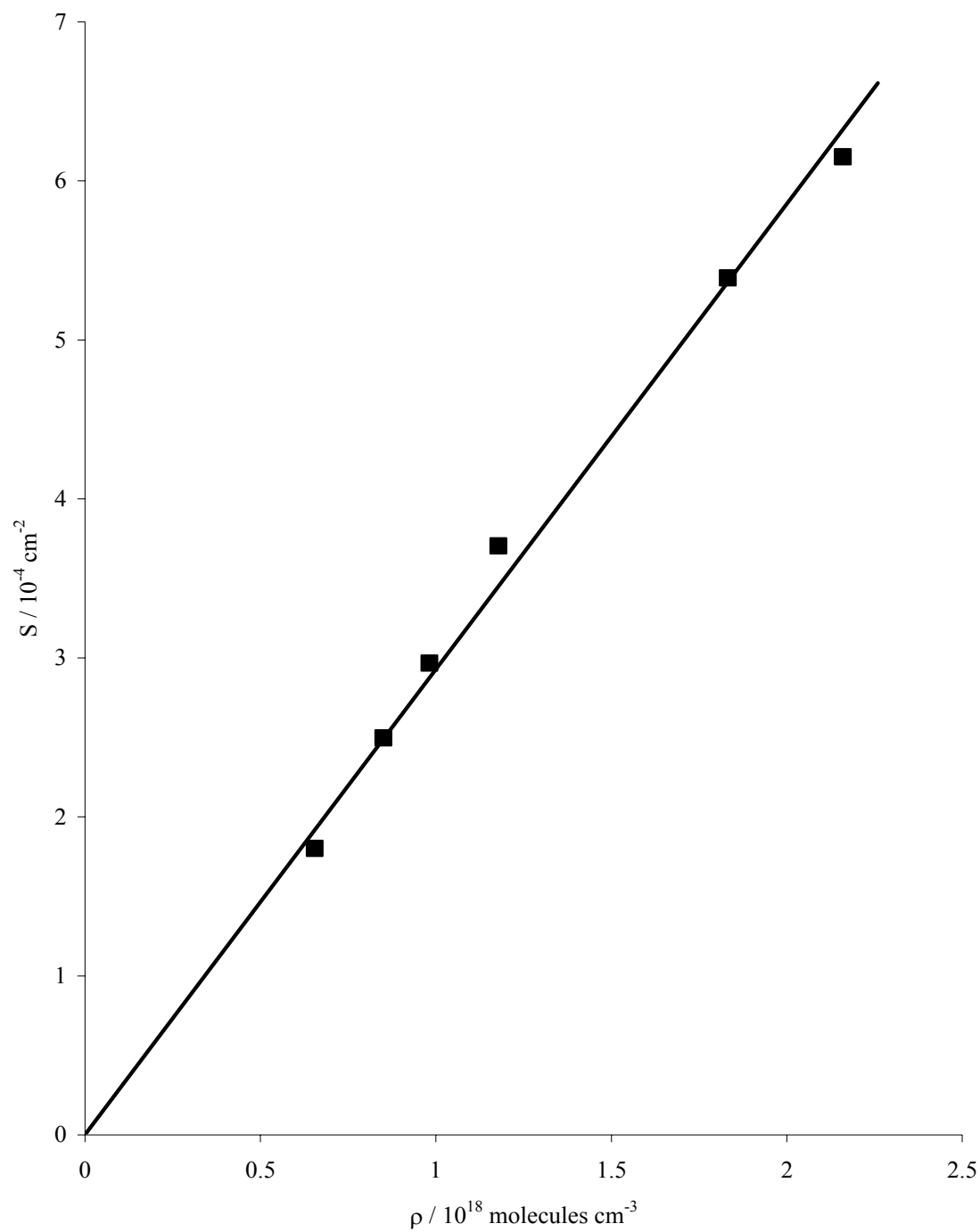
and the band strength, in $\text{cm}^2 \text{cm}^{-1} \text{molecules}^{-1}$:

$$S_0 = \frac{S}{\rho} = \frac{1}{\rho} \int \alpha(\nu) d\nu \quad (23)$$

where ρ is molecular density. The actual band strength is obtained by plotting the integrated absorptions vs. densities to obtain a linear plot, since measurements for multiple pressures are obtained. The resulting slope of the line obtained gives the S_0 value. Figure 20 is a plot of the integrated absorption (S), versus the molecular density (ρ) at each pressure. The figure shows that the integrated absorption is linear over the range of densities covered and the slope of the fitted line gives the band strength S_0 . In Table 6 the calculated molecular densities (ρ), integrated absorption areas (S) and calculated band strengths (S_0) are given.

Table 6. ($\Delta\nu=5$) C_2H_4 at 295K, Pressure, ρ , S and S_0 .

Pressure torr	ρ $10^{18} \text{ molecules cm}^{-3}$	S 10^{-3} cm^{-2}	S_0 $10^{-22} \text{ cm}^2 \text{cm}^{-1} \text{molecule}^{-1}$
66	2.1597	6.15	2.85
56	1.8324	5.39	2.94
36	1.1780	3.70	3.14
30	0.9817	2.97	3.02
26	0.8501	2.50	2.94
20	0.6544	1.80	2.75
Avg			2.9 ± 0.1



$$S_0 = (2.9 \pm 0.1) \times 10^{-22} \text{ cm}^2 \text{ cm}^{-1} \text{ molecules}^{-1}$$

$$R^2 = 0.992$$

Figure 20. ($\Delta v = 5$) of C_2H_4 at 295 K S vs. ρ . Slope is S_0 .

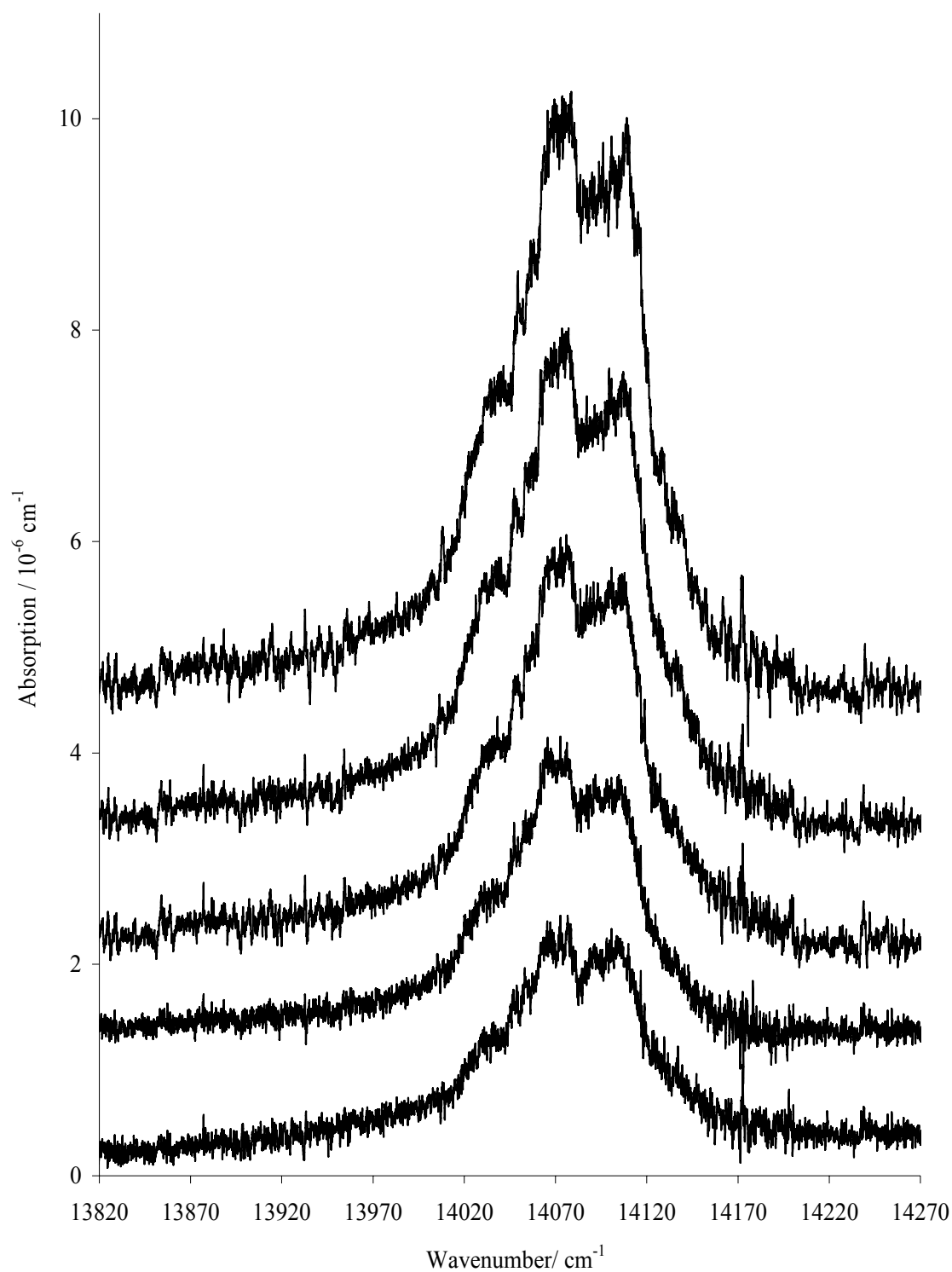


Figure 21. ($\Delta v = 5$) C_2H_4 Absorption pressure series at 140 K.

The C-H ($\Delta v = 5$) transition of ethylene was also measured at low temperatures to demonstrate the effectiveness of the low temperature system. Figure 21 shows a pressure series of ethylene at 140K. Spectra were obtained at pressures of 30, 25, 20, 15, 10, 5 Torr. Table 7 shows the band maximum, band intensity and the FWHM for each pressure. Comparison with Table 7 shows that the FWHM of the low temperature spectra is about 18 cm^{-1} less than the room temperature spectra. This is the result of the decrease in inhomogeneous broadening caused by the reduction of the number of thermally populated levels within the molecule. Table 8 reports the density, the integrated absorption band, and the band strength values for each individual pressure. Figure 22 shows the plot of S versus ρ to find the S_o value for ethylene.

Table 7. ($\Delta v=5$) C_2H_4 at 140K, Pressure, Band Maximum, Band Absorption, and FWHM

Pressure (Torr)	Band Maximum (cm^{-1})	Band Absorption (10^{-6} cm^{-1})	FWHM (cm^{-1})
30	14078.65	5.63	84.4
25	14077.12	4.70	84.0
20	14077.34	3.69	84.2
15	14078.00	2.59	84.5
10	14076.98	2.16	85.4
Avg.	14077.6 ± 0.6		84.5 ± 0.5

The band strength for Ethylene at 140K is $(3.0 \pm 0.1)10^{-22} \text{ cm}^2 \text{ cm}^{-1} \text{ molecules}^{-1}$ which is very good agreement with the room temperature value of $(2.9 \pm 0.1) 10^{-22} \text{ cm}^2 \text{ cm}^{-1} \text{ molecules}^{-1}$. A plot of the two different pressure series data shown in Figure 23

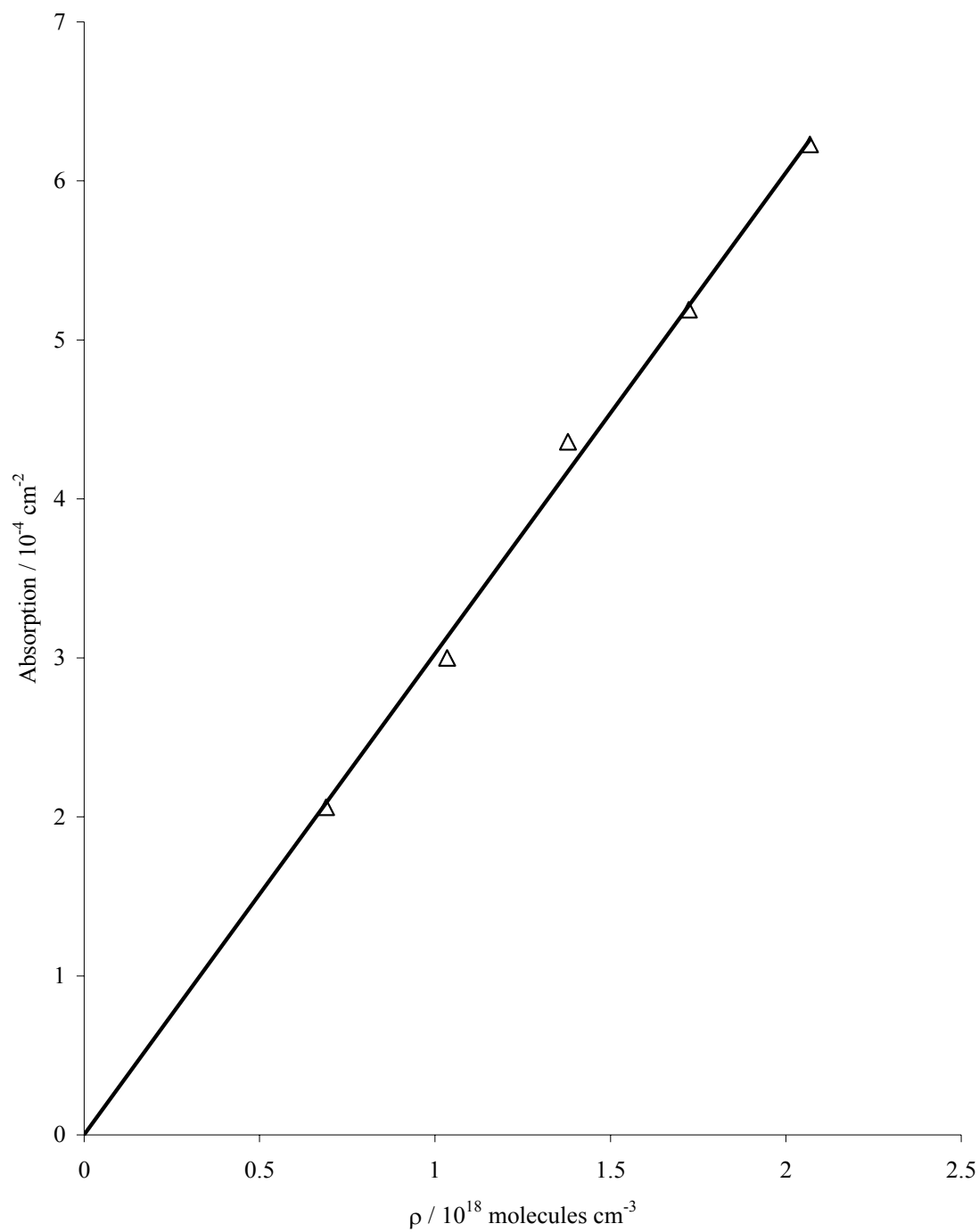
yields a linear line showing that the results for room and low temperature correlate very well and the band strength value is temperature independent. Also, these values are compared in Table 9 with some values reported in the literature.

Table 8. ($\Delta v=5$) C_2H_4 at 140K, Pressure, ρ , S and S_0 .

Pressure torr	ρ $10^{18} \text{ molecules cm}^{-3}$	S 10^{-3} cm^{-2}	S_0 $10^{-22} \text{ cm}^2 \text{ cm}^{-1} \text{ molecule}^{-1}$
30	2.07	6.23	3.01
25	1.72	5.19	3.01
20	1.38	4.36	3.16
15	1.03	3.00	2.90
10	0.69	2.06	2.99
Avg			3.0 ± 0.1

Table 9. ($\Delta v=5$) C_2H_4 S_0 Comparison

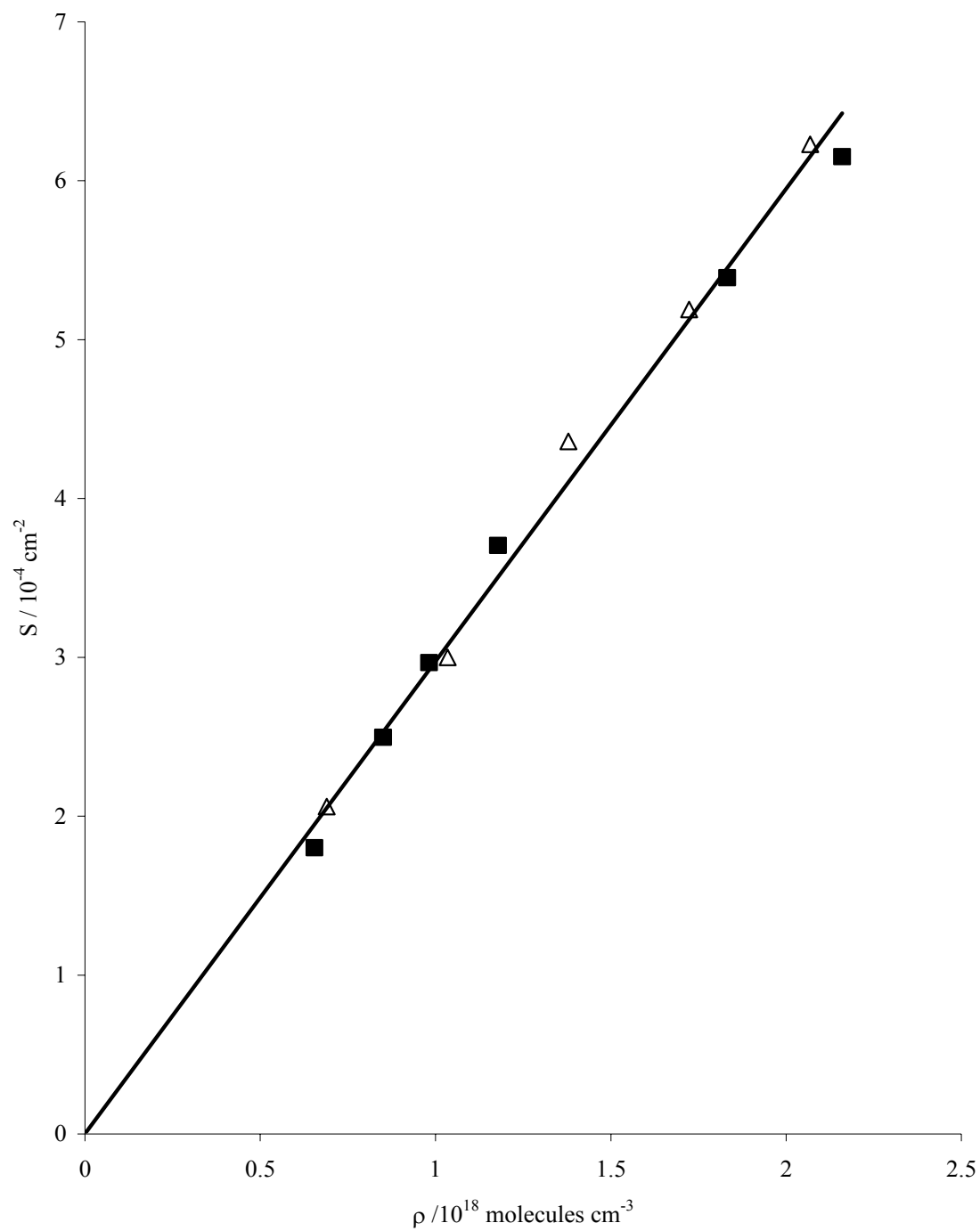
	S_0 $10^{-22} \text{ cm}^2 \text{ cm}^{-1} \text{ molecule}^{-1}$
298 K	2.9 ± 0.1
100 K	3.0 ± 0.1
Gutow (LPA) ¹⁰⁹	2.9 ± 0.2
Lewis (PS-CRD) ⁶⁴	2.85 ± 0.07
Lewis (FT-VIS) ⁶⁴	2.83 ± 0.05



$$S_0 = (3.0 \pm 0.1) \times 10^{-22} \text{ cm}^2 \text{ cm}^{-1} \text{ molecules}^{-1}$$

$$R^2 = 0.995$$

Figure 22. ($\Delta v = 5$) of C_2H_4 at 140 K S vs. ρ . Slope is S_0 .



$$S_0 = (2.9 \pm 0.1) \times 10^{-22} \text{ cm}^2 \text{ cm}^{-1} \text{ molecules}^{-1}$$

$$R^2 = 0.992$$

Figure 23. ($\Delta v = 5$) of C_2H_4 S vs. ρ . Marker ■ = measurements at 295 K and Marker Δ = measurements at 155 K

Dideuteromethane (CH₂D₂): C-H ($\Delta\nu=5$) Vibrational Overtone Absorption

The fourth ($\Delta\nu=5$) C-H overtone of CH₂D₂ in gas phase and in liquid argon solutions have been measured using a photoacoustic and a Fourier transform spectrophotometer, respectively.^{111, 112} Energy levels have also been calculated using a local mode model.¹¹² Studies of ($\Delta\nu = 5$) overtone of CH₂D₂ at temperatures between 125K and 250K, using PS-CRD have reported integrated intensities for this band.⁶⁶ In order to complete this information, the vibrational ($\Delta\nu = 5$) C-H overtone spectra of CH₂D₂ at room temperature were acquired using the PS-CRD technique. Figure 24 presents the stacked measurements taken at various pressures starting from the lowest pressure at the baseline to the highest pressure at the top. Each congested spectrum shows three peaks. The main absorption belongs to the degenerate pairs of local mode vibrations [5,0] at the low energy side lie the combination bands $4\nu_{\text{CH}} + 2\nu_9$ and $4\nu_{\text{CH}} + \nu_3 + \nu_4$.^{113 112, 112} Table 10 lists the band positions and the absorptions for each pressure.

Table 10. ($\Delta\nu=5$) CH₂D₂ at 295K, Pressure, Band Positions, and Band Absorptions

Pressure (Torr)	Main Peak (cm ⁻¹)	Peak Absorption (10 ⁻⁶ cm ⁻¹)	Minor Peaks (cm ⁻¹)	Peak Absorption (10 ⁻⁶ cm ⁻¹)
100	13786.0	7.14	13620.2 / 13611.4	0.89 / 0.83
85	13786.1	6.22	13620.8 / 13612.0	0.70 / 0.74
65	13785.9	4.80	13619.0 / 13609.9	0.56 / 0.58
46	13786.2	3.42	13619.1 / 13609.7	0.42 / 0.43
23	13785.6	1.77	-----	-----

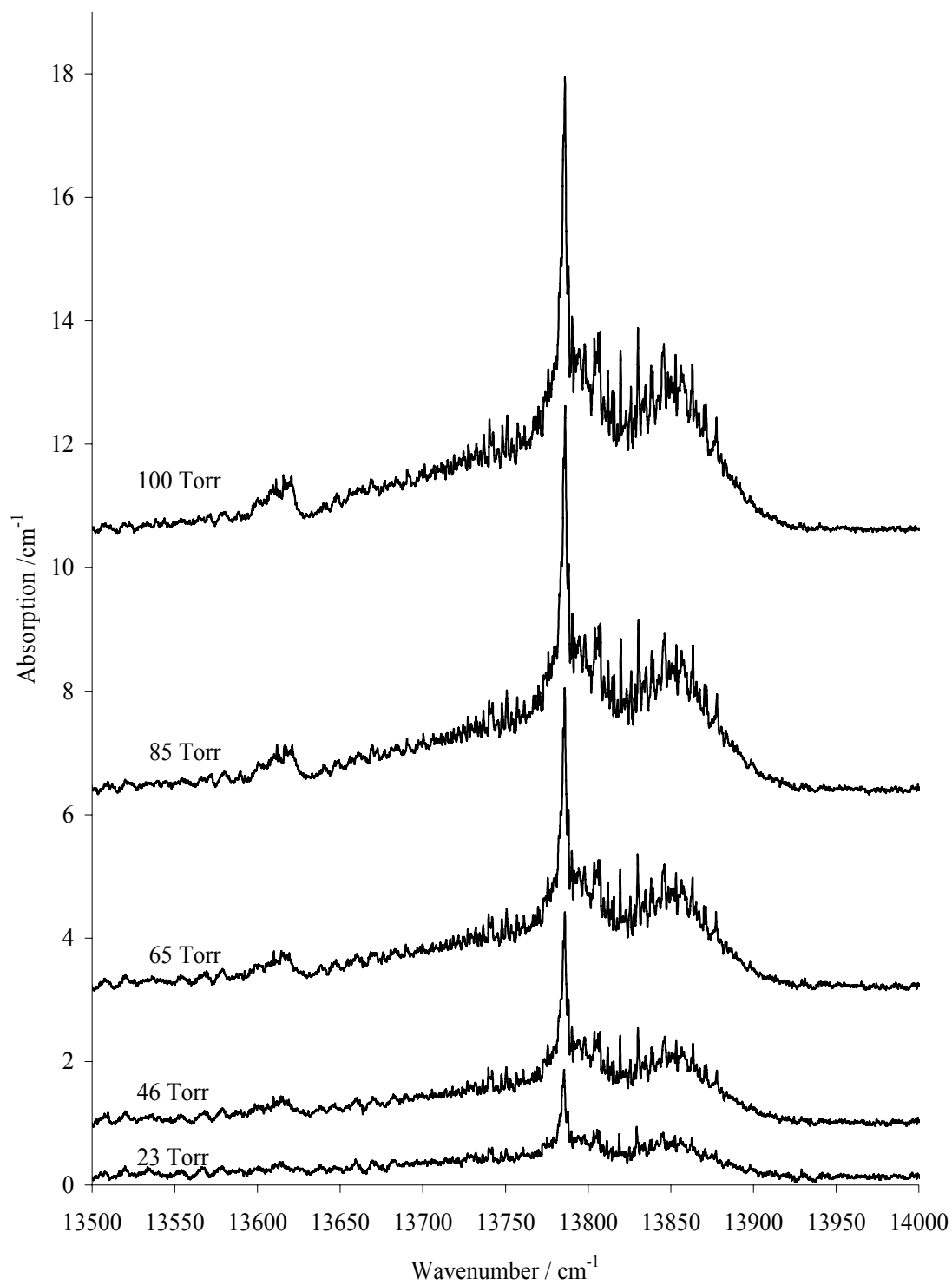


Figure 24. ($\Delta\nu=5$) CH_2D_2 Absorption pressure series at 295 K.

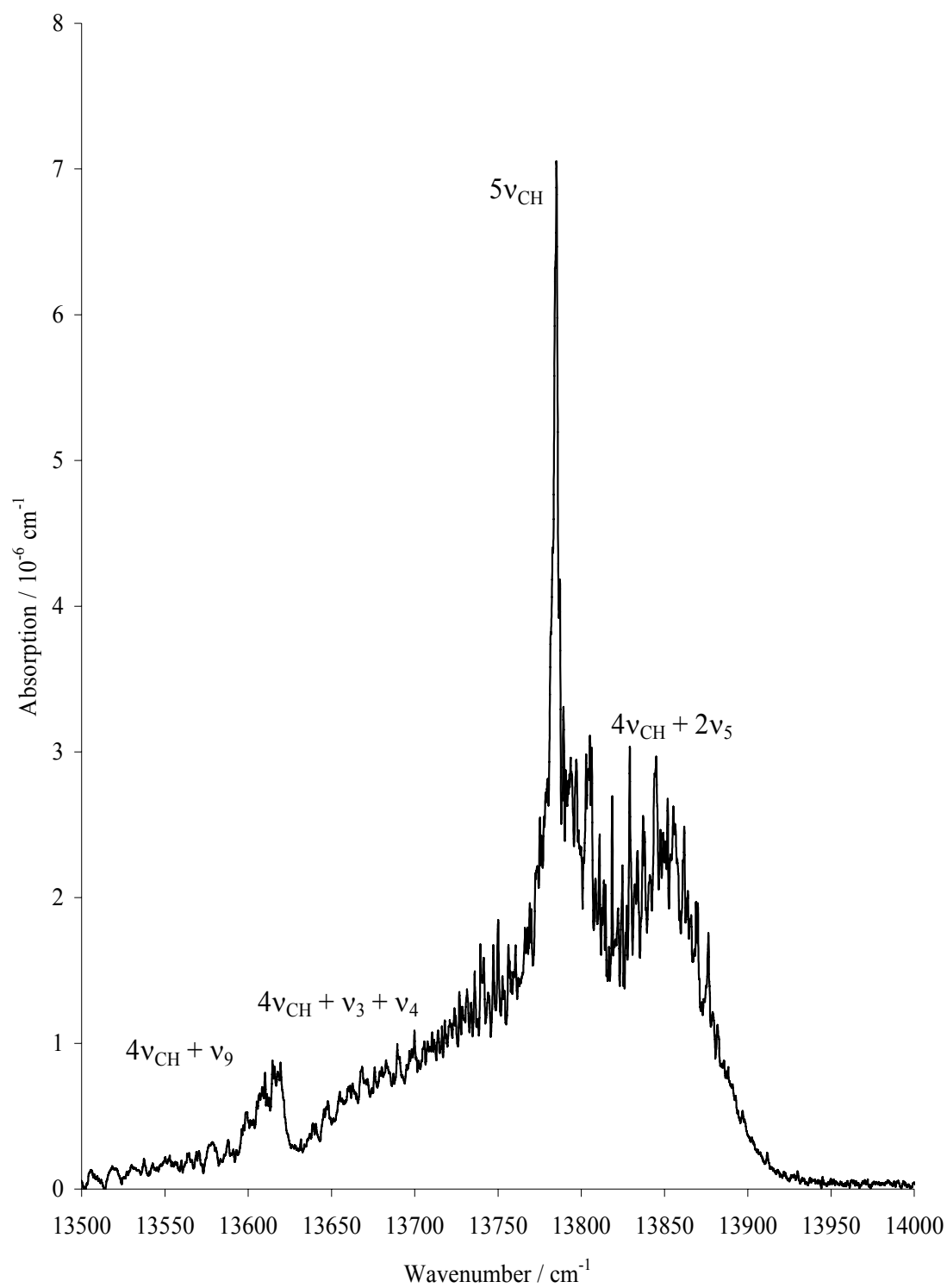
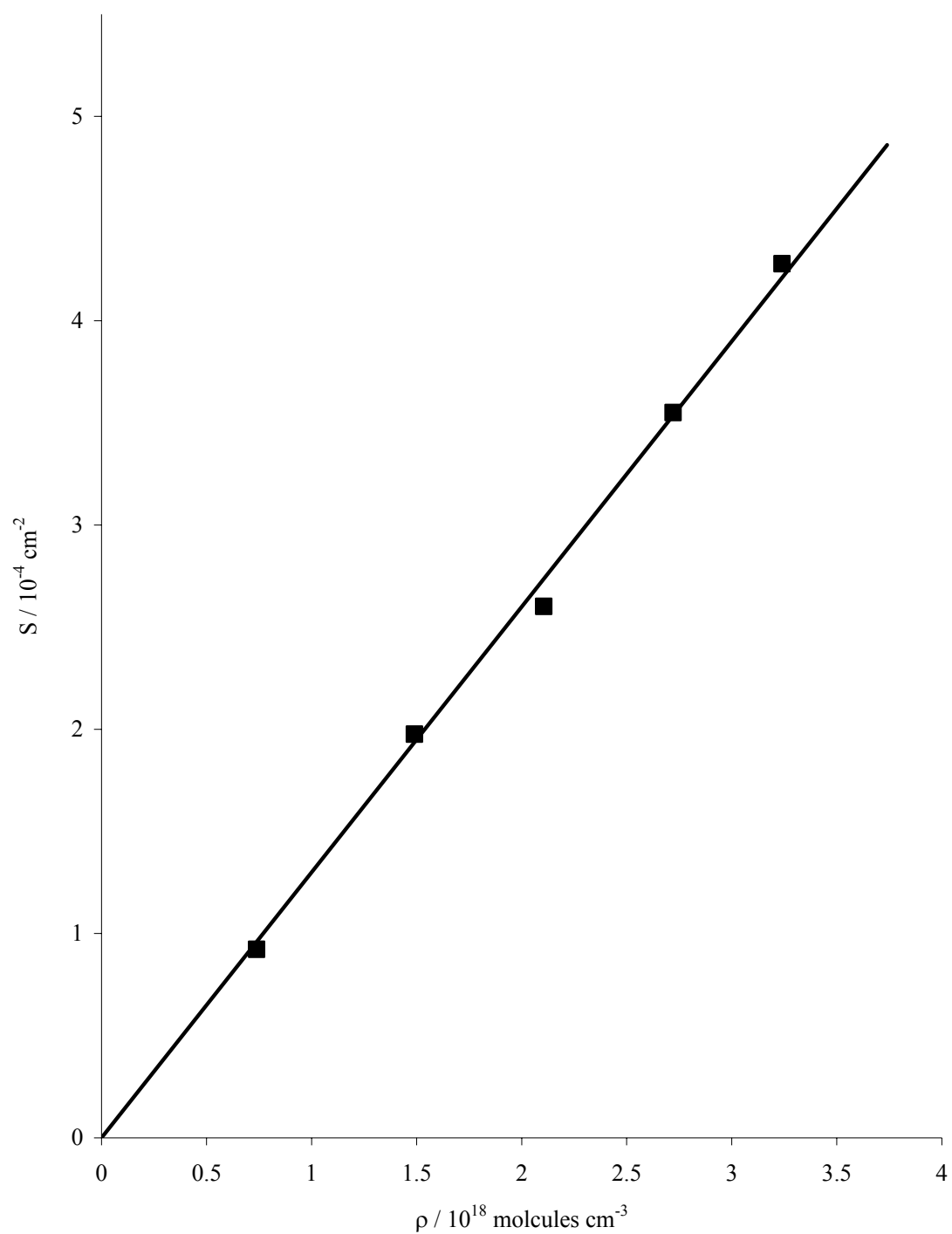


Figure 25. ($\Delta v = 5$) CH₂D₂ Absorption spectrum with a pressure of 100 Torr at 295 K, and assignments.



$$S_0 = (1.33 \pm 0.02) \times 10^{-22} \text{ cm}^2 \text{ cm}^{-1} \text{ molecules}^{-1}$$

$$R^2 = 0.998$$

Figure 26. ($\Delta\nu=5$) of CH_2D_2 at 295 K S vs. ρ . Slope is S_0

The band at around 13845 cm^{-1} is assigned to $[4, 0] + 2\nu_5$ (See Figure 25). The ρ , S , S_0 values are presenting in Table 11. Figure 26 presents the plot of S versus ρ to give the S_0 value.

Table 11. ($\Delta\nu=5$) CH_2D_2 at 295K, Pressure, ρ , S and S_0 .

Pressure torr	ρ $10^{18}\text{ molecules cm}^{-3}$	S 10^{-3} cm^{-2}	S_0 $10^{-22}\text{ cm}^2\text{ cm}^{-1}\text{ molecule}^{-1}$
100	3.24	4.28	1.32
85	2.72	3.55	1.30
65	2.11	2.60	1.24
46	1.49	1.98	1.33
23	0.74	0.92	1.25
Avg			1.33 ± 0.02

The band strength value, $S_0 = (1.37 \pm 0.07) \times 10^{-22}\text{ cm}^2\text{ cm}^{-1}\text{ molecule}^{-1}$ reported by Lewis using PS-CRD at 126K⁶⁶ is in good agreement with the value reported above $S_0 = (1.33 \pm 0.02)\text{ cm}^2\text{ cm}^{-1}\text{ molecule}^{-1}$.

C-H Spectra ($\Delta\nu=1-4$) of CH_3D .

Studies of high energy levels of CH_3D have been important because cross-sections of CH_3D have been used for the determination of deuterium abundance in planets and their satellites, which is believed in turn to give useful information about the formation and evolution of the solar system.^{114, 115} The C-H stretch absorption spectra ($\Delta\nu = 1-6$) of CH_3D in gas phase and in liquid argon solution have been studied using

different techniques.^{66, 113, 116-119} However, the $\Delta v = 4$ transition at 11264cm^{-1} has been reported¹¹⁴ but the spectrum has not been shown.

This section of the chapter presents the fundamental and overtone spectra of CH_3D around the C-H stretch at room temperature. Measurements were made using a White cell and a commercial (FT) spectrophotometer. The harmonic frequency (ω), anharmonicity (ωx); and interbond coupling parameter (λ) were used with HCAO model to calculate frequencies and assign absorption bands.

Absorption spectrum of the fundamental ($\Delta v = 1$) C-H stretch is shown in Figure 27. Two prominent maxima at 2969 and 3016.8 cm^{-1} are assigned to ν_1 symmetric (A_1) and ν_4 anti-symmetric (E), C-H stretching modes, respectively.^{116, 120} Figure 28 shows the first overtone ($\Delta v = 2$) which lies between $5450 - 6200\text{ cm}^{-1}$, in a region heavily populated by combination bands. The second overtone region ($\Delta v = 3$) covers from 8400 to 8800 cm^{-1} . The strongest band is located at 8616 cm^{-1} in Figure 29 and corresponds to the pure transition ($\Delta v = 3$). Finally, the region between 11000 and 11500 cm^{-1} contains the third overtone ($\Delta v = 4$) (Figure 30). A summary of transition frequencies and pressure used in each spectrum is presented in Table 12. Frequencies of the fourth and fifth vibrational overtone of CH_3D were reported by Lewis⁶⁶ using the PS-CRD technique. The results are summarized in Table 12.

The local mode parameters, harmonic frequency, and anharmonicity for CH_3D were calculated using Birge-Sponer plot. Figure 31 shows the corresponding plot. Local-mode parameters are summarized in Table 13

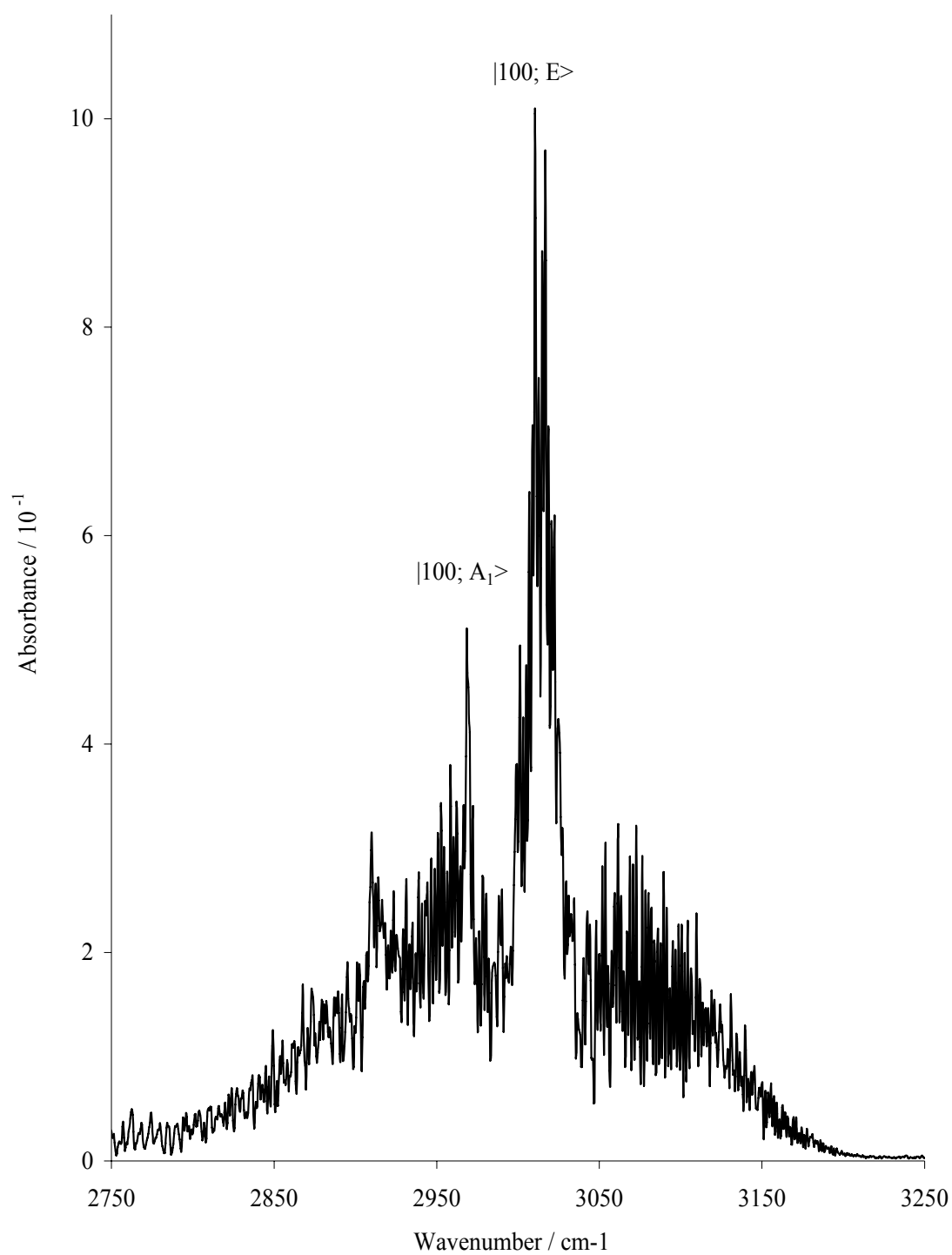


Figure 27. Absorption spectrum of the fundamental ($\Delta v = 1$) C-H stretch of CH_3D at 298 K

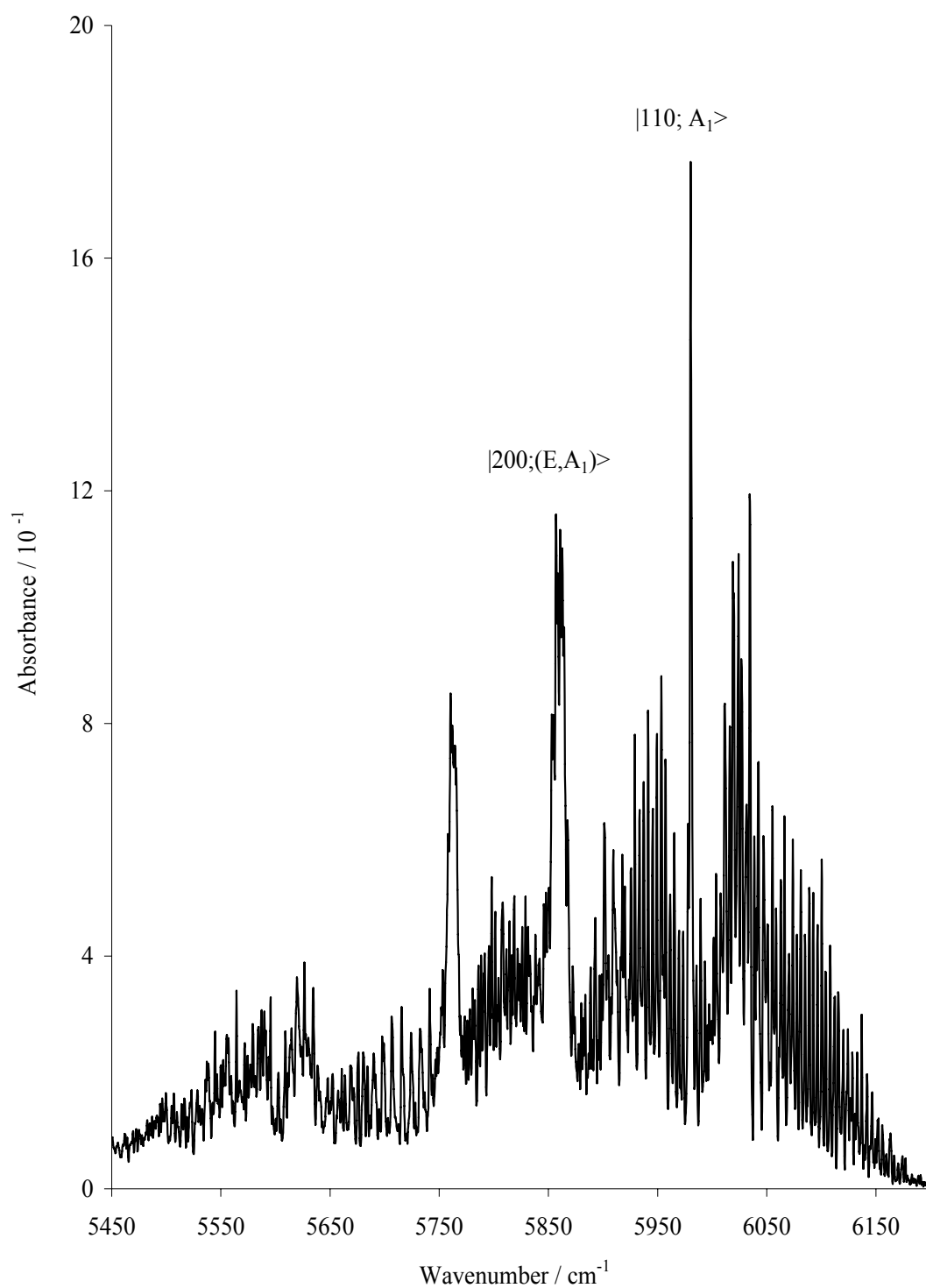


Figure 28. Absorption spectrum around the first C-H overtone ($\Delta v = 2$) of CH_3D at 298 K

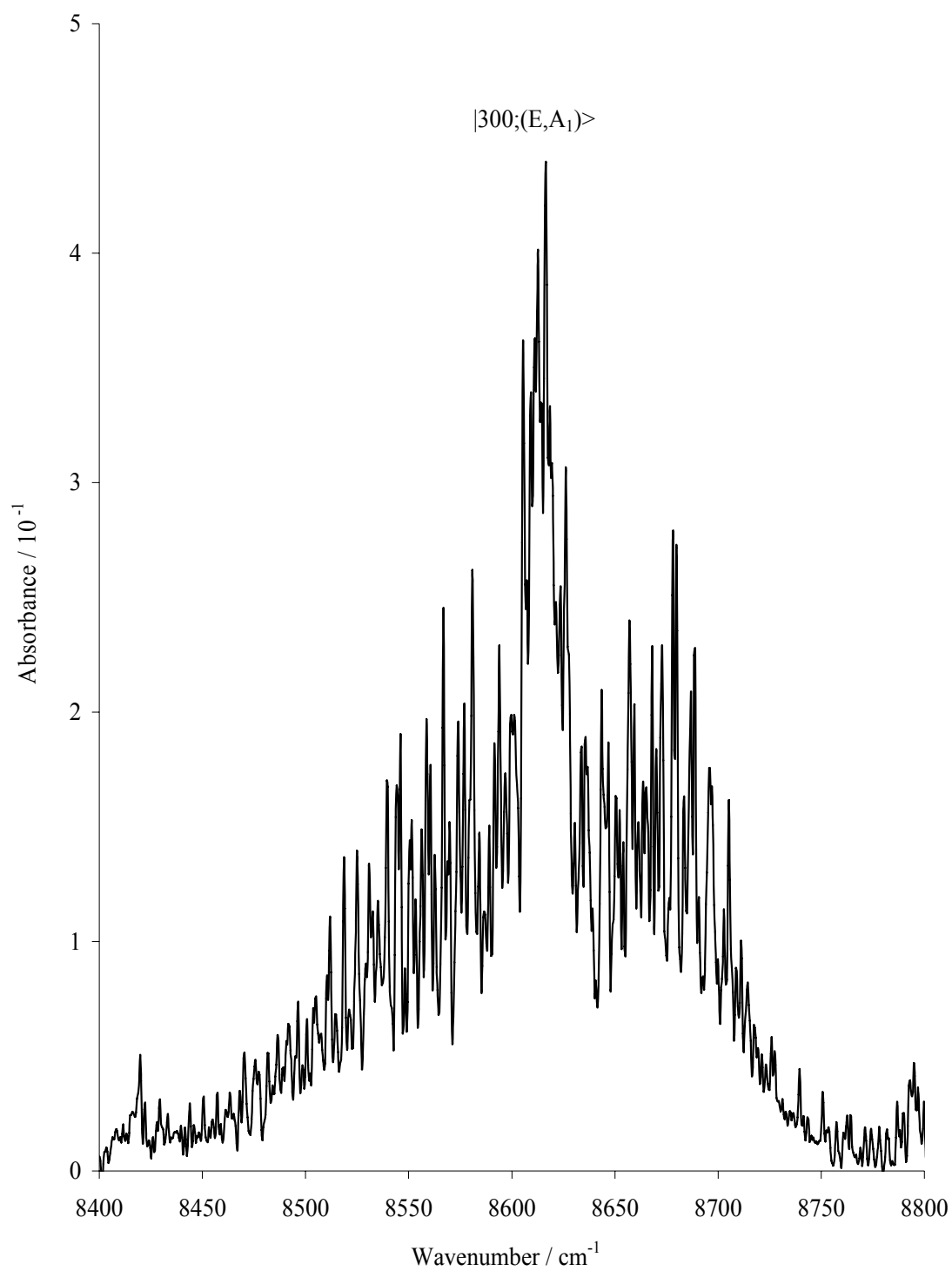


Figure 29. Absorption spectrum around the second C-H overtone ($\Delta\nu = 3$) of CH₃D at 298 K

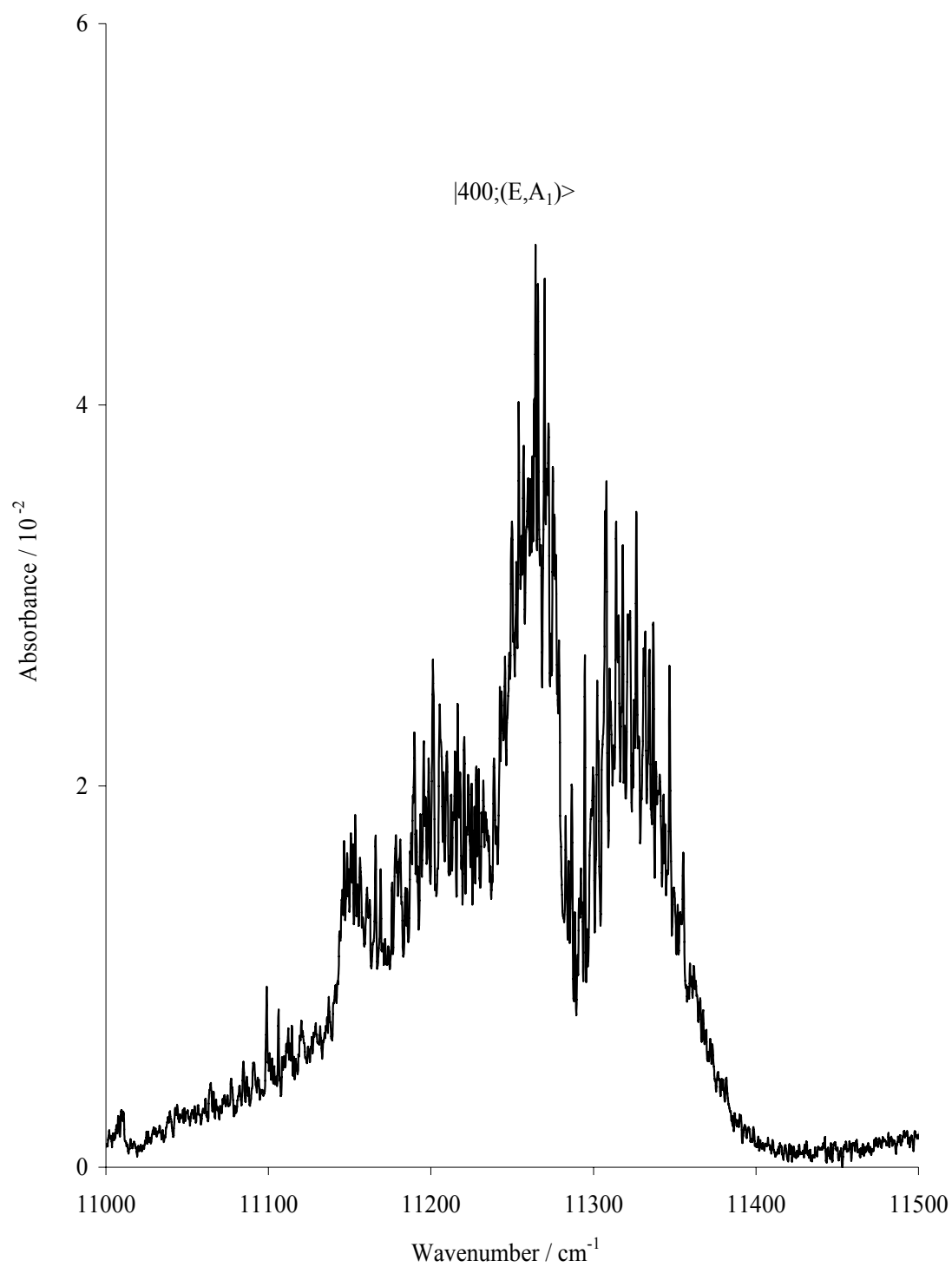


Figure 30. Absorption spectrum around the third C-H overtone ($\Delta v = 4$) of CH₃D 298 K

Table 12. Observed frequencies in the C-H fundamental and overtone spectra of CH₃D

$\Delta\nu_{\text{CH}}$	Frequency (cm ⁻¹)	Pressure (Torr)
1	2968.8	7.2
2	5860.7	102.0
3	8616.4	296.0
4	11264.0	296.0
5	(13749.0) ^a	-----
6	(16207.8) ^a	-----

^a The values in parentheses were taken from Lewis ⁶⁶

Table 13. Local-mode parameters of CH₃D in gas phase at room temperature.

Harmonic frequency cm ⁻¹	Anharmonicity cm ⁻¹
3108 ± 9	59 ± 2

The local mode theory of harmonically coupled anharmonic oscillators (HCAO)^{95-97, 121-124} was used to calculate the energies of the local mode states of three C–H bonds of CH₃D.

The HCAO model allows states within a given manifold (intra) or adjacent manifolds (inter) to interact. If intra and inter-manifold coupling of stretching vibrations are included the Hamiltonian is as follows⁹⁵

$$H = \sum_{\alpha} H_{\alpha}^o + \sum_{\alpha < \beta} H_{\alpha\beta} \quad (24)$$

where α and β denote different bonds and the summations run over all possible combinations. $H_{\alpha\beta}$ is a two bond coupling term

$$H_{\alpha\beta} = g_{rr'} p_{\alpha} p_{\beta} + f_{rr'} r_{\alpha} r_{\beta} \quad (25)$$

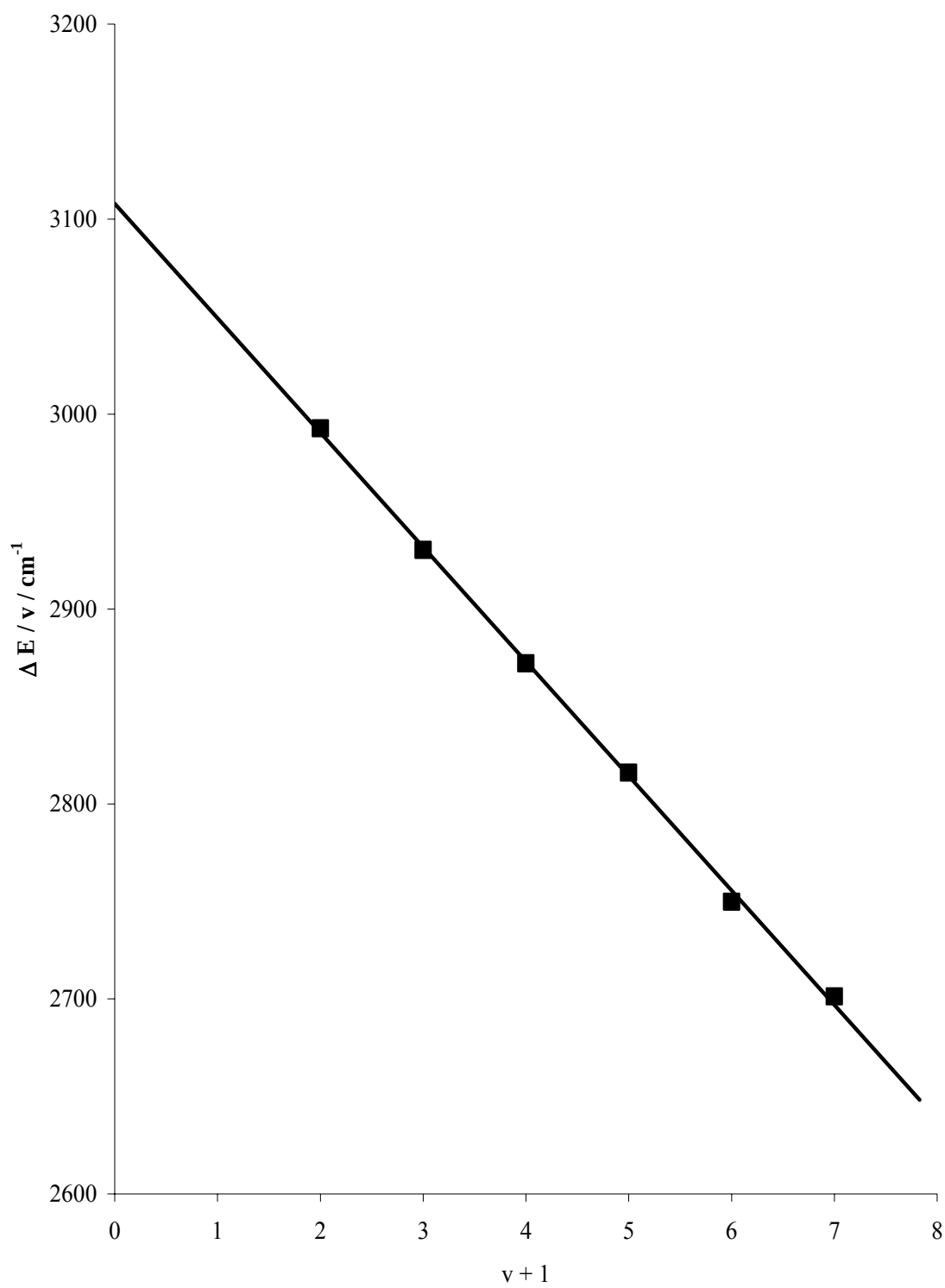


Figure 31. Birge-Sponer plot for pure local-mode C-H absorptions of CH₃D

where g_{rr} and f_{rr} are the kinetic and potential interaction coefficients, r is the XH bond displacement coordinate and the conjugate momentum (p).

Eigenvalues are obtained by diagonalizing the Hamiltonian (H) within a Morse oscillator basis set. Morse basis functions are denoted by $|n_1 n_2 n_3 \dots n_k\rangle$, where k is the number of equivalent oscillators. It is convenient to combine potential and kinetic energy coupling into a single interbond coupling parameter λ

$$\lambda = \frac{\omega}{2} \left(\frac{g_{rr'}}{g_{rr}} + \frac{f_{rr'}}{f_{rr}} \right) \quad (26)$$

where ω is the Morse frequency. If intermanifold coupling is ignored, then an effective Hamiltonian matrix H_{eff} is obtained. Matrix elements are given by:

$$\begin{aligned} \langle n'_1 n'_2 n'_3 \dots n'_k | H_{\text{eff}} | n_1 n_2 n_3 \dots n_k \rangle = & \left[\omega \nu - \sum_{\alpha=1}^k n_{\alpha} (n_{\alpha} + 1) \omega x \right] \delta_{n_1 n'_1} \delta_{n_2 n'_2} \delta_{n_3 n'_3} \dots + \\ & \lambda \sum_{\alpha \beta \gamma} [(n_{\alpha} + 1) n_{\beta}]^{1/2} \delta_{n'_{\alpha} n_{\alpha+1}} \delta_{n'_{\beta} n_{\beta-1}} \delta_{n'_{\gamma} n_{\gamma}} \dots \end{aligned} \quad (27)$$

The first term in the above equation is identical to the Birge-Sponer equation and is zero for off-diagonal elements. The second term contains the interbond coupling parameter λ and produces the off-diagonal matrix elements. In this case, only two basis functions with quantum numbers differing by ± 1 , can interact simultaneously. The quantum number ν is the index of the manifold, $\nu = n_1 + n_2 + n_3$. The matrices are block diagonal in ν .

Monodeuteromethane (CH_3D) is a symmetric top molecule belonging to the point group C_{3v} . This molecule has six fundamental vibrations: three totally symmetric (A_1) and three doubly degenerate (E) modes, all of which are infrared active. The frequencies and symmetries of the different fundamental modes are listed in Table

14¹²⁵. The interbond coupling splits the fundamental C-H vibration into symmetric, $|100, A_1\rangle$, and antisymmetric, $|100, E\rangle$, states. The interbond coupling parameter (λ) is determined from experimental peak positions and the following equations:

$$\nu_1 = \nu(|100, A_1\rangle) = \omega - 2\alpha x + 2\lambda \quad (28)$$

$$\nu_4 = \nu(|100, E\rangle) = \omega - 2\alpha x - \lambda \quad (29)$$

The harmonic frequency ($\omega = 3107.1 \text{ cm}^{-1}$), anharmonicity ($\alpha x = 57.9 \text{ cm}^{-1}$) and interbond coupling parameter ($\lambda = -16.1 \text{ cm}^{-1}$) were substituted into symmetrized effective Hamiltonian matrices¹²⁴ (equation 27) and frequencies $\nu(|100, A_1\rangle)$ and $\nu(|100, E\rangle)$ were obtained. Hamiltonian matrices are given in Appendix B for the overtone manifolds $\nu = 2$ to 6.

Table 14. Fundamental Vibrational Frequencies of CH₃D

Assignment	Symmetry	Mode	Frequency / cm^{-1}
ν_1	A_1	C-H s-stretch	2973
ν_2	A_1	C-D stretch	2200
ν_3	A_1	C-H ₃ s-bend	1300
ν_4	E	C-H a-stretch	3017
ν_5	E	C-H ₃ a-bend	1471
ν_6	E	C-D bend	1155

The experimental and calculated frequencies are presented in Table 15. Vibrational states are given in local-mode notations. Local-mode states are represented by $|n_1, n_2, n_3; \Gamma\rangle$, where $n_1 \dots n_3$ indicate equivalent oscillators, and Γ represents the state symmetry species.

Table 15. Calculated and observed vibrational frequencies of CH₃D in gas phase

ν	Assignment	Frequency / cm ⁻¹		ν	Assignment	Frequency / cm ⁻¹	
		HCAO	obs			HCAO	obs
1	100,A ₁ >	2959	2969	4	400,A ₁ >	11264	11264
1	100,E>	3007	3017	4	400,E>	11265	
	2ν ₃ + ν ₅	4071	4070	4	310,A ₁ >	11574	
	100,A ₁ >+ ν ₆	4114	4129	4	310,1E>	11592	11598
	100,E>+ ν ₃	4307	4304	4	310,2E>	11620	11628
	2> (C-D)	4338	4343	4	220,A ₁ >	11741	
	100,E>+ ν ₅	4478	4472	4	220,E>	11756	
	100,A ₁ >+ ν ₂	5159	5164	4	211,A ₁ >	11812	
	100,E>+ ν ₂	5207	5212	4	211,E>	11890	
	100,E>+ 2ν ₆	5317	5312				
	100,E>+ ν ₃ +ν ₅	5778	5761				
				5	500,A ₁ >	13793	13749
2	200,A ₁ >	5847	5861	5	500,E>	13793	
2	200,E>	5863		5	410,A ₁ >	14228	
2	110,A ₁ >	5971	5980	5	410,1E>	14241	
2	110,E>	6003		5	410,2E>	14253	
	3> (C-D)	6428	6428	5	311,A ₁ >	14443	
	2> +2ν ₆	6648	6665	5	311,E>	14483	
	200,E>+ ν ₃	7163	7150	5	320,1E>	14514	
	110,E>+ ν ₃	7302	7292	5	320,A ₁ >	14575	
	110,E>+ ν ₅	7474	7473	5	320,3E>	14620	
				5	221,A ₁ >	14722	
3	300,A ₁ >	8619	8616	6	600,A ₁ >	16206.1	16207.8
3	300,E>	8620		6	600,E>	16206.1	
3	210,A ₁ >	8814		6	510,A ₁ >	16766.7	
3	210,1E>	8834	8840	6	510,1E>	16767.1	
3	210,2E>	8889		6	510,2E>	16798.6	
3	111,A ₁ >	8979		6	411,A ₁ >	17095.1	
	210, 2E>+ ν ₅	10044	10029	6	411,E>	17100.3	
	110,E>+ 2ν ₂	10403	10403	6	420,A ₁ >	17241.5	
				6	420,1E>	17141.6	
				6	420,2E>	17258.8	
				6	330,A ₁ >	17290.7	
				6	330,E>	17294.0	
				6	321,A ₁ >	17393.7	
				6	321,1E>	17447.8	
				6	321,2E>	17530.6	
				6	222,A ₁ >	17642.2	

A comparison of the calculated frequencies with the observed frequencies shows that HCAO model provides a good description of the energies of the transitions. Agreement is particularly good for the highest overtones $\Delta\nu = 4, 5$ and 6 .

Conclusions

High overtone spectrum ($\Delta\nu = 5$) of C_2H_4 was obtained at 295 and 140K using PS-CRD spectroscopy. The S_0 value for this transition was calculated and is in agreement with the literature values.

The absorption spectrum of ($\Delta\nu = 5$) of CH_2D_2 was obtained at 295K using PS-CRD spectroscopy. S_0 value obtained at room temperature shows a good correlation with the one obtained before at 120K. Those results show the reproducibility of the PS-CRD measurements.

The spectra of the C–H stretch fundamental and overtones ($\Delta\nu = 1-4$) of CH_3D were recorded. A comparison of the calculated frequencies with the observed frequencies shows that HCAO model provides a good description of the energies of the peaks. Agreement is particularly good for the higher overtones $\Delta\nu = 3, 4, 5$ and 6 .

CHAPTER FOUR

Absorption Spectroscopy of the Oxygen Atmospheric Bands ($b^1\Sigma_g^+ \leftarrow X^3\Sigma_g^-$) and ($\Delta v = 4$) Overtone Band of HD

The absorption spectra of molecular oxygen recorded for the (0 $\leftarrow$ 0) and (2 $\leftarrow$ 0) bands of the $b^1\Sigma_g^+ \leftarrow X^3\Sigma_g^-$ transition using cavity ring down spectroscopy are presented in this chapter. Quantitative measurements of the individual rotational line intensities were made for the oxygen γ -band at 628nm. The measurements were made at room and low temperature. A comparison between experimental and simulated spectra confirmed the molecular temperature measured by a sensor localized in the cell.

Furthermore, the spectrum of hydrogen deuteride, HD, at temperatures of 295 and 90K was studied in the region of the third ($\Delta v = 4$) overtone. Absorption strength values of three transitions, R(0), R(1) and R(2), in the ($\Delta v = 4$) band were obtained. Using the Boltzmann distribution of the rotational-vibrational intensities and the simulated spectrum at low temperature, the cell temperature was confirmed.

The data obtained for both diatomic molecules were compared with literature values.

Absorption Spectroscopy of the Oxygen Atmospheric Bands ($b^1\Sigma_g^+ \leftarrow X^3\Sigma_g^-$)

Transitions between the lowest three electronic states of the oxygen molecule, $X^3\Sigma_g^-, a^1\Delta_g$ and $b^1\Sigma_g^+$ give rise to several absorption band systems in the near infrared and visible regions. Figure 32 shows a potential energy diagram for the low-lying electronic states of O₂.¹²⁶

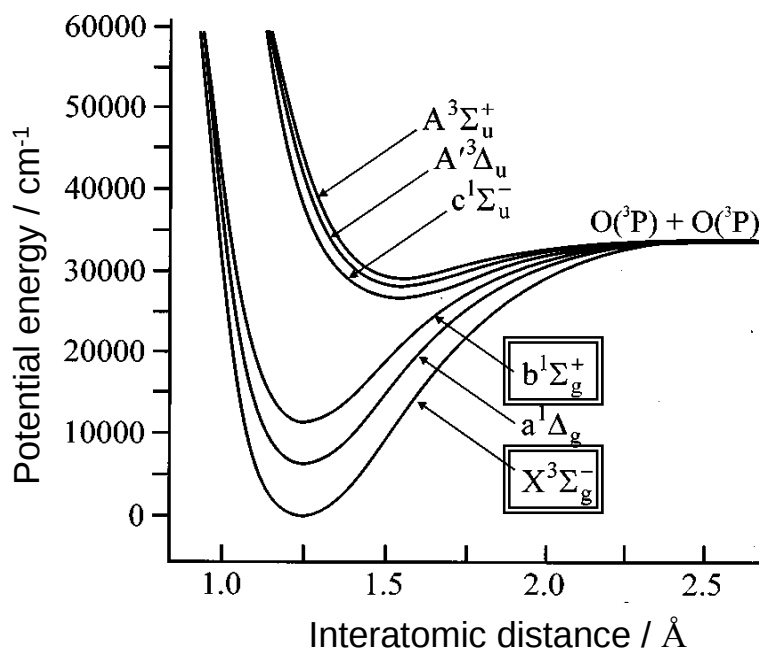


Figure 32. Potential energy diagram for the low-lying electronic states of O_2 .¹²⁶

The red atmospheric bands of molecular oxygen are due to the transition between the electronic triplet ground state $X^3\Sigma_g^-$ and the second singlet electronic state $b^1\Sigma_g^+$. The $(0 \leftarrow 0)$, $(1 \leftarrow 0)$ and $(2 \leftarrow 0)$ bands are respectively denoted as the A , B , and γ bands. In absorption from the $v = 0$ level of the ground electronic state, the Frank-Condon factors favor the vertical 0-0 transition over the 1-0 or 2-0 bands by the ratios 0.931: 0.066: 0.003.⁵ Thus, the A -band is the strongest and the γ -band the weakest.

These red atmospheric bands are very weak since the electronic dipole transition between the two states for the gerade-gerade, $\Sigma^+ - \Sigma^-$, and singlet-triplet cases are all forbidden. Hence, the transition takes place via a magnetic dipole interaction. Since the electronic ground state is the $X^3\Sigma_g^-$ state, the average electronic orbital angular momentum vanishes ($\Lambda = 0$). Still there is an instantaneous non-zero value of the orbital

angular momentum which produces a precessing magnetic dipole moment of orbital origin. The total electronic spin is $S=1$, so that molecular oxygen has a permanent magnetic dipole moment of approximately two Bohr magnetons.

The first spectroscopic study of the red system of atmospheric oxygen bands was made by Babcock *et al*¹²⁷ using a long path cell in the laboratory and open path measurements through the atmosphere with two different grating spectrometers. Quantitative measurements of intensity have been made for individual rotational lines of the atmospheric oxygen $b^1 \Sigma_g^+ (\nu' = 0, 2) \leftarrow X^3 \Sigma_g^- (\nu'' = 0)$ A band and γ band by using different techniques such “White-type” multiple traversal absorption cells^{128-132, 133, 134} intracavity laser-absorption spectroscopy (ICLAS)¹³⁵ and cavity ring down spectroscopy.^{73, 136} Only the A band has been taken at low temperatures (from 202 to 224K) to determine experimental line parameters.¹³⁴ However, spectra have not been shown.

The sensitivity of CRDS^{5, 137}, phase shift cavity ring down spectroscopy⁶ and Fourier transform phase shift cavity ring down spectroscopy¹⁰ have been demonstrated by using several bands in the very weak forbidden $b^1 \Sigma_g^+ \leftarrow X^3 \Sigma_g^-$ transitions on gaseous molecular oxygen. Using the highly sensitive CRDS, the absorption spectra of the A band of the $^{16}\text{O}^{18}\text{O}$, $^{16}\text{O}^{17}\text{O}$, $^{18}\text{O}_2$, $^{17}\text{O}^{18}\text{O}$ and $^{17}\text{O}_2$ and the γ band of $^{16}\text{O}_2$, $^{16}\text{O}^{17}\text{O}$, $^{17}\text{O}_2$ and $^{18}\text{O}_2$ isotopomers of oxygen have been investigated.^{138, 139} In addition, calculation of the atmospheric transmission function¹³⁰ and the magnetic dipole transition moment for the red atmospheric oxygen bands¹⁴⁰ has been made. Also, improved spectral parameters for those bands have been calculated and compared with HITRAN molecular absorption database.¹⁴¹

Structure of the Bands

The rotational levels of the O₂ states are designated by the quantum numbers J and K , where K represents the rotational angular momentum, and J , the total angular momentum, is the sum of the rotational and spin angular momenta, $J=K+S$. The ground state is split into levels corresponding to $J'' = K'', K''+1, K''-1$, with only odd values of K'' allowed (double primes and single primes denote lower and upper states, respectively). The upper electronic level, which has zero spin, is composed of single states with $J'=K'$, where only even values of K' are allowed.

The red atmospheric oxygen bands is comprised of four branches, two R -form branches forming a head and two P -form branches, separated from the former by a zero gap. The observed four branches of the red atmospheric oxygen bands can be accounted for only by the selection rules for magnetic dipole radiation,

$$\Delta J = 0, \pm 1 \quad (J = 0 \xleftarrow{NO} J = 0) + \leftrightarrow +, - \leftrightarrow -, - \xleftarrow{NO} + \quad (30)$$

The corresponding transitions are indicated in Figure 33 using full lines. There is an $^R R$ branch ($\Delta J = +1, \Delta K = +1$), a $^P P$ branch ($\Delta J = -1, \Delta K = -1$), an $^R Q$ branch ($\Delta J = 0, \Delta K = +1$), and a $^P Q$ branch ($\Delta J = 0, \Delta K = -1$).¹²⁷

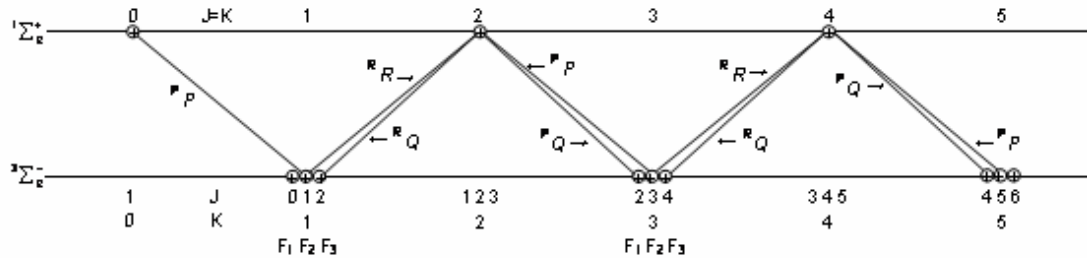


Figure 33. Combinations associated with branches of the red system of atmospheric oxygen

As indicated in Figure 33, the three components of the $X^3 \Sigma_g^-$ ground state of oxygen are designated by F_1 , F_2 , and F_3 , according as $J = K + 1$, $J = K$, and $J = K - 1$. The $^P P$ and $^R R$ branches of the red atmospheric bands correspond to transitions from the F_2 component, the $^R Q$ and $^P Q$ branches to transitions from F_1 and F_3 components, respectively. The rotational terms F_i , are given by Watson¹²⁸

For $J'' = K'' + 1$,

$$F_i = J''(J'' + 1)B'' + (2\lambda - \gamma) + (B'' - \lambda - 1/2\gamma) - \left[(B'' - \lambda - 1/2\gamma)^2 + 4J''(J'' + 1)(B'' - 1/2\gamma)^2 \right]^{1/2} \quad (31)$$

For $J'' = K''$,

$$F_i = J''(J'' + 1)B'' + (2\lambda - \gamma) \quad (32)$$

For $J'' = K'' - 1$,

$$F_i = J''(J'' + 1)B'' + (2\lambda - \gamma) + (B'' - \lambda - 1/2\gamma) + \left[(B'' - \lambda - 1/2\gamma)^2 + 4J''(J'' + 1)(B'' - 1/2\gamma)^2 \right]^{1/2} \quad (33)$$

where the inertial and coupling constants are $B'' = 1.43777 \text{ cm}^{-1}$, $\lambda = 1.984 \text{ cm}^{-1}$, and $\gamma = -0.084 \text{ cm}^{-1}$. The parameter λ indicates a coupling of the spin to the internuclear axis and thus indicates a deviation from Hund's case b which would normally be expected for an unperturbed $^3\Sigma$ state. The parameter γ represents a magnetic coupling between the electron spin and the axis of rotation.

Absorption Spectra for the (0, 0) A-Band of O_2 using PS-CRD Spectroscopy

Absorption spectra of oxygen from 12990 cm^{-1} to 13180 cm^{-1} were measured using PS-CRD. The path length used was 3.7 km. The resolution at which the spectra were recorded was 0.17 cm^{-1} , determined by the resolution of the continuous wave Ti:Sapphire ring. The A band plotted in Figure 34 arises from the $(0 \leftarrow 0)$ vibration levels of the $b^1 \Sigma_g^+ - X^3 \Sigma_g^-$ electronic transitions of molecular oxygen through its

magnetic dipole moment. Given by the low resolution, the four branches were not well resolved. However, in Figure 34 the $^P P$ and $^P Q$ branch components are indicated above the absorption peaks. The intensity distribution in these two branches was used to prove the ability of PS-CRD system to measure weak absorption bands at low temperatures. Figure 4 shows the temperature series of four separate measurements. Spectra were obtained at the temperatures: 295, 150, 130 and 90K. In Figure 35 is possible see as higher K values disappear at lower temperatures. Also, the shift in the distribution of rotational line intensity as function of the temperature can be observed. All of these show the population redistribution in the rotational levels of the ground state, $X^3 \Sigma_g^-$, given by the temperature change. Table 16 summarizes the maximum K value and strongest line observed for both branches, $^P P$ and $^P Q$, at different temperatures. Figures 34 and 35 also show the reproducibility and sensitivity of the PS-CRD measurements at different temperatures.

Table 16. Maximum K value and strongest line observed in $^P P$ and $^P Q$ branches at different temperatures

T (K)	$K_{\max}$	K value of the Strongest Line
90	11	5
130	13	5 and 7
150	17	7
295	25	9

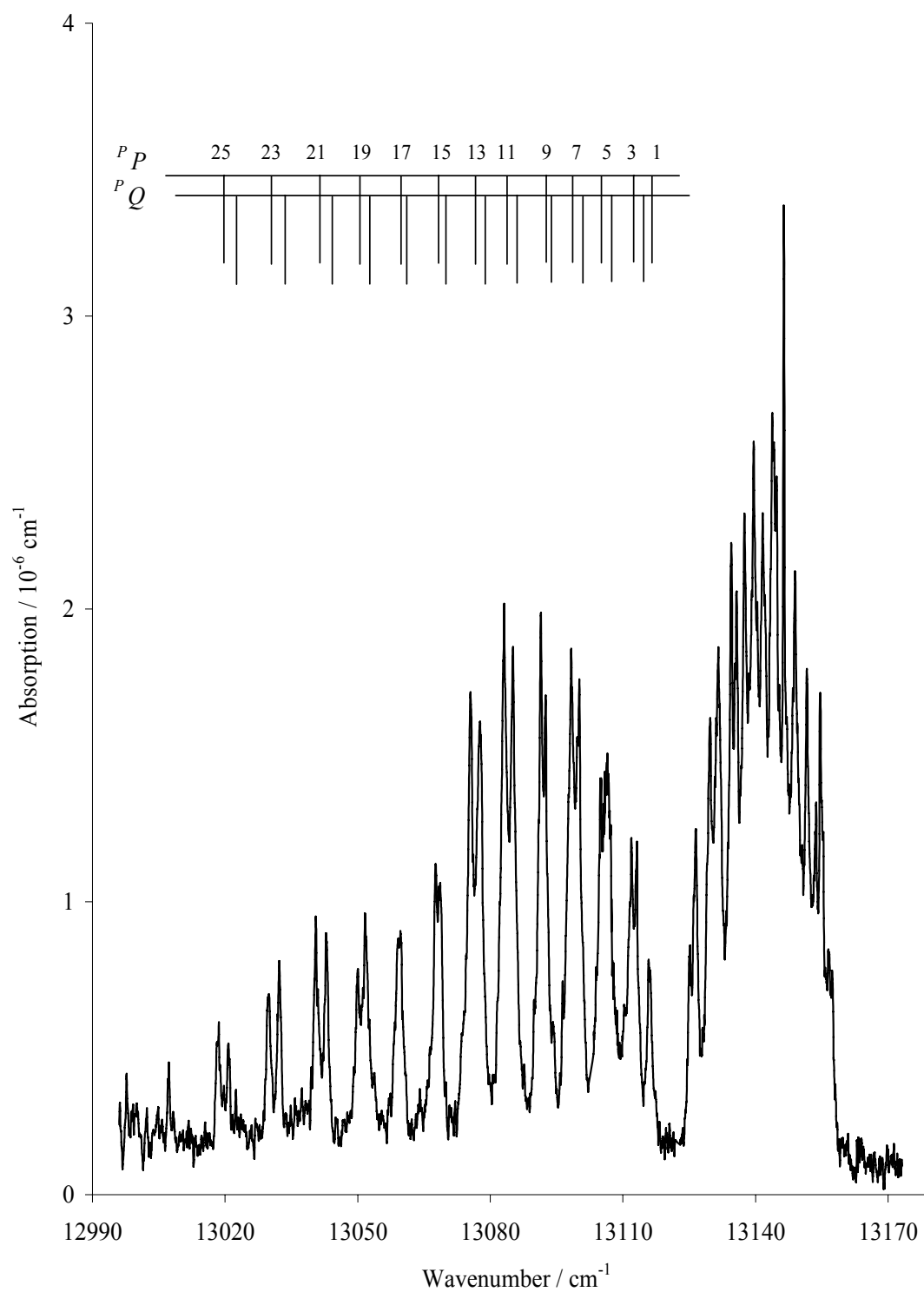


Figure 34. Absorption spectrum of the oxygen A -band with a pressure of 300 Torr at 295 K.

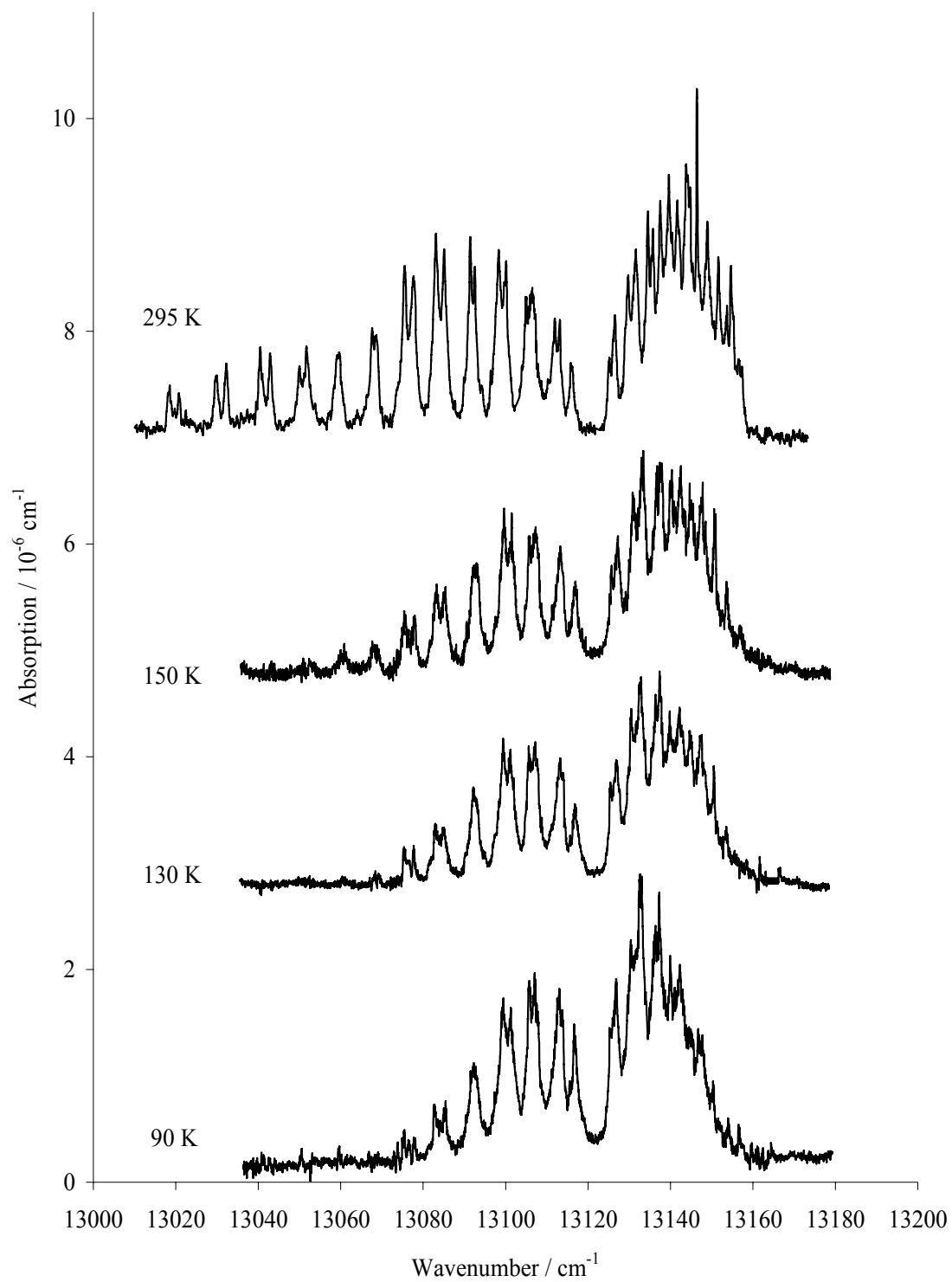


Figure 35. Temperature series of the oxygen *A*-band.

Quantitative measurements of the individual rotational line intensities of the oxygen A band were not possible because of the low spectral resolution.

In order to check the accuracy of the temperature measured by the sensor in the cell, the simulated the spectra at 295 and 90 K were obtained. The simulations used the PGOPHER program¹⁴². Vibrational and rotational constants for the electronic states $X^3 \Sigma_g^-$ and $b^1 \Sigma_g^+$ of oxygen are presented in Table 17.

Table 17. Vibrational and rotational constants for $X^3 \Sigma_g^-$ and $b^1 \Sigma_g^+$ states of oxygen¹⁴³

State	T_e	ω_e	$\omega_e x_e$	$\omega_e y_e$	B_e	α_e	D_e	Transition
$X^3 \Sigma_g^-$	0	1580.19	11.98	0.047	1.4377	0.0159	4.839×10^{-6}	
$b^1 \Sigma_g^+$	13195.1	1432.77	14.00	-----	1.40037	0.0182	5.351×10^{-6}	$b \leftrightarrow X$
<i>Units in cm^{-1}</i>								

For each vibronic transition, with a particular ν' and ν'' a separate set of constants is required. Thus, to the transition $b^1 \Sigma_g^+ - X^3 \Sigma_g^-$, the band origin can be calculated by evaluating the following equation for each vibrational state:

$$E(\nu) = T_e + \omega_e(\nu + 1/2) - \omega_e x_e(\nu + 1/2)^2 + \omega_e y_e(\nu + 1/2)^3 + \omega_e z_e(\nu + 1/2)^4 \quad (34)$$

where T_e is the electronic energy, ω_e is harmonic frequency, x_e , y_e , z_e are the anharmonicities and ν the vibrational quantum number. For $b^1 \Sigma_g^+$ $\nu'=0$, $E(0) = 13907.985 \text{ cm}^{-1}$ and for $X^3 \Sigma_g^-$ $\nu''=0$, $E(0) = 787.11 \text{ cm}^{-1}$. The band origin for the transition, $b^1 \Sigma_g^+(\nu'=0) - X^3 \Sigma_g^-(\nu''=0)$ is then $13907.985 - 787.11 = 13120.875 \text{ cm}^{-1}$.

A similar process is required for the rotational constant; B_v , and the centrifugal distortion constant, D_v . The equations are:

$$B_v = B_e - \alpha_e(\nu + 1/2) + \gamma_e(\nu + 1/2)^2 + \dots \quad (35)$$

$$D_v = D_e - \beta_e(\nu + 1/2) + \dots \quad (36)$$

where α_e , γ_e , β_e are vibration-rotational constants. For $b^1 \Sigma_g^+$ $v'=0$, $B_0 = 1.39127 \text{ cm}^{-1}$ and $D_0 = D_e = 5.351 \times 10^{-6} \text{ cm}^{-1}$. In Table 18 other molecular constants are shown. The centrifugal distortion constants of oxygen ($X^3 \Sigma_g^-$ $v''=0$) included in the simulation input.

Table 18. Molecular constants of oxygen O_2 ($X^3 \Sigma_g^-$ $v''=0$)

Constants	(cm^{-1}) ¹⁴⁴
H_0	1.2675×10^{-12}
λ_D	1.9661×10^{-6}
λ_H	1.0441×10^{-11}
γ_D	-8.1790×10^{-9}
γ_H	-5.2370×10^{-14}

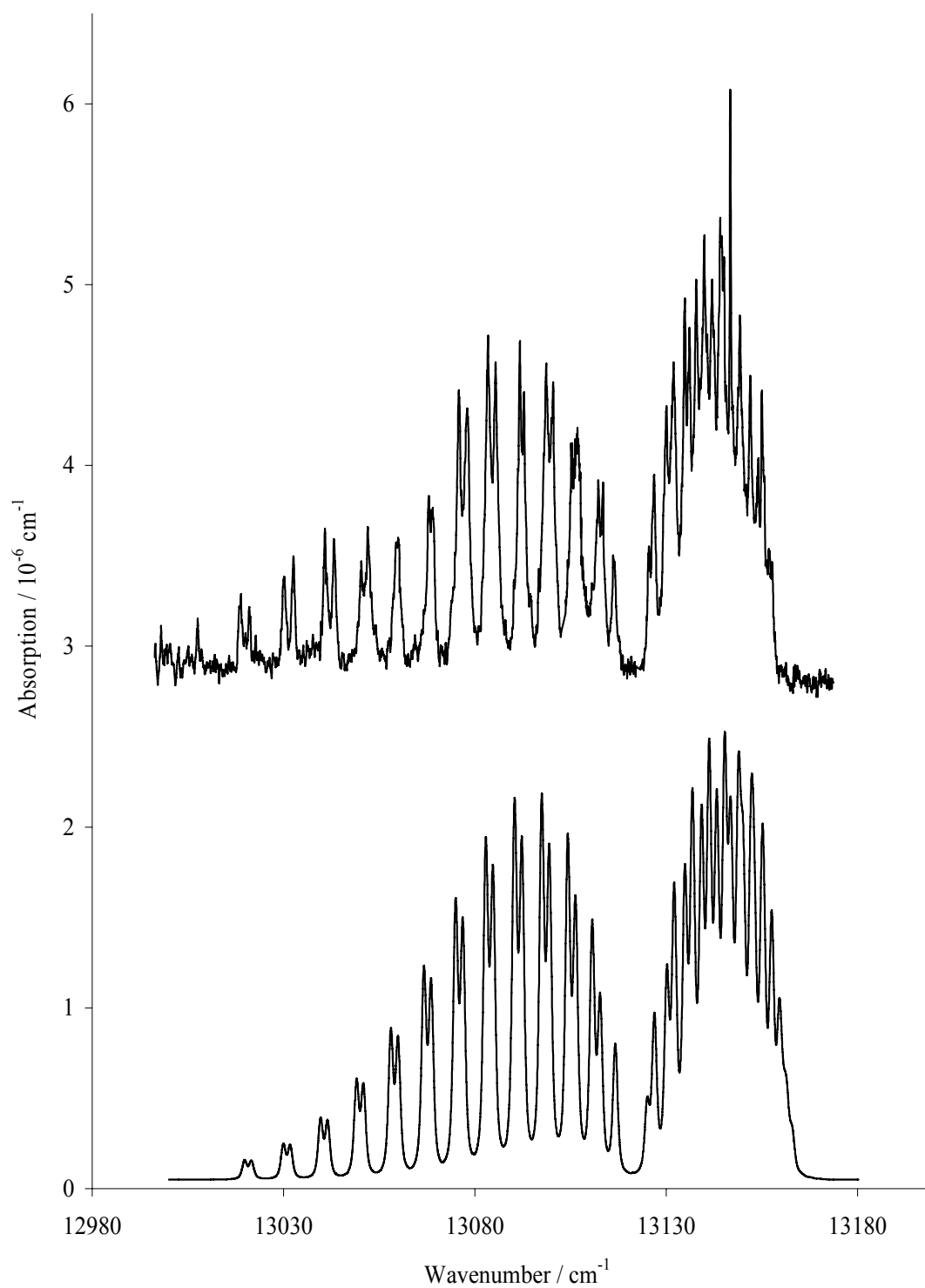


Figure 36. Comparison of absorption spectrum of oxygen *A* band with a pressure of 300 Torr at 295 K. Top= experimental. Bottom= simulated

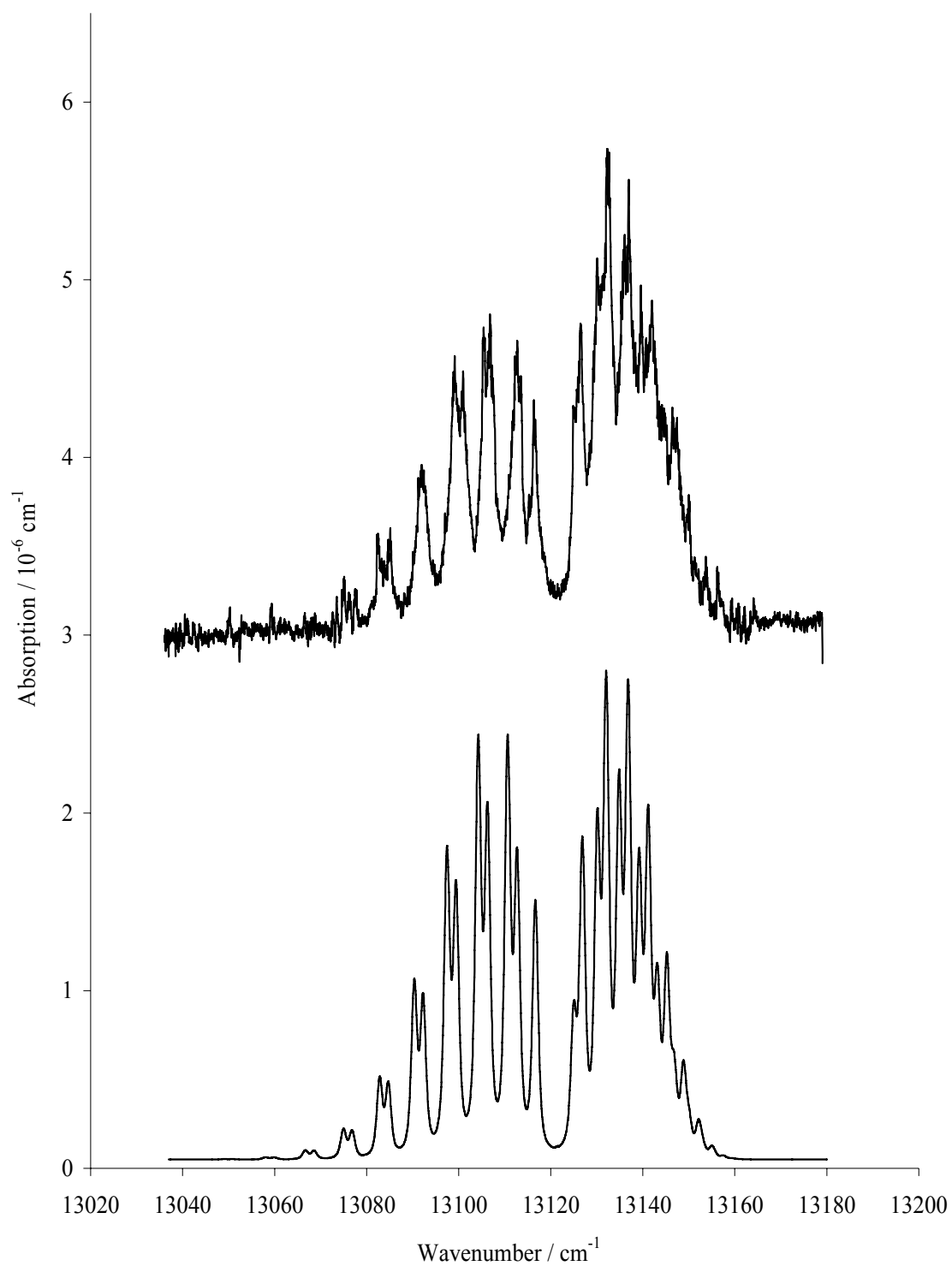


Figure 37. Comparison of absorption spectrum of oxygen *A* band with a pressure of 80 Torr at 90 K. Top= experimental. Bottom= simulated

Figure 36 and Figures 37 show the comparison between the experimental and simulated spectrum of the oxygen *A* band at 295 and 90K, respectively. The good correlation between the experimental and simulated spectra show that the temperature measured in the cell and the actual temperature of the molecule are the same.

