MICROWAVE LINE WIDTHS OF THE ASYMMETRIC TOP FORMIC ACID MOLECULE

THESIS

Presented to the Graduate Council of the North Texas State University in Partial Fulfillment of the Requirements For the Degree of

MASTER OF ARTS

By

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This work consisted of an experimental investigation of the formic acid (HCOOH) molecule's rotational spectrum. Measurements of line widths were obtained for $J = 5, 12, 13, 19,$ and 20 for a pressure range from 1 to 10 microns. A linear behavior between $\Delta \nu$ and $p$ was observed as predicted by theory. The line width parameter $\Delta \nu_p$ was observed to depend on the quantum number $J$. Hard sphere collision diameters $b_\perp$ were calculated using the obtained $\Delta \nu_p$ values. These deduced hard sphere values were found to be larger than the physical size of the molecule. This result was found to be in general agreement with other investigation in which long range forces (dipole-dipole) dominate.
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CHAPTER I

INTRODUCTION

MICROWAVE SPECTROSCOPY

The electromagnetic spectrum is thought to be bounded by $10^{21}$ Hertz, all the way down to 1 Hertz. The experimental part of this investigation was performed in the microwave region due to rotational molecular phenomena being associated with these frequencies.

Microwave radiation is of a wavelength from $\lambda = 1$ millimeter to $\lambda = 30$ centimeters. The first experiments in this region were carried out by Cleeton and Williams (1:2, p. 45) at approximately $\lambda = 1.5$ centimeters with NH$_3$ gas. Due to the crude apparatus and poor techniques the resolution was not sufficient to provide any significant information. Further development came after World War II with the invention of the klystron and associated microwave equipment.

Microwave spectroscopy is associated with frequencies of the rotational energies rather than vibrational or electronic energies. Hard sphere collision diameters of molecules can be deduced by measuring the width of rotational spectral lines at various pressures.

It was the objective of this experiment to relate line width with pressure, quantum number $J$ and hard sphere
collision diameters.

The molecule under investigation was the formic acid molecule (HCOOH). The molecular structure is shown in Figure 1. Values of bond lengths and bond angles are presented in Table 1 (6,p.).

Microwave spectroscopy usually deals with two different types of molecules: asymmetric top molecules and symmetric top molecules. Formic acid is a molecule of the asymmetric class. The asymmetric top molecule possesses the characteristic of three distinct principle moments of inertia, that is, \( I_{xx} \neq I_{yy} \neq I_{zz} \).

Pertinent data was compiled using a source of variable frequency microwave, an absorption cell, a microwave detector and an indicating device such as an oscilloscope for a visual microwave frequency display.

Since formic acid is a molecule of the slightly asymmetric prolate class a discussion is given for the reader's convenience.

**ASYMMETRIC TOP MOLECULES**

Any "top" is specified by three principle moments of inertia or rotational constants. The asymmetric top molecule has three different moments of inertia. Symmetric top molecules have two moments of inertia that are equal.

The energy of a rigid rotor is expressed as follows:

\[

\hbar \omega = \frac{4\pi^2 A}{h} p_x^2 + \frac{4\pi^2 B}{h} p_y^2 + \frac{4\pi^2 C}{h} p_z^2

\]  

(1-1)
Figure 1. Molecular Structure of HCOOH
where \( W \) is the energy of rotation, \( x, y, \) and \( z \) are the directions along the principal axes of inertia and \( P_x^2 + P_y^2 + P_z^2 = p^2 \). \( p^2 \) is quantized and must equal \( J(J+1)\hbar^2/4\pi^2 \) where \( J \) is an integer. \( A, B, \) and \( C \) are constants used to absorb \( I_x, I_y, \) and \( I_z \). It is conventional to write these constants in order of decreasing magnitude (i.e. \( A>B>C \)). In the oblate case \( A = B \) and in the prolate case \( B = C \).

Using this definition we can describe a slightly asymmetric top in the prolate or oblate category.

The formic acid molecule, HCOOH, has rotational constants of \( A = 77,512.25 \) MHz, \( B = 12,055.012 \) MHz, and a value for \( C = 10,416.205 \) MHz (1, p. 1333). With this information HCOOH is placed in the slightly asymmetric prolate top category.

Various values of \( B \) in a range bounded by \( A \) and \( C \) correspond to degrees of asymmetry. The most extreme would be for \( B \) midway between \( A \) and \( C \). An expression relating \( A, B, \) and \( C \) was formulated by B. S. Ray (7, p. 74) in 1932. The "Ray parameter" is expressed as follows:

\[
\kappa = \frac{2B-A-C}{A-C}
\]  

(1-2)

This value ranges from 1 to -1 for the oblate and prolate cases respectively. For HCOOH \( \kappa = -0.951 \). An asymmetry parameter for the slightly prolate case (7, p. 78) is:

\[
b_p = \frac{C-B}{2A-B-C} = \frac{\kappa + 1}{\kappa + 3}
\]  

(1-3)
For formic acid \( b_p = 0.0123 \). The value of \( b_p \) is zero for the prolate case and increases as the prolate criteria are departed. An analogous measure for the slightly asymmetric oblate top (7, p. 78) is expressed as:

\[
\frac{A-B}{2C-B-A} = \frac{\kappa-1}{\kappa+3}
\]

For the HCOOH molecule \( b_p \) will be of interest.

The quantum number \( J \) for the asymmetric top molecule is used to describe the energy levels. The quantum number \( K \) which is the projection of \( J \) along the symmetry axis is a "good quantum number" with the qualification of referring to the extreme cases of the prolate or oblate symmetry only. The subscript \( 1 \) and \( -1 \) will denote the oblate and prolate cases where the subscript correspond to the previously discussed asymmetry parameter of Ray. We can now designate any particular energy level by \( J, K \) (4, p. 11).

Alternately we can use the symbol \( J_\tau \) (9, P. 84) to describe an energy level. \( J \) is the total angular momentum and \( \tau \) is given by:

\[
\tau = K_{-1} - K_{+1}
\]

and is an integer between \(-J\) and \( J\).

The energy of the formic acid molecule or any asymmetric top is described as follows (9, p. 86):

\[
\frac{\hbar}{\Omega} = \frac{B+C}{2} J(J+1) + [A - \frac{B+C}{2}] \Omega
\]
Since formic acid is the slightly asymmetric prolate case $w$ can be expressed in an infinite series in terms of its asymmetry parameter, tabulated constants (9, pp. 522-6), and values for $K^2$ (9, pp. 522-6). The equation is as follows:

$$w = K^2 + C_1 b_p + C_2 b_p^2 + C_3 b_p^3 + \cdots$$  \hspace{1cm} (1-7)

For the oblate case energy is expressed as:

$$\frac{W}{\hbar} = \frac{A+B}{2} J(J+1) + \left[ C - \frac{A+B}{2} \right] w$$  \hspace{1cm} (1-8)

but in this case $w$ is expressed:

$$W = K^2 + C_1 b_0 + C_2 b_0^2 + C_3 b_0^3 + \cdots$$  \hspace{1cm} (1-9)

The series for $w$ arises from a perturbation approach where the asymmetry is the perturbation. From the above expansions for $w$ it can be concluded that these expressions will only be valid if the asymmetry parameters $b_0$ and $b_p$ are small. Although equations (1-6) and (1-8) are adequate for only slightly asymmetric tops a similar equation for large asymmetric cases is given by the following:

$$\frac{W}{\hbar} = \frac{1}{2}(A+C) J(J+1) + \frac{1}{2}(A-C) E_T$$  \hspace{1cm} (1-10)

$E_T$ is evaluated for the particular case in question and is only an even function of Ray's asymmetry parameter.
WIDTHS of SPECTRAL LINES

Due to various disturbances spectral lines have a width varying from their center frequency. Below is a list of sources that contribute to line width.

1. Natural line breadth
2. Doppler effect
3. Pressure broadening
4. Saturation broadening
5. Collisions between the molecules and the walls of the containing vessel.

Pressure broadening and the Doppler effect are the only two sources with any consequences in this investigation.

Natural line breadth is principally due to radiation damping. For a line associated with a decay from an excited state to a ground state, zero point electromagnetic fields produce a line with a half-width at half maximum (HWHM) of:

\[ \Delta \nu = \frac{32 \pi^3 \nu^3}{3hc^3} |\vec{\mu}|^2 \text{ Hz} \]  \hspace{1cm} (1-11)

In the above equation (9, p. 336) \( \mu \) = quantum-mechanical matrix element of the dipole moment. In the microwave region this yields \( \Delta \nu = 10^{-7} \) Hertz; therefore, it is considered negligible.