Absorption Spectra for the (2, 0) γ -Band of O_2 using CRD Spectroscopy

This γ band corresponds to the (2,0) band of the $b^1 \Sigma_g^+ - X^3 \Sigma_g^-$ electronic system of the O_2 molecule. The oxygen γ band is a weaker absorption than the *A* band absorption. It is a highly forbidden transition, since it is gerade - gerade, $\Sigma^+ - \Sigma^-$ and a singlet-triplet transition. Also the Franck-Condon factor is very small (0.00264).⁵

Absorption spectra of oxygen γ band were measured in the range (15795-15945) cm^{-1} using a pulsed dye laser with DCM as dye. Thus, exponential fitting to measure the decay time was used in the CRD system. The resolution of the pulsed dye laser was $0.07 cm^{-1}$. In this case, the path length used was 6.4 km. Figure 38 shows the absorption spectrum of the oxygen γ band in the region between 15900 and 15795 cm^{-1} . The $^P P$ and $^P Q$ branches are very well resolved. They assignments are indicated above the absorption peaks. Also, a congested region is observed between 15940 to 15900 cm^{-1} . This region corresponds to the $^R R$ and $^R Q$ branches of the γ band. A pressure series of 598, 495 and 384 Torr was measured and is displayed in Figure 39. Since individual rotational lines have been obtained in these spectra, quantitative measurements of intensities can be made for individuals rotational lines of the oxygen γ band.

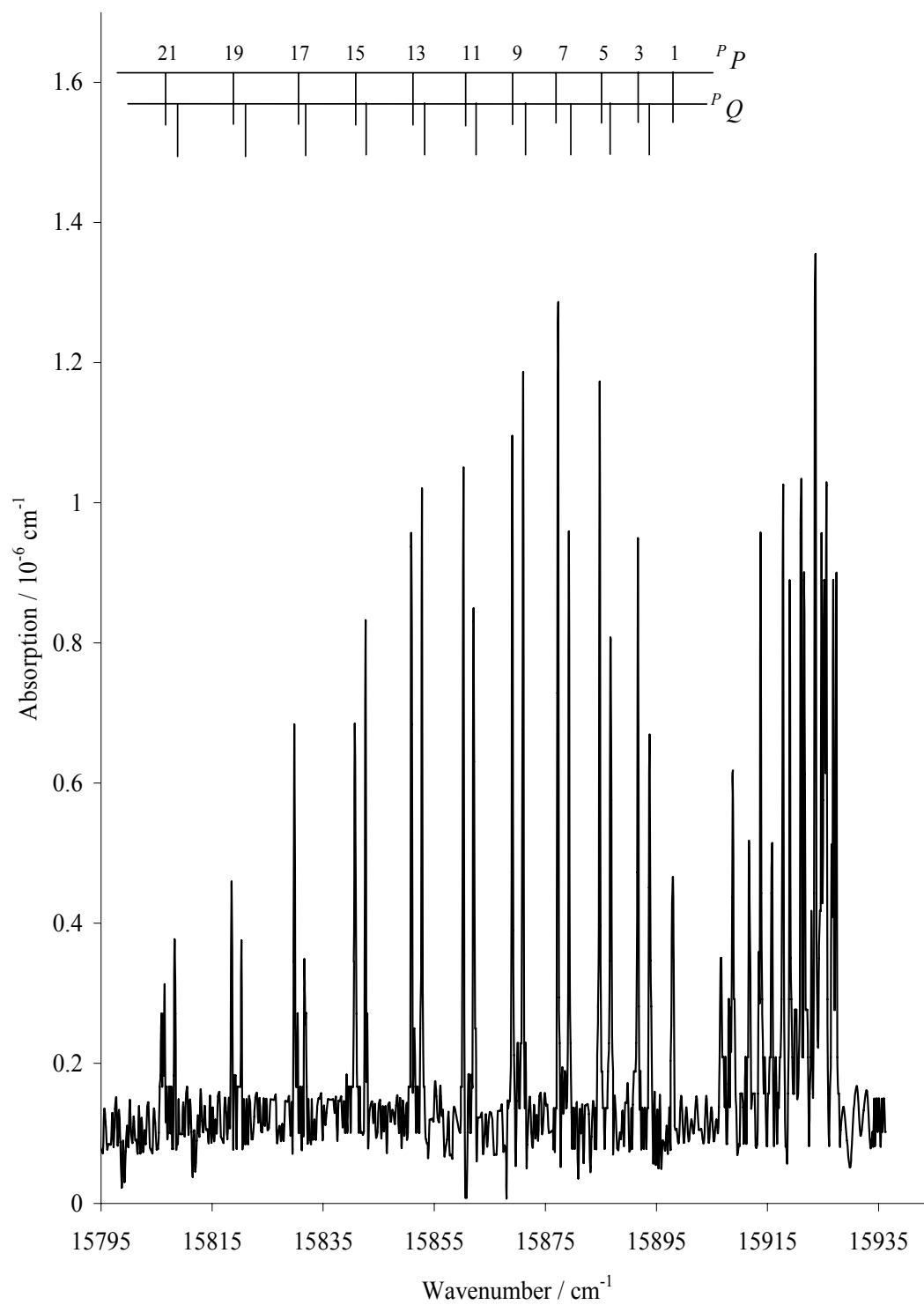


Figure 38. Absorption spectrum of the oxygen γ -band with a pressure of 598 Torr at 295 K.

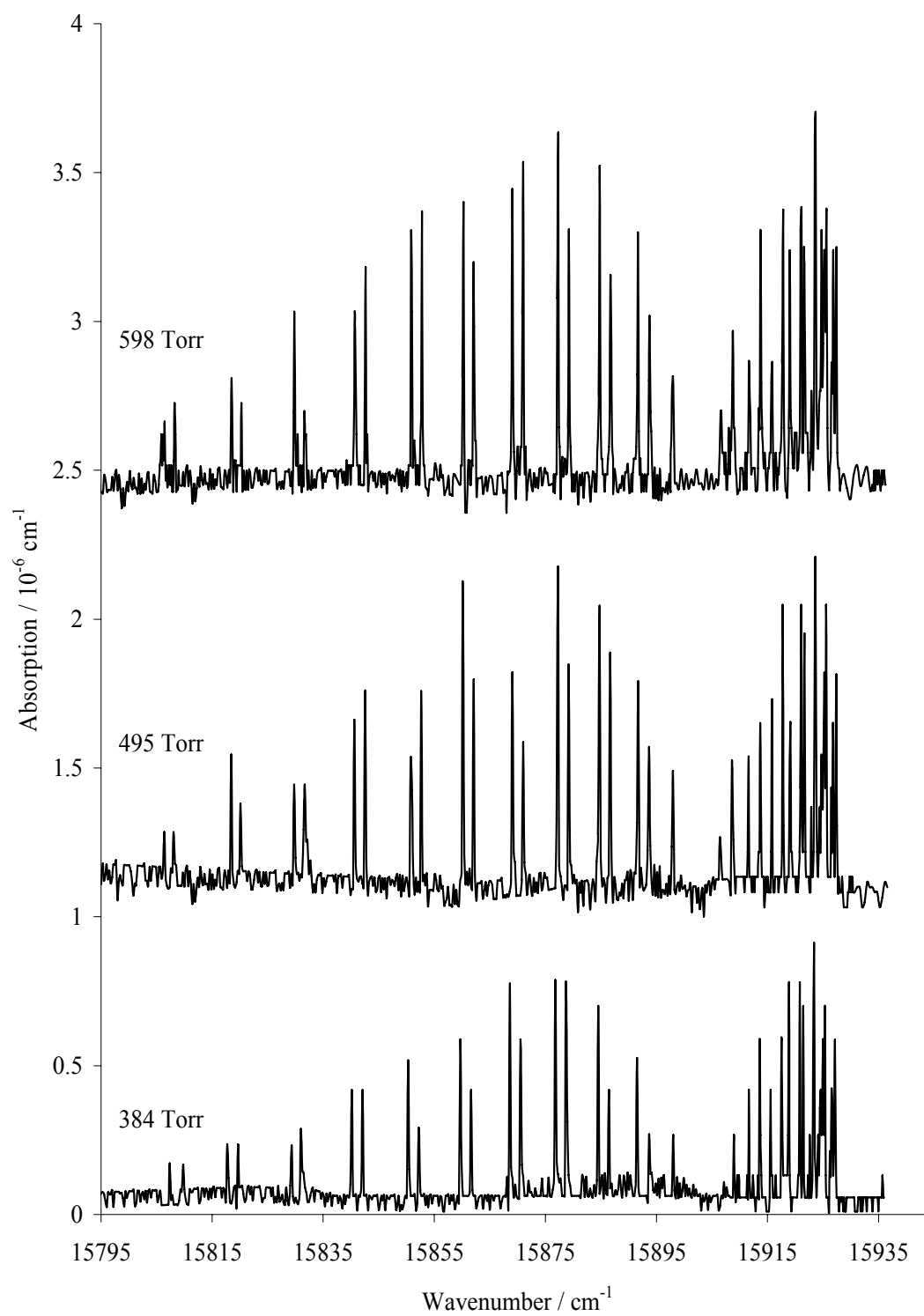


Figure 39. Oxygen γ band. Absorption pressure series at 295K

The total band intensity (vibrational band intensity) can be derived from these line intensity measurements.

The intensity of each rotational line in the oxygen γ band is given by

$$S_{J''V''}^{J'V'} = S_{V''}^{V'} \left(\frac{\nu_0}{Q(T)} \right) i_J \exp[-F_i hc / kT] [1 - \exp(-hc\nu_0 / kT)] = S_{V''}^{V'} S_{J''}^{J'} \quad (37)$$

where $Q(T)$ is the rotational partition function, ν_0 is the frequency at the line center, i_J is the Hönl-London factor, F_i is the energy of the lower state and the other symbols have their usual meaning. The observed values $S_{J''V''}^{J'V'}$ of the ^PP and ^PQ branches from $K''=1$ to $K''=21$ were obtained using equation 22. These values were calculated for the three different pressures used.

In order to calculate $S_{J''}^{J'}$ values for the ^PP and ^PQ lines of the γ band, in equation (37) the contribution of the last term was neglected and it is assumed that the spectral range covered is small. Thus, the resulting equation is the following

$$S_{J''}^{J'} = \frac{i_J}{Q(T)} \exp((-F_i hc / kT)) \quad (38)$$

where F_i values were calculated using equations (31), (32) and (33). The rotational partition function is given by

$$Q(T) = \sum (2J'' + 1) \exp\left(\frac{-hcF_{J''}}{kT}\right) \approx \frac{3}{2} \frac{kT}{Bhc} \quad (39)$$

where B is the ground state rotational constant $B = 1.4377 \text{ cm}^{-1}$ and the other constants, h , c , k , T , have their standard meanings. Because the choice between the Hönl-London factors calculated by Watson or by Schlapp makes no significant difference¹²⁸, the Hönl-London factors of Schlapp were used and the values used are shown in Table 19.

To obtain the total intensity of the γ band, the observed values $S_{J''V''}^{J'V'}$ of the ^PP and ^PQ

branches from $K''=1$ to $K''=21$ were plotted as a function of calculated $S_{J''}^{J'}$ value, the slope of the straight line that results is the vibrational band intensity $S_{V''}^{V'}$.

Table 19. Hönl-London factor of Schlapp¹³⁵

Branch	i_J
^P P	$\frac{1}{2}(J''+1)$
^P Q	$\frac{1}{2}(J''+0.75)$

The $S_{J''V''}^{J'V'}$ values plotted are the averages for the three different pressures used. Figure 40 shows the dispersion between $S_{J''V''}^{J'V'}$ and the calculated $S_{J''}^{J'}$. The straight line gives the best fit of $S_{V''}^{V'}$. This fit gave $S_{V''}^{V'} = (5.1 \pm 0.1) \times 10^{-25} \text{ cm}^2 \text{ cm}^{-1} \text{ molecules}^{-1}$. However, in the literature the vibrational band intensity is reported in units of $\text{cm}^{-1} \text{ km}^{-1} \text{ atm}^{-1} \text{ STP}$. The following relationship is used to convert from units of $\text{cm}^2 \text{ cm}^{-1} \text{ molecules}^{-1}$ to $\text{cm}^{-1} \text{ km}^{-1} \text{ atm}^{-1}$.¹⁴¹

$$S_{V''}^{V'} \left(\frac{\text{cm}^{-1}}{\text{molecule cm}^{-2}} \right) \times \frac{N_L}{p(\text{atm})} \times 10^5 \frac{\text{cm}}{\text{km}} = S_{V''}^{V'} (\text{cm}^{-1} \text{ km}^{-1} \text{ atm}^{-1} \text{ STP}) \quad (40)$$

where N_L is Loschmidt's number, the number of molecules per cubic centimeter of perfect gas at standard temperature and pressure (STP) and p is the pressure. Thus we have

$$S_{V''}^{V'} \left(\frac{\text{cm}^{-1}}{\text{molecule cm}^{-2}} \right) \times 2.6867 \times 10^5 \frac{\text{cm}^2 \text{ molecules}}{\text{atm km}} = S_{V''}^{V'} (\text{cm}^{-1} \text{ km}^{-1} \text{ atm}^{-1} \text{ STP}) \quad (41)$$

Thus, $S_{V''}^{J''} = (1.38 \pm 0.04) \text{ cm}^{-1} \text{ km}^{-1} \text{ atm}^{-1}$ (STP). Using this value, we compute the quantities $S_{J''V''calc}^{J''V''} = S_{V''}^{J''} S_{J''}^{J''}$. Table 20 summarizes $S_{J''V''obs}^{J''V''}$, $S_{J''}^{J''}$ and $S_{J''V''calc}^{J''V''}$ values for each rotational line. The calculated line intensities, $S_{J''V''calc}^{J''V''}$, are plotted and compared with the experimental values in Figure 41 for the $^P P$ and $^P Q$ branches. This plot shows a good agreement between the calculated and experimental values.

Absorption spectra for the $(2 \leftarrow 0) \gamma$ band of $O_2 \ b^1 \Sigma_g^+ - X^3 \Sigma_g^-$ were also recorded at 90K. Figure 42 shows a comparison between the absorption spectrum for the γ band taken at 295K and 90K. Two features stand out in the comparison. The low temperature decreases the number of rotational lines in each branch. Second, there is a change in the rotational intensity distribution. Table 21 review the maximum K value and strongest line observed for both branches, $^P P$ and $^P Q$, at 90K and 295 K.

Also, a pressure series of the γ band for oxygen were measured at 90K. Figure 43 presents the stacked measurements taken at various pressures starting from the lowest pressure at the baseline to the highest pressure at the top.

The intensity of the individual rotational lines, $S_{J''V''Obs}^{J''V''}$, of these spectra were obtained and $S_{J''}^{J''}$ values were calculated to 90K. These values are plotted together with the data found at room temperature (Table 20) in Figure 44. From the slope of the straight line obtained, the intensity for the oxygen γ band is $S_{V''}^{J''} = (1.38 \pm 0.04) \text{ cm}^{-1} \text{ km}^{-1} \text{ atm}^{-1}$ which is the same obtained before. Using this information, equation (37) was calculated to obtain $S_{J''V''calc}^{J''V''}$.

Table 20. $S_{J''V''_{obs}}^{J'V'}$, $S_{J''}^{J'}$ and $S_{J''V''_{calc}}^{J'V'}$ values for the γ band of O₂ at 295K

Line	$\frac{S_{J''V''_{obs}}^{J'V'} \times 10^2}{\text{cm}^{-1} \text{ km}^{-1} \text{ atm}^{-1}}$	$S_{J''}^{J'} \times 10^2$	$\frac{S_{J''V''_{calc}}^{J'V'} \times 10^2}{\text{cm}^{-1} \text{ km}^{-1} \text{ atm}^{-1}}$
$^P P_1$	2.09	1.36	1.87
$^P Q_3$	3.13	1.76	2.42
$^P P_3$	3.96	2.53	3.49
$^P Q_5$	3.88	2.67	3.69
$^P P_5$	5.03	3.35	4.61
$^P Q_7$	4.78	3.17	4.37
$^P P_7$	5.28	3.72	5.13
$^P Q_9$	4.26	3.23	4.46
$^P P_9$	4.87	3.66	5.05
$^P Q_{11}$	3.48	2.96	4.08
$^P P_{11}$	4.27	3.27	4.51
$^P Q_{13}$	3.00	2.47	3.41
$^P P_{13}$	3.76	2.69	3.71
$^P Q_{15}$	2.28	1.90	2.62
$^P P_{15}$	2.86	2.04	2.82
$^P Q_{17}$	2.51	1.36	1.87
$^P P_{17}$	1.87	1.45	2.00
$^P Q_{19}$	1.80	0.91	1.25
$^P P_{19}$	1.80	0.96	1.32

Table 20 $S_{J''V''Obs}^{J'V'}$, $S_{J''}^{J'}$ and $S_{J''V''calc}^{J'V'}$ values for the γ band of O₂ at 295K

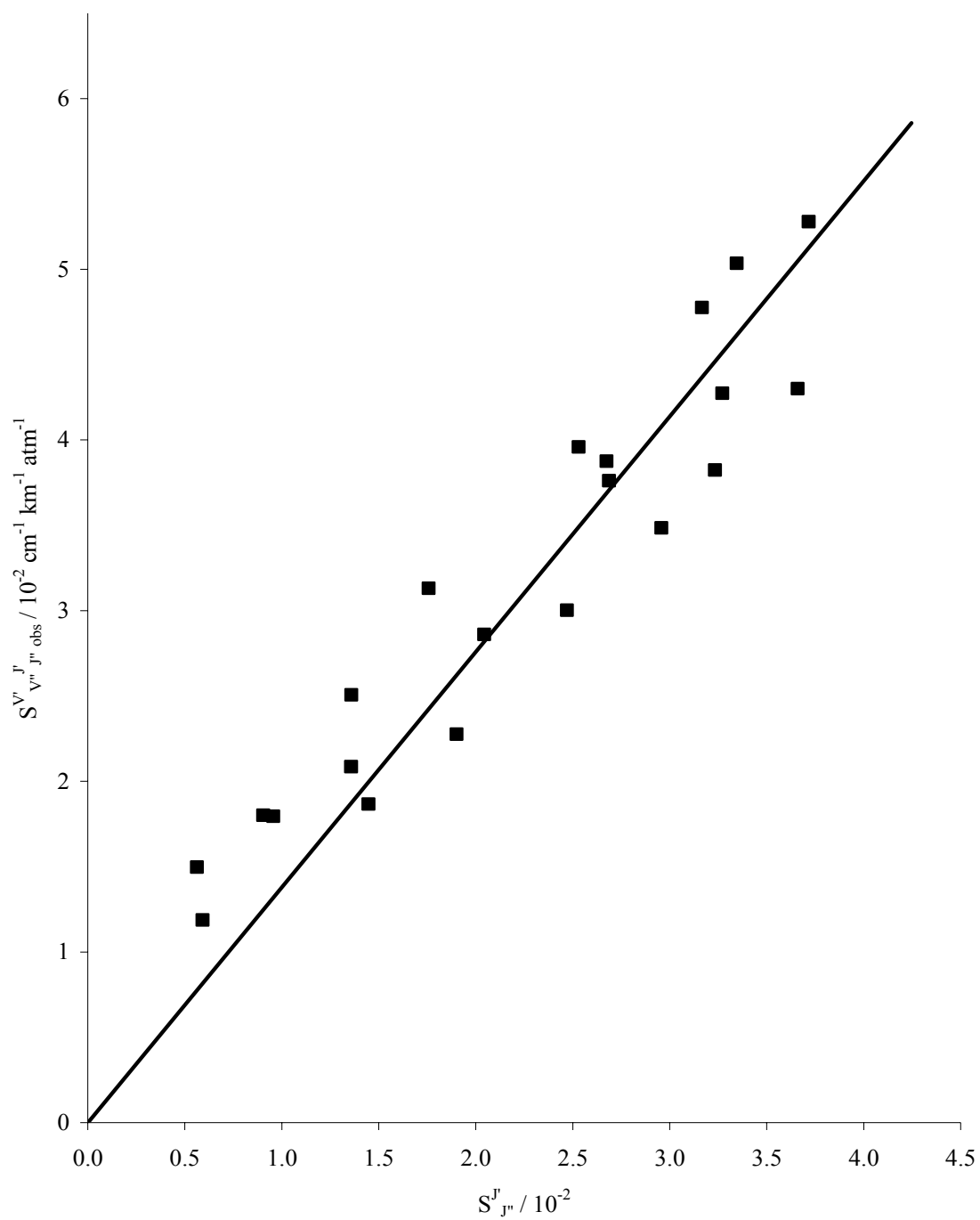
Line	$\frac{S_{J''V''Obs}^{J'V'} \times 10^2}{\text{cm}^{-1} \text{ km}^{-1} \text{ atm}^{-1}}$	$S_{J''}^{J'} \times 10^2$	$\frac{S_{J''V''calc}^{J'V'} \times 10^2}{\text{cm}^{-1} \text{ km}^{-1} \text{ atm}^{-1}}$
$^P Q_{21}$	1.50	0.56	0.77
$^P P_{21}$	1.19	0.59	0.82

Table 21. Maximum K value and strongest line observed in $^P P$ and $^P Q$ branches at 295,90K

T (K)	K_{max}	K value of the Strongest Line
90	11	5
295	25	7

Table 22 reviews the $S_{J''V''Obs}^{J'V'}$, $S_{J''}^{J'}$ and $S_{J''V''calc}^{J'V'}$ values obtained at 90K. Figure 45 presents a comparison between experimental and calculated values of $S_{J''V''}^{J'V'}$ at 90 K for the $^P P$ and $^P Q$ branches. This figure show that the rotational lines with $K'' = 5$ are the most intense ones.

In order to compare our values for the total band intensity for the γ band of oxygen, Table 23 summarizes the values of vibrational band intensities determined by several investigators. From this information, we find that our value $S_{V''}^{V'} = (1.38 \pm 0.04) \text{ cm}^{-1} \text{ km}^{-1} \text{ atm}^{-1}$ agree with the values found in the literature.



$$S_{V''}^{V'} = (1.38 \pm 0.04) \text{ cm}^{-1} \text{ km}^{-1} \text{ atm}^{-1}$$

$$R^2 = 0.922$$

Figure 40. Oxygen γ band at 295 K $S_{J''}^{J' V'}$ vs. $S_{J''}^{J'}$ Slope is $S_{V''}^{V'}$

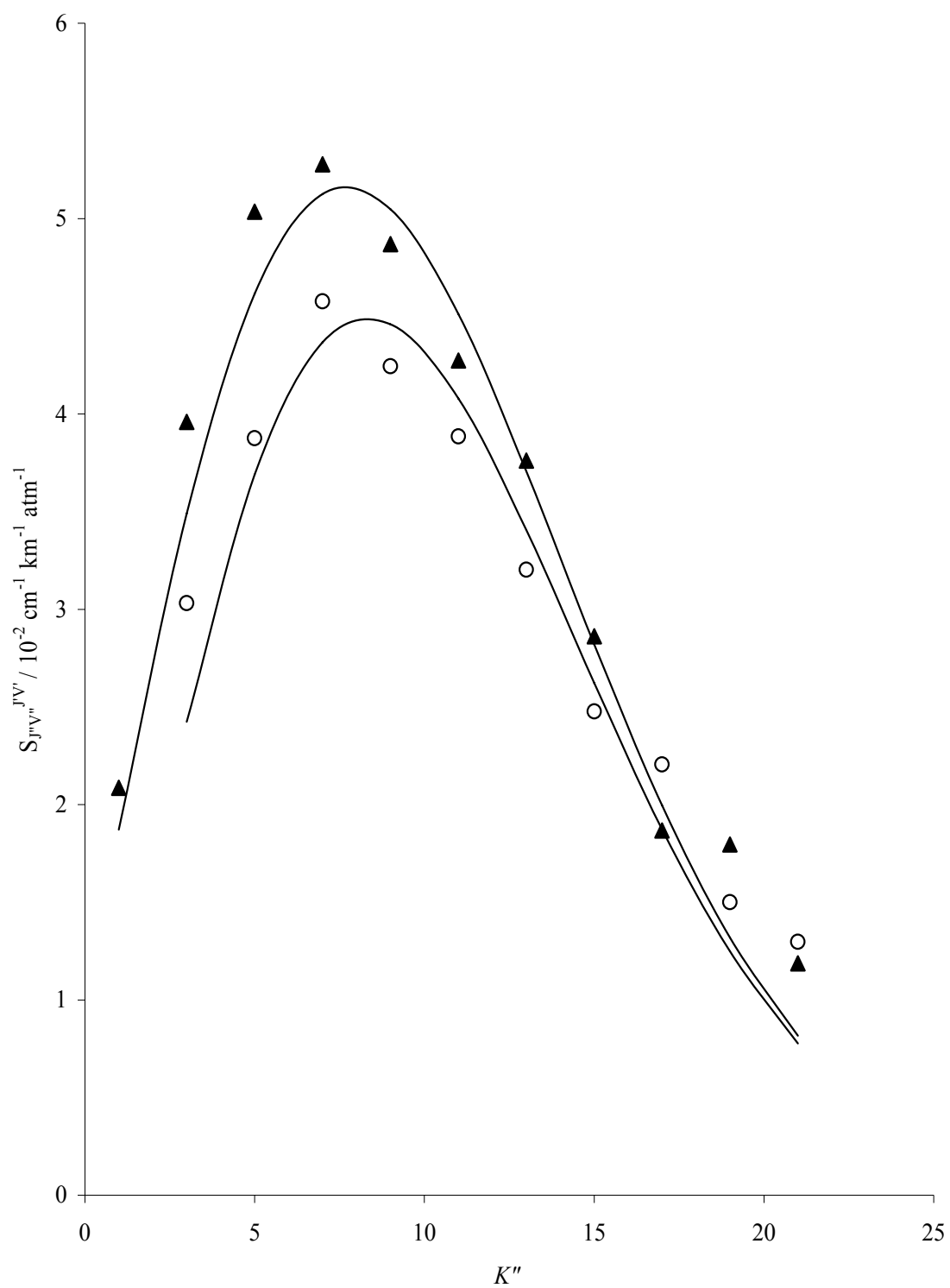


Figure 41. Comparison between calculated and observed values of line $S_{J''V''}^{JV''}$ at 295 K. Marker $\blacktriangle$ = values for $^P P$ branch and Marker $\circ$ = values for $^P Q$ branch. The continuous line refers to the calculated values

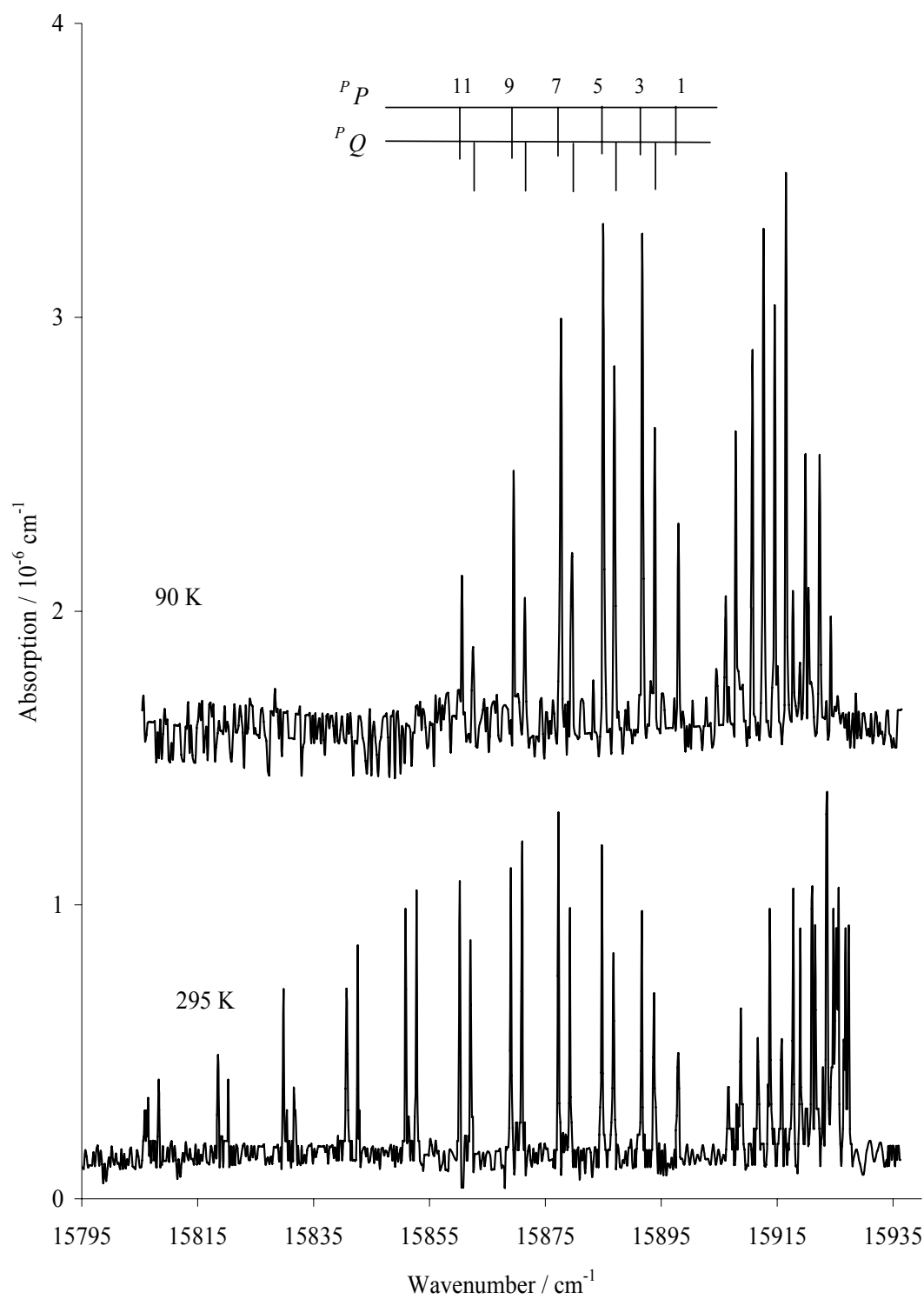


Figure 42. Oxygen γ band with a pressure of 147 Torr at 90 K- top, and 598 Torr at 295K- bottom

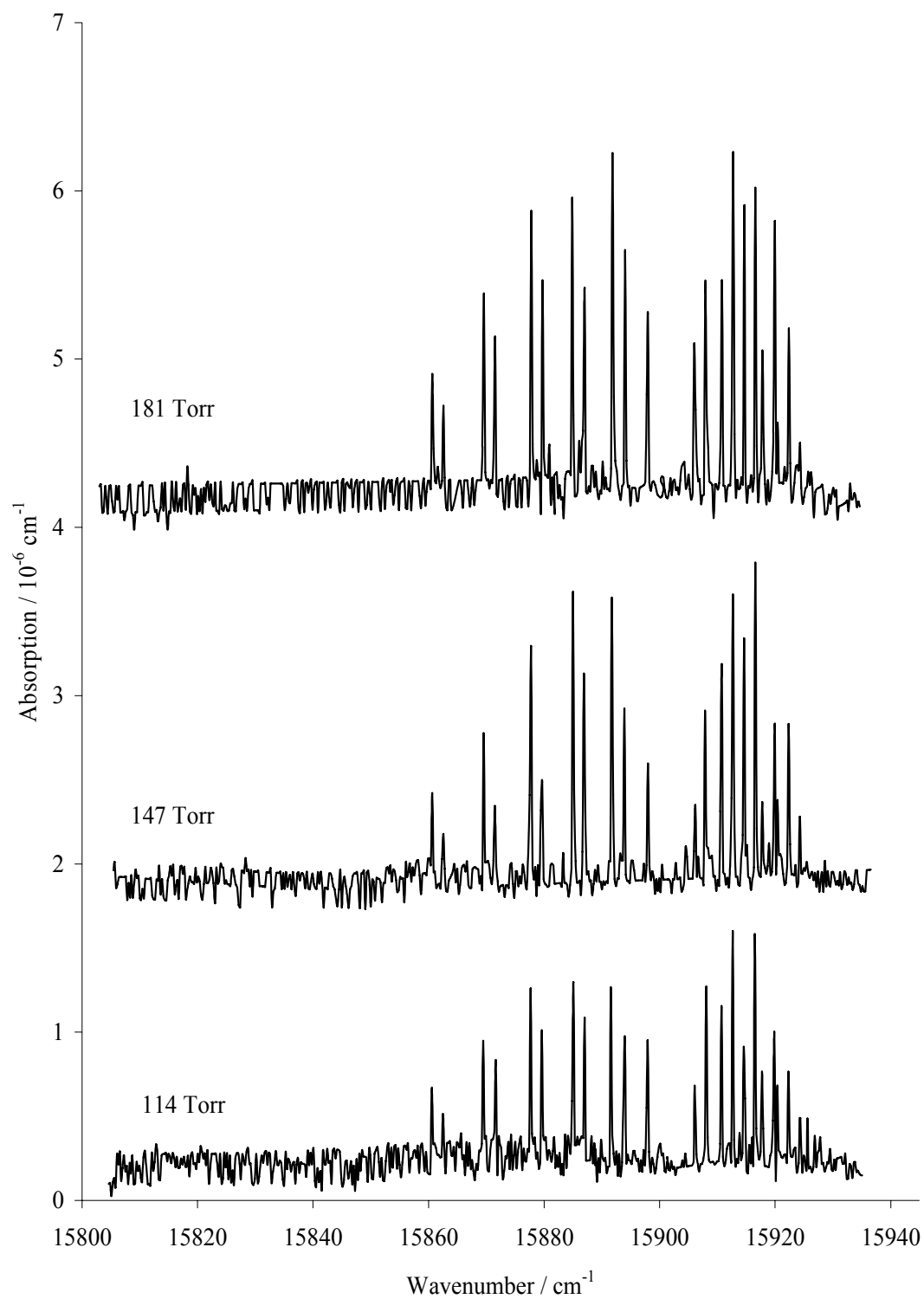
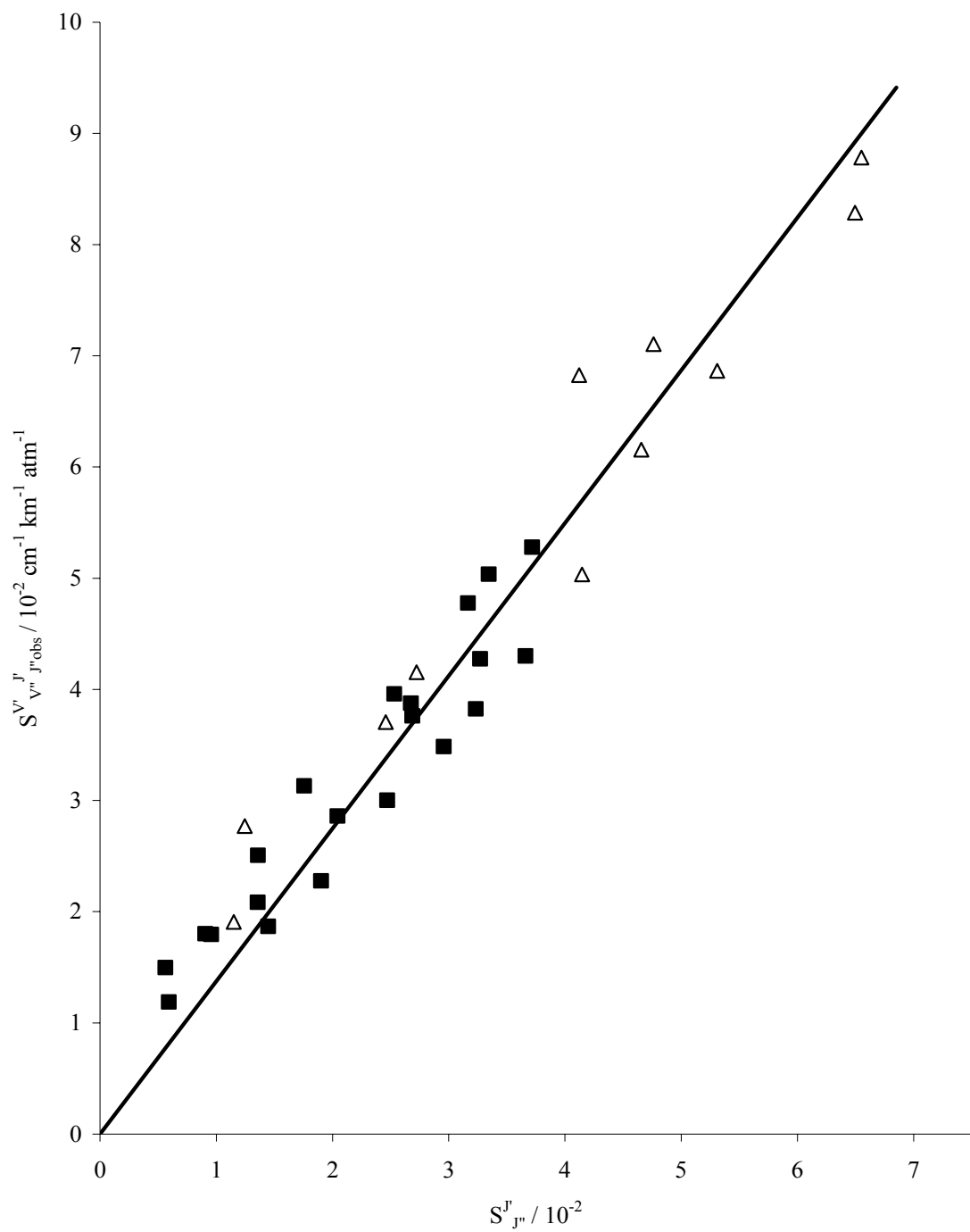


Figure 43. Oxygen γ band. Absorption pressure series at 90K



$$S_{V''}^{J'} = (1.38 \pm 0.04) \text{ cm}^{-1} \text{ km}^{-1} \text{ atm}^{-1}$$

$$R^2 = 0.941$$

Figure 44. Oxygen γ band at 295 K $S_{J''}^{J'}$ vs. $S_{J''}^{J'}$ Slope is $S_{V''}^{J'}$. Marker ■ = measurements at 295 K and Marker Δ = measurements at 90 K

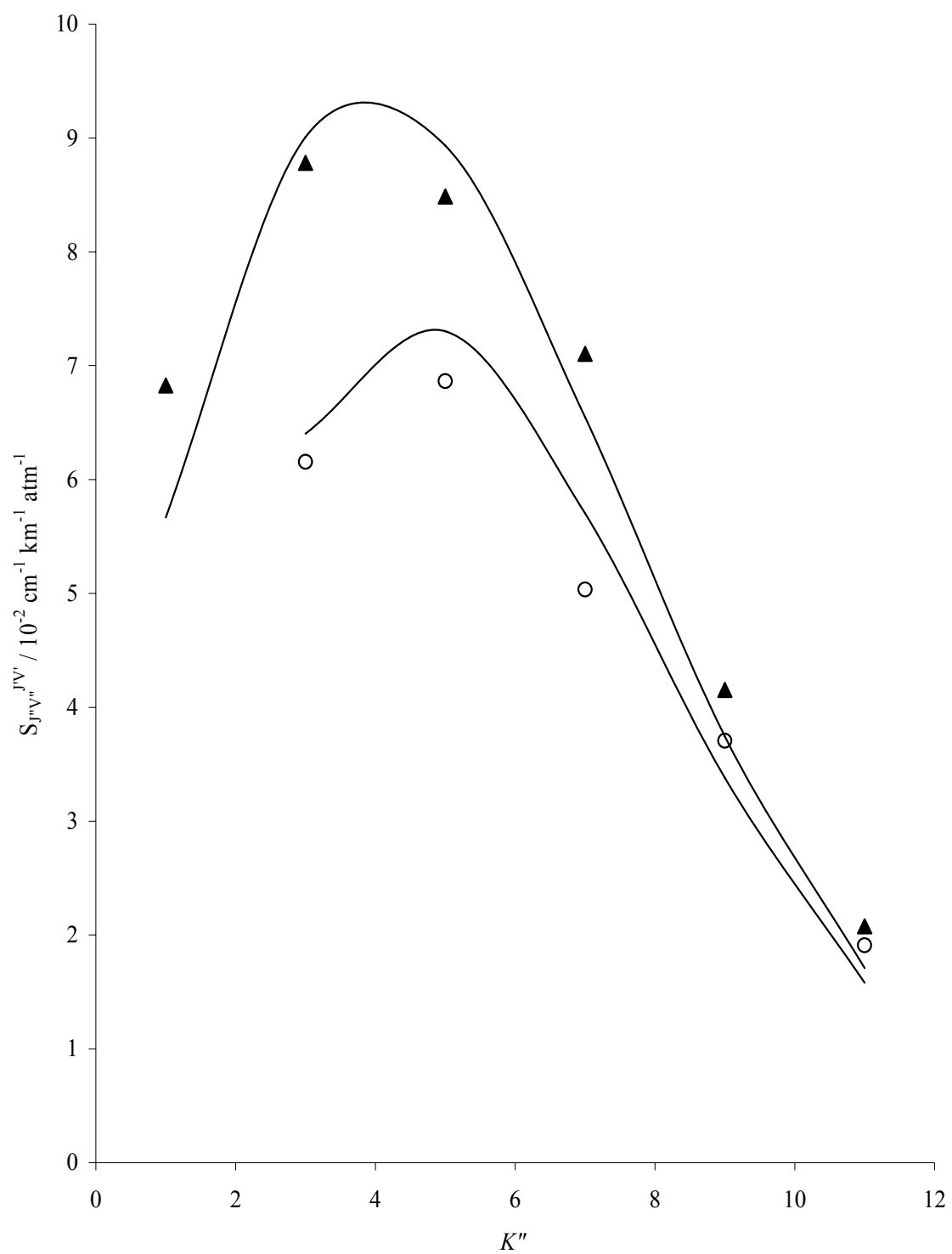


Figure 45. Comparison between calculated and observed values of line $S_{J''V''}^{J'V'}$ at 90 K. Marker $\blacktriangle$ = values for $^P P$ branch and Marker $\circ$ = values for $^P Q$ branch. The continuous line refers to the calculated values

Table 22. $S_{J''V''obs}^{J'V'}$, $S_{J''}^{J'}$ and $S_{J''V''calc}^{J'V'}$ values for the γ band of O₂ at 90K

Line	$\frac{S_{J''V''Obs}^{J'V'} \times 10^2}{\text{cm}^{-1} \text{ km}^{-1} \text{ atm}^{-1}}$	$S_{J''}^{J'} \times 10^2$	$\frac{S_{J''V''calc}^{J'V'} \times 10^2}{\text{cm}^{-1} \text{ km}^{-1} \text{ atm}^{-1}}$
$^P P_1$	6.83	4.12	5.67
$^P Q_3$	6.16	4.65	6.40
$^P P_3$	8.78	6.55	9.01
$^P Q_5$	6.87	5.31	7.30
$^P P_5$	8.29	6.50	8.93
$^P Q_7$	5.03	4.15	5.70
$^P P_7$	7.10	4.76	6.55
$^P Q_9$	3.71	2.45	3.38
$^P P_9$	4.15	2.72	3.74
$^P Q_{11}$	1.91	1.15	1.58
$^P P_{11}$	2.77	1.24	1.71

Absorption Spectra of γ band of oxygen at 295 and 90 K were simulated using the PGOPHER program.¹⁴² Table 24 shows the rotational constant, B₂, and centrifugal distortion, D_v, used in the program to the excited state $b^1 \Sigma_g^+ (v'=2)$. Figure 46 and 47 show the comparison between experimental and simulated spectrum of the γ band at 295 and 90 K, respectively. The similarity between the rotational intensity distribution in the experimental spectra and the simulated spectra confirms the temperature measured in the cell.

Table 23. Band intensities $S_{\nu''}^{\nu'}$ in ($\text{cm}^{-1} \text{ km}^{-1} \text{ atm}^{-1}$) for the γ ($2 \leftarrow 0$) O_2 band

Reference	$S_{\nu''}^{\nu'}$ ($\text{cm}^{-1} \text{ km}^{-1} \text{ atm}^{-1}$)
Allen ¹⁴⁵	1.22
Van de Hulst ¹⁴⁶	1.31
Babcock ¹²⁷	1.50
Miller ¹²⁹	1.52 ± 0.07
Stoeckel ¹³⁵	1.26 ± 0.05
Mizushima ¹⁴⁷	1.52
This work	1.38 ± 0.04

Table 24. Parameters for the $b^1 \Sigma_g^+$ ($\nu'=2$) state.

$b^1 \Sigma_g^+$	cm^{-1}
Band Origin	15902.42
B_2	1.35487
D_v	5.351×10^{-6}

Conclusions

The rotational vibrational spectra for three different transition, for O_2 the ($0 \leftarrow 0$) and ($2 \leftarrow 0$) bands of the $b^1 \Sigma_g^+ \leftarrow X^3 \Sigma_g^-$ transition were obtained using CRD spectroscopy. The spectra were measurement at room and low temperatures.

The intensity of the individual rotational lines of the $b^1 \Sigma_g^+ (\nu'=2) \leftarrow X^3 \Sigma_g^- (\nu''=0)$ oxygen molecules was measured. From these measurements the total band intensity was determined. The total band intensity derived from the line intensities is $(1.38 \pm 0.04) \text{ cm}^{-1} \text{ km}^{-1} \text{ atm}^{-1}$. This value is in good agreement with the literature values.

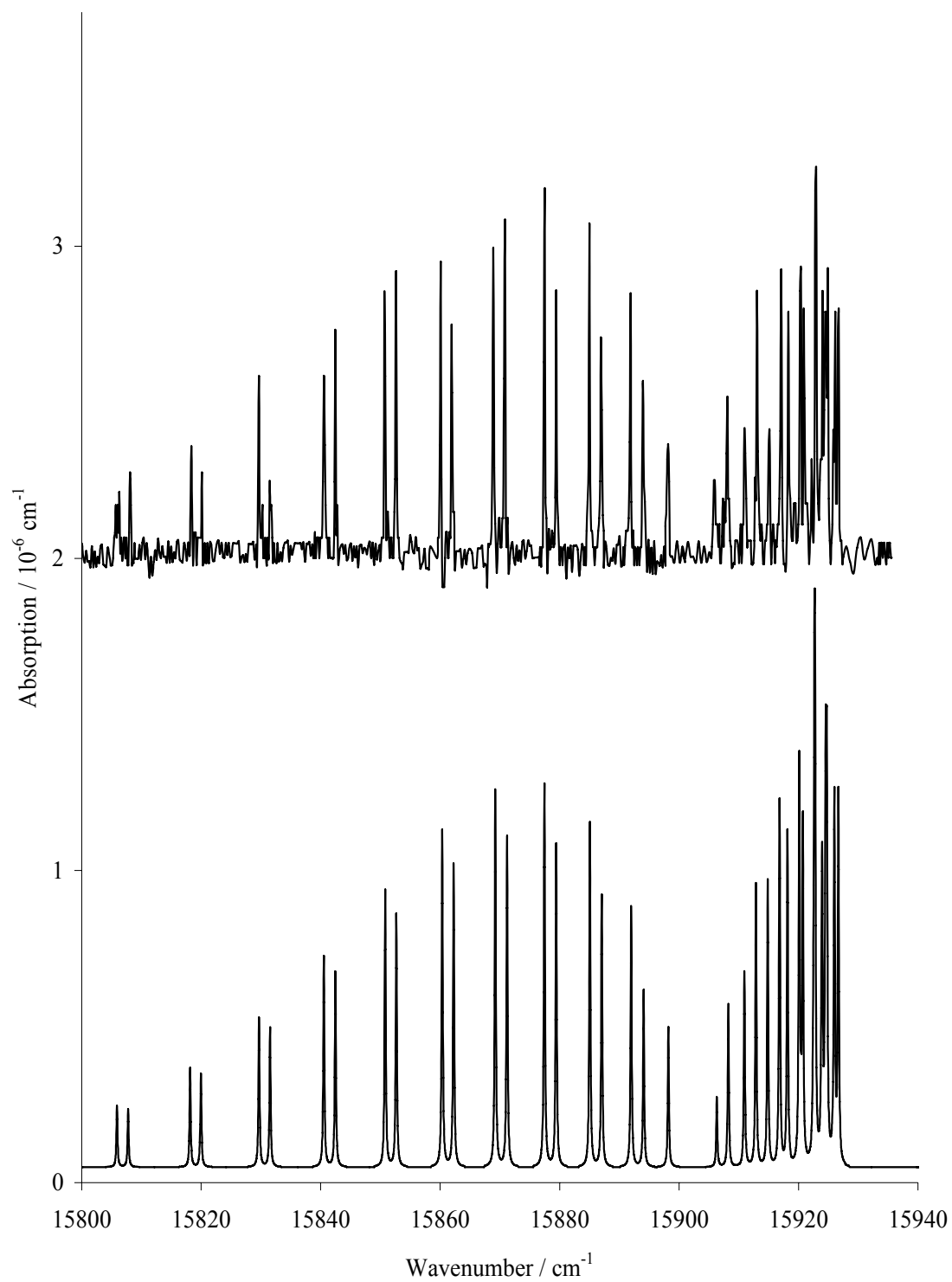


Figure 46. Comparison of absorption spectrum of γ band for O_2 with a pressure of 598 Torr at 295 K. Top= experimental. Bottom= simulated

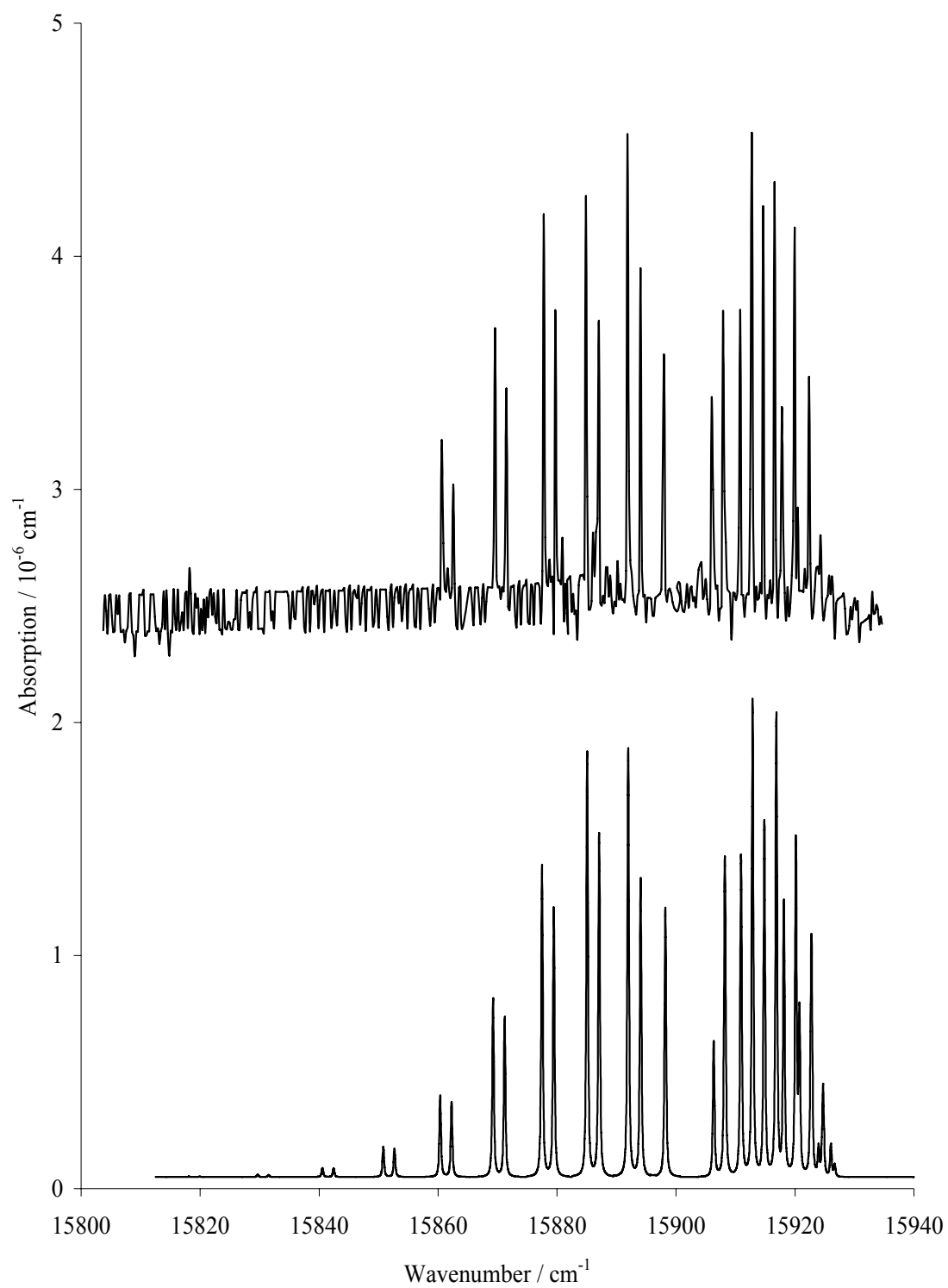


Figure 47. Comparison of absorption spectrum of γ band for O_2 with a pressure of 147 Torr at 90 K. Top= experimental. Bottom= simulated

Rotation-Vibration Spectra of HD.

Intensity Measurements of the $\Delta v=4$ Overtone Band

There is a particular interest in the measurements of the rotation-vibration bands of HD because they have been detected in the atmospheres of giant planets.¹⁴⁸ The estimation of HD abundance by this means, which of course requires knowledge of the transition intensity, is presently the best way to determine the D/H ratio in their atmosphere. Observations of the D/H ratio in the atmospheres of giant planets provide an understanding of the evolution of solar system and even the origin of the universe.¹⁴⁸

Because the mass of the deuteron is twice the mass of the proton, the electrons in HD approach the former in average slightly closer than the latter. In a hydrogen atom the average proton-electron distance is 1.0005456 bohr and in the deuterium atom the deuteron-electron distance is 1.0002724 bohr. The asymmetry in the electron behavior near the deuterium and hydrogen nuclei results in an appearance of a small dipole moment HD¹⁴⁹. Due to this dipole moment rotational-vibrational transitions are visible in the HD experimental spectrum, although they are very weak.

Rovibrational transitions $\Delta v=3$ and $\Delta v=4$ in the HD were observed by Herzberg¹⁵⁰ for first time using a White multiple reflection cell and preliminary values for the constants of HD were given. Later studies of fundamental and some overtones ($\Delta v = 1, 2, 3, 4, 5, 6$) were used to determine molecular constants for the $v = 0$ and $v = 6$ vibrational levels of HD ground electronic state.¹⁵¹⁻¹⁵⁴ Due to the observation of HD, P (1) of the $\Delta v = 4$ transition, on Jupiter¹⁴⁸, several group have studies intensities of the $\Delta v=1, 2, 3, 4, 5, 6$ at room and low temperatures^{68, 153-160}. Intensities of the dipole transitions have been measured in order to determine the permanent dipole moment of

HD in its ground vibrational state and transition dipole moments.^{154, 156, 157, 161-165} Also, theoretical calculations have been made for this molecule.^{149, 157, 166, 167}

The weak $\Delta v=4$ overtone band of the rotation-vibration spectrum of HD was studied using PS-CRD absorption spectroscopy. The resolution of the continuous wave Ti:Sapphire laser was 0.17cm^{-1} . In order to increase the coupling-time efficiency of the laser light inside the cavity, the off-axis alignment has been used. In the off-axis alignment, the laser beam is injected into the cavity at an angle to the center axis (off-axis), the beam may couple continuously into the cavity up to 100% of the time. The path length used was 6 km.

The rotational-vibrational overtone transition ($\Delta v=4$) of HD was measured at 295 and 104 K. Low temperature measurements of this transition are important because they provide a relevant comparison to planetary spectra measurements because of the coldness of their atmospheres ranging between 50 and 150K.

The HD ($\Delta v=4$) overtone spectrum at 891 Torr and 295K is shown in Figure 48. As can be seen, the lines form a clear R and P branch with a zero gap between the branches. The intensities of the rotational lines of the R branch were analyzed and compared to literature values. Figure 49 shows a pressure series of 6 separate measurements ranging from 891 to 519 Torr of HD taken at 295K. From these spectra, it is possible measure the integrated intensity and absorption strength of the R (0), R (1) and R (2) bands of the third overtone transition.

For many purposes it is convenient to define an absorption strength value, S_J which is independent of temperature,¹⁵³

$$S_J = \frac{S}{\rho * P_J} \quad (42)$$

where S is the integrated absorption in $\text{cm}^{-1} \text{ km}^{-1}$, ρ is the density in amagat and $P_J(T)$ is the fraction of molecules in the initial rotational level J at temperature T . P_J is calculated using the relation:⁸⁷

$$P_J = \frac{(2J+1)e^{-\frac{B_e J(J+1)hc}{kT}}}{\sum_{J=0}^{\infty} (2J+1)e^{-\frac{B_e J(J+1)hc}{kT}}} \quad (43)$$

where J is the rotational quantum number, B_e is the equilibrium rotational constant, ($B_e = 45.655 \text{ cm}^{-1}$). The other symbols have their usual meaning. The calculated Boltzmann factors for HD at 295K are presented in Table 25.

Table 25. Calculated Boltzmann factors at 295K

P_J	295K
0	0.207
1	0.397
2	0.272

The actual absorption strength values are obtained by plotting the integrated absorption (S), versus the density (ρ) multiplied by the Boltzmann population factor (P_J).

The slope of the resulting straight line gives the S_J value. Rotational line, R(0), R(1) and R(2) were analyzed individually. Table 26 displays the pressure, the density multiplied by P_J , integrated absorption value (S), and the temperature independent absorption strengths (S_0) of the R (0) line at 295K.

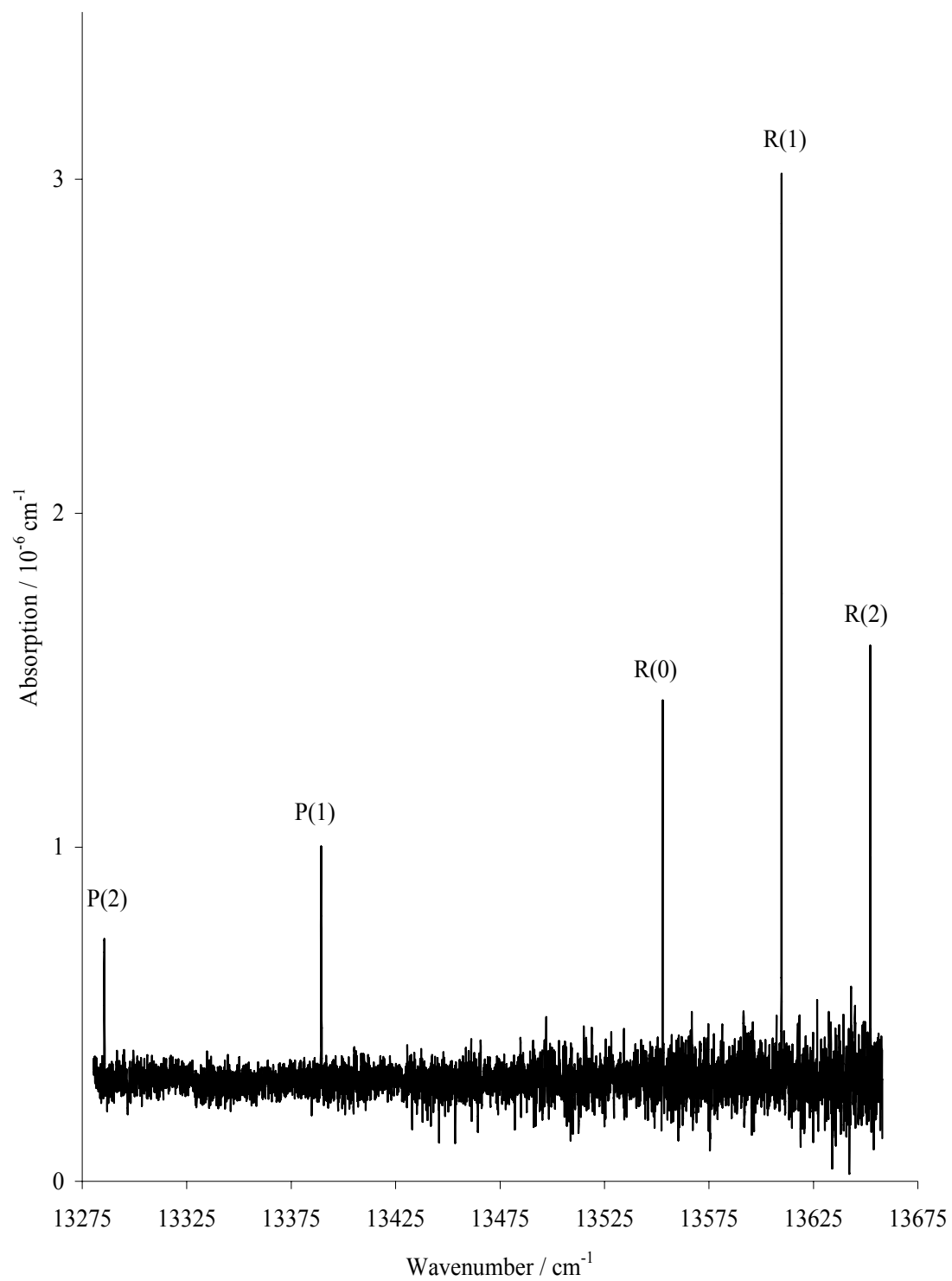


Figure 48. ($\Delta v=4$) HD with a pressure of 891 Torr at 295 K

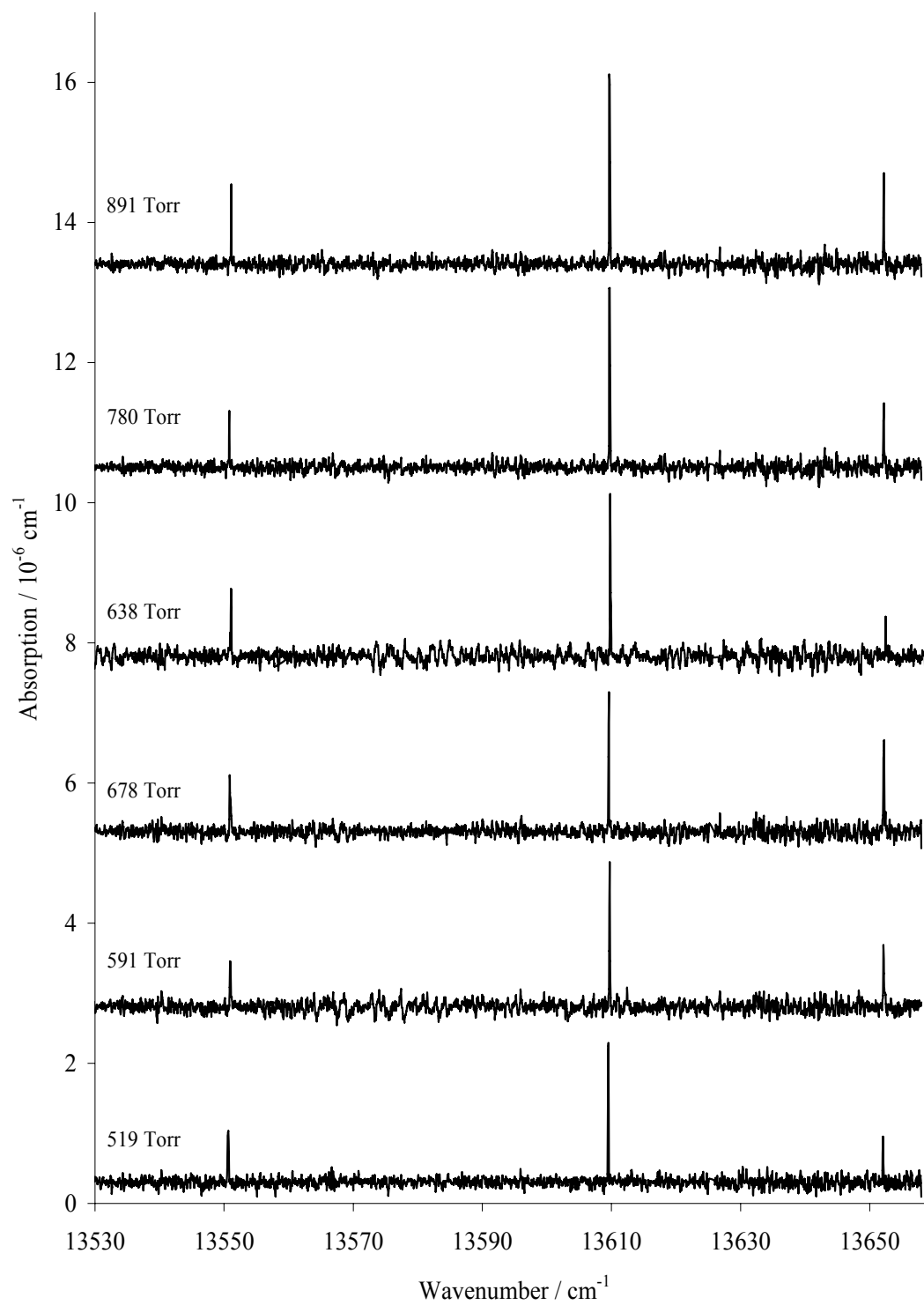


Figure 49. ($\Delta v=4$) HD. Absorption pressure series at 295K

Table 26. ($\nu=0 \rightarrow 4$) R(0) of HD at 295 K, Pressure, ρ^*P_0 , S , and S_0 .

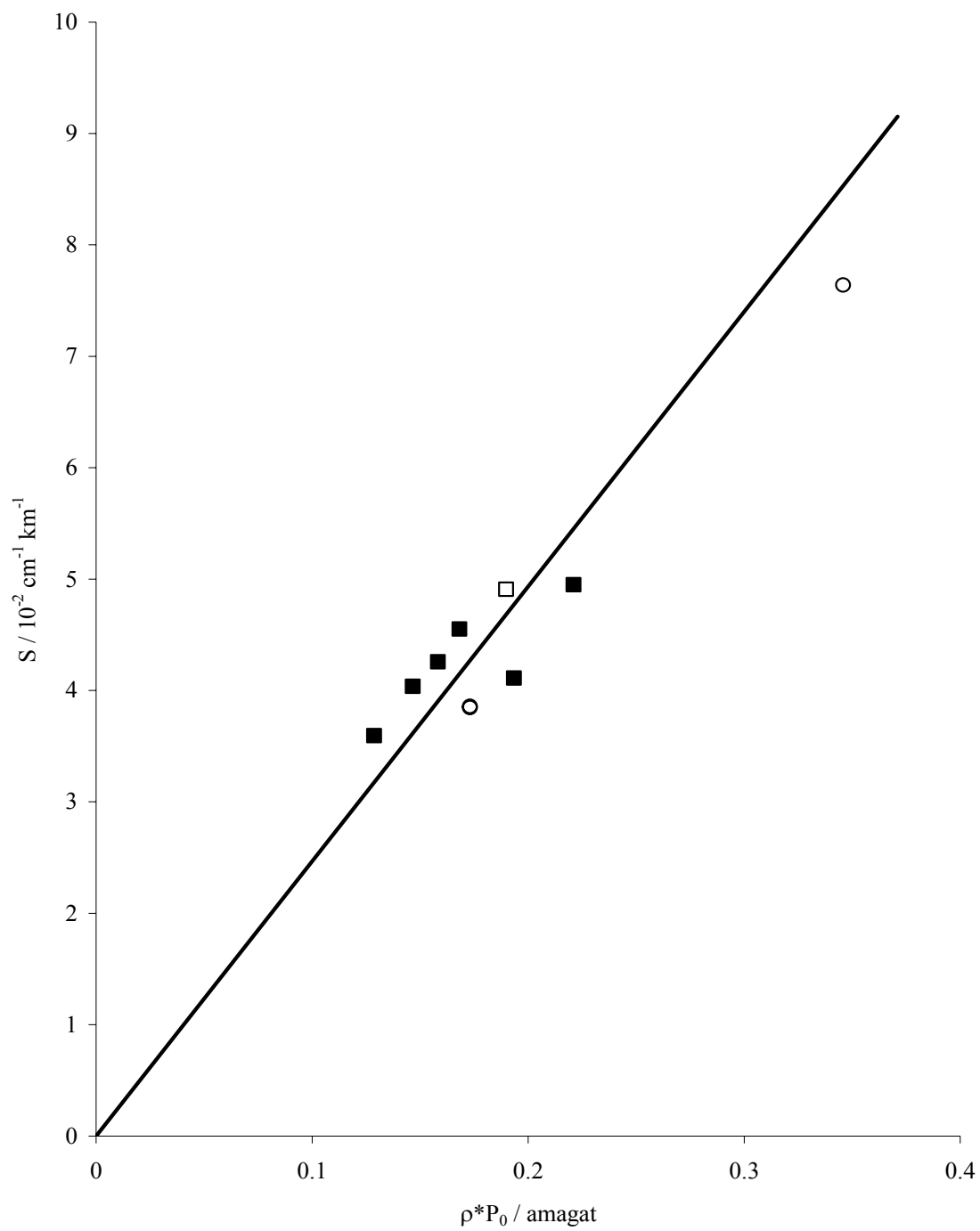
Pressure	ρ^*P_J	S	S_0
torr	amagat	$10^{-2} \text{ cm}^{-1} \text{ km}^{-1}$	$\text{cm}^{-1} (\text{km amagat})^{-1}$
891	0.221	4.948	0.227
780	0.193	4.111	0.216
678	0.168	4.552	0.275
638	0.158	4.257	0.273
591	0.147	4.036	0.279
519	0.129	3.594	0.283
Avg.			0.25 ± 0.01

In Figure 50 the values of S are plotted versus ρ^*P_J (full square) for the R (0) absorption at 295K and fitted to a straight line. For comparison, (without including the points in the fit), the values reported by Trauger and Mickelson.¹⁵⁹ (open circle) and McKellar et al.¹⁵³ (open square) are presented. Figure 50 shows that there is very good agreement between our measurements and the values reported in the literature.

The same analysis was made for the R(1) and R(2) absorptions at 295K. Table 27 and Table 28 present the pressure, ρ^*P_J , S and S_J values of the R (1) and R (2) absorptions at 295K, respectively.

The values reported in Tables 27 and 28 with literatures values for R(1) and R(2) are plotted in Figures 51 and 52.

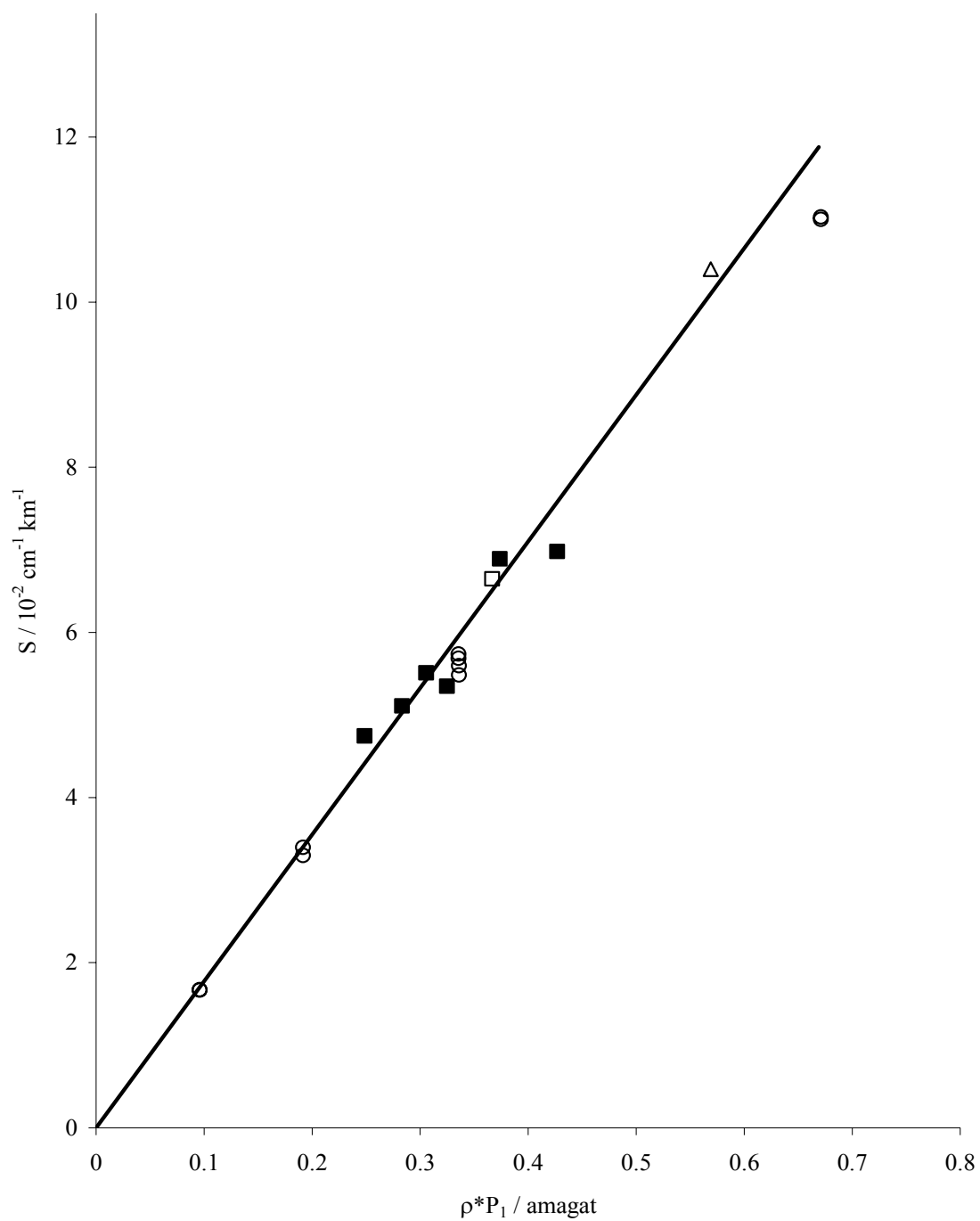
The resulting absorption strength values are listed together with previously reported laboratory and theoretical values in Table 29. There is good agreement between our measurements and values reported before.^{153, 158, 159, 163} Measurements of the ($\Delta \nu = 4$) overtone band of the rotation-vibration spectrum of HD were also done at 90K using the low temperature setup of the PS-CRD system.



$$S_0 = (0.25 \pm 0.01) \text{ cm}^{-1} (\text{km atm})^{-1}$$

$$R^2 = 0.960$$

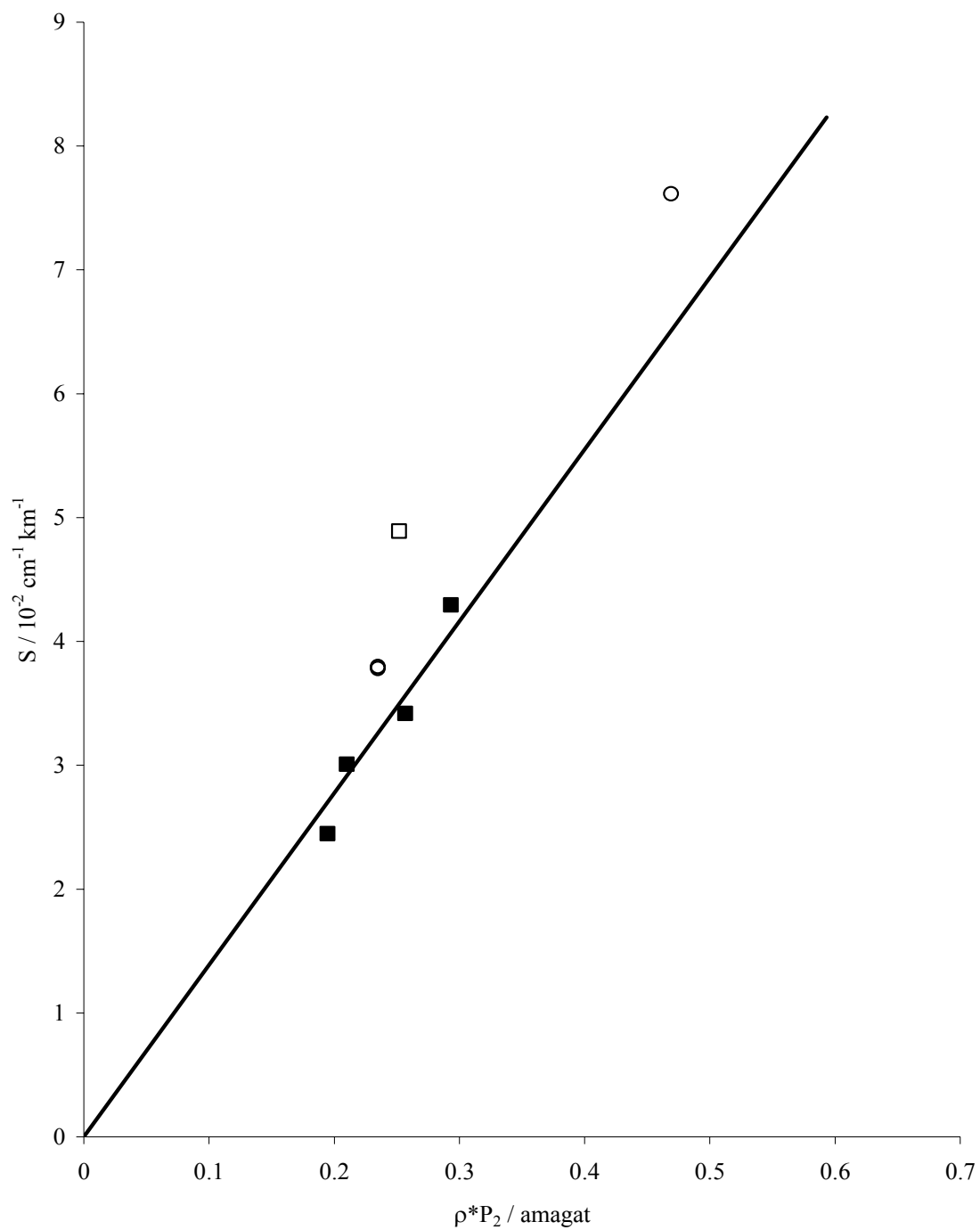
Figure 50. $(\Delta v = 4)$ HD R(0) at 295K S vs $\rho * P_0$. Marker ■ = present work, □ = McKellar¹⁵³ and ○ = Trauger¹⁵⁹



$$S_0 = (0.175 \pm 0.004) \text{ cm}^{-1} (\text{km atm})^{-1}$$

$$R^2 = 0.990$$

Figure 51. ($\Delta v=4$) HD R(1) at 295K S vs $\rho * P_1$. Marker ■ = present work, □ = McKellar ¹⁵³ and ○ = Trauger ¹⁵⁹



$$S_0 = (0.134 \pm 0.004) \text{ cm}^{-1} (\text{km atm})^{-1}$$

$$R^2 = 0.993$$

Figure 52. ($\Delta v=4$) HD R(2) at 295K S vs $\rho * P_2$. Marker ■ = present work, □ = McKellar ¹⁵³ and ○ = Trauger ¹⁵⁹

Table 27. ($\nu=0\rightarrow4$) R(1) of HD at 295 K, Pressure, ρ^*P_0 , S , and S_0 .

Pressure	ρ^*P_J	S	S_0
torr	amagat	$10^{-2}\text{cm}^{-1}\text{km}^{-1}$	$\text{cm}^{-1}(\text{km amagat})^{-1}$
891	0.427	6.980	0.163
780	0.374	6.890	0.184
678	0.325	5.350	0.165
638	0.306	5.510	0.180
591	0.283	5.110	0.181
519	0.249	4.747	0.191
Avg.			0.175 ± 0.004

Table 28. ($\nu=0\rightarrow4$) R(2) of HD at 295 K, Pressure, ρ^*P_0 , S , and S_0 .

Pressure	ρ^*P_J	S	S_0
torr	amagat	$10^{-2}\text{cm}^{-1}\text{km}^{-1}$	$\text{cm}^{-1}(\text{km amagat})^{-1}$
891	0.293	4.294	0.146
780	0.257	3.418	0.133
638	0.210	3.008	0.143
591	0.195	2.447	0.126
Avg.			0.139 ± 0.004

Figure 53 shows a comparison of the overtone spectrum of HD at room and low temperature. As can be seen in this figure the distribution of the rotational lines has changed, at room temperature the intensities are in the order $R(1) > R(0) \approx R(2)$ and at low temperature the intensities are in the order $R(0) > R(1) > R(2)$. This is because the thermal distribution of the rotational levels changes when the temperature is reduced. This is in agreement with the calculated Boltzmann factors for HD at 90K shown in Table 30.

Table 29. ($\Delta v = 4$) HD absorption strengths values

	S_J (this work)	S_J (other work)
	(cm ⁻¹ (km amagat) ⁻¹)	
R(0)	0.25 ± 0.01	0.226 ± 0.004 ¹⁵⁹ 0.224 ± 0.011 ¹⁵⁸ 0.26 ± 0.03 ¹⁵³ 0.230 ¹⁶³
R(1)	0.175 ± 0.004	0.171 ± 0.003 ¹⁵⁹ 0.18 ± 0.02 ¹⁵³ 0.162 ¹⁶³
R(2)	0.134 ± 0.004	0.165 ± 0.003 ¹⁵⁹ 0.19 ± 0.02 ¹⁵³ 0.161 ¹⁶³

Table 30. Calculated Boltzmann factors at 90K

P_J	295K
0	0.568
1	0.395
2	0.036

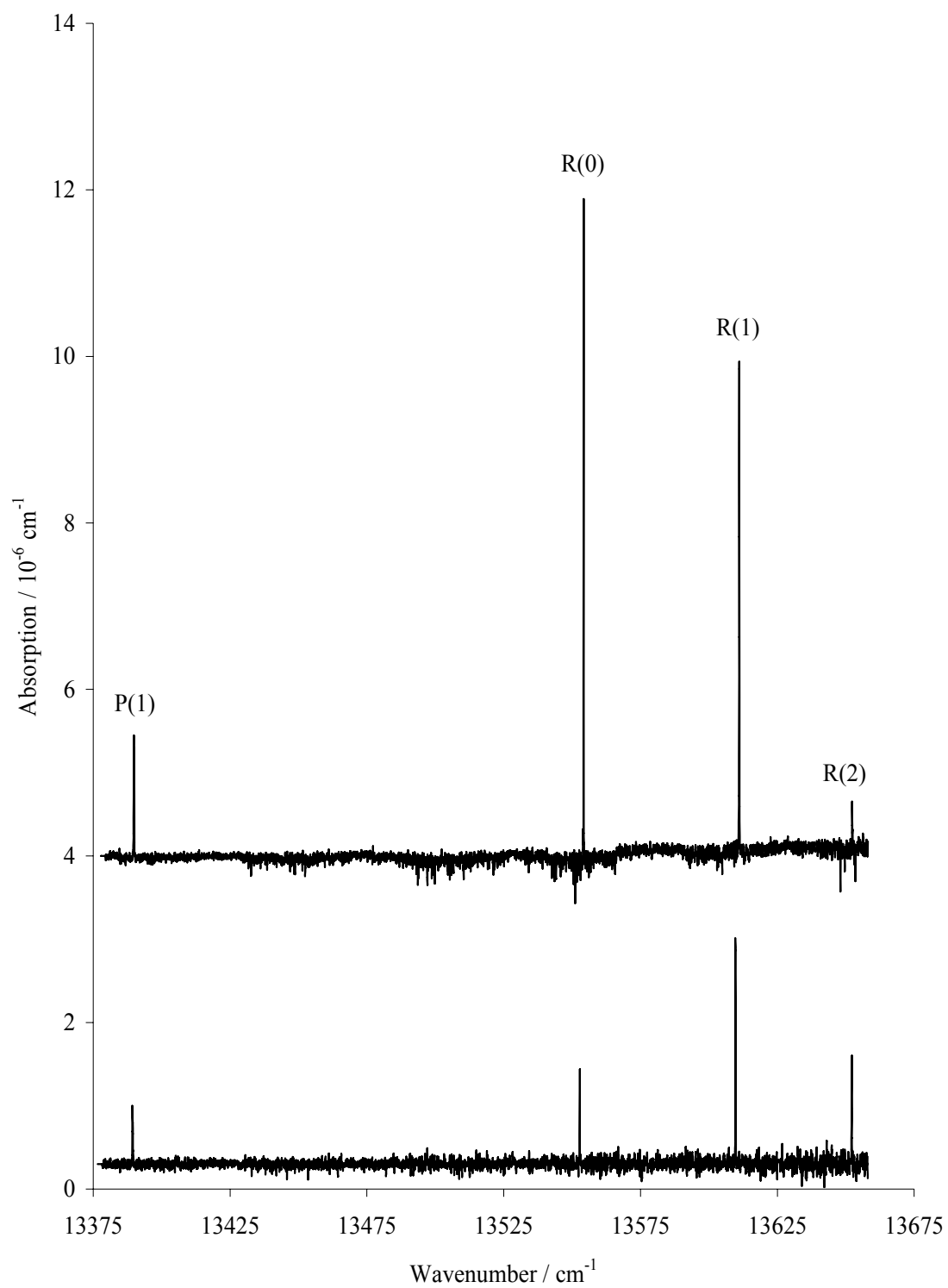


Figure 53. ($\Delta v = 4$) HD with a pressure of 401 Torr at 90 K- top, and 891 Torr at 295K- bottom

The integrated absorption was also calculated using the low temperature spectrum (S) for R(0), R(1), and R(2). Table 31 summarizes the values of ρ^*P , S and S_J at 90 K.

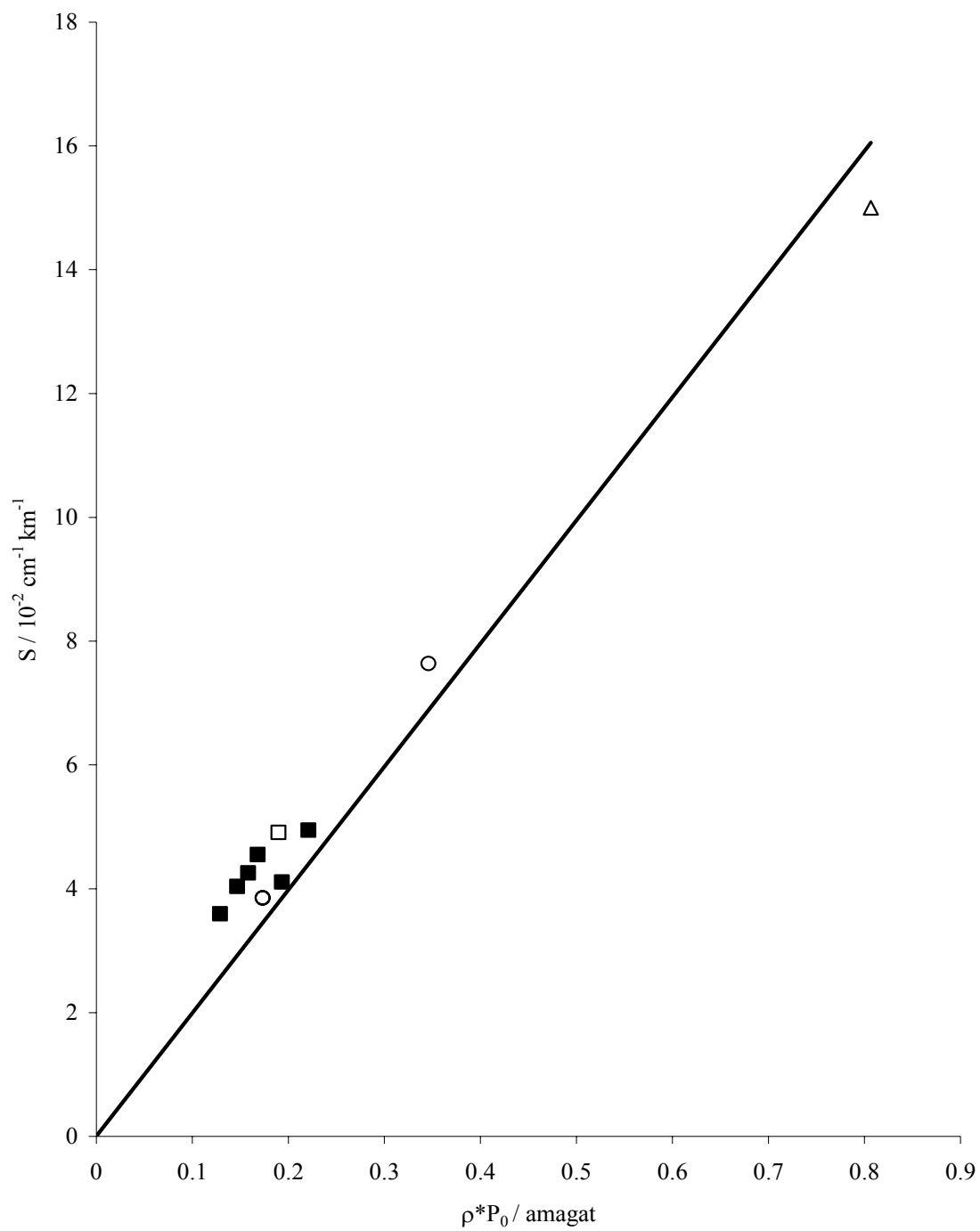
These data were added to the information obtained at 295K and the resulting plots of ρ^*P_J versus S are shown in Figures 54 through 56. As before, for comparison are presented, without including the points in the fit, the values reported by Trauger and Mickelson.¹⁵⁹ (open circle) and McKellar et al.¹⁵³ (open square).

Table 31. ($\nu=0\rightarrow4$) HD. Pressure, ρ^*P_0 , S , and S_0 values at 90K

$R(J)$	ρ^*P_J	S	S_0
	amagat	$10^{-2} \text{ cm}^{-1} \text{ km}^{-1}$	$\text{cm}^{-1} (\text{km amagat})^{-1}$
0	0.806	0.150	0.190
1	0.569	0.104	0.183
2	0.058	0.013	0.220

The 90 K data fitted well in the straight lines obtained in these figures (54 through 56), this shows the ability PS-CRD system to measure rotational- vibrational overtone transitions at 295 and 90K.