The Doppler effect on line width is due to a molecule moving parallel to the propagation of the radiation it is absorbing. This leads to a frequency without the Doppler
shift, \( v \) is the velocity of the molecule, and \( v_p \) is the propagational phase velocity of the radiation. The HWHM associated with the Doppler effect is more pronounced in small line widths and at transitions of high frequencies (i.e. 40 GHz and above). An expression for the HWHM due to the Doppler effect is shown below (9, p. 337).

\[
\Delta \nu = \frac{v}{c} \sqrt{2kT N_0 \ln 2} \sqrt{\frac{1}{M}}
\]  

(1-12)

where \( M \) is the molecular weight, \( T \) is the temperature in degrees Kelvin, \( k \) in Boltzmann's constant, \( N_0 \) is Avogadro's number, and \( c \) is the velocity of light. For formic acid \( \Delta \nu/v = 9.15 \times 10^{-7} \).

Saturation broadening and broadening due to collisions between molecules and the walls of a containing vessel are assumed to be unimportant.

The most important component of a spectral line's width is that due to the effects of pressure. In this work pressures from zero to ten microns was the pressure range of interest. This type of broadening also tells us something about the behavior of molecules as they collide and therefore about molecular force fields.

Theory assumes that molecules undergo very violent but brief collisions which cause them to stop radiating and to start radiating again after the collision independent of their mode before the collision. The orientation of a rotating molecule after a collision is therefore
assumed random. This is because the collisions are violent.

Observed line widths are usually larger than those obtained by classical kinetic theory. In fact broadening of microwave lines are several times larger than kinetic theory would indicate. This is because microwave lines are affected by the long range interaction of van der Waals forces.

Due to the complexity of pressure broadening many different treatments have been developed to represent a wide range of phenomena. This paper focuses on the treatment compatible with the microwave region.

All intermolecular forces are embraced by van der Waals forces. These forces all depend on $r^{-n}$ where $r$ is the distance separating two molecules and $n$ is an integer. Associated with lower $n$ values are the long-range molecular forces to which we can attribute the major portion of pressure broadening. Pressure broadening can tell us much about molecular forces (9, p. 338).

More specifically we need to discuss line width theory at this point since the dominant influence on a spectral line width is due to pressure effects for a range from approximately zero to ten microns.

Distribution of spectral due to finite life of oscillations was first formulated by Lorentz (9, p. 338). If an oscillator's radiation decreases exponentially with time the distribution of radiation generates a "resonance
curve" as shown in Figure 2. This example also corresponds to the finite life of molecular oscillations due to their strong interaction with other molecules which terminates their oscillation.

Debye (3), van Vleck (10,p. 17), and Weisskopf (10,p. 41) have developed theories of pressure broadening.

Consider a fixed dipole with no rotational or translational energy. The dipole is oriented with respect to the electric field present in accordance with the Boltzmann distribution \( (E \cdot \mu/kT) \). \( E \) is the electric field strength existing, \( \mu \) is the dipole moment, \( k \) is Boltzmann's constant and \( T \) is the temperature in degrees Kelvin.

If the field changes many times before another collision process the dipole has no special orientation with respect to the field. After another collision it again orientates itself with the field and it absorbs a small amount of energy from the field while being oriented. Debye's characteristic theoretical expression for absorption per unit length is expressed:

\[
\gamma = \frac{\omega}{c} \frac{4\pi N \mu^2}{3\sqrt{\pi T}} \frac{\omega}{1 + \omega^2 \tau^2}
\]

(1-13)

where:

\( \omega = 2\pi v \)

\( \tau = \text{mean lifetime between collisions} \)

\( \mu = \text{dipole moment} \)

\( c = \text{velocity of light} \)
Figure 2. "Resonance Curve"
k = Boltzmann's constant

γ = absorption per unit length

N = number of molecules per cubic centimeter

The theoretical van Vleck-Weisskopf line shape has the following general features (9, p. 344).

1. The HWHM (Δν) is proportional to pressure over a wide range of low pressure.

2. The peak absorption intensity is independent of pressure over a wide range of low pressures.

The features above are used as criteria for acceptable data in the experimental section of this work.