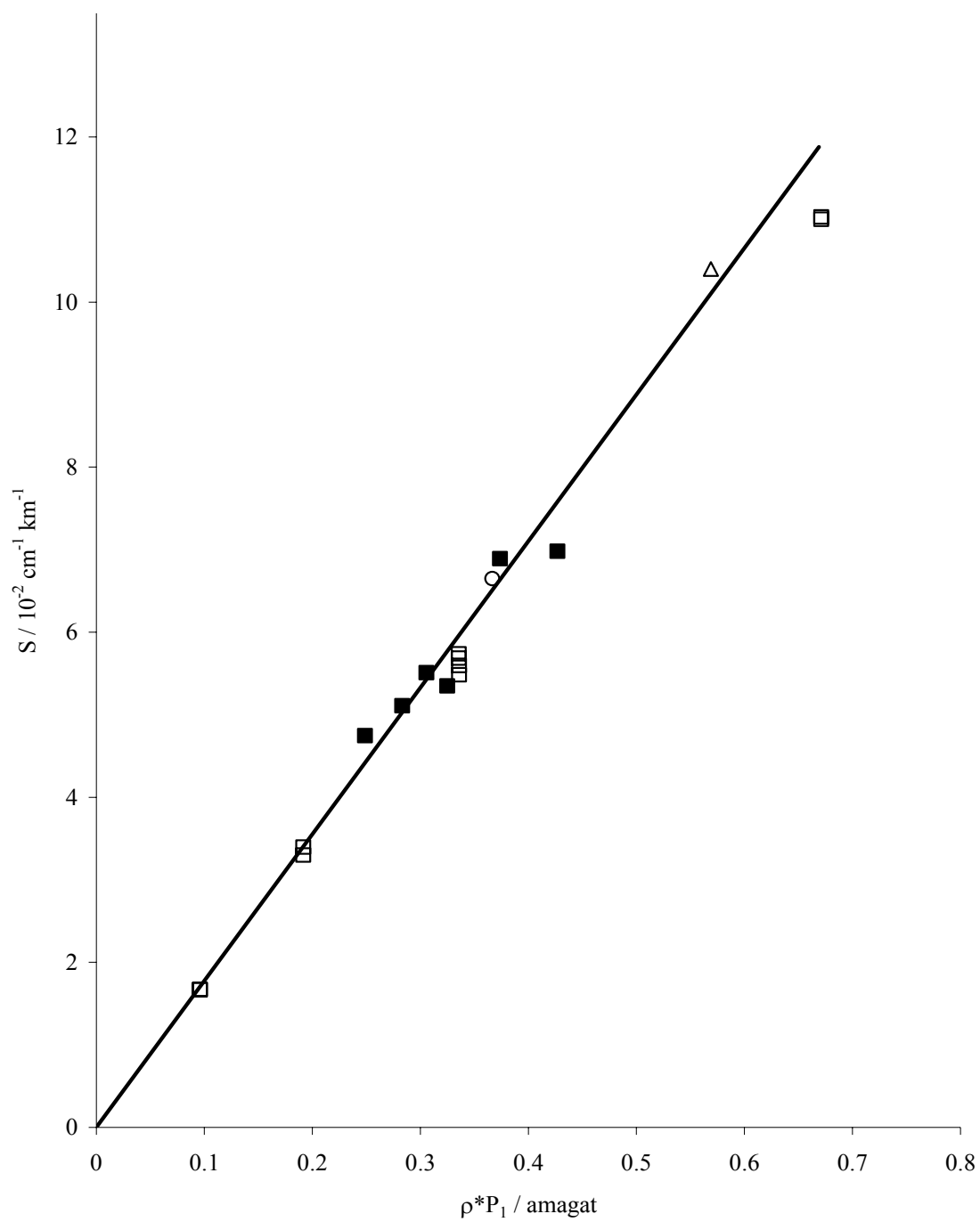
The molecular temperature can be determined using the position and intensities of the rotational lines of HD. The variation of the intensity of the lines in a rotation-vibration band as a function of the J values is the result of the thermal distribution of the rotational levels.



$$S_0 = (0.20 \pm 0.01) \text{ cm}^{-1} (\text{km atm})^{-1}$$

$$R^2 = 0.980$$

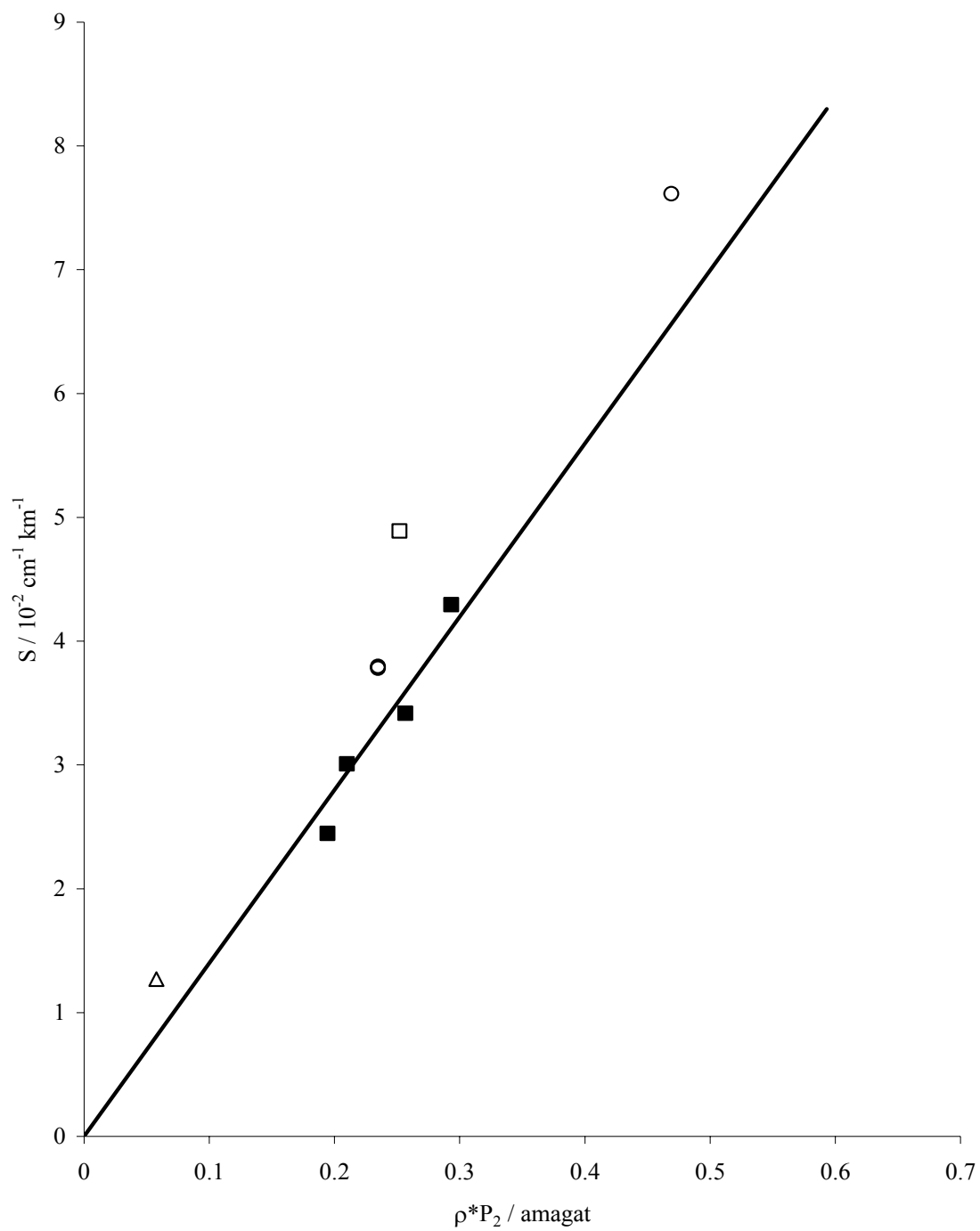
Figure 54. ($\Delta v = 4$) HD R(0). S vs $\rho * P_0$. Marker ■ = 295K, Δ = 90K, □ = McKellar¹⁵³ and ○ = Trauger¹⁵⁹



$$S_0 = (0.178 \pm 0.003) \text{ cm}^{-1} (\text{km atm})^{-1}$$

$$R^2 = 0.993$$

Figure 55. ($\Delta v = 4$) HD R(1). S vs $\rho * P_1$. Marker ■ = 295K, Δ = 90K, □ = McKellar¹⁵³ and ○ = Trauger¹⁵⁹



$$S_0 = (0.140 \pm 0.006) \text{ cm}^{-1} (\text{km atm})^{-1}$$

$$R^2 = 0.985$$

Figure 56. ($\Delta v = 4$) HD R(2). S vs $\rho * P_2$. Marker $\blacksquare$ = 295K, Δ = 90K, $\square$ = McKellar¹⁵³ and $\circ$ = Trauger¹⁵⁹

Thus, the intensities of the lines of rotation- vibrational band for a diatomic molecule is given by ⁸⁷

$$I_{abs} = \frac{C_{abs}\nu}{Q_r}(J' + J'' + 1)e^{-\frac{B''J''(J''+1)hc}{kT}} \quad (44)$$

where Q_r is the rotational partition function, ν is the frequency at the line center, J'' is the rotational quantum number in the lower state, J' is the rotational number in the upper state, B'' is the rotational constant of the ground state, C_{abs} is a constant depending on the change of the dipole moment and the total number of molecules in the initial vibrational level and the other symbols have their usual meaning. For a given rotational-vibrational band at a given temperature the factor C_{abs}/Q_r is constant.

Therefore, to obtain the rotational temperature the energy of the lower state, $F_{J''}$, versus the natural logarithm of the absorption intensity for each R lines must be plotted.

The energy of the lower state is ⁸⁷

$$F_{J''} = B''J''(J'' + 1) \quad (45)$$

The natural logarithm of the absorption intensity is represented by:

$$\ln\left(\frac{I_{abs}}{\nu(J' + J'' + 1)}\right) \quad (46)$$

The plot of natural logarithm of the absorption intensity versus $F_{J''}$ yields a linear line whose slope is equal to

$$Slope = -\frac{1}{kT} \quad (47)$$

The slope has units of cm. Thus, the k value is given as $0.694 \text{ K}^{-1} \text{ cm}^{-1}$. Using ($\Delta\nu=4$) HD spectrum at 401 Torr and 90K, the F_J , ν , and natural logarithm of the

absorption intensity values were determined for each R(J) and data is shown in Table 32.

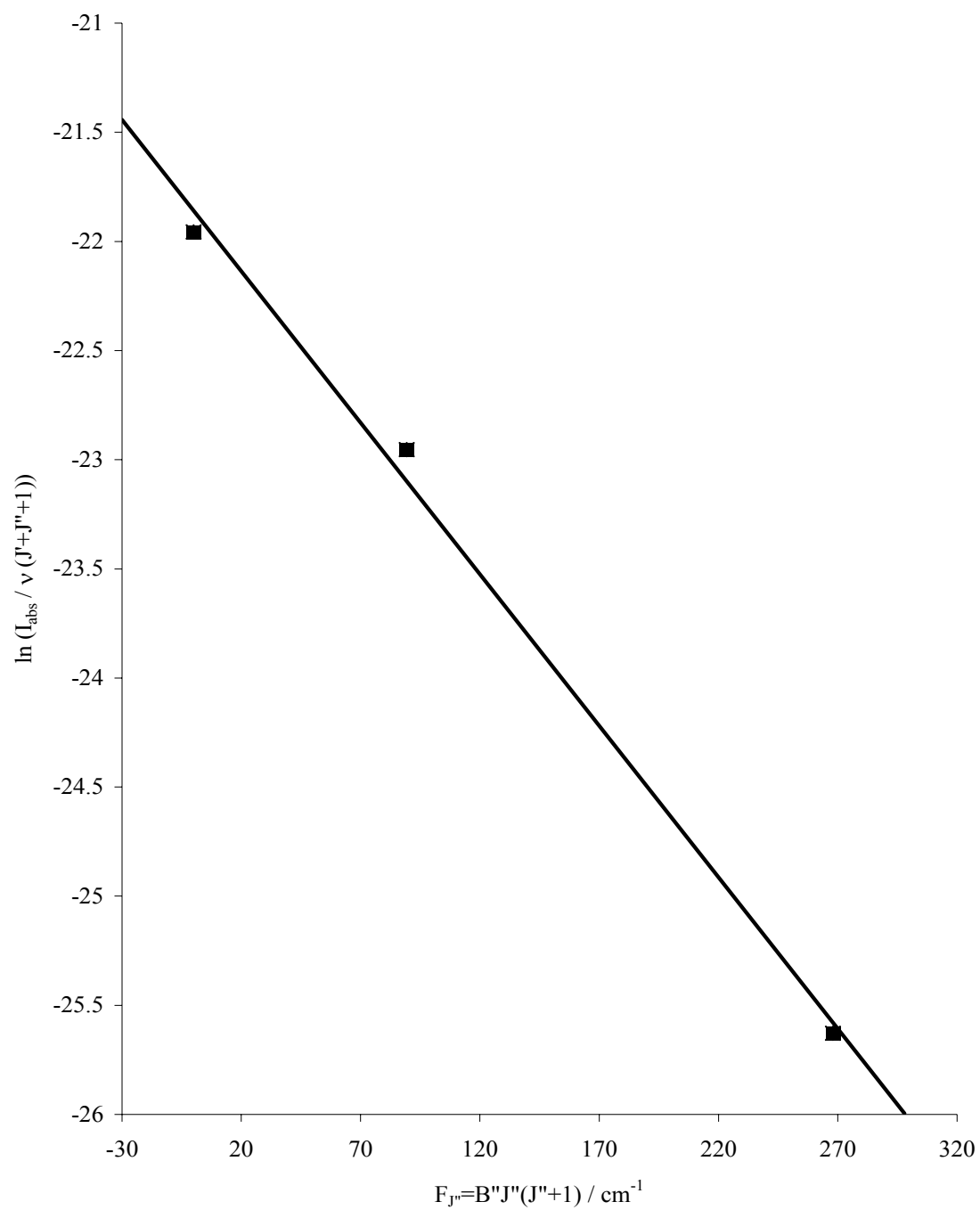
Table 32. ($\nu=0\rightarrow4$) HD 401 Torr at 90 K, Temperature Calculation Data.

R(J)	$\frac{F_{J''} = B''J''(J''+1)}{cm^{-1}}$	$\frac{\nu}{cm^{-1}}$	$\ln\left(\frac{I_{abs}}{\nu(J'+J''+1)}\right)$
R(0)	0	13552.80	-21.957
R(1)	89.33	13609.66	-22.954
R(2)	267.99	13652.20	-25.628

Figure 57 shows the temperature calculation plot for data in Table 32. From the slope, temperature obtained was $(104 \pm 8)K$. Also, PGOPHER¹⁴² was used to simulated the ($\Delta\nu=4$) HD spectrum at 90K. The rotational constant, (B_0) centrifugal distortion, (D_0) and band origins, ν_0 , used in this simulation are summarized in Table 33. Figure 23 shows the comparison between experimental and simulated spectrum of ($\Delta\nu=4$) of HD at 90 K. Figures 57 and Figure 58 confirm a good correlation between temperature measured by sensor localized in the cell and the actual temperature of the molecule.

Table 33. Rotational constants and Band origins¹⁵³ for HD (in cm^{-1})

ν	ν_0	B_0	D_0
0	0	44.668	0.0263
4	13476.87	37.140	0.0231



Slope = $(-0.0139 \pm 0.0009) \text{ cm}$

$T = (104 \pm 8) \text{ K}$

$R^2 = 0.998$

Figure 57. Temperature calculation for HD with a pressure of 401 Torr at 90K

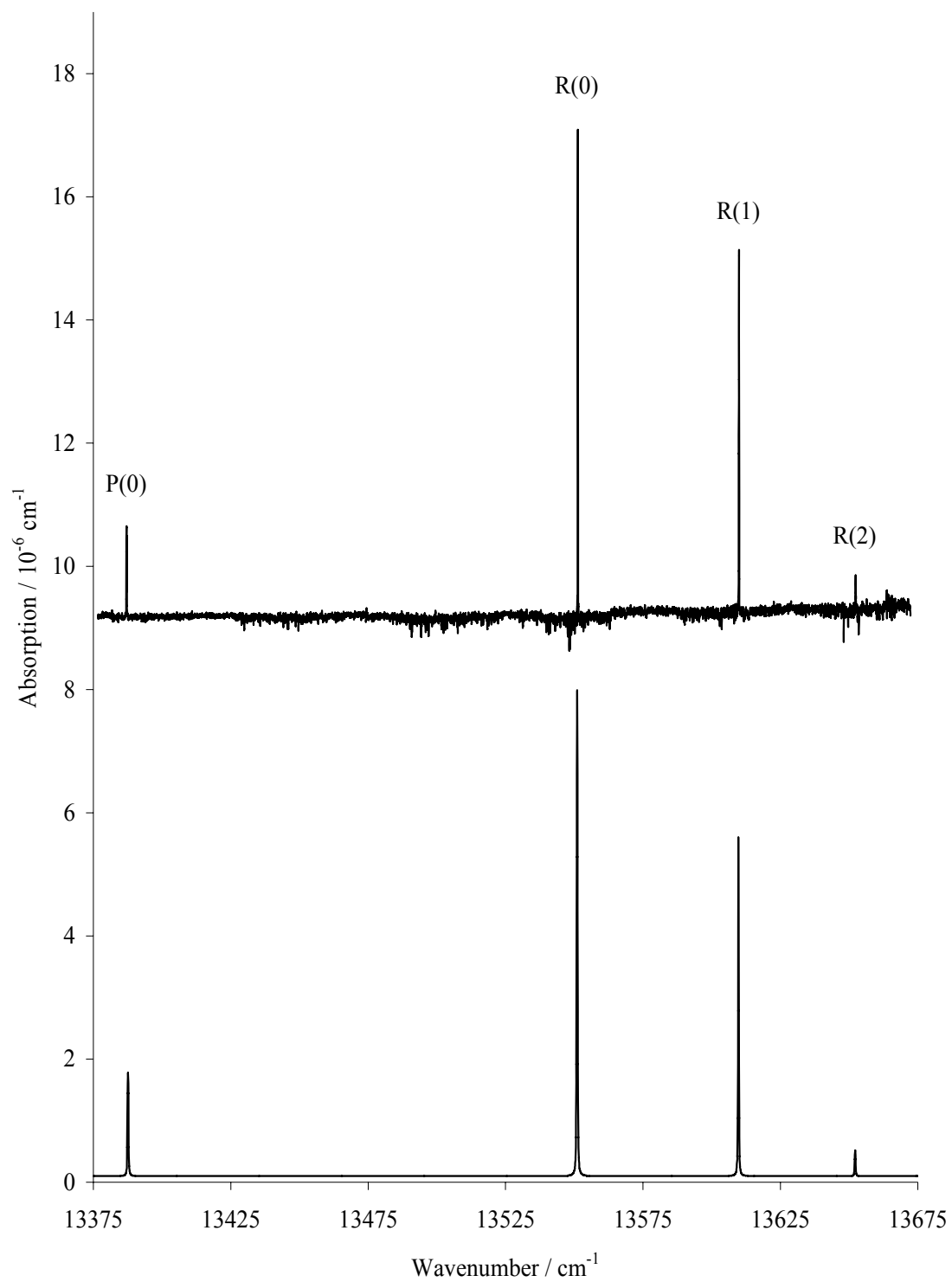


Figure 58. Comparison of ($\Delta v = 4$) HD spectrum with a pressure of 401 Torr at 90 K. Top= experimental. Bottom= simulated

Conclusions

Accurate absorption strength values were obtained for the R(0), R(1) and R(2) lines in the ($\Delta v = 4$) rotational vibrational band of HD. Good agreement is seen between these measured values and values found in the literature.

To confirm temperature measured by sensor localized in the cell was using the Boltzmann distribution of the rotational-vibrational intensities and the simulated spectrum at low temperature.

The temperatures found are in good agreement with the temperature recorded by sensor in the cell.

These results show the ability of the CRD system to measure weak absorption spectra of HD in the visible region at any temperature. Because absorption spectra of these molecules are using to obtain information of planetary atmospheres, our CRD system is interest setup to acquire absorption spectrum at temperatures of the planetary atmospheres which are range between 165 and 100 K.

CHAPTER FIVE

Vibrational Overtone Spectroscopy of Trideuteromethane (CHD_3) at Room and Low Temperatures

Trideuteromethane (CHD_3) is the lightest symmetric top molecule with one C-H bond. Due to the high values of rotational constants, $B'' = 3.27916 \text{ cm}^{-1}$, $C'' = 2.62896 \text{ cm}^{-1}$ in the vibrational ground state, CHD_3 is a good candidate for the study of rotational structure of high excited vibrational states. The vibrational fundamental and overtone spectra ($\Delta v = 1, 2, 3, 4, 5, 6, 7$) of the C-H stretch of CHD_3 have been studied previously using different techniques. Infrared spectra of CHD_3 between 900 and 3400 cm^{-1} have been used to identify fundamental vibrational frequencies as well to calculate ground-state and fundamental parameters.^{120, 168-171} Studies of C-H overtone levels near $\Delta v = 2, 3, 4$ include high resolution spectra, with K-subband structure clearly resolved, have been made using photographic infrared, intracavity laser absorption spectroscopy (ICLAS) and FT-spectrometer.^{170, 172-175}

An analysis of the Fermi resonances of CHD_3 has been made for high-energy overtones ($\Delta v = 5, 6, 7$) which indicates strong interactions of the CH stretch with degenerate bending modes. The C-H overtone ($\Delta v = 5, 6, 7$) absorption spectra have been obtained using photoacoustic spectroscopy^{113, 176}, ICLAS^{174, 175, 177, 178}, FT-spectrophotometer¹⁷⁹. Hence, the rotational constants of the ground state and some vibrationally excited states up to 16500 cm^{-1} are well known.

The spectrum around $\Delta v = 6$ at 77 K using a specially designed photoacoustic cell has been obtained.¹⁷⁶ Also, Vibrational fundamental and overtone spectra ($\Delta v = 1$,

2, 3, 5) have been obtained in liquid argon solutions at temperatures around 94K using FT spectrophotometer and a photo-acoustic cell at low temperature.¹⁸⁰

In addition, calculations of highly excited C-H stretch states¹¹⁸, potential energy surface^{170, 181, 182}, and dipole moment function^{179, 181} of the CH chromophore in CHD₃ have been performed by several groups and have been shown good correlation with the experimental data. Due to adequate information about vibrational energies, relative intensities, and rotational constants, the CHD₃ overtone spectra was studied to test our CRD system at low temperatures.

The fourth and fifth C-H stretching overtones of CHD₃ were taken with the Cavity Ring Down (CRD) system using the phase shift and exponential detection methods, respectively. The spectra around $\Delta\nu = 5$ and 6 were obtained at room temperature and at low temperatures of 111 K and 124 K, respectively. These spectra were obtained to probe the ability of CRD system to measure rovibrational spectra at low temperatures. Also, rotational intensities were used to confirm the temperature of the cell. The vibrational spectra of CH were recorded using a Fourier transformer spectrophotometer at room temperature. Observation of the spectra of the overtone progression shows the increase of the interaction between the CH stretch with degenerate bending modes.

The absorption strength (S_0) values were obtained from the fundamental and overtone ($\Delta\nu = 1, 2, 3, 4, 5, 6$) spectra of C-H stretch. Also, absorption strength values were calculated with *ab initio* dipole moment functions. The experimental and calculated S_0 values were compared.

Fundamental and Overtones of CHD₃, in the Region Between 2700 and 11400cm⁻¹

The vibrational spectra of CHD₃ were measured at 295 K from the C-H stretching fundamental through to the third overtone, using a white cell with a path length of 7.2 m and a FT-spectrophotometer with a resolution of 1 cm⁻¹. CHD₃ belongs to the point group C_{3v} and has six fundamental vibrations: three totally symmetric (A₁) and three doubly degenerate (E) modes, all of which are infrared active.¹²⁵ The frequencies and symmetry of the various fundamental modes are listed in Table 34. Absorption spectrum of the fundamental ($\Delta v = 1$) C-H stretching vibration is shown in Figure 59. The strong peak at 2991.34 cm⁻¹ is assigned as the center (*Q* branch) of the ν_1 C-H stretching mode. This band has associated *P* and *R* branches with it which exhibit an unusual rotational structure, because of overlapping with other transitions. The band around to 3051 cm⁻¹ (*R* branch) was assigned as $2\nu_6 + \nu_3$ by Bernstein and Wilmschurst.¹²⁰ To higher wavenumbers around to 3178 cm⁻¹ lie the combination band $\nu_2 + \nu_6$.

Table 34. Fundamental Vibrational Frequencies of CHD₃

Assignment	Symmetry	Mode	Frequency / cm ⁻¹
ν_1	A ₁	C-H stretch	2993
ν_2	A ₁	C-D ₃ s-stretch	2142
ν_3	A ₁	C-D ₃ s-bend	1003
ν_4	E	C-D ₃ a-stretch	2263
ν_5	E	C-D ₃ a-bend	1291
ν_6	E	C-D ₃ bend	1036

Overtones, $\Delta v = 2, 3$, and 4 around the C–H stretch were recorded in the range from 5400 to 11400 cm⁻¹. Individual overtone regions are presented in Figures 60.to 62.

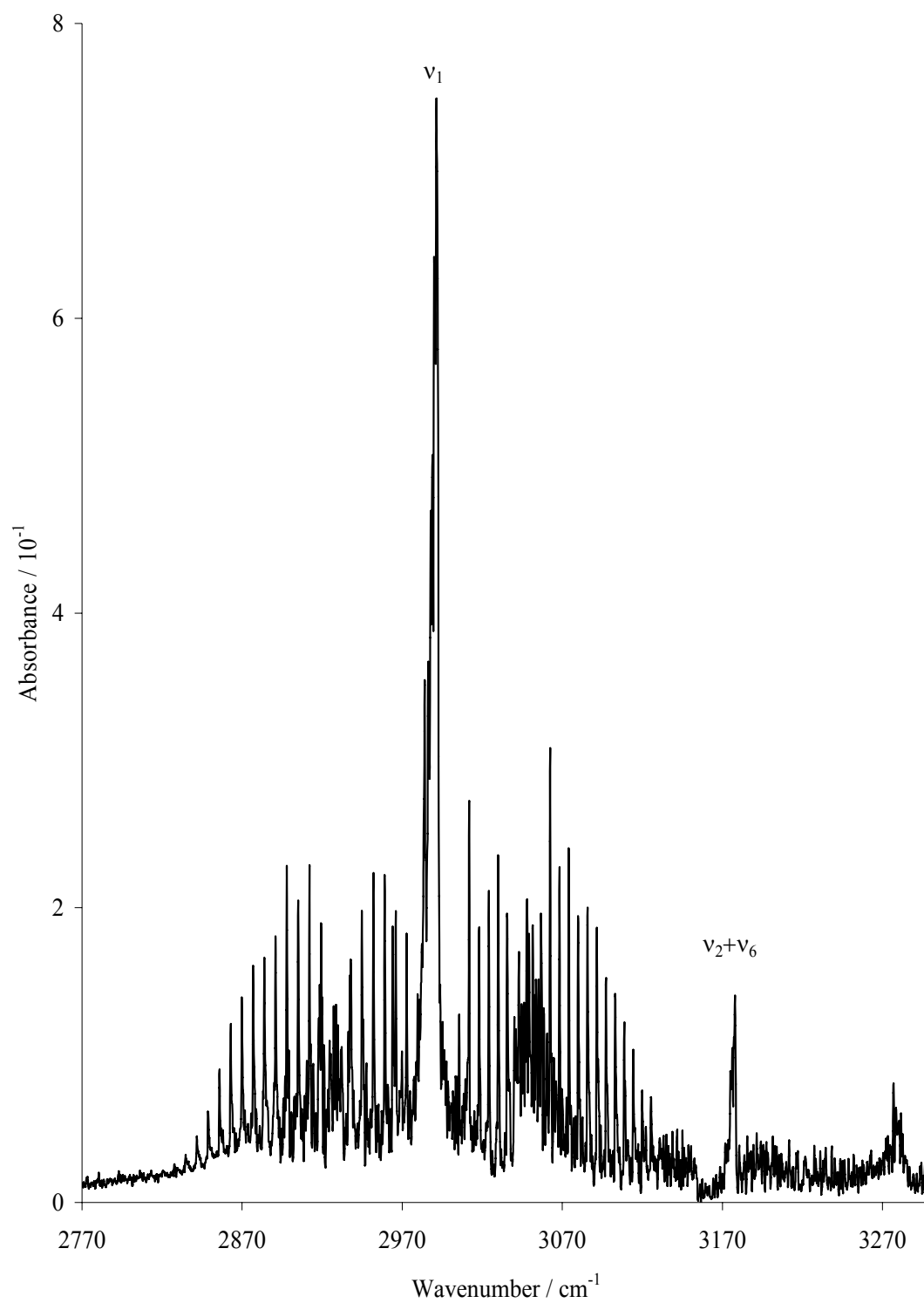


Figure 59. Absorption spectrum of the fundamental ($\nu = 0 \rightarrow 1$) C-H stretch of CHD₃ at 295K. Pressure = 1.5 Torr. Pathlength = 7.2 m

Instead of one overtone transition, two bands are observed. In the CHD_3 molecule, a Fermi resonance occurs between the C-H stretching mode ν_1 (A_1) and twice the frequency of the C-H bending mode ν_5 (E).¹⁶⁹ These states have fairly similar energies, because the bending fundamental is at 1291 cm^{-1} , about half the wavenumber of the stretching fundamental at 2993 cm^{-1} . This resonance explains the observation of vibrational bands forming polyads which can be characterized by introducing a new quantum number $N = \nu_s + \frac{1}{2} \nu_b$ ¹⁸³⁻¹⁸⁵, where ν_s is the quantum number of the C-H stretching mode ν_1 (A_1) and ν_b is the quantum number of the H-C-D bending mode ν_5 (E). The result is that combination bands involving states in Fermi resonance are often much stronger than they would otherwise be, since they can “borrow” some of the character of the main overtone transition. This point will be presented more in detail later in this Chapter. (See Analysis of the Fermi resonance).

Figures 60 to 61 show essentially unperturbed intensities in the rotational structure, PQR , of the absorption spectrum of overtones bands. Figure 62 shows initial overlap between the two bands at higher overtones. In region of the third overtone, there is overlapping between the R branch of $3\nu_1+2\nu_5$ and the P branch of $4\nu_1$, as in shown in Figure 62.

Absorption Spectra of CHD_3 in the Fundamental Region ($\Delta\nu = 1$) at Low Temperatures

A temperature series of the fundamental of this vibration were recorded with a resolution of 0.06 cm^{-1} using a FT-spectrophotometer and a low temperature cell inside a cryostat. The path length used was 5 cm to a molecular density of CHD_3 equal to $3.33 \times 10^{18}\text{ molecules cm}^{-3}$.

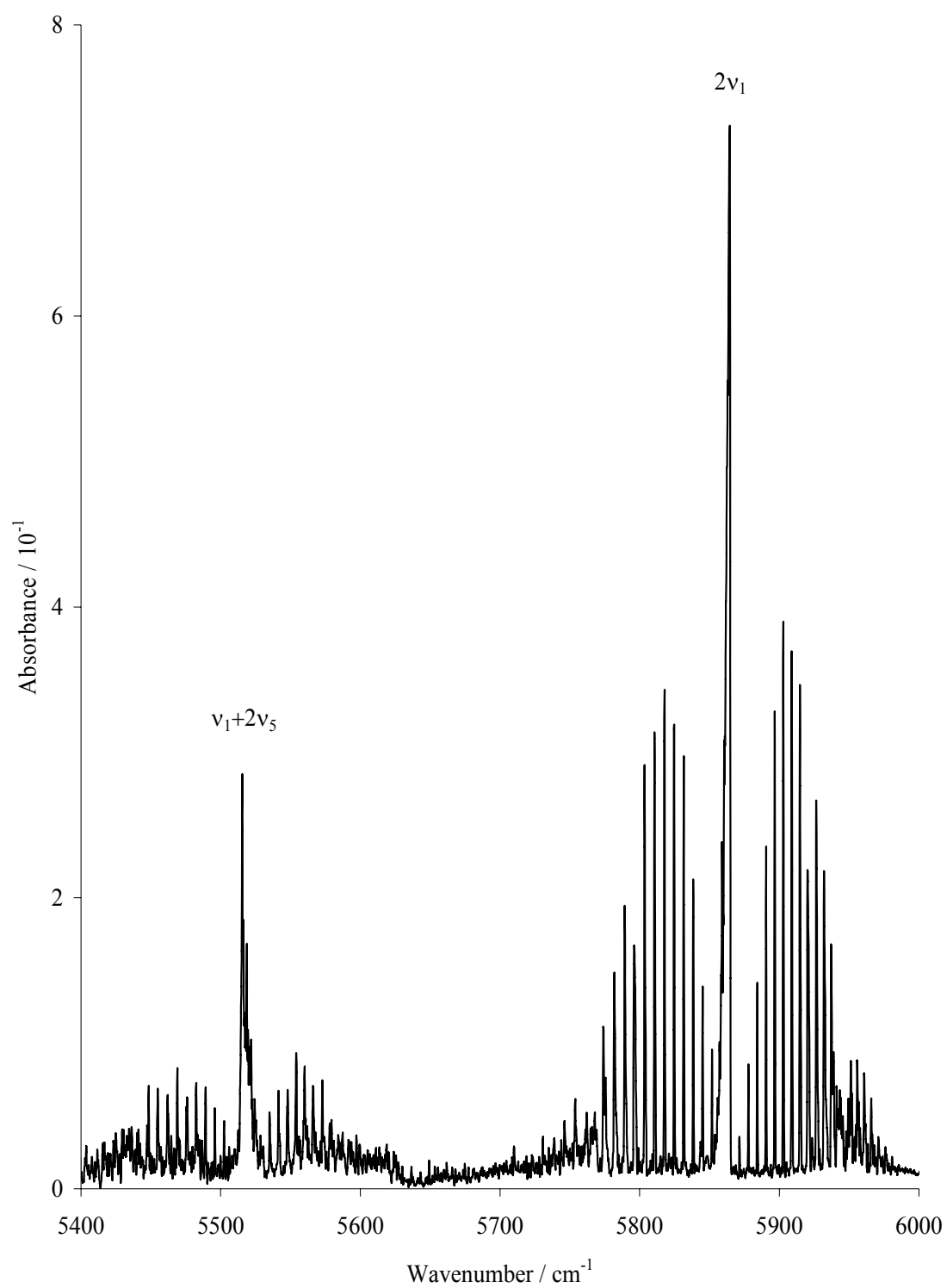


Figure 60. Absorption spectrum of the first overtone ($\nu=0\rightarrow2$) C-H stretch of CHD_3 at 295K. Pressure = 32 Torr. Pathlength = 7.2 m

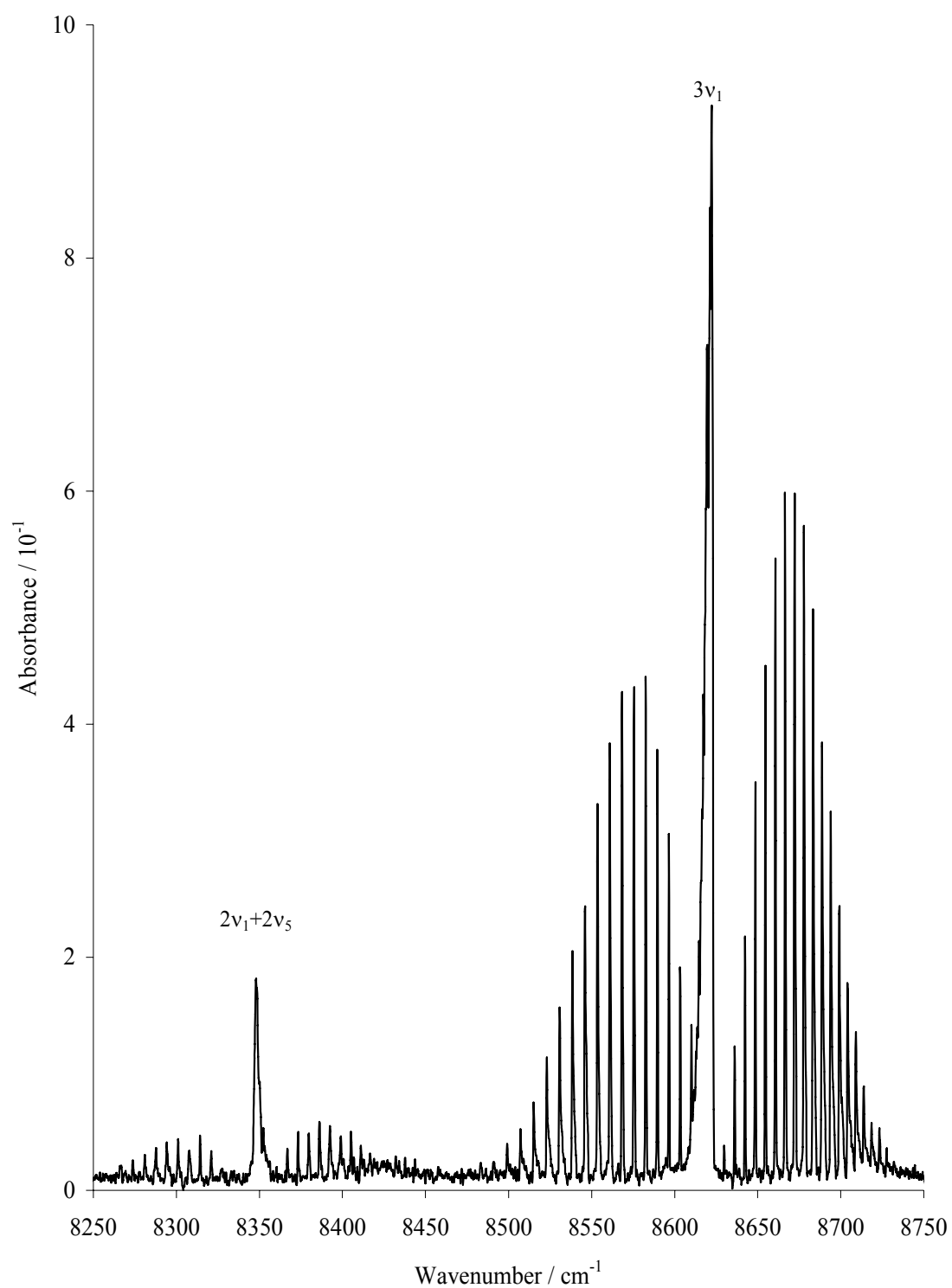


Figure 61. Absorption spectrum of the second overtone ($\nu=0\rightarrow3$) C-H stretch of CHD_3 at 295K. Pressure = 295 Torr. Pathlength = 7.2 m

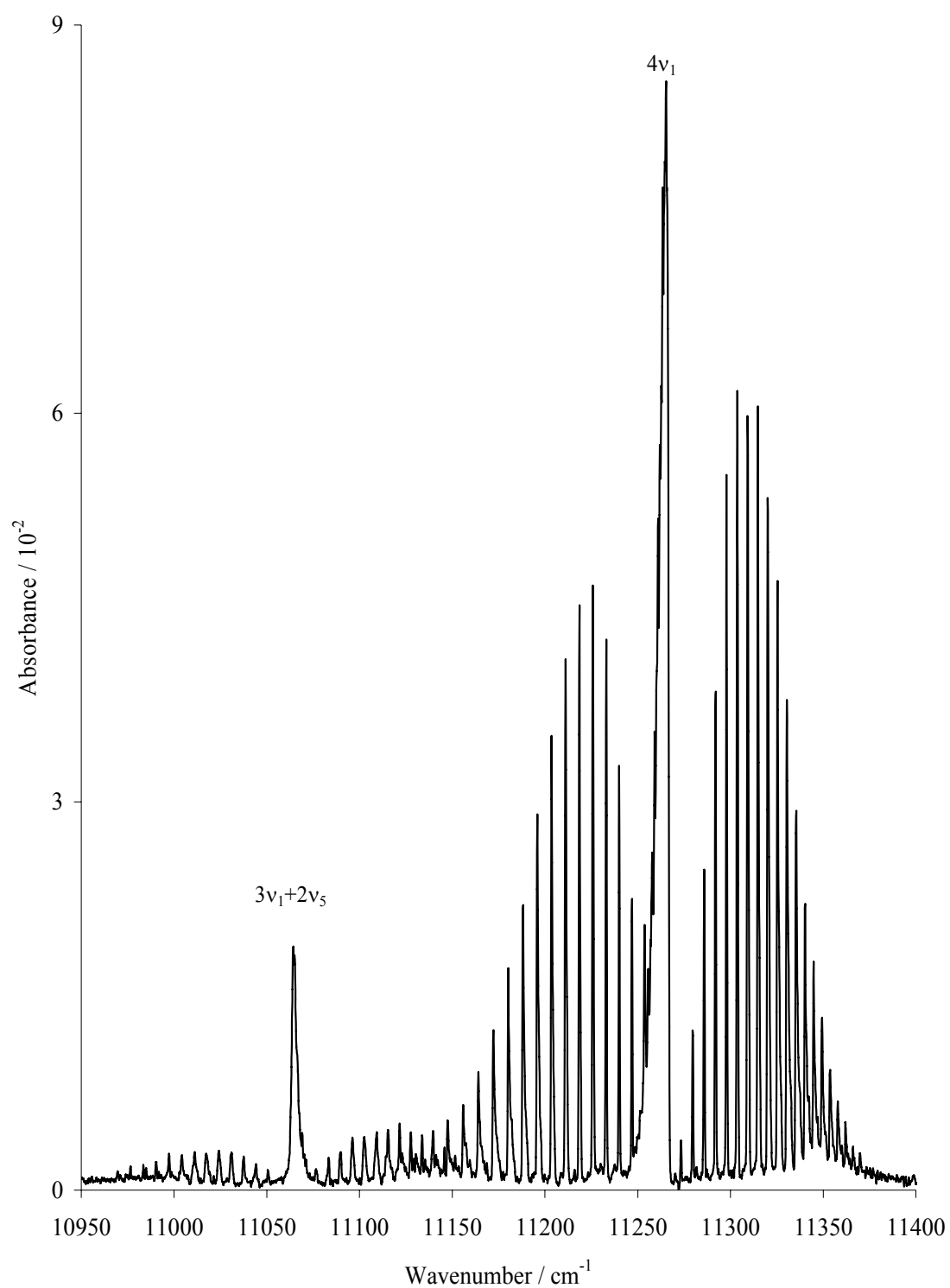


Figure 62. Absorption spectrum of the third overtone ($\nu=0\rightarrow4$) C-H stretch of CHD_3 at 295K. Pressure = 295 Torr. Pathlength = 7.2 m

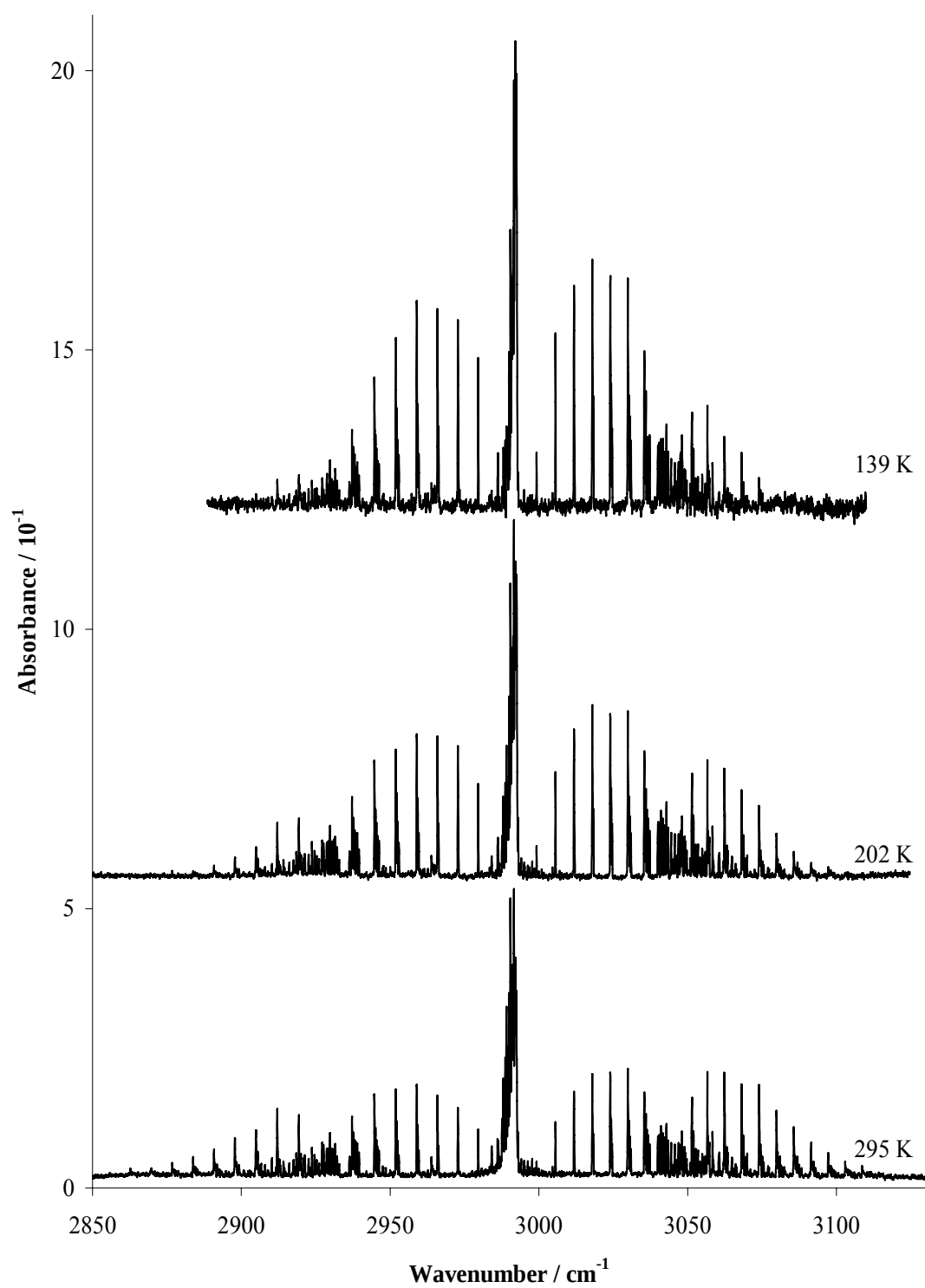


Figure 63. ($\nu = 0 \rightarrow 1$) CHD_3 Temperature Series

Figure 63 presents the stacked measurements taken at various temperatures starting from the highest temperature at the baseline to the lowest temperature at the top. Absorption spectrum of the fundamental ($\Delta v = 1$) C-H stretching at 295 K is a congested spectrum. Several perturbations appear in the R and P branches, one around 3042 cm^{-1} which is close to the R(7) and R(8) lines and another at 2929 cm^{-1} close to the P(9) and P(10) lines. Thus, these branches present an unusual rotational structure. Reduction of this perturbation can be observed when the temperature decreases. Due to redistribution in the rotational levels, a change in the intensity distribution of the P and R branches is observed and a decrease of the number of lines is shown in the spectra at 202 and 139K. Also, the Q branch becomes narrower at low temperatures. However, greater changes can be observed when the absorption spectrum is taken at 84K. Figure 64 shows the IR spectra of the fundamental of the C-H stretching at 84 K which shows basically an unperturbed PQR structure. It is a less congested spectrum in comparison with the one of Figure 59. The strongest lines in the R and P branch are R(3) and P(4) lines, respectively. That is in agreement with the temperature of the sample. Table 35 summarizes the highest J value (J max) observed in the spectrum and the J value of the strongest line observed for each branch at different temperatures.

Table 35. Maximum J value observed and strongest intensity of the line observed at different temperatures.

T (K)	J max		Strongest Line	
	R branch	P branch	R branch	P branch
295	19	19	J = 5	J = 6
202	17	16	J = 4	J = 6
139	11	11	J = 3	J = 6
84	7	9	J = 3	J = 4

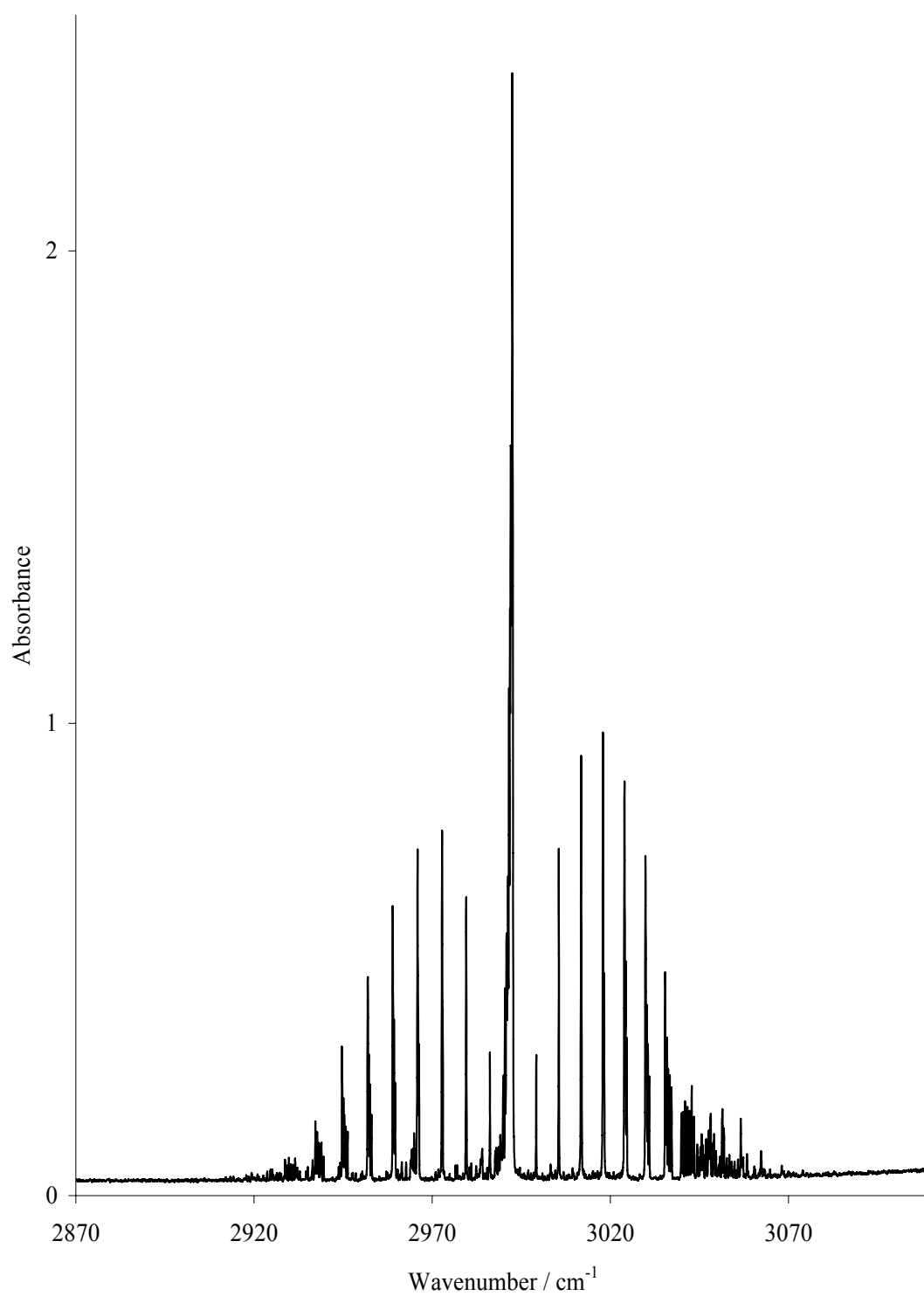


Figure 64. Absorption spectrum of the fundamental C-H stretch of CHD₃ at 84K.

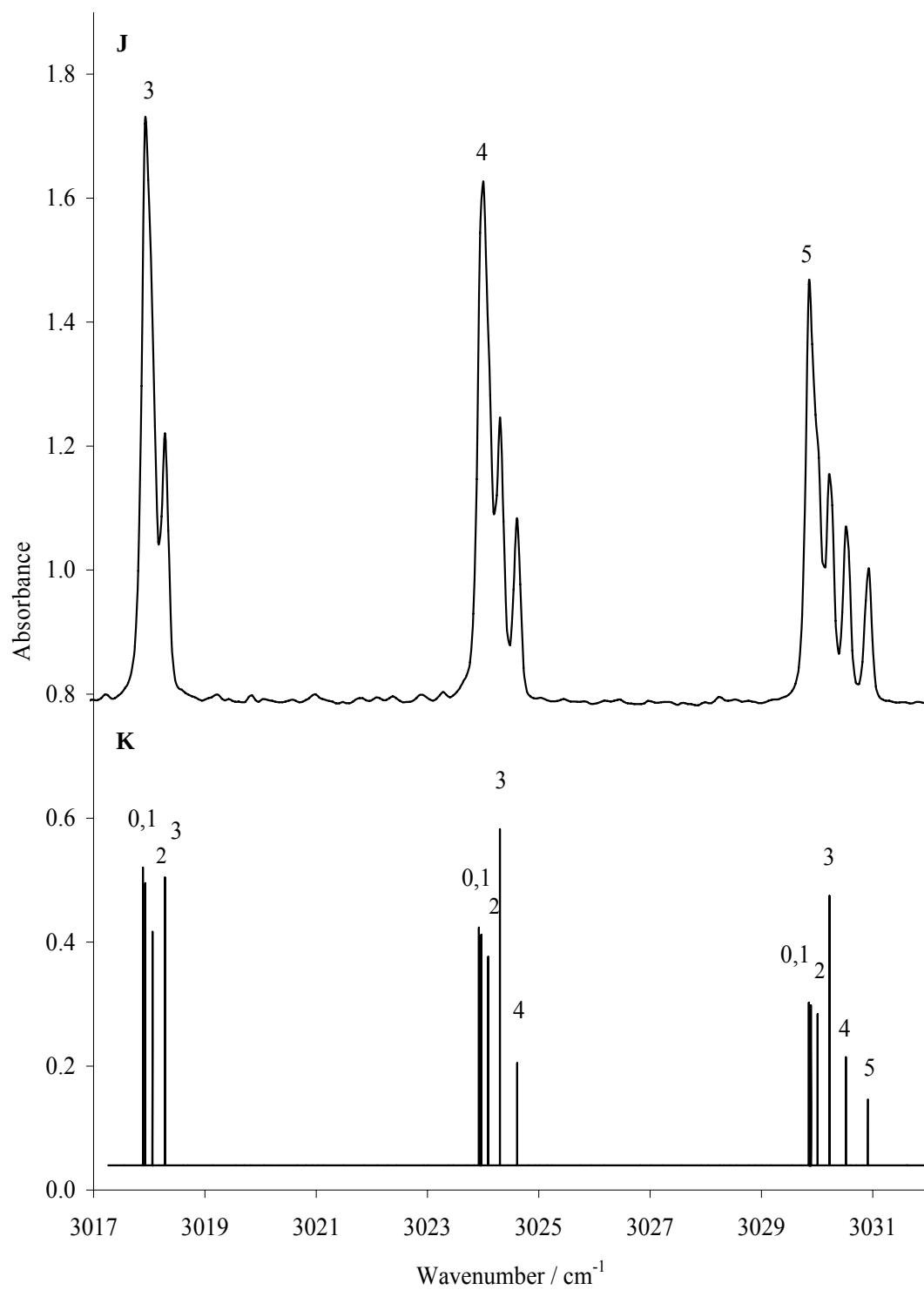


Figure 65. Details of the experimental spectrum of R(3), R(4), and R(5) (J being given on top of the lines) (top). Simulated R(3), R(4) and R(5) (K being given on top of the lines) (bottom).

Due to the resolution used, some K structure can be observed in the absorption spectrum of the fundamental ($\Delta v = 1$) C-H stretching at 84 K. Figure 65 shows in detail the experimental (top) and simulated (bottom) R(3), R(4) and R(5) lines. Because the nuclear spin of deuterium is 1, the alternation of intensity as a function of K is 11, 8, 8, 11, 8, 8, 11, that means the intensity is higher for lines with K multiple of three than of other lines. This effect can be observed in Figure 65.

Calculations of Band Strength S_0 Values for FT- Spectrometer Measurements.

The absorption strength (S_0) values can be obtained from the fundamental and overtones ($\Delta v = 1, 2, 3, 4$) spectra of the C-H stretch. When using the FT-spectrophotometer equation (23) can be rewritten as

$$S_0 = \frac{1}{Pl} \int A(\nu) d(\nu) \quad (48)$$

where P is the gas pressure in Torr, l is the path length in meters, and $A(\nu)$ is the absorbance as a function of frequency in wavenumbers. Using this equation was obtained the (S_0) values for the fundamental and overtones ($\Delta v = 1, 2, 3$ and 4) of CH stretching. It has been reported that the Q branch represents 0.36 of the total band intensity.¹⁷⁸ Table 36 presents the band strength values for each transition.

Table 36. ($\Delta v = 1, 2, 3$ and 4) CHD_3 , S_0 values

ν	S_0 $\text{cm}^2 \text{cm}^{-1} \text{molecule}^{-1}$
1	1.08×10^{-18}
2	2.44×10^{-20}
3	4.64×10^{-21}
4	5.36×10^{-22}

Spectra Simulation

CHD₃ is an oblate ($I_z > I_x = I_y$) symmetric top molecule belonging to the C_{3v} point group. The intensity of the rotational lines in the bands of symmetric top molecules is given by:¹⁸⁶

$$I(J,K) = C A_{KJ} \nu g_{KJ} e^{-F(K,J)hc/kT} \quad (49)$$

where, **C** is a constant independent of K and J values but dependent on the vibrational transition, **g_{KJ}** is the statistical weight. Because the nuclear spin of deuterium is 1, the alternation of statistical weights as a function of K is 11, 8, 8, 11, 8, 8, 11, that means the statistical weight (and therefore the intensity) is higher for lines with K multiple of 3 than of other lines. **A_{KJ}** is proportional to the square of the transition moment $R_{xf}^2 + R_{yf}^2 + R_{zf}^2$ summed over all orientations of J. The quantities A_{KJ} in the present case ($\Delta K=0$) are:

$$\text{for } \Delta J = +1: \quad A_{KJ} = \frac{(J+1)^2 - K^2}{(J+1)(2J+1)}, \quad (50)$$

$$\text{for } \Delta J = 0: \quad A_{KJ} = \frac{K^2}{J(J+1)}, \quad (51)$$

$$\text{for } \Delta J = -1: \quad A_{KJ} = \frac{J^2 - K^2}{J(2J+1)}, \quad (52)$$

where, as always, K and J refer to the lower state. The rotational energy levels of an oblate symmetric top molecule in a specific vibrational level are given by^{186, 187}

$$F(J,K) = BJ(J+1) + (C-B)K^2 - D_J J^2(J+1)^2 - D_{JK}(J+1)K^2 - D_K K^4. \quad (53)$$

where B is the rotational constant perpendicular to symmetric axis; C is the rotational constant about symmetric axis; D_J is J²(J+1)² is the quartic centrifugal distortion; D_{JK} is

the $J(J+1)K^2$ quartic centrifugal distortion; and D_K is the K^4 quartic centrifugal distortion. The rotational selection rules for a parallel band are:

$$\Delta K=0 \text{ and } \Delta J= \pm 1 \text{ if } K=0 \quad (54)$$

$$\Delta K=0 \text{ and } \Delta J= 0, \pm 1 \text{ if } K \neq 0 \quad (55)$$

The rovibrational frequencies (ν) for the P branch ($\Delta J = -1$) and the R branch ($\Delta J = +1$) are given by¹⁸⁸

$$\begin{aligned} \nu^{P,R}(m,K) = & [\nu_o + (2B'' + \Delta B)m + (\Delta B - \Delta D_J)m^2 - 2(2D_J'' + \Delta D_J)m^3 - \Delta D_J m^4] + \\ & [(\Delta C - \Delta B) - (2D_{JK}'' + \Delta D_{JK})m - \Delta D_{JK} m^2]K^2 - \Delta D_K K^4 \end{aligned} \quad (56)$$

where $m = -J$ for the P branch ($m < -1$) and $m = J + 1$ for the R branch ($m \geq 1$). and ν_o is the frequency of the band center. The rovibrational frequencies for the Q branch ($\Delta J=0$) are given by

$$\nu^Q(J,K) = \nu_o + \Delta B J(J+1) + (\Delta C - \Delta B)K^2 - \Delta D_J J^2(J+1)^2 - \Delta D_{JK} J(J+1)K^2 + \Delta D_K K^4 \quad (57)$$

Figures 66 to 69 present the comparison between experimental and simulated spectra of the fundamental of CHD₃ at different temperatures, 84, 139, 202 and 295 K respectively. The PGOPHER program was used to make the simulations¹⁴². The important influence of the overlapping in the intensities of the rotational structure is observed from the comparison. Also, these simulations confirmed the temperature of the molecule in the cell during the experiments. Tables 37 and 38 show spectroscopic parameters for CHD₃ used to simulate the absorption spectra.^{168, 170}

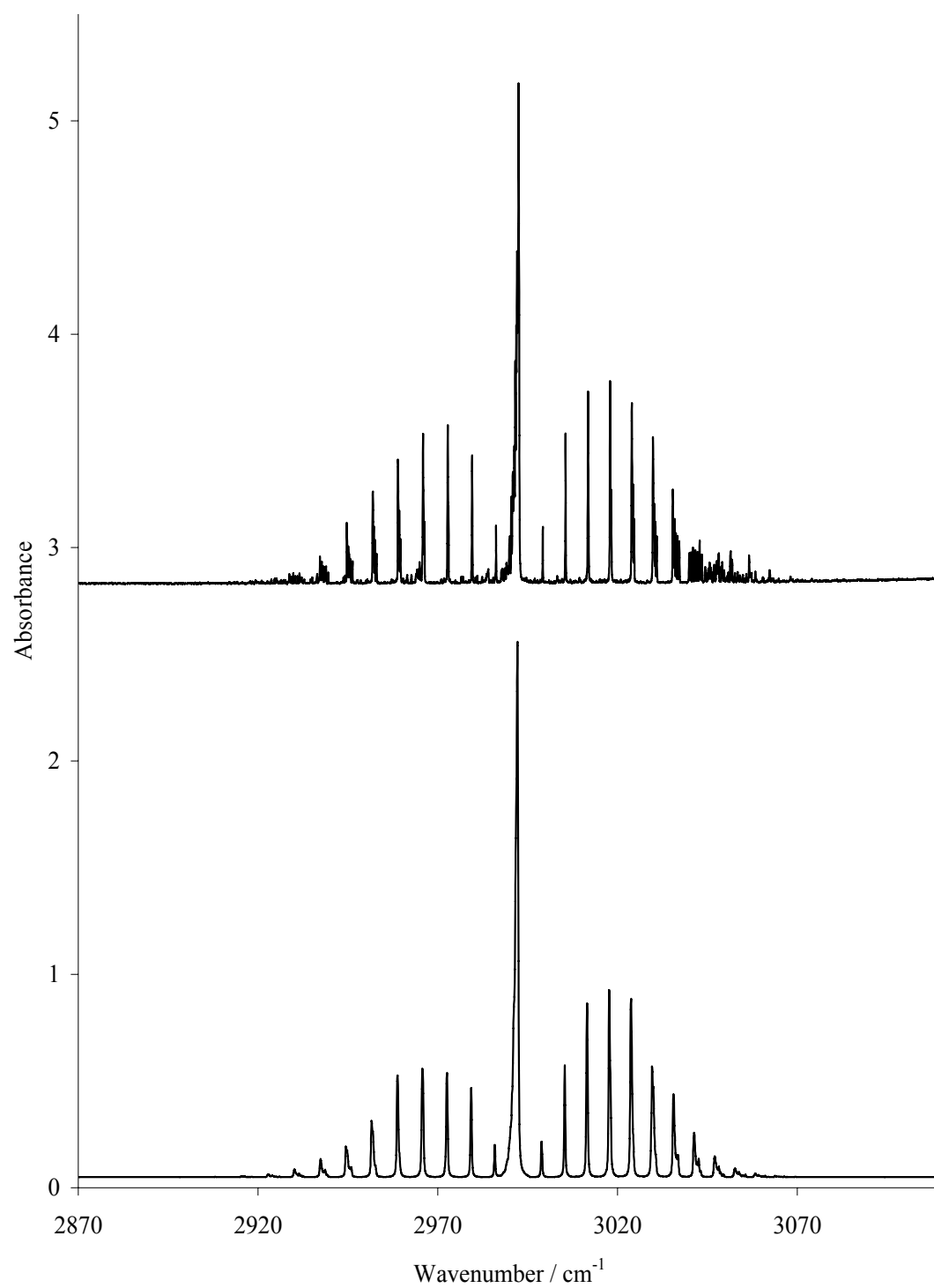


Figure 66. Comparison of the absorption spectrum of the fundamental of CHD_3 at 84K. Top= experimental. Bottom= simulated.

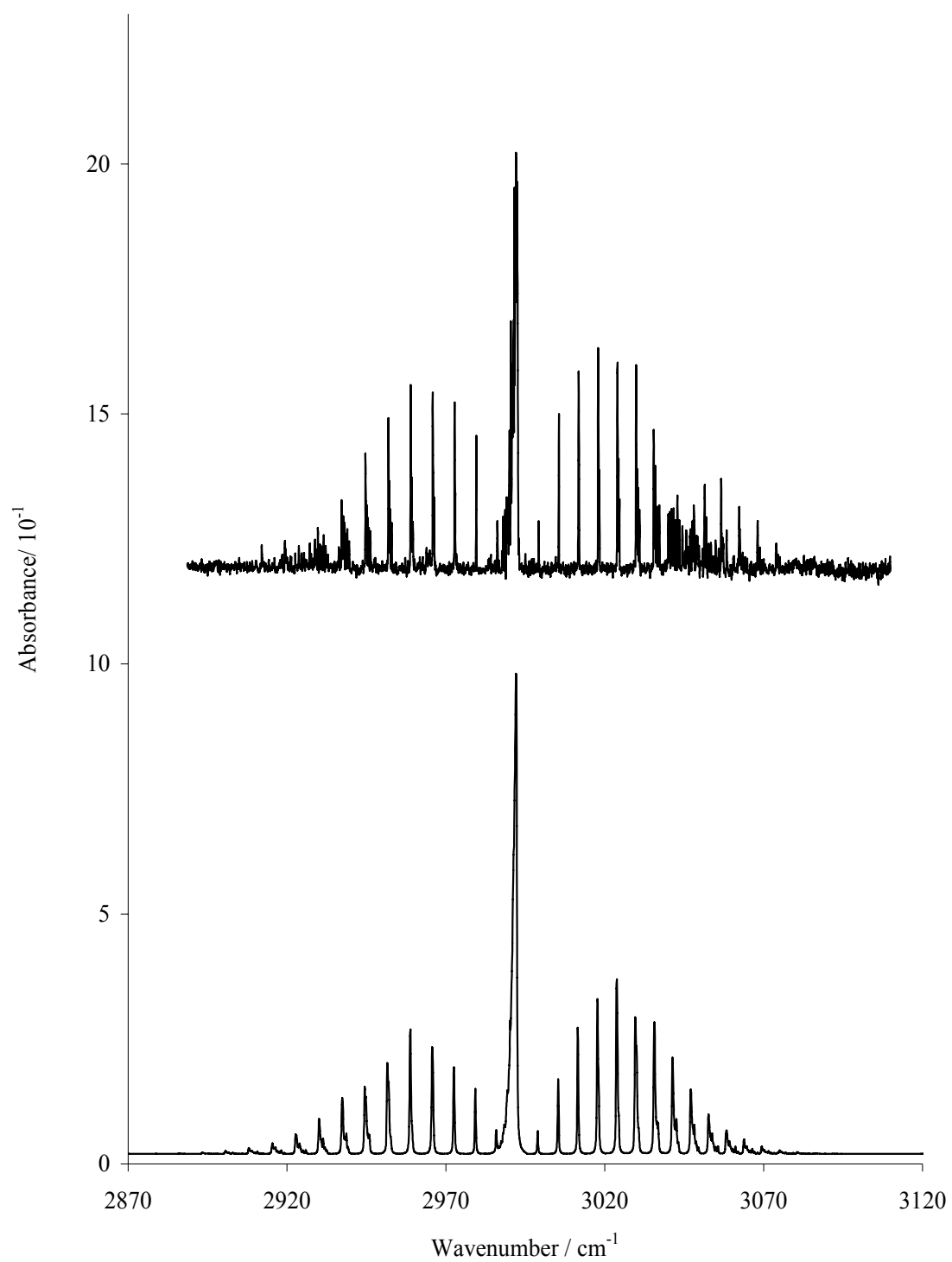


Figure 67. Comparison of the absorption spectrum of the fundamental of CHD_3 at 139K. Top= experimental. Bottom= simulated.

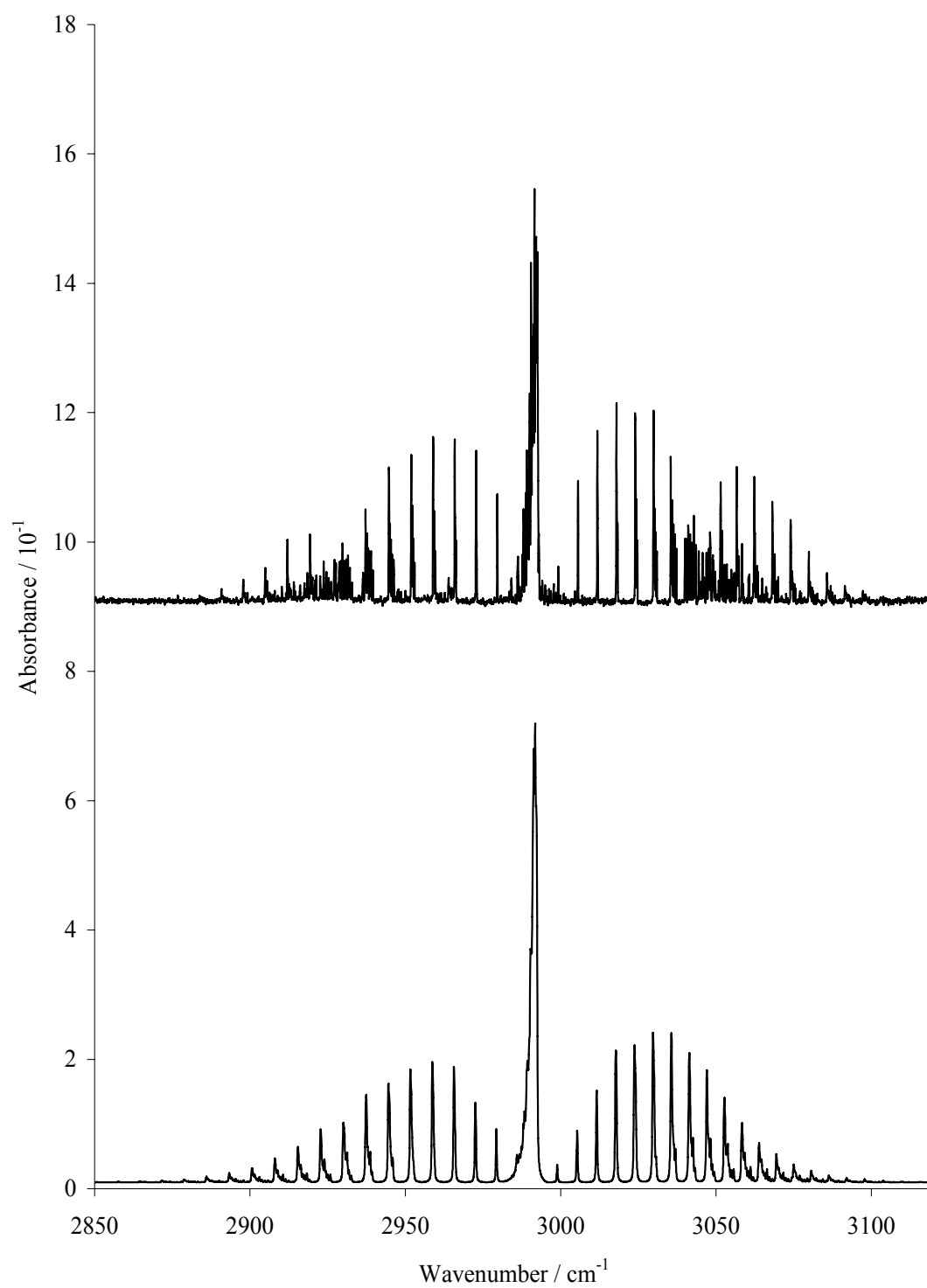


Figure 68. Comparison of the absorption spectrum of the fundamental of CHD_3 at 202K. Top= experimental. Bottom= simulated.

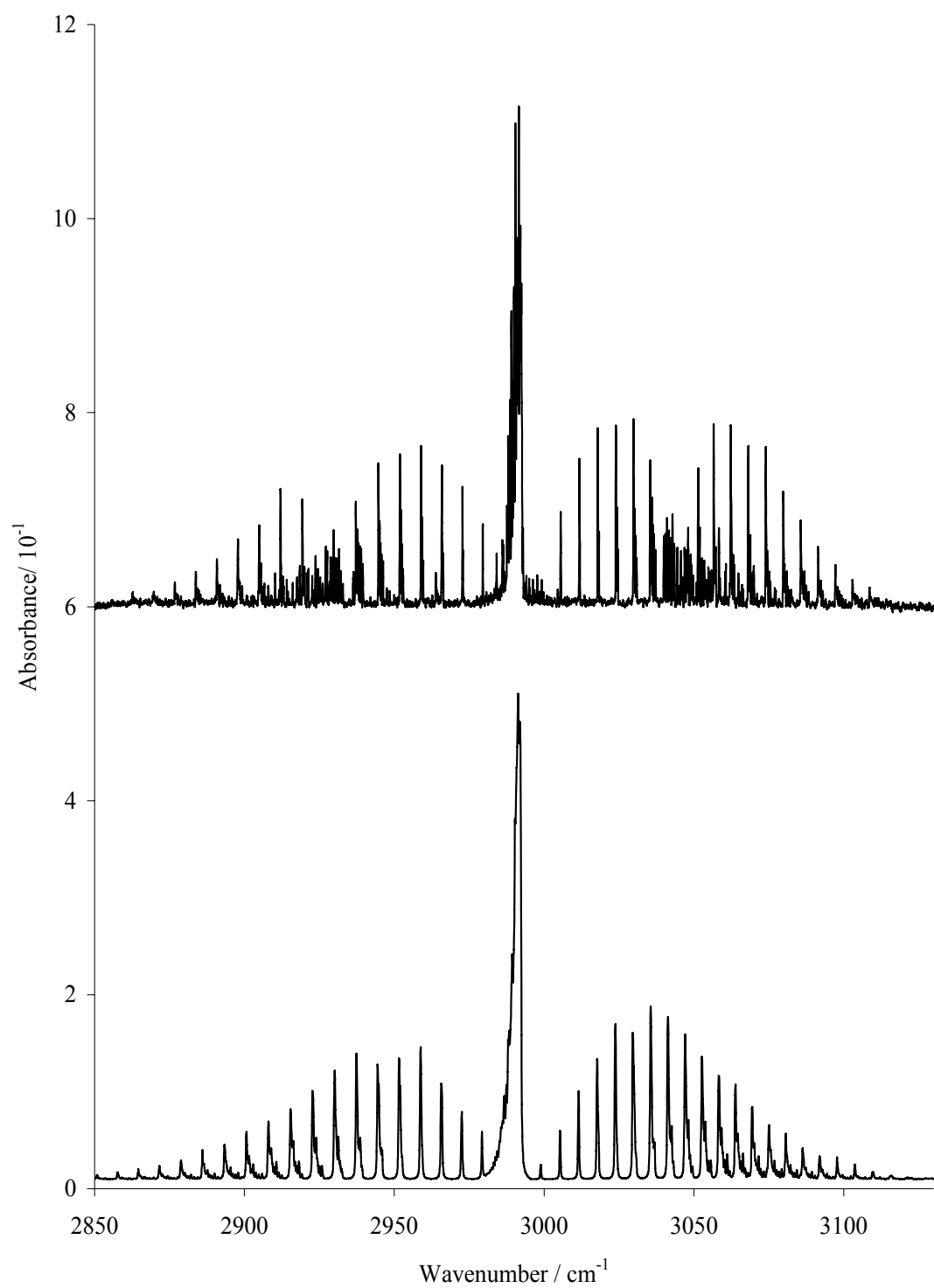


Figure 69. Comparison of the absorption spectrum of the fundamental of CHD_3 at 295K. Top= experimental. Bottom= simulated.

Table 37. Ground state parameters for CHD₃

Parameter	Value (cm ⁻¹)
B''	3.279053
C''	2.6297
D'' _J	5.010 x 10 ⁻⁵
D'' _{JK}	-4.030 x 10 ⁻⁵
D'' _K	1.8 x 10 ⁻⁵

Table 38. Excited state parameters for CHD₃

<i>N</i>	<i>v</i> _s , <i>v</i> _b	<i>v</i> _o / cm ⁻¹	<i>B</i> ' - <i>B</i> '' / cm ⁻¹	<i>C</i> ' - <i>C</i> '' / cm ⁻¹	<i>D</i> ' _J - <i>D</i> '' _J /10 ⁻⁶ cm ⁻¹	<i>D</i> ' _{JK} - <i>D</i> '' _{JK} /10 ⁻⁶ cm ⁻¹	<i>D</i> ' _K - <i>D</i> '' _K /10 ⁻⁶ cm ⁻¹
1	1,0	2992.745	-0.05545	-0.0099	-63.12	143.37	-100.3

*PS-CRD Spectra of CHD₃ in the ($\Delta v = 5$) C-H Stretching Region
at Room and Low Temperatures*

The fourth ($\Delta v = 5$) C-H stretching overtone of CHD₃ was measured using PS-CRD absorption spectroscopy with a continuous laser. The PS-CRD method monitors the phase shift of a modulated beam exiting the cavity. The continuous wave Ti:Sapphire ring laser used has a resolution of 0.17 cm⁻¹. The optical path length used was 3.4 km. The ($\Delta v=5$) C-H overtone spectrum of CHD₃ shows some interesting features, one is the weak intensity or no appearance of the lower R lines (R(1) and R(2)) and other is the perturbed intensities in the rotational structures of the $\Delta v = 5$ C-H stretch overtone. The spectra reported by Perry *et al*¹¹³ and Hollenstein *et al*¹⁷⁹ show normal intensities for lower R lines. Those problems with intensities of rotational structure have been attributed to the short time that the light is coupled into the cavity when using the PS-CRD spectroscopy. In this technique a laser beam is typically aligned along the center axis of the cavity and as a result, the coherent laser beam

couples into the cavity on average only 5%- 10% of the time. In order to increase the coupling-time efficiency, the off-axis alignment has been used. In the off-axis alignment, the laser beam is injected into the cavity at an angle to the center axis (off-axis). The beam may couple continuously into the cavity up to 100% of the time.^{83, 86}

Figure 70 shows the absorption spectrum of the $\Delta\nu=5$ (C-H) overtone of CHD_3 at 295K using off-axis PS-CRD spectroscopy. The spectrum displays two major vibrational bands, $5\nu_1$ at 13797.49 cm^{-1} and $4\nu_1+2\nu_5$ at 13666.14 cm^{-1} , each containing resolved P and R branch and sharp central Q branch characteristic of symmetric top parallel type transitions¹⁸⁶. At higher values of J, some unresolved K structure is observed at this resolution. The overlap between the two bands ($5\nu_1$ and $4\nu_1+2\nu_5$) becomes stronger than the overlap shown for the absorption spectrum of the third overtone ($\Delta\nu = 4$). The interaction between the two levels is reflected in the intensity ratio of the combination band $4\nu_1+2\nu_5$ and the intensity of $5\nu_1$. The ratio is higher in Figure 70 than in Figures 61 and 62.

Although the off-axis alignment was used, intensity of R(2) still was lower than R(1). The reported absorption for the ($\Delta\nu = 5$) spectrum of CHD_3 using a photoacoustic technique¹¹³ and FT-spectrophotometer¹⁷⁹ showed normal intensities for lower R lines, this problem can be explained as an instrumental problem of our PS-CRD system. It is possible that even with the off-axis configuration there is poor overlap between the cavity mode and the R(2) transition at this particular frequency.

In order to get the band strength value for ($\Delta\nu=5$) C-H stretching, the absorption spectrum of ($\Delta\nu=5$) of CHD_3 was measured at different pressures. Figure 71 shows the pressure series of seven separate measurements ranging from 30 to 245

Torr of CHD₃ taken at 295 K. The actual band strength value is obtained by plotting the integrated absorption versus densities to obtain a linear plot. The resulting slope of the line obtained gives the S_0 value. From the simulation by Campargue¹⁷⁸, it is known that the Q branch in the rovibrational spectrum represents 0.36 of the total band intensity. Thus, the integrated absorption area for the total band was obtained by dividing the S value for Q branch by 0.36. Table 39 reports the calculated density (ρ) integrated absorption areas (S), and the band strength (S_0) for each pressure. The S_0 value is reported from the slope of Figure 72.

Table 39. ($\nu=0\rightarrow5$) CHD₃ at 295K, Pressure, ρ , S and S_0

Pressure torr	ρ 10^{18} molecules cm^{-3}	S 10^{-4} cm^{-2}	S_0 $10^{-23} \text{ cm}^2 \text{ cm}^{-1} \text{ molecule}^{-1}$
245	7.97	3.21	4.03
157	5.10	2.04	3.99
95	3.09	1.07	3.47
71	2.31	0.86	3.72
51	1.66	0.63	3.78
30	0.98	0.42	4.34
Avg			4.1 ± 0.1

Figures 71 and 72 show the reproducibility and sensitivity of the PS-CRD instrument to measure rovibrational spectra of high overtones. Band absorption intensities decrease with decreasing pressure as expected.

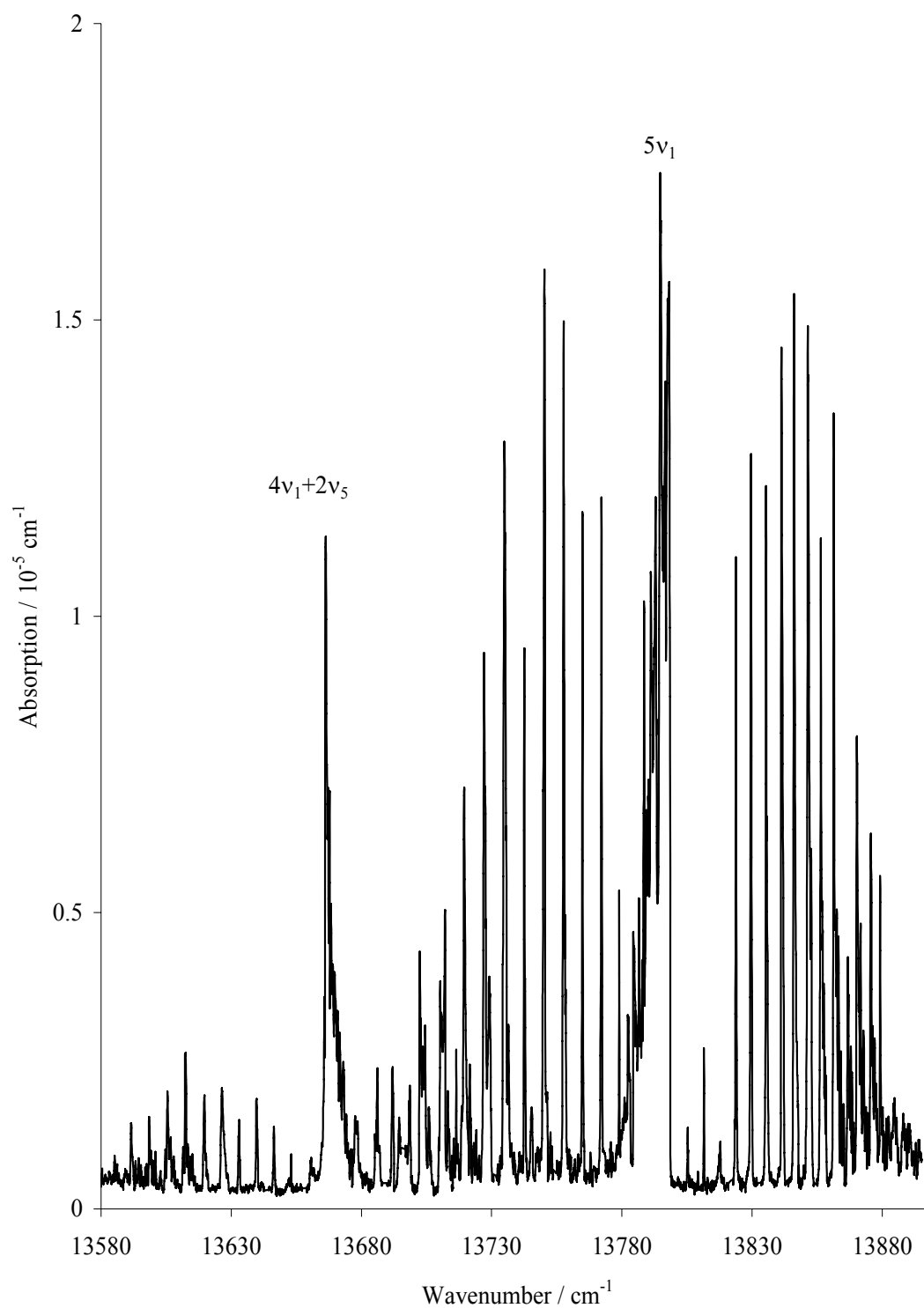


Figure 70. Absorption spectrum of ($v=0 \rightarrow 5$) C-H stretch of CHD_3 with a pressure of 247 Torr at 295K.

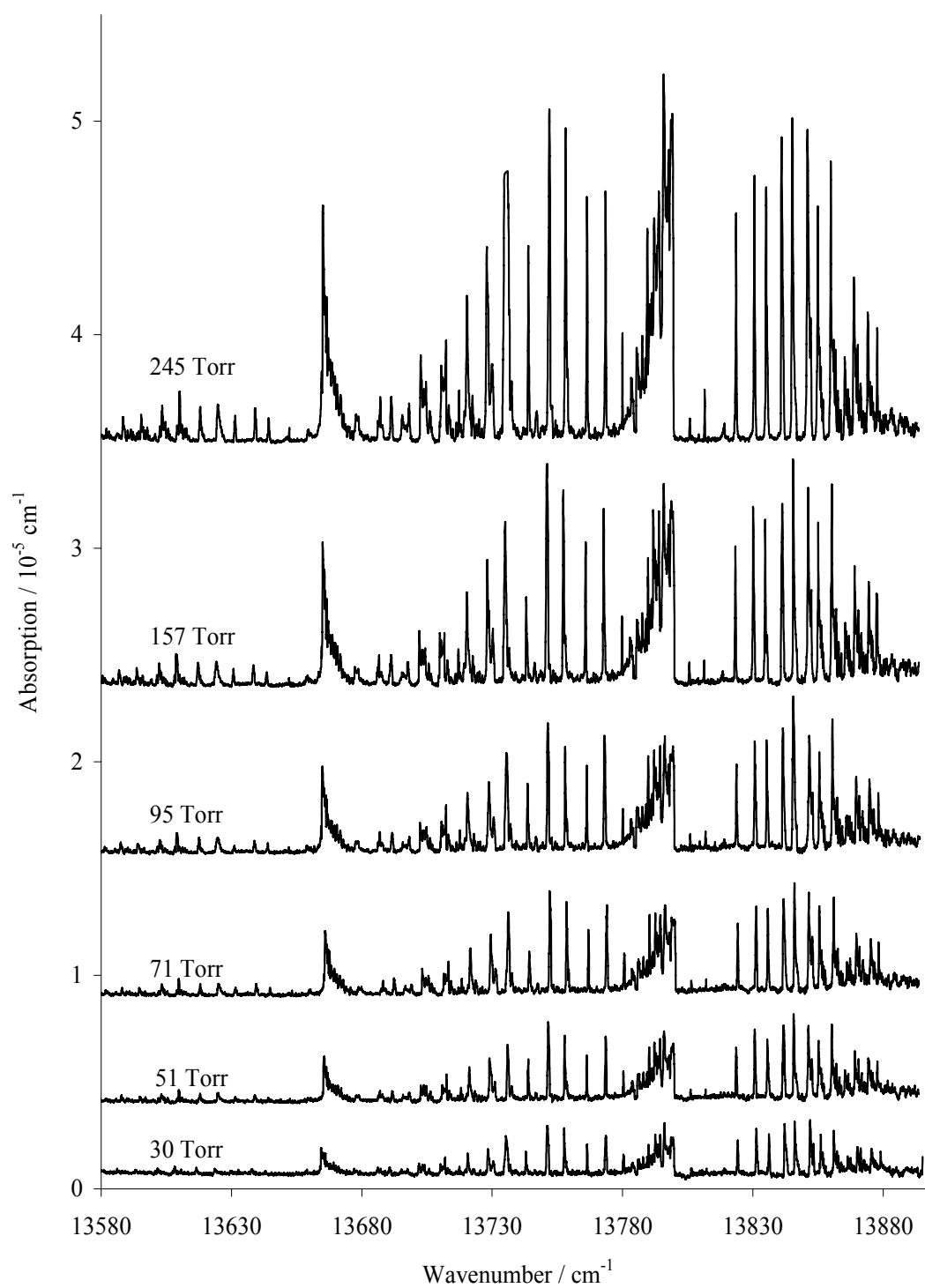
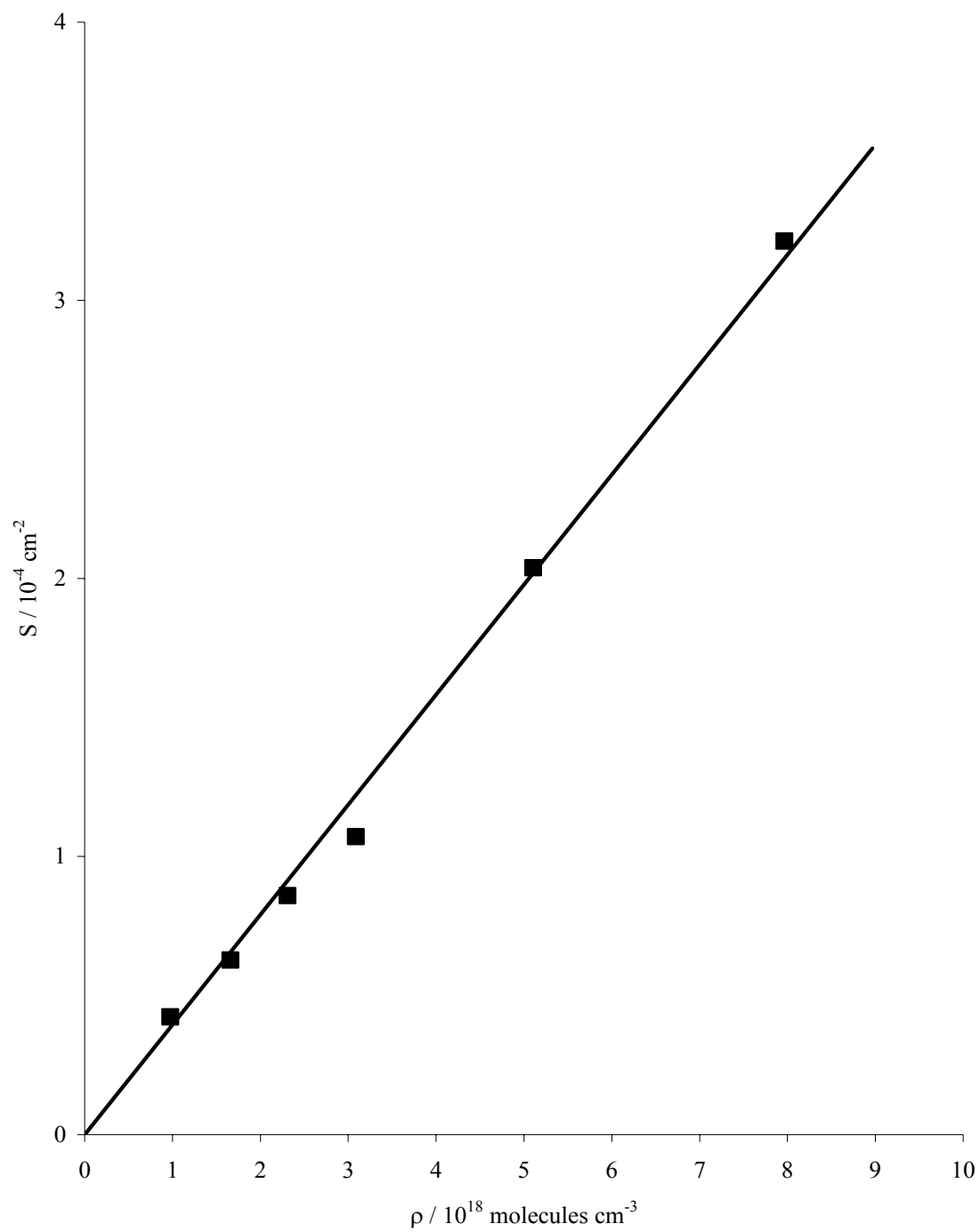


Figure 71. ($\nu=0 \rightarrow 5$) CHD_3 absorption pressure series at 295K



$$S_0 = (4.1 \pm 0.1) \times 10^{-23} \text{ cm}^2 \text{ cm}^{-1} \text{ molecules}^{-1}$$

$$R^2 = 0.998$$

Figure 72. ($\nu = 0 \rightarrow 5$) of CHD_3 at 295 K S vs. ρ . Slope is S_0

The fourth overtone ($\Delta v = 5$) of C-H stretching of CHD_3 was also measured at low temperature (111K). A comparison of the overtone spectrum at room and low temperature is shown in Figure 73. From this figure it is noted that there is a shift in the intensity of the rotational lines. The population of lower rotational levels increases with a corresponding reduction of the population of high rotational levels. In Figure 73 there is a reduction or disappearance of the higher rotational lines whereas lines with lower J values are more intense. The intensity of the Q branch at 111K is twice the intensity of the same branch at 295K. A change in the population of the rotational levels also produces change in the width of the Q branch. The Q branch is narrower at low temperature in comparison with its width at room temperature. Thus, the P(2) line can be observed at low temperature. However, the intensity of R(2) line is still lower than R(0) and R(1). This anomaly is probably due to mode mismatch as was explained before. The most intense lines in the top spectrum of Figure 73 are R(4) and P(4). These are in agreement with the temperature of the sample. In addition, a reduction of the spectral congestion around to $(13690-13730) \text{ cm}^{-1}$ can be observed at 111 K. The overtone spectrum at low temperature shows the two bands $4\nu_1 + 2\nu_5$ and $5\nu_1$ almost separated.

Figure 74 displays the absorption spectrum of ($v = 0 \rightarrow 5$) C-H stretch of CHD_3 at 113 Torr and 91Torr at 111 K. From this data the integrated absorption areas (S) to each pressure was calculated. The ρ , S and S_0 values are presented in Table 40. Figure 75 presents a straight line showing that the results for room and low temperatures correlate very well and the band strength value is temperature independent.

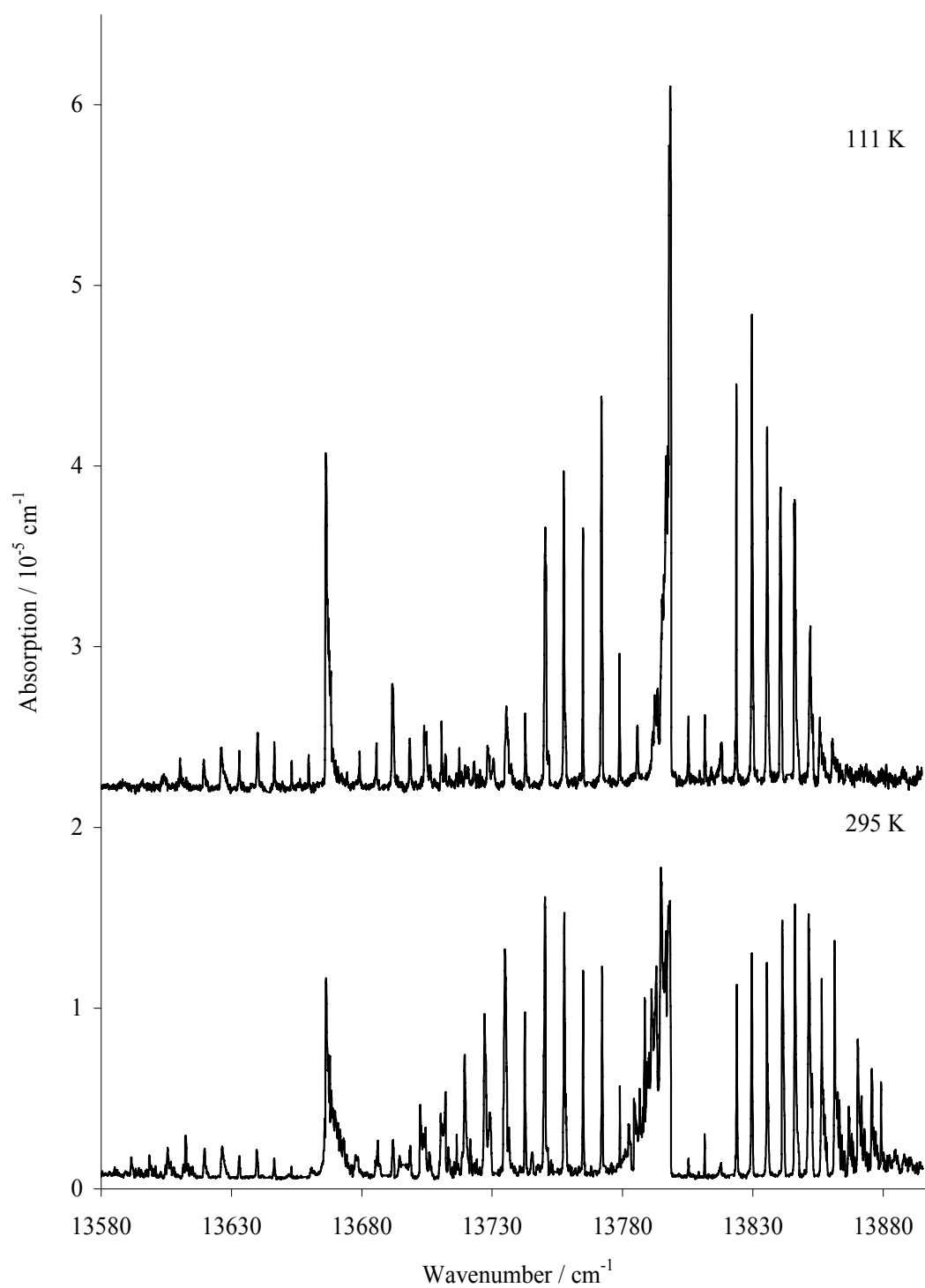


Figure 73. ($\nu = 0 \rightarrow 5$) transition of CHD₃ with a pressure of 91 Torr at 111 K- top, and 247 Torr at 295K- bottom

Table 40. ($\nu=0\rightarrow5$) CHD₃ at 111K, Pressure, ρ , S and S_0 .

Pressure torr	ρ 10^{18} molecules cm^{-3}	S 10^{-4} cm^{-2}	S_0 $10^{-23} \text{ cm}^2 \text{ cm}^{-1} \text{ molecule}^{-1}$
113	9.83	4.27	4.35
90	7.91	2.93	3.70

The S_0 is equal to $(4.2 \pm 0.2) \times 10^{-23} \text{ cm}^2 \text{ cm}^{-1} \text{ molecules}^{-1}$ for the ($\Delta\nu=5$) C-H stretch of CHD₃. This value is very close to the $S_0 = 4.28 \times 10^{-23} \text{ cm}^2 \text{ cm}^{-1} \text{ molecules}^{-1}$ value reported by Campargue¹⁷⁸. The S_0 value reported by Campargue was obtained from only two measurements using a laser intracavity technique (ICLAS).

The intensities of the rotational lines in the ($\Delta\nu=5$) absorption spectrum of CHD₃ can be used to confirm the temperature of the cell and the molecule as well. Since, the cell is thermally isolated so therefore the entire cell and sample inside should be at an equilibrium temperature. From a comparison between experimental and simulated spectra, the temperature measured by the sensor localized in the cell is confirmed. Absorption Spectra of ($\nu=0\rightarrow5$) C-H stretch of CHD₃ at 295 and 111 K were simulated following the same treatment used before to simulate the fundamental spectrum. The rotational constants of CHD₃ using the PGOPHER program are shown in Table 41. The relation between intensities of the two bands was taken from the experimental spectra.

Figures 76 and 77 show the comparison between the experimental and simulated spectra of the ($\Delta\nu=5$) of CHD₃ at 295 and 111 K, respectively. These figures confirm a good correlation between temperature measured by the sensor located in the cell and the

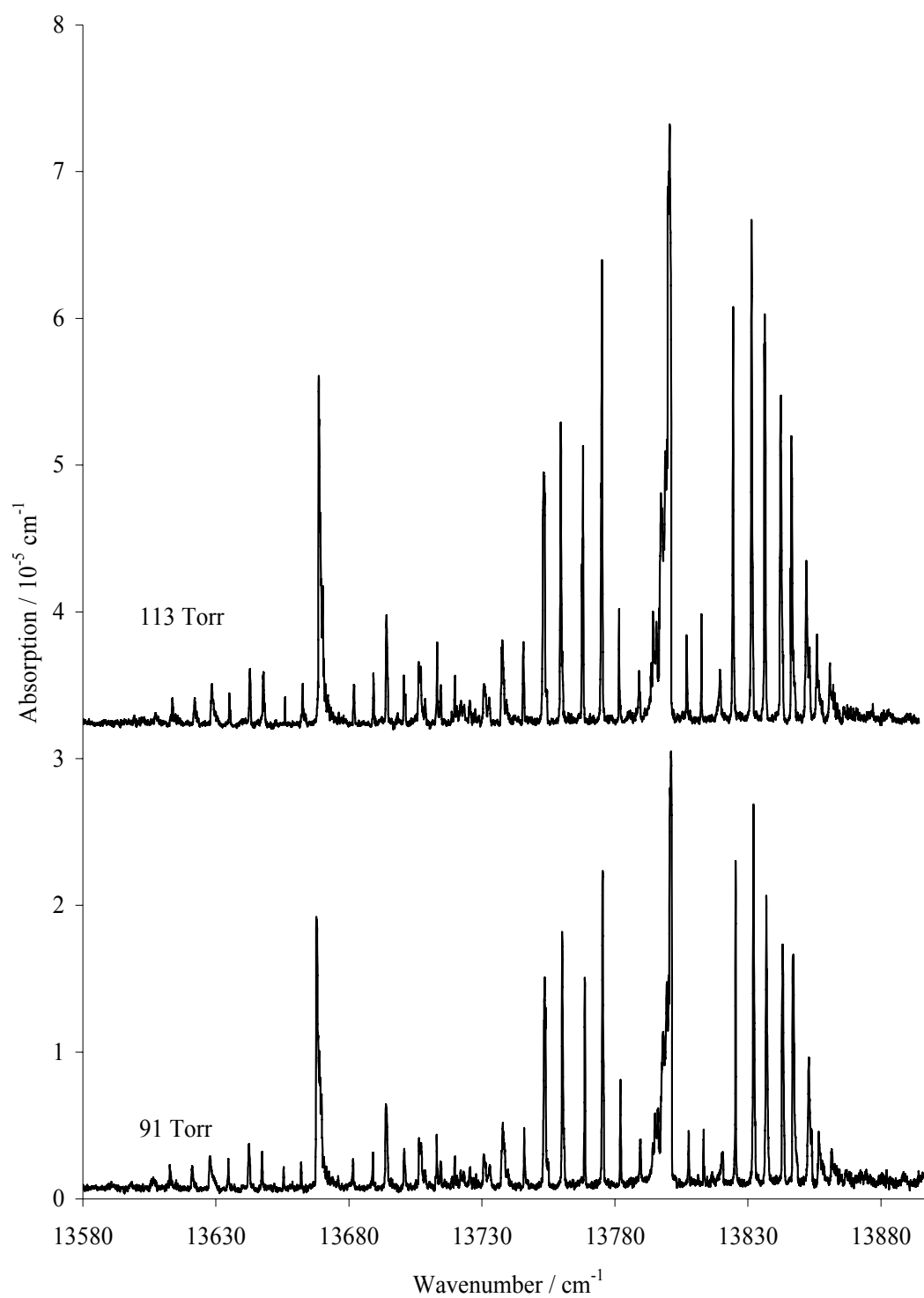
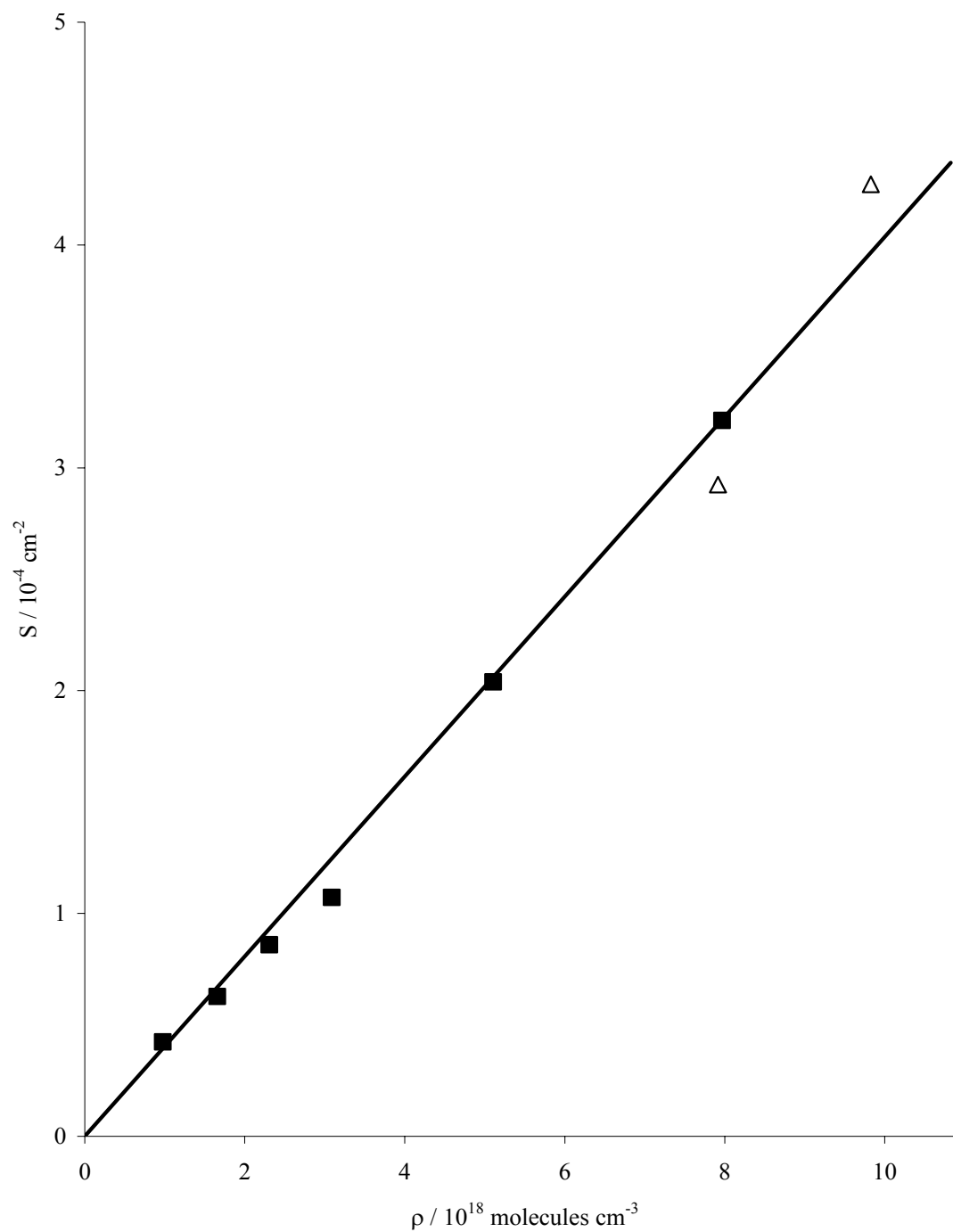


Figure 74. $(\nu=0 \rightarrow 5)$ transition of CHD_3 with a pressure of 113 Torr (top), and 91 Torr (bottom) at 111K



$$S_0 = (4.2 \pm 0.2) \times 10^{-23} \text{ cm}^2 \text{ cm}^{-1} \text{ molecules}^{-1}$$

$$R^2 = 0.994$$

Figure 75. ($v=0 \rightarrow 5$) transition of CHD_3 S vs. ρ . Marker ■ = measurements at 295 K and Marker Δ = measurements at 111 K

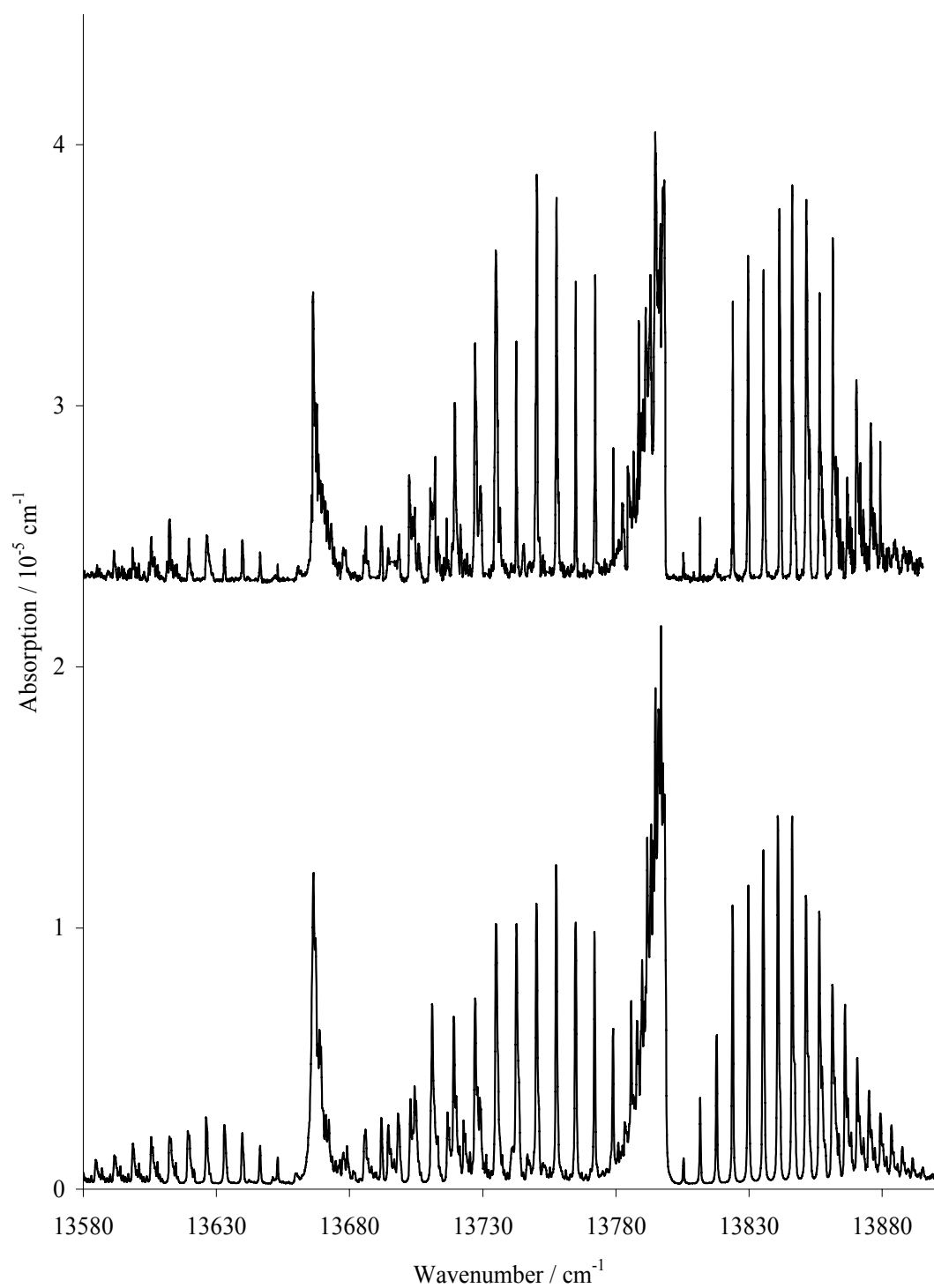


Figure 76. Comparison of absorption spectra of ($\nu = 0 \rightarrow 5$) C-H stretch of CHD_3 with a pressure of 247 Torr at 295 K. Top= experimental. Bottom= simulated

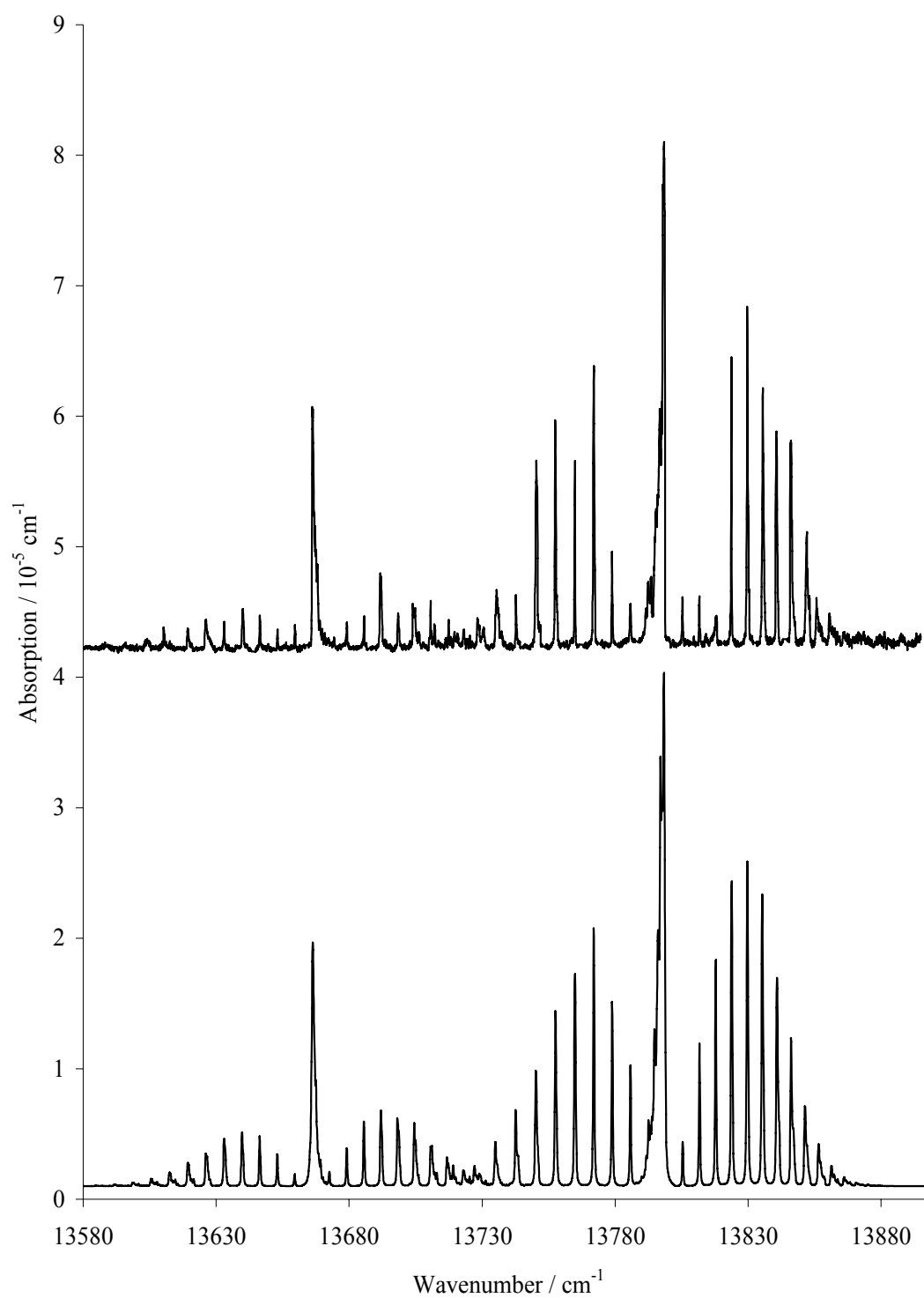


Figure 77. Comparison of absorption spectra of ($\nu=0\rightarrow5$) C-H stretch of CHD_3 with a pressure of 91 Torr at 111 K. Top= experimental. Bottom= simulated

actual temperature of the molecule. It demonstrates the capabilities of the PS-CRD instrument to measure low temperature rovibrational overtone spectra.

Table 41. Excited state parameters for CHD₃

N	ν_s, ν_b	ν_o / cm ⁻¹	$B' - B''$ / cm ⁻¹	$C' - C''$ / cm ⁻¹	$D'_J - D''_J$ /10 ⁻⁶ cm ⁻¹	$D'_{JK} - D''_{JK}$ /10 ⁻⁶ cm ⁻¹	$D'_K - D''_K$ /10 ⁻⁶ cm ⁻¹
5	5,0	13799.454	-0.0747	-0.0441	-7.4	8.9	-3.8
5	4,2	13666.142	-0.0272	0.0396	-22.6	-13	5.5

*CRD Spectra of CHD₃ in the ($\Delta\nu = 6$) CH-Stretching Region
at Room and Low Temperatures*

The overtone spectrum and integrated band strength (S_0) for the fifth ($\Delta\nu = 6$) C-H stretching overtone of CHD₃ was measured using the CRD absorption spectroscopy with a pulsed dye laser. The CRD method uses an exponential fitting to measure the decay time, or the time a given packet of light spends within an optical cavity. The pulsed dye laser used DCM as dye and has a resolution of 0.07 cm⁻¹. For these experiments the optical path length used was 6.4 km.

Figure 78 presents the absorption spectrum of the fifth overtone ($\Delta\nu = 6$) of the C-H stretching of CHD₃. The spectrum shows the two major vibrational bands, $6\nu_1$ at 16226.84 cm⁻¹ and $5\nu_1 + 2\nu_5$ at 16157.15 cm⁻¹, having almost the same intensity and closer than in the fourth overtone region, demonstrating that the mixing between the two bands, $\nu\nu_1$ and $(\nu - 1)\nu_1 + 2\nu_5$, becomes stronger for higher overtones ($\nu > 5$). This point will be discussed in more detail later. From this spectrum it is more difficult to distinguish between the R branch of $6\nu_1$ and the P branch of $5\nu_1 + 2\nu_5$ because of the strong overlapping between the two bands. Figure 78 shows an unperturbed

distribution intensities in R branch of $6\nu_1$, where the most intense line correspond to R(6). The highest J value recorded in this band was R(14). Note that Figure 78 presents a weaker $6\nu_1$ transition in comparison to Figure 70. The difference between them is one order of magnitude.

A pressure series of absorption spectrum ($\Delta\nu=6$) of CHD_3 at 295 K is illustrated in Figure 79. Spectra were obtained at pressures 300, 248, 214, 177 120 and 77 Torr. From spectra, where the Q branch represents 36 % of the total band intensity¹⁷⁸, the integrated absorption areas (S) were calculated and plotted versus the molecular density (ρ) as is shown in Figure 80, where the slope of the straight line represents the band strength (S_0) values. Table 42 reports the calculated ρ , S , and S_0 value for each pressure.

Table 42. ($\nu=0\rightarrow6$) CHD_3 at 295K, Pressure, ρ , S and S_0

Pressure torr	ρ $10^{18} \text{ molecules cm}^{-3}$	S 10^{-5} cm^{-2}	S_0 $10^{-24} \text{ cm}^2 \text{ cm}^{-1} \text{ molecule}^{-1}$
300	9.82	5.44	5.54
248	8.12	5.19	6.40
214	7.00	4.26	6.08
177	5.79	3.35	5.79
120	3.93	2.50	6.35
77	2.52	1.70	6.76
Avg			5.5 ± 0.4

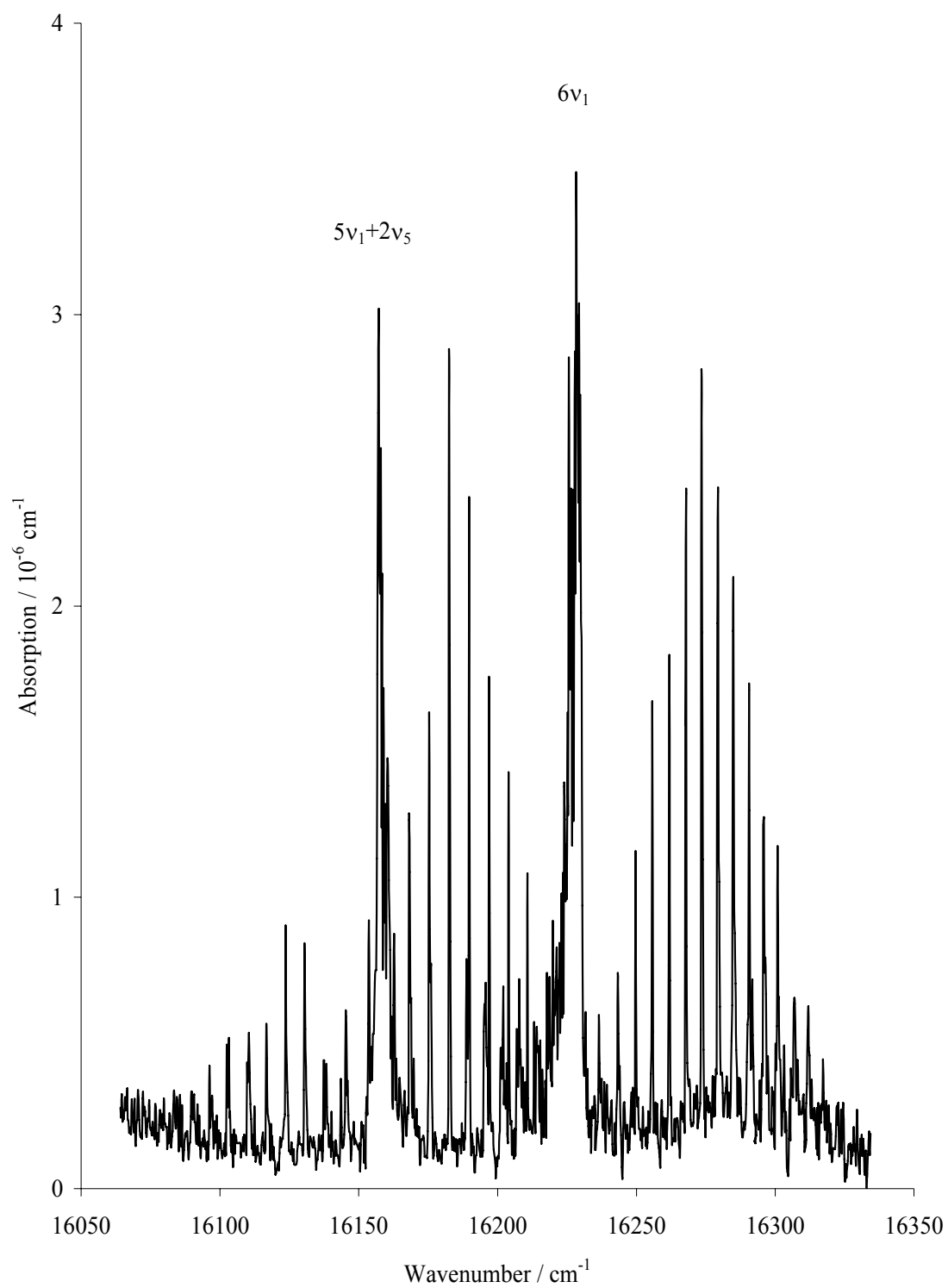


Figure 78. Absorption spectrum of ($\nu = 0 \rightarrow 6$) C-H stretch of CHD₃ with a pressure of 248 Torr at 295K.

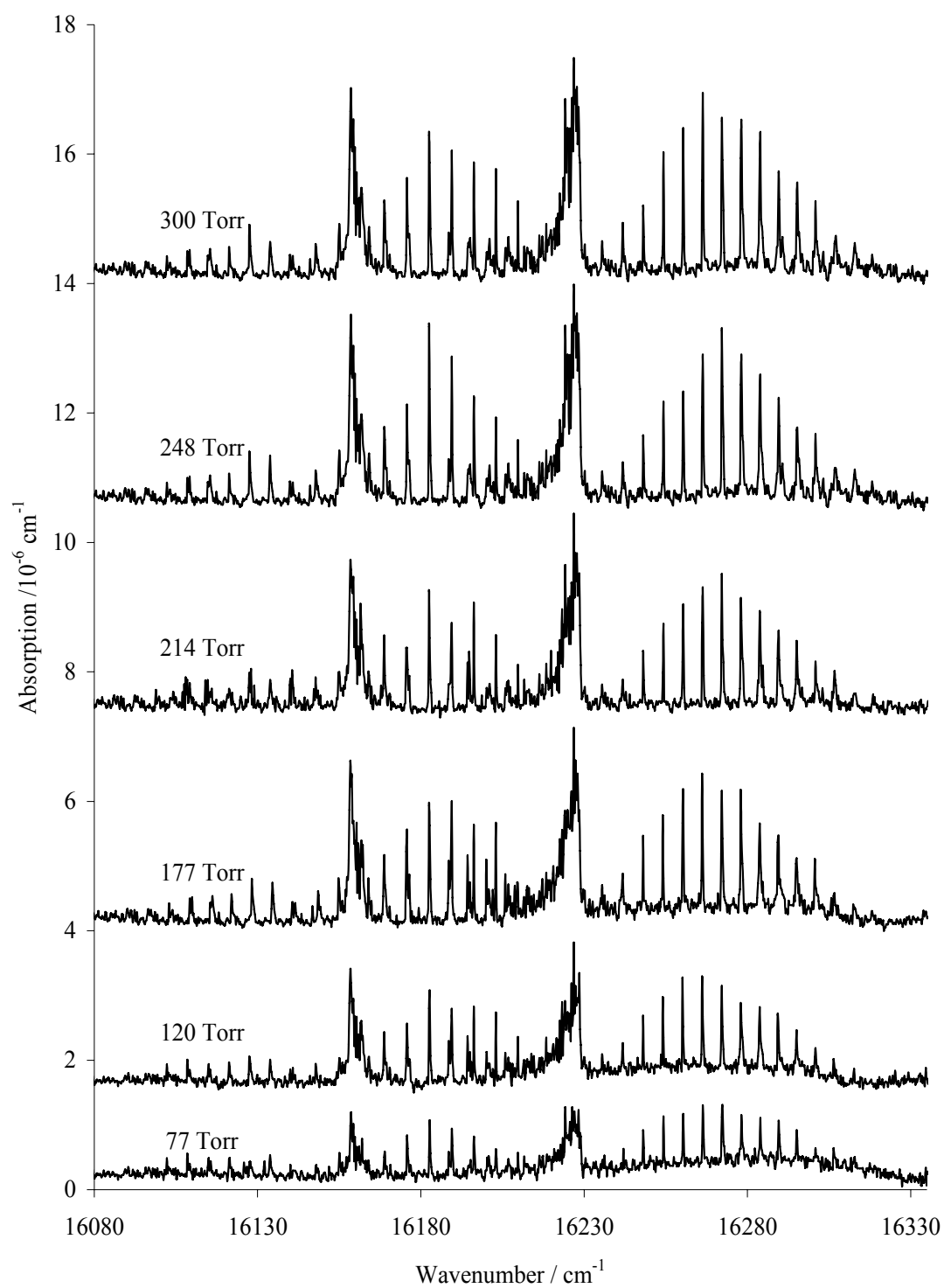
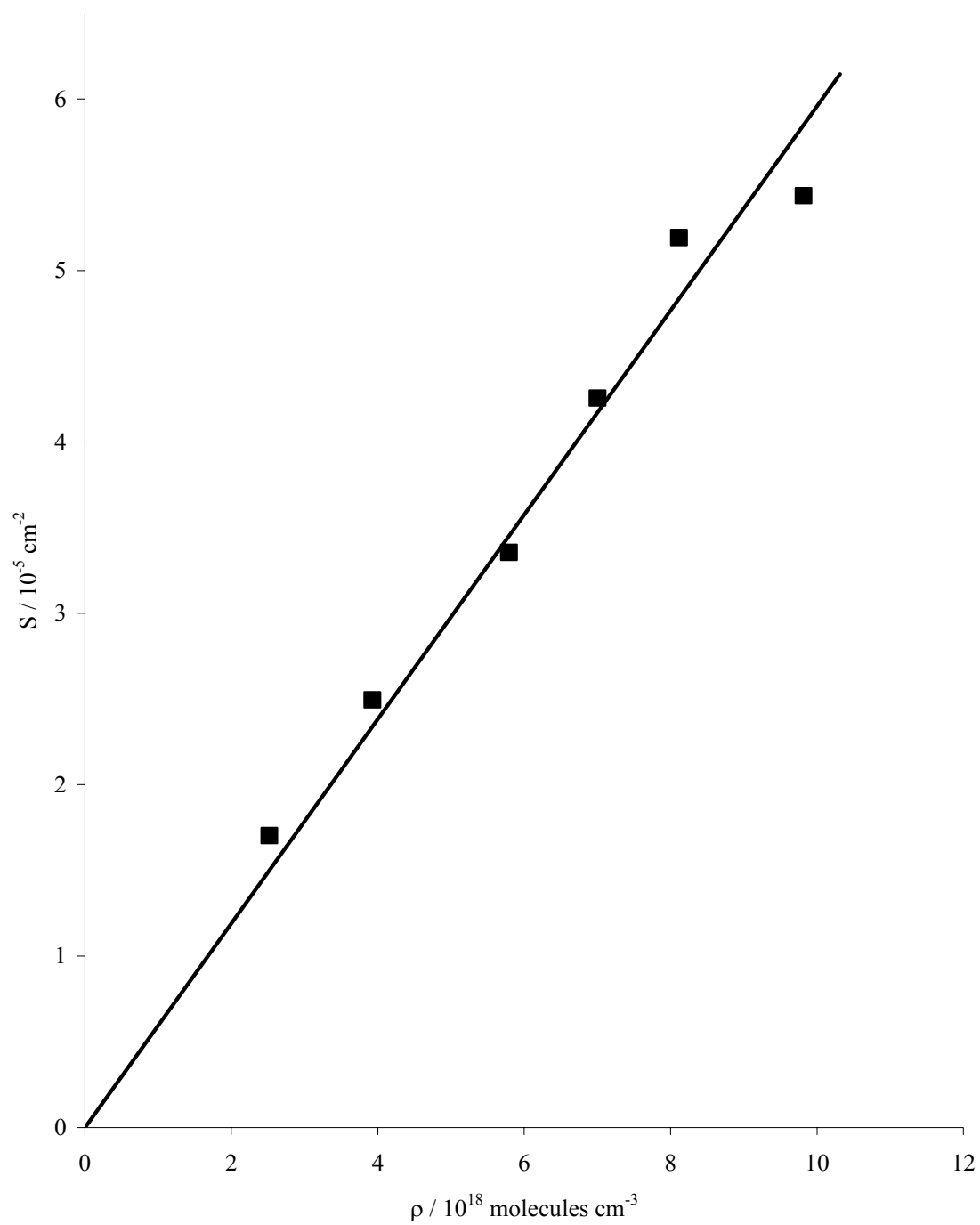


Figure 79. ($\nu=0\rightarrow6$) CHD_3 absorption pressure series at 295K



$$S_0 = (5.5 \pm 0.4) \times 10^{-24} \text{ cm}^2 \text{ cm}^{-1} \text{ molecules}^{-1}$$

$$R^2 = 0.988$$

Figure 80. ($\nu=0 \rightarrow 6$) of CHD_3 S vs. ρ . Slope is S_0

Figure 81 shows a temperature series of the ($\Delta v = 6$) of CHD_3 at 124, 195 and 295 K displaying the shift in rotational line intensity and a reduction of the width of the Q branch. The top spectrum was taken for 105 Torr at 124K, the middle spectrum was for 130 Torr at 195 K, and the bottom spectrum was for 248 Torr at 100K. The top spectrum is twice as intense as the one at 295 K because the increase of the populations in the lower rotational levels and decrease in higher rotational levels at low temperatures.

The intensities of the spectra at 295 and 124 K can be comparable, because both have similar molecular densities. Table 43 summarizes the maximum J value observed and the most intense line observed for the R branch of the vibrational band $6\nu_1$ at different temperatures. In Table 43, the R branch is only considered since in the P branch there is strong overlapping with R branch of the $5\nu_1 + 2\nu_5$ band.

A pressure series of the ($\Delta v = 6$) C-H overtone of CHD_3 at 124 K was also measured and is shown in Figure 82. Pressures of 105, 81 and 54 Torr were used and their integrated absorption areas were calculated.

Table 43. Maximum J value observed and strongest intensity of the line observed in $6\nu_1$ at different temperatures

T (K)	J max	Strongest Line
	R branch	R branch
124	10	J = 4
195	12	J = 5
295	14	J = 6

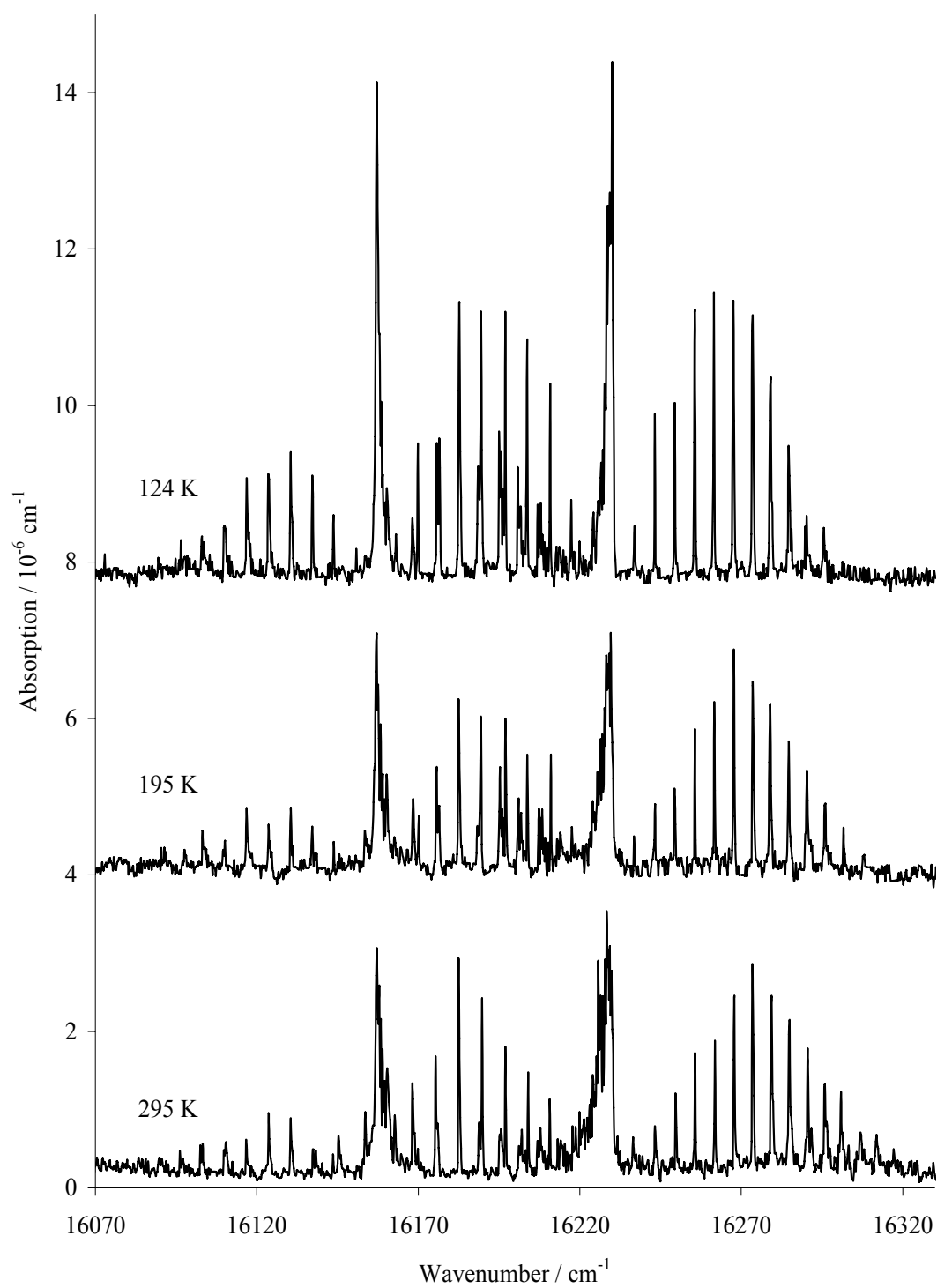


Figure 81. $(\nu=0 \rightarrow 6)$ CHD_3 with a pressure of 105 Torr at 124 K-top, 130 Torr at 195K- middle, and 295 Torr at 295K-bottom.

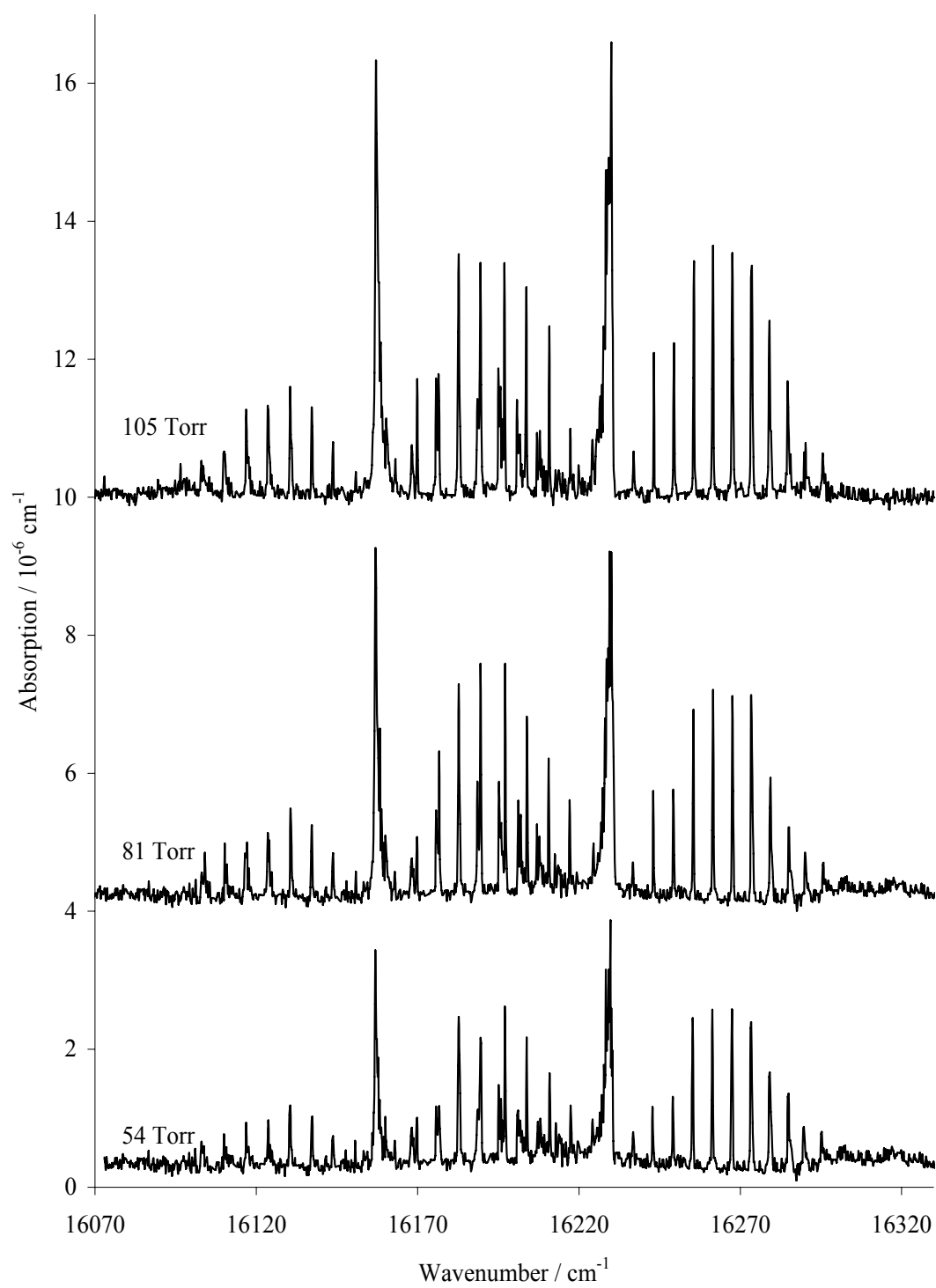


Figure 82. ($\nu=0 \rightarrow 6$) CHD_3 absorption pressure series at 124K

Table 44 reports the density, S , and S_0 for each pressure at 124 and 195K. These values were plotted together with values obtained at room temperature in Figure 83 which demonstrate the linearity of the results taken at different temperatures.

From the slope, the S_0 value is $(5.4 \pm 0.3) \times 10^{-24} \text{ cm}^2 \text{ cm}^{-1} \text{ molecules}^{-1}$. This value is in good agreement with $5.68 \times 10^{-24} \text{ cm}^2 \text{ cm}^{-1} \text{ molecules}^{-1}$ reported by Campargue *et al*¹⁷⁸

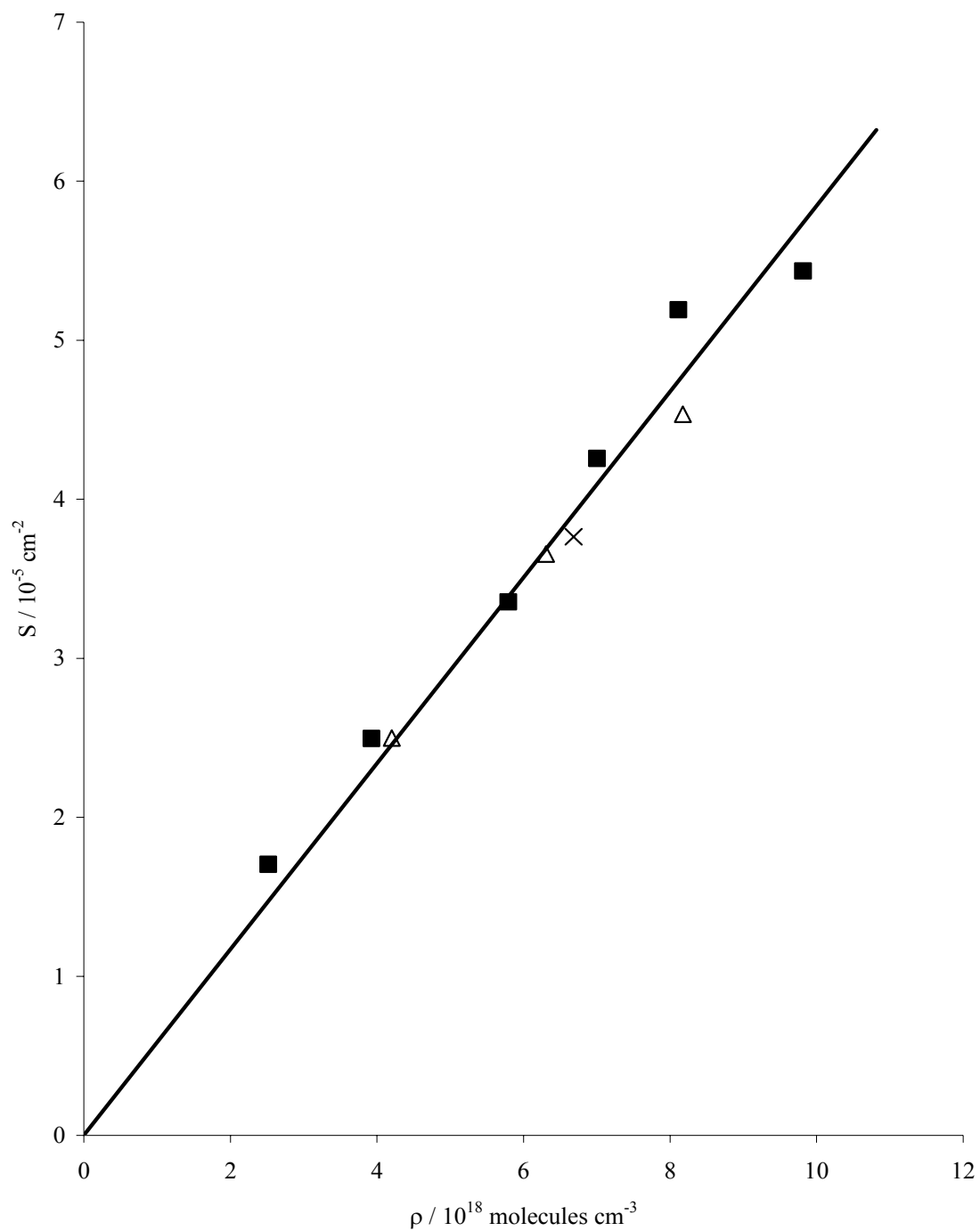
Table 44. ($\nu = 0 \rightarrow 6$) CHD₃ at 124K, Pressure, ρ , S and S_0 .

T	Pressure	ρ	S	S_0
Torr	Torr	$10^{18} \text{ molecules cm}^{-3}$	10^{-5} cm^{-2}	$10^{-24} \text{ cm}^2 \text{ cm}^{-1} \text{ molecule}^{-1}$
124 K	105	8.17	4.53	5.55
	81	6.31	3.65	5.80
	54	4.20	2.50	5.94
195 K	130	6.68	3.76	5.63
Avg				5.5 ± 0.4

The three different temperatures were used to measure the absorption spectra of ($\nu = 0 \rightarrow 6$) of CHD₃. The results were confirmed by spectra simulations at each temperature. This is possible because intensities of the rotational lines are related to the temperature by equation (49). The rotational constants for the excited states $6\nu_1$ and $5\nu_1+2\nu_5$ necessary to simulate the spectra are given in Table 45

Table 45. Excited state parameters for CHD₃

N	ν_s, ν_b	ν_o	$B' - B''$	$C' - C''$	$D'_J - D''_J$	$D'_{JK} - D''_{JK}$	$D'_K - D''_K$
		/ cm^{-1}	/ cm^{-1}	/ cm^{-1}	/ 10^{-6} cm^{-1}	/ 10^{-6} cm^{-1}	/ 10^{-6} cm^{-1}
6	6,0	16230.660	-0.0552	-0.0430	29	-120	59
6	5,2	16156.933	-0.033	0.044	-20	-205	275



$$S_0 = (5.4 \pm 0.3) \times 10^{-24} \text{ cm}^2 \text{ cm}^{-1} \text{ molecules}^{-1}$$

$$R^2 = 0.988$$

Figure 83. The ($v=0 \rightarrow 6$) transition of CHD_3 . S vs. ρ . Marker ■ = measurements at 295 K, Marker × = measurement at 195 K, and Marker Δ = measurements at 124 K

Figures 84 to **86** show the comparison between the experimental spectra with the simulated spectra. The PGOPHER program ¹⁴² was used to simulate the spectra at different temperatures. The agreement between the experimental and simulated spectra confirms a good correlation between temperature measured by the sensor located in the cell and the actual temperature of the molecule.

Analysis of the Fermi Resonance

In this section the mathematical formulation for Fermi resonance will be used to show how the perturbation between the two vibrational levels, $\nu\nu_1$ and $(\nu-1)\nu_1+2\nu_5$ is involved in each overtone level of CHD₃ and increases for higher overtones ($\nu \geq 5$). The approximation of treating only the purely vibrational interaction between the levels is made; that is, Coriolis coupling is ignored to nearby E states. It is expected that a Fermi resonance interaction of the totally symmetric overtone and combination state will dominate the relative intensities.¹¹³

The magnitude of the perturbation depends on the value of the corresponding matrix element W_{ni} of the perturbation function W .¹⁸⁶

$$W_{ni} = \int \psi_n^o W \psi_i^{o*} d\tau \quad (58)$$

The perturbation function W is essentially given by the anharmonic (cubic, quartic, ...) terms in the potential energy, while ψ_n^o and ψ_i^o are the zero order eigenfunctions of the two vibrational levels that perturb each other. Since W is totally symmetric, ψ_n^o must have the same symmetry type as ψ_i^o in order to give a non-zero value to W_{ni} and therefore to the magnitude of the perturbation.¹⁸⁶

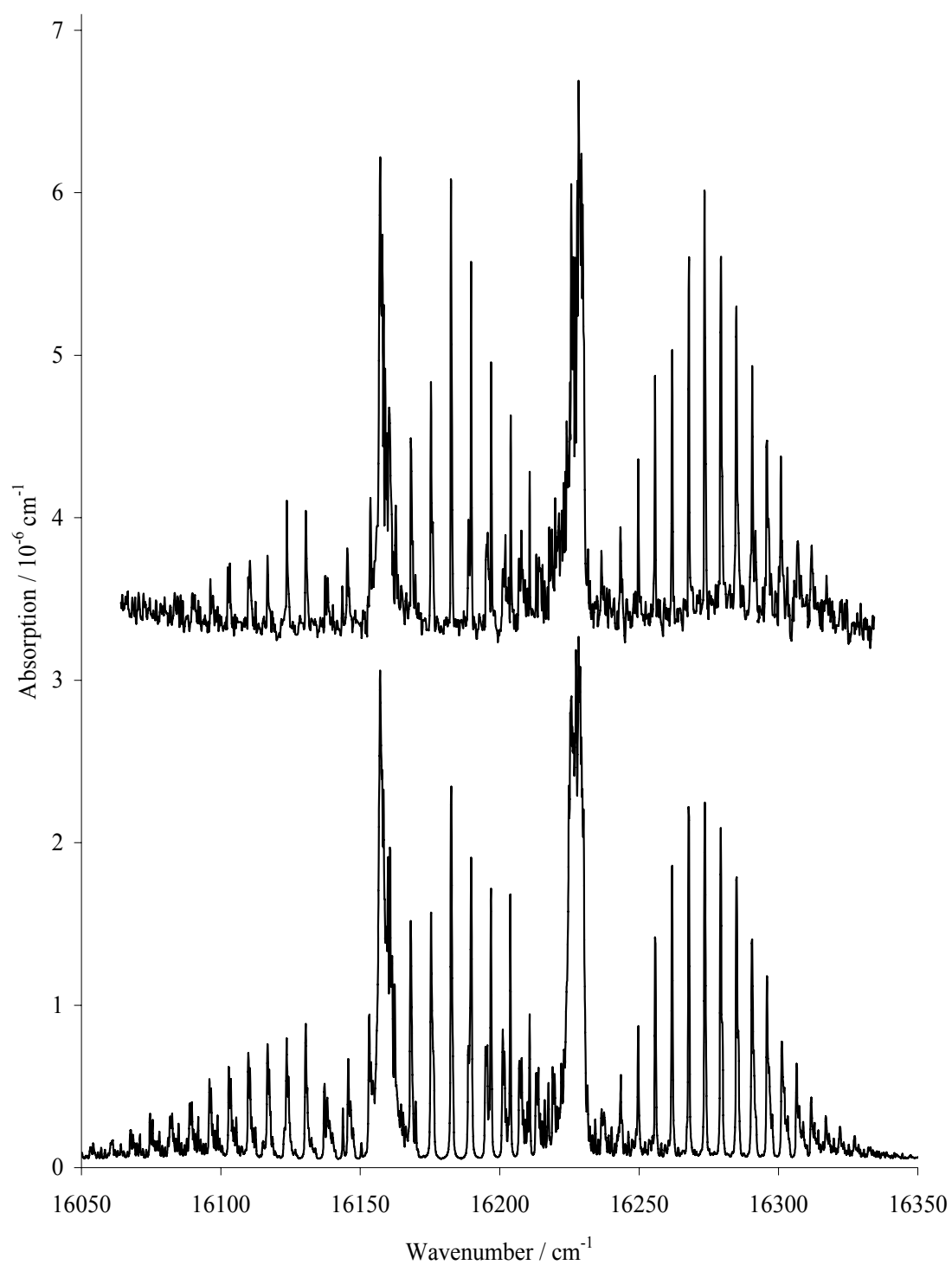


Figure 84. Comparison of absorption spectra of ($\nu=0\rightarrow6$) C-H stretch of CHD_3 with a pressure of 248 Torr at 295 K. Top= experimental. Bottom= simulated

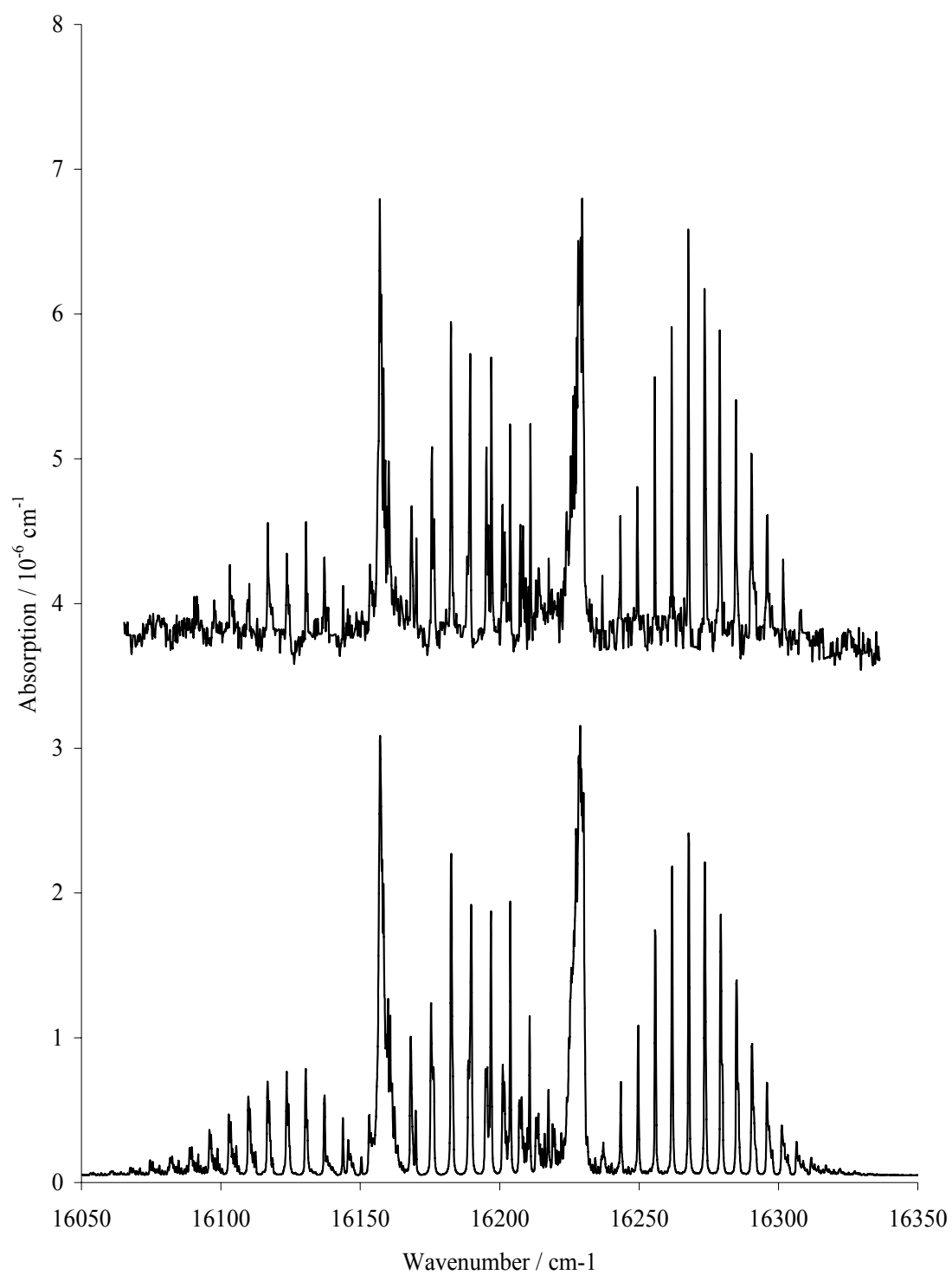


Figure 85. Comparison of absorption spectra of ($\nu=0\rightarrow6$) C-H stretch of CHD_3 with a pressure of 130 Torr at 195 K. Top= experimental. Bottom= simulated

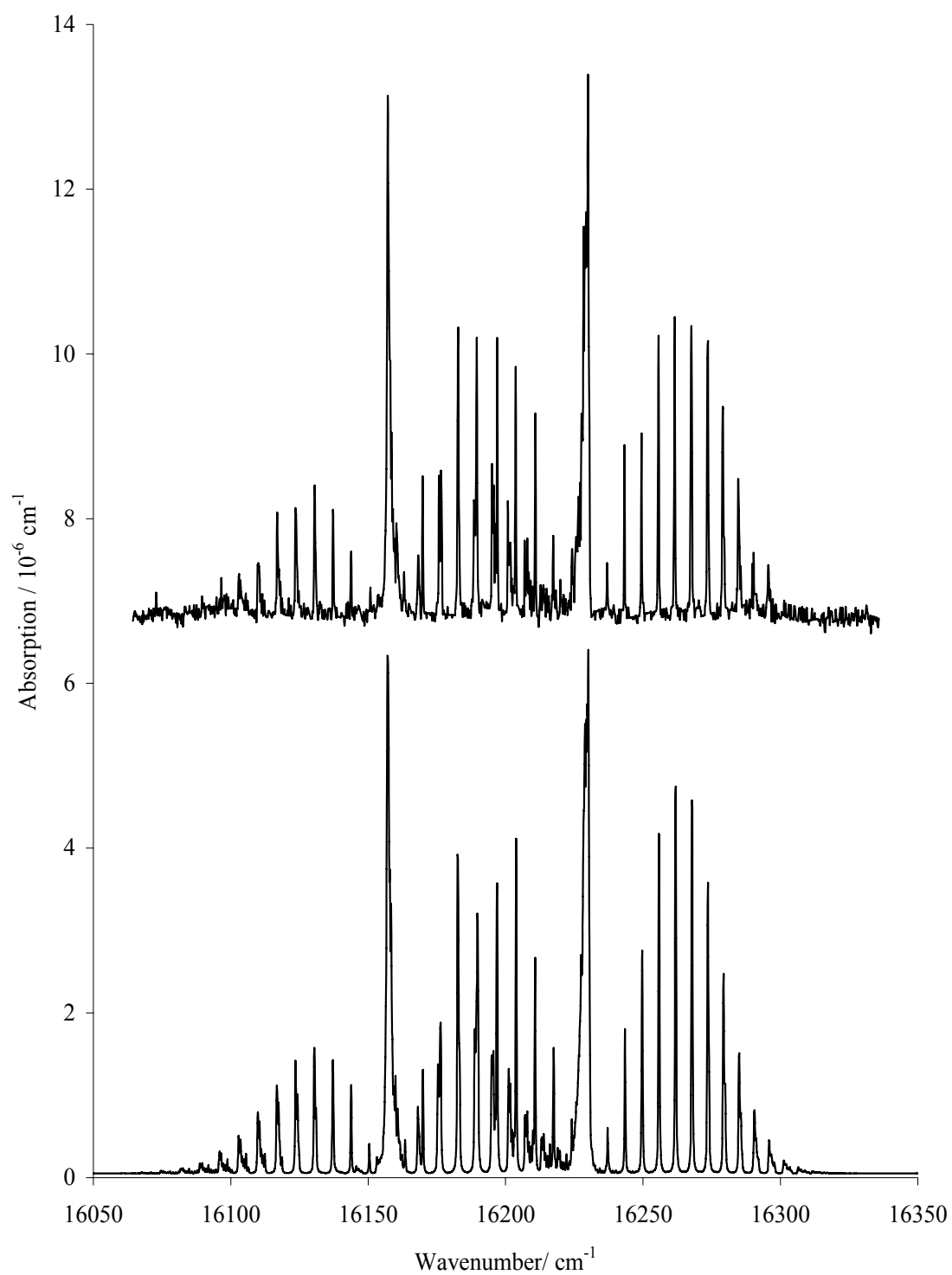


Figure 86. Comparison of absorption spectra of ($\nu=0\rightarrow6$) C-H stretch of CHD_3 with a pressure of 105 Torr at 124 K. Top= experimental. Bottom= simulated

Thus, it is obtained the important rule: only vibrational levels of the same species can perturb one another, or, Fermi resonance can occur only between levels of the same species. This rule restricts very greatly the occurrence of vibrational perturbations (Fermi resonance) in symmetrical polyatomic molecules. The C-H stretching fundamental has A_1 symmetry in the C_{3v} molecular point group. Thus, all overtones of this mode have A_1 symmetry also. The symmetry of mode ν_5 is E, however, the level $2\nu_5$ split into A_1 and E sublevels of which the A_1 level may, with or without combination with the A_1 C-H stretch overtones, interact with A_1 C-H- stretching levels.

If the resonance is fairly close the magnitude of the shift can be obtained according to first-order perturbation theory from the secular determinant¹⁸⁶

$$\begin{vmatrix} E_n^o - E & W_{ni} \\ W_{in} & E_i^o - E \end{vmatrix} = 0 \quad (59)$$

where E_n^o and E_i^o are the unperturbed energies. From this equation one obtains for the perturbed energies $E_{\pm}$, since according to equation (58) $W_{in} = W_{ni}^*$,

$$E_{\pm} = \bar{E}_{ni} \pm \frac{1}{2} \sqrt{4|W_{ni}|^2 + \delta^2} \quad (60)$$

where $\bar{E}_{ni} = \frac{1}{2}(E_i^o + E_n^o)$ is the mean of the unperturbed levels and $\delta = E_n^o - E_i^o$ is the separation of the unperturbed levels. From this equation the magnitude of the perturbation, W_{ni} , can be obtained.

Following the same procedure used by Perry *et al*¹¹³ and Campargue,¹⁷⁷ Fermi resonances of CHD_3 are studied. The $\Delta\nu = 6$ region is used as a model. Thus, the subscripts in equation (60) are defined as $n = 6\nu_1$ and $i = 5\nu_1 + 2\nu_5$.

First, the unperturbed or zero-order (E^o) overtone energies have to be obtained. These are obtained from the extrapolation of the Birge-Sponer equation. Figure 87 shows the Birge-Sponer plot for the CHD_3 ν_1 overtones. Using a linear least squares fit to experimental points for $\nu=1$ through 7 the following equation was determined: $\frac{\Delta E_{0 \rightarrow \nu}}{\nu} = 3107 - 58.12\nu$. Table 46 lists energies for the CHD_3 ν_1 overtones ($\nu \nu_1$) obtained experimentally in previous sections (E_{obs}), extrapolated energies from the Birge-Sponer equation (E_{ext}^o), the Fermi resonance shift (FRS) which is obtained from the difference in the observed energy of the pure overtone and the extrapolated value ($F_s = E_{obs} - E_{ext}^o$), and the harmonic frequency (ω), and anharmonicity (ωx) for CHD_3 .

Thus, from Table 46 the zero-order energy to $6\nu_1$ can be obtained, $E_n^o = 16202.59 \text{ cm}^{-1}$. Since the shifts due to the resonance interaction are of equal magnitude for the two level problem, the shift of the observed $6\nu_1$ energy from the zero-order calculated energy (FRS) can be used to correct the observed $5\nu_1 + 2\nu_5$ energy, $E_{corr}^o = E_{obs} + \text{FRS} = 16157.15 \text{ cm}^{-1} + 24.25 \text{ cm}^{-1} = 16181.4 \text{ cm}^{-1} = E_i^o$. Hence, we are able to obtain the zero-order energy for the combination band. Table 47 lists the energies for the CH-stretch- bend combination ($(\nu-1)\nu_1 + 2\nu_5$) obtained experimentally E_{obs} , and the corrected, E_{corr}^o .

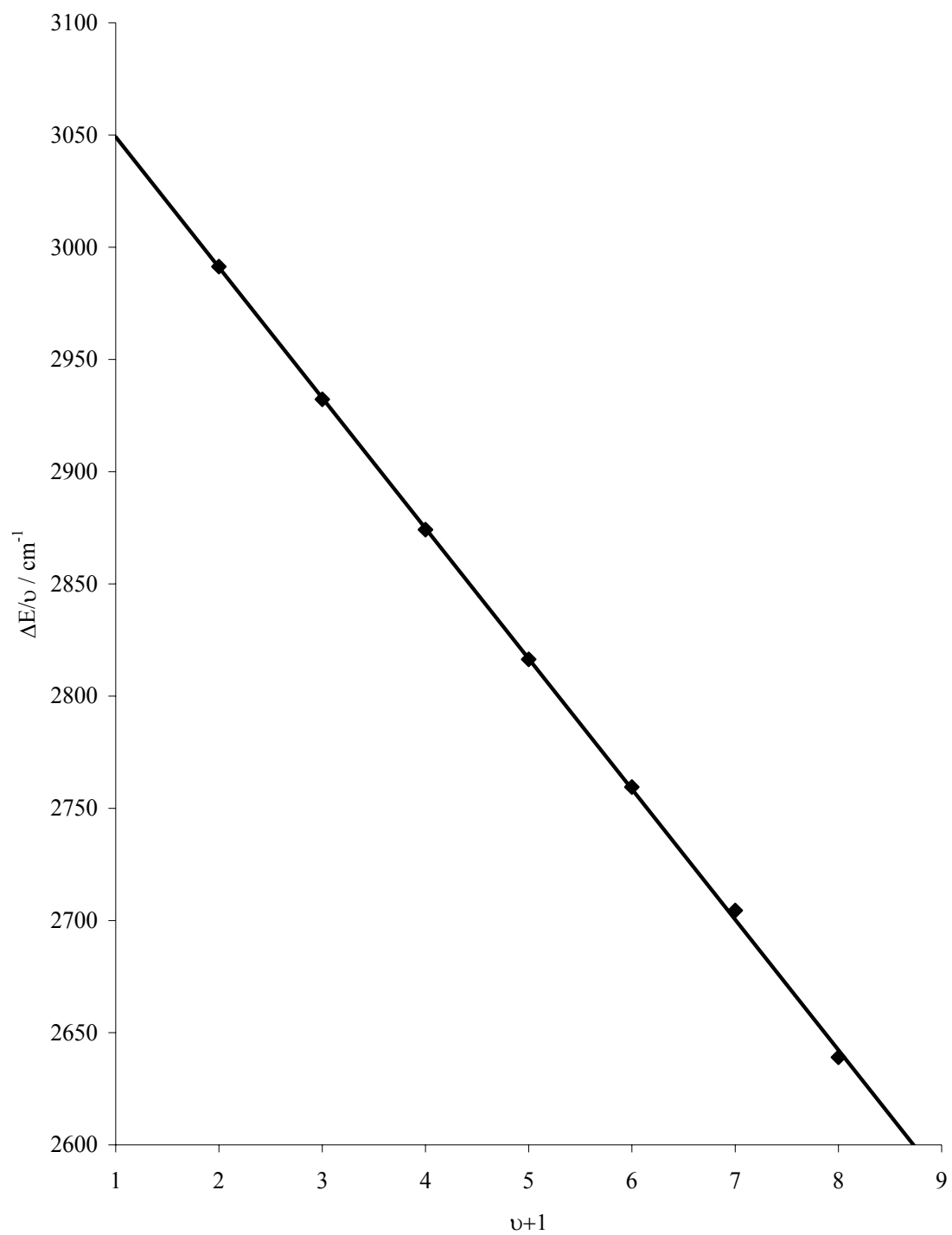


Figure 87. Birge-Sponer plot for CHD₃, C-H stretching states.

Table 46. Observed and extrapolated energies of C-H stretch overtones ($\nu \nu_1$) of CHD₃

ν	E_{obs} / cm^{-1}	$E_{ext}^o / \text{cm}^{-1}$	FRS / cm^{-1}
1	2991.34	2990.77	0.57
2	5864.56	5866.66	-2.09
3	8622.32	8625.31	-2.99
4	11265.32	11267.52	-2.20
5	13797.44	13793.28	4.16
6	16226.84	16202.59	24.25
7	(18473.00) ^a	18495.46	-22.46
Harmonic Frequency / cm^{-1}	3107 ± 2	Anharmonicity / cm^{-1}	58.1 ± 0.4

^a The values in parentheses were taken from Perry *et al*¹¹³

Table 47. Energies of CH-stretch-bend combination ($(\nu - 1)\nu_1 + 2\nu_5$) of CHD₃

ν	State	E_{obs} / cm^{-1}	$E_{corr}^o / \text{cm}^{-1}$
4	$3\nu_1 + 2\nu_5$	11064.28	11066.48
5	$4\nu_1 + 2\nu_5$	13666.14	13670.30
6	$5\nu_1 + 2\nu_5$	16157.15	16181.40

The perturbed energies ($E_{\pm}$) are the values obtained experimentally, called earlier E_{obs} . E_+ refers to experimental energy of ν_1 overtones ($\nu \nu_1$) and E_- is the energy for the CH-stretch-bend combination ($(\nu - 1)\nu_1 + 2\nu_5$). For our model $E_+ = 16226.84 \text{ cm}^{-1}$ and $E_- = 16157.15 \text{ cm}^{-1}$. The W_{ni} value can now be calculated. Table 48. shows E_+ , E_- , E_n^o , E_i^o , $\bar{E}_{ni}$ and δ . These values are used to calculate W_{ni} for $\Delta\nu = 4, 5$ and 6 region. The W_{ni} values are also summarized in Table 48.

Table 48. E_+ , E_- , E_n^o , E_i^o , $\bar{E}_{ni}$, δ and W_{ni} values for CHD_3

ν	E_+	E_-	E_n^o	E_i^o	$\bar{E}_{ni}$	δ	W_{ni}
	/ cm^{-1}						
4	11265.32	11064.28	11267.52	11066.48	11164.8	201.04	1.35×10^{-5}
5	13797.44	13666.14	13793.28	13670.30	13670.30	122.98	23
6	16226.84	16157.15	16202.59	16181.40	16181.40	21.19	33

For $\Delta\nu=4$ region, the value of the perturbation is very small. Hence, the weak coupling is observed in the spectrum of Figure 62 where very little overlap is observed and confirms the perturbation value obtained. On the other hand, the magnitude of the perturbation increases for higher overtones, W_{ni} for $\Delta\nu = 6$ is larger than W_{ni} for $\Delta\nu = 5$, which is in agreement with the absorption spectra of these regions. Figures 78 and 70 show that the mixing between the pure CH stretching overtone with the CH-stretch-bend combination is stronger for the $\Delta\nu = 6$ region than for the $\Delta\nu = 5$.

The eigenfunctions for the mixed states can be shown to be the following mixtures of the zero approximation eigenfunctions ψ_n^o and ψ_i^o :¹⁸⁶

$$\psi_n = a\psi_n^o - b\psi_i^o \quad (61)$$

$$\psi_i = b\psi_n^o + a\psi_i^o \quad (62)$$

where

$$a = \left(\frac{\sqrt{4|W_{ni}|^2 + \delta^2} + \delta}{2\sqrt{4|W_{ni}|^2 + \delta^2}} \right)^{\frac{1}{2}}, \quad b = \left(\frac{\sqrt{4|W_{ni}|^2 + \delta^2} - \delta}{2\sqrt{4|W_{ni}|^2 + \delta^2}} \right)^{\frac{1}{2}} \quad (63)$$

Where $a^2 + b^2 = 1$. If $\delta=0$, a fifty-fifty mixture is obtained and if δ is very large $\psi_n \rightarrow \psi_n^0$ and $\psi_i \rightarrow \psi_i^0$. Using equation (61) to (63), the eigenfunctions for the mixed states in $\Delta v=5$ and 6 region were obtained. These eigenfunctions together with a and b values are shown in Table 49.

Eigenfunctions show that the perturbation W_{ni} destroys the “pure” character of the CH stretching overtone ($v \nu_1$). Thus, those confirm that combinations bands involving states in Fermi resonance are often much stronger than they would otherwise be, since they have “borrowed” some of the character of the more strongly allowed transition^{186, 189}.

Table 49. Eigenfunctions for the mixed states in $\Delta v=5$ and 6 region

v	a	b	Eigenfunctions
5	0.98	0.17	$\psi_{5\nu_1} = 0.98\psi_{5\nu_1}^o - 0.17\psi_{4\nu_1+2\nu_5}^o$
			$\psi_{4\nu_1+2\nu_5} = 0.17\psi_{5\nu_1}^o + 0.98\psi_{4\nu_1+2\nu_5}^o$
6	0.81	0.59	$\psi_{6\nu_1} = 0.81\psi_{6\nu_1}^o - 0.59\psi_{5\nu_1+2\nu_5}^o$
			$\psi_{5\nu_1+2\nu_5} = 0.59\psi_{6\nu_1}^o + 0.81\psi_{5\nu_1+2\nu_5}^o$

Theoretical Calculations of Band Strength Values for C-H Stretching of CHD₃

In this section, band strength values obtained experimentally (in a previous section) for the C-H stretch of CHD₃ are compared with calculated S_o values. The calculation is based on the following theoretical considerations. The oscillator strength, f , of a vibrational transition within the same electronic state between the ground state g and an excited vibrational state e can be written as:¹⁹⁰

$$f_{e \leftarrow g} = 4.70165 \times 10^{-7} (cmD^{-2}) \tilde{\nu}_{eg} |\mu_{eg}|^2, \quad (64)$$

where $\tilde{\nu}_{eg}$ is the transition frequency for a particular eigenstate in cm^{-1} and $|\mu_{eg}| = \langle e | \mu | g \rangle$ is the transition dipole moment in debye (D). Since the transition frequencies are known from the measured spectra (see Table 46) what is left to be calculated are the transitions dipole moments.

The dipole moment as a function of all or even a fraction of the internal coordinates is a nontrivial quantity to determine. Intensity calculations for local mode overtone spectra have been presented through two approximations to calculate the dipole moment function. They are an exponential bond dipole form^{191,192} or a set of *ab initio* calculated coefficients in a series expansion in the internal displacement coordinates.¹⁹³

The dipole moment function (DMF), for an XH_n is modeled as a polynomial expansion in the internal bond displacement coordinates q_i ^{190, 194,195}

$$\mu(q_1, q_2, \dots, q_n) = \sum_{i_1, i_2, \dots, i_n} \mu_{i_1, i_2, \dots, i_n} q_1^{i_1} q_2^{i_2} \dots q_n^{i_n} \quad (65)$$

where

$$\mu_{i_1, i_2, \dots, i_n} = \frac{1}{i_1! i_2! \dots i_n!} \frac{\partial \sum_j i_j \mu}{\partial q_1^{i_1} \partial q_2^{i_2} \dots \partial q_n^{i_n}} \quad (66)$$

The $q_1, q_2, \dots, q_n$ coordinates represent the displacement of the appropriate H atom from its equilibrium position. To calculate the transition dipole moments for a single C-H stretching bond, it considers only the single bond (one-dimensional) DMF. This simplifies equations (65) and (66) considerably¹⁹⁶:

$$\mu(q) = \sum_i \mu_i q^i \quad (67)$$

and

$$\mu_i = \frac{1}{i!} \frac{\partial^i \mu}{\partial q^i} \quad (68)$$

To calculate the μ_i in equation (67), the bond length is changed in small steps and then the dipole moment at the new geometry is calculated for each step. The resulting dipole moment values with the corresponding displacement values are fitted to polynomial function. From that fitting the μ_i coefficients can be obtained

The transition dipole moment of equation (64) can be expanded as¹⁹⁷

$$\langle e | \hat{\mu} | g \rangle = \langle \nu | \hat{\mu} | 0 \rangle = \frac{\partial \mu}{\partial q} \langle \nu | q | 0 \rangle + \frac{1}{2} \frac{\partial^2 \mu}{\partial q^2} \langle \nu | q^2 | 0 \rangle + \frac{1}{6} \frac{\partial^3 \mu}{\partial q^3} \langle \nu | q^3 | 0 \rangle + \dots \quad (69)$$

The $\langle \nu | q^n | 0 \rangle$ values correspond to the matrix elements of the powers of the coordinates over the Morse oscillator wave functions^{198, 199}. These matrix elements are relatively insensitive to the C-H stretch harmonic frequency (ω) and the Morse anharmonicity (ωx) parameters. Therefore, the values calculated by Kjaergaard and Henry¹⁹³ were adopted and give in Table 50.

One-dimensional dipole moment functions for the CH bond in CHD₃ were calculated using Hartree-Fock (HF) and MP2 levels of theory using 6-311++G(d,2p), 6-311++G(d,3pd), 6-311++G(2d,pd), 6-311++G(d,2pd) and 6-311++G(d,pd) basis sets. The computations were performed using the Gaussian 03 Program Package.²⁰⁰

The calculations utilized the C_{3v} symmetry of the CHD₃ molecule. Table 51 contains the select parameters¹⁸¹ for the optimized geometries, and compares available experimental data.

To calculate the μ_i in equation (67), the CH bond length was changed in the range of $0.4 \text{ \AA}$ to $-0.4 \text{ \AA}$, in steps of $0.1 \text{ \AA}$.¹⁹⁶ This procedure required nine calculations and provided accordingly nine dipole moment values.

Table 50. Matrix elements $\langle \nu | q^n | 0 \rangle$ for a Morse oscillator (in unit of $\text{\AA}^n$)

ν	n=1	n=2	n=3	n=4	Exponent
1	7.847	0.453	0.170	0.020	-2
2	-8.210	8.127	0.878	0.401	-3
3	1.417	-2.128	0.898	0.137	-3
4	-3.213	5.890	-4.398	0.921	-4
5	0.878	-1.822	1.778	-0.804	-4
6	-2.768	6.264	-7.205	4.558	-5
7	0.980	-2.367	3.050	-2.361	-5

Table 51. Calculated parameters for CHD_3

		μ (Debye)	B_0 /MHz	C_0 /MHz
HF	6-311++G(d,2p)	0.0133	97.59	77.89
	6-311++G(d,3pd)	0.0130	97.60	77.89
	6-311++G(2d,pd)	0.0127	97.57	77.88
	6-311++G(d,2pd)	0.0134	97.61	77.90
MP2	6-311++G(d,2p)	0.0104	97.43	77.87
	6-311++G(d,pd)	0.0099	97.41	77.86
	6-311++G(d,3pd)	0.0103	97.45	77.88
	6-311++G(2d,pd)	0.0097	97.40	77.86
Experimental		0.0058	98.37	78.89

Figure 88 shows the dipole moment as a function of the CH bond length. The coefficients in equation (67) were found by least-squares fitting of an n th order

polynomial in the coordinate q^{201} , where n is the chosen maximum order. Tables 52 to 59 show the dipole derivatives fitted to a polynomial for different orders at each level of theory. The values $n = 4, 5, 6, 7$ and 8 were used to denote the maximum order of the polynomial.

Table 52. HF/ 6-311++G(d,2p)Dipole moment derivate coefficients

μ	$n=4$	$n=5$	$n=6$	$n=7$	$n=8$
$D(\hat{A}^{-1})$	-0.828	-0.826	-0.826	-0.826	-0.825
$D(\hat{A}^{-2})$	-1.138	-1.137	-1.137	-1.137	-1.127
$D(\hat{A}^{-3})$	0.140	0.098	0.098	0.078	0.078
$D(\hat{A}^{-4})$	0.041	0.041	0.028	0.028	0.372

Table 53. HF/ 6-311++G(d,3pd)Dipole moment derivate coefficients

μ	$n=4$	$n=5$	$n=6$	$n=7$	$n=8$
$D(\hat{A}^{-1})$	-0.797	-0.792	-0.792	-0.793	-0.793
$D(\hat{A}^{-2})$	-1.139	-1.139	-1.167	-1.168	-1.166
$D(\hat{A}^{-3})$	0.050	-0.071	-0.071	-0.032	-0.032
$D(\hat{A}^{-4})$	0.183	0.182	0.673	0.673	0.613

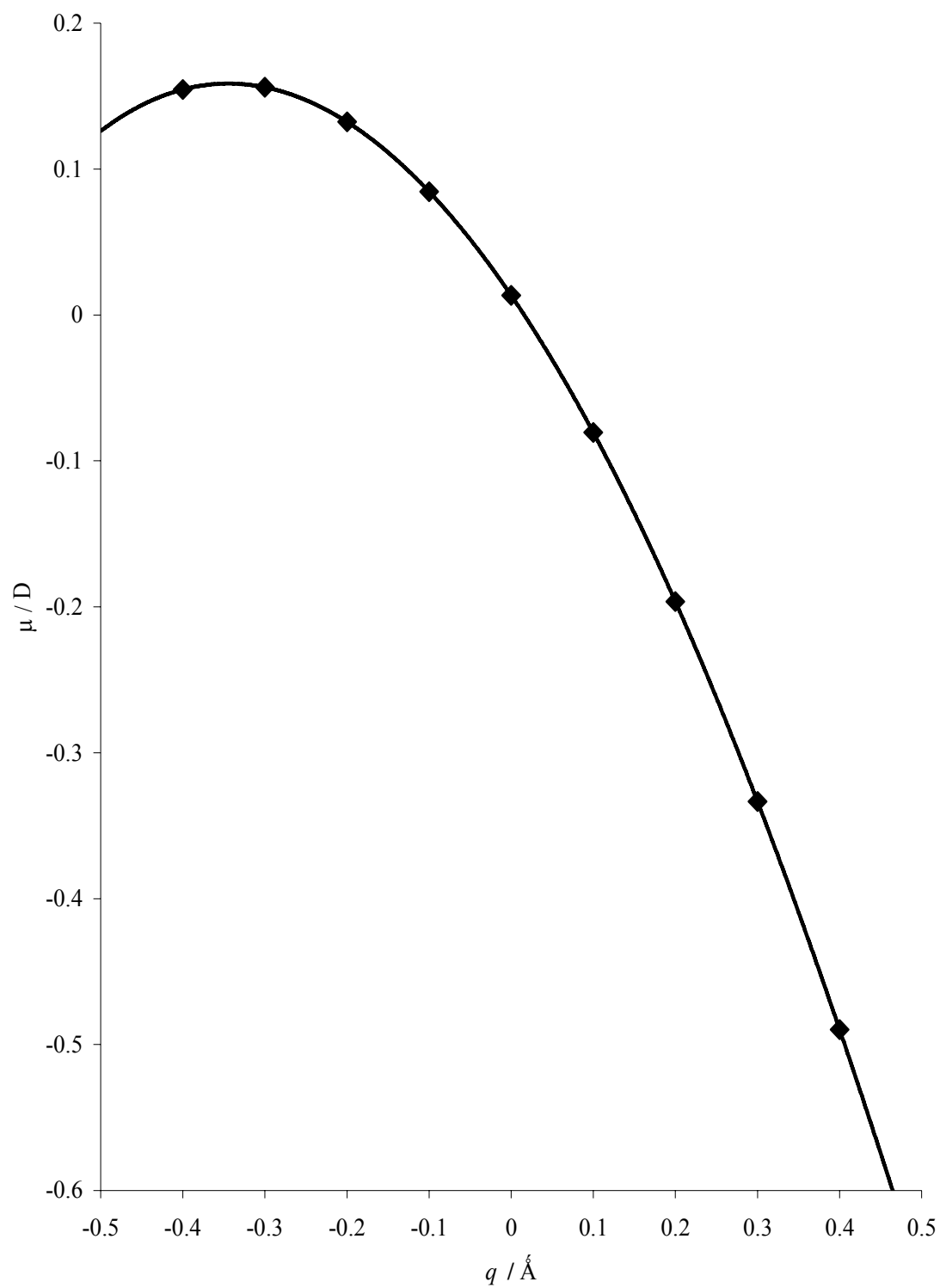


Figure 88. Dipole moment as a function of the CH bond length using the HF / 6-311++G(d,2p)

Table 54. HF/ 6-311++G(2d,pd)Dipole moment derivate coefficients

μ	$n=4$	$n=5$	$n=6$	$n=7$	$n=8$
$D(\text{\AA}^{-1})$	-0.818	-0.813	-0.813	-0.813	-0.813
$D(\text{\AA}^{-2})$	-1.085	-1.085	-1.101	-1.101	-1.095
$D(\text{\AA}^{-3})$	0.081	-0.061	0.061	-0.057	-0.057
$D(\text{\AA}^{-4})$	0.060	0.060	0.212	0.212	-0.018

Table 55. HF/ 6-311++G(d,2pd)Dipole moment derivate coefficients

μ	$n=4$	$n=5$	$n=6$	$n=7$	$n=8$
$D(\text{\AA}^{-1})$	-0.809	-0.805	-0.805	-0.806	-0.806
$D(\text{\AA}^{-2})$	-1.138	-1.138	-1.151	-1.151	-1.155
$D(\text{\AA}^{-3})$	0.064	-0.045	-0.045	-0.021	-0.021
$D(\text{\AA}^{-4})$	0.120	0.120	0.359	0.359	0.492

Table 56. MP2/ 6-311++G(d,2p) Dipole moment derivate coefficients

μ	$n=4$	$n=5$	$n=6$	$n=7$	$n=8$
$D(\text{\AA}^{-1})$	-0.838	-0.836	-0.836	-0.836	-0.836
$D(\text{\AA}^{-2})$	-1.136	-1.136	-1.140	-1.140	-1.142
$D(\text{\AA}^{-3})$	0.140	0.088	0.088	0.107	0.107
$D(\text{\AA}^{-4})$	0.041	0.041	0.101	0.102	0.174

Table 57. MP2/ 6-311++G(d,pd) Dipole moment derivate coefficients

μ	$n=4$	$n=5$	$n=6$	$n=7$	$n=8$
$D(\hat{A}^{-1})$	-0.832	-0.829	-0.829	-0.829	-0.829
$D(\hat{A}^{-2})$	-1.210	-1.210	-1.238	-1.238	-1.237
$D(\hat{A}^{-3})$	0.087	-0.010	-0.010	0.017	0.017
$D(\hat{A}^{-4})$	0.256	0.256	0.744	0.744	0.708

Table 58. MP2/ 6-311++G(d,3pd) Dipole moment derivate coefficients

μ	$n=4$	$n=5$	$n=6$	$n=7$	$n=8$
$D(\hat{A}^{-1})$	-0.806	-0.802	-0.802	-0.802	-0.802
$D(\hat{A}^{-2})$	-1.140	-1.140	-1.169	-1.169	-1.173
$D(\hat{A}^{-3})$	0.048	-0.061	-0.061	-0.018	-0.018
$D(\hat{A}^{-4})$	0.189	0.189	0.694	0.694	0.851

Table 59. MP2/ 6-311++G(d,2p) Dipole moment derivate coefficients

μ	$n=4$	$n=5$	$n=6$	$n=7$	$n=8$
$D(\hat{A}^{-1})$	-0.829	-0.823	-0.823	-0.824	-0.824
$D(\hat{A}^{-2})$	-1.088	-1.088	-1.104	-1.104	-1.101
$D(\hat{A}^{-3})$	0.080	-0.066	-0.066	-0.053	-0.053
$D(\hat{A}^{-4})$	-0.040	-0.040	0.248	0.248	0.120

The dipole moment derivate coefficients from the best order polynomial fitting, the matrix elements $\langle \nu | q^n | 0 \rangle$ for a Morse oscillator, and the transition frequencies shown in Table 13 were used to calculate the oscillator strength (f). The f values were calculated using equation (64) for the fundamental and overtones ($\Delta \nu = 1, 2, 3, 4, 5$, and 6) of CH stretch in CHD₃. Comparison with the experimental data, indicated that the seventh order polynomial is the best polynomial fitting for the DMF.

In order to compare the calculated oscillator strength with the S_0 values obtained from the absorption spectra, the relation between the oscillator strength and the band strength is given by:

$$f = \frac{4 \times 10^{-2} \varepsilon_0 m c^2}{e^2} S_0 = 1.1296 \times 10^{12} S_0 \quad (70)$$

where ε_0 is the permittivity of free space, m and e are the mass and charge of the electron respectively, c is the speed of light and S_0 is the band strength.

Table 60 shows the comparison between the S_0 calculated at different levels of theory and the experimental values. The S_0 values are in units of $\text{cm}^2 \text{ cm}^{-1} \text{ molecule}^{-1}$.

In general, the calculated S_0 values are in good agreement with the experimental values. From Table 60 is possible to observe that the S_0 value decreases for higher transitions. For the fundamental intensity the best calculated value is about 18% higher than the experimental value. This difference in the fundamental region has been reported before for other molecules.¹⁹⁵ Calculated fundamental intensities were found to improve with the addition of electron correlation. The importance of electron correlation for the fundamental is perhaps related to the fact that fundamental intensities depend primarily on the first derivative of the dipole moment expansion.

However, the overtone intensities for the fundamental and the $\Delta\nu = 2-6$ regions are relatively unaffected by electron correction and the levels of the theory chosen. A possible explanation for this lies in the assumption that the vibrational wavefunctions can be separated into contributions from CH-stretching and all the other low frequency modes.

Table 60. Observed and calculated band strength values for CHD_3

	ν	I	II	III	IV	V	obs
HF	1	6.07×10^{-18}	6.18×10^{-18}	5.90×10^{-18}	5.82×10^{-18}		1.08×10^{-18}
	2	1.38×10^{-20}	2.11×10^{-20}	1.22×10^{-20}	1.67×10^{-20}		2.44×10^{-20}
	3	6.28×10^{-21}	8.92×10^{-21}	4.90×10^{-21}	6.43×10^{-21}		4.64×10^{-21}
	4	8.92×10^{-22}	7.57×10^{-22}	5.50×10^{-22}	6.66×10^{-22}		5.36×10^{-22}
	5	1.23×10^{-22}	5.29×10^{-23}	5.97×10^{-23}	6.50×10^{-23}		4.22×10^{-23}
	6	1.88×10^{-23}	3.24×10^{-24}	7.20×10^{-24}	6.88×10^{-24}		5.43×10^{-24}
MP2	1	6.20×10^{-18}	5.78×10^{-18}	6.04×10^{-18}		6.18×10^{-18}	
	2	1.25×10^{-20}	1.72×10^{-20}	1.14×10^{-20}		2.11×10^{-20}	
	3	6.55×10^{-21}	7.34×10^{-21}	4.91×10^{-21}		8.92×10^{-21}	
	4	9.10×10^{-22}	6.04×10^{-22}	5.42×10^{-22}		7.57×10^{-22}	
	5	1.21×10^{-22}	4.01×10^{-23}	5.70×10^{-23}		5.29×10^{-23}	
	6	1.78×10^{-23}	2.21×10^{-24}	6.61×10^{-24}		3.24×10^{-24}	

^a I: 6-311++G(d,2p), II: 6-311++G(d,3pd), III: 6-311++G(2d,pd), IV: 6-311++G(d,2pd), V: 6-311++G(d,pd)

Conclusions

The fundamental and overtone spectra, $\Delta\nu = 1, 2, 3$, and 4 around the C-H stretch of CHD_3 were measured at room temperature using a FT-spectrophotometer and their band strength values were determined.

The fundamental ($\Delta\nu = 1$) spectrum of CHD_3 was recorded at different temperatures, 84, 139, 202 and 295 K. Comparison of the spectra show as the

overlapping of fundamental ($\Delta v = 1$) C-H stretch with other transitions produces an anomalous intensity in the rotational distribution.

The off-axis alignment of the cavity was used with the PS-CRD technique, to increase the time that the coherent laser beam couples into the cavity. Unlike to the on-axis alignment where the coupling the light into the cavity is only 5%- 10% of the time, in the off-axis alignment the beam may couple continuously into the cavity up to 100% of the time.

The fourth overtone ($\Delta v = 5$) spectra at different pressures were measured using the PS-CRD instrument at 295K. The spectra probed the ability of PS-CRD system to measure rovibrational spectra of high overtones. However, an anomalous intensity in the rotational structure of the R branch was observed. The R(2) line showed a lower absorption than R(0) and R(1). This problem could be explained as an instrumental problem of our PS-CRD system.

The fifth overtone ($\Delta v = 6$) spectra of CHD_3 were also measured using the CRD technique, but in this case a pulsed dye laser was used. The exponential fitting method was used to measure the decay time. In this region the overlap between the two bands ($6\nu_1$ and $5\nu_1+2\nu_5$) is strong and the intensities of both are almost the same. It was shown that the mixing between the two states is stronger than the mixing of the lower overtones

High overtone spectra ($\Delta v = 5$ and 6) of CHD_3 were also measured at low temperatures of 111, 124 and 195K using the PS-CRD and the pulsed CRD spectroscopy, respectively. Shift and increase of the intensities of the rotational lines at

low temperatures was observed. These spectra show the ability of our systems to measure spectra at any temperature.

The comparison between simulated and experimental spectra confirmed a good correlation between temperature measured by the sensor localized in the cell and the actual temperature of the molecule. The PGOPHER program¹⁴² was used to simulate the spectra.

The high energy overtone spectra ($\Delta\nu = 5$ and 6) of CHD_3 are strongly affected by Fermi resonance of the pure overtone $\nu \nu_1$ with combinations $(\nu-1)\nu_1 + 2\nu_5$. The spectra are reasonably well described using degenerate perturbation theory.

The band strength values for $\Delta\nu = 1-6$ regions for CHD_3 were calculated using *ab initio* dipole moment functions. The local mode parameters, frequency and anharmonicity, were obtained from experimental data. The dipole derivatives were obtained for fitted polynomials of different order ($n = 4, 5, 6, 7$ and 8). It was found that the best polynomial fitted for the DMF was the seventh order polynomial. The calculations give results that are in good agreement with experimental values.

CHAPTER SIX

C-H Fundamental and Overtone Spectroscopy of Methyl acetylene, Tert-butylacetylene and Trimethyl-silyl-acetylene.

Methyl acetylene ($\text{CH}_3\text{C}\equiv\text{CH}$), Tert-butyl acetylene $(\text{CH}_3)_3\text{CC}\equiv\text{CH}$ and Trimethyl-silyl-acetylene $[(\text{CH}_3)_3\text{CSi}\equiv\text{CH}]$ are interesting molecules, since they include two types of C-H stretches, involving acetylenic and methyl hydrogens.

Methyl acetylene (propyne) was chosen as a model to study similar molecules $\text{RC}\equiv\text{CH}$ because its vibrational overtone absorption has been extensively investigated in the near infrared and visible ranges using standard infrared techniques, and photoacoustic (PA) spectroscopy.²⁰²⁻²⁰⁶ Also, high resolution spectroscopy using intracavity absorption spectroscopy (ICLAS), cavity ring down spectroscopy (CRDS)^{207,208} and photodissociation spectroscopy^{201,209} have been employed for studying the intramolecular dynamic of Propyne.²¹⁰⁻²¹²

The fundamental and first overtone region for the series of trimethyl substituted acetylenes $(\text{CH}_3)_3\text{XC}\equiv\text{C-H}$ ($\text{X} = \text{C}$ and Si) and its deuterium compounds, tert-butylacetylene- d_9 and (trimethylsilyl)acetylene- d_9 , have been previously studied by Lehmann *et al*²¹³⁻²¹⁵ using an optothermal detection method using molecular beam infrared spectroscopy to study the intramolecular vibrational relaxation of the acetylene CH vibration. Also, a theoretical study has been reported for these molecules.²¹⁶

This chapter presents the vibrational overtone spectra of the ($\Delta\nu=4$) acetylenic and ($\Delta\nu=5$) methyl C-H stretches of propyne using the PS-CRD technique at 295 and

240K. With this information the band strength values (S_0) for these transitions were obtained.