COLLISION DIAMETERS

The hard sphere collision diameter \( b_1 \) is related to \( \Delta \nu \) by (8, p. 34):

\[
\Delta \nu_p = b_1^2 \left( \frac{\pi M k T}{4 N_0} \right)^{-\frac{1}{2}}
\]

where \( \Delta \nu_p \) is the line width parameter, \( N_0 \) is Avogadro's number, \( k \) is Boltzmann's constant, \( M \) is the molecular weight and \( T \) is the temperature in degrees Kelvin. Therefore, we can calculate \( b_1 \) with the formula below.

\[
b_1 = \Delta \nu_p \left( \frac{\pi M k T}{4 N_0} \right)^{\frac{1}{4}}
\]

In chapter II the reader will find a discussion of the spectrometer used to obtain the experimental data from which hard sphere collision diameters were deduced.
CHAPTER BIBLIOGRAPHY


CHAPTER II

EXPERIMENTAL TECHNIQUE AND EQUIPMENT

MICROWAVE SPECTROGRAPH

A microwave line width spectrograph is comprised of three basic sections, a source of microwave energy, a vacuum system and a microwave detector. With these components shown in Figure 3 a microwave absorption experiment can be performed. Basically a microwave signal was fed into an absorption cell which contained a sample of approximately 1 to 10 microns of gas and the transmitted signal gave rise to an absorption line of finite width.

The microwave source used in this work was a reflex type klystron. In order to obtain a rough frequency range of approximately 3 MHz a cavity wave meter was attached to the klystron. This allows a rough frequency measurement of a spectral line. Using the wave meter it is possible to excluded other lines in the range of the klystron. A small amount of the klystron signal was coupled to a crystal mixer where it was mixed with a signal from the marker multipliers. This resulted in heterodyne power for the marker system.

In order to eliminate saturating the molecules in
FIGURE 3. MICROWAVE SPECTROGRAPH.
the absorption cell with microwave power a variable attenuator was employed prior to the absorption cell. A transition section channelled the microwave power into the absorption cell. The microwave signal interacted with the gas in the absorption cell and the exiting signal was detected and amplified. An oscilloscope was used for a visual display and a chart recorder for permanent record. A detailed block diagram is provided in Figure 4 for the reader's convenience.

THEORY of OPERATION

The klystron signal oscillates slowly about a fixed center frequency. By suitably modulating the klystron with a sine wave signal the second derivative of the absorbed power is obtained. This takes place when the klystron frequency sweeps through a range corresponding to a spectral line characteristic of the molecule under investigation. The detected signal is first amplified by a tuned preamplifier. The output of the preamplifier is then fed into the input of a lock-in amplifier. Signals from the lock-in amplifier can then be used for the chart recorder or oscilloscope.

In order to measure the width of a spectral line a frequency marker system was employed. A signal which was representative of actual data is displayed in Figure 5. Frequency markers were generated from the signal coupled
FIGURE 4. Detailed Block Diagram of a Microwave Spectrograph.
into a mixer from the klystron. This signal was then mixed with a signal from a highly stable oscillator. This generated a series of signals which could be detected by a receiver. The receiver was set for a frequency for example of 250 kHz. The receiver then detected two markers separated by 500 kHz which were monitored on the oscilloscope. Using these signals called "markers" it is possible to measure the width of a spectral line, within their range.

A measurement of the line width is the magnitude of the frequency range of the two half power points on the absorption line. The full width at half maximum (FWHM) is noted in Figure 5. The half width at half maximum (HWHM) is simply FWHM/2 and is noted as $\delta v$.

In order to deduce the parameters in the objective of the experiment it is necessary to measure $\delta v$ over a range of pressures and to measure the slope of the function produced as well as the intercept. The intercept will give an estimate of line width at a pressure of "zero". The reader may see plots of this behavior in Appendix B.

SAMPLE

Gaseous formic acid obtained from Eastman Chemical Company Lot #F2B was investigated. This chemical was obtained in liquid form with vapor off of the liquid introduced via the vacuum system. The formic acid molecule
FIGURE 5. Representative Chart Recorder Data, \(2\delta\nu\) is the FWHM.
is a near prolate asymmetric top. The rotational spectra examined ranged in \( J \) quantum number from 5 to 20. These \( J \) numbers correspond to a frequency range of 23,203.40 MHz to 36,818.61 MHz. The pressure in the experiment ranged from approximately .5 microns to 12 microns.