Complete spectra of the fundamental and overtones of the C-H stretches of the large polyatomic molecules $(\text{CH}_3)_3\text{XC}\equiv\text{C-H}$ ($\text{X} = \text{C}$ and Si) are shown in this chapter. Spectra at 240K were recorded using PS-CRD spectroscopy. Thus, band strength values for the higher overtones were obtained. In addition a harmonically coupled anharmonic oscillator (HCAO)^{92, 96, 190, 194, 217, 218} model was used to determine the overtone energy levels and assign the absorption bands to transitions in C_6H_{10} and $\text{C}_5\text{SiH}_{10}$.

Overtone Spectroscopy of Propyne (C_3H_4)

Propyne is a symmetric top molecule with two types of CH oscillators. The CH_3 group does not internally rotate (this is not true). In this molecule the acetylenic CH oscillator is around $\sim 3335\text{ cm}^{-1}$ and the methyl C-H stretches around $\sim 2940\text{ cm}^{-1}$. Both types of CH bonds are decoupled. Table **61** shows the fundamental vibrational frequencies of propyne.²¹⁹ Hence, the propyne overtones are dominated by features arising from these two oscillator types.

The vibrational overtone spectra of the ($\Delta v = 4$) acetylenic and ($\Delta v = 5$) methyl C-H stretches of propyne at 295 and 185K were obtained using the PS-CRD technique. From the spectra, the integrated band strength was calculated for both oscillators and compared with literatures values. The resolution of the continuous wave Ti:Sapphire ring was 0.17 cm^{-1} . The optical path length was 3.67 km.

Table 61. Fundamental Vibrational Frequencies of Propyne

Assignment	Symmetry	Mode	Frequency / cm^{-1}
ν_1	A_1	acetylenic C-H stretch	3335.1
ν_2	A_1	methyl C-H s-stretch	2941.4
ν_3	A_1	$\text{C} \equiv \text{C}$ stretch	2137.9
ν_4	A_1	methyl deformation	1385.0
ν_5	A_1	C-C stretch	930.3
ν_6	E	methyl C-H a-stretch	2980.8
ν_7	E	methyl skeletal deformation	1450.3
ν_8	E	methyl skeletal rock	1036.1
ν_9	E	$\text{C} \equiv \text{C}$ - H bend	633.3
ν_{10}	E	C - $\text{C} \equiv \text{C}$ bend	327.5

Acetylenic C-H Stretch

Absorption spectrum in the range of $(12550\text{-}12850) \text{ cm}^{-1}$ is shown in Figure 89. The spectrum shows three different bands. The stronger one around 12712 cm^{-1} is assigned as the pure $4\nu_1$ transition. The second band, around 12764 cm^{-1} , is assigned as $3\nu_1 + \nu_3 + \nu_5$. These two bands are in Fermi resonance^{202, 203}. The assignments $4\nu_1$ and $3\nu_1 + \nu_3 + \nu_5$, were established by Crofton *et al.*²⁰² and is based on the integrated intensity of a combination band being weaker than that of a pure overtone band if strong multilevel coupling is absent. These authors also calculated the locations of the unperturbed $4\nu_1$ and $3\nu_1 + \nu_3 + \nu_5$ levels and estimated the magnitude of the coupling between these states.

The small peak to lower frequencies corresponds to a hot band, $4\nu_1 + \nu_9 - \nu_9$. This band arises from nonresonant intramolecular coupling of the acetylenic C-H stretch (ν_1) and the $\equiv \text{C}$ - H bending mode (ν_9). This small peak at low frequencies have been also observed at $\nu = 2, 3, 4, 5, 6$ in the region of the acetylenic stretch. It has been

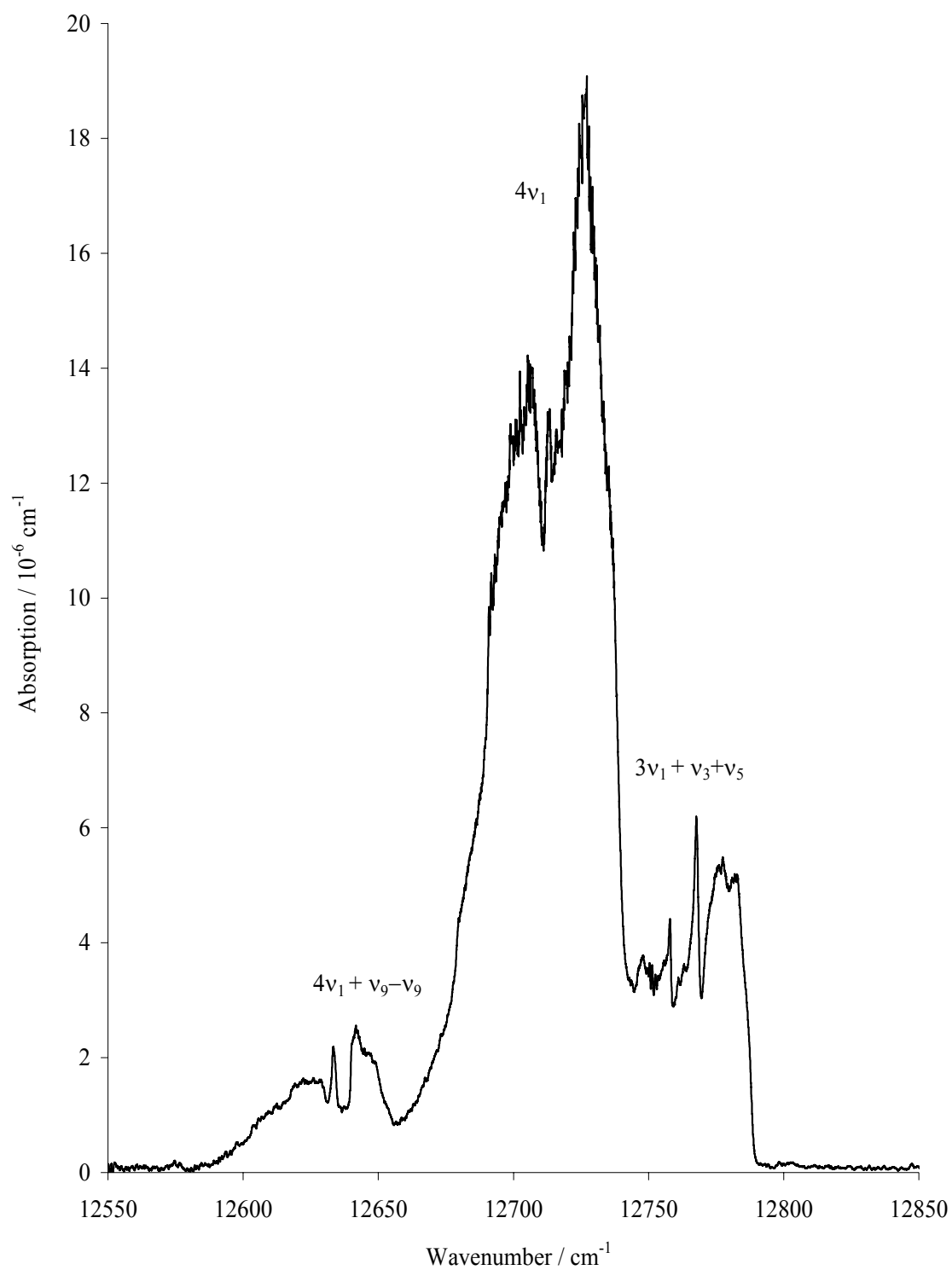


Figure 89. Absorption spectrum of ($\Delta v = 4$) acetylenic C-H stretch of propyne with a pressure of 92 Torr at 295K.

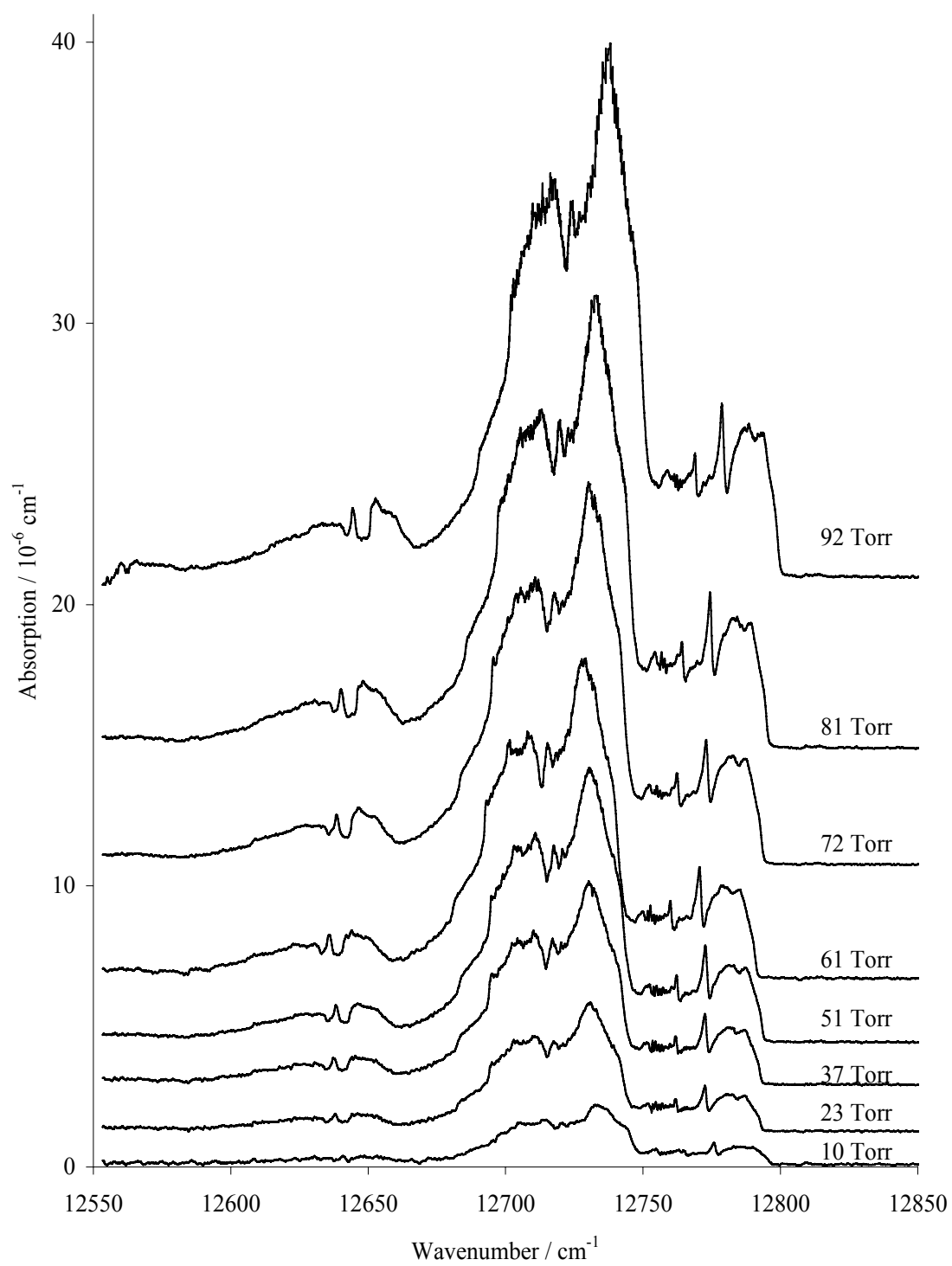
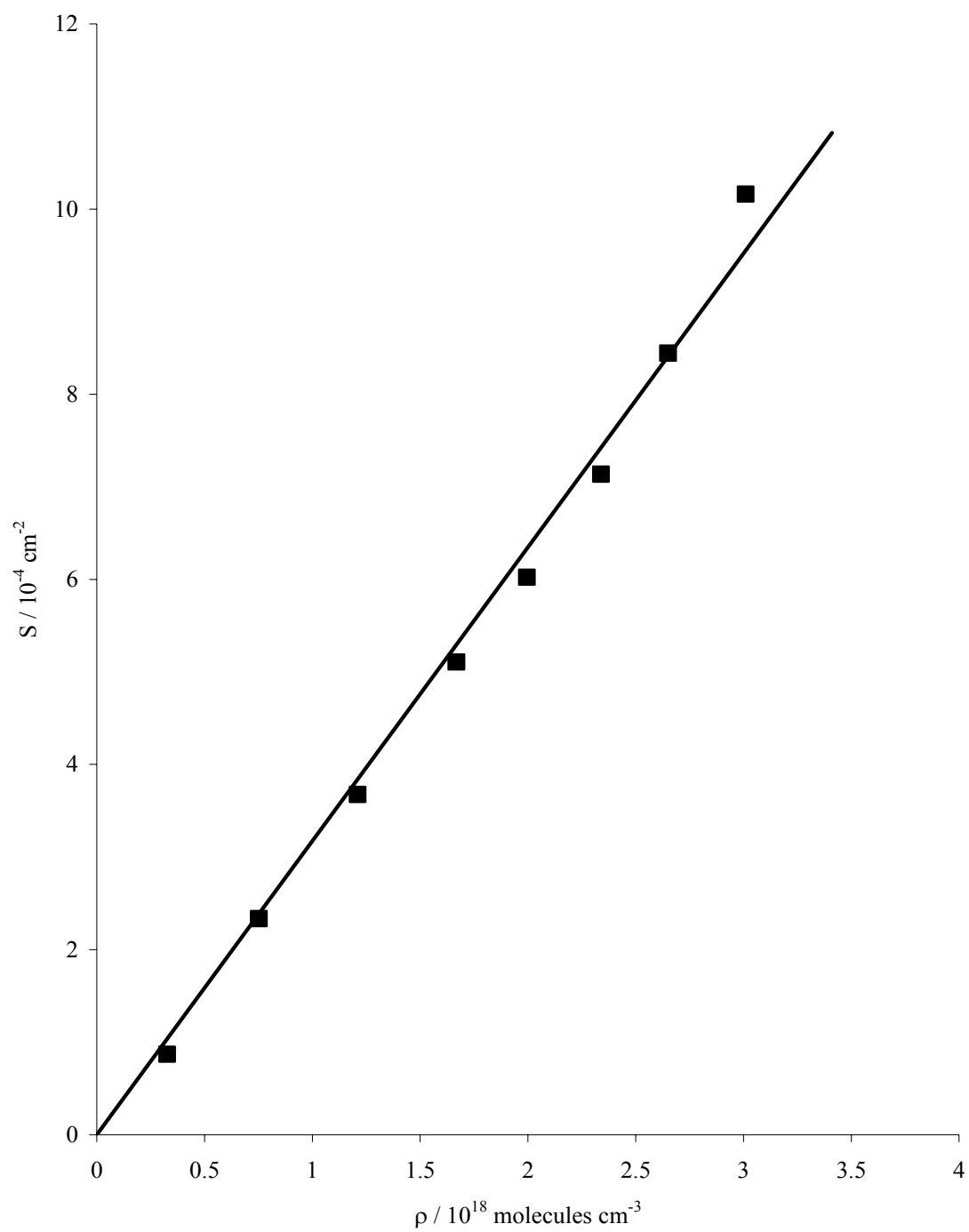


Figure 90. ($\Delta v = 4$) acetylenic C-H stretch of propyne. Absorption pressure series at 295K



$$S_0 = (3.3 \pm 0.1) \times 10^{-22} \text{ cm}^2 \text{ cm}^{-1} \text{ molecules}^{-1}$$

$$R^2 = 0.997$$

Figure 91. ($\Delta\nu=4$) acetylenic C-H stretch of propyne. S vs. ρ . Slope is S_0

demonstrated that the transitions are due to the hot bands $\nu\nu_1 + \nu_9 - \nu_9$.²⁰³ In a similar molecule, 3,3,3-trifluoropropyne, these series of transitions were also seen at $\nu = 2-6$.²²⁰

In order to obtain the integrated band strength (S_0) of this region $\Delta\nu=4$ for the acetylenic stretch for a series of eight different pressures, 92, 81, 72, 61, 51, 37, 23 and 10 Torr. The pressure series was obtained and is shown in Figure 90. Table 62 reports the density, integrated absorption band, and band strength values for each individual pressure. The S_0 value is found by plotting S versus ρ (see Figure 91)

Table 62. ($\Delta\nu=4$) acetylenic C-H of C_3H_4 at 295K, Pressure, ρ , S and S_0 .

Pressure torr	ρ $10^{18} \text{ molecules cm}^{-3}$	S 10^{-4} cm^{-2}	S_0 $10^{-22} \text{ cm}^2 \text{ cm}^{-1} \text{ molecule}^{-1}$
92	3.01	10.61	3.38
81	2.65	8.44	3.19
72	2.34	7.14	3.05
61	2.00	6.02	3.02
51	1.67	5.11	3.06
37	1.21	3.68	3.04
23	0.75	2.33	3.10
10	0.33	0.87	2.66
Avg			3.3 ± 0.1

The absorption spectrum of the ($\Delta\nu=4$) acetylenic C-H stretch of propyne was recorded at 185K. A comparison between the spectrum at room and low temperature is shown in Figure 92. This figure shows that the red shoulder of band $4\nu_1$ is reduced dramatically at low temperature. This is expected since the population of the hot band decreases. Also, it is possible to see from this comparison that the hot band disappears at 185 K. Other feature of the spectrum at low temperature is the increase of the main absorption.

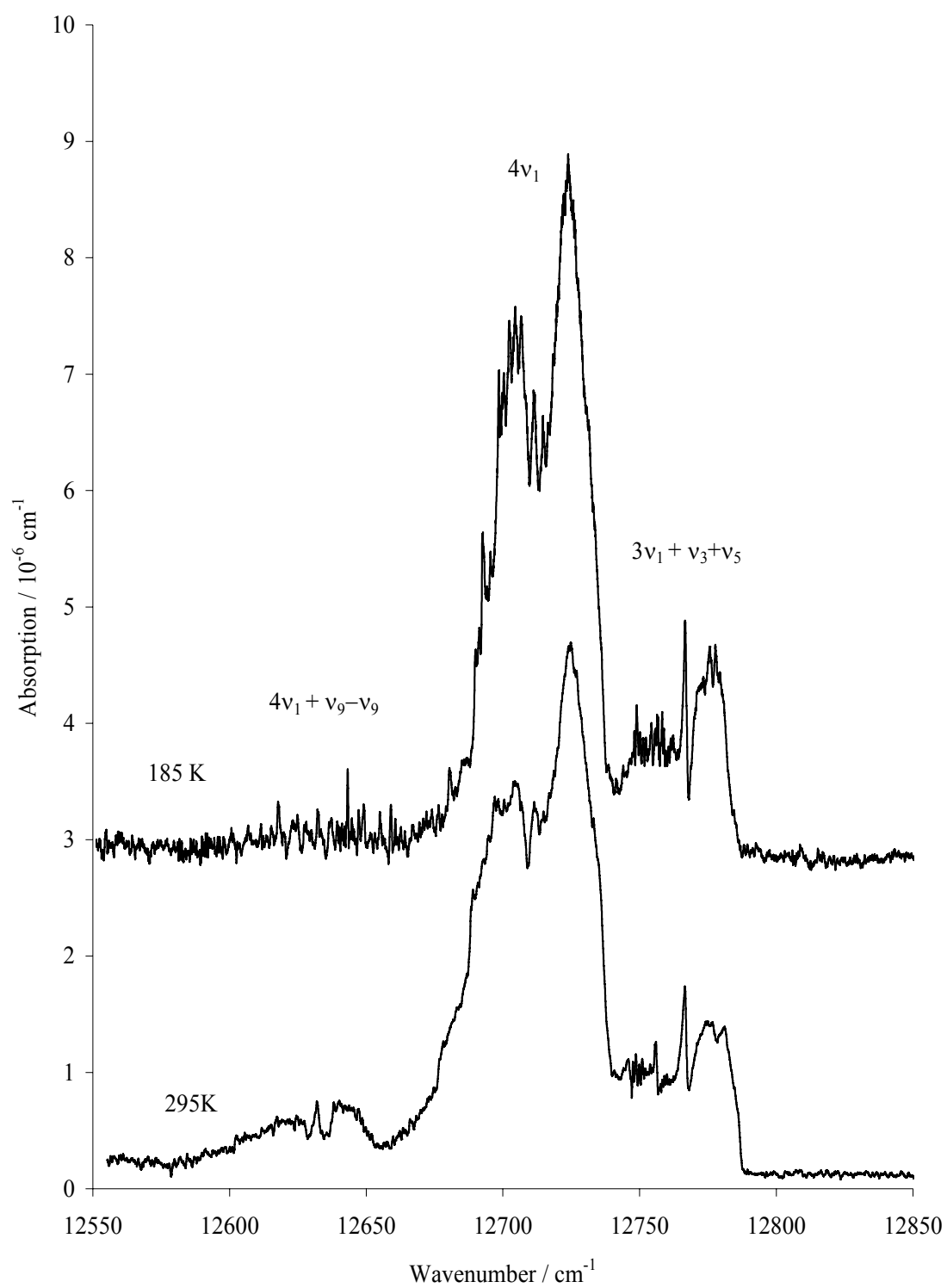


Figure 92. ($\Delta v = 4$) acetylenic C-H stretch of propyne with a pressure of 10 Torr at 185 K (top), and 23 Torr at 295 K (bottom)

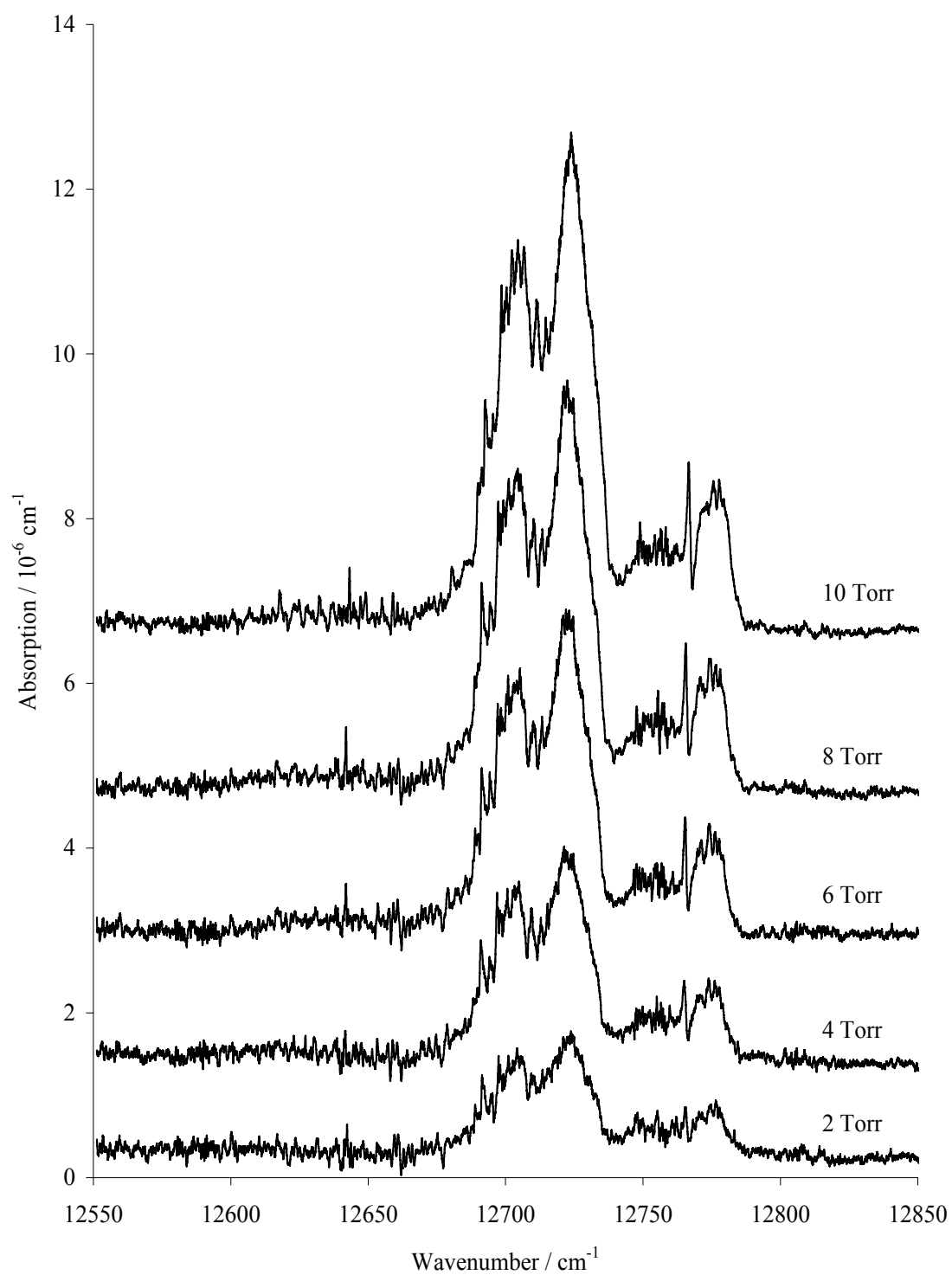
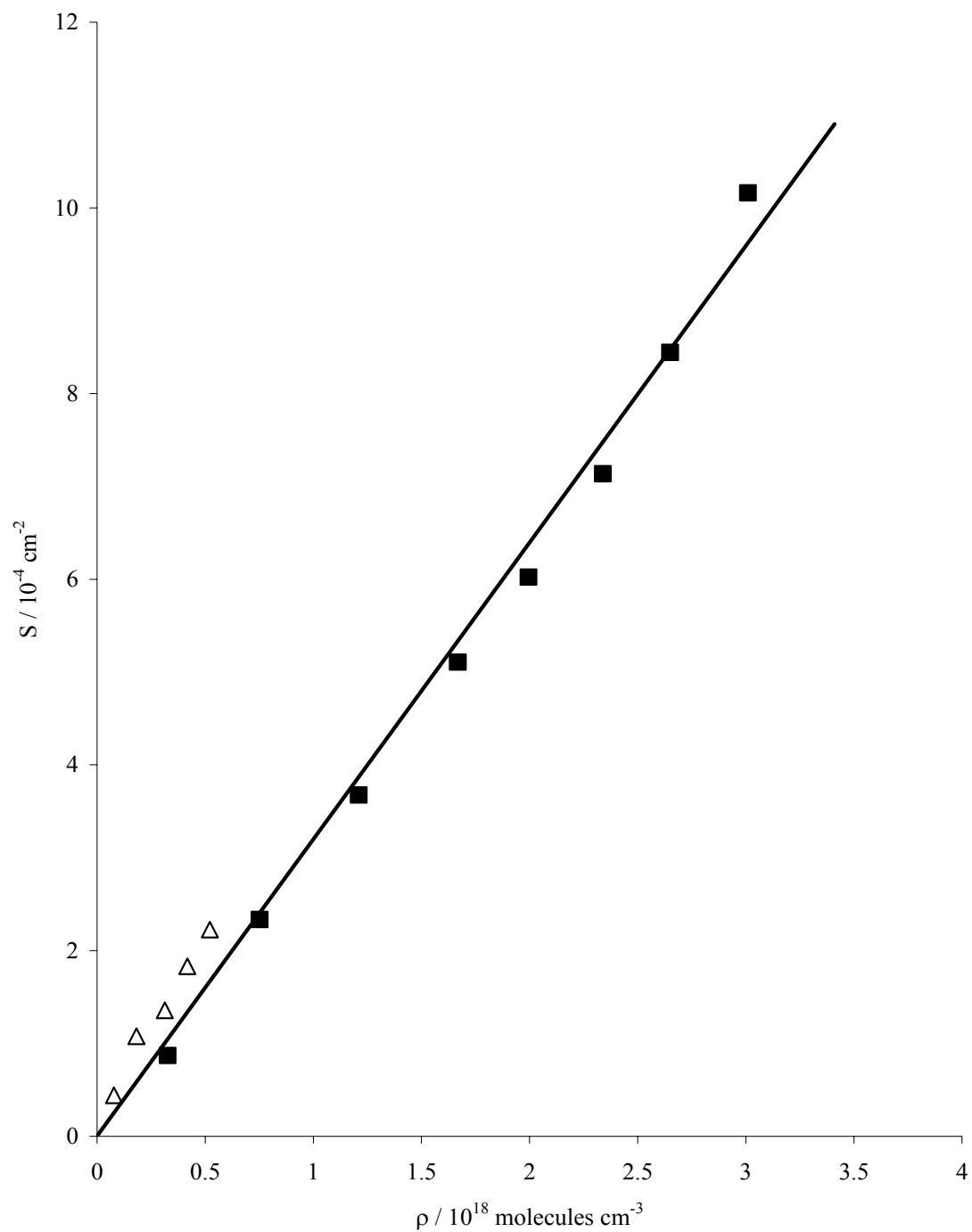


Figure 93. $(\Delta v = 4)$ acetylenic C-H stretch of propyne. Absorption pressure series at 185K



$$S_0 = (3.1 \pm 0.1) \times 10^{-22} \text{ cm}^2 \text{ cm}^{-1} \text{ molecules}^{-1}$$

$$R^2 = 0.994$$

Figure 94. ($\Delta\nu=4$) acetylenic C-H stretch of propyne. S vs. ρ . Slope is S_0 . Marker ■ = measurements at 295 K and Marker Δ = measurements at 185 K.

Although the density used to take the low temperature ($\rho = 7.52 \times 10^{17}$ molecules cm^{-3}) spectrum is smaller than the density used for the spectrum at 295 K ($\rho = 5.22 \times 10^{17}$ molecules cm^{-3}) the absorption of $4\nu_1$ and $3\nu_1 + \nu_3 + \nu_5$ at 185 K is 30% more intense than the absorption at 295K. This is because the bands are narrower at low temperature. However, the integrated band strength of the total band remains constant at any temperature.

A pressure series of ($\Delta\nu=4$) acetylenic C-H stretch of C_3H_4 at 185 K was also measured and is shown in Figure 93. Pressures of 10, 8, 6, 4 and 2 Torr were used and their integrate absorption areas were calculated.

Table 63 reports the density, S , and S_0 for each pressure at 185K. These values and values obtained at room temperature were plotted together in Figure 94. The results are linear for measurements taken at different temperatures.

Table 63. ($\Delta\nu=4$) acetylenic C-H of C_3H_4 at 185K, Pressure, ρ , S and S_0

Pressure torr	ρ 10^{18} molecules cm^{-3}	S 10^{-4} cm^{-2}	S_0 $10^{-22} \text{ cm}^2 \text{ cm}^{-1} \text{ molecule}^{-1}$
10	0.52	2.23	4.26
8	0.42	1.83	4.38
6	0.31	1.36	4.33
4	0.18	1.08	5.89
2	0.08	0.44	5.62
Avg			3.1 ± 0.1

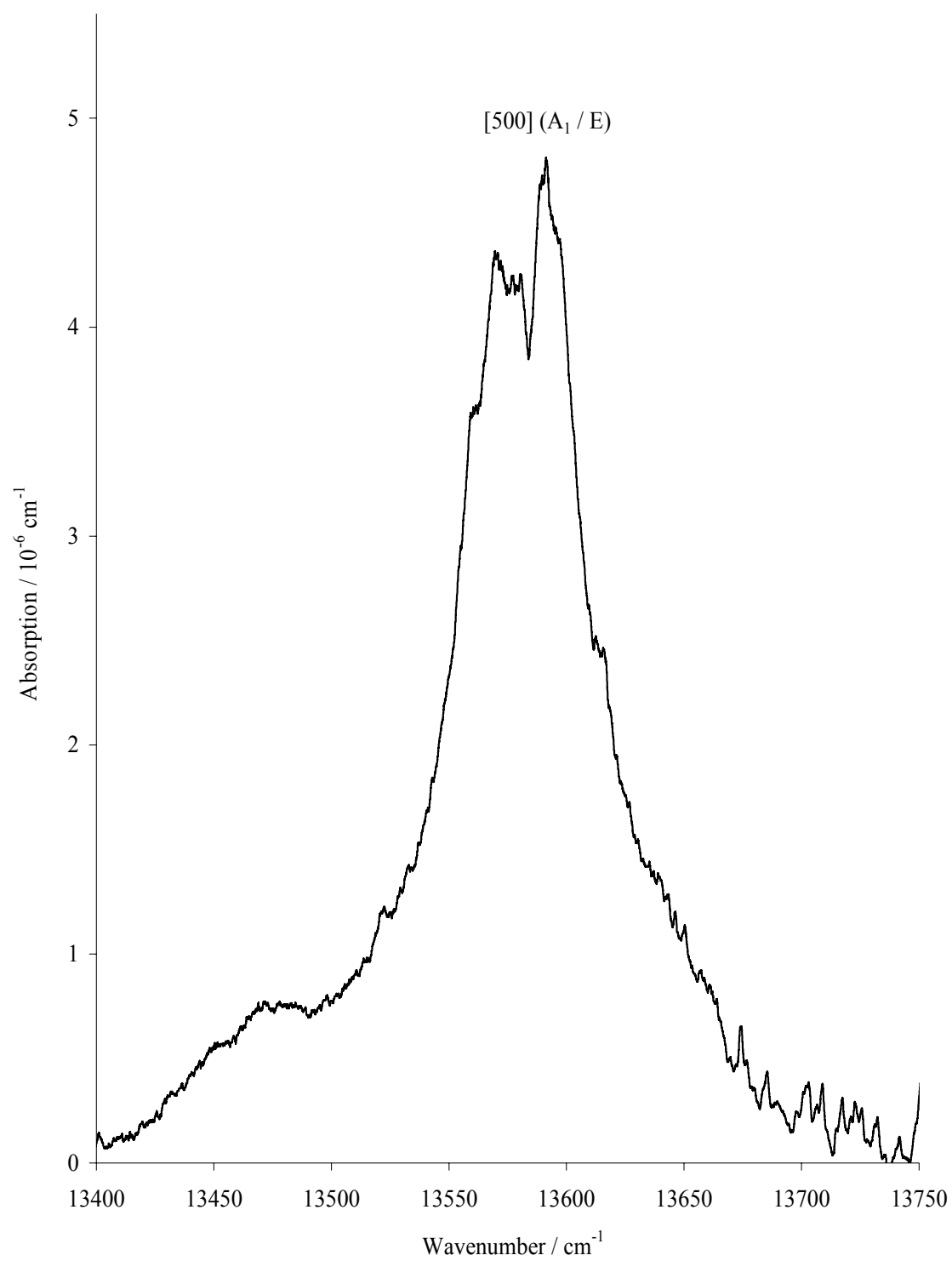


Figure 95. Absorption spectrum of ($\Delta v=5$) methyl C-H stretch of propyne with a pressure of 92 Torr and 295K.

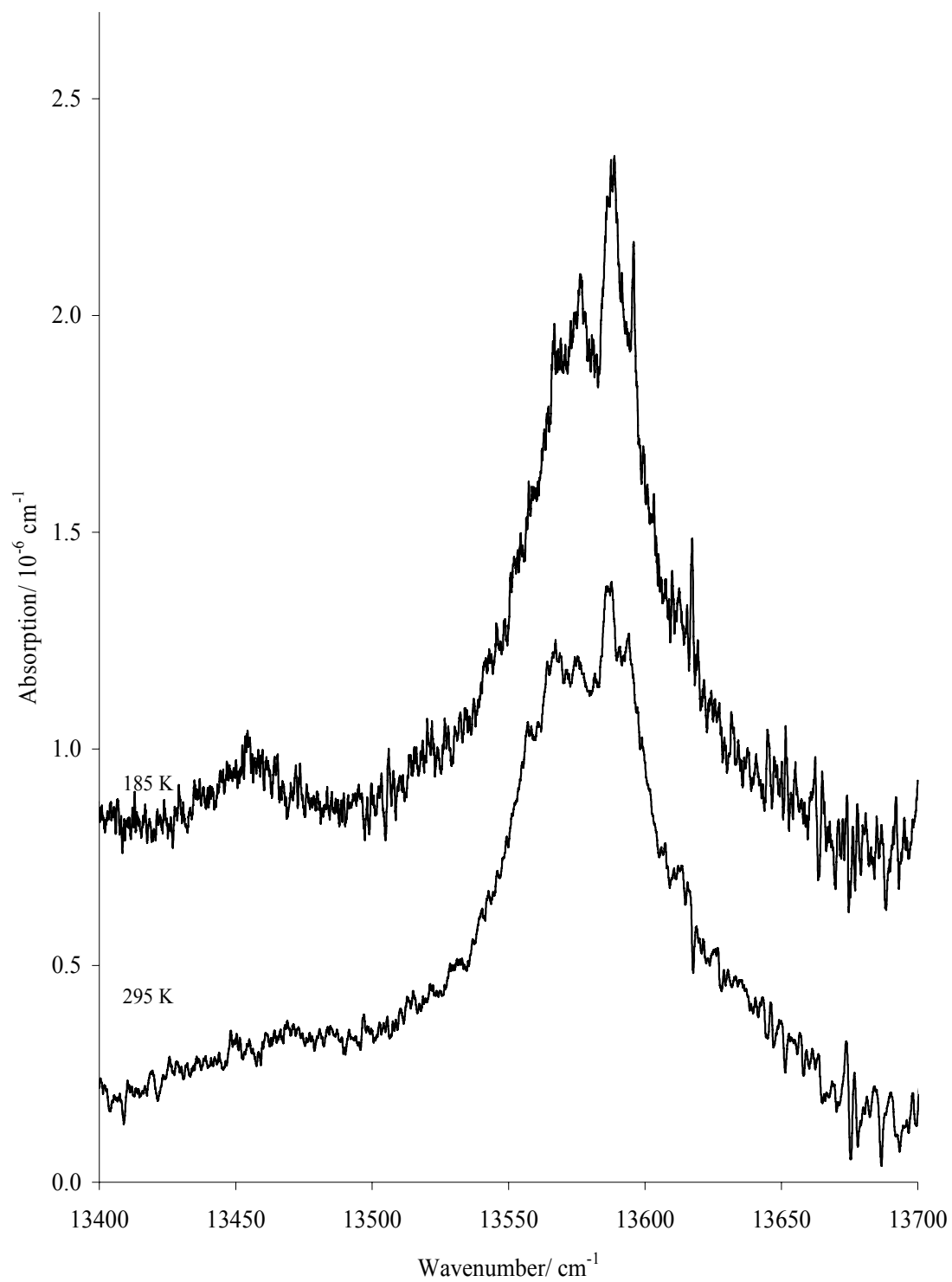


Figure 96. ($\Delta v = 5$) methyl C-H stretch of propyne with a pressure of 10 Torr at 185 K- top, and 23Torr at 295K- bottom

Methyl C-H Stretch

The fourth overtone spectrum of the propyne methyl group C-H stretch is shown in Figure 95. This band is more complex than the band presented above. In the local mode limit there are now three independent oscillators. The linear basis functions for each oscillator can be combined to form A_1 and E symmetry states, consistent with the C_{3v} point group of the molecule. Bands involving the A_1 state are associated with parallel type bands whereas E states are associated with perpendicular type bands. Thus, the band in Figure 95 is associated with parallel and perpendicular type bands. This information has been confirmed in previous work by Crofton *et al*²⁰² and Bar *et al*^{201, 209}.

Figure 96 shows stacked spectra of ($\Delta\nu=5$) methyl C-H stretch at 295 and 185 K. The narrowing of the band at the lower temperature can be observed from this comparison. It is especially large on the low frequency side.

In order to get the band strength value, the absorption spectrum of ($\Delta\nu=5$) methyl C-H stretch of propyne was measured at different pressures. Figure 97 shows the pressure series of eight separate measurements ranging from 10 to 92 Torr of C_3H_4 taken at 295 K, and Figure 98 shows the pressure series at 185K. Table 64 reports the density, S , and S_0 for each pressure at 295 and 185K. These values were plotted together and are displayed in Figure 99. The resulting slope corresponds to the S_0 value, $S_0 = (1.34 \pm 0.02) \times 10^{-22} \text{ cm}^2 \text{ cm}^{-1} \text{ molecules}^{-1}$. This value is closer to the S_0 value calculated by Bar *et al*²⁰¹, $S_0 = 2.08 \times 10^{-22} \text{ cm}^2 \text{ cm}^{-1} \text{ molecules}^{-1}$.

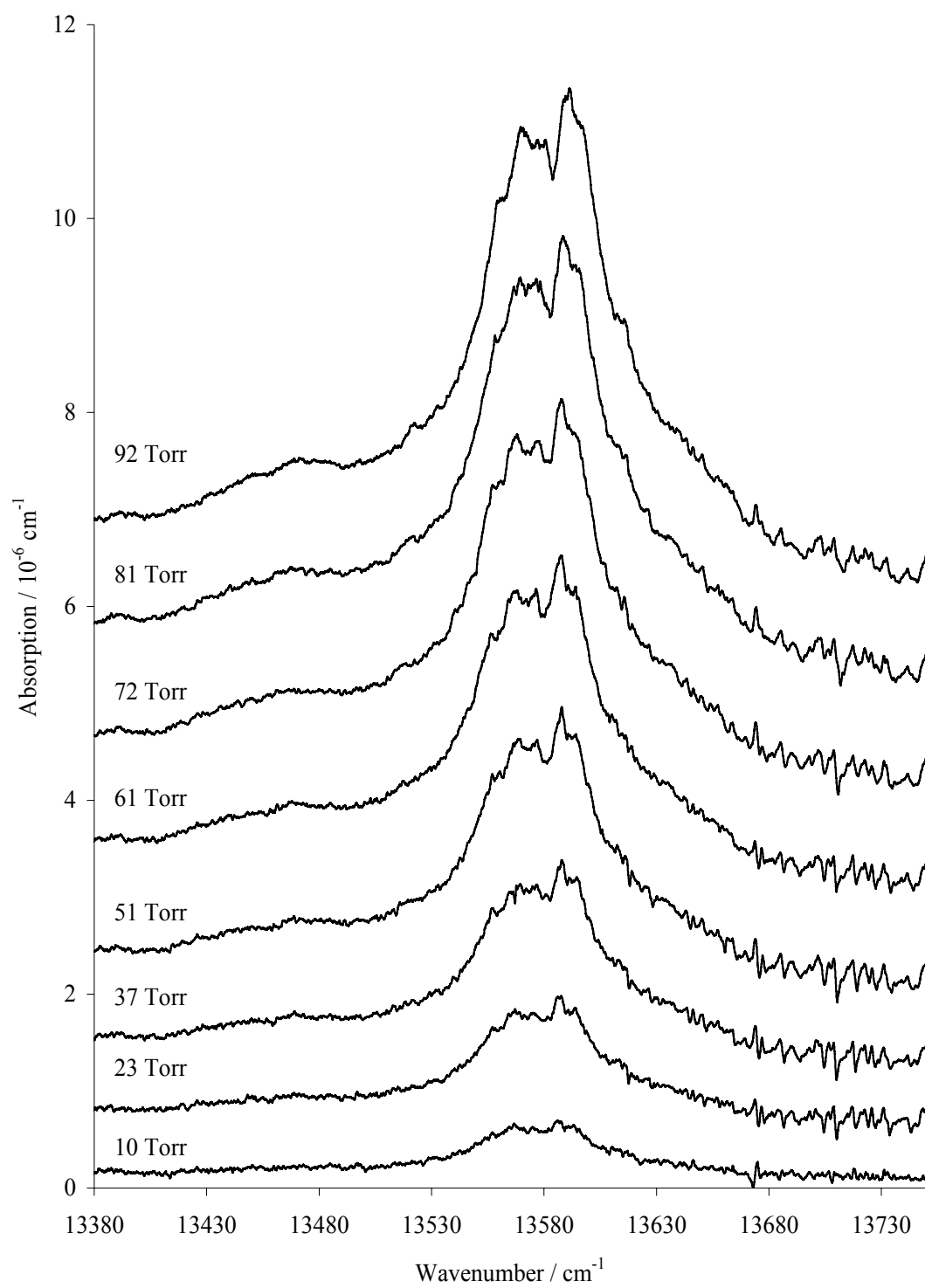


Figure 97. ($\Delta\nu=5$) methyl C-H stretch of propyne. Absorption pressure series at 295K

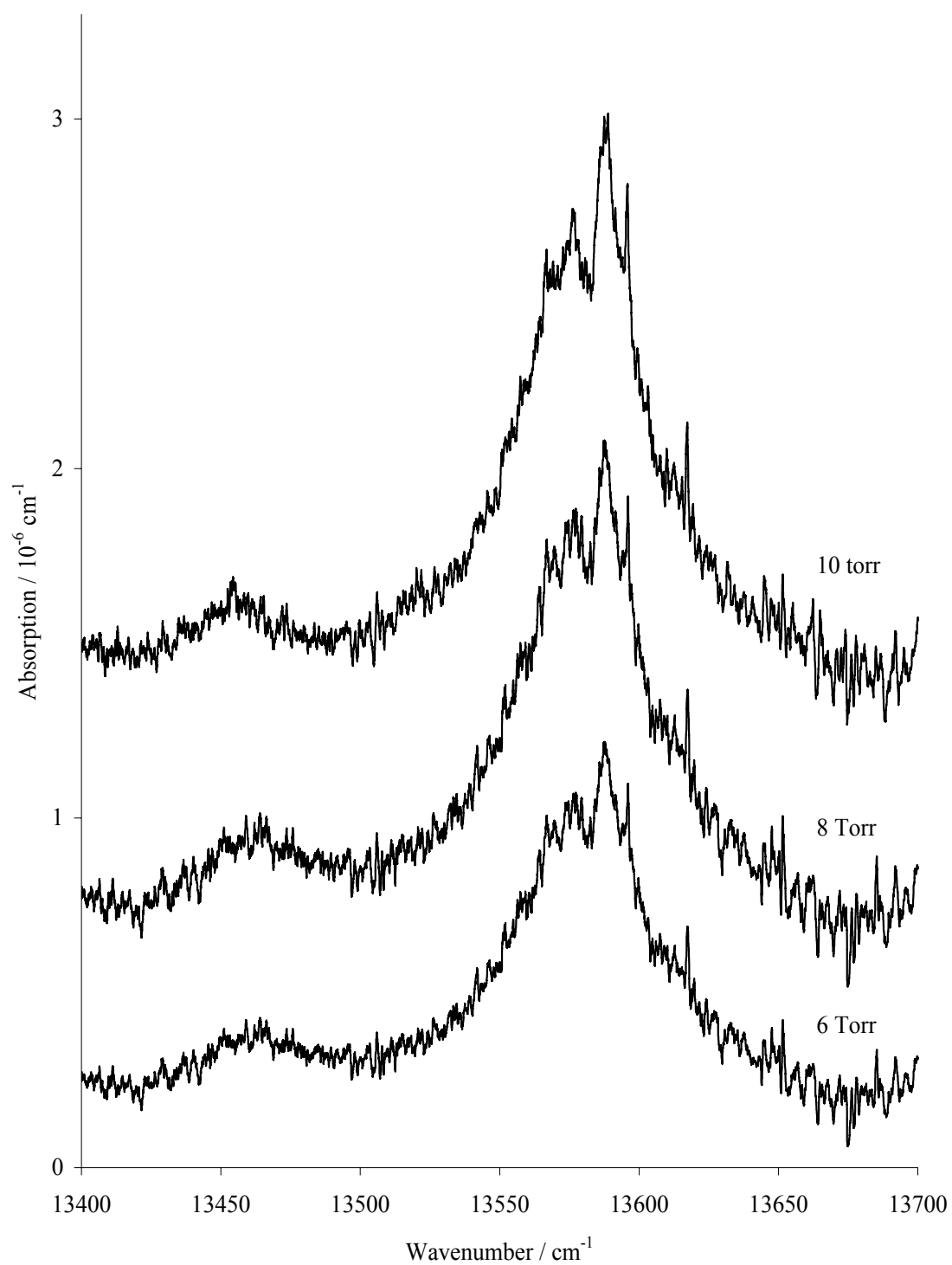
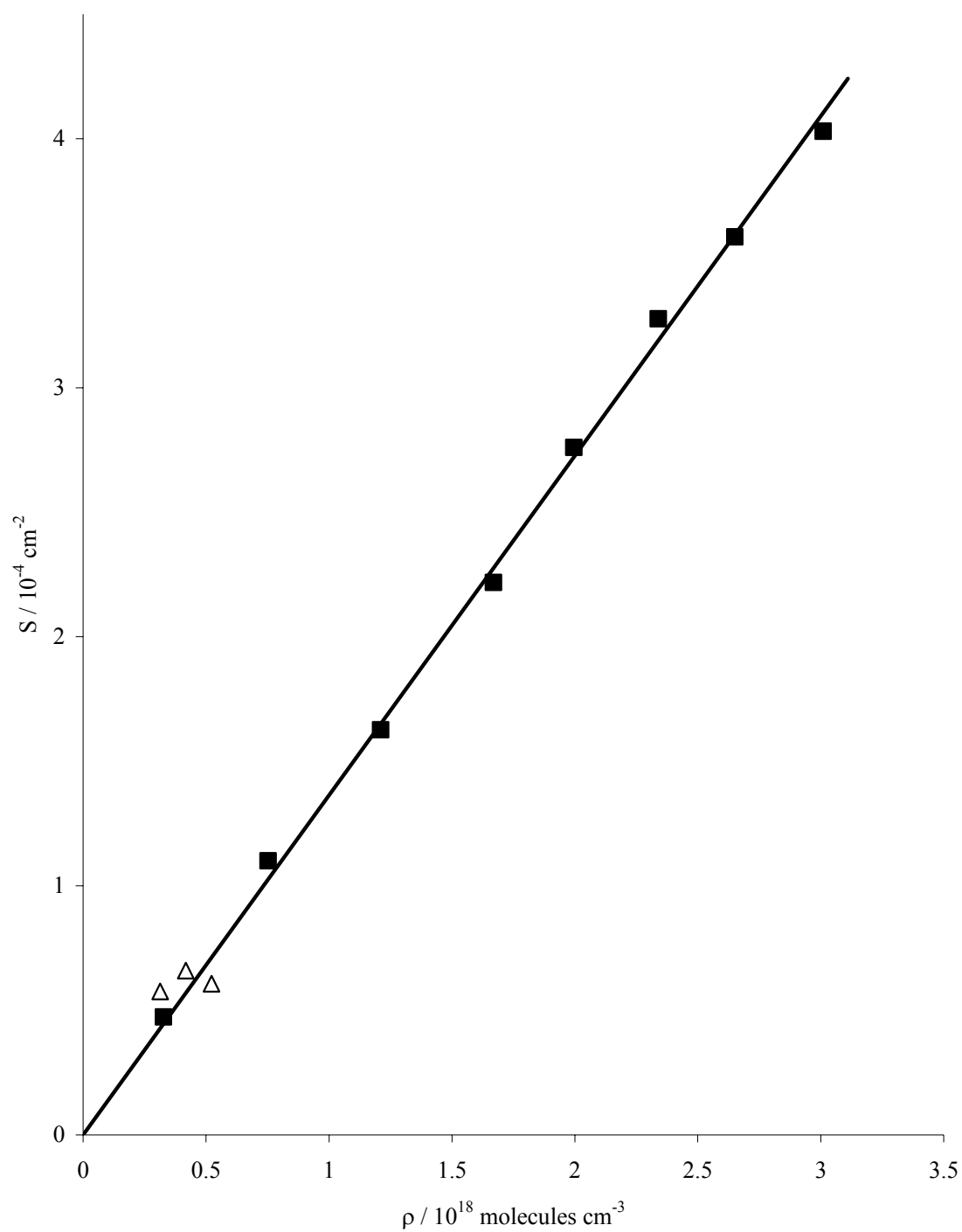


Figure 98. ($\Delta v = 5$) methyl C-H stretch of propyne. Absorption pressure series at 185K



$$S_0 = (1.34 \pm 0.02) \times 10^{-22} \text{ cm}^2 \text{ cm}^{-1} \text{ molecules}^{-1}$$

$$R^2 = 0.998$$

Figure 99. ($\Delta\nu=5$) methyl C-H stretch of propyne. S vs. ρ . Slope is S_0 . Marker ■ = measurements at 295 K and Marker Δ = measurements at 185 K.

Table 64. ($\Delta\nu=4$) methyl C-H of C_3H_4 at 295 and 185K, Pressure, ρ , S and S_0 .

T	Pressure	ρ	S	S_0
Torr	Torr	$10^{18} \text{ molecules cm}^{-3}$	10^{-4} cm^{-2}	$10^{-22} \text{ cm}^2 \text{ cm}^{-1} \text{ molecule}^{-1}$
295 K	92	3.01	4.03	1.34
	81	2.65	3.61	1.36
	72	2.34	3.28	1.40
	61	1.99	2.76	1.38
	51	1.67	2.22	1.33
	37	1.21	1.63	1.34
	23	0.75	1.10	1.46
	10	0.33	0.47	1.44
185 K	10	0.52	0.61	1.16
	8	0.42	0.66	1.58
	6	0.31	0.58	1.84
Avg				1.34 ± 0.02

The S_0 values obtained for the acetylenic C-H stretch, $S_0 = (3.1 \pm 0.1) \times 10^{-22} \text{ cm}^2 \text{ cm}^{-1} \text{ molecules}^{-1}$, and methyl C-H stretch, $S_0 = (1.34 \pm 0.02) \times 10^{-22} \text{ cm}^2 \text{ cm}^{-1} \text{ molecules}^{-1}$. are used as reference for the molecules to be presented in the following sections.

Overtone Spectroscopy of Tert-butylacetylene

The vibrational overtone spectra of the acetylenic and methyl C-H stretches of tert-butylacetylene (C_6H_{10}) were obtained for the $\nu=1$ to $\nu=4$ and $\nu=1$ to $\nu=5$ levels, respectively. These spectral regions were measured using Fourier transform spectrophotometer with a resolution of 1 cm^{-1} and white cell with an optical path length of 6.6 m. The overtones spectra, $\nu=4$ for the acetylenic and $\nu=5$ for the methyl C-H stretches, were also obtained at 295 and 240 K using PS-CRD technique, with a path length of 4.34 km and resolution of 0.17 cm^{-1} given by the continuous wave Ti:Sapphire

ring laser used. S_0 values were obtained from the data obtained. The C-H stretches in C_6H_{10} were analyzed in terms of the local-mode model. Harmonic frequencies (ω_i) and anharmonicities (X_{ii}) were calculated. A harmonically coupled anharmonic oscillator (HCAO)^{190, 218} model was used to determine the overtone energy levels and assign the absorption bands to vibrational transitions. *Ab initio* molecular orbital calculations of geometries and vibrational frequencies were also performed.

Acetylenic C-H Stretch

The spectra shown in Figures 100 to 103 correspond to transitions from $\nu=0$ to levels 1, 2, 3 and 4 of the acetylenic C-H stretch. These spectra were taken on the FT-spectrophotometer.

Figure 100 shows the PQR structure for the acetylenic C-H fundamental centered at $\nu_1 = 3328\text{ cm}^{-1}$, and a small shoulder at the low frequency end of the P branch. This fundamental spectrum looks similar to similar molecules of the type $RC \equiv CH$ such as $(CF_3)_3C \equiv CH$ ²²¹, 3,3,3-trifluoropropyne²²⁰ and propyne²⁰³. Also, the fundamental acetylenic C-H stretch of C_6H_{10} and these similar molecules nearly coincide in frequency. Hence, the weaker band centered at 3308 cm^{-1} could be assigned as a hot band originating from the ν_{24} vibrational frequency at 634 cm^{-1} , following the notation used in Table 65.^{222, 223}

The first overtone is shown in Figure **101** and exhibits the strong narrow acetylenic C-H absorption (Q branch), as well as a small peak to the low frequency side.

A similar low frequency absorption is observable for the $\Delta\nu_1 = 3$ and 4 transitions in Figure **102** and Figure 103. Because of its lower frequency relative to the

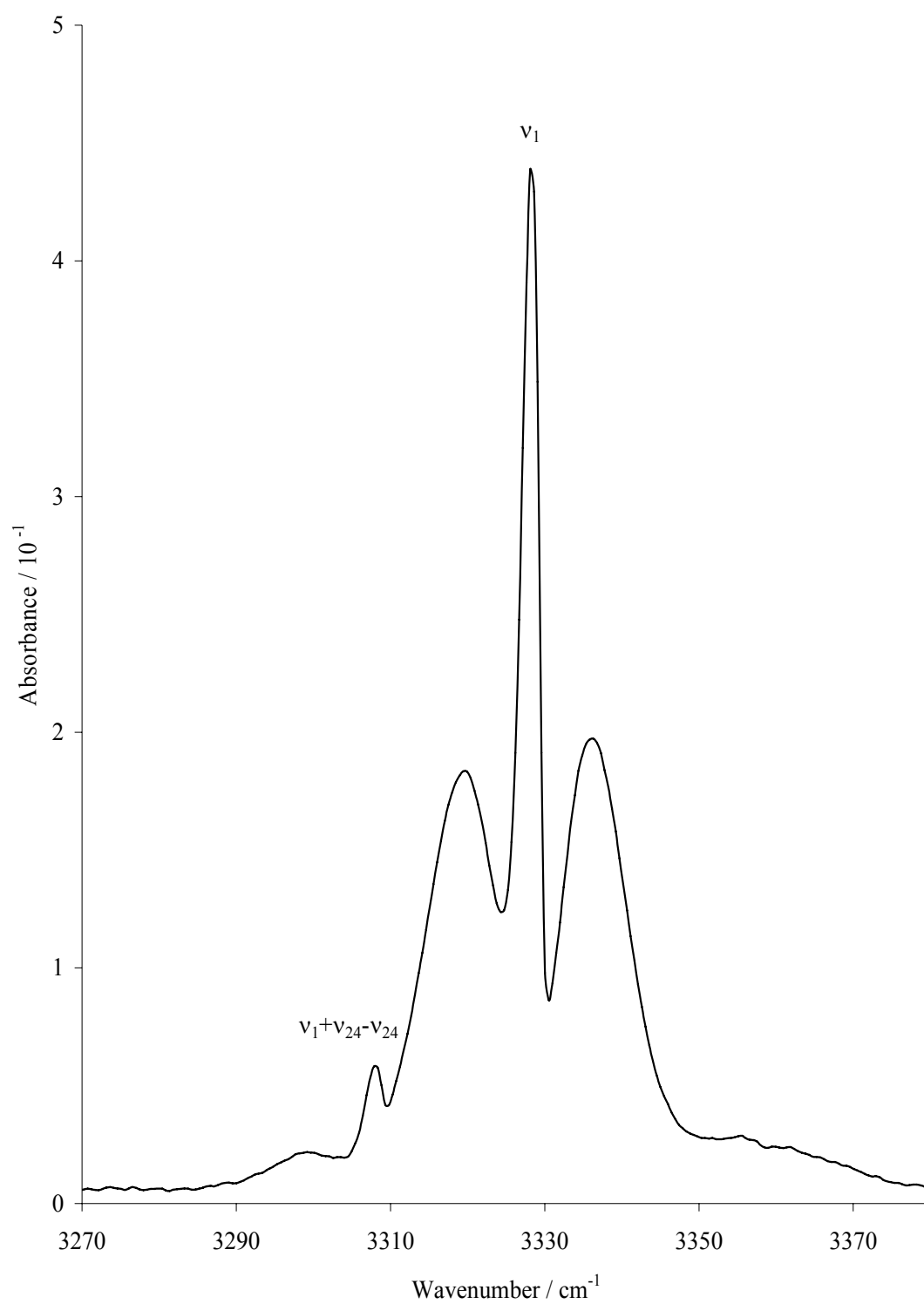


Figure 100. Absorption spectrum of the fundamental ($\Delta v = 1$) acetylenic C-H stretch of C_6H_{10} at 295K. Pressure = 0.2Torr.

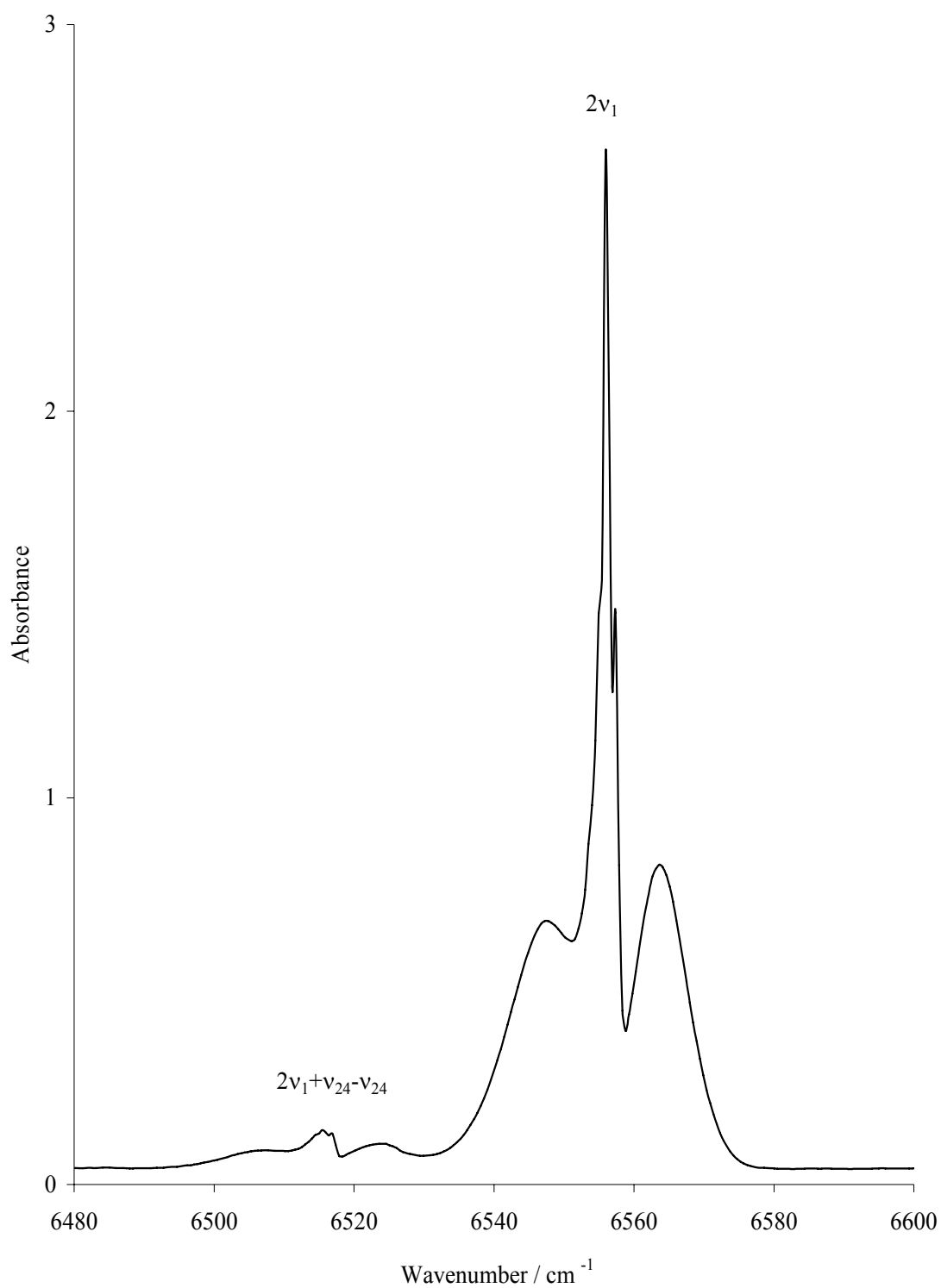


Figure 101. Absorption spectrum of the first overtone ($\Delta v=2$) acetylenic C-H stretch of C_6H_{10} at 295K. Pressure = 9.2Torr.

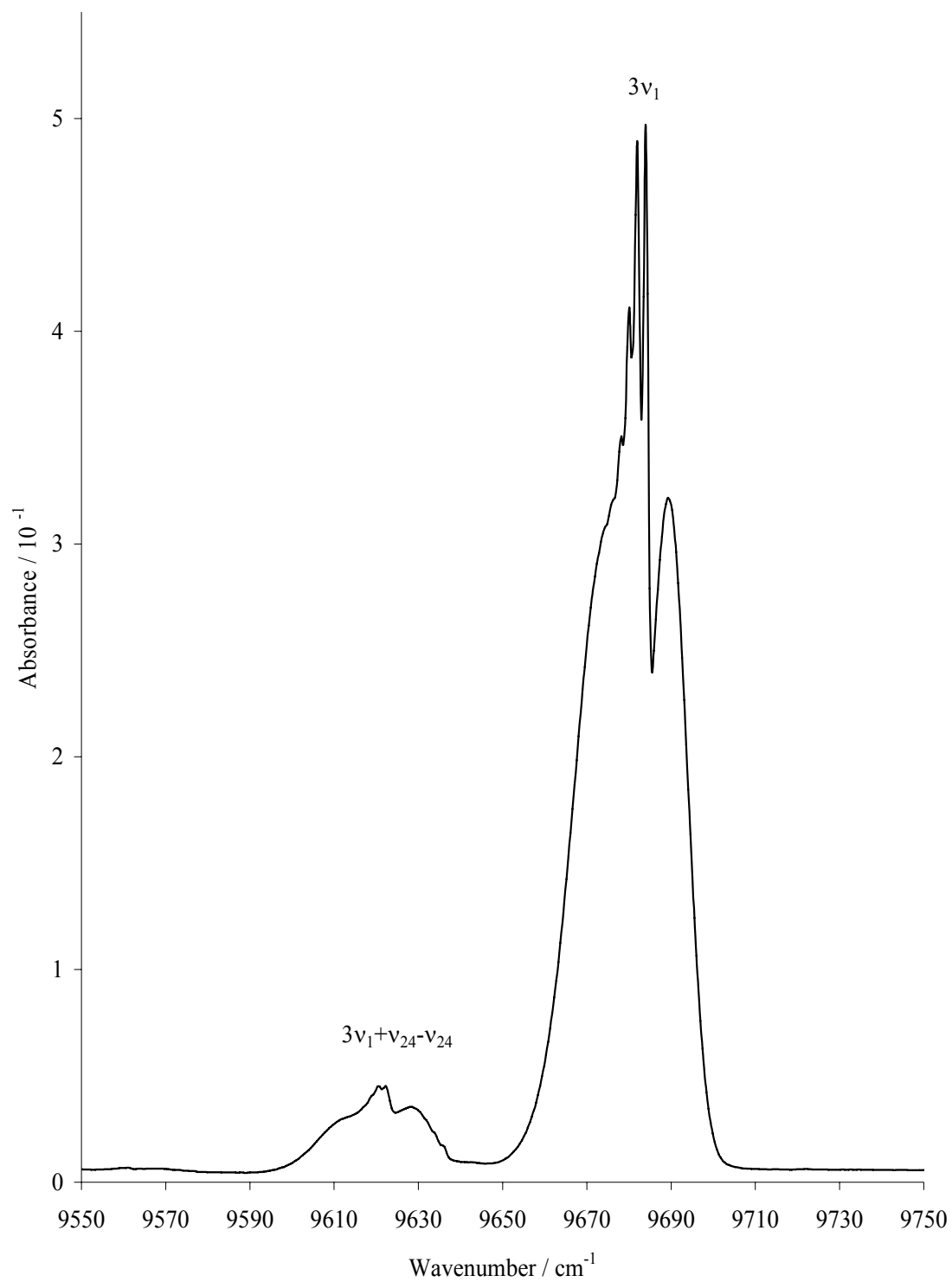


Figure 102. Absorption spectrum of the second overtone ($\Delta v=3$) acetylenic C-H stretch of C_6H_{10} at 295K. Pressure = 200Torr.

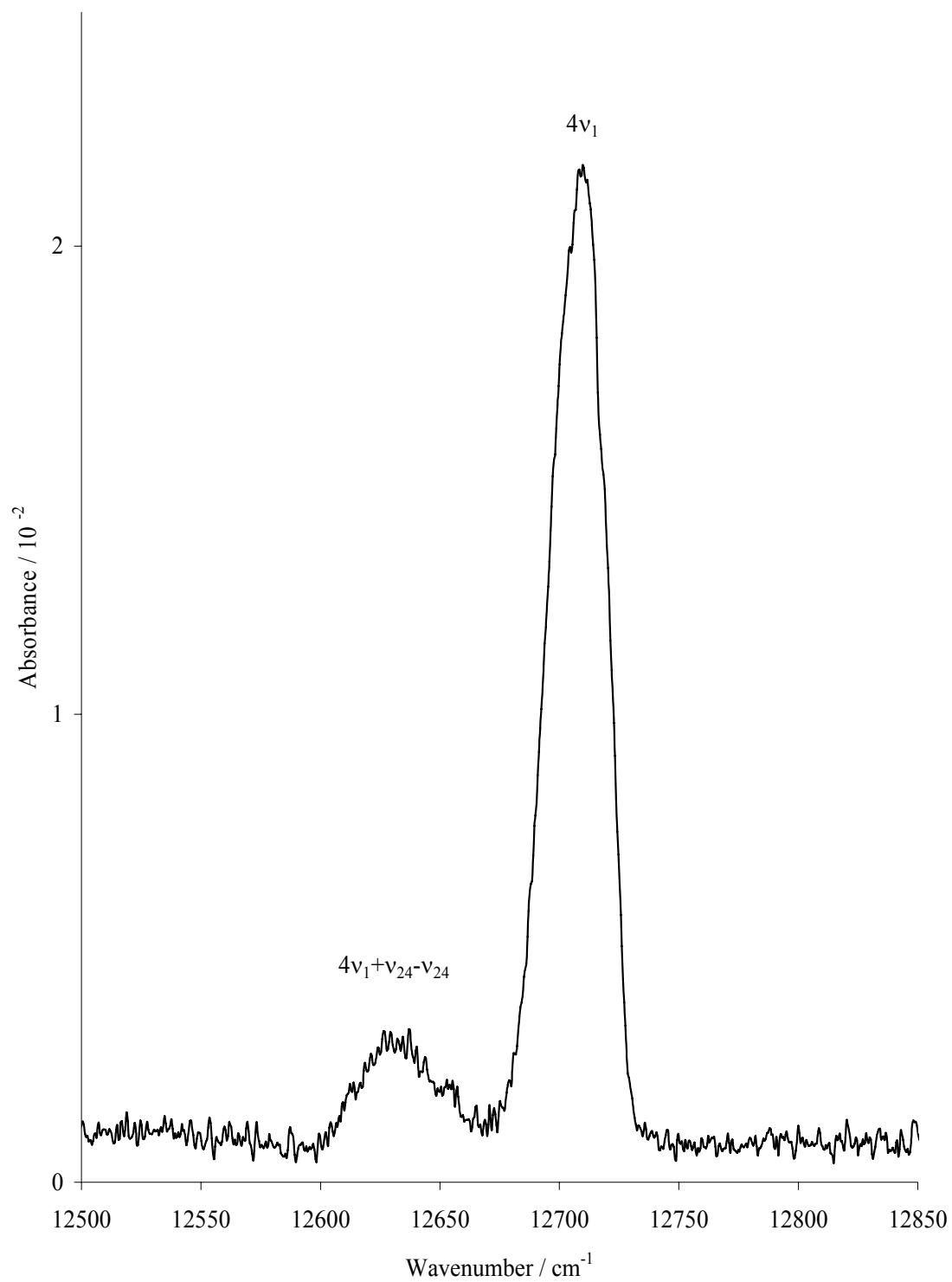


Figure 103. Absorption spectrum of the third overtone ($\Delta v = 4$) acetylenic C-H stretch of C_6H_{10} at 295K. Pressure = 200Torr.

Table 65. Fundamental Vibrational Frequencies of C₆H₁₀

Assignment	Symmetry	Mode	Frequency / cm ⁻¹
ν_1	A ₁	acetylenic C-H stretch	3329
ν_2	A ₁	methyl C-H a-stretch	2977
ν_3	A ₁	methyl C-H s-stretch	2889
ν_4	A ₁	C $\equiv$ C stretch	2107
ν_5	A ₁	H-C-H a-bend	1475
ν_6	A ₁	H-C-H s-bend	1363
ν_7	A ₁	C-C stretch	1248
ν_8	A ₁	CH ₃ rock	885
ν_9	A ₁	C - C $\equiv$ C stretch	691
ν_{10}	A ₁	C-C ₃ bend	382
ν_{11}	A ₂	CH ₃ a- stretch	2974
ν_{12}	A ₂	CH ₃ a- bend	1459
ν_{13}	A ₂	CH ₃ rock	995
ν_{14}	A ₂	CH ₃ twist	216
ν_{15}	E	acetylenic C-H stretch	2978
ν_{16}	E	methyl C-H a-stretch	2976
ν_{17}	E	methyl C-H s-stretch	2889
ν_{18}	E	CH ₃ a-bend	1475
ν_{19}	E	CH ₃ a-bend	1456
ν_{20}	E	CH ₃ s-bend	1393
ν_{21}	E	C-C a-stretch	1205
ν_{22}	E	CH ₃ a-rock	1032
ν_{23}	E	CH ₃ a-rock	930
ν_{24}	E	$\equiv$ C - H bend	634
ν_{25}	E	C-C ₃ a-bend	542
ν_{26}	E	C - C $\equiv$ C rock	362
ν_{27}	E	CH ₃ twist	287
ν_{28}	E	C - C $\equiv$ C bend	181

ν_1 overtones and its proximity to them, it is most probably a hot band corresponding to one observed in the fundamental. In addition, the separation in energy between the maximum of main absorption and the low-frequency peak increases by a multiple of the vibrational quantum number of the excited level.

For a polyatomic molecule the local-mode representation of a vibrational energy level is usually expressed as ²²⁰

$$E = E_0 + \sum_i \nu_i \omega_i + \sum_{i \geq j} c_{ij} \omega_{ij} + \sum_{i \geq j} \nu_i \nu_j X_{ij} \quad (71)$$

where ω_i and ν_i are the harmonic frequency and vibrational quantum number, respectively, and ω_{ij} 's are harmonic coupling terms that are usually small and can be neglected. Besides the diagonal X_{ii} local-mode anharmonicities, off-diagonal X_{ij} local-mode-local-mode and local-mode-normal mode anharmonicities are sometimes necessary to assign the spectra.

With eq 71, the energy difference $E(\nu_i) - E(0)$, corresponding to a pure local-mode transition $0 \rightarrow \nu_i$ is

$$\Delta E = \nu_i \omega_i + \nu_i^2 X_{ii} \quad (72)$$

Similarly for a hot-band transition $(0, \nu_j) \rightarrow (\nu_i, \nu_j)$ the energy difference $E(\nu_i, \nu_j) - E(0, \nu_j)$ is given by

$$\Delta E' = \nu_i \omega_i + \nu_i^2 X_{ii} + \nu_i X_{ij} \quad (73)$$

With the experimental points for the acetylenic CH stretch transitions $0 \rightarrow \nu_i$, a plot of $\Delta E/\nu$ versus ν was obtained and the results are shown on the upper straight line of Figure **104**. A similar plot was made with the experimental energies obtained for the small absorption on the low energy side of each transition. A straight line was obtained from this data as shown in the lower line of Figure **104**. From this result it can be concluded that the weaker band, close to and at a lower frequency than the main overtone transition, is a hot band of the type $(\nu_1 = 0, \nu_{24} = 1) \rightarrow (\nu_1 = \nu, \nu_{24} = 1)$. These are in agreement with the suggestion made by Manzanares *et al*²²⁰ that the coupling between the CH stretch and CH bend of the acetylenic compounds should be common to other similar molecules of the type $RC \equiv CH$. The observed and calculated

frequencies for these transitions are presented in Table 66. The frequencies were calculated by use of equation 72 and 73 and the harmonic frequency, ω_l , anharmonic constant, X_{ll} , and anharmonic interaction constant, $X_{l\ 24}$ also presented in Table 66.

The best absorption spectrum the third overtone ($\Delta v=4$) acetylenic C-H stretch of C_6H_{10} was recorded using PS-CRD spectroscopy and is shown in Figure 105. Both bands can be observed in this spectrum, the strong acetylenic C-H absorption, $4\nu_1$, and the small peak at low frequency side due to the hot band $\nu_{24} \rightarrow (\nu_{24} + 4\nu_1)$.

Using the PS-CRD technique, the absorption spectrum of the ($\Delta v=4$) acetylenic C-H stretch of C_6H_{10} was recorded at 240K. Give by the vapor pressure of tert-butylacetylene (26 Torr at 240K), it was 240K the lower temperature reached. Figure 106 shows that the band $4\nu_1$ is narrower at 240K than at 295 K.

It is possible to see from this comparison that the hot band intensity decreases at 240K. Pressure series at 295 and 240 K were taken and are shown in Figure 107 and Figure 108. This information was used to calculate the S_0 value for this overtone transition. Table 67 reports the calculated density (ρ), integrated absorption areas (S), and the band strength (S_0) for each pressure at 295 and 240K. Also, in this table the data obtained for this transition using FT spectrometer at 200 Torr and 295 K is included. The S_0 value reported is found by plotting S vs. ρ found in Figure 109.

The S_0 value equal to $(3.0 \pm 0.1) \times 10^{-22} \text{ cm}^2 \text{ cm}^{-1} \text{ molecules}^{-1}$ is similar to the value obtained for propyne, $S_0 = (3.1 \pm 0.1) \times 10^{-22} \text{ cm}^2 \text{ cm}^{-1} \text{ molecules}^{-1}$. This result shows that the acetylenic C-H oscillator is isolated from other parts of the molecule.

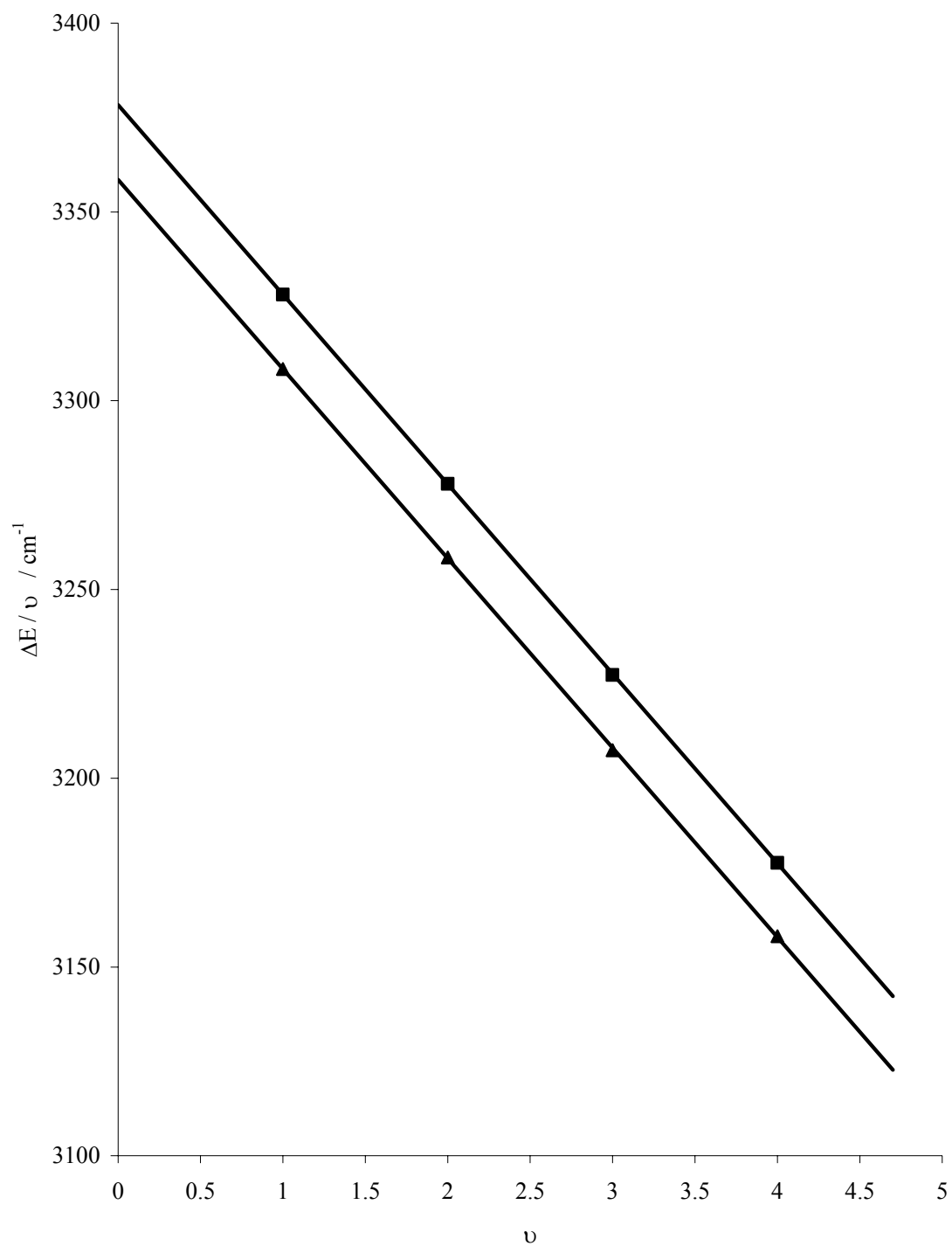


Figure 104. Birge-Sponer plot of the acetylenic C-H stretch of C_6H_{10} and an associated hot-band transition. Marker $\blacksquare$ represents the $v v_1$ overtones and Marker $\blacktriangle$ represents the $v_{24} \rightarrow (v_{24} + v v_1)$ hot bands.

Table 66. Observed and Calculated Frequencies, ω_l , X_{ll} and $X_{l\ 24}$ (cm^{-1}) for the Acetylenic CH stretch of C_6H_{10}

ν	Obs. Freq	Calc freq	Assigned Transition
1	3308.34 3328.11	3308.34 3328.07	$\nu_{24} \rightarrow (\nu_{24} + \nu_1)$ $0 \rightarrow \nu_1$
2	6516.96 6555.93	6516.36 6555.70	$\nu_{24} \rightarrow (\nu_{24} + 2\nu_1)$ $0 \rightarrow 2\nu_1$
3	9622.25 9682.03	9624.05 9682.87	$\nu_{24} \rightarrow (\nu_{24} + 3\nu_1)$ $0 \rightarrow 3\nu_1$
4	12632.63 12710.25	12631.42 12709.58	$\nu_{24} \rightarrow (\nu_{24} + 4\nu_1)$ $0 \rightarrow 4\nu_1$
Harmonic Frequency	3378.3 ± 0.3	Anharmonic constants	-50.2 ± 0.1
	Anharmonic interaction constant	-19.8 ± 0.7	

Table 67. ($\Delta\nu=4$) acetylenic C-H of C_6H_{10} at 295 and 240K, Pressure, ρ , S and S_0 .

T	Pressure	ρ	S	S_0
Torr	Torr	$10^{18} \text{ molecules cm}^{-3}$	10^{-4} cm^{-2}	$10^{-22} \text{ cm}^2 \text{ cm}^{-1} \text{ molecule}^{-1}$
295 K	65	2.105	5.12	2.43
	52	1.684	4.06	2.41
	32	1.037	2.73	2.63
	19	0.615	1.64	2.66
	11	0.356	1.33	3.72
	4	0.130	0.59	4.58
	2	0.065	0.40	6.22
	200	6.567	20.23	3.08
240 K	5.5	0.221	0.732	3.31
	1.6	0.064	0.261	4.06
	0.9	0.039	0.216	5.47
Avg				3.0 ± 0.1

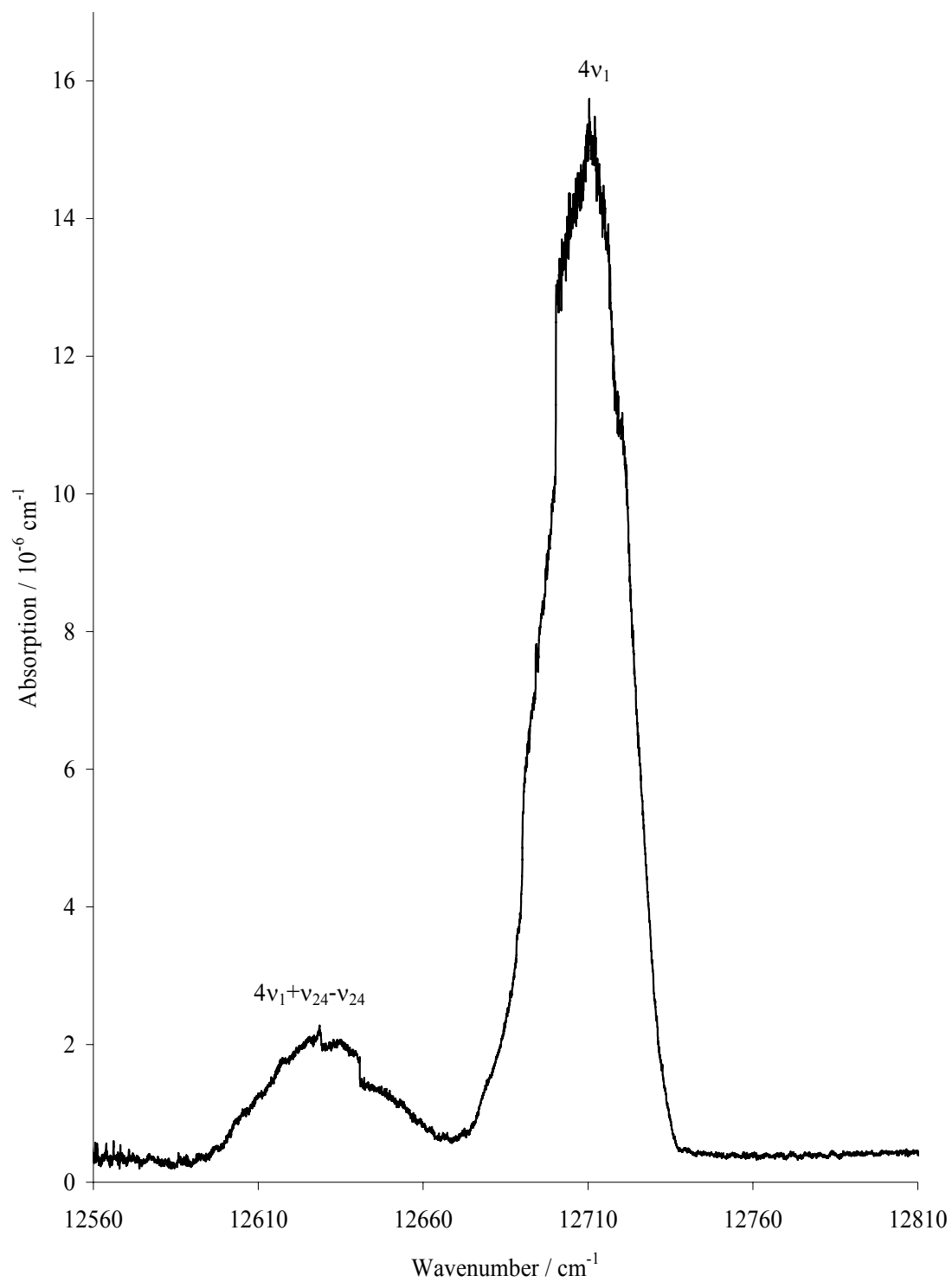


Figure 105. Absorption spectrum of ($\Delta v=4$) acetylenic C-H stretch of C_6H_{10} with a pressure of 65 Torr at 295K

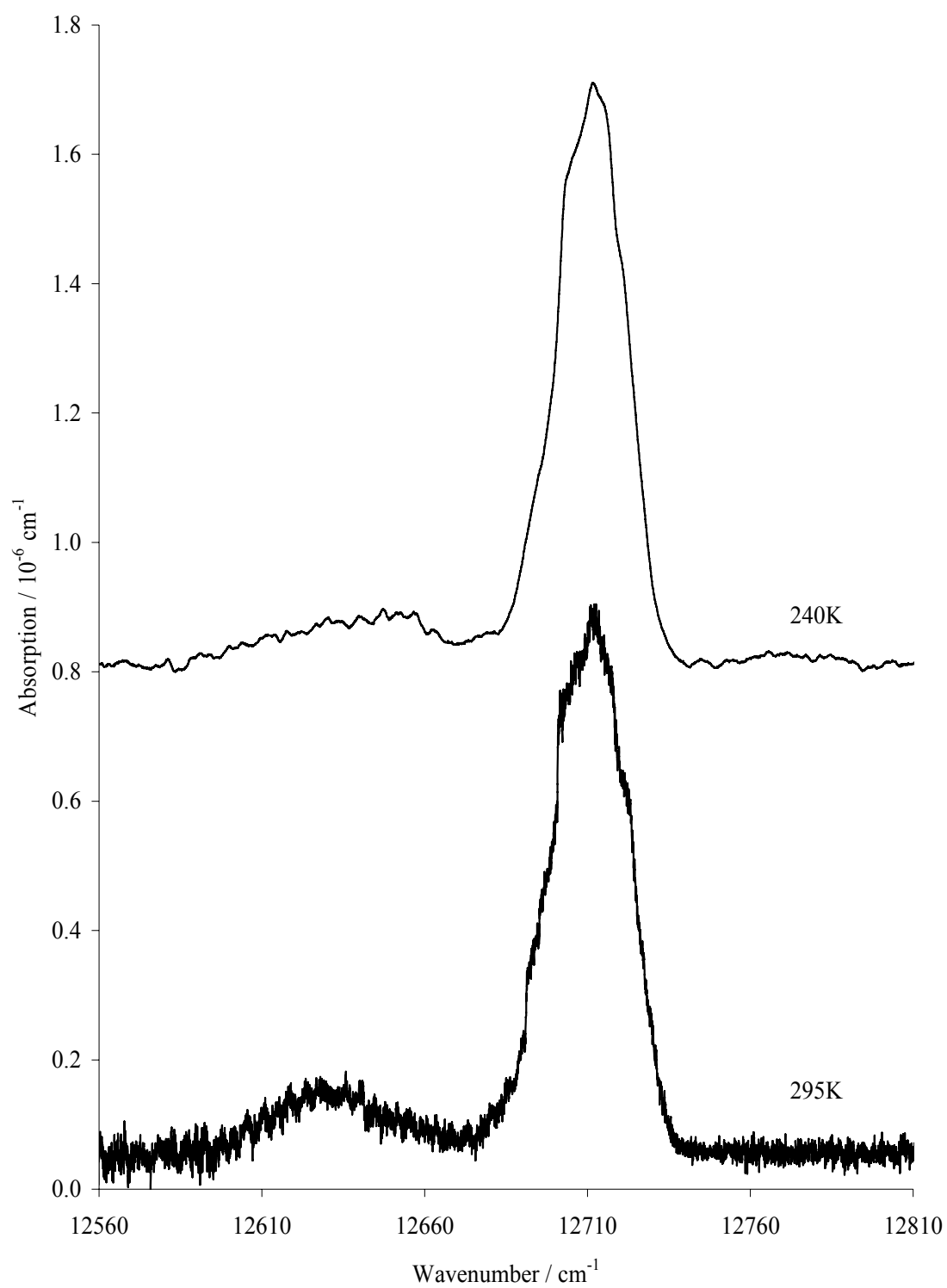


Figure 106. ($\Delta v=4$) acetylenic C-H stretch of C_6H_{10} with a pressure of 1.6 Torr at 240 K- top, and 2 Torr at 295K- bottom

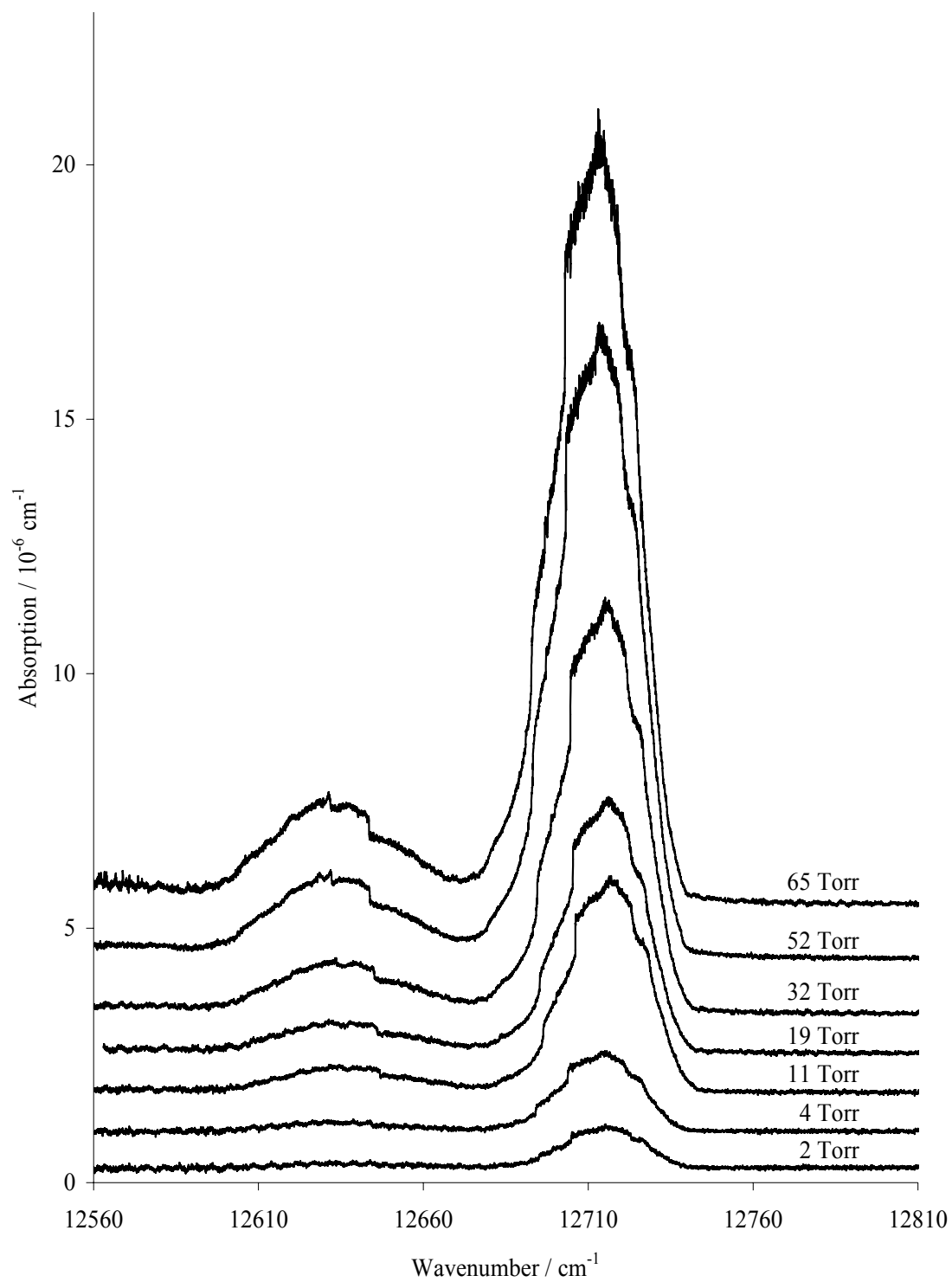


Figure 107. $(\Delta v=4)$ acetylenic C-H stretch of C_6H_{10} . Absorption pressure series at 295K

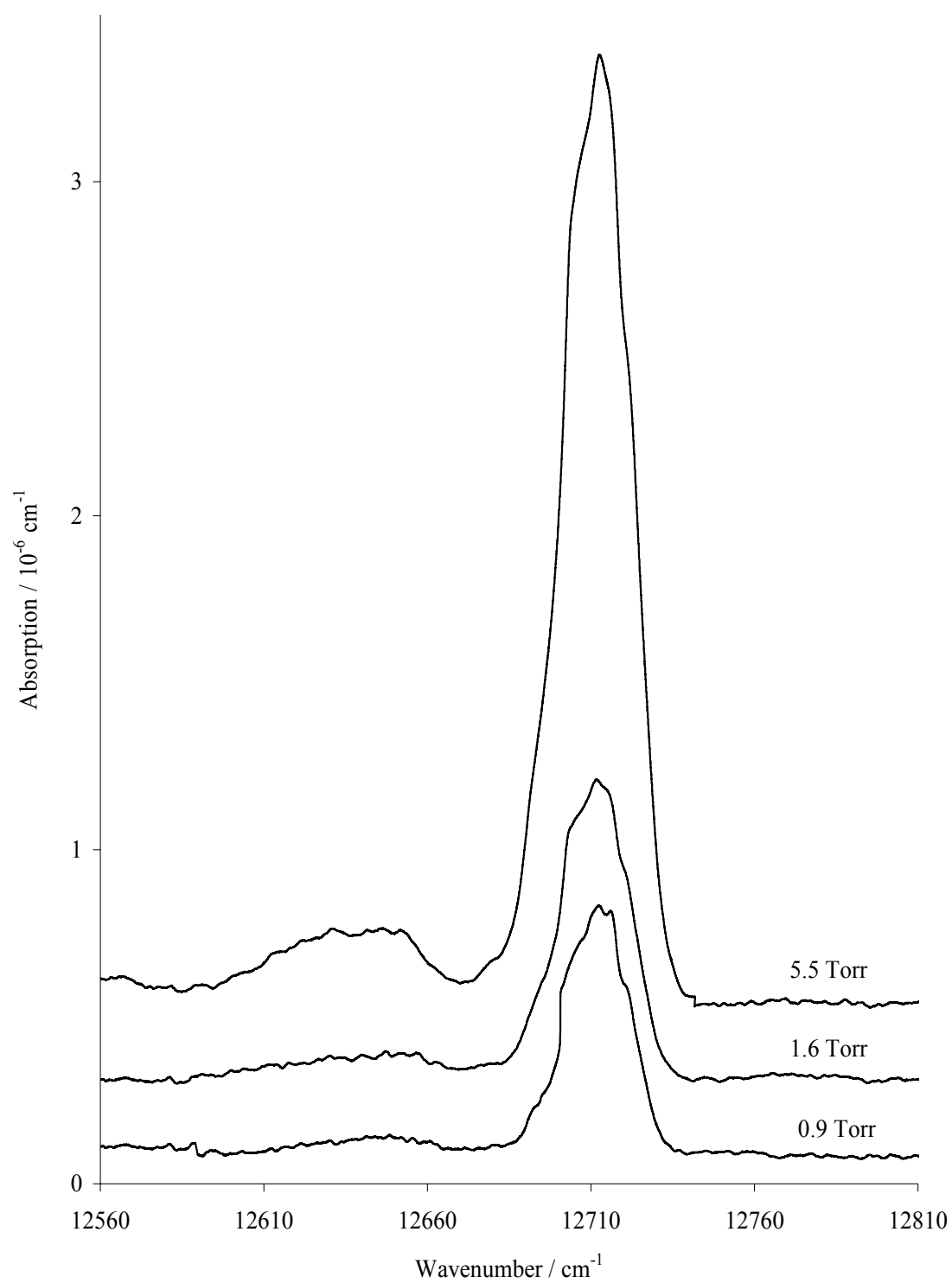
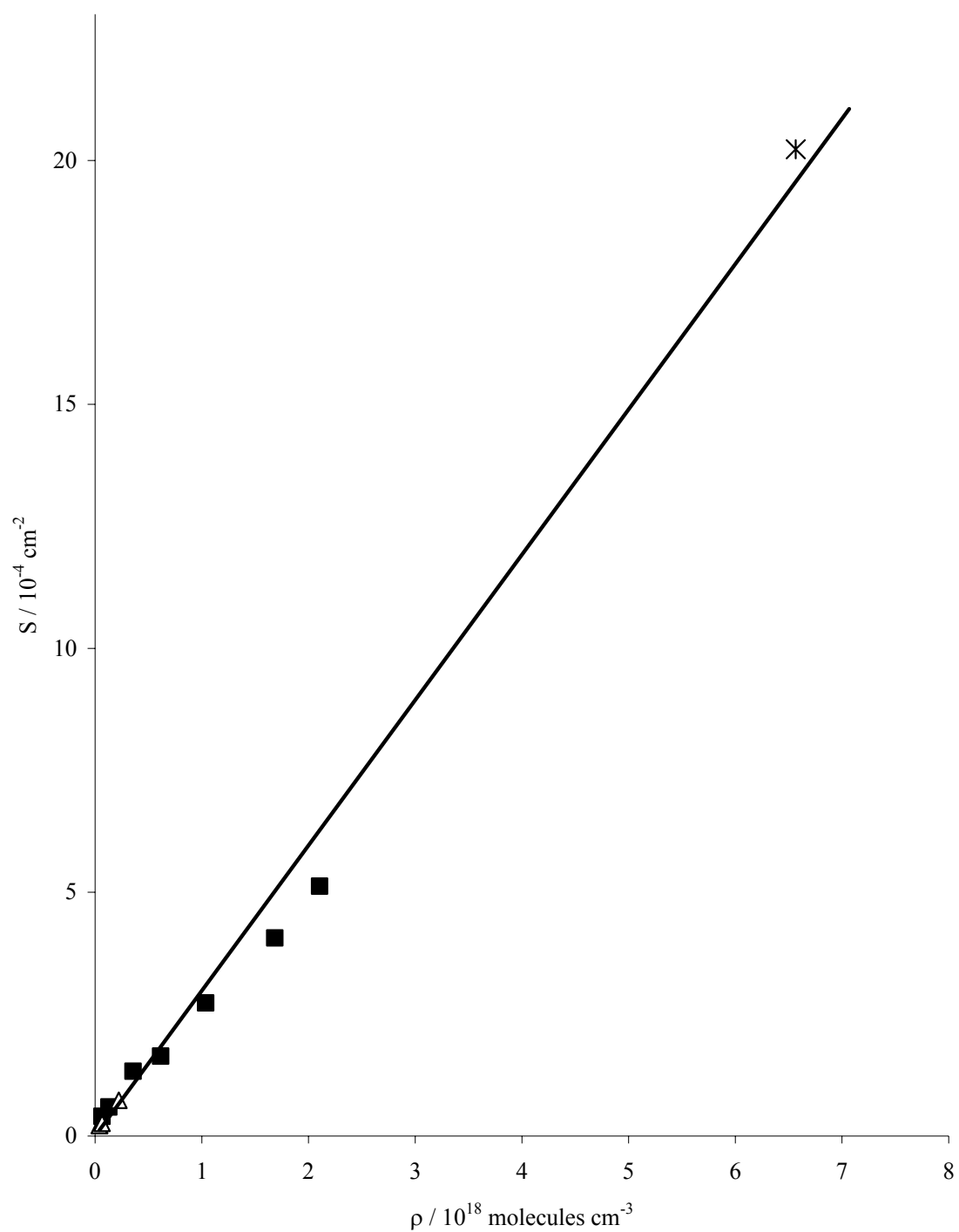


Figure 108. $(\Delta v=4)$ acetylenic C-H stretch of C_6H_{10} . Absorption pressure series at 240K



$$S_0 = (3.0 \pm 0.1) \times 10^{-22} \text{ cm}^2 \text{ cm}^{-1} \text{ molecules}^{-1}$$

$$R^2 = 0.992$$

Figure 109. ($\Delta\nu=4$) acetylenic C-H stretch of C_6H_{10} . S vs. ρ . Slope is S_0 . Marker ■ = measurements at 295 K, Marker × = FT-spectrum, Marker Δ = measurements at 240 K.

Since the S_0 value for the acetylenic C-H stretch in molecules like $RC \equiv CH$ is not affected by changing the R group.

Methyl C-H stretch

Tert-butylacetylene is a symmetry top molecule belongs to the point group C_{3v} . For this reason at the equilibrium geometry, each CH_3 group is aligned with a C-H bond in the C_{3v} plane (CH_s) and the other two C-H bonds out of the molecular C_{3v} plane (CH_a). It is expected that this molecule will show two overtone bands in the methyl C-H regions corresponding to the two non-equivalent CH bonds in the methyl groups.

The methyl C-H stretch spectra are shown from Figure **110** to Figure 114. Figure **110** and Figure **111** correspond to the fundamental and first overtone C-H region. The expected two bands for two non-equivalent CH bonds in the methyl groups do not appear because they have similar energies at this level of excitation. For higher overtones from $\Delta v = 3$ up to $\Delta v = 5$, these two bands can be distinguished. This is because the two C-H bonds have different anharmonicity constants. The contribution from the anharmonicity begins to show the separation between energy levels for vibrational transitions larger than $\Delta v = 3$.^{203, 224}

Absorption spectrum of the fourth overtone ($\Delta v = 5$) methyl C-H stretch of C_6H_{10} was also obtained using the PS-CRD technique. The spectra were obtained at 295 and 240K. A small decrease in the bandwidth was observed in the spectrum taken at 240 K. Using the same procedure explained before for the ($\Delta v = 4$) transition of the acetylenic C-H stretch, a pressure series at each temperature were obtained and are shown in Figure **115** and Figure **116**.

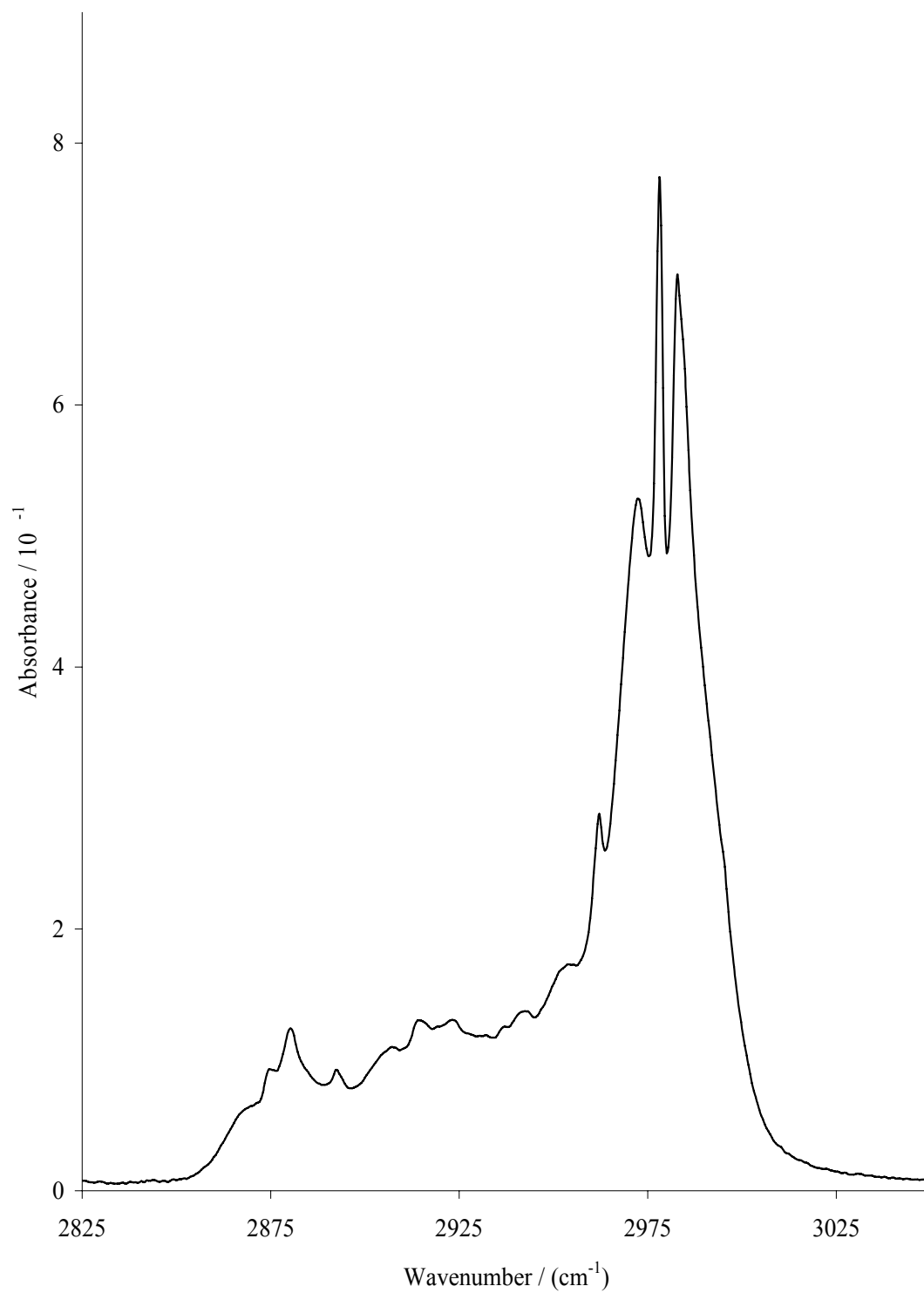


Figure 110. Absorption spectrum of the fundamental ($\Delta v=1$) methyl C-H stretch of C₆H₁₀ at 295K. Pressure = 0.2Torr.

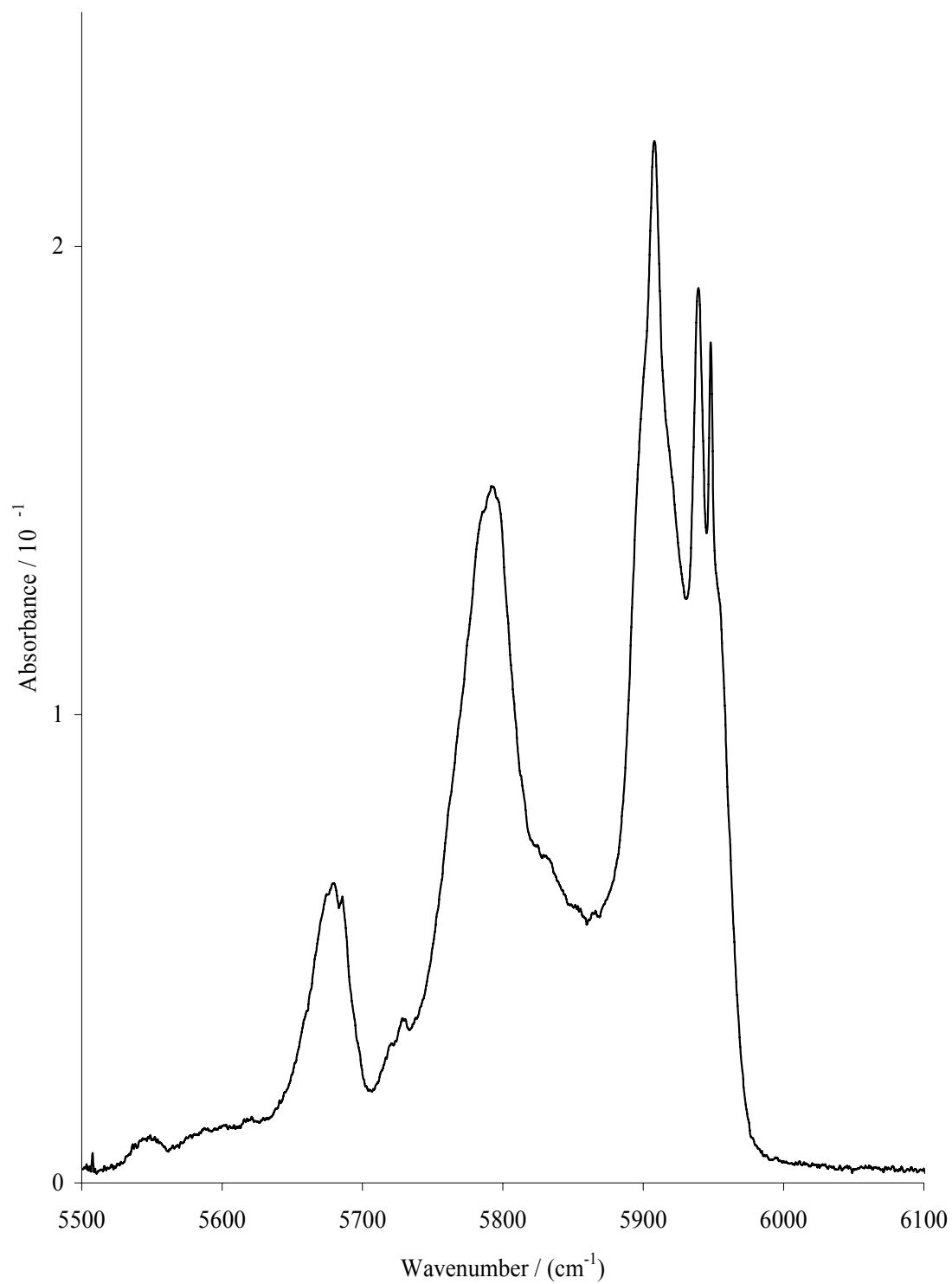


Figure 111. Absorption spectrum of the first overtone ($\Delta\nu = 2$) methyl C-H stretch of C_6H_{10} at 295K. Pressure = 9.2Torr.

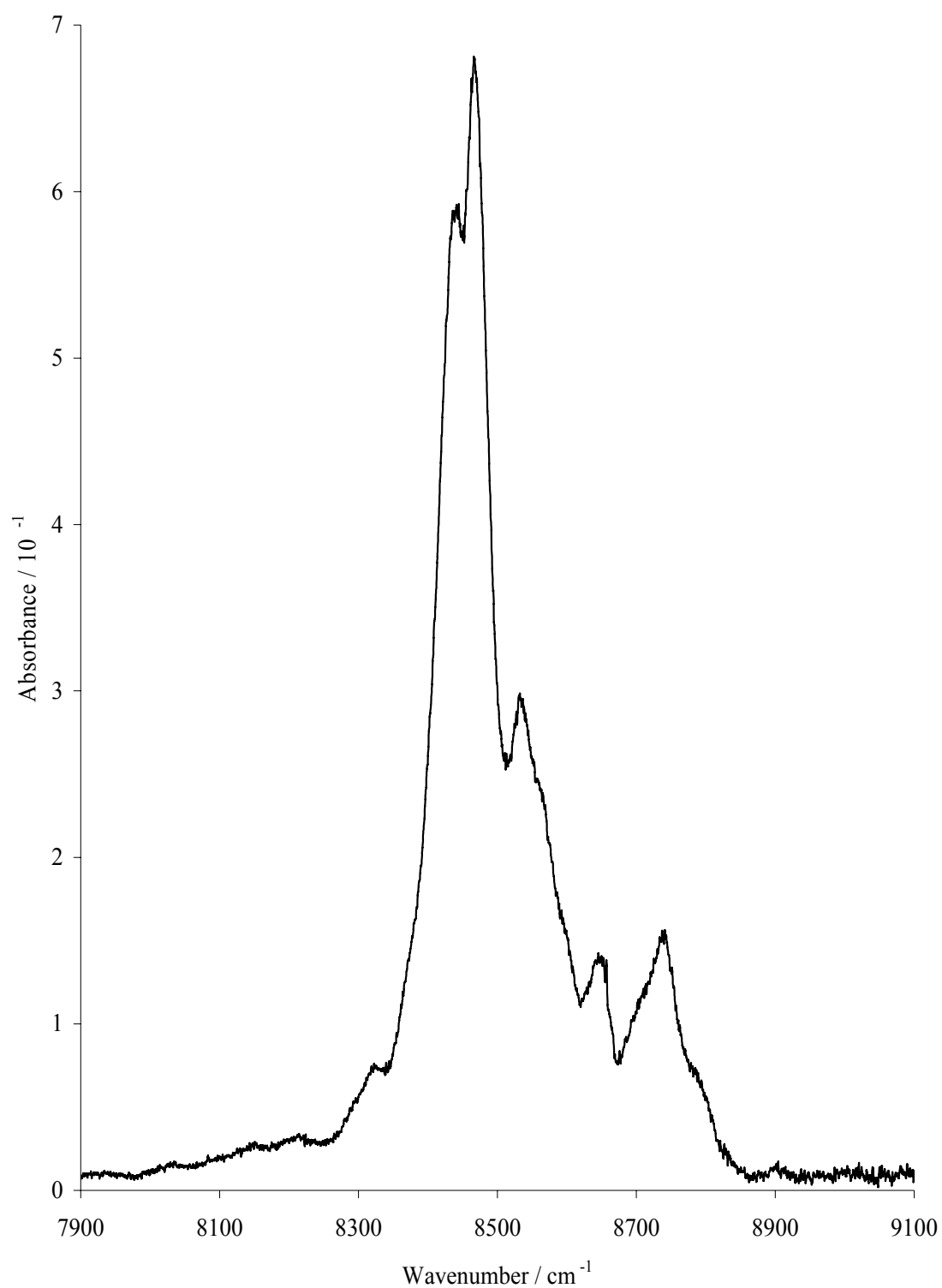


Figure 112. Absorption spectrum of the second overtone ($\Delta v = 3$) methyl C-H stretch of C_6H_{10} at 295K. Pressure = 200Torr.

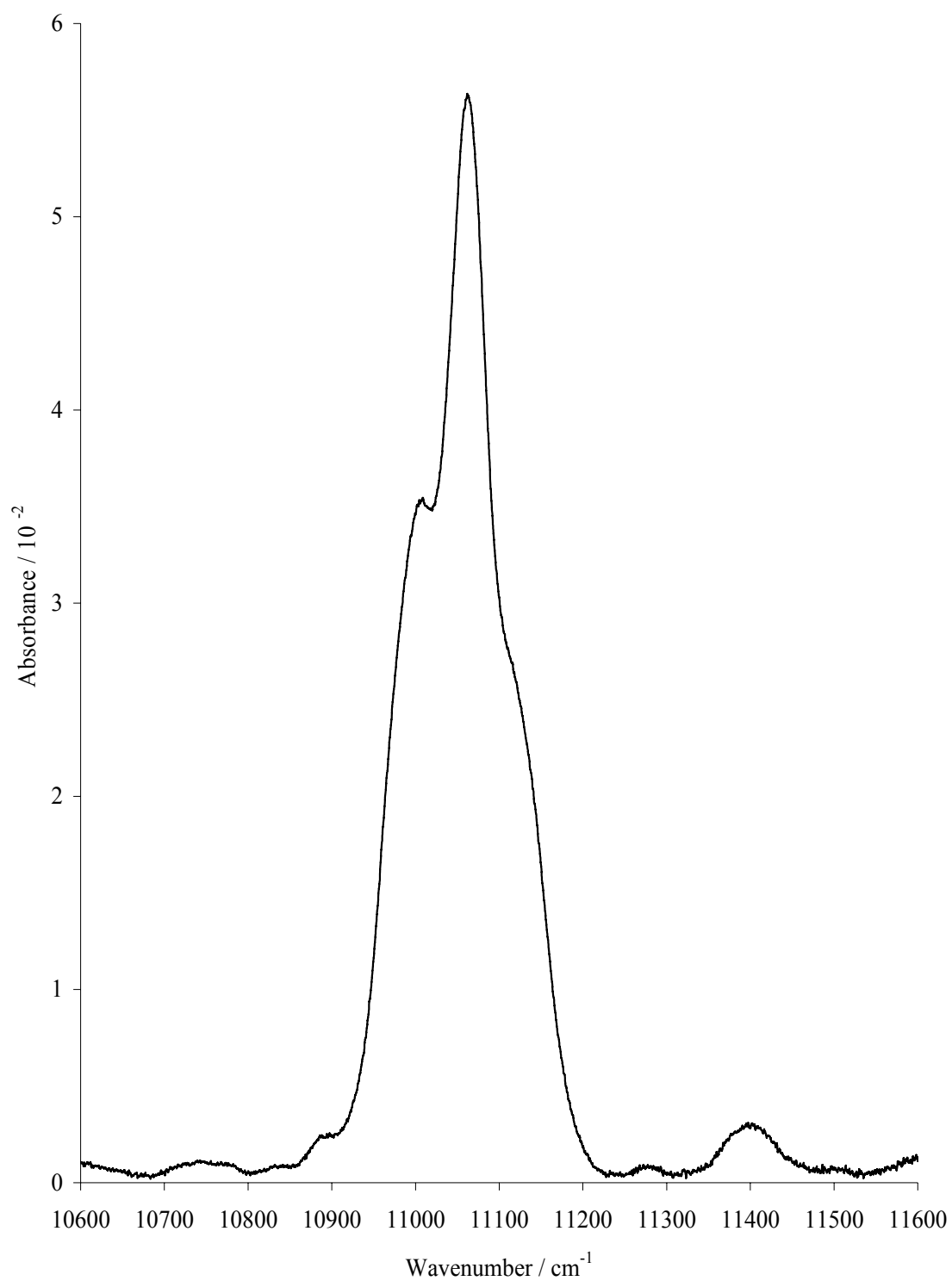


Figure 113. Absorption spectrum of the third overtone ($\Delta v = 4$) methyl C-H stretch of C_6H_{10} at 295K. Pressure = 200 Torr.

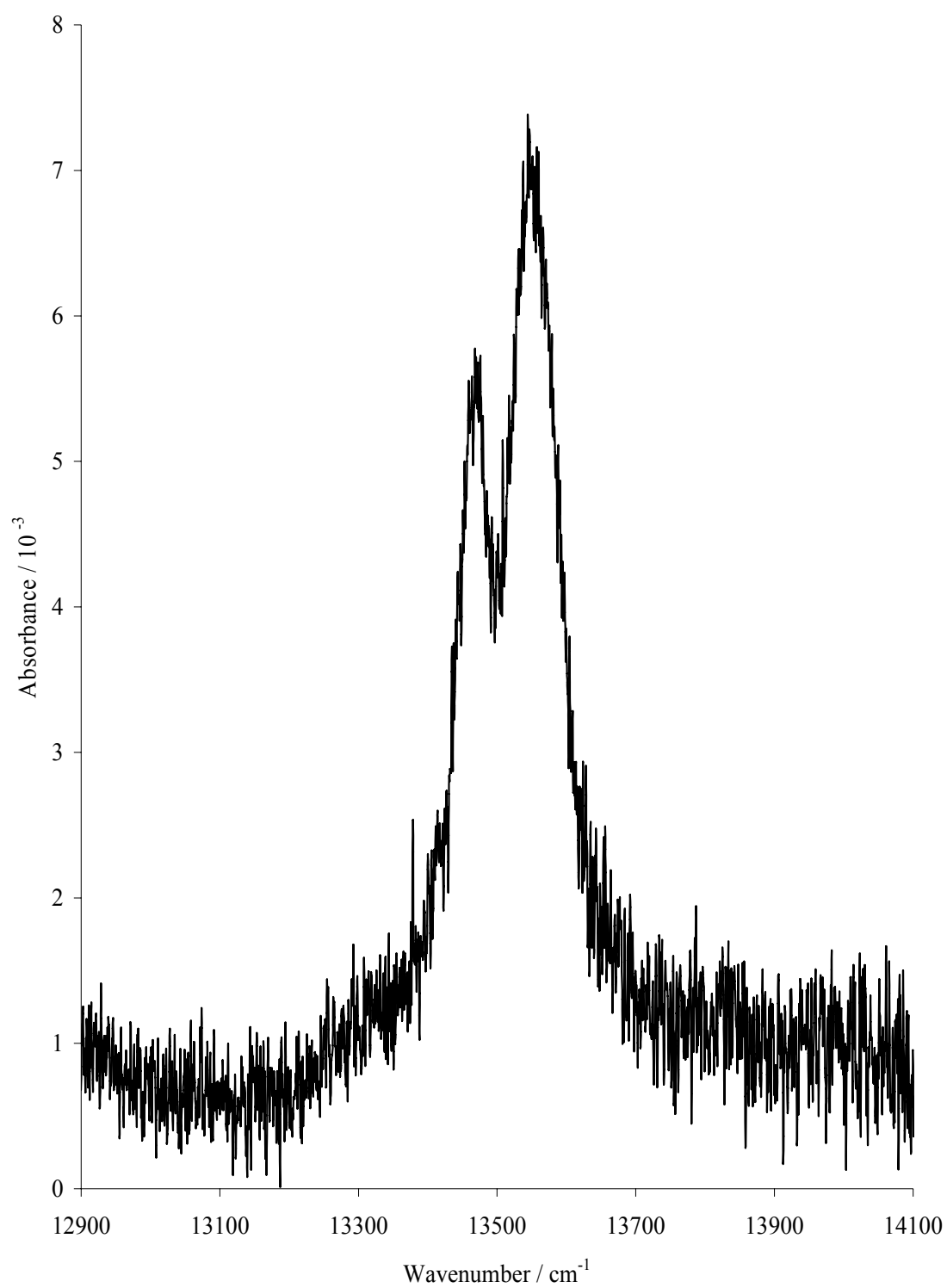


Figure 114. Absorption spectrum of the fourth overtone ($\Delta v = 5$) methyl C-H stretch of C_6H_{10} at 295K. Pressure = 200Torr.

Table 68. ($\Delta\nu=5$) methyl C-H of C_6H_{10} at 295 and 240K, Pressure, ρ , S and S_0 .

T	Pressure	ρ	S	S_0
Torr	Torr	$10^{18} \text{ molecules cm}^{-3}$	10^{-4} cm^{-2}	$10^{-22} \text{ cm}^2 \text{ cm}^{-1} \text{ molecule}^{-1}$
295 K	65	2.105	8.04	3.82
	52	1.684	6.51	3.87
	32	1.037	4.13	3.98
	19	0.615	2.46	4.00
	11	0.356	1.84	5.17
	4	0.130	0.85	6.55
	2	0.065	0.20	3.08
	200	6.567	27.6	4.20
240 K	5.5	0.221	1.34	6.06
	1.6	0.064	3.85	5.98
	0.9	0.039	3.37	7.69
Avg				4.14 ± 0.06

In order to obtain the band strength value for ($\Delta\nu=5$) methyl C-H stretch, integrated band values were plotted as a function of the molecular density. The results are shown in Figure 117. Table 68 reports the density, integrated absorption band, and band strength values for each individual pressure. The integrated band obtained from the FT- spectrum was also plotted.

The S_0 value obtained $(4.14 \pm 0.06) \times 10^{-22} \text{ cm}^2 \text{ cm}^{-1} \text{ molecules}^{-1}$ is three times the S_0 value obtained for propyne $((1.34 \pm 0.02) \times 10^{-22} \text{ cm}^2 \text{ cm}^{-1} \text{ molecules}^{-1})$ which confirms that the triple bond in molecules like $RC \equiv CH$ effectively isolates the acetylenic C-H stretch from the methyl group vibrational modes and that the converse is also true.²⁰³

The harmonically coupled anharmonic oscillators (HCAO) model was used to obtain suitable vibrational energies for the methyl groups.^{217, 218} Following the same treatment given by Henry *et al*¹⁹⁴, the model neglects interactions among the three

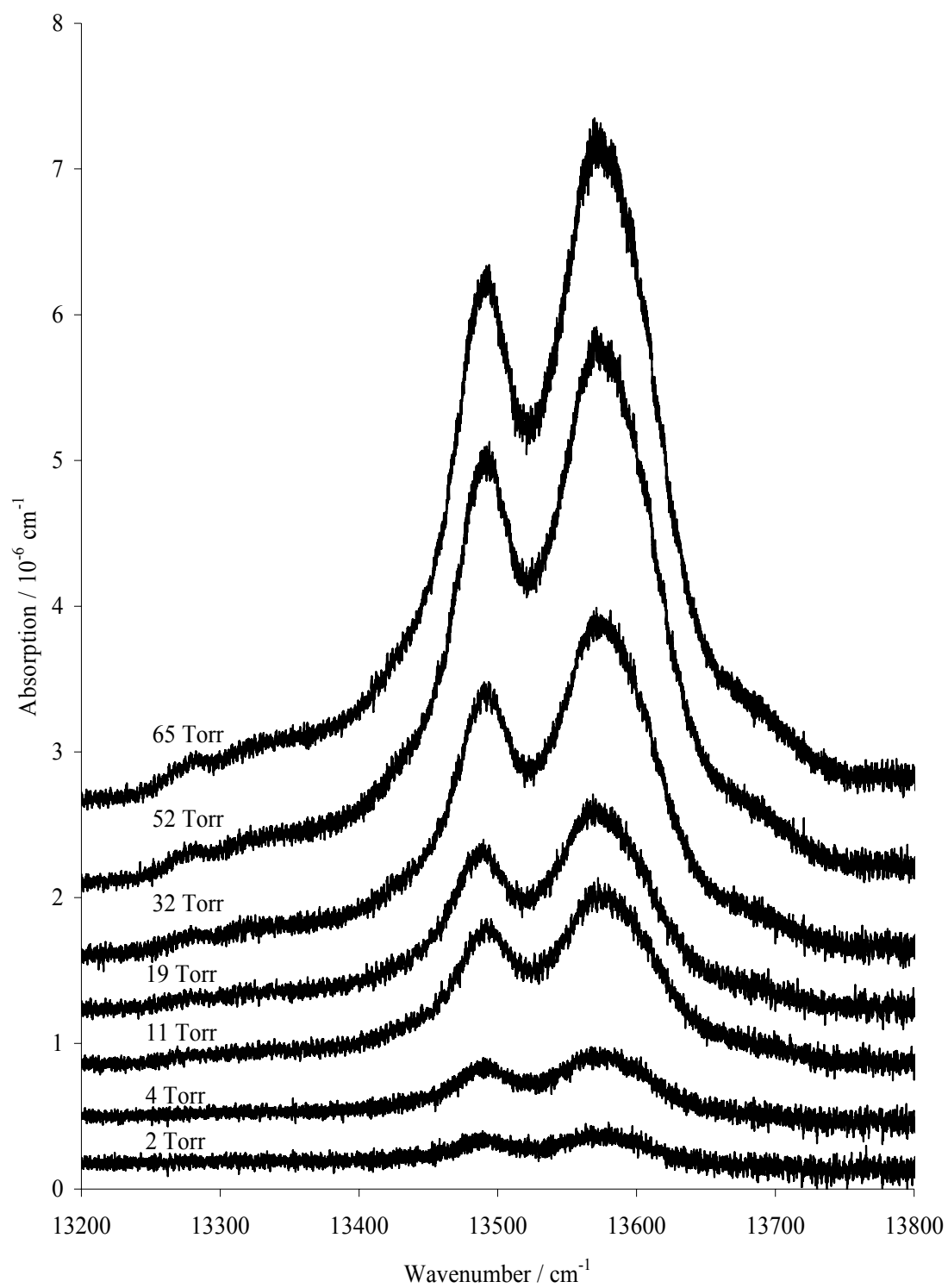


Figure 115. ($\Delta\nu=5$) methyl C-H stretch of C_6H_{10} . Absorption pressure series at 295K

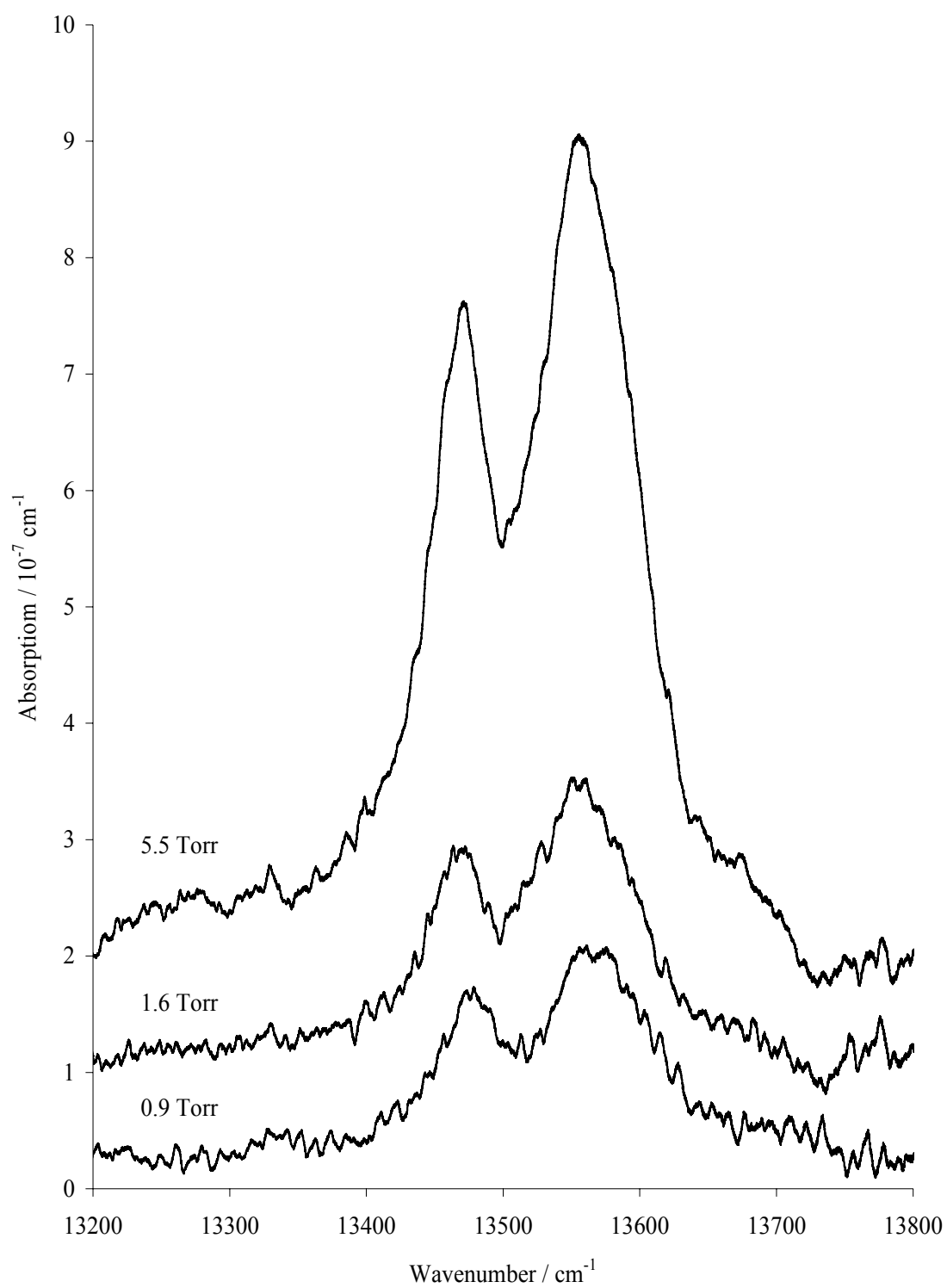
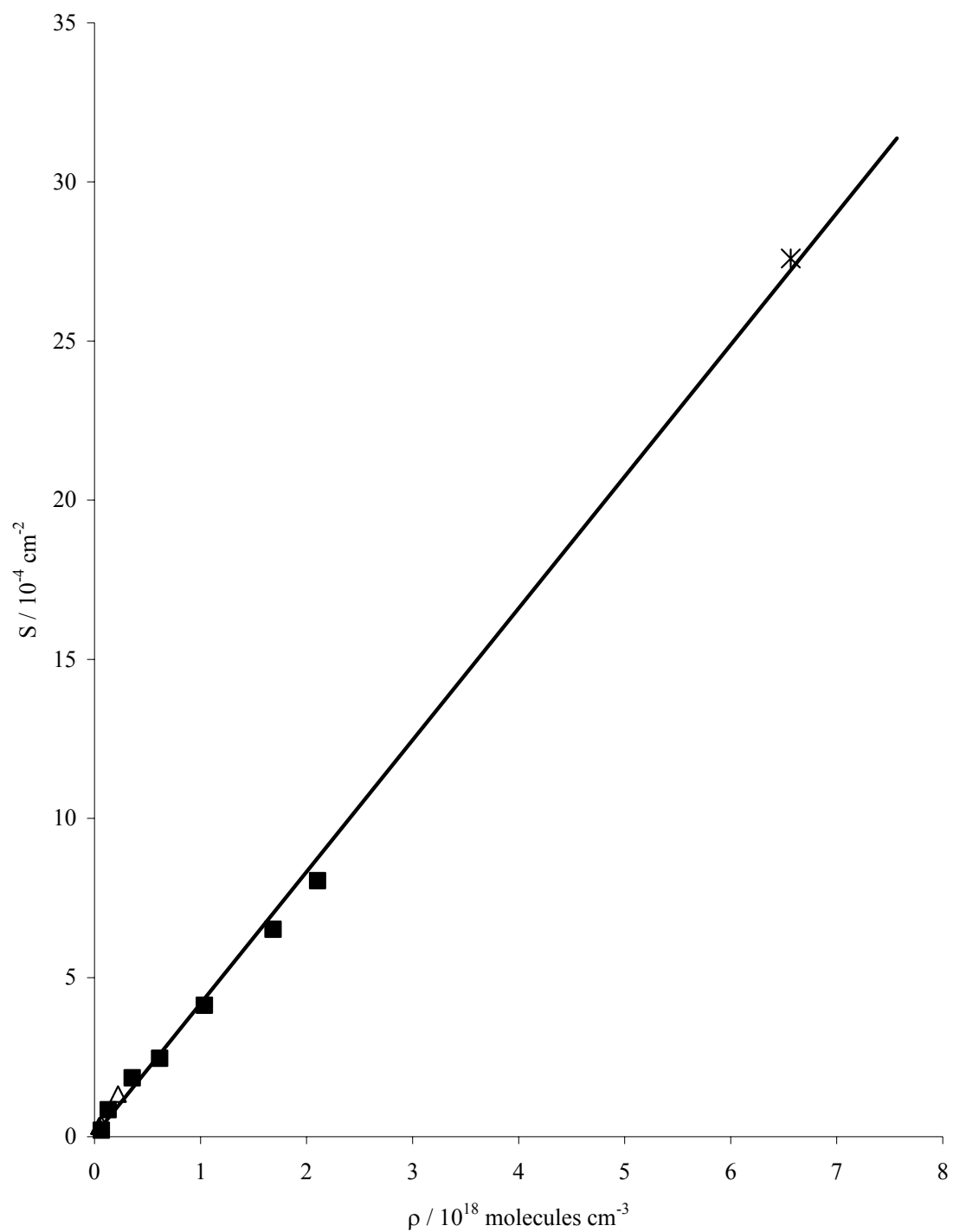


Figure 116. ($\Delta\nu=5$) methyl C-H stretch of C_6H_{10} . Absorption pressure series at 240K



$$S_0 = (4.14 \pm 0.06) \times 10^{-22} \text{ cm}^2 \text{ cm}^{-1} \text{ molecules}^{-1}$$

$$R^2 = 0.998$$

Figure 117. ($\Delta\nu=5$) methyl C-H stretch of C_6H_{10} . S vs. ρ . Slope is S_0 . Marker ■ = measurements at 295 K , Marker × =FT-spectrum , Marker Δ = measurements at 240 K.

methyl groups of the molecule. In a methyl group, the coupling between the C-H stretching modes and the bending modes is also neglected and the Hamiltonian is the sum of three (two of which are identical) Morse oscillators which are harmonically coupled.

The states in each methyl group are described by three quantum numbers with the notation $| \nu_1 \nu_2 \nu_3 \rangle$, where ν_1 and ν_2 are the vibrational quanta in the two C-H_a oscillators, respectively, and ν_3 is the number of vibrational quanta in the C-H_s oscillator. The $\pm$ refers to the symmetry of the two equivalent C-H, wave functions with respect to reflection in the skeletal plane. The zeroth-order Hamiltonian H^o can be written as

$$\frac{(H^o - E_{|00\rangle|0\rangle}^o)}{hc} = (\nu_1 + \nu_2)\omega_1 - (\nu_1^2 + \nu_2^2 + \nu_1 + \nu_2)\omega_1 x_1 + \nu_3\omega_3 - (\nu_3^2 + \nu_3)\omega_3 x_3 \quad (74)$$

where ω_l and $\omega_l x_l$ are the local mode frequency and anharmonicity of the two equivalent C-H_a oscillators, and ω_3 and $\omega_3 x_3$ are the corresponding local mode parameters for the C-H_s oscillator. $E_{|00\rangle|0\rangle}^o$ is the zeroth-order energy of the ground state. States that have the same total number of vibrational quanta $\nu = \nu_1 + \nu_2 + \nu_3$ are said to belong to the same manifold.

The HCAO local model includes in the perturbation only terms that are quadratic in the momentum or the position operators. Henry *et al*^{98, 190} introduced the creation a^+ and annihilation a operators in place of the momentum and position operators. Thus the perturbation can be written as $H^1 = H_{int ra}^1 + H_{int er}^1$, where

$$\frac{H_{int ra}^1}{hc} = -\gamma'_{12}(a_1 a_2^+ + a_1^+ a_2) - \gamma'_{13}(a_1 a_3^+ + a_1^+ a_3 + a_2 a_3^+ + a_2^+ a_3) \quad (75)$$

and

$$\frac{H_{inter}^1}{hc} = -\gamma_{12}^*(a_1 a_2 + a_1^+ a_2^+) - \gamma_{13}^*(a_1 a_3 + a_1^+ a_3^+ + a_2 a_3 + a_2^+ a_3^+), \quad (76)$$

where the coupling parameters are defined by

$$\gamma'_{12} = (\gamma_{12} - \phi_{12})\omega_1, \quad \gamma'_{13} = (\gamma_{13} - \phi_{13})\sqrt{\omega_1\omega_3} \quad (77)$$

and

$$\gamma_{12}^* = (\gamma_{12} + \phi_{12})\omega_1, \quad \gamma_{13}^* = (\gamma_{13} + \phi_{13})\sqrt{\omega_1\omega_3} \quad (78)$$

The parameters γ and ϕ are defined by^{96, 194}

$$\gamma_{ij} = -\frac{1}{2} \frac{G_{ij}^o}{\sqrt{G_{ii}^o G_{jj}^o}} \quad \text{and} \quad \phi_{ij} = \frac{1}{2} \frac{F_{ij}}{\sqrt{F_{ii} F_{jj}}} \quad (79)$$

Where the G_{ij}^o are the elements of the Wilson G matrix evaluated at the optimized geometry, and the F_{ij} , the usual force constants. Henry *et al*¹⁹⁴ assume that the operators a^+ and a , to good approximation, have the step-up and step-down properties known from harmonic oscillators even though they here operate on Morse oscillators.⁹⁶ With this approximation, $H_{int ra}^1$ will only couple states within the same manifold and only those that differ by one vibrational quantum in two CH oscillators. H_{inter}^1 is the contribution to the energy from the coupling between vibrational manifolds. It has been shown¹⁹⁰ that this second contribution to the perturbation is very small because it couples states where v is changed by ± 2 , which are states that are well separated in energy. Hence, H_{inter}^1 is neglected in the present calculation. The problem of obtaining peak positions is reduced to diagonalization of a block diagonal Hamiltonian matrix with one block for each manifold.

The intramanifold coupling parameters γ' can usually be obtained from the observed frequencies of the fundamental peaks and/or some of the observed peak frequencies in the first CH-stretching overtone. However, this is not our case since *ab initio* molecular orbital calculations were performed to obtain γ' .

The vibrational frequencies of C₆H₁₀ were calculated at the Hartree-Fock, DFT (B3LYP) level of theory using the standard 6-311G (3d,p) and 6-311G(d,p) basis sets, respectively. The computations were performed by using the Gaussian 03 Program Package.²⁰⁰ The most stable configuration is presented in Figure **118**.

Table 69 contains the selected computed geometric parameters for the C_{3v} symmetry of C₆H₁₀ and compares available experimental data.^{225, 226}

The most stable configuration of C₆H₁₀ was used to calculate the vibrational frequencies. The configuration with C_{3v} symmetry possesses 3N-6 = 42 normal modes with the symmetry representations 10A₁ + 4A₂ + 14E. Tables **70** and Table **71** lists the vibrational frequencies calculated at the HF / 6-311G (3d,p) and DFT (B3LYP) / 6-311G(d,p) levels, respectively.

Table 69. Optimized geometry (C_{3v}) and experimental bond lengths (Å) and bond angle (degree) for C₆H₁₀

Parameter	HF / 6-311G (3d,p)	DFT (B3LYP) / 6-311G(d,p)	Experimental ²²⁵ ²²⁶	
C ₁ ≡C ₂	1.1822	1.2025	1.206	1.210
C ₂ -C ₃	1.4799	1.4720	1.500	1.498
C ₃ -C ₄	1.5370	1.5454	1.531	1.529
C ₄ -H ₆	1.0859	1.0942		
C ₄ -H ₇	1.0843	1.0924		
C ₁ -H ₈	1.0548	1.0622	1.056	1.10
C ₅ -C ₃ -C ₄	109.9321	109.7587	111.1	110.9
C ₃ -C ₄ -H ₆	109.9846	110.0392		
C ₃ -C ₄ -H ₇	110.9314	110.8969		

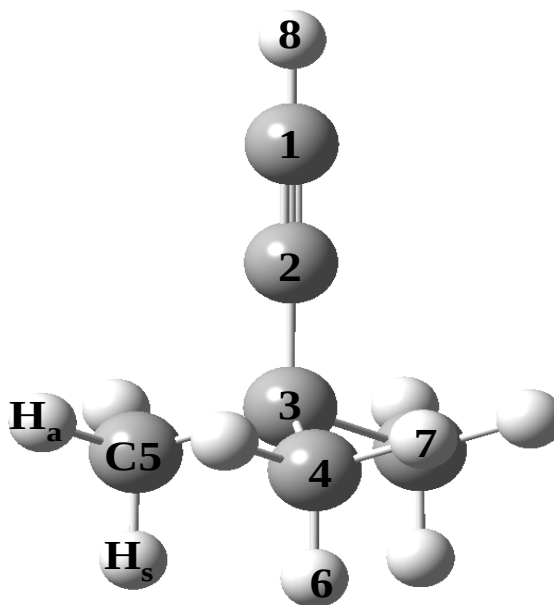


Figure 118. Equilibrium geometry (C_{3v} symmetry) of tert-butylacetylene.

These tables also show the corresponding calculated IR intensities. The calculated frequencies are scaled (scaling factors: 0.92(HF) and 0.96 (DFT (B3LYP)) and compared with the observed IR frequencies²²².

Therefore, the intra-manifold coupling parameters (γ') were estimated from frequencies obtained from *ab initio* calculations using the same method that was used for dimethyl ether.¹⁹⁴

The isolated fundamental C-H_a and C-H_s stretching frequencies for (CD₂H) (CD₃)₂C₃D and the fundamental CH stretching frequencies of (CH₃) (CD₃)₂C₃D were calculated at the Hartree-Fock 6-311G (3d,p) and DFT (B3LYP) 6-311G(d,p) levels of theory. The results are presented in Table 72.

Since the calculated isolated fundamental frequencies, C-H_a and C-H_s, for (CD₂H) (CD₃)₂C₃D are independent of any coupling, these two CH frequencies are

made equal to the pure local mode frequencies, $(\omega_I - 2\omega_I x_I) = 3219 \text{ cm}^{-1}$ and $(\omega_3 - 2\omega_3 x_3) = 3199 \text{ cm}^{-1}$, respectively. These values were obtained when HF 6-311G (3d,p) level of theory was used. The latter calculation produces three frequencies (ν) that correspond in increasing order to the energies of the states $\nu|00\rangle|1\rangle = 3163 \text{ cm}^{-1}$, $\nu|10\rangle_+|0\rangle = 3228 \text{ cm}^{-1}$, $\nu|10\rangle_-|0\rangle = 3240 \text{ cm}^{-1}$ of the HCAO model.

The parameter γ'_{12} is calculated from the equation

$$\gamma'_{12} = \nu|10\rangle_-|0\rangle - (\omega_1 - 2\omega_1 x_1) \quad (80)$$

and γ'_{13} is obtained from the calculated frequencies of the in-plane fundamental $|00\rangle|1\rangle$ and the following energy matrix

$$\begin{vmatrix} |10\rangle_+|0\rangle & \omega_1 - 2\omega_1 x_1 - \gamma'_{12} & -\sqrt{2}\gamma'_{13} \\ |00\rangle|1\rangle & -\sqrt{2}\gamma'_{13} & \omega_3 - 2\omega_3 x_3 \end{vmatrix} \quad (81)$$

which involves the two symmetric states $|10\rangle_+|0\rangle$ and $|00\rangle|1\rangle$ and their interaction through γ'_{13} . The *ab initio* calculated fundamental frequencies are higher than the experimental ones but because the present analysis depends only on the differences in frequencies between (CD_2H) $(\text{CD}_3)_2\text{C}_3\text{D}$ and (CH_3) $(\text{CD}_3)_2\text{C}_3\text{D}$, it is expected that the calculated parameters (γ') are as reliable as the ones obtained from experimental frequencies. The analysis yields values of $\gamma'_{12} = 21 \text{ cm}^{-1}$ and $\gamma'_{13} = 25 \text{ cm}^{-1}$

In order to obtain the CH local model parameters for C_6H_{10} , the peak frequencies of the absorption bands in Figures 110 to 113 were fitted to the equation for the transition energy for a one-dimensional anharmonic oscillator:

$$\frac{\Delta E}{\nu} = \omega_i - (\nu + 1)\omega_i x_i \quad (i = 1, 3) \quad (82)$$

where ω_i is the harmonic frequency, $\omega_i x_i$ is the anharmonicity and v is the vibrational quantum number. The sub-index $i=1, 3$ refers to the two C-H_a and one C-H_s oscillators, respectively.

Table 70. Normal modes for C₆H₁₀ calculated at the HF 6-311G(3d,p) level of theory

Symmetry	Normal Mode	IR Intensity	Calculated Frequency	Scaled Frequency	Experimental Frequency
A ₁	v ₁	63	3620	3330	3329
	v ₂	96	3233	2974	2977
	v ₃	32	3170	2916	2889
	v ₄	3	2370	2180	2107
	v ₅	7	1637	1505	1475
	v ₆	1	1557	1432	1363
	v ₇	24	1379	1268	1248
	v ₈	0	951	874	885
	v ₉	2	729	670	691
	v ₁₀	0	409	376	382
A ₂	v ₁₁	0	3232	2974	2974
	v ₁₂	0	1597	1469	1459
	v ₁₃	0	1047	963	995
	v ₁₄	0	202	186	216
E	v ₁₅	56	3239	2980	2978
	v ₁₆	5	3223	2965	2976
	v ₁₇	26	3160	2907	2889
	v ₁₈	6	1620	1490	1475
	v ₁₉	0	1606	1478	1456
	v ₂₀	5	1526	1404	1393
	v ₂₁	5	1341	1233	1205
	v ₂₂	0	1142	1050	1032
	v ₂₃	0	1008	927	930
	v ₂₄	40	805	740	634
	v ₂₅	12	607	558	542
	v ₂₆	0	383	352	362
	v ₂₇	0	299	275	287
	v ₂₈	1	202	186	181

Table 71. Normal modes for C₆H₁₀ calculated at DFT (B3LYP) 6-311G(d,p)

Symmetry	Normal Mode	IR Intensity	Calculated Frequency	Scaled Frequency	Experimental Frequency
A ₁	v ₁	65	3477	3338	3329
	v ₂	68	3098	2975	2977
	v ₃	28	3031	2910	2889
	v ₄	5	2209	2121	2107
	v ₅	9	1518	1458	1475
	v ₆	2	1429	1371	1363
	v ₇	22	1272	1221	1248
	v ₈	1	892	856	885
	v ₉	1	693	667	691
	v ₁₀	0	382	367	382
A ₂	v ₁₁	0	3102	2977	2974
	v ₁₂	0	1477	1418	1459
	v ₁₃	0	967	929	995
	v ₁₄	0	218	209	216
E	v ₁₅	42	3106	2982	2978
	v ₁₆	5	3091	2968	2976
	v ₁₇	23	3024	2903	2889
	v ₁₈	8	1501	1441	1475
	v ₁₉	0	1489	1429	1456
	v ₂₀	7	1397	1341	1393
	v ₂₁	6	1224	1175	1205
	v ₂₂	0	1050	1008	1032
	v ₂₃	0	930	893	930
	v ₂₄	44	672	645	634
	v ₂₅	6	556	534	542
	v ₂₆	1	353	339	362
	v ₂₇	0	271	260	287
	v ₂₈	1	179	172	181

Figure 119 shows a plot of Eq (82) for the two different CH oscillators in C₆H₁₀. The upper line corresponds to the C-H_a oscillators and from its intercept and slope ω_l and $\omega_l x_l$ are obtained, respectively. For the C-H_s oscillators, ω_3 and $\omega_3 x_3$ values were

obtained from intercept and slope of the lower line. The points for $\nu=2$ were not included in the fit. The local mode parameters are presented in Table 72.

Table 72. Local mode parameters. *ab initio* calculated isolated frequencies ν_{CH}^{iso}

	(cm^{-1})	C-H _a	C-H _s
Local Mode parameters	ω_i $\omega_i x_i$	3099 66.2	3091 67.1
HF/ 6-311G (3d,p)	ν_{CH}^{iso}	3219	3199
	$\nu_{ 00\rangle 1\rangle}$		3163
	$\nu_{ 10\rangle_+ 0\rangle}$	3228	
	$\nu_{ 10\rangle_- 0\rangle}$	3240	
	γ'_{12}		21
	γ'_{13}	25	
DFT (B3LYP) 6-311G(d,p)	ν_{CH}^{iso}	3216	3197
	$\nu_{ 00\rangle 1\rangle}$		3163
	$\nu_{ 10\rangle_+ 0\rangle}$	3225	
	$\nu_{ 10\rangle_- 0\rangle}$	3236	
	γ'_{12}		20
	γ'_{13}	23	

The matrices for each vibrational manifold from $\nu=1$ to 5 were obtained using the local mode parameters and the coupling parameters γ'_{12} and γ'_{13} (see Appendix B)^{217, 218}. The frequencies corresponding to pure local modes were calculated from the matrices. Table 73 summarizes the experimental and calculated peak positions.

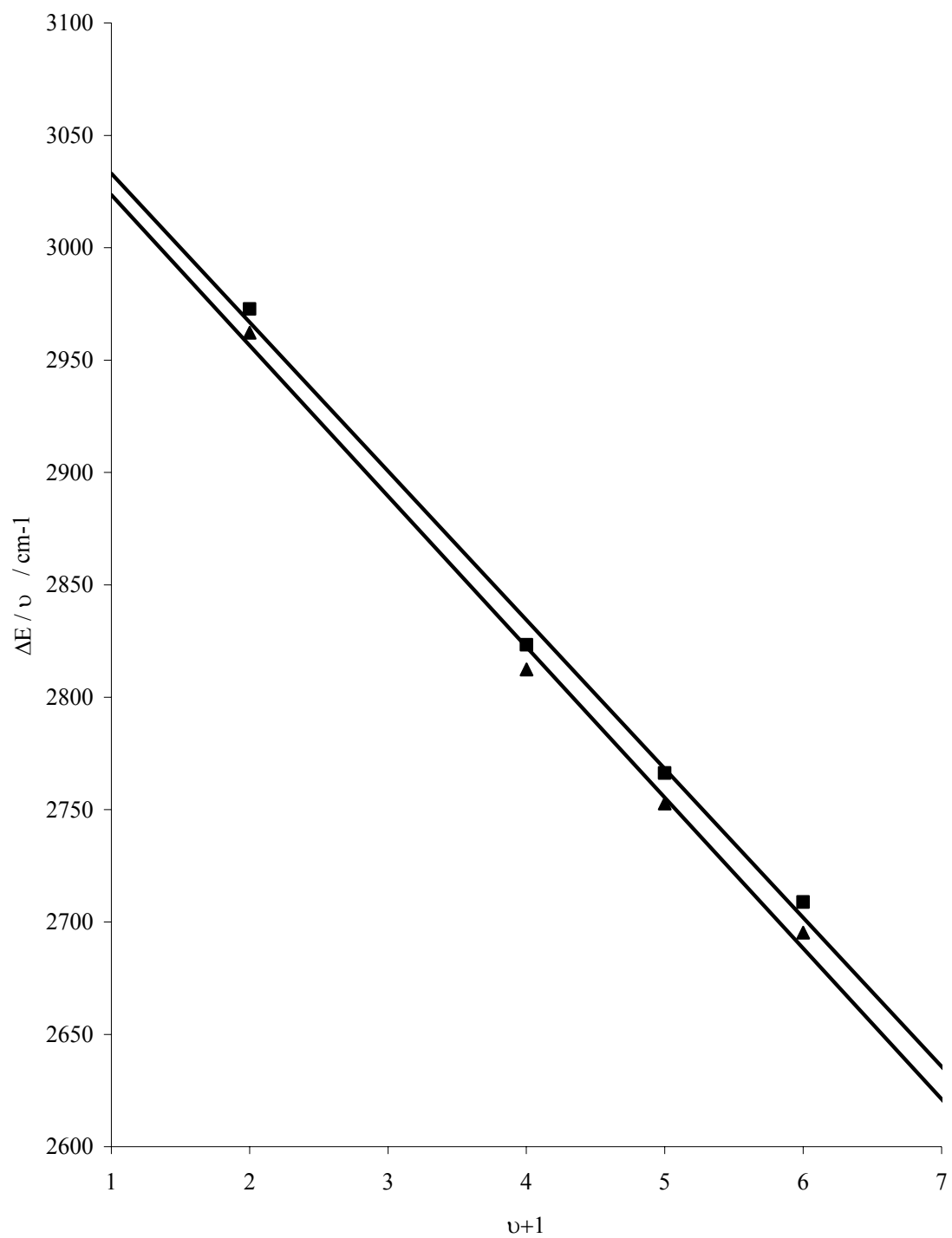


Figure 119. Birge-Sponer plot of the C-H_a and C-H_s oscillators in C₆H₁₀ Marker ■ = CH_a data and Marker ▲ = CH_s data.

Table 73. Calculated and experimental vibrational frequencies (cm⁻¹)

ν	Assignment	HCAO		Observed Frequencies
		HF	DFT	
1	$ 00\rangle 1\rangle$	2916	2917	2889
1	$ 10\rangle_+ 0\rangle$	2987	2985	2978
1	$ 10\rangle_- 0\rangle$	2987	2987	
2	$ 00\rangle 2\rangle$	5753	5755	5731
2	$ 20\rangle_+ 0\rangle$	5785	5785	5788
2	$ 20\rangle_- 0\rangle$	5792	5792	5795
2	$ 10\rangle_+ 1\rangle$	5915	5915	5908
2	$ 10\rangle_- 1\rangle$	5952	5952	5939
2	$ 11\rangle 0\rangle$	5961	5960	5948
3	$ 00\rangle 3\rangle$	8454	8455	8445
3	$ 30\rangle_+ 0\rangle$	8487	8488	8468
3	$ 30\rangle_- 0\rangle$	8489	8490	
3	$ 10\rangle_+ 2\rangle$	8672	8674	8650
3	$ 20\rangle_- 1\rangle$	8715	8717	
3	$ 21\rangle_+ 0\rangle$	8729	8730	8737
3	$ 10\rangle_- 2\rangle$	8802	8801	8780
3	$ 20\rangle_+ 1\rangle$	8805	8803	
3	$ 21\rangle_- 0\rangle$	8829	8827	
3	$ 11\rangle 1\rangle$	8920	8919	
4	$ 00\rangle 4\rangle$	11010	11012	11011
4	$ 40\rangle_+ 0\rangle$	11060	11060	11064
4	$ 40\rangle_- 0\rangle$	11073	11072	
4	$ 10\rangle_+ 3\rangle$	11371	11375	11394
4	$ 10\rangle_- 3\rangle$	11407	11410	
4	$ 30\rangle_+ 1\rangle$	11413	11414	

Continued. Table 73. Calculated and experimental vibrational frequencies (cm⁻¹)

ν	Assignment	HCAO		Observed Frequencies
		HF	DFT	
4	$ 30\rangle_- 1\rangle$	11448	11448	
4	$ 31\rangle_+ 0\rangle$	11459	11460	
4	$ 31\rangle_- 0\rangle$	11483	11483	
4	$ 20\rangle_+ 2\rangle$	11603	11601	
4	$ 20\rangle_- 2\rangle$	11624	11621	
4	$ 22\rangle 0\rangle$	11634	11634	
4	$ 21\rangle_+ 1\rangle$	11667	11667	
4	$ 11\rangle 2\rangle$	11780	11777	11766
4	$ 21\rangle_- 1\rangle$	11780	11779	
5	$ 00\rangle 5\rangle$	13432	13433	13470
5	$ 50\rangle_+ 0\rangle$	13497	13498	13550
5	$ 50\rangle_- 0\rangle$	13497	13498	
5	$ 10\rangle_+ 4\rangle$	13948	13950	
5	$ 10\rangle_- 4\rangle$	13986	13989	
5	$ 40\rangle_+ 1\rangle$	13987	13989	
5	$ 40\rangle_- 1\rangle$	13995	13996	
5	$ 41\rangle_+ 0\rangle$	14038	14038	
5	$ 41\rangle_- 0\rangle$	14043	14042	
5	$ 20\rangle_+ 3\rangle$	14203	14204	
5	$ 20\rangle_- 3\rangle$	14216	14217	
5	$ 32\rangle_+ 0\rangle$	14240	14241	
5	$ 30\rangle_+ 2\rangle$	14351	14349	
5	$ 30\rangle_- 2\rangle$	14357	14355	
5	$ 11\rangle 3\rangle$	14357	14358	
5	$ 32\rangle_- 0\rangle$	14371	14370	
5	$ 31\rangle_+ 1\rangle$	14426	14425	
5	$ 31\rangle_- 1\rangle$	14453	14451	

Continued. Table 73. Calculated and experimental vibrational frequencies (cm⁻¹)

ν	Assignment	HCAO		Observed Frequencies
		HF	DFT	
5	$ 21\rangle_+ 2\rangle$	14559	14557	
5	$ 21\rangle_- 2\rangle$	14597	14597	
5	$ 22\rangle 1\rangle$	14629	14625	

The local mode states are labeled $|\nu_1\nu_2\rangle_\pm|\nu_3\rangle$. Pure local mode assignments corresponding to the least intense low energy overtone (C-H_s) are denoted by $|00\rangle|\nu\rangle$ and assignments corresponding to the most intense high energy overtone (C-H_a) are denoted by $|\nu 0\rangle_\pm|0\rangle$, where $\nu=3-5$ is the vibrational quantum number. Assignments of pure local modes were also confirmed with the help of the Birge-Sponer plot.

Overtone Spectroscopy of (Trimethylsilyl)acetylene

Overtone spectra of (Trimethylsilyl)acetylene, C₅SiH₁₀, for the acetylenic and methyl C-H stretch were recorded between 3250 and 13900 cm⁻¹. Spectral regions were measured using Fourier transform spectrophotometer with a resolution of 1 cm⁻¹ and using a white cell with a path length of 6.6 m. As in C₆H₁₀, higher level overtones spectra ($\nu=4$) for the acetylenic and ($\nu=5$) for the methyl C-H stretches, were obtained with the PS-CRD technique. The path length and resolution used were 4.34 km and 0.17cm⁻¹, respectively. The spectra were taken at 295 and 240K. Birge-Sponer plots were constructed for each C-H oscillator and local-mode parameters were calculated. S_0 values were obtained from the data obtained

Acetylenic C-H stretch

Individual overtone regions of the acetylene C-H stretch of C_5SiH_{10} are presented in Figures 120 to 123. In general, these spectra show the same features exhibited by C_6H_{10} spectra (see Figures 100-102). A strong narrow acetylenic C-H absorption, as well as a small peak to the low-frequency side are shown. This weaker band has been identified as a hot band. It arises from nonresonant intramolecular coupling of the acetylenic C-H stretch and the $\equiv C-H$ bending mode. Equation (73) was used to fit the frequencies of the hot band $\nu_{24} \rightarrow (\nu_{24} + \nu_1)$, using the notation in Table 74.²²⁷ The fundamental region and the small peaks observed at $\nu=2-4$ were used for the plot. The fit is shown in Figure 124 (lower line). The good linear fit indicates that these absorptions are all due to the hot bands $\nu_{24} \rightarrow (\nu\nu_{24} + \nu_1)$ and that this absorption can be described as a local mode. The ν_1 overtones were analyzed based on Eq(72). A plot of $\Delta E/\nu$ versus ν was constructed and is shown in Figure 124 (upper line). The resulting good linear fit indicates that the vibration can be adequately described by a two-parameter local-mode model. Table 75 summarizes observed frequencies and calculated frequencies by use of eq (72) and (73). Also, values for the local parameters; ω_l , X_{1l} , and $X_{l\ 24}$ are shown.

It was found that the line width of the C_5SiH_{10} spectra is significantly narrower than the tert-butylacetylene spectra. This feature has been observed before for the fundamental and first overtone of acetylenic C-H stretch of C_6H_{10} and C_5SiH_{10} in studies of intramolecular vibrational relaxation (IVR)²¹³⁻²¹⁵

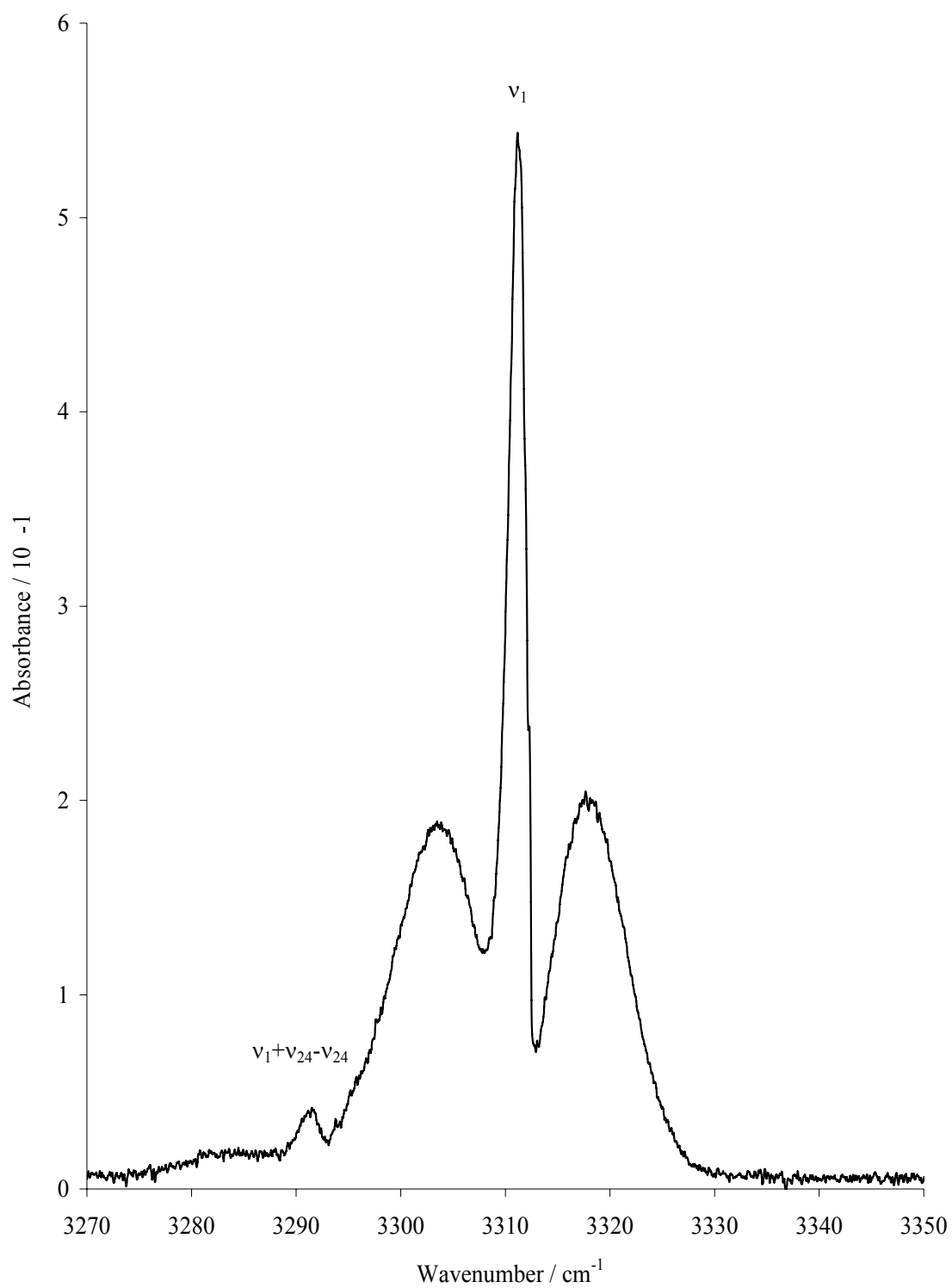


Figure 120. Absorption spectrum of the fundamental ($\Delta v=1$) acetylenic C-H stretch of C_5SiH_{10} at 295K. Pressure = 0.5Torr.

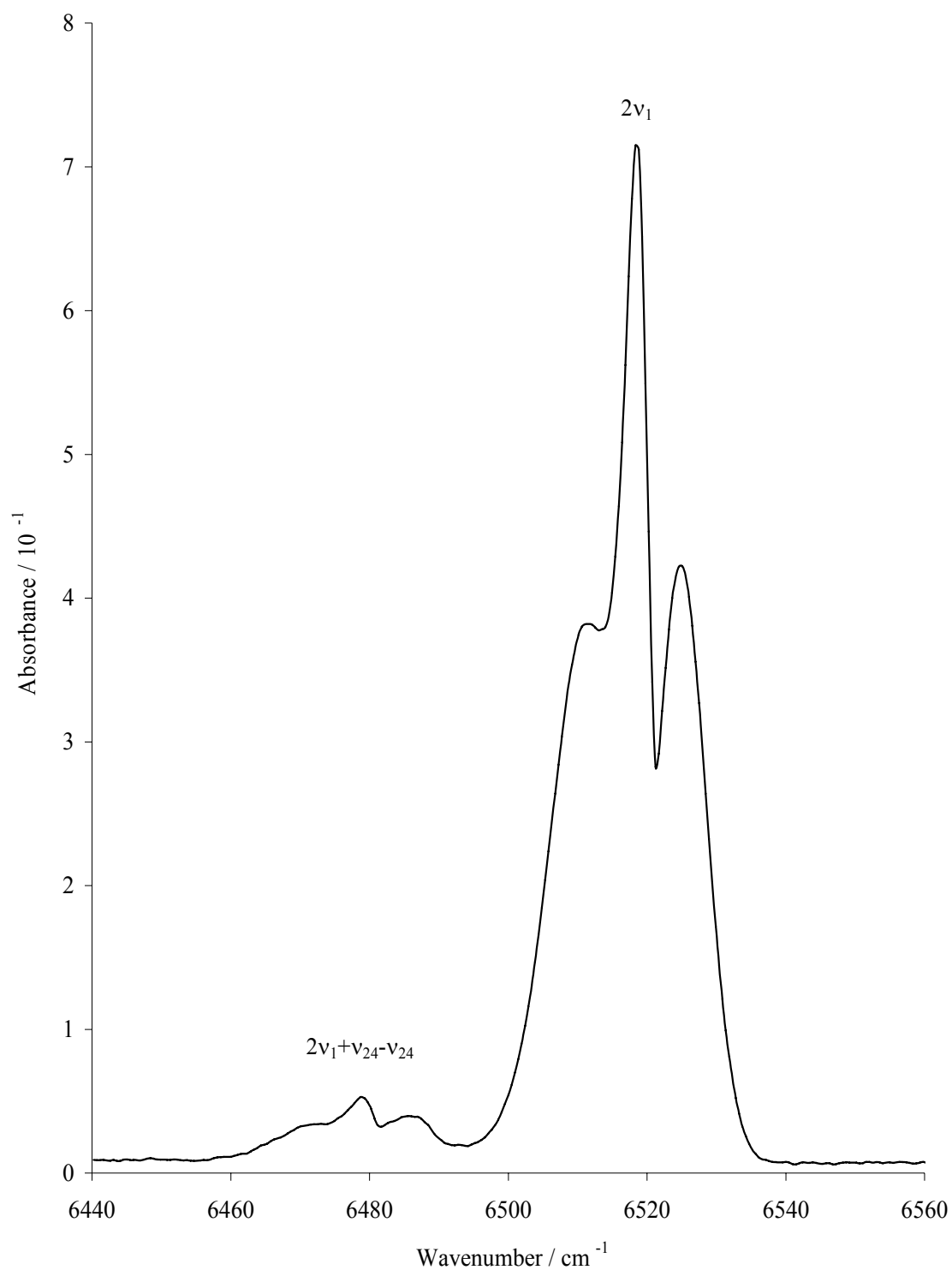


Figure 121. Absorption spectrum of the first overtone ($\Delta v=2$) acetylenic C-H stretch of C_5SiH_{10} at 295K. Pressure = 28 Torr.

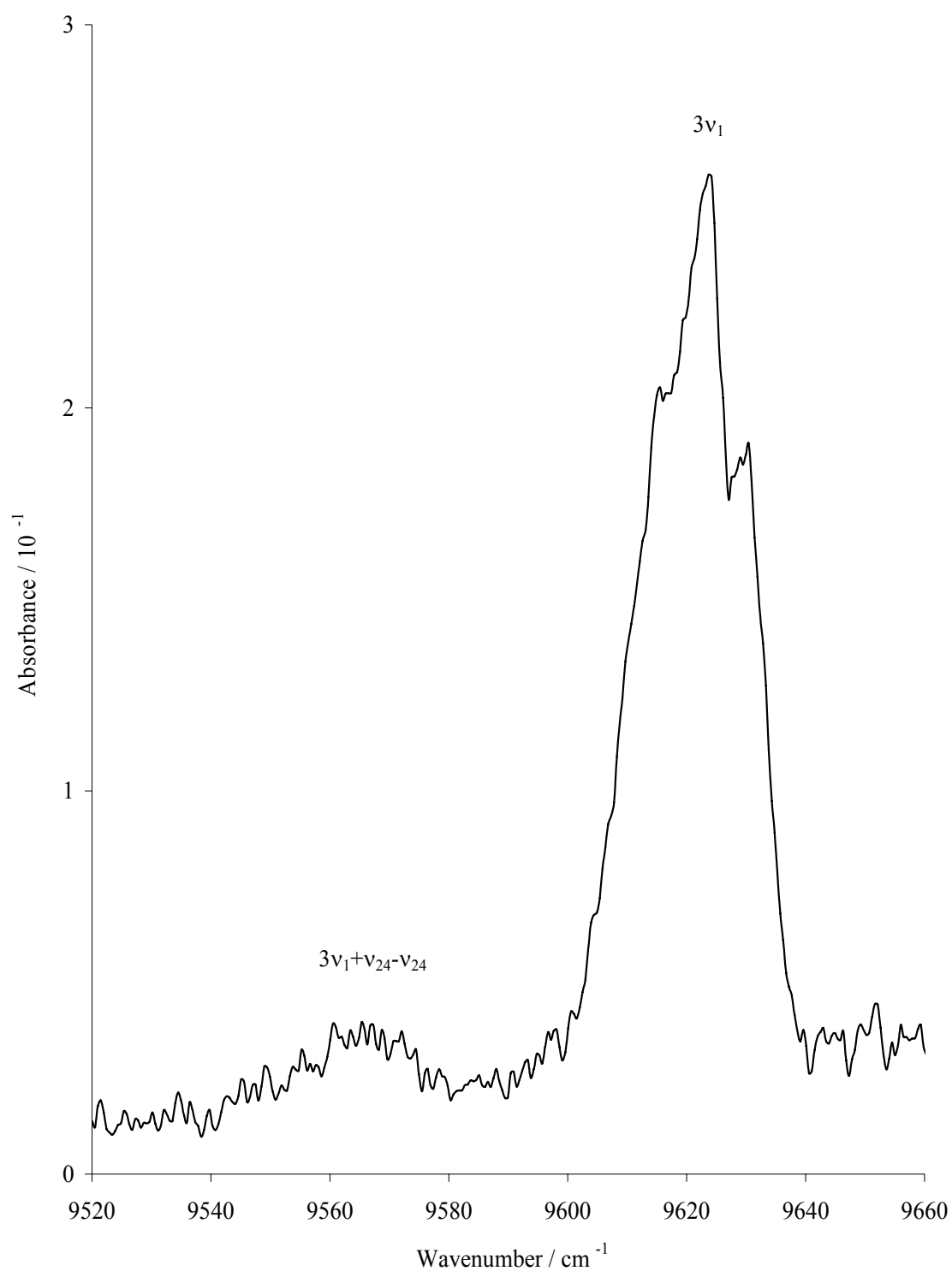


Figure 122. Absorption spectrum of the second overtone ($\Delta v=3$) acetylenic C-H stretch of C_5SiH_{10} at 295K. Pressure = 180 Torr

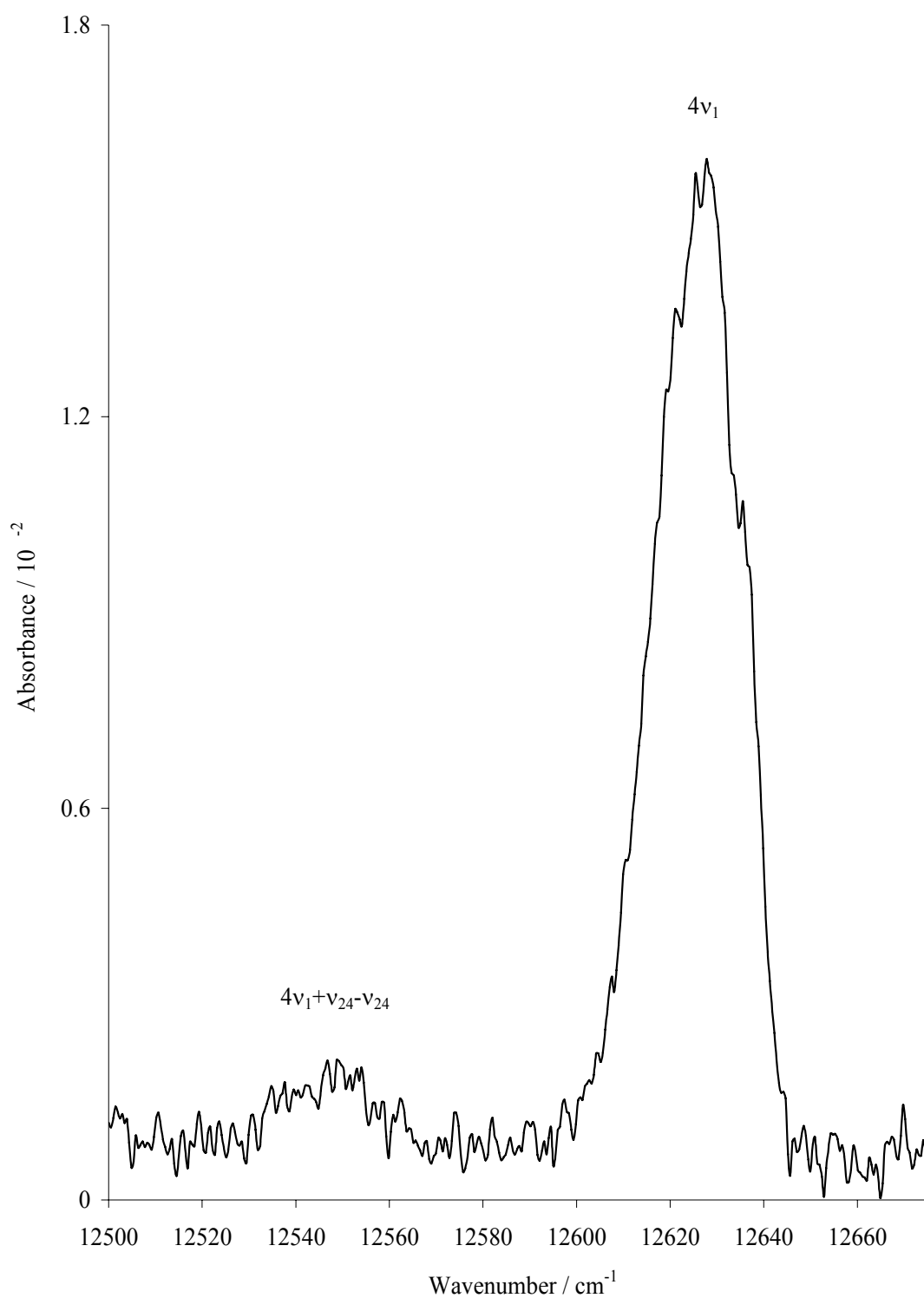


Figure 123. Absorption spectrum of the third overtone ($\Delta v=4$) acetylenic C-H stretch of C_5SiH_{10} at 295K. Pressure = 180 Torr.

The observation of dramatically different lifetimes in both molecules was explained first by the increase of the mass of the central atom.²²⁸⁻²³⁰ However, quantum calculations for the intramolecular vibrational energy redistribution and absorption spectra of the first two excited states of the acetylenic CH stretch vibration in the polyatomic molecules $(CX_3)_3YCCH$, where $X=H$ or D and $Y=C$ or Si found that an increase of the mass alone of the central atom from C to Si cannot explain the observed difference in the C and Si molecules.²¹⁶

Moreover, this theoretical study found that a model of intramolecular vibrational relaxation based on the assumption of sequential off-resonance transitions via third and fourth order vibrational couplings (as opposed to direct high order couplings) is in agreement with experimental results on spectral linewidths. In a semiclassical limit this type of relaxation corresponds to a dynamic tunneling in phase space. It was shown that the local density of resonances of third and fourth order, rather than the total density of states, plays a central role for the relaxation. It is found that in the Si molecule an accidental absence of appropriate resonances results in a bottleneck in the initial stages of relaxation. As a result, an almost complete localization of the initially prepared excitation occurs. Vibrational states for C_6H_{10} and C_5SiH_{10} molecules, $v = 1$, are shown in Figure 125.

Because of the extremely high density of states in higher tiers and the limited resolution of the plot only the first few tiers are shown. In Figure 125 a qualitative difference can be seen in the densities of coupled states in the first tiers for the C and Si molecules.

Table 74. Fundamental Vibrational Frequencies of C₅SiH₁₀

Assignment	Symmetry	Mode	Frequency / cm ⁻¹
ν_1	A ₁	acetylenic C-H stretch	3312
ν_2	A ₁	methyl C-H a-stretch	2966
ν_3	A ₁	methyl C-H s-stretch	2900
ν_4	A ₁	C $\equiv$ C stretch	2037
ν_5	A ₁	H-C-H a-bend	1420
ν_6	A ₁	H-C-H s-bend	1265
ν_7	A ₁	Si-C stretch	654
ν_8	A ₁	CH ₃ rock	860
ν_9	A ₁	Si - C $\equiv$ C stretch	557
ν_{10}	A ₁	Si-C ₃ bend	218
ν_{11}	A ₂	CH ₃ a- stretch	2974
ν_{12}	A ₂	CH ₃ a- bend	1459
ν_{13}	A ₂	CH ₃ rock	995
ν_{14}	A ₂	CH ₃ twist	----
ν_{15}	E	acetylenic C-H stretch	2966
ν_{16}	E	methyl C-H a-stretch	2966
ν_{17}	E	methyl C-H s-stretch	2900
ν_{18}	E	CH ₃ a-bend	1420
ν_{19}	E	CH ₃ a-bend	1420
ν_{20}	E	CH ₃ s-bend	1255
ν_{21}	E	Si-C a-stretch	700
ν_{22}	E	CH ₃ a-rock	845
ν_{23}	E	CH ₃ a-rock	765
ν_{24}	E	$\equiv$ C - H bend	680
ν_{25}	E	Si-C ₃ a-bend	236
ν_{26}	E	Si - C $\equiv$ C rock	132
ν_{27}	E	CH ₃ twist	----
ν_{28}	E	Si - C $\equiv$ C bend	350

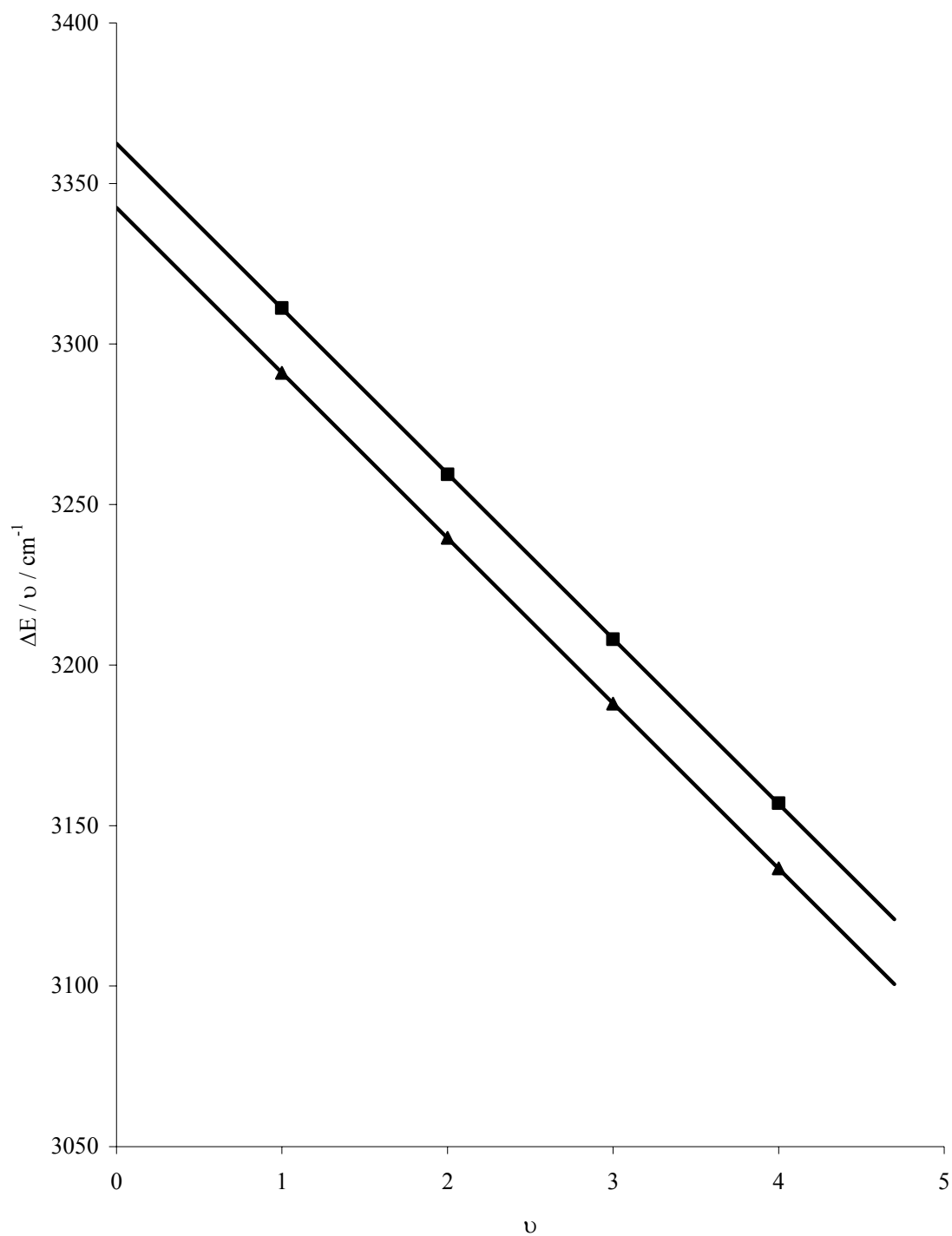


Figure 124. Birge-Sponer plot of the acetylenic C-H stretch of $\text{C}_5\text{SiH}_{10}$ and an associated hot-band transition. Marker ■ represents the νv_1 overtones and Marker ▲ represents the $\nu_{24} \rightarrow (\nu_{24} + \nu v_1)$ hot bands.

Table 75. Observed and Calculated Frequencies, ω_l , X_{ll} and $X_{l\ 24}$ (cm^{-1}) for the Acetylenic CH stretch of $\text{C}_5\text{SiH}_{10}$.

ν	Obs. Freq	Calc freq	Assigned Transition
1	3291.00	3291.05	$\nu_{24} \rightarrow (\nu_{24} + \nu_1)$
	3311.23	3311.08	$0 \rightarrow \nu_1$
2	6479.27	6479.19	$\nu_{24} \rightarrow (\nu_{24} + 2\nu_1)$
	6518.81	6519.33	$0 \rightarrow 2\nu_1$
3	9564.00	9564.423	$\nu_{24} \rightarrow (\nu_{24} + 3\nu_1)$
	9624.17	9624.74	$0 \rightarrow 3\nu_1$
4	12546.81	12546.75	$\nu_{24} \rightarrow (\nu_{24} + 4\nu_1)$
	12627.81	12627.31	$0 \rightarrow 4\nu_1$
Harmonic Frequency	3362.5 ± 0.3	Anharmonic constants	-51.4 ± 0.4
	Anharmonic interaction constant	-20.0 ± 0.3	

Despite the fact that the total density of states in the Si molecule is approximately thirty times higher in this energy region, the local density of directly coupled states in the Si molecule is found to be substantially smaller than in the C molecule. A particularly low number of strongly coupled states in the tier 3 (the light state is tier zero) of the Si molecule produces a bottleneck for the energy transfer from the acetylenic CH vibrational state. For the C molecule there are already a number of quasi-resonant states in tier 3, as one can see in Figure 125 (a).

The third ($\Delta\nu=4$) acetylenic C-H stretch of $\text{C}_5\text{SiH}_{10}$ spectra were obtained at 295 and 240K using the PS-CRD technique. Figure 126 displays the spectra of 4 Torr of $\text{C}_5\text{SiH}_{10}$ at 295 K and 240 K.