**PRESSURE MEASUREMENT**

Pressure measurements were obtained using a McLeod gauge as shown in Figure 6. Three readings were taken at each pressure, the height of mercury in the closed tube, the height of the mercury in the open tube and the height of the "plugged" tube. These values were noted as \( h_c \), \( h_o \), and \( h_p \) respectively. When these values were substituted in the following equation for each pressure point the pressure of the gas in microns was calculated \( (1) \).

\[
\text{Pressure} = 4.44 \times 10^{-1} \left[ (h_p - h_c)(h_o - h_c) \right]
\]

\( (2-1) \)

The formula above was used each time a new pressure point was investigated. The formic acid gas was initially introduced into the vacuum system in small amounts via a "doser" shown in Figure 7. The "doser" admitted 5 microns of gas into the absorption cell each time the stopcock was opened. This procedure of dosing was repeated along with intermediate periods of stabilization until the spectral line lost definition. Next a small amount of gas was pumped from the absorption cell. After the
Figure 6. McLeod Gauge
To absorption cell

Small dosing chamber

Doser

Sample introduced here

Figure 7. Doser
system stabilized in pressure the spectral line was examined. If it looked like it would provide a reasonable measurement (i.e. the half power points were defined) it would be the first data point. The pumping and stabilization procedure was repeated until 5 or 6 points were obtained over an equally subdivided pressure range. For each pressure point four line width measurements were recorded, then an average was taken.

Using formula (2-1) each pressure point was calculated and was plotted against the corresponding line width. If the data had a linear behavior it was considered acceptable. After the entire range of pressures was measured a check was made by returning to a previous point for measurement to insure consistency in the data. If this was in agreement with the previous data a linear least-square fit was carried out by a computer. If a fit had a low coefficient of determination possible problems in measurement technique, sample of gas and equipment were investigated. This procedure was carried out for the five transitions in Table II of Appendix A.

LINE WIDTH MEASUREMENT

The width of a spectral line was measured from the data obtained with the chart recorder. This was carried out by measuring the distance between peaks of the second derivative of the absorption line. This interval was
compared with that between the markers. The measured interval was then divided by two to yield the HWHM.

Silicon point contact crystals were used as detectors. Changing detectors for the same spectral line until the best signal was obtained provided choice of a signal with best suited detector. Each time a new spectral line was investigated the detector choosing procedure was repeated. The following procedure was used to maximize detector response. Figure 8 is provided for the reader's convenience.

1. Adjust plunger to obtain maximum current from detector.
2. Rotate detector for maximum response.
3. Move detector in and out for a maximum current output.
4. Rotate waveguide to align the detector antennae with microwave electric field vector.
5. Reduce microwave power with the attenuator to 1 microampere.

Following the above procedure gave a sharp resonance line with minimum saturation broadening.

ELECTRONICS

The klystrons used were Model 35V11 for the frequency range of 32 kHz to 37 kHz and the Model 22V10 for frequency of 20 kHz to 24 kHz. The klystron power supply manufactured by FXR Machine Works Incorporated was a Tupe Z815B. The receiver used was a Wells-Gardner
Figure 8. Detector Set Up
and Company Model BC-348-0 manufactured for the U. S. Army Signal Corps. The dual trace oscilloscope employed was a Model 561B manufactured by Tektronix Incorporated. The lock-in amplifier was a Princeton Applied Research Model 122. The frequency generator for modulation was a Heath EUW-27.

OTHER EQUIPMENT

The absorption cell was constructed with copper pipe 10.5 meters long and 20 millimeters in diameter. It was sealed on both ends with Teflon window .77 millimeters thick and A12 epoxy obtained from Armstrong Products Company. Different wave meters were used for different ranges of frequency. The 36,818.63 MHz line, the 30,521.65 MHz line, and the 27,758.48 MHz line were measured with the Model R532A Hewlett Packard wave meter. The 23,203.40 MHz line and the 24,568.96 MHz line were measured with the Model K325A Hewlett Packard wave meter.

TURN on PROCEDURE

A very careful procedure (2, pp. 32) should be adhered to when preparing the spectrograph for operation. The following steps will help prevent any damage to the electronics.

1. Turn on klystron filament and allow to warm for one minute.

2. Adjust the klystron power supply to proper
potential range for the repeller and control electrode.

3. Set resonator potential to a minimum.

4. Turn on the oscilloscope and other equipment.

5. Set sweep rate to desired value.

6. Adjust resonator to draw the suggested current indicated on the klystron.

7. Adjust repeller to maximize beam current.

In summary, first turn on klystron filament and allow at least one minute. Next, turn on the repeller and control electrode. Finally, the resonator potential should be applied. About three hours is necessary to allow the klystron to reach thermal equilibrium before any data is taken. Additional current adjustments may be required after this period.

Experimental results are presented and discussed in Chapter III.
CHAPTER BIBLIOGRAPHY

1. Klages, John, unpublished calibration for McLeod Gauge, Department of Physics, North Texas State University, Denton, Texas, 1973.

2. Yang, Wei Han, "Pressure Dependence of Line Widths of Microwave Spectra of Sulphur Dioxide," unpublished master's thesis, Department of Physics, North Texas State University, Denton, Texas, August, 1972.
CHAPTER III

ANALYSIS AND CONCLUSION

OBJECTIVE

As mentioned earlier in this work isolated, undisturbed, and stationary molecules would have definite fixed energy levels. However, due to thermal motion, collisions, and radiation damping energy levels and therefore spectral lines have a finite width.

A system such as that of formic acid gas is composed of many small oscillating systems moving about due to thermal energy. Due to the molecules undergoing collisions with one another their oscillations are interrupted. Post collision oscillations are assumed to have no relationship to oscillations prior to the collision. This phenomenon is the source of pressure broadening of spectral lines examined in the work. Theoretical studies carried out by van Vleck and Weisskopf (2, p.17) indicated that the width of spectral lines due to the above behavior is proportional to pressure. This pressure dependence was investigated for the near prolate asymmetric top HCOOH.
PROCEDURE

The first step was to prepare the equipment for taking measurements. The vacuum system was pumped out for two days to purge the system of any foreign substance. Next, the electronics portion of the spectrograph was turned on as described in Chapter II. The sample was then introduced into the dosing chamber so it could be admitted into the absorption cell in small amounts. After admitting the gas to the cell the spectrograph was adjusted to the frequency of the desired transition (see Table II, p. 40). When the absorption line was in view the system was pumped down to "zero" pressure. If the line had disappeared after this process it could be attributed to the presence of the gas and not to standing waves or other causes. Gas was then readmitted to the cell for measurements.

The second derivative of the absorption line was then adjusted for suitable data measurements. The markers were also adjusted to a compatible frequency interval for the line width measurement. For five measurements were taken for each pressure. If these repeated line width measurements for a given pressure were not within ten per cent of one another the measurement was carried out again.

These measurements were made for J values of:
J = 5, 12, 13, 19, and 20. The resulting data is tabulated in Appendix C and plotted in Appendix B.

The data collected in this investigation represents an extension of some work carried out by David Rogers (1) on the formaldehyde molecule. The formic acid molecule is similar to that of formaldehyde except that formaldehyde HCHO, has one less oxygen atom than formic acid, HCOOH. More measurements on formaldehyde are presently being carried out by Arun Venkatachar of the North Texas State University physics department. The work on HCHO and HCOOH are meant to complement each other to lead to a better understanding of the behavior of these molecules in collision configuration.

Data measurements in pressure were accurate to the nearest .005 micron. Line width measurements are accurate to the nearest 10 kHz.

DOPPLER CORRECTIONS

The value of line width measured from the second derivative of the absorption line taken with the chart recorder is noted with $\delta v$. This width is composed of other effects than just pressure broadening. The Doppler effect on the line width is the only one of concern since it does have a sizable effect at widths below 100 kHz. The effect is more pronounced at high frequency transitions. Doppler corrections were carried out with the aid of a
computer. The tabulated data of Doppler effect on line width at 10 kHz intervals at room temperature was graphed for the five transitions of interest and is presented in Figure 9. The corrected line width was denoted by $\Delta \nu$. Slopes of pressure line width behavior was noted with $\delta \nu_p$ and $\Delta \nu_p$ respectively for experimental line width and Doppler corrected line width.

A plot of the quantum number $J$ and $\Delta \nu_p$ was prepared in Figure 10. Data are presented for different $J$ values. The plot was included for the sake of completeness although it is not the purpose of this work to explain the correlation.

This work concludes that:

1. A linear relationship existed between $\Delta \nu$ and a wide range of low pressures as predicted by van Vleck-Weisskopf line shape theory.

2. The line width parameter $\Delta \nu_p$ is dependent upon the quantum number $J$.

3. The hard sphere collision diameters $b_1$ (Table VIII) are greater than the physical size of HCOOH (i.e. physical size was approximately 3.5Å).

Hard sphere collision diameters are tabulated in Table VIII of Appendix C. Collision diameters were noted to depend on the quantum number $J$.

The exact dependence of $\Delta \nu_p$ with $J$ cannot be established completely until more points are obtained for Figure 10. These results will be obtained by another
FIGURE 9. Doppler Correction Curves
investigation when reflex klystrons become available to extend the frequency range of the equipment.