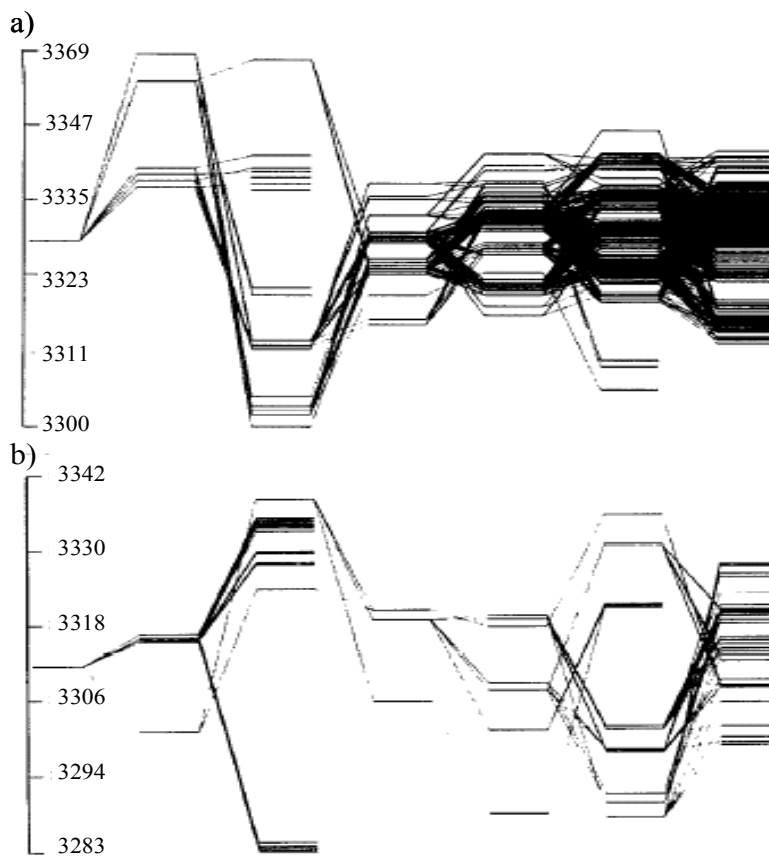


Figure 125. First six tiers of sequentially coupled zero-order states in (a) $(\text{CH}_3)_3\text{CCCH}$ and in (b) $(\text{CH}_3)_3\text{SiCCH}$. The first state on the left is the CH vibration, $\nu=1$.²¹⁶

In the low temperature spectrum (upper), the hot band intensity is reduced dramatically. The low energy shoulder of $4\nu_1$ band is reduced at 240K. This is expected since the hot bands contribute the most on this side, but the high energy shoulder shows little change at the two temperatures. A pressure series at 295K is presented in Figure 127. Table 76 reports the density, integrated absorption band, and band strength values for each individual pressure. Also, the data obtained from the FT-spectra were included. The S_0 value reported is found by plotting S vs. ρ in Figure 128. The S_0 value equal to $(2.20 \pm 0.07) \times 10^{-22} \text{ cm}^2 \text{ cm}^{-1} \text{ molecules}^{-1}$ is a lower than the S_0 value

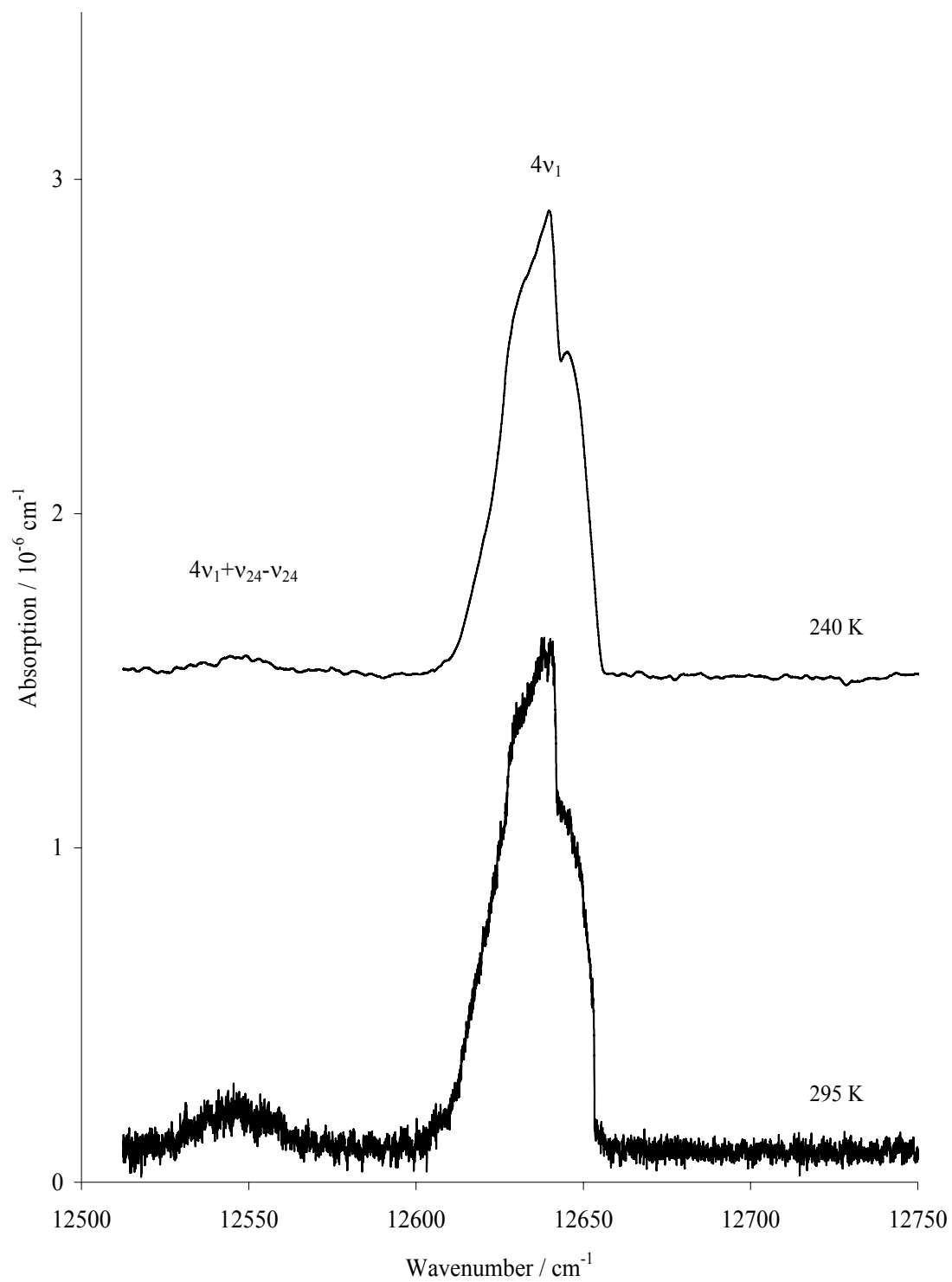


Figure 126. $(\Delta v=4)$ acetylenic C-H stretch of C_5SiH_{10} at 240 K- top, and at 295K- bottom

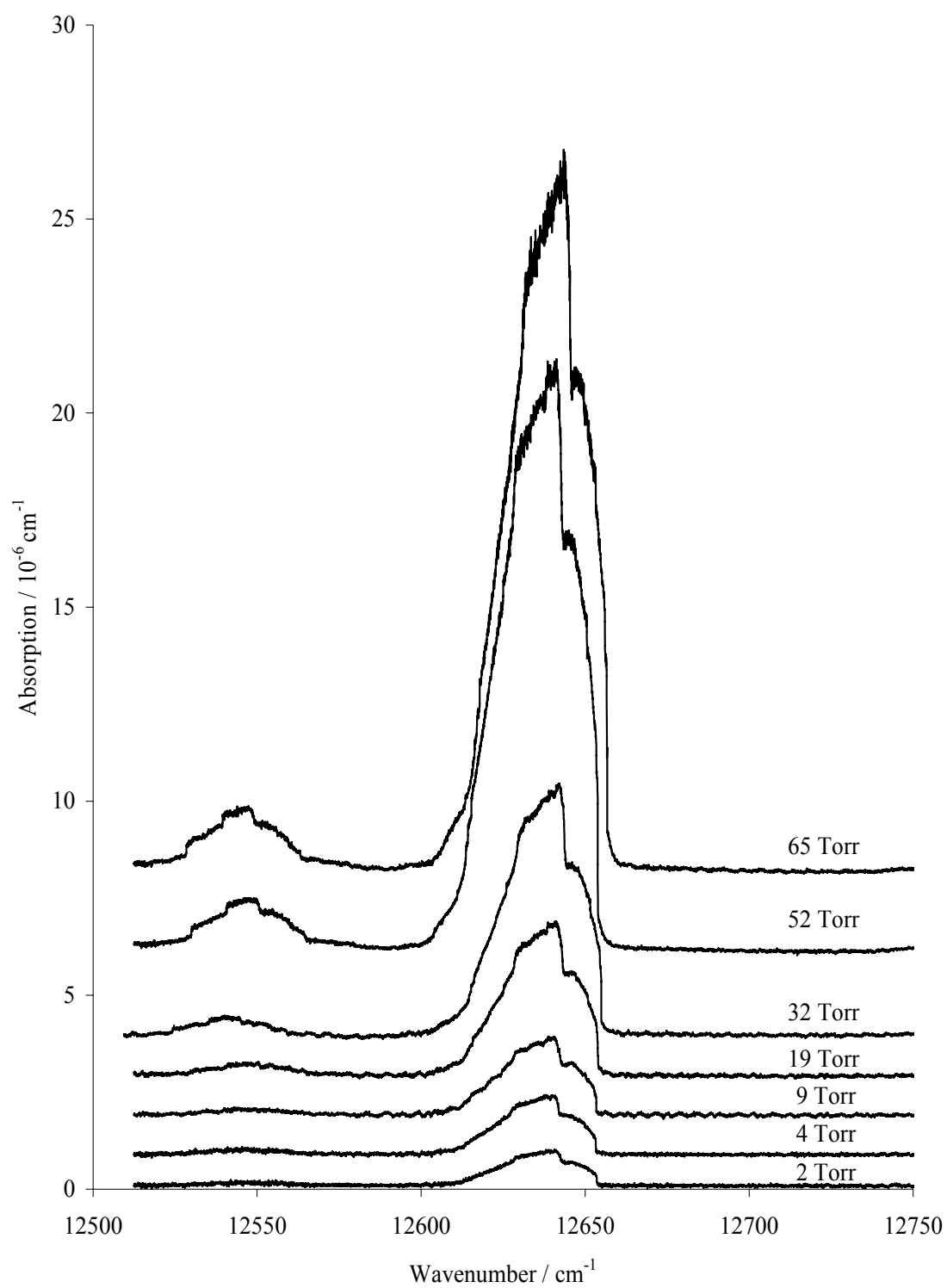
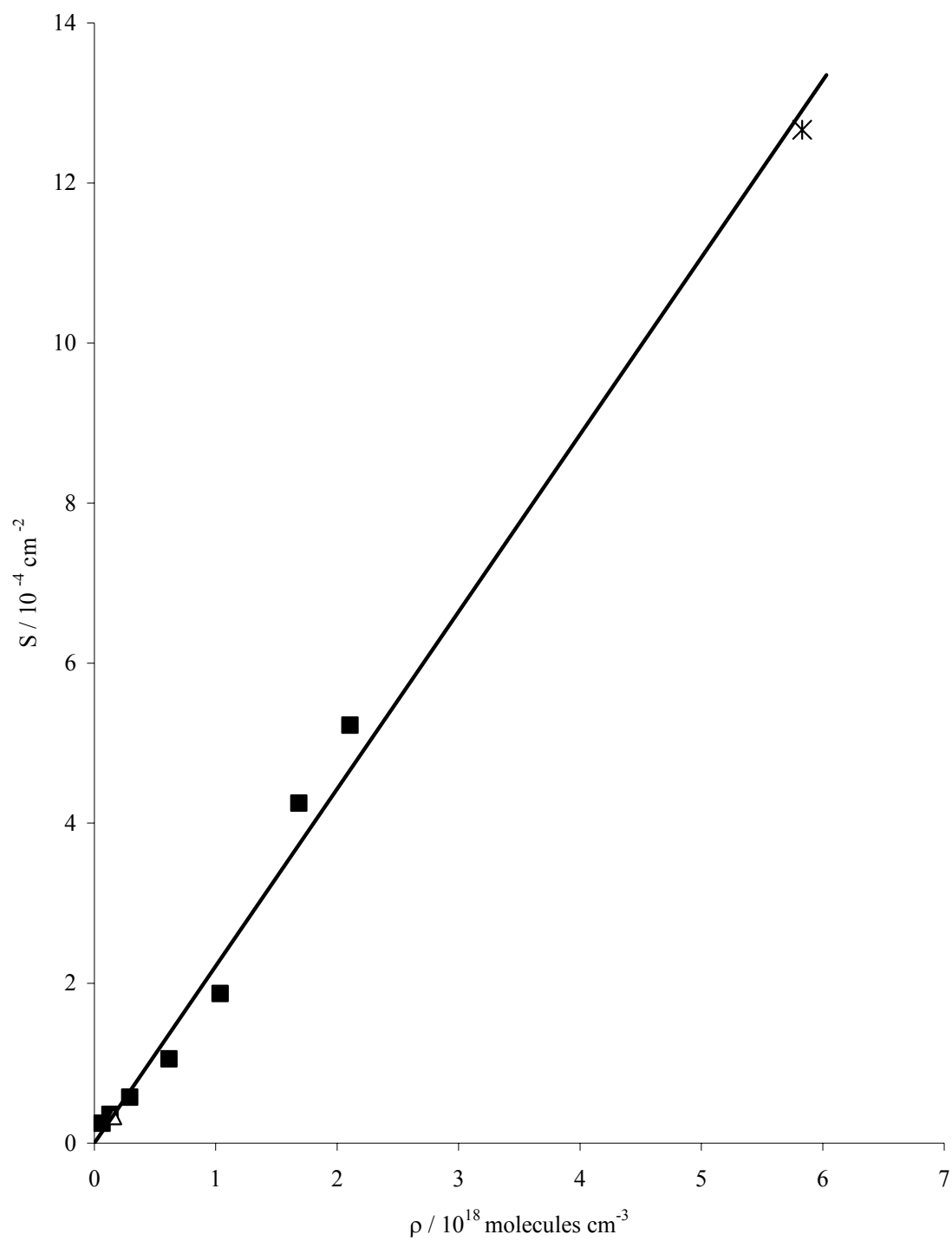


Figure 127. $(\Delta v=4)$ acetylenic C-H stretch of C_6H_{10} . Absorption pressure series at 295K



$$S_0 = (2.20 \pm 0.07) \times 10^{-22} \text{ cm}^2 \text{ cm}^{-1} \text{ molecules}^{-1}$$

$$R^2 = 0.993$$

Figure 128. ($\Delta\nu=4$) acetyl C-H stretch of $\text{C}_5\text{SiH}_{10}$. S vs. ρ . Slope is S_0 . Marker ■ = measurements at 295 K, Marker × = FT-spectrum, Marker Δ = measurement at 240 K.

Table 76. ($\Delta\nu=4$) acetylenic C-H of C_5SiH_{10} at 295 and 240K. Pressure, ρ , S and S_0

T Torr	Pressure Torr	ρ $10^{18} \text{ molecules cm}^{-3}$	S 10^{-4} cm^{-2}	S_0 $10^{-22} \text{ cm}^2 \text{ cm}^{-1} \text{ molecule}^{-1}$
295 K	65	2.105	5.22	2.48
	52	1.684	4.25	2.52
	32	1.037	1.87	1.80
	19	0.615	1.05	1.71
	9	0.292	0.57	1.97
	4	0.130	0.36	2.78
	2	0.065	0.25	3.83
	180	5.831	12.66	2.17
240 K	4	0.157	0.33	2.13
Avg				2.20 ± 0.07

found for CH_3CCH and $(CH_3)_3CCCH$. That is in agreement with the reduction of the linewidth given by the change of central atom.

Methyl C-H Stretch

Also, the fundamental and overtones spectra of the methyl C-H stretch of C_5SiH_{10} were obtained. Figures **129** to **133** show the spectra correspond to transitions to levels 1, 2, 3, 4 and 5 of the methyl C-H stretching. Since (Trimethylsilyl)acetylene is also a symmetry top molecule that belongs to the point group C_{3v} , it is expected that this molecule will show overtone bands in the methyl C-H regions corresponding to the two non-equivalent CH bonds in the methyl groups. In Figures 132 and **133** the two bands for two non-equivalent CH bonds in the methyl groups are shown. The decrease in the line width of the absorption bands is also observed in these transitions. An

unusual feature occurs in the absorption spectrum of the ($\Delta v=5$) methyl C-H stretch, where an absorption immediately to high frequency side of the C-H_a overtone may be seen. Since this feature is not present in the $\Delta v=5$ spectrum of C₆H₁₀ and even in the fundamental and lower overtone spectra of C₅SiH₁₀, it is expected that this absorption band correspond to a combination band that involve at least one mode where the silicon is involved. This band can be assigned as local mode-normal mode combination band $|00\rangle|4\rangle + \nu_{26}$, where ν_{26} is the Si - C $\equiv$ C rock mode.

Using the band absorption frequencies from Figures **129** to **133**, Birge-Spooner plots were obtained for the C-H_a and C-H_s oscillators. They are shown in Figure 134. Table 77 summarizes observed frequencies and calculated frequencies for C-H_a and C-H_s. Also, it is shown values for the local parameters; ω_l , $\omega_l x_l$ for CH_a and ω_3 , $\omega_3 x_3$ for CH_s. As in Figure 26, in Figure 134 the points for $v=2$ were not included in the fit.

The Fermi resonance between $|00\rangle|4\rangle$ and $|00\rangle|4\rangle + \nu_{26}$ is analyzed using the procedure explained in Chapter 5. The perturbed energies are given by equation (60)¹⁸⁶ where the subscripts, in this case, are defined as $n \equiv |00\rangle|4\rangle + \nu_{26}$ and $i \equiv |00\rangle|4\rangle$. From this equation the magnitude of the perturbation, W_{ni} , can be obtained. Frequency of the perturbed combination band measured from Figure **133** is $E_+ = 13570.36 \text{ cm}^{-1}$ and $E_n^0 = 13551.9 \text{ cm}^{-1}$. The magnitude of the perturbation is $W_{ni} = 25 \text{ cm}^{-1}$.

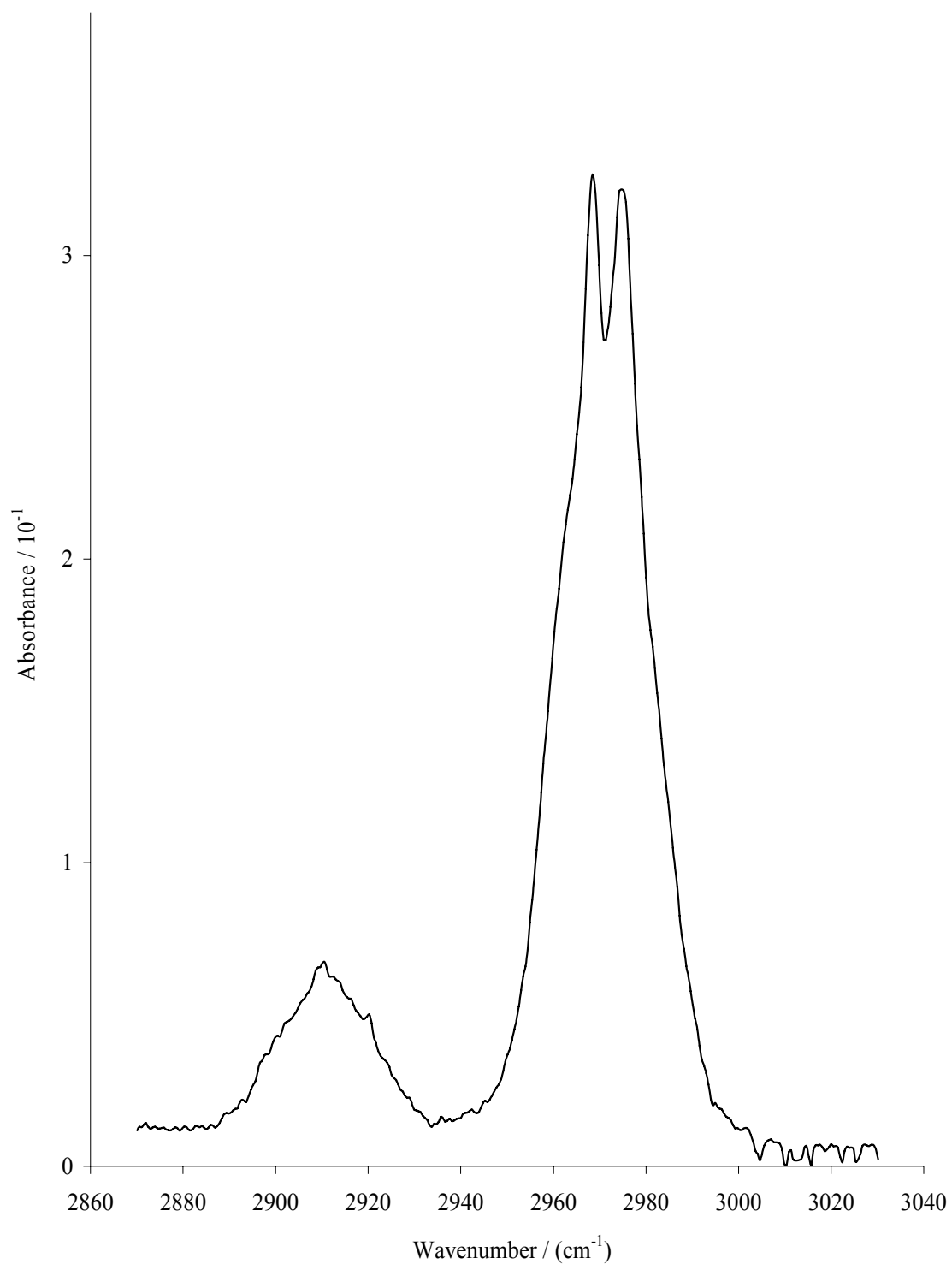


Figure 129. Absorption spectrum of the fundamental ($\Delta v=1$) methyl C-H stretch of C_5SiH_{10} at 295K. Pressure = 0.5Torr.

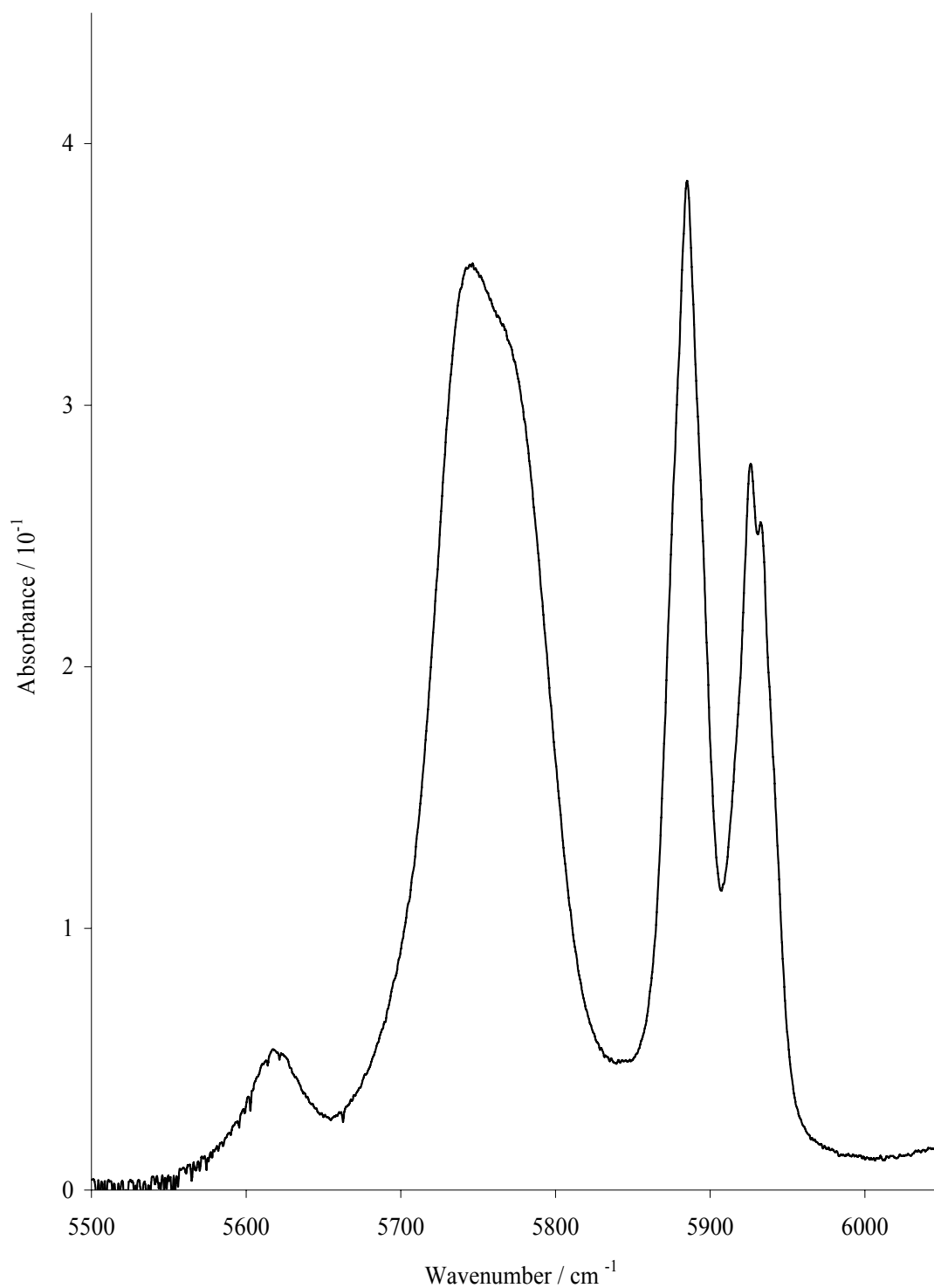


Figure 130. Absorption spectrum of the first overtone ($\Delta\nu = 2$) methyl C-H stretch of C_5SiH_{10} at 295K. Pressure = 28 Torr.

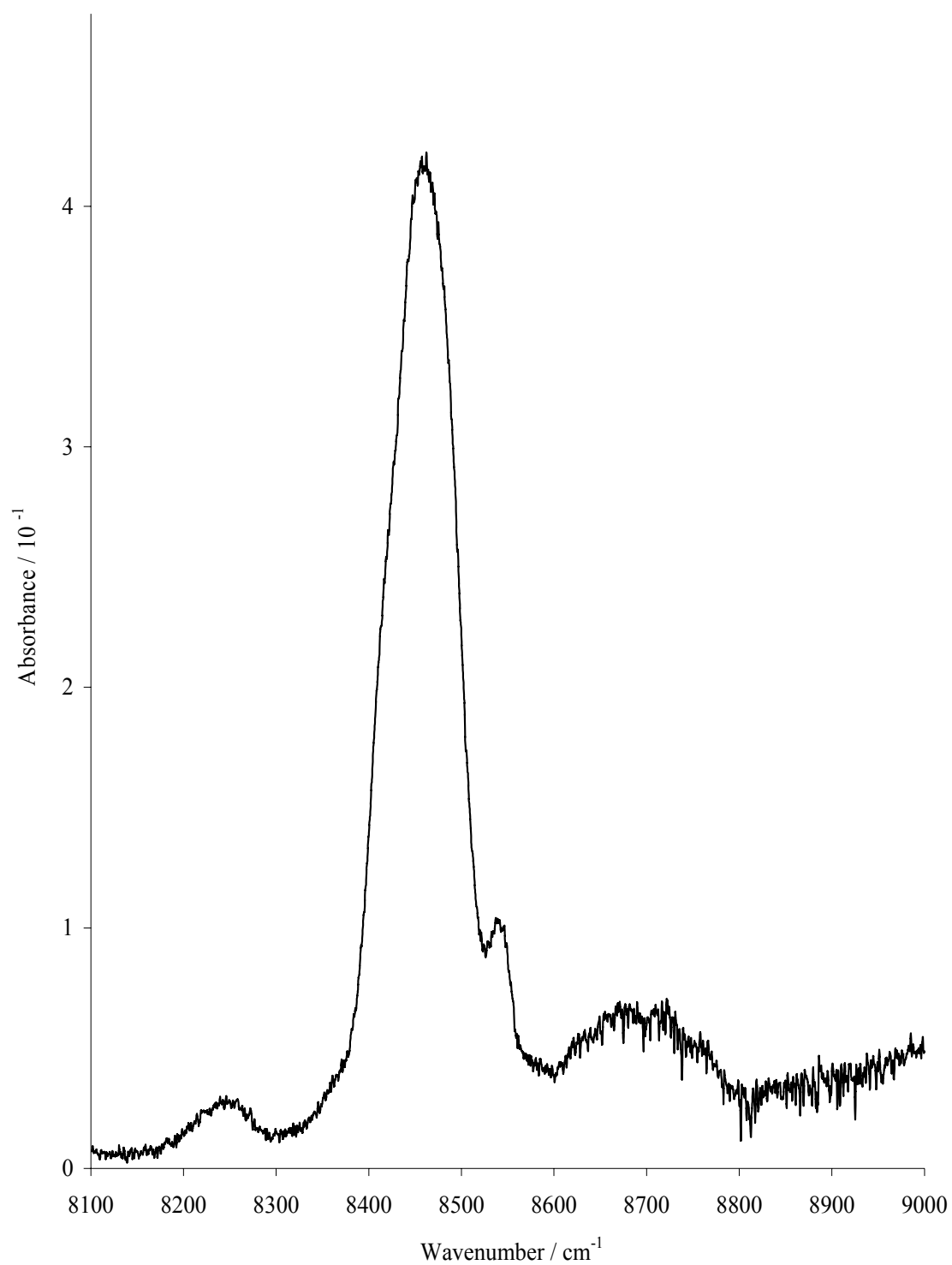


Figure 131. Absorption spectrum of the second overtone ($\Delta\nu = 3$) methyl C-H stretch of C_5SiH_{10} at 295K. Pressure = 180 Torr

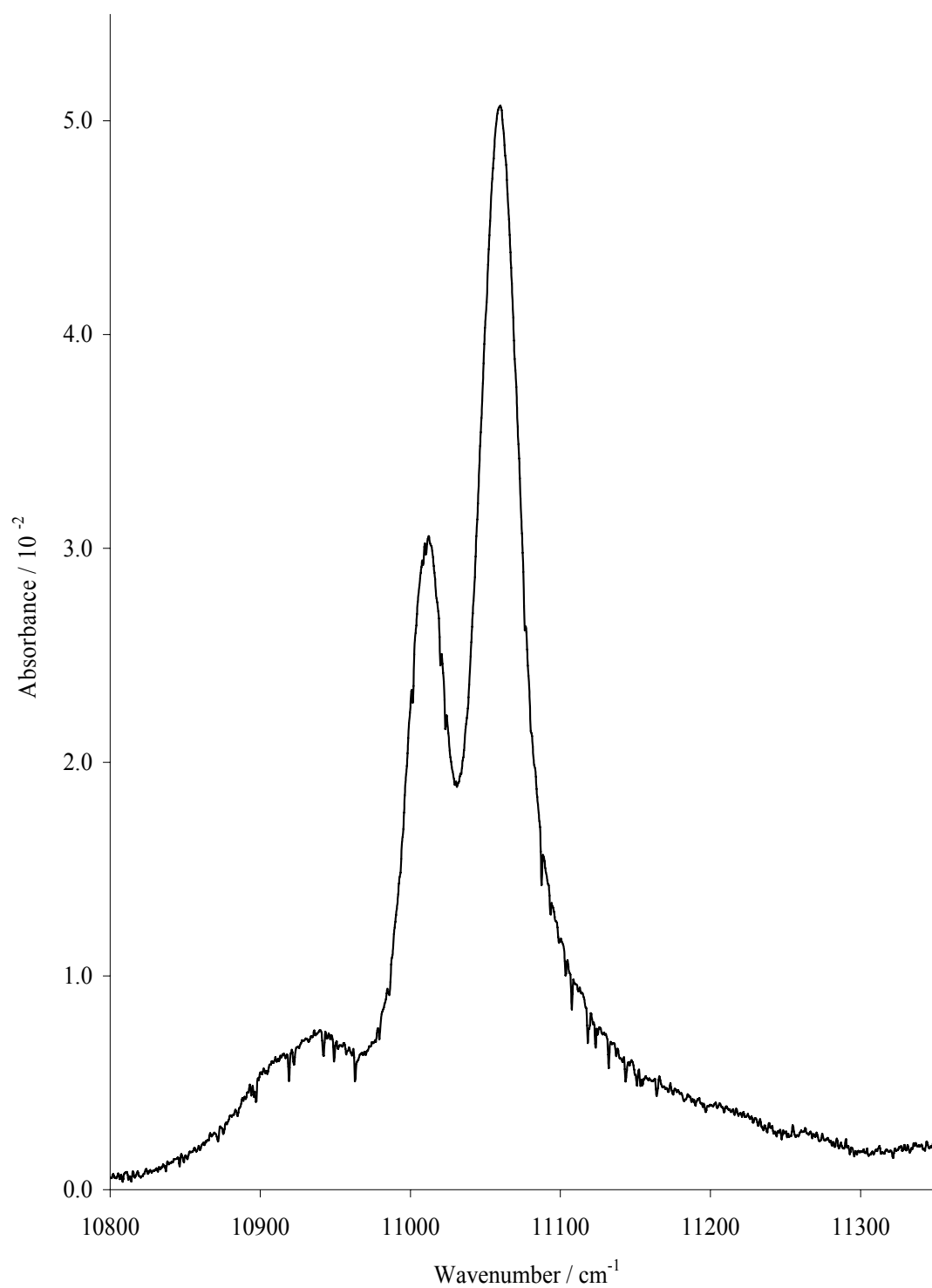


Figure 132. Absorption spectrum of the third overtone ($\Delta v = 4$) methyl C-H stretch of C_5SiH_{10} at 295K. Pressure = 180 Torr

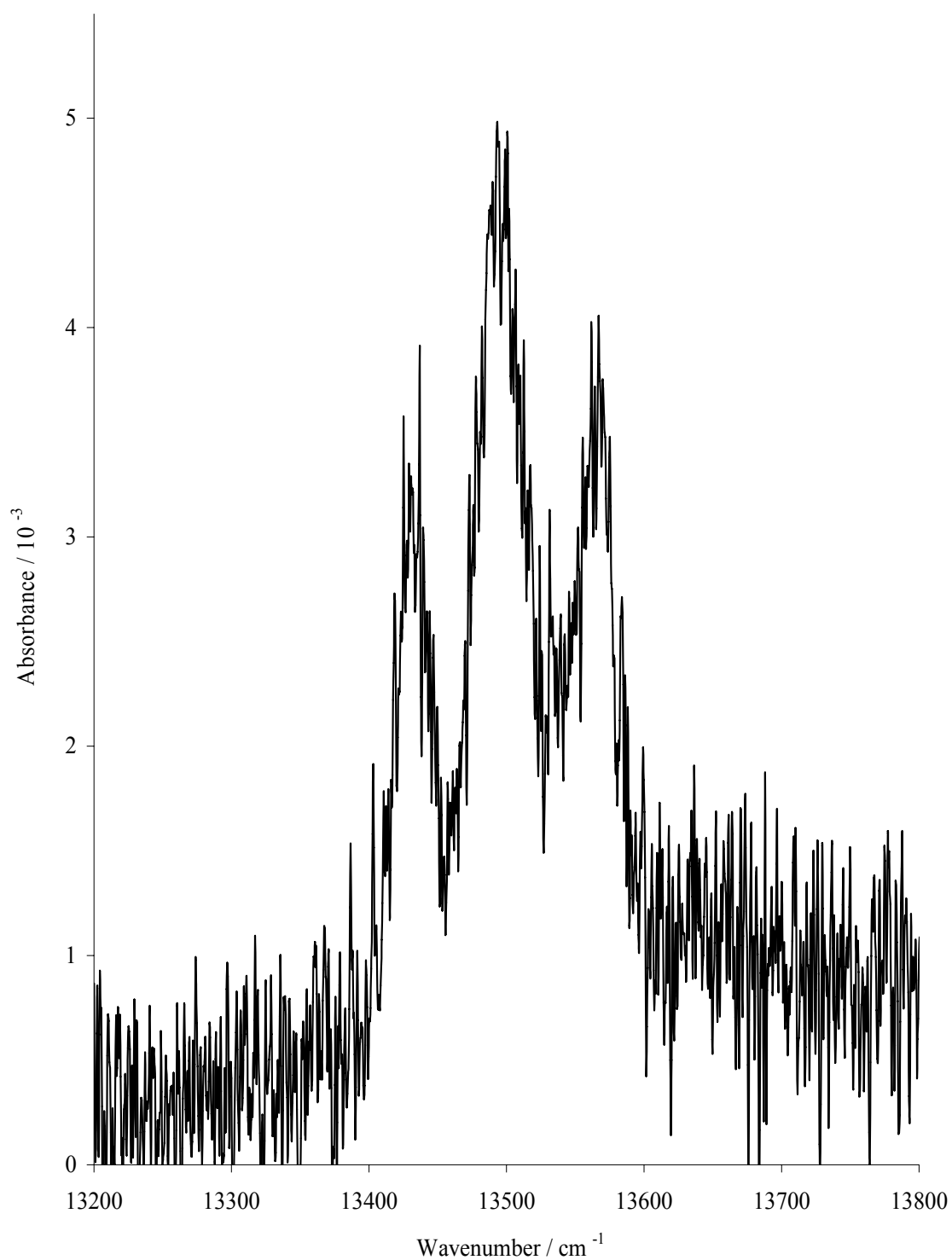


Figure 133. Absorption spectrum of the fourth overtone ($\Delta v = 5$) methyl C-H stretch of C_5SiH_{10} at 295K. Pressure = 180 Torr

Table 77. Observed and Calculated Frequencies, ω_l and $\omega_l x_l$ (cm^{-1}) for the Methyl CH_a stretch of $\text{C}_5\text{SiH}_{10}$.

ν	C- H_a		C- H_s	
	Obs. Freq	Calc. Freq	Obs. Freq	Calc. Freq
1	2975.00	2969.65	2965.00	2963.46
3	8460.32	8495.99	8463.22	8471.16
4	11060.90	11052.68	11013.17	11015.40
5	13493.22	13471.72	13429.10	13419.90
Harmonic Frequency	3107.3 ± 5		3103 ± 3	
Anharmonic Constants	-69 ± 1		-69.9 ± 0.8	

A better spectra of the fourth overtone ($\Delta\nu=5$) methyl C-H stretch of $\text{C}_5\text{SiH}_{10}$ was obtained using the PS-CRD technique. The spectra were obtained at 295 and 240K. However, only small decrease in the bandwidth was observed in the spectrum taken at 240 K. Figure 135 shows the absorption spectrum of ($\Delta\nu=5$) methyl C-H of $\text{C}_5\text{SiH}_{10}$ at 240K.

Table 78 reports the calculated density ρ , integrated absorption areas S , and the band strength S_0 for the pressure series shown in Figure 136, also it is included in this table the data obtained at 240K and from FT-spectrum. The S_0 value is reported from the linear fit of Figure 137 that is a plot of integrated absorption areas versus density.

The S_0 value $(2.87 \pm 0.08) \times 10^{-22} \text{ cm}^2 \text{ cm}^{-1} \text{ molecules}^{-1}$ for $\text{C}_5\text{SiH}_{10}$ is almost half that the S_0 value obtained for C_6H_{10} which means that the change of the central

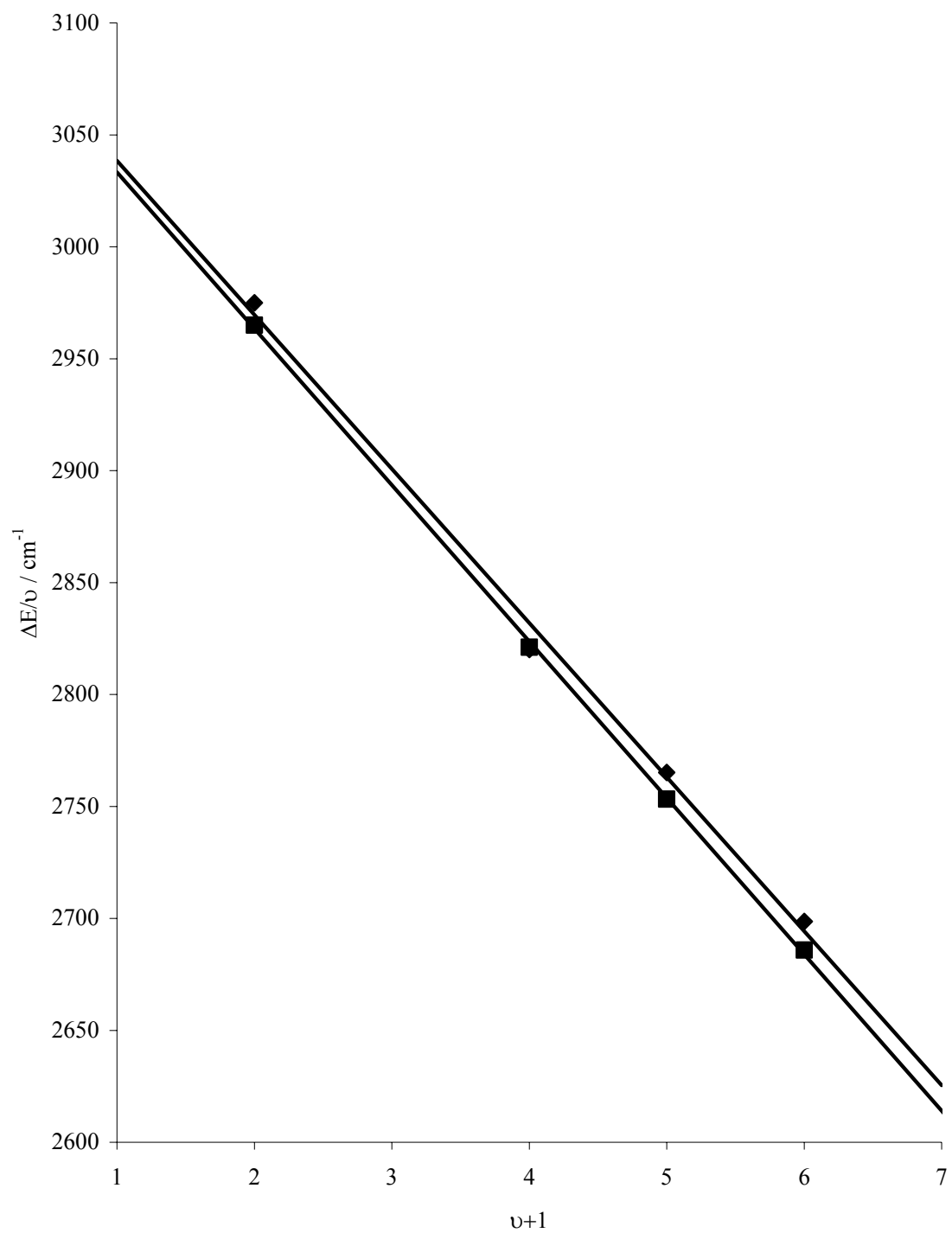


Figure 134. Birge-Sponer plot of the C-H_a and C-H_s oscillators in C₅SiH₁₀ Marker ■ = CH_a data and Marker ▲ = CH_s data.

Table 78. ($\Delta\nu=5$) methyl C-H of C_5SiH_{10} at 295 and 240K. Pressure, ρ , S and S_0

T	Pressure	ρ	S	S_0
Torr	Torr	$10^{18} \text{ molecules cm}^{-3}$	10^{-4} cm^{-2}	$10^{-22} \text{ cm}^2 \text{ cm}^{-1} \text{ molecule}^{-1}$
295 K	65	2.106	6.34	3.01
	52	1.684	5.55	3.30
	32	1.037	2.39	2.30
	19	0.615	1.48	2.40
	9	0.292	0.90	3.09
	4	0.130	0.48	3.70
	2	0.065	0.23	3.60
240 K	180	5.831	16.57	2.84
	4	0.157	0.35	2.23
Avg				2.87 ± 0.08

atom from C to Si affect more the C-H oscillators in the methyl groups than the acetylenic C-H stretch.

The harmonically coupled anharmonic oscillators (HCAO) model was also used to obtain suitable vibrational energies for the methyl groups present in C_5SiH_{10} . Following the same treatment shown before for C_6H_{10} , fundamental vibrational frequencies of C_5SiH_{10} were calculated at the Hartree-Fock and DFT (B3LYP) level of theory using the standard 6-311G (df,p) and 6-311G(3d,p) basis sets, respectively. The computations were performed by using the Gaussian 03 Program Package.²⁰⁰

The most stable configuration is presented in Figure138. Table 79 contains the selected computed geometric parameters for the C_{3v} symmetry of C_5SiH_{10} and compares them to available experimental data.²²⁷ This configuration was used to calculate the fundamental vibrational frequencies.

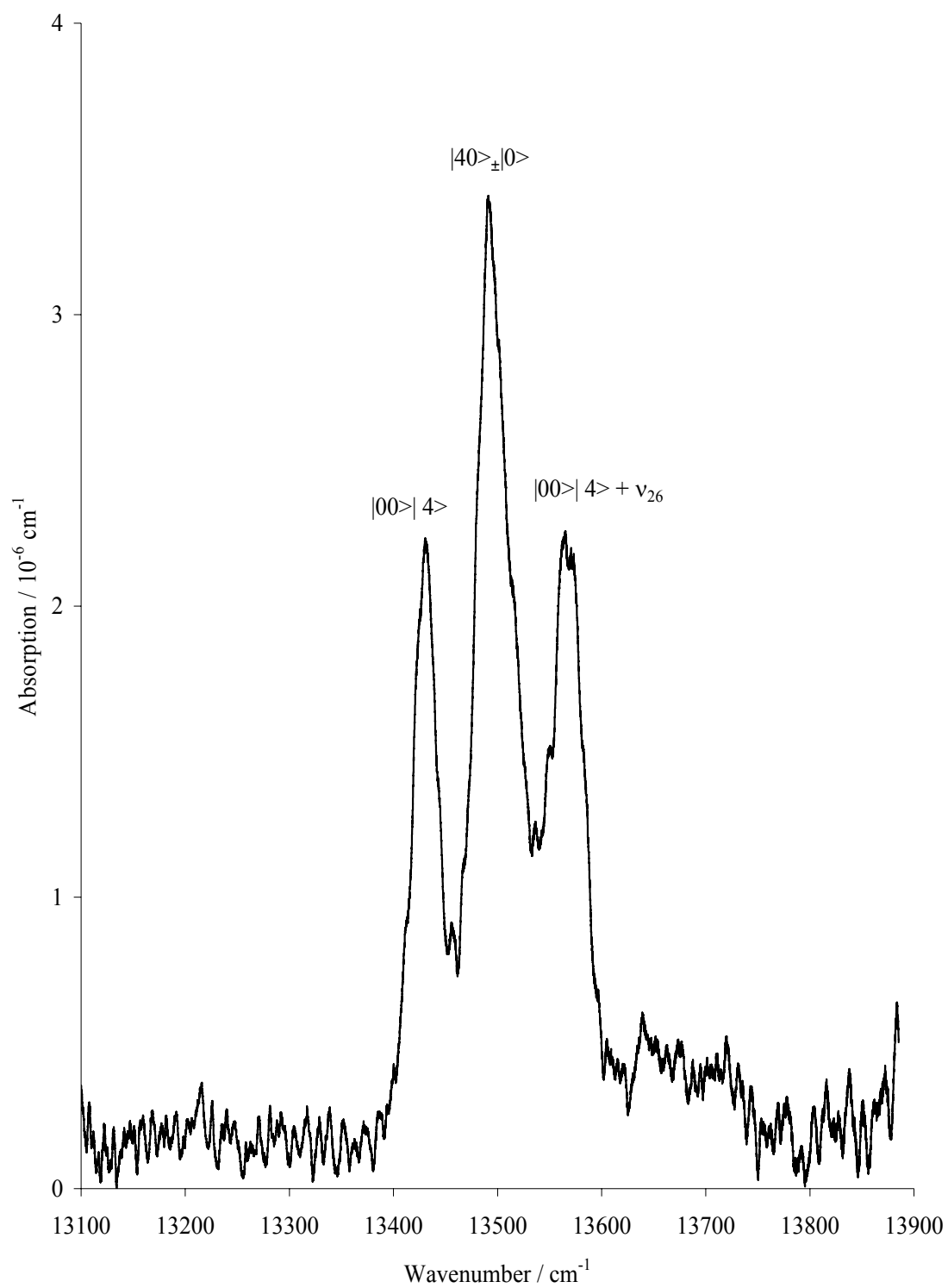


Figure 135. ($\Delta v=5$) methyl C-H stretch of $\text{C}_5\text{SiH}_{10}$ at 4 Torr and 240 K

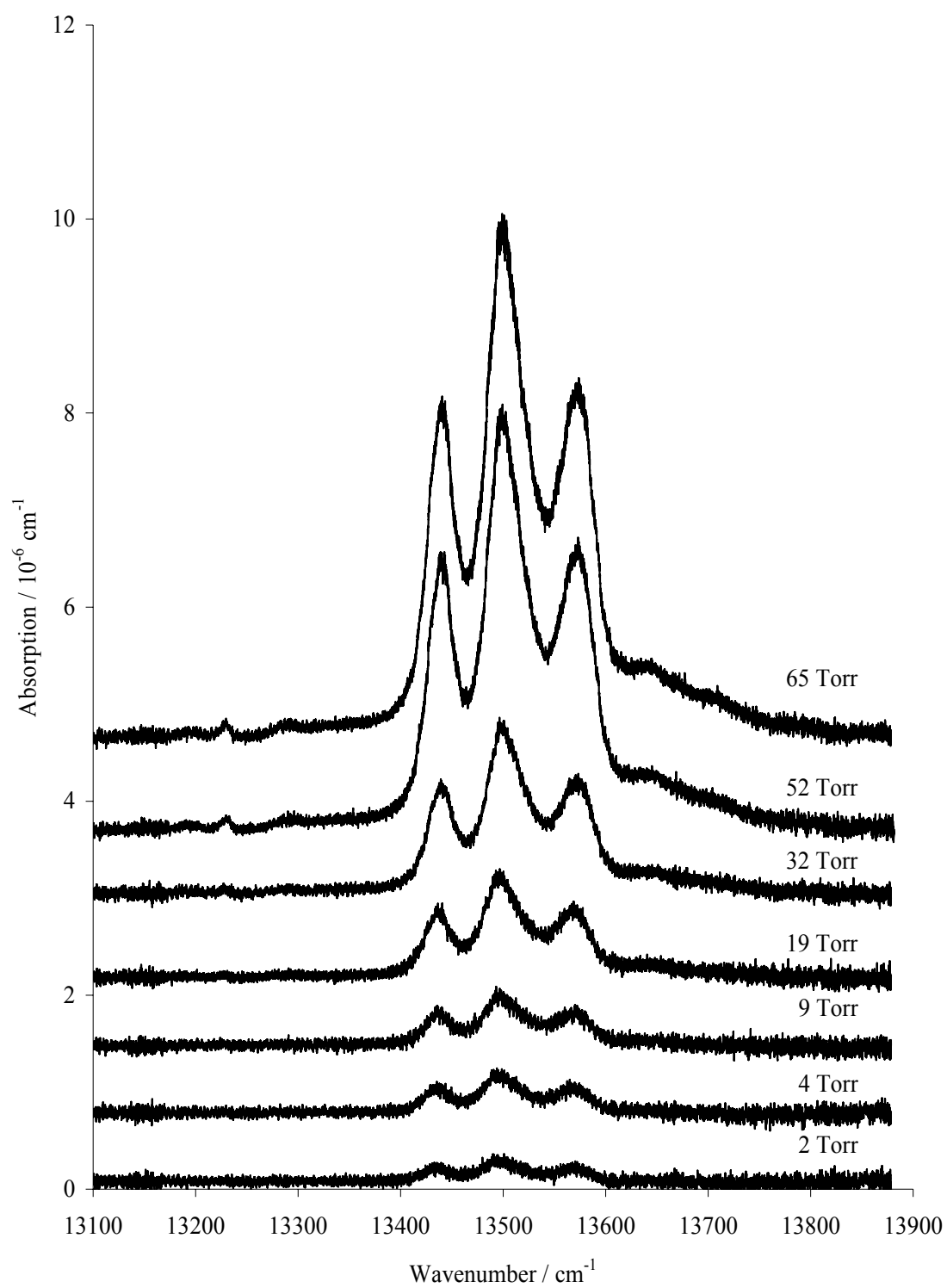
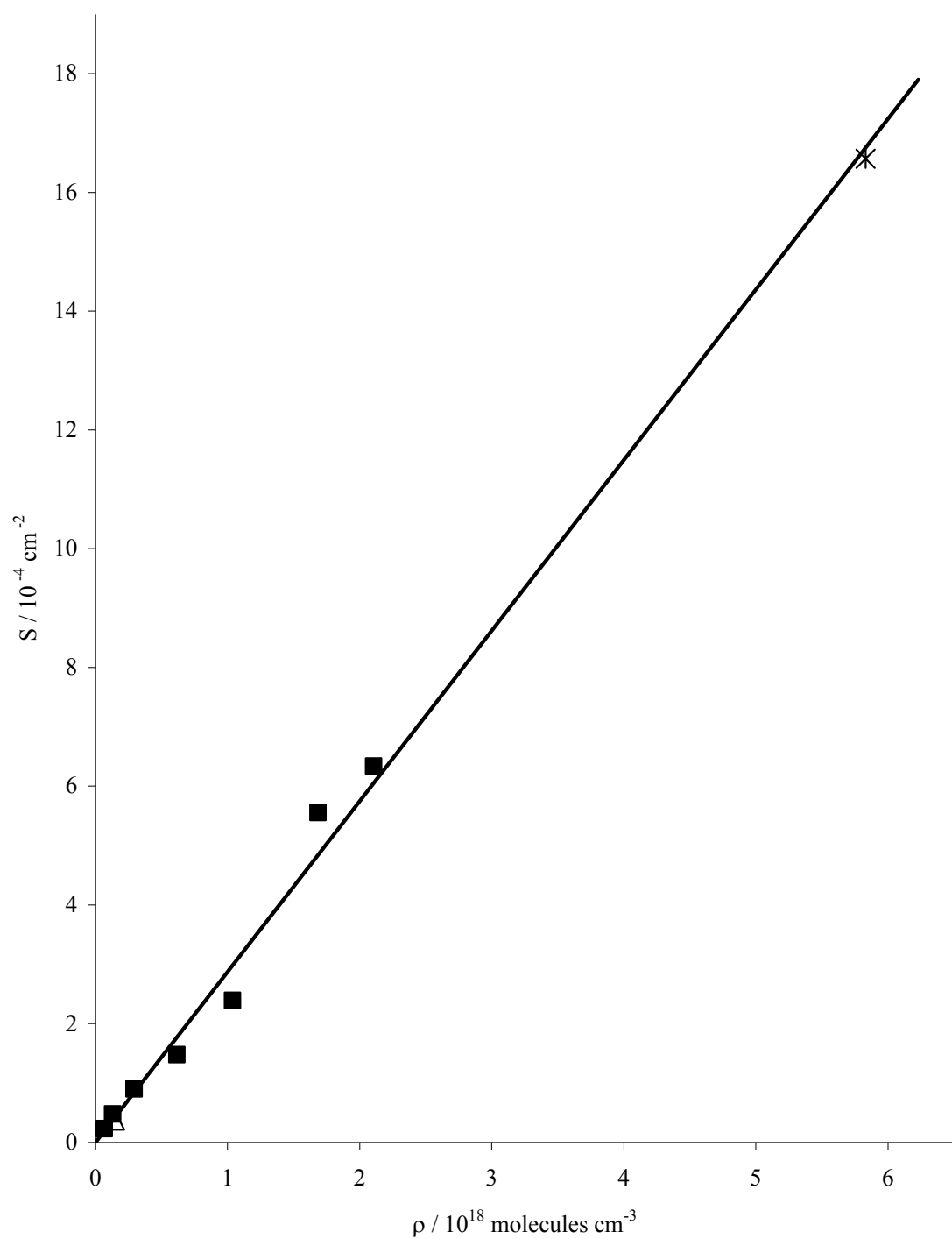


Figure 136. ($\Delta\nu=5$) Methyl C-H stretch of C_5SiH_{10} . Absorption pressure series at 295K



$$S_0 = (2.87 \pm 0.07) \times 10^{-22} \text{ cm}^2 \text{ cm}^{-1} \text{ molecules}^{-1}$$

$$R^2 = 0.995$$

Figure 137. ($\Delta\nu=5$) methyl C-H stretch of $\text{C}_5\text{SiH}_{10}$. S vs. ρ . Slope is S_0 . Marker ■ = measurements at 295 K , Marker x =FT-spectrum , Marker Δ = measurement at 240 K.

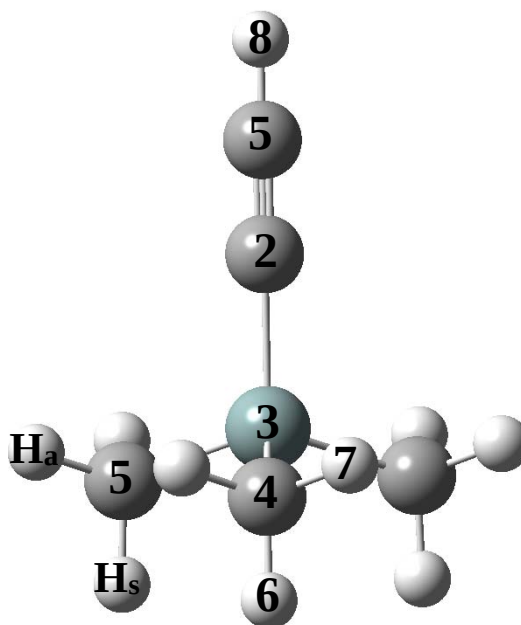


Figure 138. Equilibrium geometry (C_{3v} symmetry) of (Trimethylsilyl)acetylene.

Table 79. Optimized geometry (C_{3v}) and experimental bond lengths ($\text{\AA}$) and bond angle (degree) for C_5SiH_{10}

Parameter	HF / 6-311G(df,p)	DFT (B3LYP) / 6-311G(3d,p)	²³¹	Experimental ²³²
$C_1 \equiv C_2$	1.1904	1.2063		1.204
C_2-Si_3	1.8579	1.8455		1.833
Si_3-C_4	1.8794	1.8774		1.868
C_4-H_6	1.0878	1.0942		
C_4-H_7	1.0865	1.0929		
C_1-H_8	1.0569	1.0640	1.098	1.064
$C_2-Si_3-C_4$	108.2327	108.3573		109.7
$Si_3-C_4-H_6$	110.7444	110.6310		
$Si_3-C_4-H_7$	111.1381	111.2248		

Tables 80 and **81** list the vibrational frequencies calculated at the HF / 6-311G (df,p) and DFT (B3LYP) / 6-311G(3d,p) levels, respectively. Tables 80 and **81** also show the corresponding calculated IR intensities. The calculated frequencies are scaled

(scaling factors: 0.919(HF) and 0.959 (DFT (B3LYP)) and compared with the observed IR frequencies.²²⁷

Table 80. Normal modes for C₅SiH₁₀ calculated at the HF 6-311G(df,p) level of theory

Symmetry	Normal Mode	IR Intensity	Calculated Frequency	Scaled Frequency	Experimental Frequency
A ₁	v ₁	40	3612	3319	3312
	v ₂	63	3226	2965	2966
	v ₃	11	3153	2898	2900
	v ₄	41	2304	2117	2037
	v ₅	7	1579	1451	1420
	v ₆	10	1413	1298	1265
	v ₇	50	682	626	654
	v ₈	189	941	864	860
	v ₉	25	573	526	557
	v ₁₀	4	240	220	218
A ₂	v ₁₁	0	3226	2965	2967
	v ₁₂	0	1558	1432	1410
	v ₁₃	0	739	679	739
	v ₁₄	0	159	146	----
E	v ₁₅	31	3228	2967	2966
	v ₁₆	2	3217	2957	2966
	v ₁₇	10	3151	2896	2900
	v ₁₈	5	1571	1443	1420
	v ₁₉	0	1564	1436	1420
	v ₂₀	38	1405	1291	1255
	v ₂₁	98	830	762	700
	v ₂₂	44	927	852	845
	v ₂₃	30	856	786	765
	v ₂₄	13	736	676	680
	v ₂₅	0	219	202	236
	v ₂₆	1	136	125	132
	v ₂₇	0	179	164	----
	v ₂₈	34	388	356	350

Table 81. Normal modes for C₅SiH₁₀ calculated at DFT (B3LYP) 6-311G(3d,p)

Symmetry	Normal Mode	IR Intensity	Calculated Frequency	Scaled Frequency	Experimental Frequency
A ₁	v ₁	40	3455	3314	3312
	v ₂	63	3093	2966	2966
	v ₃	11	3025	2900	2900
	v ₄	41	2133	2046	2037
	v ₅	7	1478	1417	1420
	v ₆	10	1304	1250	1265
	v ₇	50	651	625	654
	v ₈	189	883	847	860
	v ₉	25	549	526	557
	v ₁₀	4	224	215	218
A ₂	v ₁₁	0	3100	2973	2967
	v ₁₂	0	1454	1395	1410
	v ₁₃	0	693	665	739
	v ₁₄	0	145	139	----
E	v ₁₅	31	3101	2974	2966
	v ₁₆	2	3091	2964	2966
	v ₁₇	10	3023	2899	2900
	v ₁₈	5	1467	1407	1420
	v ₁₉	0	1460	1400	1420
	v ₂₀	38	1294	1241	1255
	v ₂₁	98	714	685	700
	v ₂₂	44	869	833	845
	v ₂₃	30	778	746	765
	v ₂₄	13	697	668	680
	v ₂₅	0	207	199	236
	v ₂₆	1	122	117	132
	v ₂₇	0	163	156	----
	v ₂₈	34	354	339	350

Isolated fundamental C-H_a and C-H_s stretching frequencies for (CD₂H) (CD₃)₂C₃D and the fundamental CH stretching frequencies of (CH₃) (CD₃)₂C₃D were calculated at the Hartree-Fock 6-311G (df,p) and DFT (B3LYP) 6-311G(3d,p) levels of theory. The results are presented in Table **82**.

Since the calculated isolated fundamental frequencies, C-H_a and C-H_s, for (CD₂H) (CD₃)₂C₃D are independent of any coupling, these two CH frequencies are made equal to the pure local mode frequencies, $(\omega_l - 2\omega_l x_l)$ and $(\omega_3 - 2\omega_3 x_3)$, respectively. The latter calculation produces three frequencies (ν) that correspond in increasing order to the energies of the states $\nu|00\rangle|1\rangle$, $\nu|10\rangle_+|0\rangle$, $\nu|10\rangle_-|0\rangle$ of the HCAO model.

The parameter γ'_{12} was calculated from equation (80) and γ'_{13} was obtained from the calculated frequency of the in-plane fundamental $|00\rangle|1\rangle$ and the energy matrix (81) which involves the two symmetric states $|10\rangle_+|0\rangle$ and $|00\rangle|1\rangle$ and their interaction through γ'_{13} . The *ab initio* calculated fundamental frequencies are higher than the experimental ones but because the present analysis depends only on the differences in frequencies between (CD₂H) (CD₃)₂C₃D and (CH₃) (CD₃)₂C₃D, it is expected that the calculated parameters (γ') are as reliable as the ones obtained from experimental frequencies.

Frequencies corresponding to pure local modes were calculated from the matrices for each vibrational manifold from $\nu=1$ to 5. These matrices were obtained using the local mode parameters and the coupling parameters γ'_{12} and γ'_{13} (see

Appendix B).^{217, 218} The parameters required for these calculations are presented in Table 82.

Table 82. Ab initio calculated isolated frequencies ν_{CH}^{iso} for C₅SiH₁₀

	(cm ⁻¹)	C-H _a	C-H _s
HF/ 6-311G (df,p)	ν_{CH}^{iso}	3205	3191
	$\nu_{ 00\rangle 1\rangle}$		3152
	$\nu_{ 10\rangle_+ 0\rangle}$	3218	
	$\nu_{ 10\rangle_- 0\rangle}$	3227	
	γ'_{12}		22
	γ'_{13}	24	
DFT (B3LYP) 6-311G(3d,p)	ν_{CH}^{iso}	3078	3064
	$\nu_{ 00\rangle 1\rangle}$		3024
	$\nu_{ 10\rangle_+ 0\rangle}$	3091	
	$\nu_{ 10\rangle_- 0\rangle}$	3100	
	γ'_{12}		22
	γ'_{13}	25	

Table 83 summarizes the experimental and calculated peak positions for C₅SiH₁₀. The local mode states are labeled $|\nu_1\nu_2\rangle_\pm|\nu_3\rangle$. Frequencies involving local mode-normal mode combination bands were not calculated using the HCAO model and correspond to the simple addition of the calculated local mode frequency (HCAO) and the normal mode frequency taken from Table 74. Pure local mode assignments corresponding to the least intense low energy overtone (C-H_s) are denoted by $|00\rangle|\nu\rangle$ and assignments corresponding to the most intense high energy overtone (C-H_a) are denoted

by $|\nu 0\rangle_{\pm}|0\rangle$, where $\nu=3-5$ is the vibrational quantum number. Assignments of pure local modes were also confirmed with the help of the Birge-Sponer plot. Comparison of the calculated frequencies with the observed frequencies shows that the HCAO model provides a good description of the energies of the peaks.

Table 83. Calculated and experimental vibrational frequencies (cm^{-1}) of C_6H_{10}

ν	Assignment	HCAO		Observed Frequencies
		HF	DFT	
1	$ 00\rangle 1\rangle$	2924	2922	2911
1	$ 10\rangle_{+} 0\rangle$	2993	2995	2975
1	$ 10\rangle_{-} 0\rangle$	2995	2995	
2	$ 00\rangle 2\rangle$	5766	5764	5750
2	$ 20\rangle_{+} 0\rangle$	5794	5794	5770
2	$ 20\rangle_{-} 0\rangle$	5800	5800	
2	$ 10\rangle_{+} 1\rangle$	5929	5930	5888
2	$ 10\rangle_{-} 1\rangle$	5968	5969	5928
2	$ 11\rangle 0\rangle$	5974	5975	5935
3	$ 00\rangle 3\rangle$	8467	8466	8466
3	$ 30\rangle_{+} 0\rangle$	8491	8490	8466
3	$ 30\rangle_{-} 0\rangle$	8493	8493	
3	$ 10\rangle_{+} 2\rangle$	8690	8688	8679
3	$ 20\rangle_{-} 1\rangle$	8735	8733	8733
3	$ 21\rangle_{+} 0\rangle$	8743	8744	
3	$ 10\rangle_{-} 2\rangle$	8819	8819	
3	$ 20\rangle_{+} 1\rangle$	8819	8822	
3	$ 21\rangle_{-} 0\rangle$	8844	8846	
3	$ 11\rangle 1\rangle$	8940	8942	

Continued. Table 83. Calculated and experimental vibrational frequencies (cm⁻¹)

v	Assignment	HCAO		Observed Frequencies
		HF	DFT	
4	$ 00\rangle 4\rangle$	11016	11015	11013
4	$ 40\rangle_+ 0\rangle$	11054	11053	11061
4	$ 40\rangle_- 0\rangle$	11066	11066	
4	$ 10\rangle_+ 3\rangle$	11389	11386	11394
4	$ 10\rangle_- 3\rangle$	11425	11422	
4	$ 30\rangle_+ 1\rangle$	11426	11425	
4	$ 31\rangle_- 0\rangle$	11463	11462	
4	$ 20\rangle_+ 2\rangle$	11471	11471	
4	$ 20\rangle_- 2\rangle$	11494	11495	
4	$ 22\rangle 0\rangle$	11620	11622	
4	$ 21\rangle_+ 1\rangle$	11640	11643	
4	$ 11\rangle 2\rangle$	11651	11651	11766
4	$ 21\rangle_- 1\rangle$	11689	11689	
5	$ 00\rangle 5\rangle$	13424	13423	13429
5	$ 50\rangle_+ 0\rangle$	13476	13476	13493
5	$ 50\rangle_- 0\rangle$	13476	13476	
5	$ 00\rangle 5\rangle + \nu_{26}$	13556	13555	13570
5	$ 10\rangle_+ 4\rangle$	13959	13958	
5	$ 10\rangle_- 4\rangle$	13991	13989	
5	$ 40\rangle_+ 1\rangle$	13993	13991	
5	$ 40\rangle_- 1\rangle$	14005	14004	
5	$ 41\rangle_+ 0\rangle$	14039	14039	
5	$ 41\rangle_- 0\rangle$	14044	14044	
5	$ 20\rangle_+ 3\rangle$	14220	14218	
5	$ 20\rangle_- 3\rangle$	14234	14232	
5	$ 32\rangle_+ 0\rangle$	14250	14249	
5	$ 30\rangle_+ 2\rangle$	14367	14369	

Continued. Table 83. Calculated and experimental vibrational frequencies (cm⁻¹)

ν	Assignment	HCAO		Observed Frequencies
		HF	DFT	
5	$ 30\rangle_- 2\rangle$	14371	14373	
5	$ 11\rangle_- 3\rangle$	14378	14376	
5	$ 32\rangle_- 0\rangle$	14385	14386	
5	$ 31\rangle_+ 1\rangle$	14445	14447	
5	$ 31\rangle_- 1\rangle$	14469	14470	
5	$ 21\rangle_+ 2\rangle$	14581	14583	
5	$ 21\rangle_- 2\rangle$	14625	14626	
5	$ 22\rangle_- 1\rangle$	14650	14654	

Conclusions

The acetylenic and methyl C-H overtone spectra of propyne, tert-butylacetylene and (trimethylsilyl)acetylene were investigated using standard infrared technique (FT-spectrophotometer) and PS-CRD spectroscopy.

The acetylenic C-H stretch of C₆H₁₀ and C₅SiH₁₀ behaves as a local mode for all vibrational levels investigated ($\nu=1-4$).

The absorption spectra of ($\Delta\nu=1, 2, 3, 4$) acetylenic C-H stretch of C₆H₁₀ and C₅SiH₁₀ look similar a previous reported results for propyne²⁰³ and 3, 3, 3-trifluoropropyne.²²⁰ These results indicate that the acetylenic C-H stretch is a relatively long-lived mode that does not significantly interact in a resonant manner with the rest of the molecule.

A hot band transition ($\nu_{24} \rightarrow (\nu_{24} + \nu\nu_1)$) was observed for $\Delta\nu=1-6$ in acetylenic C-H stretch overtones of these molecules that is almost identical to the transitions observed in C_3H_4 and C_3HF_3 .

The behavior of the methyl C-H stretches in C_6H_{10} and C_5SiH_{10} is almost identical. For the fundamental and first overtone levels, there are separate symmetric and antisymmetric (normal mode) C-H stretches. At higher levels ($\Delta\nu=3, 4$ and 5) two bands can be distinguished in the spectra, these correspond to the two non-equivalent CH bonds in the methyl groups. In these transitions the methyl C-H stretch is a local mode.

An unexpected absorption occurs in the absorption spectrum of the ($\Delta\nu=5$) methyl C-H stretch, where an absorption immediately to high frequency side of the $C-H_a$ overtone was observed. This band was assigned as local mode-normal mode combination band $|00\rangle|4\rangle + \nu_{26}$, where ν_{26} is the Si - $C \equiv C$ rock mode.

A noticeable change in the bandwidth of the absorption spectra was observed when the central atom in the like molecules $(CH_3)_3XC \equiv CH$ was $X=C$ or $X=Si$. Spectral bandwidth of the tert-butylacetylene compound was much larger than that of the silicon-substituted compound. This bandwidth difference has been explained by theoretical study. It has been found that in Si molecule an accidental absence of appropriate resonance states results in a bottleneck in the initial stages of relaxation. As a result, an almost complete localization of the initially prepared excitation occurs.

For C_6H_{10} and C_5SiH_{10} , the corresponding local mode parameters and the HCAO model were used to assign vibrational transitions. A comparison of the calculated frequencies with the observed frequencies shows that the HCAO model

provides a good description of the energies of the peaks. Agreement is particularly good for the higher overtones $\Delta v = 3, 4$ and 5 .

Using the spectra obtained from the PS-CRD technique, the band strength values, S_0 , for acetylenic and methyl C-H were obtained. S_0 values for C_5SiH_{10} are smaller than the values obtained for C_6H_{10} .

High overtone spectra ($\Delta v = 4$ and 5) of C_3H_4 , C_6H_{10} and C_5SiH_{10} were also measured at low temperatures of 185 and $240K$, using PS-CRD spectroscopy. However, only smaller changes in the bandwidth were observed. Because of the low vapor pressure of C_6H_{10} and C_5SiH_{10} at $240K$, this was the lowest temperature reached.

CHAPTER SEVEN

Photolysis of Ethyl Acetate by Visible Radiation

Sunlight is the driving force for reactions in the Earth's atmosphere. The major flux of solar radiation is mostly in the ultraviolet (UV), visible (VIS) and near infrared (NIR) with a maximum in the visible. Excitation of electronic molecular states at energies corresponding to the UV, induce chemical reaction by accessing and breaking covalent bonds. The electronic states of oxygen (O_2 and O_3) are photo reactive, and this light induced chemistry in the upper and middle atmosphere leads to formation of a stratospheric ozone layer, controlling the UV radiation available for chemistry in the troposphere below. Hence, at the lowest altitudes, basically all of the higher energy ultraviolet radiation is attenuated, leaving light of $\lambda > 305$ nm to affect any photochemistry.²³³

Although visible radiation is more abundant than UV radiation at any altitude and zenith angle (angle between the direction of the Sun's light and the vertical at a given point),²³⁴ excitation energies corresponding to these wavelengths are below the bond dissociation energy of most covalent bonds, and so visible radiation is not usually considered as a driving force in atmospheric chemistry.

However, Vaida *et al*²³⁵ proposed that OH-containing species, such as HNO_x ($HONO$, $HONO_2$, HO_2NO_2) would absorb visible radiation into vibrational overtones of the OH stretch of sufficient energy to cause dissociation to $HO_x + NO_x$. In the mechanism which leads to radical formation by OH overtone excitation, direct overtone photodissociation (DOP), a strongly-absorbing local mode oscillator (via the O-H

stretch) is excited into a vibrational level which contains sufficient energy to break some other bond (N-O or O-O) in the molecule. This bond dissociation occurs by a rapid (on the order of picoseconds) intramolecular vibrational energy redistribution which then transfers sufficient energy to the weaker bond(s) in the molecule to dissociate them.

For example, in nitric acid, the 0 K dissociation energy (D_0) of the HO-NO₂ bond lies at 16 740 cm⁻¹ so the lowest vibrational overtone transition which causes dissociation in this molecule is that to the $\Delta v=5$ level, centered at 16 165 cm⁻¹. Although this value is lower in energy than D_0 , bond rupture does occur following excitation of this overtone from thermally populated rotational states.²³⁵ Thus, there is a temperature dependence to the dissociation quantum yield which is related to the internal energy of the molecule prior to the overtone excitation.²³⁶ Therefore, transitions to $v=5$ and higher of the O-H stretch provide the molecule with sufficient energy to rupture the HO-NO₂ bond. This energy is initially localized in the O-H stretching vibration. Then, a rapid intramolecular vibrational redistribution (IVR) occurs as a consequence of the anharmonic coupling between the H-O stretching motion and the other vibrations of the nitric acid molecule, giving rise to migration of energy out of the OH stretch.²³⁷ Because of potential and kinetic couplings among the internal motions of the molecule, this energy will eventually become distributed statistically into the “bath” of internal quantum states, which is the nitric acid molecule, providing sufficient thermal energy for the O-N bond to break.^{236, 238}

Furthermore, Vaida *et al* (2) proposed that excitation of vibrational overtones of sulfuric acid (H₂SO₄) and its hydrate (H₂SO₄·H₂O) in the near-infrared and visible leads

to photolysis, forming sulfur trioxide (SO₃) and water. The reactions of interest to this study involve the dehydration of H₂SO₄ (Eqn. 1) and H₂SO₄·H₂O (Eqn. 2).



The energy required to achieve the transition state for reaction 1 has been predicted to lie in the range of 32 to 40 kcal/mol (11192 to 13990 cm⁻¹).^{239,240} The energy of the Δν = 4 O-H stretch level, calculated using HCAO model, is 38.6 kcal/mol (13500 cm⁻¹)²³⁶, so even if the barrier lies at the high end of its calculated range, dissociation of either molecule upon excitation to the ν=4 level is expected to occur, promoted by rotational energy. For dissociation of the H₂SO₄·H₂O complex, an energy of ~ 25 kcal/mol, corresponding to ν ≥ 3 of the OH stretch, is required.^{239,240} The estimated *J* values were sufficiently large to explain SO₂ stratospheric and mesospheric concentration and the related observation of the sulfate layer.²³⁶

Hence, it is also possible that the overtones of C-H vibration could induce reactions in organic molecules such as ethers, aldehydes, ketones, nitrates and alcohols.

Atmospheric Photolysis Rates

The rate of formation of photoproduct B from the photolysis of atmospheric species A is expressed as a first order rate law, with a rate coefficient *J*(s⁻¹)²³³

$$\frac{d[B]}{dt} = J[A] \quad (85)$$

The value of *J* is given by a convolution of the absorption spectrum of A, scaled by the quantum yield of formation of B, with the spectrum of available atmospheric radiation

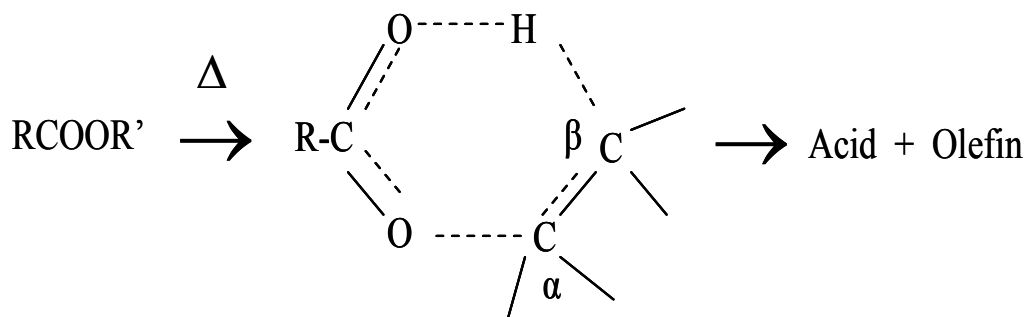
$$J = \int \{\sigma(\lambda)\phi(\lambda)I(\lambda)\}d\lambda \quad (86)$$

where $\sigma(\lambda)$ gives the absorption cross section of A at wavelength λ , $I(\lambda)$ represents the intensity of solar radiation (in photons $\text{cm}^{-2} \text{ nm}^{-1} \text{ s}^{-1}$) at λ , and $\phi(\lambda)$ gives the wavelength-dependent quantum yield for formation of B via photolysis. The integration is carried out over the absorption spectrum of the molecule A. Thus, absorption cross-sections and quantum yields of overtone-induced chemistry must be known as a function of wavelength. To provide quantitative J values, the temperature and pressure dependence of these parameters should also be known. In general, electronic transitional cross sections of atmospheric species are available in the literature.²³⁴ However, due to vibrational transitions having much lower cross sections than electronic transitions, by several orders of magnitude; these are more difficult to measure accurately, especially the higher overtones, which are more reactive.

Vibrational overtone spectra are measured using sensitive techniques such as photoacoustic and cavity ring down spectroscopic.^{64, 65, 113} Also, overtone intensities may be calculated using *ab initio* quantum chemical methods.²⁴¹

Photolysis of Esters via Vibrational Overtone Absorption

Esters RCOOR' , where R' contains a β -hydrogen atom, decompose into olefins and acids in the gas phase at high temperatures (230-600°C). A cyclic transition state (Scheme 1) is usually accepted for these reactions. Thermal decomposition of esters have been widely studied by several groups.²⁴²⁻²⁴⁸ Table **84** summarizes the activation energy (E_a) for thermal decomposition of some esters with $\text{R}' = \text{ethyl (CH}_2\text{CH}_3)$ and different R groups. The activation energy is reported in units of Kcal/mol, cm^{-1} and nm.



Scheme 1. Decomposition of RCOOR'

Table 84. Activation Energy for Thermal Decomposition of RCOOCH₂CH₃

R Group	E _a / (Kcal/mol)	E _a / cm ⁻¹	E _a / nm
CH ₃ - ²⁴²	47.9	16751.9	597
CH ₃ CH ₂ - ²⁴³	48.5	16960.9	590
CH ₃ CH ₂ CH ₂ - ²⁴⁴	49.5	17312.0	578
(CH ₃) ₃ C- ²⁴⁵	44.0	15389.3	650
C ₆ H ₅ - ²⁴⁶	47.7	16676.7	600
C ₆ H ₅ CH ₂ - ²⁴⁶	47.8	16718.5	598
Trans- CH ₃ CH=CH- ²⁴⁴	46.8	16375.7	611
ClCH ₂ - ²⁴⁷	47.1	16467.7	607
ClCH ₂ CH ₂ - ²⁴⁷	47.0	16451.0	608
ClCH ₂ CH ₂ - ²⁴⁷	47.5	16609.8	602

From these values, it is proposed that decomposition of esters, containing a β-hydrogen atom, to an acid and an olefin could occur by excitation of vibrational overtone of C-H stretch via absorption of visible light. Because of the high frequency and anharmonicity of this local mode, it might be expected to have reasonable energy in Δν = 6 or 7, as required to exceed the threshold energy for decomposition of the esters tabulated in Table 84.

Ethyl acetate (C₄H₈O₂) is volatile organic compound (VOC) and is emitted into the atmosphere by various anthropogenic and natural sources. The molecule C₄H₈O₂ is used extensively in industry, particularly as a solvent and in the manufacture of

perfumes and flavorings. This compound is also produced in nature by a process in vegetation. Thus, a substantial proportion of ethyl acetate could escape then to the atmosphere where it is available for photochemical transformation, such as the proposed mechanism here. The next section outlines why ethyl acetate has been chosen as a model to demonstrate this possible mechanism.

Fundamental and Overtones Spectra of Ethyl Acetate

Investigation of reactions controlled by vibrational overtone excitation requires knowledge of basic spectroscopic information of overtones, such as transition energies and intensities. For this reason, fundamental and overtone ($\Delta v = 1, 2, 3, 4$, and 5) spectra of $C_4H_8O_2$ have been recorded at 295K. The spectral region between 2800 and 11500cm^{-1} was recorded for $C_4H_8O_2$ using a Fourier transform spectrometer with a resolution of 1 cm^{-1} and a white cell with a path length of 6.6 m. The higher level overtone spectrum $\Delta v=5$ was obtained using the PS-CRD technique, with a path length of 2.17 km and a resolution of 0.17cm^{-1} given by the continuous wave Ti:Sapphire ring laser used.

Individual fundamental and overtone regions ($\Delta v = 1, 2, 3, 4, 5$) are presented in Figures 139 to **143**. These figures show very spectrally congested spectra due to the overlap of the different C-H oscillators present in this molecule. Using the main band absorption frequencies from Figure 139 to Figure **143**, the Birge-Sponer plot was obtained for ethyl acetate and is shown in Figure**144**. Table **85** shows the observed frequencies for the main band of ethyl acetate. Using the Birge-Sponer equation, Table **85**, predicted the position for overtones $\Delta v = 6$ and $\Delta v = 7$ of ethyl acetate at 15847 cm^{-1} (631nm) and 18019 cm^{-1} (555nm), respectively. Hence, decomposition of ethyl

acetate to acetic acid and ethylene could occur by excitation of vibrational overtone ($\Delta v = 6$ or 7) of C-H stretch. On the other hand, the integrated band strength (S_0) was calculated for the fourth overtone ($\Delta v=5$) of ethyl acetate. A series of nine different pressures of this absorption was obtained and is shown in Figure 145. Table 86 reports the density (ρ), integrated absorption band (S), and band strength values (S_0) for each individual pressure. The S_0 value reported, $S_0 = (4.6 \pm 0.1) \times 10^{-22} \text{ cm}^2 \text{ cm}^{-1} \text{ molecules}^{-1}$, was found from the slope of Figure 146.

Table 85. Observed Frequencies and Birge-Sponer Equation for Ethyl Acetate

v	Obs. Freq (cm^{-1})
1	2982
2	5820
3	8484
4	11092
5	13580
Birge-Spooner Equation $\Delta E/v = -66.9 (v+1) + 3109.4$	

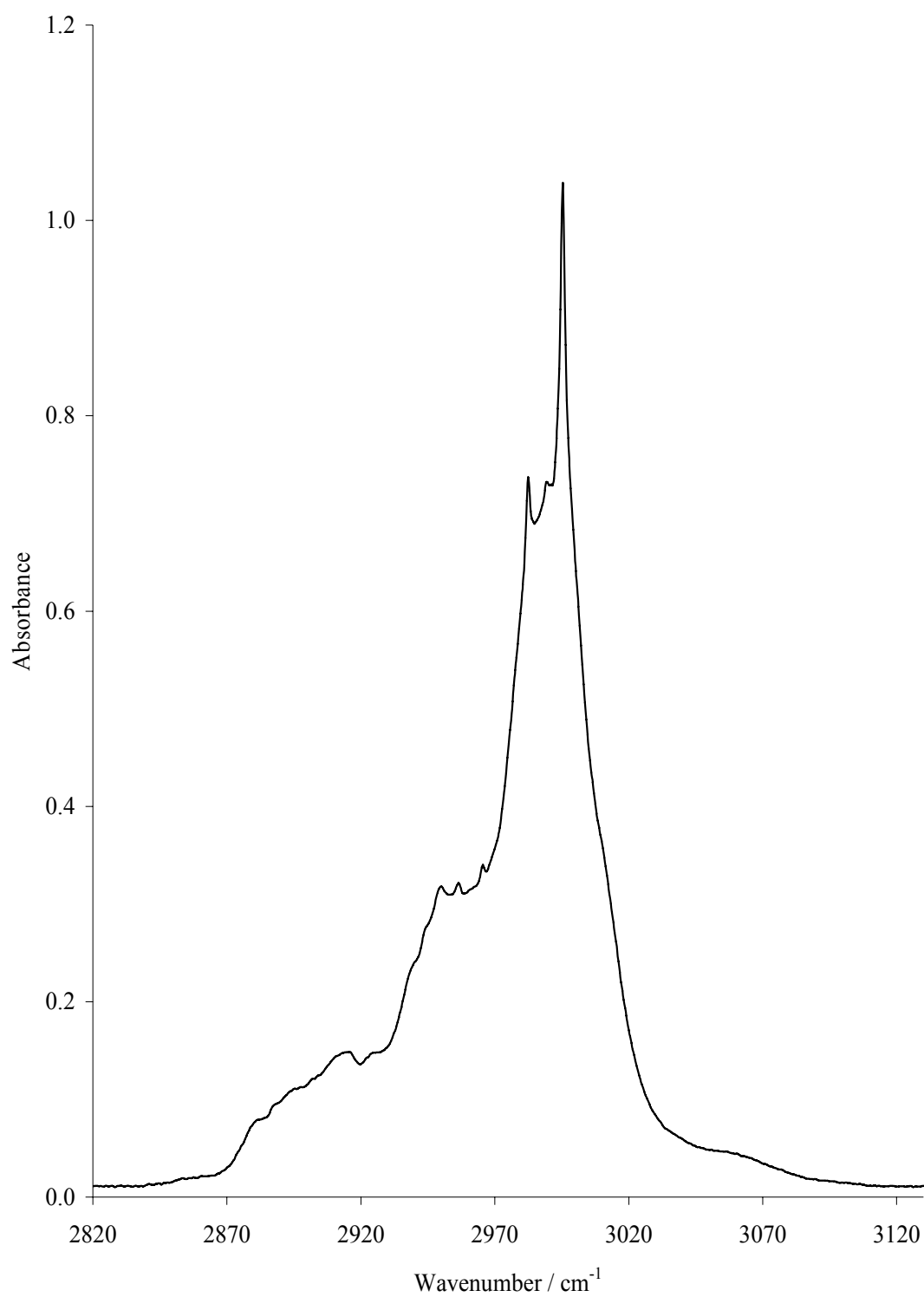


Figure 139. Absorption spectrum of the fundamental ($\Delta v = 1$) of ethyl acetate at 295K. Pressure = 0.2Torr.

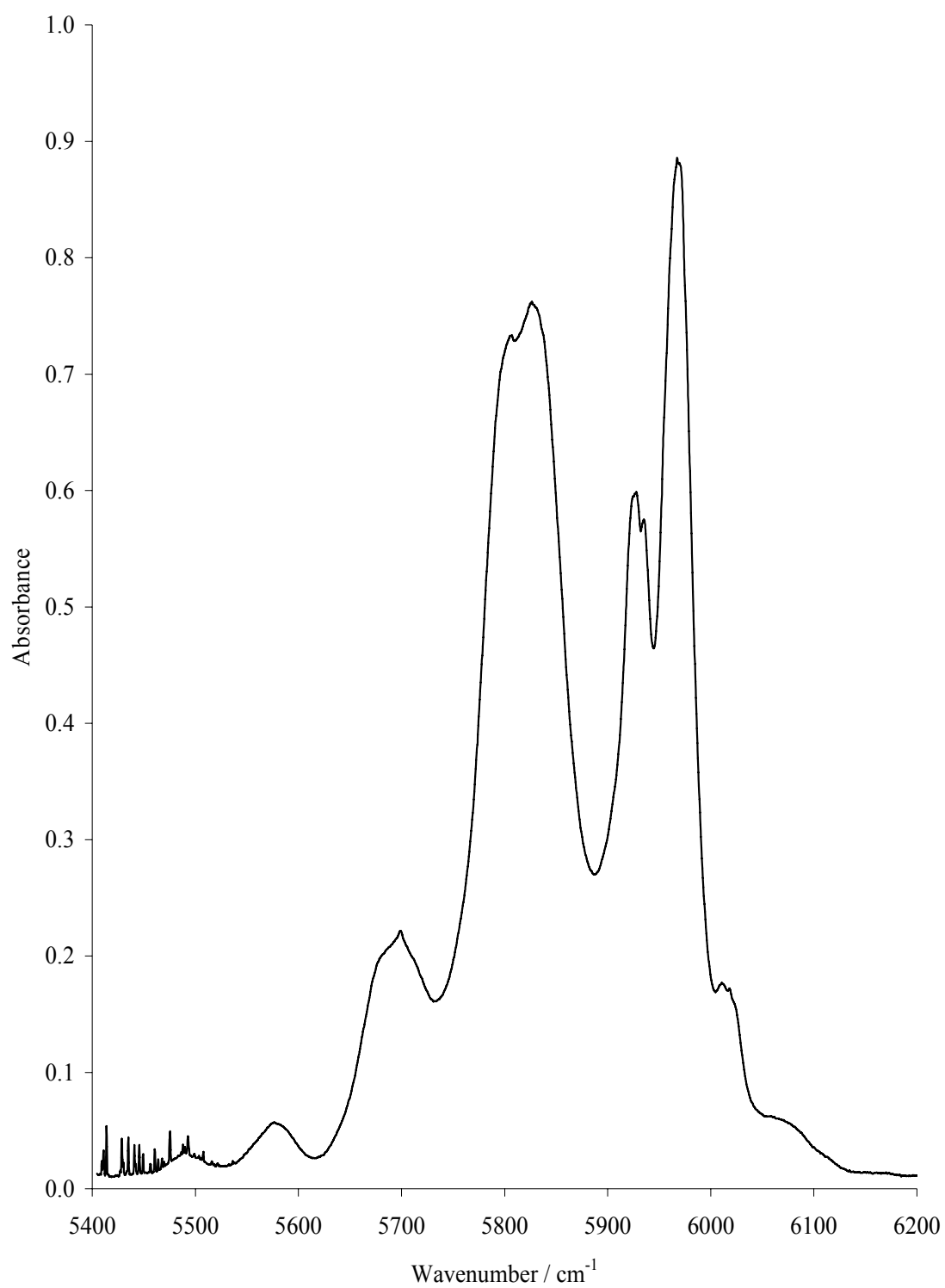


Figure 140. Absorption spectrum of the first overtone ($\Delta\nu = 2$) of ethyl acetate at 295K. Pressure = 60 Torr.

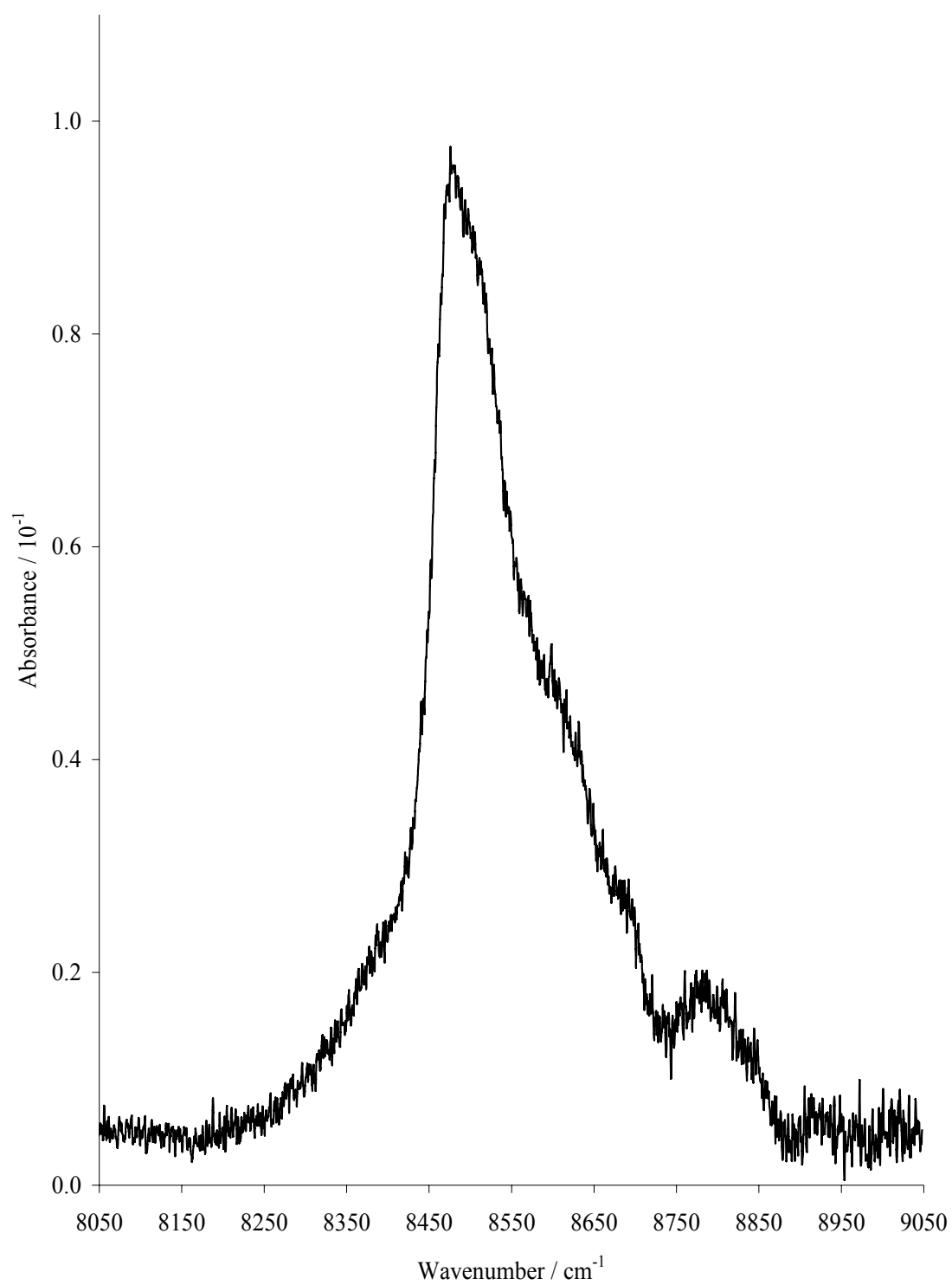


Figure 141. Absorption spectrum of the second overtone ($\Delta v = 3$) of ethyl acetate at 295K. Pressure = 60 Torr.