This work was felt to be completed in that sufficient data has been obtained to demonstrate a quantum number J dependence for the line width parameters $\Delta v_p$. 
CHAPTER BIBLIOGRAPHY


APPENDIX-A

MOLECULAR CONSTANTS AND TRANSITIONAL FREQUENCIES
TABLE I

ROTATIONAL AND DERIVED MOLECULAR CONSTANTS FOR HCOOH

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>77,512.25 MHz</td>
</tr>
<tr>
<td>B</td>
<td>12,055.012 MHz</td>
</tr>
<tr>
<td>C</td>
<td>10,416.205 MHz</td>
</tr>
<tr>
<td>r_{\text{C-H}}</td>
<td>1.085A + 0.025A</td>
</tr>
<tr>
<td>r_{\text{C=O}}</td>
<td>1.245A ± 0.002A</td>
</tr>
<tr>
<td>r_{\text{C-O}}</td>
<td>1.312A ± 0.002A</td>
</tr>
<tr>
<td>r_{\text{O-H}}</td>
<td>0.95A ± 0.020A</td>
</tr>
<tr>
<td>\angle \text{OCO}</td>
<td>124^018' ± 10'</td>
</tr>
<tr>
<td>\angle \text{COH}</td>
<td>107^048' ± 1^0</td>
</tr>
<tr>
<td>r_{\text{O-O}}</td>
<td>2.261A ± 0.004A</td>
</tr>
<tr>
<td>C-O/C=O</td>
<td>1.054 ± 0.003</td>
</tr>
<tr>
<td>( J_{K-1K'1+1} )</td>
<td>( J_{K-1K+1} )</td>
</tr>
<tr>
<td>-----------------</td>
<td>-----------------</td>
</tr>
<tr>
<td>5 (1, 4) + 5 (1, 5)</td>
<td>24568.96</td>
</tr>
<tr>
<td>12 (2,10) + 12 (2,11)</td>
<td>27758.32</td>
</tr>
<tr>
<td>13 (2,11) + 13 (2,12)</td>
<td>36818.58</td>
</tr>
<tr>
<td>19 (3,16) + 19 (2,17)</td>
<td>23203.41</td>
</tr>
<tr>
<td>20 (3,17) + 20 (3,18)</td>
<td>30521.70</td>
</tr>
</tbody>
</table>
APPENDIX B

LINE WIDTH CURVES FOR ROTATIONAL STATES OF HCOOH
SLOPE = 38.76
INTERCEPT = 39.22

**Figure 11.** 5(1,4) → 5(1,5)
SLOPE = 16.82
INTERCEPT = 122.23

\[ \Delta \nu \] (Doppler Corrected) vs. \( p \) (MICRONS)

FIGURE 12. 12(2,10) \rightarrow 12(2,11) 27,758.48 MHz
SLOPE = 24.13
INTERCEPT = 107.65

\[ \Delta \nu \text{ (Doppler Corrected)} \]

\[ \text{p(MICRONS)} \]

FIGURE 13. 13(2,11) \rightarrow 13(2,12) 36,818.63 MHz
SLOPE = 26.20
INTERCEPT = 94.55

FIGURE 14. (3,16) $\rightarrow$ 19(3,17) 23,20,340 MHz

$\Delta \nu_{\text{KHz}}$ (Doppler Corrected)
SLOPE = 31.91
INTERCEPT = 38.49

FIGURE 15. 20(3,17) → 20(3,18)
30521.65 MHz

p(MICRONS)
SLOPE = 37.31   INTERCEPT = 47.50

\[ \Delta v \] (kHz) (w/o Doppler Correction)

\[ p \text{ (MICRONS)} \]

FIGURE 16. 5(1,4) \rightarrow 5(1,5)  24,568.96 MHz
\( SLOPE = 23.25 \quad INTERCEPT = 117.90 \)
SLOPE = 26.20   INTERCEPT = 96.55

FIGURE 19. 19(3,16) → 19(3,17)  23,203.40 MHz
APPENDIX C

TABULATED DATA FOR THE ROTATIONAL TRANSITIONS OF HCOOH
<table>
<thead>
<tr>
<th>Pressure (microns)</th>
<th>$\delta\nu$ (kHz)</th>
<th>$\Delta\nu$ (kHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.505</td>
<td>97.</td>
<td>91.</td>
</tr>
<tr>
<td>1.609</td>
<td>111.</td>
<td>105.</td>
</tr>
<tr>
<td>1.807</td>
<td>119.</td>
<td>114.</td>
</tr>
<tr>
<td>2.307</td>
<td>136.</td>
<td>131.</td>
</tr>
<tr>
<td>2.936</td>
<td>149.</td>
<td>145.</td>
</tr>
<tr>
<td>3.424</td>
<td>179.</td>
<td>176.</td>
</tr>
</tbody>
</table>
### TABLE IV