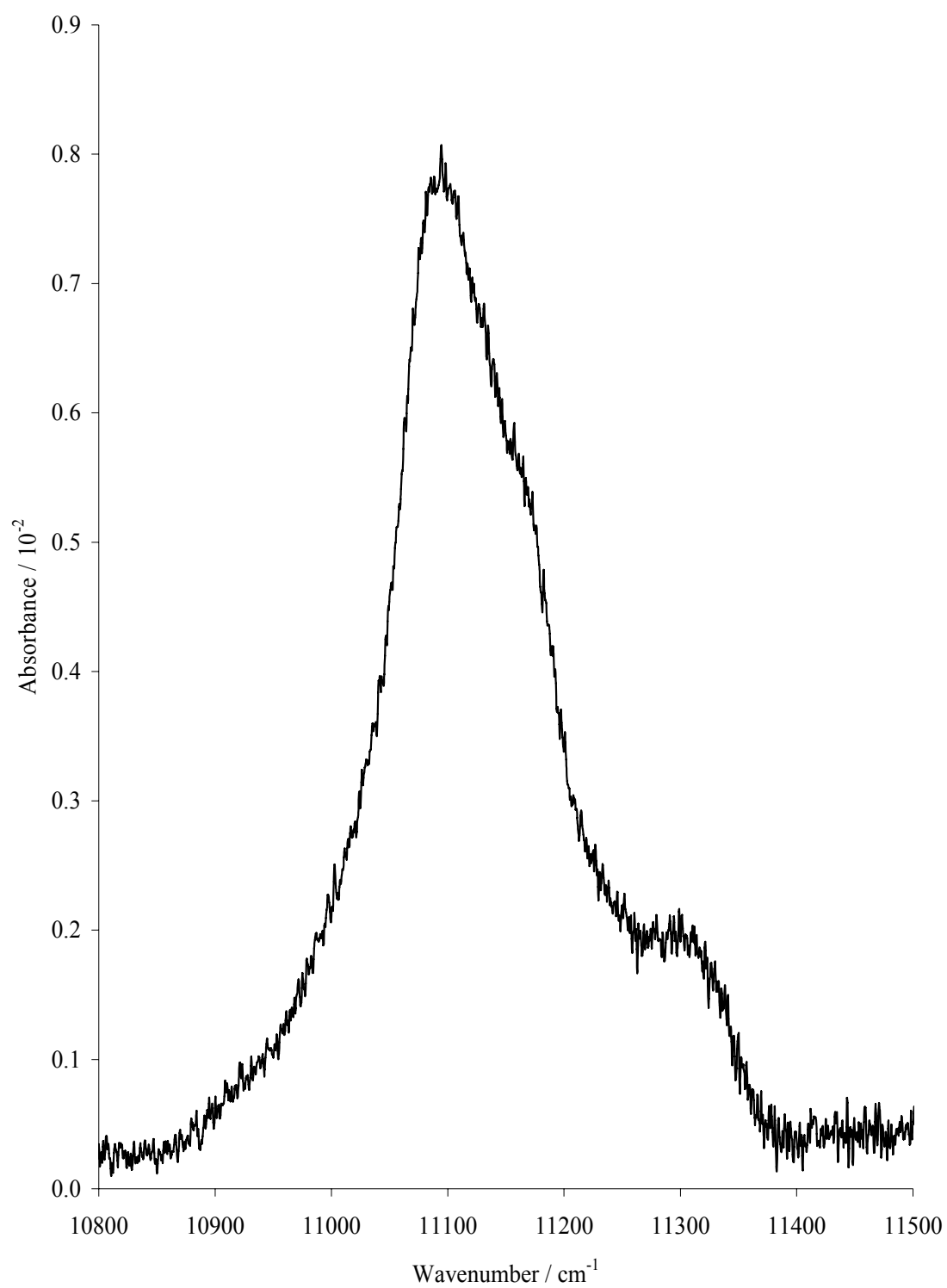


Figure 142. Absorption spectrum of the third overtone ($\Delta v = 4$) of ethyl acetate at 295K. Pressure = 60 Torr.

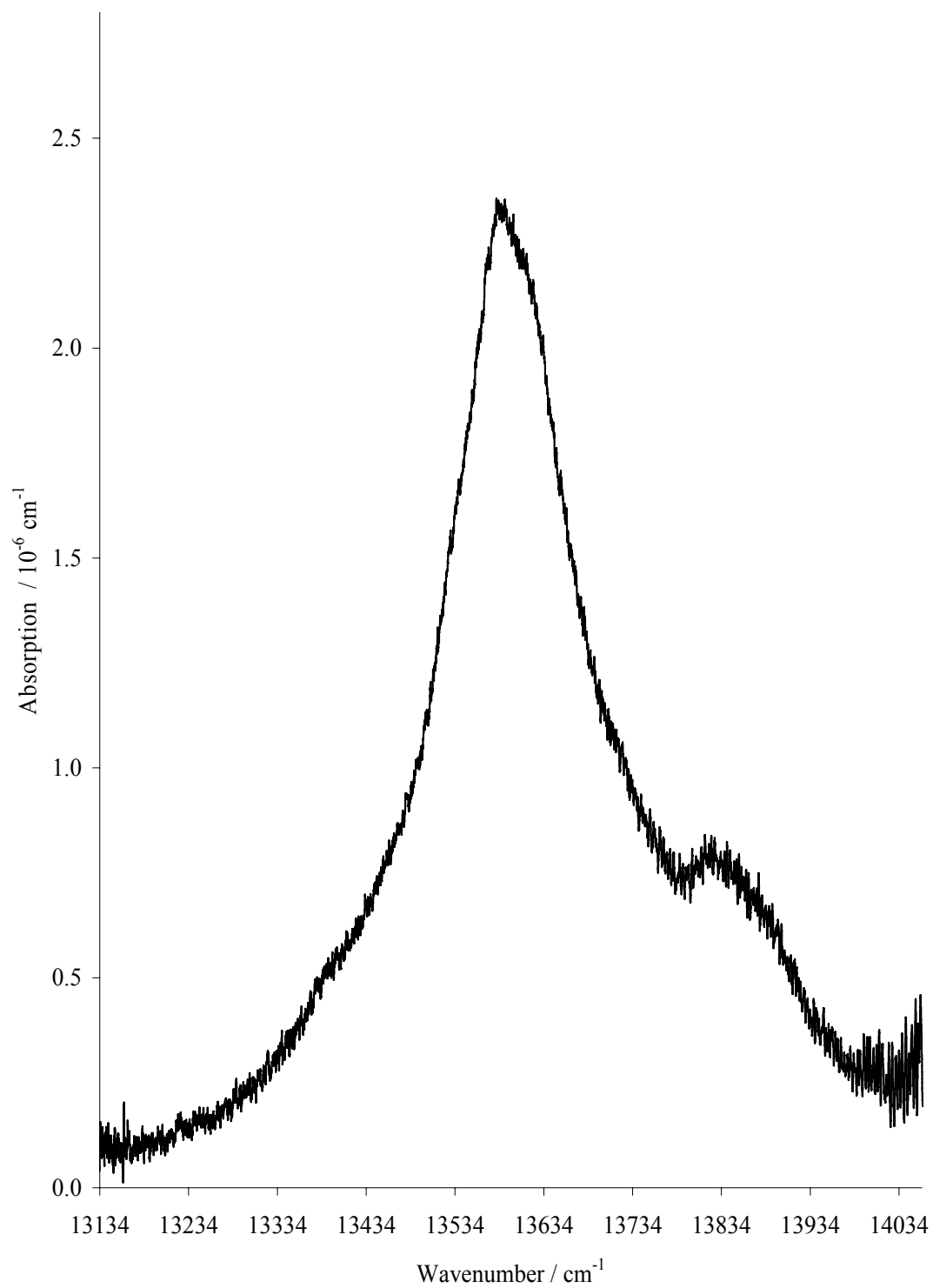


Figure 143. CRD Absorption spectrum of the fourth overtone ($\Delta v = 5$) of ethyl acetate with a pressure of 38 Torr at 295K.

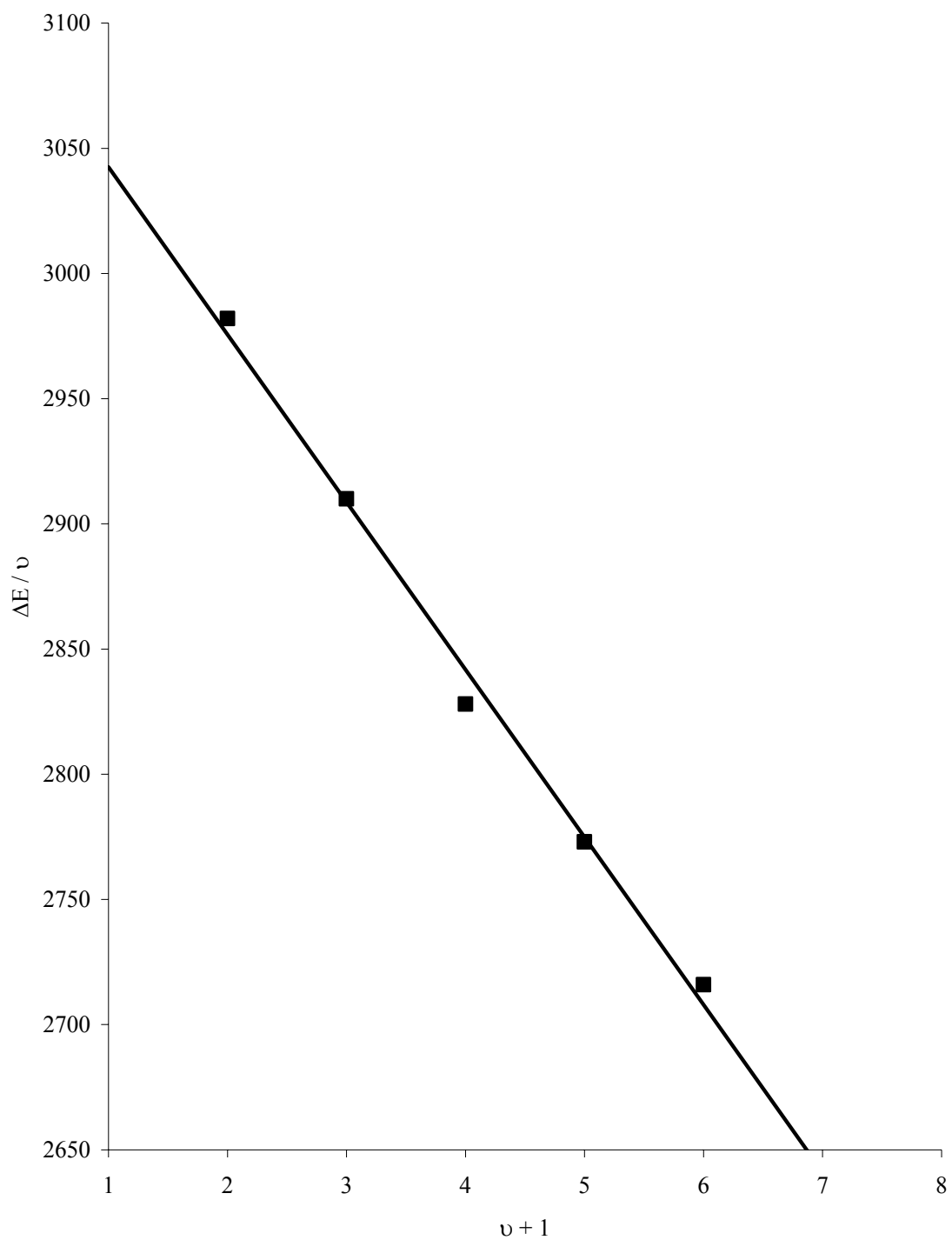


Figure 144. Birge-Sponer plot for ethyl acetate

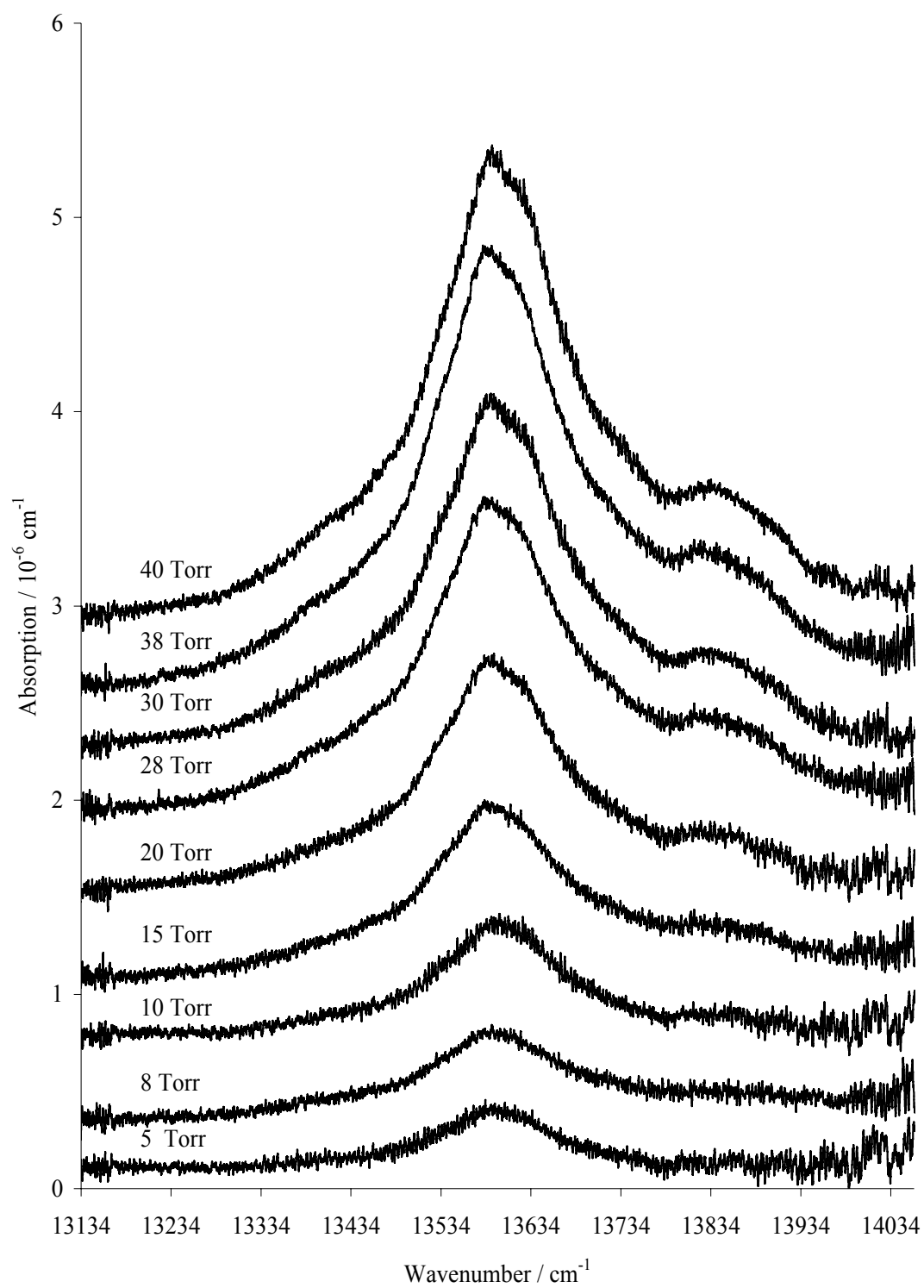
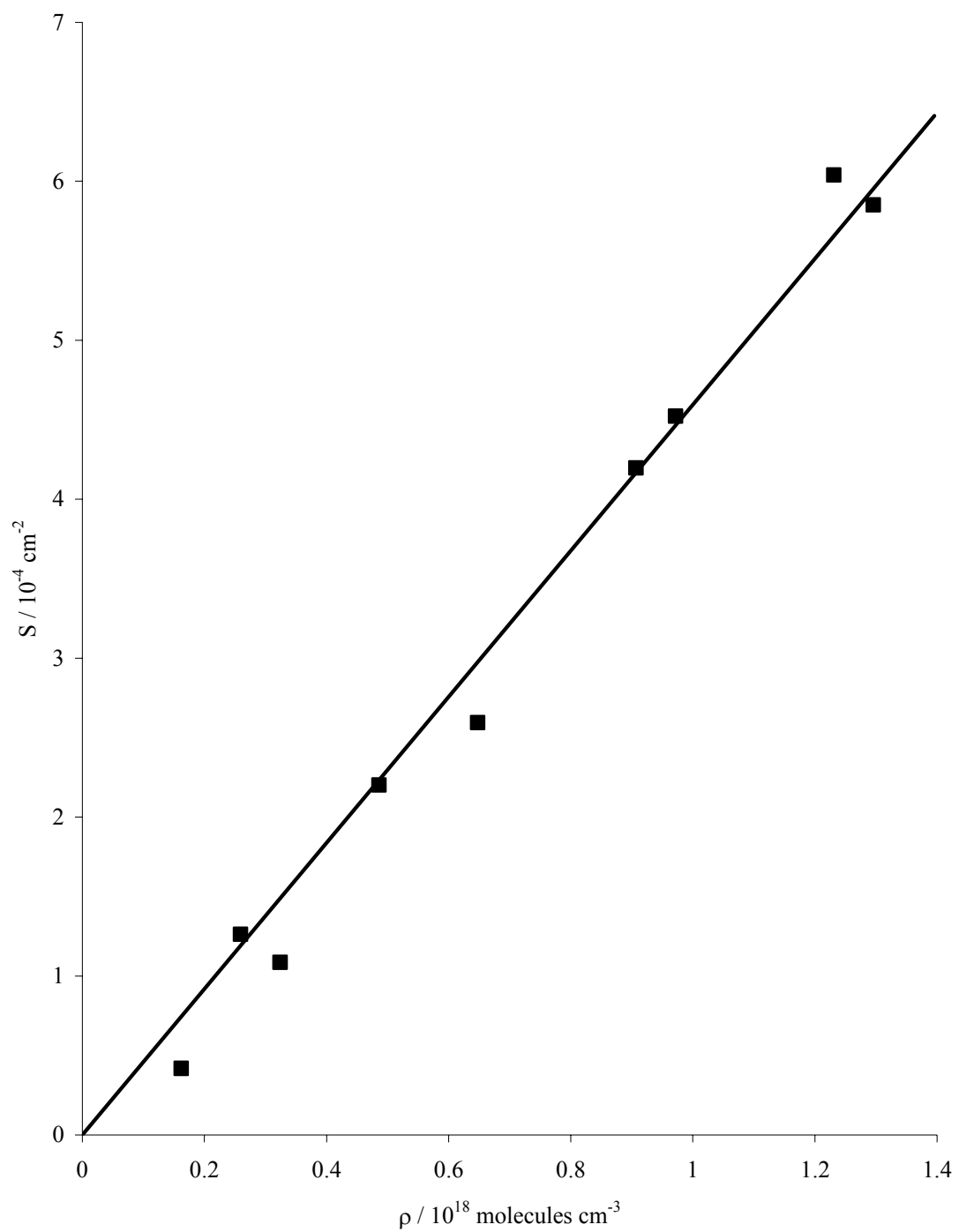


Figure 145. ($\Delta\nu = 5$) $\text{C}_4\text{H}_8\text{O}_2$ absorption pressure series at 295 K



$$S_0 = (4.6 \pm 0.1) \times 10^{-22} \text{ cm}^2 \text{ cm}^{-1} \text{ molecules}^{-1}$$

$$R^2 = 0.992$$

Figure 146. $(\Delta\nu = 5)$ of $\text{C}_4\text{H}_8\text{O}_2$ at 295 K S vs. ρ . Slope is S_0

Table 86. ($\Delta\nu=5$) $C_4H_8O_2$ at 295K, Pressure, ρ , S and S_0 .

$\frac{Pressure}{torr}$	$\frac{\rho}{10^{18} molecules\ cm^{-3}}$	$\frac{S}{10^{-4} cm^{-2}}$	$\frac{S_0}{10^{-22} cm^2 cm^{-1} molecule^{-1}}$
40	1.30	5.85	4.52
38	1.23	6.04	4.91
30	0.97	4.52	4.65
28	0.91	4.20	4.63
20	0.65	2.59	4.00
15	0.49	2.20	4.53
10	0.32	1.09	3.36
8	0.26	1.26	4.87
5	0.16	0.42	2.59
Avg			4.6 ± 0.1

Conclusions and Research Outlook

Conclusions

Photolysis of esters with a β -hydrogen atom by visible radiation has been proposed in this chapter. In the mechanism, which leads to acid and olefin formation by C-H overtone excitation, a strongly absorbing local mode oscillator (the C-H stretch) is excited into a high vibrational level. This vibrational mode contains sufficient energy to achieve the activation energy for decomposition of ester. Thus, this process may be potentially important in the atmosphere as a source of acid formation.

The spectra of fundamental and overtones ($\Delta\nu = 1-5$) of ethyl acetate were recorded. From this information, the Birge-Sponer plot was obtained to predict the frequencies of overtones $\Delta\nu = 6$ and $\Delta\nu = 7$ of ethyl acetate.

Using the spectra obtained with the PS-CRD technique, the band strength values (S_0), was obtained for the fourth overtone ($\Delta\nu = 5$) of ethyl acetate.

Research Outlook

Future work should be focused on obtaining the absorption spectra of $\Delta\nu=6$ and $\Delta\nu=7$ of ethyl acetate in gas phase. Also, kinetic studies should perform by pumping the $\Delta\nu=6$ and $\Delta\nu=7$ C-H overtones of ethyl acetate together with theoretical studies of this possible reaction at different levels of theory in order to confirm the proposed mechanism.

Due to the demonstrated ability of our CRD spectrometer to measure very weak transition at any temperature between 90 and 295 K, this system can be used to perform the studies proposed above.

APPENDICES

APPENDIX A

Remote Control and Data Acquisition System

This appendix describes the basic system used to achieve remote operation of the CRD spectrometer. National Instruments LabView offers the ability to performed together operations of wavelength tuning and data acquisition in the CRD system.

Data Acquisition Hardware

Phase shift-CRD.

Two types of computer cards are required in our system to collect PS-CRD spectrum. The first is a DAQ card and it is used to send an analog pulse in the form of a wave train to the stepper motor driver. The pulse is received and is transformed into a signal to move the step motor one step. Connection between the card and the motor is carried out with a suitable connector panel. The second card is a PCI-GPIB card and it is used to acquire the phase angle from the Sr830 lock-in amplifier. Connection to the lock-in amplifier is carried out with a GPIB cable, which requires a compatible port in the measuring device.

Exponential-CRD

In this case the pulsed dye laser (PDL) motor is connected to the computer using a 9-pin (DB-9) serial interface connector. A R232 tester (from Radio Shack) is necessary to find out what binary number is associated to each pin. A PCI-GPIB card allows signal readout from the LeCroy 9310C oscilloscope.

CRD LabView Software Programs

LabView is a graphical program which provides a user friendly environment without needing to know complex programming. The key is the graphical environment that facilitates connectivity between ideas and actual coding. The principal behind LabView is to create programs called virtual instruments (VI's) to produce the data acquisition system. In general, one VI, called main, is in charge of coordinating all subroutines, so that each chore is achieved in an orderly mode. Saving all VI's created by the programmer into a library (*.llb) is usually recommended to facilitate execution.

The main measurement panel wiring diagram for the CRD acquisition system is illustrated in Figure 147 which connects all the components of the program together and orders them in sequences that the computer can follow and execute in a particular. The sequence follow by the program is:

- 1) Move the step motor.
- 2) Wait specified time.
- 3) Take data point from the lock-in amplifier or oscilloscope.
- 4) Calculate the absorption.
- 5) Write the data to a file,
- 6) Repeat until the final position is reached.

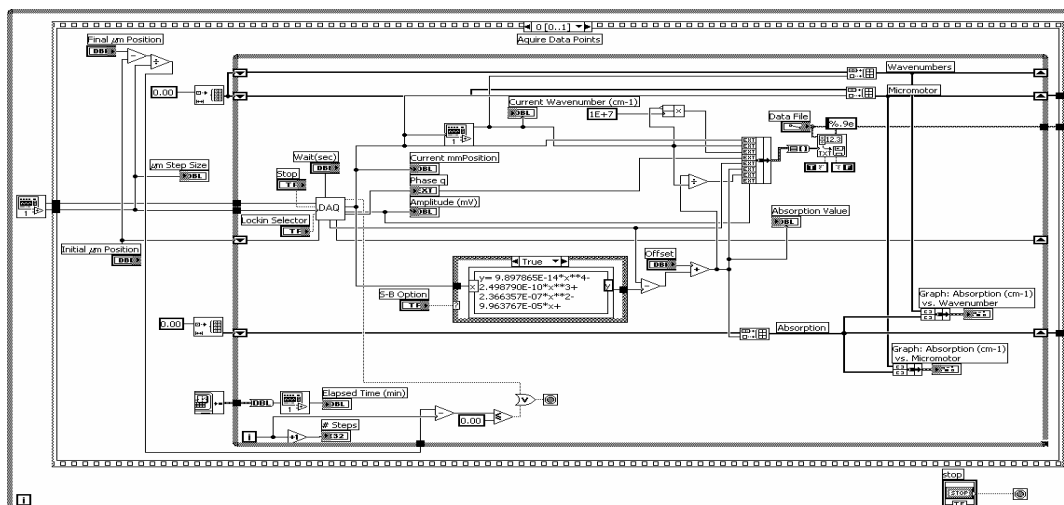


Figure 147. Measurement Panel Wiring Diagram.

The DAQ vi is the essential vi in the CRD program. This contains several frames operation within it. It starts the data acquisition by moving the step motor or PDL motor. It then has a sequence to allow the lock-in or oscilloscope to respond to the signal after the step by waiting a predetermined amount of time set by the operator. The vi then communicates with the lock-in or oscilloscope to acquire the data following by calculation the ring down time (τ) and then absorption using the equations presented in chapter one. After the data point is processed the computer sends a signal back to the lock-in or oscilloscope re-establishing communication. The program can then be stopped if desired using the next sequence or it will keep collecting data points until the final position is reached, previously set by the user.

Although in general for both phase shift and exponential cavity ring down, the DAQ sequence is similar, for reasons of clearer understanding, the DAQ vi's are presented separately in the following sections.

PS-CRD

Figure 148 shows the first sequence of the DAQ program. This starts the process by moving the motor one step. The next sequence is shown in Figure 149 and notifies

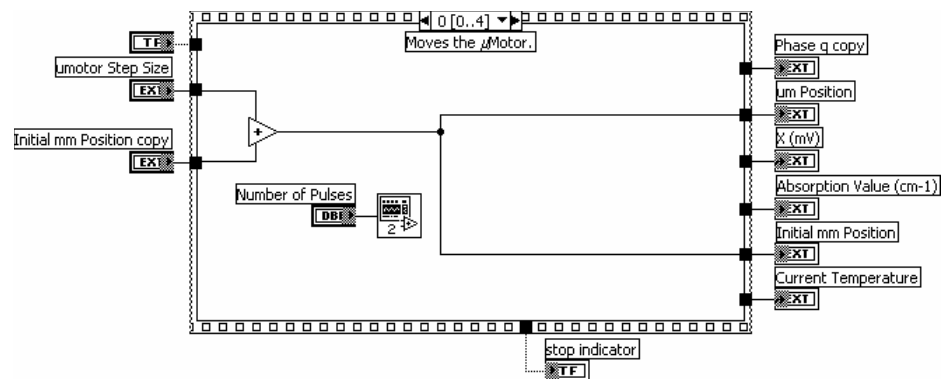


Figure 148. DAQ Movement of the motor

the program to wait a specified time before collecting the data point. Figure 150 shows the follow sequence where the data point is acquired and the absorption calculated.

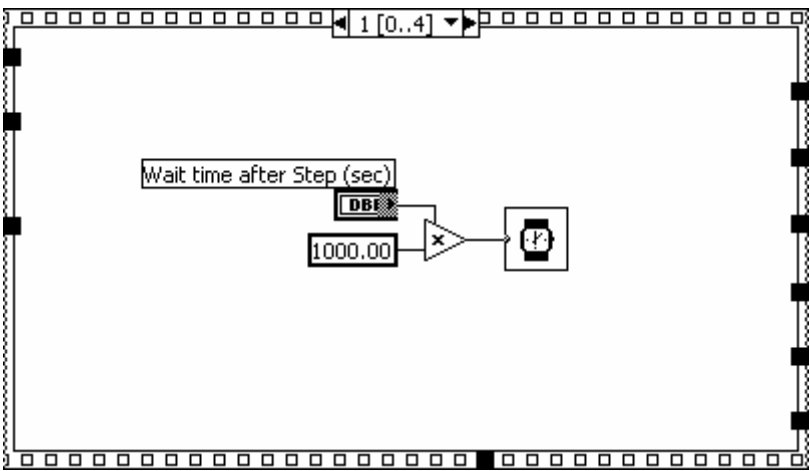


Figure 149. Delay time

The Pscrd 830 snap vi is in charge to communicate with the lock-in and is illustrated in Figure 151. This vi takes the string obtained from the lock-in and

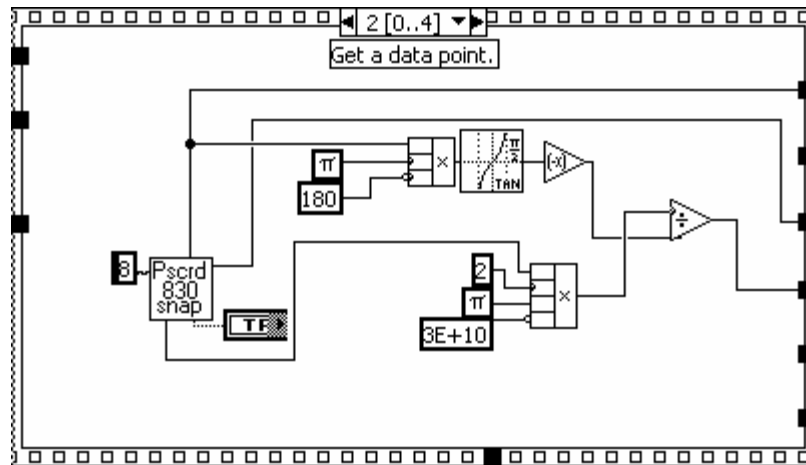


Figure 150. Acquire Data Point and Calculated Absorption.

separates it into useable data. As shown in Figure 151, the string is separated into an X, Y, intensity in mV, phase angle, and the reference frequency supplied to the lock-in. Also, calculation of the absorption value was setup. Figure 152 shows the last vi. It is wired to a button on the measurement panel that when pushed tells the data acquisition process to end. All of the information collected is sent out of the DAQ vi and assembled in the measurement diagram where it is processed and shown on the main panel.

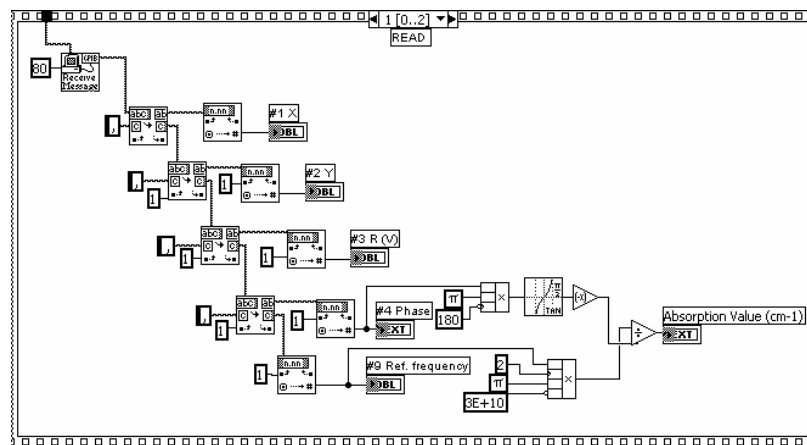


Figure 151. Pscrd 830 Snap vi.

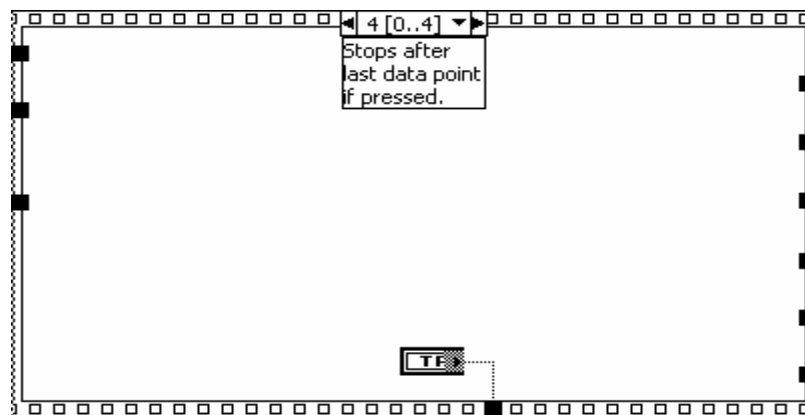


Figure 152. Stop Data Collection

Exponential-CRD

In this case the sequences presented in Figures 148 and 149 are the same. However, the next sequence where the data point is acquired and the absorption calculated is different in this system. Figure 153 shows acquire data point and calculated absorption sequence. This uses a separate vi to communicate with the oscilloscope. This vi is denoted as LeCroy Wv Frm and is presented in Figure 154. This figure presents the method for receiving information from the oscilloscope. It has also been setup to calculate the absorption value and this is shown in Figure 155.

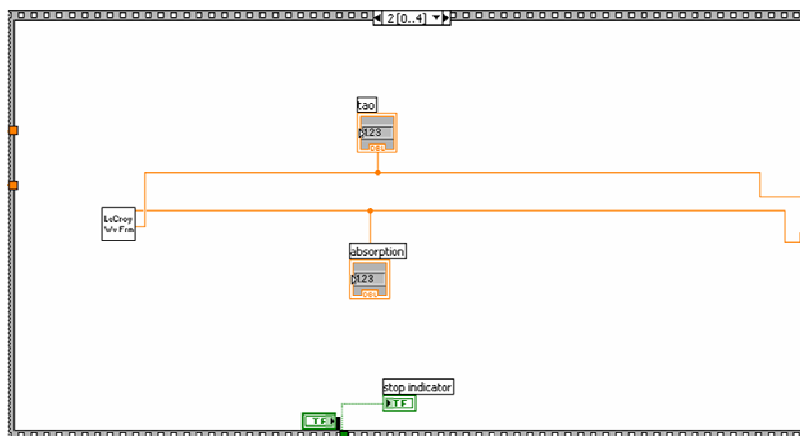


Figure 153. Exponential-CRD. Acquire Data Point and Calculated Absorption

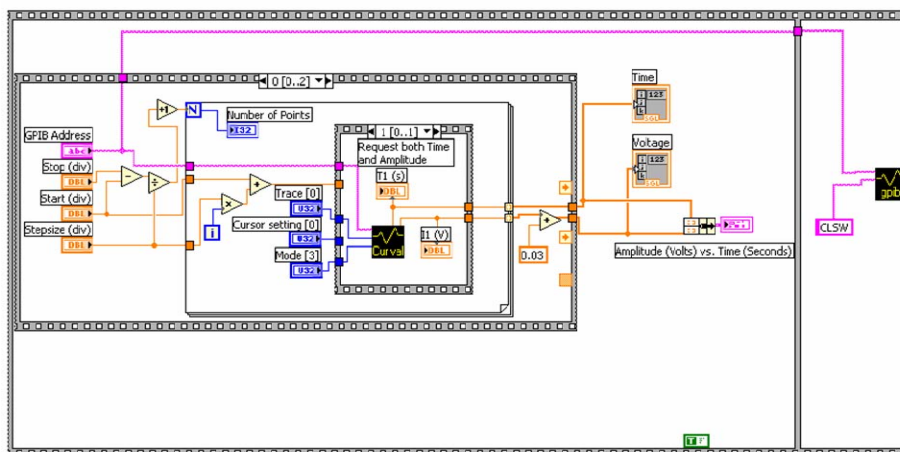


Figure 154. . LeCroy Wv Frm.vi

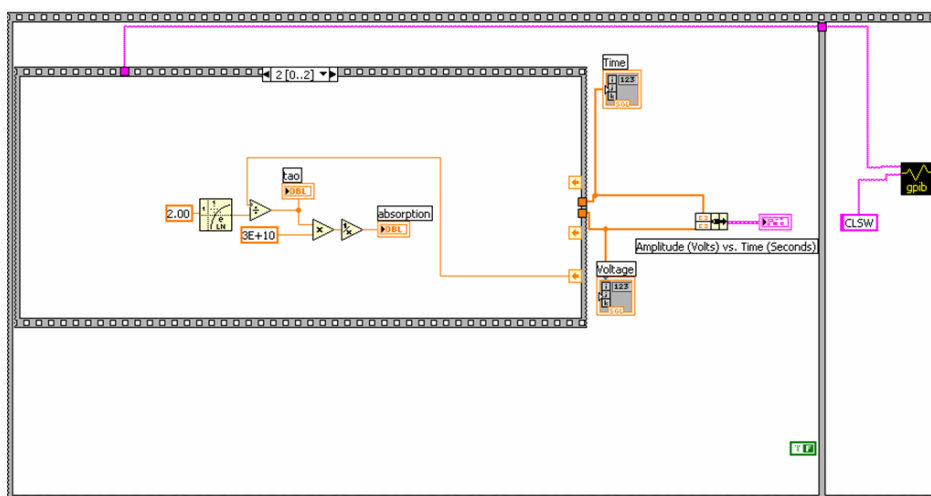


Figure 155. Calculation of Absorption using LeCroy Wv Frm.vi

The last sequence is the same that is shown in Figure 155. As in the PS-CRD system, all of the information collected is sent out of the DAQ vi and assembled in the measurement diagram where it is processed and shown on the main panel.

APPENDIX B

Hamiltonian Matrices to HCAO model

Hamiltonian Matrices to Calculate Frequencies of CH₃D

$$\Delta v = 1$$

$$|100; A_1\rangle: \omega - 2\omega_K + 2\lambda$$

$$|100; E\rangle: \omega - 2\omega_K - \lambda$$

$$\Delta v = 2$$

$$\begin{array}{cc} |200; A_1\rangle & |110; A_1\rangle \\ \begin{bmatrix} 2\omega - 6\omega_K & 2\sqrt{2}\lambda \\ 2\sqrt{2}\lambda & 2\omega - 4\omega_K + 2\lambda \end{bmatrix} \end{array}$$

$$\begin{array}{cc} |200; E\rangle & |110; E\rangle \\ \begin{bmatrix} 2\omega - 6\omega_K & -\sqrt{2}\lambda \\ -\sqrt{2}\lambda & 2\omega - 4\omega_K - \lambda \end{bmatrix} \end{array}$$

$$\Delta v = 3$$

$$\begin{array}{ccc} |300; A_1\rangle & |210; A_1\rangle & |111; A_1\rangle \\ \begin{bmatrix} 3\omega - 12\omega_K & \sqrt{6}\lambda & 0 \\ \sqrt{6}\lambda & 3\omega - 8\omega_K + 3\lambda & -\sqrt{3}\lambda \\ 0 & -\sqrt{3}\lambda & 3\omega - 6\omega_K \end{bmatrix} \end{array}$$

$$\begin{array}{ccc} |300; E\rangle & |210; 1E\rangle & |210; 2E\rangle \\ \begin{bmatrix} 3\omega - 12\omega_K & \sqrt{6}\lambda & 0 \\ \sqrt{6}\lambda & 3\omega - 8\omega_K & -\sqrt{3}\lambda \\ 0 & -\sqrt{3}\lambda & 3\omega - 8\omega_K \end{bmatrix} \end{array}$$

$$\Delta v = 4$$

$$\begin{array}{c} |400; A_1\rangle \quad |310; A_1\rangle \quad |220; A_1\rangle \quad |211; A_1\rangle \\ \left[\begin{array}{cccc} 4\omega - 20\omega x & 2\sqrt{2}\lambda & 0 & 0 \\ 2\sqrt{2}\lambda & 4\omega - 14\omega x + \lambda & 2\sqrt{3}\lambda & \sqrt{6}\lambda \\ 0 & 2\sqrt{3}\lambda & 4\omega - 12\omega x & 2\sqrt{2}\lambda \\ 0 & \sqrt{6}\lambda & 2\sqrt{2}\lambda & 4\omega - 10\omega x + 4\lambda \end{array} \right] \end{array}$$

$$\begin{array}{c} |400; E\rangle \quad |310; 1E\rangle \quad |310; 2E\rangle \quad |220; E\rangle \quad |211; E\rangle \\ \left[\begin{array}{ccccc} 4\omega - 20\omega x & 2\sqrt{2}\lambda & 0 & 0 & 0 \\ 2\sqrt{2}\lambda & 4\omega - 14\omega x + \lambda & 0 & -\sqrt{3}\lambda & \sqrt{6}\lambda \\ 0 & 0 & 4\omega - 14\omega x - \lambda & 3\lambda & 0 \\ 0 & -\sqrt{3}\lambda & 3\lambda & 4\omega - 12\omega x & -\sqrt{2}\lambda \\ 0 & \sqrt{6}\lambda & 0 & -\sqrt{2}\lambda & 4\omega - 10\omega x - 2\lambda \end{array} \right] \end{array}$$

$$\Delta v = 5$$

$$\begin{array}{c} |500; A_1\rangle \quad |410; A_1\rangle \quad |311; A_1\rangle \quad |320; A_1\rangle \quad |221; A_1\rangle \\ \left[\begin{array}{ccccc} 5\omega - 30\omega x & \sqrt{10}\lambda & 0 & 0 & 0 \\ \sqrt{10}\lambda & 5\omega - 22\omega x + \lambda & 4\lambda & 2\sqrt{2}\lambda & 0 \\ 0 & 4\lambda & 5\omega - 16\omega x & 2\lambda & 2\sqrt{6}\lambda \\ 0 & 2\sqrt{2}\lambda & 2\lambda & 5\omega - 18\omega x + 3\lambda & \sqrt{6}\lambda \\ 0 & 0 & 2\sqrt{6}\lambda & \sqrt{6}\lambda & 5\omega - 14\omega x + 4\lambda \end{array} \right] \end{array}$$

$$\begin{array}{c} |500; E\rangle \quad |410; 1E\rangle \quad |410; 2E\rangle \quad |311; E\rangle \quad |320; 1E\rangle \quad |320; 2E\rangle \\ \left[\begin{array}{ccccc} 5\omega - 30\omega x & \sqrt{10}\lambda & 0 & 0 & 0 & 0 \\ \sqrt{10}\lambda & 5\omega - 22\omega x + \lambda & 0 & 2\lambda & 2\sqrt{2}\lambda & 0 \\ 0 & 0 & 5\omega - 22\omega x & 0 & 0 & 2\sqrt{2}\lambda \\ 0 & \sqrt{2}\lambda & 0 & 5\omega - 16\omega x & 2\lambda & 0 \\ 0 & 2\sqrt{2}\lambda & 0 & 2\lambda & 5\omega - 18\omega x - \sqrt{3}/2\lambda & 0 \\ 0 & 0 & 2\sqrt{2}\lambda & 0 & 0 & 5\omega - 18\omega x + \sqrt{3}/2\lambda \end{array} \right] \end{array}$$

$$\begin{array}{c}
\Delta v=6 \\
\begin{array}{c}
|600; A_1\rangle \quad |510; A_1\rangle \quad |411; A_1\rangle \quad |420; A_1\rangle \quad |330; A_1\rangle \quad |321; A_1\rangle \quad |222; A_1\rangle \\
\left[\begin{array}{cccccccc}
6\omega - 42\omega\kappa & 2\sqrt{3}\lambda & 0 & 0 & 0 & 0 & 0 \\
2\sqrt{3}\lambda & 6\omega - 32\omega\kappa + \lambda & \sqrt{10}\lambda & \sqrt{10}\lambda & 0 & 0 & 0 \\
0 & \sqrt{10}\lambda & 6\omega - 24\omega\kappa & \lambda & 0 & 2\sqrt{3}\lambda & 0 \\
0 & \sqrt{10}\lambda & \lambda & 6\omega - 26\omega\kappa & 2\sqrt{6}\lambda & 2\lambda & 0 \\
0 & 0 & 0 & 2\sqrt{6}\lambda & 6\omega - 24\omega\kappa & \sqrt{6}\lambda & 0 \\
0 & 0 & 2\sqrt{3}\lambda & 2\lambda & \sqrt{6}\lambda & 6\omega - 20\omega\kappa + 5\lambda & 6\lambda \\
0 & 0 & 0 & 0 & 0 & 6\lambda & 6\omega - 18\omega\kappa
\end{array} \right]
\end{array} \\
\\
\begin{array}{c}
|600; E\rangle \quad |510; 1E\rangle \quad |510; 2E\rangle \quad |411; E\rangle \quad |420; 1E\rangle \quad |420; 2E\rangle \quad |330; E\rangle \quad |321; 1E\rangle \quad |321; 2E\rangle \\
\left[\begin{array}{cccccccccc}
6\omega - 42\omega\kappa & 2\sqrt{3}\lambda & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
2\sqrt{3}\lambda & 6\omega - 32\omega\kappa + \lambda & 0 & \sqrt{10}\lambda & \sqrt{10}\lambda & 0 & 0 & 0 & 0 \\
0 & 0 & 6\omega - 32\omega\kappa - \lambda & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & \sqrt{10}\lambda & 0 & 6\omega - 24\omega\kappa & \lambda & \sqrt{10}\lambda & 0 & \lambda & 0 \\
0 & \sqrt{10}\lambda & 0 & \lambda & 6\omega - 26\omega\kappa & 0 & -\sqrt{6}\lambda & 2\lambda & 0 \\
0 & 0 & \sqrt{10}\lambda & 0 & 0 & 6\omega - 26\omega\kappa & 3\sqrt{2}\lambda & 0 & 2\lambda \\
0 & 0 & 0 & 0 & -\sqrt{6}\lambda & 3\sqrt{2}\lambda & 6\omega - 24\omega\kappa & -\sqrt{3}/2\lambda & \sqrt{1}/2\lambda \\
0 & 0 & 0 & \lambda & 2\lambda & 0 & -\sqrt{3}/2\lambda & 6\omega - 20\omega\kappa + \lambda/2 & -3/2\sqrt{3}\lambda \\
0 & 0 & 0 & 0 & 0 & 2\lambda & \sqrt{1}/2\lambda & -3/2\sqrt{3}\lambda & 6\omega - 20\omega\kappa - \lambda/2
\end{array} \right]
\end{array}
\end{array}$$

Hamiltonian Matrices to Calculate Frequencies of C₆H₁₀ and C₅SiH₁₀

$\Delta v = 2$ Energy Matrices for all states

$$\begin{array}{cc} \langle 20|_+ \langle 0| & \langle 10|_+ \langle 1| \\ \left[\begin{array}{cc} 2\omega_1 - 6\omega_1 X_1 & -\sqrt{2}\gamma_{12} \\ -\sqrt{2}\gamma_{12} & \omega_1 + \omega_2 - 2\omega_1 X_1 - 2\omega_2 X_2 + \gamma_{12} \end{array} \right] \end{array}$$

$$\begin{array}{cccc} \langle 20|_+ \langle 0| & \langle 10|_+ \langle 1| & \langle 11| \langle 0| & \langle 00| \langle 2| \\ \left[\begin{array}{cccc} 2\omega_1 - 6\omega_1 X_1 & -\sqrt{2}\gamma_{12} & -2\gamma_{12} & 0 \\ -\sqrt{2}\gamma_{12} & \omega_1 + \omega_2 - 2\omega_1 X_1 - 2\omega_2 X_2 + \gamma_{12} & -\sqrt{2}\gamma_{12} & -2\gamma_{12} \\ -2\gamma_{12} & -\sqrt{2}\gamma_{12} & 2\omega_1 - 4\omega_1 X_1 & 0 \\ 0 & -2\gamma_{12} & 0 & 2\omega_2 - 6\omega_2 X_2 \end{array} \right] \end{array}$$

$\Delta v = 3$ Energy Matrices for all states

$$\begin{array}{cccc} \langle 30|_+ \langle 0| & \langle 21|_+ \langle 0| & \langle 20|_+ \langle 1| & \langle 10|_+ \langle 2| \\ \left[\begin{array}{cccc} 3\omega_1 - 12\omega_1 X_1 & -\sqrt{3}\gamma_{12} & -\sqrt{3}\gamma_{12} & 0 \\ -\sqrt{3}\gamma_{12} & 3\omega_1 - 8\omega_1 X_1 + 2\gamma_{12} & -\gamma_{12} & 0 \\ -\sqrt{3}\gamma_{12} & -\gamma_{12} & 2\omega_1 + \omega_2 - 6\omega_1 X_1 - 2\omega_2 X_2 & -2\gamma_{12} \\ 0 & 0 & -2\gamma_{12} & \omega_1 + 2\omega_2 - 2\omega_1 X_1 + \gamma_{12} - 6\omega_2 X_2 \end{array} \right] \end{array}$$

$\Delta v = 4$ Energy Matrices for all states

$<40 <0 $	$<31 <0 $	$<30 <1 $	$<21 <1 $	$<20 <2 $	$<10 <3 $
$4\varpi_1 - 20\varpi_1 X_1$	$-2\gamma_{12}$	$-2\gamma_{13}$	0	0	0
$-2\gamma_{12}$	$4\varpi_1 - 14\varpi_1 X_1$	$-\gamma_{13}$	$-\sqrt{3}\gamma_{13}$	0	0
$-2\gamma_{13}$	$-\gamma_{13}$	$3\varpi_1 + \varpi_3 - 12\varpi_1 X_1 - 2\varpi_3 X_3$	$-\sqrt{3}\gamma_{12}$	$-\sqrt{6}\gamma_{13}$	0
0	$-\sqrt{3}\gamma_{13}$	$3\varpi_1 + \varpi_3 - 6\varpi_1 X_1 - 2\varpi_3 X_3 + \gamma_{13}$	$-\sqrt{2}\gamma_{13}$	$-\sqrt{2}\gamma_{13}$	0
0	0	$-\sqrt{6}\gamma_{13}$	$2\varpi_1 + 2\varpi_3 - 6\varpi_1 X_1 - 6\varpi_3 X_3$	$-\sqrt{6}\gamma_{13}$	$-\sqrt{6}\gamma_{13}$
0	0	0	$-\sqrt{6}\gamma_{13}$	$\varpi_1 + 3\varpi_3 - 2\varpi_1 X_1 - 12\varpi_3 X_3 + \gamma_{13}$	0

$ 40> 0>$	$ 31> 0>$	$ 22> 0>$	$ 30> 1>$	$ 21> 1>$	$ 20> 2>$	$ 11> 2>$	$ 10> 3>$	$ 00> 4>$
$4\varpi_1 - 20\varpi_1 X_1$	$-2\gamma_{12}$	0	$2\gamma_{13}$	0	0	0	0	0
$-2\gamma_{12}$	$4\varpi_1 - 14\varpi_1 X_1$	$-\sqrt{12}\gamma_{12}$	$-\gamma_{13}$	$-\sqrt{3}\gamma_{13}$	0	0	0	0
0	$-\sqrt{12}\gamma_{12}$	$4\varpi_1 - 12\varpi_1 X_1$	0	$-\gamma_{13}$	0	0	0	0
$-2\gamma_{13}$	$-\gamma_{13}$	0	$3\varpi_1 + \varpi_3 - 12\varpi_1 X_1 - 2\varpi_3 X_3$	$-\sqrt{3}\gamma_{12}$	$-\sqrt{6}\gamma_{13}$	0	0	0
0	$-\sqrt{3}\gamma_{13}$	$-\gamma_{13}$	$3\varpi_1 + \varpi_3 - 6\varpi_1 X_1 - 2\varpi_3 X_3 - 2\gamma_{12}$	$-\sqrt{2}\gamma_{13}$	$-\sqrt{2}\gamma_{13}$	$-2\sqrt{2}\gamma_{13}$	0	0
0	0	0	$-\sqrt{6}\gamma_{13}$	$-\sqrt{2}\gamma_{13}$	$2\varpi_1 + 2\varpi_3 - 6\varpi_1 X_1 - 6\varpi_3 X_3$	$-2\gamma_{12}$	$-\sqrt{6}\gamma_{13}$	0
0	0	0	0	$-2\sqrt{2}\gamma_{13}$	$-2\gamma_{12}$	$2\varpi_1 + 2\varpi_3 - 4\varpi_1 X_1 - 6\varpi_3 X_3$	$-\sqrt{6}\gamma_{13}$	0
0	0	0	0	$-\sqrt{6}\gamma_{13}$	$-2\gamma_{12}$	$2\varpi_1 + 2\varpi_3 - 4\varpi_1 X_1 - 6\varpi_3 X_3$	$-\sqrt{6}\gamma_{13}$	0
0	0	0	0	0	$-\sqrt{6}\gamma_{13}$	$2\varpi_1 + 2\varpi_3 - 4\varpi_1 X_1 - 6\varpi_3 X_3$	$-\sqrt{6}\gamma_{13}$	$-2\sqrt{2}\gamma_{13}$
0	0	0	0	0	0	$-\sqrt{6}\gamma_{13}$	$2\varpi_1 + 2\varpi_3 - 4\varpi_1 X_1 - 6\varpi_3 X_3$	$-2\sqrt{2}\gamma_{13}$
0	0	0	0	0	0	0	$-2\sqrt{2}\gamma_{13}$	$4\varpi_3 - 20\varpi_3 X_3$

$\frac{\Delta v = 5}{}$

$ 50\rangle, 0\rangle$	$ 41\rangle, 0\rangle$	$ 32\rangle, 0\rangle$	$ 40\rangle, 1\rangle$	$ 31\rangle, 1\rangle$	$ 30\rangle, 2\rangle$	$ 21\rangle, 2\rangle$	$ 20\rangle, 3\rangle$	$ 10\rangle, 4\rangle$
$5\pi_1 - 33\pi_1 X_1$	$-\sqrt{5}\gamma_{12}$	0	$-\sqrt{5}\gamma_{13}$	0	0	0	0	0
$-\sqrt{5}\gamma_{12}$	$5\pi_1 - 22\pi_1 X_1$	$-\sqrt{6}\gamma_{12}$	$-\gamma_{13}$	$-2\gamma_{13}$	0	0	0	0
0	$-\sqrt{6}\gamma_{12}$	$5\pi_1 - 18\pi_1 X_1 + 3\gamma_{12}$	0	$-\sqrt{2}\gamma_{13}$	0	0	0	0
$-\sqrt{5}\gamma_{13}$	$-\gamma_{13}$	0	$4\pi_1 + \pi_3 - 20\pi_1 X_1 - 2\pi_1 X_3$	$-2\gamma_{12}$	$-2\sqrt{2}\gamma_{13}$	0	0	0
0	$-2\gamma_{13}$	$-\sqrt{2}\gamma_{12}$	$-2\gamma_{12}$	$4\pi_1 + \pi_3 - 14\pi_1 X_1 - 2\pi_1 X_3$	$-\sqrt{2}\gamma_{13}$	$-\sqrt{6}\gamma_{13}$	0	0
0	0	0	$-2\sqrt{2}\gamma_{13}$	$-\sqrt{2}\gamma_{13}$	$3\pi_1 + 2\pi_3 - 11\pi_1 X_1 - 6\pi_1 X_3$	$-\sqrt{3}\gamma_{12}$	$-3\gamma_{13}$	0
0	0	0	0	$-\sqrt{6}\gamma_{13}$	$-\sqrt{3}\gamma_{12}$	$3\pi_1 + 2\pi_3 - 8\pi_1 X_1 - 6\pi_1 X_3 + 2\gamma_{12}$	$-\sqrt{3}\gamma_{13}$	0
0	0	0	0	0	$-\sqrt{3}\gamma_{12}$	$3\pi_1 + 2\pi_3 - 8\pi_1 X_1 - 6\pi_1 X_3 + 2\gamma_{12}$	$-\sqrt{3}\gamma_{13}$	0
0	0	0	0	0	$-3\gamma_{13}$	$3\pi_1 + 2\pi_3 - 8\pi_1 X_1 - 6\pi_1 X_3 + 2\gamma_{12}$	$-2\sqrt{2}\gamma_{13}$	$-2\sqrt{2}\gamma_{13}$
0	0	0	0	0	0	0	$-2\sqrt{2}\gamma_{13}$	$\pi_1 + 4\pi_3 - 2\pi_1 X_1 - 20\pi_1 X_3 + \gamma_{12}$

$\Delta U = 5$

$ 50\rangle, +10\rangle$	$ 41\rangle, +10\rangle$	$ 32\rangle, +10\rangle$	$ 40\rangle, +11\rangle$	$ 31\rangle, +11\rangle$	$ 22\rangle, +11\rangle$	$ 30\rangle, +12\rangle$	$ 21\rangle, +12\rangle$	$ 20\rangle, +13\rangle$	$ 11\rangle, +13\rangle$	$ 10\rangle, +14\rangle$	$ 00\rangle, +15\rangle$
$5w_1 - 30w_2\bar{X}_1$	$-\sqrt{2}\gamma_{12}$	0	$-\sqrt{5}\gamma_{13}$	0	0	0	0	0	0	0	0
$-\sqrt{5}\gamma_{13}$	$5w_1 - 22w_2\bar{X}_1$	$-\sqrt{5}\gamma_{12}$	$-\gamma_{13}$	$-\gamma_{13}$	0	0	0	0	0	0	0
0	$-\sqrt{5}\gamma_{12}$	$5w_1 - 13w_2\bar{X}_1 - 3\gamma_{12}$	0	$-\sqrt{2}\gamma_{13}$	$-\sqrt{5}\gamma_{13}$	0	0	0	0	0	0
$-\sqrt{5}\gamma_{13}$	$-\gamma_{13}$	0	$4w_1 + w_2 - 20w_2\bar{X}_1 - 2w_2\bar{X}_3$	$-\gamma_{13}$	0	$-2\sqrt{2}\gamma_{13}$	0	0	0	0	0
0	$-2\gamma_{13}$	$-\gamma_{13}$	$4w_1 + w_2 - 14w_2\bar{X}_1 - 2w_2\bar{X}_3$	$-\sqrt{12}\gamma_{12}$	$-\sqrt{12}\gamma_{12}$	$-\sqrt{2}\gamma_{13}$	$-\sqrt{6}\gamma_{13}$	0	0	0	0
0	0	$-\sqrt{6}\gamma_{13}$	$-\sqrt{12}\gamma_{12}$	$-\sqrt{12}\gamma_{12}$	$\frac{1}{2}w_1 + w_2 - 12w_2\bar{X}_1 - 2w_2\bar{X}_3$	0	$-2\sqrt{2}\gamma_{13}$	0	0	0	0
0	0	0	$-2\sqrt{2}\gamma_{13}$	$-\sqrt{2}\gamma_{13}$	$3w_1 + 2w_2 - 12w_2\bar{X}_1 - 6w_2\bar{X}_3$	$-\sqrt{2}\gamma_{12}$	$-\sqrt{6}\gamma_{13}$	$-3\gamma_{13}$	0	0	0
0	0	0	0	0	$-\sqrt{6}\gamma_{13}$	$3w_1 + 2w_2 - 8w_2\bar{X}_1 - 6w_2\bar{X}_3 - 2\gamma_{12}$	$-\sqrt{2}\gamma_{13}$	$-3\gamma_{13}$	0	0	0
0	0	0	0	0	0	$2w_1 + 3w_2 - 6w_2\bar{X}_1 - 12w_2\bar{X}_3$	$-2\gamma_{12}$	$-2\gamma_{12}$	$-2\sqrt{2}\gamma_{13}$	0	0
0	0	0	0	0	0	$2w_1 + 3w_2 - 4w_2\bar{X}_1 - 12w_2\bar{X}_3$	$-2\sqrt{2}\gamma_{13}$	$-2\gamma_{12}$	$-2\sqrt{2}\gamma_{13}$	0	0
0	0	0	0	0	0	0	0	$w_1 + 4w_2 - 2w_2\bar{X}_1 - 20w_2\bar{X}_3 - \gamma_{12}$	$-\sqrt{10}\gamma_{13}$	$-\sqrt{10}\gamma_{13}$	0
0	0	0	0	0	0	0	0	$-10\gamma_{13}$	0	$5w_2 - 30w_2\bar{X}_3$	0

REFERENCES

- (1) Busch, K. W.; Busch, M. A. In *Cavity-Ringdown Spectroscopy: An Ultratrace-Absorption Measurement Technique*; ACS Symposium Series; 1999;pp 269.
- (2) Berden, G.; Peeters, R.; Meijer, G. *Int Rev Phys Chem* **2000**, *19*, 564-607.
- (3) Herbelin, J. M.; McKay, J. A.; Kwok, M. A.; Ueunten, R. H.; Urevig, D. S.; Spencer, D. J.; Benard, D. J. *Appl Optics* **1980**, *19*, 144-147.
- (4) Anderson, D. Z.; Frisch, J. C.; Masser, C. S. *Appl Optics* **1984**, *23*, 1238-1245.
- (5) O'Keefe, A.; Deacon, D. A. G. *Rev. Sci. Instrum.* **1988**, *59*, 2544-2551.
- (6) Engeln, R.; von Helden, G.; Berden, G.; Meijer, G. *Chem Phys Lett* **1996**, *262*, 105-109.
- (7) Romanini, D.; Sadeghi, N.; Stoeckel, F. *Chem Phys Lett* **1997**, *264*, 316-322.
- (8) Engeln, R.; Meijer, G. *Rev. Sci. Instrum.* **1996**, *67*, 2708-2713.
- (9) Martin, J.; Paldus, B. A.; Zalicki, P.; Wahl, E. H.; Owano, T. G.; Harris Jr., J. S.; Kruger, C. H.; Zare, R. N. *Chem. Phys. Lett* **1996**, *258*, 63-70.
- (10) Hamers, E.; Schram, D.; Engeln, R. *Chem Phys Lett* **2002**, *365*, 237-243.
- (11) Barros, J. P. P.; Engeln, R. A. H.; Schram, D. C. Development of a Phase Shift-, Fourier Transform- Cavity Ring Down Spectrometer, Univ. Drukkerij, Tech. Univ. Eindhoven, 2000.
- (12) Jones-Bey, H. *Optoelectronics World* **2000**, *March*, S19-S22.
- (13) Romanini, D.; Kachanov, A. A.; Stoeckel, F. *Chem. Phys. Lett.* **1997**, *270*, 538-545.
- (14) He, Y.; Orr, B. J. *Chem. Phys. Lett.* **2000**, *319*, 131-137.
- (15) Ball, S. M.; Povey, I. M.; Norton, E. G.; Jones, R. L. *Chem. Phys. Lett.* **2001**, *342*, 113-120.
- (16) Scherer, J. J.; Paul, J. B.; Jiao, H., O'Keefe *Appl Optics* **2001**, *40*, 6725-6732.
- (17) Scherer, J. J. *Chem. Phys. Lett.* **1998**, *292*, 143-153.

- (18) Pipino, A. C. R.; Hudgens, J. W.; Huie, R. E. *Rev. Sci. Instrum.* **1997**, *68*, 2978-2989.
- (19) Engeln, R.; Letourneur, K. G. Y.; Boogarts, M. G. H.; van de Sanden, M. C. M. *Chem. Phys. Lett.* **1999**, *310*, 405-410.
- (20) Hallock, A. J.; Berman, E. S. F.; Zare, R. N. *App. Spec.* **2003**, *57*, 571-573.
- (21) Xu, S.; Sha, G.; Xie, J. *Rev. Sci. Instrum.* **2002**, *73*, 255-258.
- (22) Hallock, A. J.; Berman, E. S. F.; Zare, R. N. *Anal. Chem.* **2002**, *74*, 1741-1743.
- (23) Benedikt, J.; Letourneur, K. G. Y.; Wisse, M.; Schram, D. C.; van de Sanden, M. C. M. *Diamonds and Related Materials* **2002**, *11*, 989-993.
- (24) John, P.; Rabeau, J. R.; Wilson, J. I. B. *Diamonds and Related Materials* **2002**, *11*, 608-611.
- (25) Hoefnagels, J. P. M.; Stevens, A. A. E.; Boogarts, M. G. H.; Kessels, W. M. M.; van de Sanden, M. C. M. *Chem. Phys. Lett.* **2002**, *360*, 189-193.
- (26) Birza, P.; Motylewski, T.; Khoroshev, D.; Chirokolava, A.; Linnartz, H.; Maier, J. P. *Chem. Phys. Lett.* **2002**, *283*, 119-124.
- (27) Hippler, M.; Quack, M. *Chem. Phys. Lett.* **1999**, *314*, 273-281.
- (28) Scherer, J. J.; Paul, J. B.; O'Keefe, A.; Saykally, R. J. *Chem. Rev.* **1997**, *97*, 25-51.
- (29) Ito, F.; Nakanaga, T.; Futami, Y.; Nakata, M. *Chem. Phys. Lett.* **2003**, *286*, 337-345.
- (30) Ito, F.; Nakanaga, T. *Chem Phys* **2002**, *277*, 163-169.
- (31) Hippler, M.; Quack, M. *Chem. Phys. Lett.* **1999**, *314*, 273-281.
- (32) Evertsen, R.; Van Oijen, J. A.; Hermanns, R. T. E.; DeGoey, L. P. H.; Ter Meulen, J. J. *Combustion and Flame* **2003**, *132*, 34-42.
- (33) Mercier, X.; Therssen, E.; Pauwels, J. F.; Desgroux, P. *Combustion and Flame* **2001**, *125*, 656-667.
- (34) Lozovsky, V. A.; Derzy, I.; Cheskis, S. *Chem. Phys. Lett.* **1998**, *284*, 407-411.
- (35) Mercier, X.; Pillier, L.; Pauwels, J. F.; Desgroux, P. *C. R. Acad. Sci. Paris* **2001**, *2*, 965-972.

- (36) Stolk, R. L.; ter Meulen, J. J. *Diamonds and Related Materials* **1999**, 8, 1251-1255.
- (37) Lommatzsch, U.; Wahl, E. H.; Owano, T. G.; Kruger, C. H.; Zare, R. N. *Chem. Phys. Lett* **2000**, 320, 339-344.
- (38) Wahl, E. H.; Owano, T. G.; Kruger, C. H.; Zalicki, P.; Ma, Y.; Zare, R. N. *Diamonds and Related Materials* **1996**, 5, 373-377.
- (39) Wahl, E. H.; Owano, T. G.; Kruger, C. H.; Ma, Y.; Zalicki, P.; Z., R.N. *Diamonds and Related Materials* **1997**, 6, 476-480.
- (40) Atkinson, D. B.; Hudgens, J. W.; Orr-Ewing, A. J. *J. Phys. Chem. A* **1999**, 103, 6173-6180.
- (41) Atkinson, D. B.; Hudgens, J. W. *J. Phys. Chem. A* **2000**, 104, 811-818.
- (42) Atkinson, D. B.; Hudgens, J. W. *J. Phys. Chem. A* **1999**, 103, 4242-4252.
- (43) Tonokura, K.; Koshi, M. *J. Phys. Chem. A* **2003**, 107, 4457-4461.
- (44) Czyzewski, A.; Ernst, K.; Franssen, G.; Karasinski, G.; Kmiecik, M.; Lange, H.; Skubiszak, W.; Stacewicz, T. *Chem. Phys. Lett.* **2002**, 357, 477-482.
- (45) Alexander, A. *Chem. Phys. Lett.* **2004**, 393, 138-142.
- (46) Enami, S.; Hashimoto, S.; Kawasaki, M.; Nakano, Y.; Ishiwata, T.; Tonokura, K.; Wallington, T. J. *J. Phys. Chem. A* **2005**, 109, 1587-1593.
- (47) Brown, S. S.; Stark, H.; Ravishankara, A. R. *Appl. Phys. B* **2002**, 75, 173-182.
- (48) King, M. D.; Dick, E. M.; Simpson, W. R. *Atm. Env.* **2000**, 34, 685-688.
- (49) Mazurenka, M. I.; Fawcett, B. L.; Elks, J. M. F.; Shallcross, D. E.; Orr-Ewing, A. *J. Chem. Phys. Lett.* **2003**, 367, 1-9.
- (50) Lehman, S. Y.; Bertness, K. A.; Hodges, J. T. *J. Crystal Growth* **2003**, 68, 57-63.
- (51) Stacewicz, T.; Chudzynski, S.; Czyzewski, A.; Ernst, K.; Karasinski, G.; Pietruczuk, A.; Skubiszak, W.; Stelmaszyk, K. *Rad. Phys. Chem.* **2003**, 68, 57-63.
- (52) Bulatov, V.; Fisher, M.; Schechter, I. *Anal. Chim. Acta* **2002**, 466, 1-9.
- (53) Fawcett, B. L.; Parkes, A. M.; Shallcross, D. E.; Orr-Ewing, D. E. *Phys. Chem. Chem. Phys.* **2002**, 4, 5960-5965.

- (54) Parkes, M.; Fawcett, B. L.; Austin, R. E.; Nakamichi, S.; Shallcross, D. E.; Orr-Ewing, A. J. *The Analyst* **2003**, *128*, 960-965.
- (55) Parkes, A. M.; Lindley, R. E.; Orr-Ewing, A. J. *Anal. Chem.* **2004**, *76*, 7329-7335.
- (56) Romanini, D.; Lehmann, K. K. *J. Chem. Phys.* **1993**, *99*, 6287-6301.
- (57) Kleine, D.; Stry, S.; Lauterbach, J.; Kleinerann, K.; Hering, P. *Chem. Phys. Lett.* **1999**, *312*, 185-190.
- (58) Romanini, D.; Kachanov, A. A.; Stoeckel, F. *Chem. Phys. Lett.* **1997**, *270*, 546-550.
- (59) Brown, S. S.; Wilson, R. W.; Ravishankara, A. R. *J. Phys. Chem. A* **2000**, *104*, 4976-4983.
- (60) Romanini, D.; Kachanov, A. A.; Sadeghi, N.; Stoeckel, F. *Chem. Phys. Lett.* **1997**, *264*, 316-322.
- (61) Scherer, J. J.; Voelkel, D.; Rakestraw, D. J.; Paul, J. B.; Collier, C. P.; Saykally, R. J. *A. O. Appl. Chem. Phys. Lett.* **1995**, *245*, 273-280.
- (62) He, Y.; Hippler, M.; Quack, M. *Chem. Phys. Lett.* **1998**, *289*, 527-534.
- (63) O'Keefe, A.; Lee, O. *Am. Lab* **1989**, *21*, 19.
- (64) Lewis, E. K.; Moehnke, C. J.; Manzanares, C. E. *Chem Phys Lett* **2004**, *394*, 25-31.
- (65) Lewis, E. K.; Reynolds, D.; Li, X.; de Villelea, G.; Leduca, L.; Cedeño, D. L.; Manzanares I, C. *Chem Phys Lett* **2001**, *334*, 357-364.
- (66) Lewis, E. K. *Design of a Low Temperature Phase Shift Cavity Ring Down Technique with Applications to High Vibrational Overtones Absorptions*, Baylor University, 2003.
- (67) Lewis, E. K.; Moehnke, C. J.; Navea, J. G.; Manzanares, C. E. *Rev. Sci. Instrum.* **2006**, *77*, 073107.
- (68) Moehnke, C. J.; Lopez-Calvo, A.; Manzanares, C. E. *Chem Phys Lett* **2006**, *418*, 576-580.
- (69) Moehnke, C. J. *Low Temperature Phase Shift Cavity Ring Down: Applications to High Vibrational Overtones*, Baylor University, 2005.

- (70) Martyn, D.; Wheeler, M. D.; Newman, S. M.; Orr-Ewing, A. J.; Ashfold, N. R. *J. Chem. Soc. Faraday Trans.* **1998**, *94*, 337-351.
- (71) Zalicki, P.; Zare, R. N. *J. Chem. Phys.* **1995**, *102*, 2708-2717.
- (72) Lehmann, K. K.; Romanini, D. *J. Chem. Phys.* **1996**, *105*, 10263-10277.
- (73) van Helden, J. H.; Schram, D. C.; Engeln, R. *Chem. Phys. Lett.* **2004**, *400*, 320-325.
- (74) Kasyutich, V. L.; Martin, P. A.; Holdsworth, R. J. *Meas. Sci. Technol* **2006**, *17*, 923-931.
- (75) Kasyutich, V. L.; Martin, P. A.; Holdsworth, R. J. *Chem Phys Lett* **2006**, *430*, 429-434.
- (76) Kasyuticha, V. L.; Martin, P. A. *Chem Phys Lett* **2007**, *446*, 206-211.
- (77) Kasyutich, V. L.; Canosa-Mas, C. E.; Pfrang, C.; Vaughan, S.; Wayne, R. P. *Appl. Phys. B* **2002**, *75*, 755-761.
- (78) Kasyutich, V. L.; Bale, C. S. E.; Canosa-Mas, C. E.; Pfrang, C.; Vaughan, S.; Wayne, R. P. *Appl. Phys. B* **2003**, *76*, 691-697.
- (79) Kasyutich, V. L.; Martin, P. A.; Holdsworth, R. J. *Appl. Phys. B* **2006**, *85*, 413-420.
- (80) Paul, J. B.; Lapson, L.; Anderson, J. G. *Appl Optics* **2001**, *40*, 4904-4910.
- (81) Baer, D. S.; Paul, J. B.; Gupta, M.; O'Keefe, A. *Appl. Phys. B* **2002**, *75*, 261-265.
- (82) Zhao, W.; Gao, X.; Chen, W.; Zhang, W.; Huang, T.; Wu, T.; Cha, H. *Appl. Phys. B* **2007**, *86*, 353-359.
- (83) Bakhirkin, Y. A.; Kosterev, A. A.; Roller, C.; Tittel, F. K. *Appl Optics* **2004**, *43*, 2257-2266.
- (84) Vasudev, R. *App. Spec.* **2006**, *60*, 926-930.
- (85) Ayers, J. D.; Apodaca, R. L.; Simpson, W. R.; Baer, D. S. *Appl Optics* **2005**, *44*, 7239-7242.
- (86) Herriott, D.; Kogelnik, H.; Kompfner, R. *Appl Optics* **1964**, *3*, 523-526.
- (87) Herzberg, G. In *Spectra of Diatomic Molecules*; Van Nostrand, Ed.; Princeton: New York, 1950.

- (88) Diem, M. In *Introduction to Modern Vibrational Spectroscopy*; John Wiley & Sons, Ed.; New York, 1993; , pp 1-44.
- (89) Herzberg, G. In *Molecular Spectra and Molecular Structure II. Infrared and Raman Spectra of Polyatomic Molecules*; D. van Nostrand, Ed.; New York, 1945; , pp 665.
- (90) Henry, B. R.; Kjaergaard, H. G. *Can J Chem* **2002**, *80*, 1635-1642.
- (91) Henry, B. R.; Siebrand, W. *J. Chem. Phys.* **1968**, *49*, 5369-5376.
- (92) Henry, B. R.; Tarr, A. W.; Mortensen, O. S.; Murphy, W. F.; Compton, D. A. C. *J. Chem. Phys.* **1983**, *79*, 2583-2589.
- (93) Baggott, J. E.; Law, D. W.; Lightfoot, P. D.; Mills, M. *J. Chem. Phys.* **1986**, *85*, 5414-5429.
- (94) Tarr, A. W.; Swanton, D. J.; Henry, B. R. *J. Chem. Phys.* **1986**, *85*, 3463-3468.
- (95) Child, M. S.; Lawton, R. T. *Faraday Discuss. Chem. Soc.* **1981**, *71*, 273-285.
- (96) Mortensen, O. S.; Henry, B. R.; Mohammadi, M. A. *J. Chem. Phys.* **1981**, *75*, 4800-4808.
- (97) Mills, M. I.; Robiette, A. G. *Mol Phys* **1985**, *56*, 743-765.
- (98) Kjaergaard, H. G.; Goddard, J. D.; Henry, B. R. *J. Chem. Phys.* **1991**, *95*, 5556-5564.
- (99) Turnbull, D. M.; Kjaergaard, H. G.; Henry, B. R. *Chem Phys Lett* **1995**, *195*, 129-141.
- (100) Donaldson, D. J.; Orlando, J. J.; Amann, S.; Tyndall, G. S.; Henry, B. R.; Proos, R. J.; Vaida, V. *J. Phys. Chem. A* **1998**, *102*, 5171-5174.
- (101) Fono, L.; Donaldson, D. J.; Proos, R. J.; Henry, B. R. *Chem Phys Lett* **1999**, *311*, 131-138.
- (102) Low, R. G.; Kjaergaard, H. G. *J. Chem. Phys.* **1999**, *110*, 9104-9115.
- (103) Henry, B. R.; Turnbull, D. M.; Schofield, D. P.; Kjaergaard, H. G. *J. Phys. Chem* **2003**, *107*, 3236-3243.
- (104) Ishiuchi, S.; Fujii, M.; Robison, T. W.; Miller, B. J.; Kjaergaard, H. G. *J. Phys. Chem.* **2006**, *110*, 7345-7354.

- (105) Kjaergaard, H. G.; Henry, B. R.; Wei, H.; Lefebvre, S.; Carrington Jr, T.; Mortensen, O. S.; Sage, M. L. *J. Chem. Phys.* **1994**, *100*, 6228-3239.
- (106) Manzanares I, C.; Peng, J.; Blunt, V. M. *J. Phys. Chem.* **1992**, *96*, 6212-6217.
- (107) Manzanares, I. C.; Mina-Camile, N.; Brock, A.; Peng, J.; Blunt, V. M. *Rev. Sci. Instrum.* **1995**, *66*, 2644-2651.
- (108) Mina-Camile, N.; Cedeño, D. L.; Manzanares, I. C. *Spectrochim Acta A* **1998**, *54*, 419-437.
- (109) Gutow, J. H.; Davidsson, J.; Zare, R. N. *Chem Phys Lett* **1991**, *185*, 120-124.
- (110) Wong, J. S.; Moore, C. B. *J. Chem. Phys.* **1982**, *77*, 603-615.
- (111) Blunt, V. M.; Mina-Camile, N.; Cedeño, D. L.; Manzanares, C. *Chem Phys* **1996**, *209*, 79-90.
- (112) Duncan, J. L.; Law, M. M. *Spectrochim Acta A* **1997**, *53*, 1445-1457.
- (113) Perry, J. W.; Moll, D. J.; Kuppermann, A.; Zewail, A. H. *J. Chem. Phys.* **1985**, *82*, 1195-1211.
- (114) Bardwell, J.; Herzberg, G. *Astrophys. J.* **1953**, *117*, 462.
- (115) Lutz, B. L.; de Berg, C.; Maillard, J. P.; Owen, T.; Brault, J. *Astrophys J (Letters)* **1981**, *248*, L141.
- (116) Brown, R. L.; Nikitin, A.; Benner, C. D.; Devi, V. M.; Smith, M. A. H.; Fejard, L.; Champion, J. P. T., V.G.; Sams, R. L. *J. Mol. Struct.* **2004**, *181*, 695-696.
- (117) Lin, Z.; Boraas, K.; Reilly, J. P. *J. Molec. Spectrosc.* **1995**, *170*, 266-278.
- (118) Voth, G. A.; Marcus, R. A.; Zewail, A. H. *J. Chem. Phys.* **1984**, *81*, 5494-5507.
- (119) Blunt, V. M.; Brock, A.; Manzanares I., C. *J. Phys. Chem.* **1996**, *100*, 4413-4419.
- (120) Wilmshurst, J. K.; Bernstein, H. J. *Can J Chem* **1957**, *35*, 226-235.
- (121) Halonen, L.; Child, M. S. *Mol Phys* **1982**, *46*, 239-255.
- (122) Halonen, L.; Child, M. S.; Carter, S. *Mol Phys* **1982**, *47*, 1097-1112.
- (123) Halonen, L.; Child, M. S. *J. Chem. Phys.* **1983**, *79*, 559-570.
- (124) Halonen, L.; Child, M. S. *J. Chem. Phys.* **1983**, *79*, 4355-4362.

- (125) Shimanouchi, T. *Tables of Molecular Vibrational Frequencies, Consolidate Vol. I; Natl. Bur. Stand.* **1975**, 2, 164.
- (126) Newman, S.; Lane, I. C.; Orr-Ewing, A. J.; Newnham, D. A.; Ballard, J. J. *Chem. Phys.* **1999**, 110, 10749-10757.
- (127) Babcock, H. D.; Herzberg, L. *Astrophys. J.* **1948**, 108, 167-190.
- (128) Miller, J. H.; Boese, R. W.; Giver, L. P. *J. Quant. Spectrosc. Radiat. Transfer* **1969**, 9, 1507-1517.
- (129) Miller, J. H.; Giver, L. P.; Boese, R. W. *J. Quant. Spectrosc. Radiat. Transfer* **1976**, 16, 595-598.
- (130) Nakazawa, T.; Yamanouchi, T.; Tanaka, M. *J. Quant. Spectrosc. Radiat. Transfer* **1982**, 27, 615-625.
- (131) Grossmann, B. E.; Cahen, C.; Lesne, J. L.; Benard, J.; Leboudec, G. *Appl Optics* **1986**, 25, 4261-4267.
- (132) Ritter, K. J.; Wilkerson, T. D. *J. Mol. Spectrosc.* **1987**, 121, 1-19.
- (133) Phillips, A. J.; Peters, F.; Hamilton, P. A. *J. Mol. Spectrosc.* **1997**, 184, 162-166.
- (134) Brown, L. R.; Plymate, C. *J. Mol. Spectrosc.* **2000**, 199, 166-179.
- (135) Melieres, M. A.; Chenevier, M.; Stoeckel, F. *J. Quant. Spectrosc. Radiat. Transfer* **1985**, 33, 337-345.
- (136) Xu, S.; Dai, D.; Xie, J.; Sha, G.; Zhang, C. *Chem. Phys. Lett* **1999**, 303, 171-175.
- (137) Teslja, A.; Dagdigian, P. J. *Chem. Phys. Lett* **2004**, 400, 374-378.
- (138) Naus, H.; de Lange, A.; Ubachs, W. *Phys Rev A* **1997**, 56, 4755-4763.
- (139) Naus, H.; Navaian, K.; Ubachs, W. *Spectrochim Acta A* **1999**, 55, 1255-1262.
- (140) Minaev, B.; Vahtras, O.; Agren, H. *Chem Phys* **1996**, 208, 299-311.
- (141) Gamache, R. R.; Goldman, A.; Rothman, L. S. *J. Quant. Spectrosc. Radiat. Transfer* **1998**, 59, 495-509.
- (142) PGOPHER, a Program for Simulating Rotational Structure, C. M. Western, University of Bristol, <http://pgopher.chm.bris.ac.uk>.

- (143) National Institute of Standards and Technology NIST Chemistry web book.
<http://webbook.nist.gov/chemistry/> (accessed 11/18, 2008).
- (144) Golubiatnikov, G. Y.; Krupnov, A. F. *J. Mol. Spectrosc.* **2004**, 225, 222-224.
- (145) Allen, C. W. *Astrophys. J.* **1937**, 85, I56- I64.
- (146) van de Hulst, H. C. *Ann. D' Astrophys* **1945**, 8, 12-25.
- (147) Mizushima, M.; Yamamoto, S. *J. Mol. Spectrosc.* **1991**, 148, 447-452.
- (148) Trauger, J. T.; Roesler, F. L.; Carleton, N. P.; Traub, W. A. *Astrophys J (Letters)* **1973**, 184, L137-L141.
- (149) Bubin, S.; Leonarski, F.; Stanke, M.; Adamowicz, L. *J. Chem. Phys.* **2009**, 130, 124120.
- (150) Herzberg, G. *Nature* **1950**, 166, 563.
- (151) Stoicheff, B. P. *Can J Phys* **1957**, 35, 730-741.
- (152) Durie, R. A.; Herzberg, G. *Can J Phys* **1960**, 38, 806-818.
- (153) McKellar, A. R.; Goetz, W.; Ramsay, D. A. *The Astrophysical Journal* **1976**, 207, 663-670.
- (154) Rich, N. H.; Johns, J. W. C.; McKellar, A. R. W. *J Mol Spectrosc* **1982**, 95, 432-438.
- (155) McKellar, A. R. W. *Astrophys J (Letters)* **1973**, 185, L53-L55.
- (156) McKellar, A. R. W. *Can J Phys* **1973**, 51, 389-397.
- (157) McKellar, A. R. W. *Can J Phys* **1974**, 52, 1144-1151.
- (158) Mickelson, M. E.; Larson, L. E.; Trauger, J. T. *Icarus* **1980**, 41, 142-146.
- (159) Trauger, J. T.; Mickelson, M. E. *Icarus* **1983**, 56, 176-183.
- (160) Smith, S. H.; Keffer, C. E.; Connor, C. P. *Icarus* **1991**, 91, 234-237.
- (161) Trefler, M.; Gush, H. P. *Phys Rev Lett* **1968**, 20, 703-705.
- (162) Bejar, J.; Gush, H. P. *Can J Phys* **1974**, 52, 1669-1671.
- (163) Lewis Ford, A.; Browne, J. C. *Phys Rev A* **1977**, 16, 1992-2001.

- (164) Nelson, J. B.; Tabisz, G. C. *Phys Rev Lett* **1982**, 48, 1393-1396.
- (165) Nelson, J. B.; Tabisz, G. C. *Phys Rev A* **1983**, 28, 2157-2161.
- (166) Karthikeyan, B.; Rajamanickam, N.; Bagare, S. P. *Astroparticle Physics* **2006**, 26, 186-189.
- (167) Pachucki, K.; Komasa, J. *Phys Rev A* **2008**, 78, 052508.
- (168) Jennings, D. E.; Blass, W. E. *J Mol Spectrosc* **1975**, 55, 445-451.
- (169) Peyerimhoff, S.; Lewerenz, M.; Quack, M. *Chem Phys Lett* **1984**, 109, 563-569.
- (170) Lewerenz, M.; Quack, M. *J. Chem. Phys.* **1988**, 88, 5408-5431.
- (171) Ulenikova, O. N.; Onopenkoa, G. A.; Alankob, S.; Koivusaarib, M.; Anttilab, R. *J Mol Spectrosc* **1998**, 191, 9-16.
- (172) Bovey, L. F. H. *J. Chem. Phys.* **1953**, 21, 830-836.
- (173) Charvat, A.; Kachanov, A. A.; Campargue, A.; Permogorov, D.; Stoeckel, F. *Chem Phys Lett* **1993**, 214, 495-501.
- (174) Campargue, A.; Permogorov, D. *Chem Phys* **1994**, 182, 281-290.
- (175) Permogorov, D.; Campargue, A.; Chenevier, M.; Ben Kraiem, H. *J Mol Spectrosc* **1995**, 170, 10-26.
- (176) Scherer, Kevin K. Lehmann, and W. Klemperer *J. Chem. Phys.* **1984**, 81, 5319-5325.
- (177) Campargue, A.; Stoeckel, F. *J. Chem. Phys.* **1986**, 85, 1220-1227.
- (178) Ben Kraiem, H.; Campargue, A.; Chenevier, M.; Stoeckel, F. *J. Chem. Phys.* **1989**, 91, 2148-2152.
- (179) Hollenstein, H.; Marquardt, R.; Quack, M.; Suhm, M. *J. Chem. Phys.* **1994**, 101, 3588-3602.
- (180) Blunt, V. M.; Brock, A.; Manzanares I, C. *Ber. Bunsenges Phys. Chem* **1995**, 99, 520-529.
- (181) Dubal, H.; Ha, T.; Lewerenz, M.; Quack, M. *J. Chem. Phys.* **1989**, 91, 6698-6713.
- (182) Ha, T.; Lewerenz, M.; Marquardt, R.; Quack, M. *J. Chem. Phys.* **1990**, 93, 7097-7109.

- (183) Dubal, H.; Quack, M. *Mol Phys* **1984**, *53*, 257-264.
- (184) Dubal, H.; Quack, M. *J. Chem. Phys.* **1984**, *81*, 3779-3791.
- (185) Baggott, J. E.; Chuang, M. C.; Zare, R. N. *J. Chem. Phys.* **1985**, *82*, 1186-1194.
- (186) Herzberg, G. In *Infrared and Raman Spectra*; Van Nostrand, Ed.; Princeton: New York, 1945.
- (187) Wilkinson, G. R.; Wilson, M. K. *J. Chem. Phys.* **1966**, *44*, 3867-3874.
- (188) Campargue, A.; Stoeckel, F.; Chenevier, M.; Ben Kraiem, H. *J. Chem. Phys.* **1987**, *87*, 5598-5605.
- (189) Atkins, P. W. In *Quanta. A handbook of concepts*; Oxford, Ed.; Oxford University Press: New York, 1994; .
- (190) Kjaergaard, H. G.; Yu, H.; Schattka, B. J.; Henry, B. R. *J. Chem. Phys.* **1990**, *93*, 6239-6248.
- (191) Phillips, J. A.; Orlando, J. J.; Tyndall, G. S.; Vaida, V. *Chem Phys Lett* **1998**, *296*, 377-383.
- (192) Lin, H.; Yuan, L.; Wang, D.; Zhu, Q. *Chin. Phy. Lett* **2000**, *17*, 13-15.
- (193) Kjaergaard, H. G.; Henry, B. R. *J. Chem. Phys.* **1992**, *96*, 4841-4851.
- (194) Kjaergaard, H. G.; Henry, B. R.; Tarr, A. W. *J. Chem. Phys.* **1991**, *94*, 5844-5854.
- (195) Rong, Z.; Henry, B. R.; Robison, T. W.; Kjaergaard, H. G. *J. Phys. Chem.* **2005**, *109*, 1033-1041.
- (196) Daub, C. D.; Henry, B. R.; Sage, M. L.; Kjaergaard, H. G. *Can J Chem* **1999**, *77*, 1775-1781.
- (197) Lane, J. R.; Kjaergaard, H. G. *J. Phys. Chem. A* **2007**, *111*, 9707-9713.
- (198) Sage, M. L. *Chem Phys* **1978**, *35*, 375-380.
- (199) Rong, Z.; Kjaergaard, H. G.; Sage, M. L. *Mol Phys* **2003**, *101*, 2285-2294.

- (200) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; and Pople, J. A. *Gaussian 03, Revision C.02*, Gaussian, Inc., Wallingford CT, 2004.
- (201) Portnov, A.; Blockstein, L.; Bar, I. *J. Chem. Phys.* **2006**, *124*, 164301.
- (202) Crofton, M. W.; Stevens, C. G.; Klenerman, D.; Gutow, J. H.; Zare, R. N. *J. Chem. Phys.* **1988**, *89*, 7100-7111.
- (203) Baylor, I. C.; Weitz, E.; Hofmann, P. *J. Chem. Phys.* **1989**, *90*, 615-627.
- (204) Lin, Z.; Boraas, K.; Reilly, J. P. *J Mol Spectrosc* **1992**, *156*, 147.
- (205) Ganot, Y.; Bar, I.; Rosenwaks, S. *J Mol Spectrosc* **2001**, *208*, 249-252.
- (206) Callegari, C.; Conjusteau, A.; Reinhard, I.; Lehmann, K. K.; Scoles, G. *J. Chem. Phys.* **2000**, *113*, 10535-10535.
- (207) Campargue, A.; Biennier, L.; Garnache, A.; Kachanov, A.; Romanini, D.; Herman, M. *J. Chem. Phys.* **1999**, *111*, 7888-7903.
- (208) Campargue, A.; Bertseva, E.; Graner, G.; Herman, M. *J Mol Spectrosc* **2000**, *201*, 156-163.
- (209) Portnov, A.; Bespechansky, E.; Ganot, Y.; Rosenwaks, S.; Bar, I. *J. Chem. Phys.* **2005**, *122*, 224316.
- (210) Hofmann, P.; Gerber, R. B.; Ratner, M. A.; Baylor, I. C.; Weitz, E. *J. Chem. Phys.* **1988**, *88*, 7434-7447.
- (211) Gambogi, J. E.; Timmermans, J. H.; Lehmann, K. K.; Scoles, G. *J. Chem. Phys.* **1993**, *99*, 9314-9317.

- (212) McIlroy, A.; Nesbitt, D. J.; Kerstel, E. R.; Pate, B. H.; Lehmann, K. K.; Scoles, G. *J. Chem. Phys.* **1994**, *100*, 2596-2611.
- (213) Lehmann, K. K.; Pate, B. H.; Scoles, G. *J. Chem. Phys.* **1990**, *93*, 2152-2153.
- (214) Kerstel, E. R. T.; Lehmann, K. K.; Mentel, T. F.; Pate, B. H.; Scoles, G. *J. Phys. Chem.* **1991**, *95*, 8282-8293.
- (215) Gambogi, J. E.; L'Esperance, R. P.; Lehmann, K. K.; Pate, B. H.; Scoles, G. *J. Chem. Phys.* **1993**, *98*, 1116-1122.
- (216) Stuchebrukhov, A. A.; Marcus, R. A. *J. Chem. Phys.* **1993**, *98*, 6044-6061.
- (217) Manzanares I, C.; Blunt, V. M.; Peng, J. *J. Chem. Phys.* **1993**, *99*, 9412.
- (218) Manzanares I, C.; Peng, J.; Mina-Camile, N.; Brock, A. *Can J Chem* **1995**, *190*, 247-259.
- (219) Thomas, K.; Thompson, H. W. *Spectrochim Acta A* **1968**, *24*, 1337-1352.
- (220) Manzanares I, C.; Yamasaki, N. L. S.; Weitz, E. *J. Phys. Chem.* **1986**, *90*, 3953-3958.
- (221) von Puttkamer, K.; Dubal, H.; Quack, M. *Faraday Discuss. Chem. Soc.* **1983**, *75*, 197-210.
- (222) Crowder, G. A. *Vib Spectrosc* **1991**, *1*, 317-323.
- (223) Rintoul, L.; Shurvwll, H. F. *J. Raman Spectrosc.* **1998**, *29*, 791-798.
- (224) Page, R. H.; Shen, Y. R.; Lee, Y. T. *J. Chem. Phys.* **1988**, *88*, 4621-4636.
- (225) Nugent, L. J.; Mann, D. E.; Lide, D. R. *J. Chem. Phys.* **1962**, *36*, 965-971.
- (226) Haase, J.; Zeil, W. Z. *Naturforsch* **1969**, *24a*, 1844.
- (227) Nikitin, V. S.; Polyakova, M. V.; Baburina, I. I.; Belyakov, A. V.; Bogoradovskii, e. T.; Zavgorodnii, V. S. *Spectrochim Acta A* **1990**, *46A*, 1669-1677.
- (228) Manzanares I, C.; Yamasaki, N. L. S.; Weitz, E. *J. Phys. Chem* **1987**, *91*, 3959-3969.
- (229) Swamy, K. N.; Hase, W. L. *J. Chem. Phys.* **1985**, *82*, 123-133.
- (230) Manzanares I, C.; Yamasaki, N. L. S.; Weitz, E. *Chem Phys Lett* **1985**, *117*, 477-484.

- (231) Traetteber, M.; Bakken, P.; Liebman, J. F.; Hulce, M. *J. Mol Struct.* **1995**, *346*, 101.
- (232) Zeil, W.; Haase, J.; Dakkouri, M. *Discuss. Faraday Soc.* **1969**, *47*, 149.
- (233) Vaida, V. *Int. J. Photoenergy* **2005**, *7*, 61-70.
- (234) Donaldson, D. J.; Tuck, A. F.; Vaida, V. *Chem. Rev.* **2003**, *103*, 4717-4729.
- (235) Donaldson, D. J.; Frost, G. J.; Rosenlof, K. H.; Tuck, A. F.; Vaida, V. *Geophys. Res. Lett.* **1997**, *24*, 2651-2654.
- (236) Vaida, V.; Kjaergaard, H. G.; Hintze, P. E.; Donaldson, D. J. *Science* **2003**, *299*, 1566-1568.
- (237) Fleming, P. R.; Li, M.; Rizzo, T. R. *J. Chem. Phys.* **1991**, *94*, 2425.
- (238) Sinha, A.; Vander Wal, R. L.; Crim, F. F. *J. Chem. Phys* **1990**, *92*, 401.
- (239) Morokuma, K.; Mugurama, C. *J. Am. Chem. Soc.* **1994**, *116*, 10316.
- (240) Larson, L. J.; Kuno, M.; Tao, F. M. *J. Chem. Phys* **2000**, *112*, 8830.
- (241) Kjaergaard, H. G.; Daub, C. D.; Henry, B. R. *Mol Phys* **1997**, *90*, 201.
- (242) Norfolk, B.; Taylor, R. *J. Chem. Soc. , Perkin Trans. 2.* **1976**, 280.
- (243) Blades, A. T.; Gilderson, P. W. *Can. J. Chem.* **1960**, *38*, 1412-1415.
- (244) Kairistis, D. A.; Stimson, V. R. *Aust. J. Chem* **1968**, *21*, 1349.
- (245) Cross, J. T.; Stimson, V. R. *Aust. J. Chem* **1967**, *20*, 177-181.
- (246) Taylor, R. *J. Chem. Soc. , Perkin Trnas. 2.* **1975**, 1025.
- (247) Chuchani, G.; Triana, J. L.; Rotinov, A.; Caraballo, D. F. *J. Phys. Chem* **1981**, *85*, 1243-1245.
- (248) Blake, P. G.; Shraydeh, B. F. *Int. J. Chem. Kinet.* **1982**, *14*, 739-747.