HCOOH \( 12 (2,10) + 12 (2,11) \) 27758.48 MHz

<table>
<thead>
<tr>
<th>Pressure (microns)</th>
<th>( \delta \nu ) (kHz)</th>
<th>( \Delta \nu ) (kHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.287</td>
<td>165.</td>
<td>160.</td>
</tr>
<tr>
<td>2.547</td>
<td>172.</td>
<td>167.</td>
</tr>
<tr>
<td>4.178</td>
<td>195.</td>
<td>191.</td>
</tr>
<tr>
<td>4.797</td>
<td>203.</td>
<td>199.</td>
</tr>
<tr>
<td>5.211</td>
<td>218.</td>
<td>214.</td>
</tr>
</tbody>
</table>
TABLE V

HCOOH     | 13 (2,11) + 13 (2,12) | 36818.63 MHz
--- | --- | ---

<table>
<thead>
<tr>
<th>Pressure (microns)</th>
<th>$\delta \nu$ (kHz)</th>
<th>$\Delta \nu$ (kHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.861</td>
<td>162.</td>
<td>153.</td>
</tr>
<tr>
<td>2.466</td>
<td>166.</td>
<td>158.</td>
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<tr>
<td>3.114</td>
<td>201.</td>
<td>194.</td>
</tr>
<tr>
<td>3.795</td>
<td>207.</td>
<td>200.</td>
</tr>
<tr>
<td>4.869</td>
<td>228.</td>
<td>222.</td>
</tr>
<tr>
<td>6.112</td>
<td>260.</td>
<td>255.</td>
</tr>
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</table>
TABLE VI

<table>
<thead>
<tr>
<th>Pressure (microns)</th>
<th>$\delta\nu$ (kHz)</th>
<th>$\Delta\nu$ (kHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.603</td>
<td>240.</td>
<td>238.</td>
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<tr>
<td>6.301</td>
<td>270.</td>
<td>268.</td>
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<tr>
<td>7.777</td>
<td>290.</td>
<td>288.</td>
</tr>
<tr>
<td>8.704</td>
<td>330.</td>
<td>328.</td>
</tr>
<tr>
<td>Pressure (microns)</td>
<td>$\delta \nu$ (kHz)</td>
<td>$\Delta \nu$ (kHz)</td>
</tr>
<tr>
<td>-------------------</td>
<td>-------------------</td>
<td>-------------------</td>
</tr>
<tr>
<td>.795</td>
<td>80.</td>
<td>68.</td>
</tr>
<tr>
<td>.934</td>
<td>82.</td>
<td>70.</td>
</tr>
<tr>
<td>2.367</td>
<td>105.</td>
<td>96.</td>
</tr>
<tr>
<td>2.697</td>
<td>135.</td>
<td>128.</td>
</tr>
<tr>
<td>3.279</td>
<td>158.</td>
<td>152.</td>
</tr>
<tr>
<td>3.783</td>
<td>165.</td>
<td>159.</td>
</tr>
<tr>
<td>Transition J #</td>
<td>$\delta_{vp}$</td>
<td>$\Delta_{vp}$</td>
</tr>
<tr>
<td>---------------</td>
<td>--------------</td>
<td>--------------</td>
</tr>
<tr>
<td>5</td>
<td>37.31</td>
<td>38.76</td>
</tr>
<tr>
<td>12</td>
<td>16.42</td>
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<tr>
<td>13</td>
<td>23.25</td>
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<tr>
<td>19</td>
<td>26.20</td>
<td>26.21</td>
</tr>
<tr>
<td>20</td>
<td>29.56</td>
<td>31.91</td>
</tr>
</tbody>
</table>
BIBLIOGRAPHY

Books


Articles


Unpublished Materials

Klages, John, unpublished calibration for the McLeod Gauge, Department of Physics, North Texas State University, Denton, Texas, 1973.


Yang, Wei Han, "Pressure Dependence of Line Widths of Microwave Spectra of Sulphur Dioxide," unpublished master's thesis, Department of Physics, North Texas State University, Denton, Texas, 1972.