Molecular Probing at Microwave Frequencies as a Means of Studying Atmospheric Motion and Composition

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MOLECULAR PROBING AT MICROWAVE FREQUENCIES
AS A MEANS OF STUDYING
ATMOSPHERIC MOTION AND COMPOSITION

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ABSTRACT
Environments of planets are of great interest in this age of space probing. The nature of the atmosphere and its ability to support life is of primary interest today. This paper concerns the use of spectroscopic probing as a means to determine the composition and behavior of planetary atmospheres and nebulae.

One of the most sensitive methods of obtaining properties of gaseous mixtures is the method of probing resonance conditions of one or more molecular species within the mixture. For example, a mixture containing SO₂ and other gases could be studied by observing the structure and shape of a resonance profile of SO₂ in the presence of the unknown gases and comparing these observations with the resonance nature of isolated SO₂ molecules. Such a method can be employed to study the motion of molecules within the gaseous space through Doppler shift and these results used to determine atmospheric motion.

INTRODUCTION
A number of investigators have been studying the structural properties of molecules via their rotational resonance properties for several decades. These studies have enabled structural assignments to be made for varying types of molecules from the simple diatomic HCl to highly complex molecules. Structural studies have been extended to include line width and center frequency shifts of the resonances with the recent advent of suitable apparatus which is capable of obtaining the small pressure and temperature perturbations on resonant frequency for molecules.

This investigation deals primarily with the following aspects of molecules.

1. Pressure effects upon the width of rotational resonances of molecules as a means of studying dipole-dipole and dipole-induced dipole forces.

2. Pressure effects upon the energy levels of molecular rotors. These energy level perturbations lead to shifts in the center frequency of the transitions of some molecular spectra and may cause errors to arise in structural assignments for some molecules.

3. Stark effect in molecular spectra to better understand how overlapping resonances effect centroids and widths of resonances. A better understanding of these overlap conditions is needed in order to get life times of states from line width data.

4. Double resonance pumping of molecular systems as a means of better understanding molecular state life times and radiation absorption processes.

Some of the above processes were explored experimentally in our laboratory. Both pure gases and binary gas mixes were investigated. The line shape was monitored in the measurements.

Pressure-broadened line shapes have generally been assumed to be Lorentzian, based on theoretical predictions. However, experimental evidence that the Lorentzian line shape is the true pressure-broadened shape has lately been provided by a series of measurements on the profiles of the first through fifth derivatives of spectral lines of ammonia at low pressure.

We have employed a device to select and separate such Lorentzian components by using d.c. offset Stark field to remove the
M-degeneracy in each state of interest. The desired M-component is selected and shifted via the applied field into an isolated frequency region of the scan; source modulation being used to obtain a time-varying signal for amplification and observation purposes.

Ignoring the second resonant term in the Van Vleck-Weisskopf line shape, the line shape equation reduces to (7)

$$\alpha(\nu) = \frac{8\pi^2 N f \nu^2 \Delta \nu |\mu_{ij}|^2}{3ckT(\nu - \nu_0 + (\Delta \nu)^2)}$$  (1)

Where $N$ is the number of molecules per unit volume, $f$ is the fraction of the molecules in the lower energy state involved in the transition, $\mu_{ij}$ is the dipole moment matrix element for the transition, and $\Delta \nu$ is the half-maximum half width. The symbols $c$, $k$, and $T$ have the usual meanings of speed of light, Boltzmann's constant, and absolute temperature, respectively.

Experimentally, one generally observes derivative of the absorption profile, $\alpha'(\nu)$; the derivatives are inevitable if source modulation is used, and in any case the derivatives are easier to measure accurately (the half-power points of a line are difficult to establish because of baseline noise). The points of zero slope of any derivative of $\alpha(\nu)$ may be related to the half-power points by repeated differentiation of Eq. (1). It is a simple matter to discover that the peaks of the first derivative are related to the half-width, $\Delta \nu$, by $2 \Delta \nu_1 = 2 \Delta \nu_2$, where, following convention, the separation between the peaks of a derivative profile coincide with the half-power points of $\alpha''(\nu)$. The profiles of the first two derivatives of the absorption profile are shown, along with a Lorentzian absorption profile, in Figure 1.

Care should be exercised by noting that the relations between $\delta \nu$ and $\Delta \nu$ in Figure 1 obtain only if the original shape of the line is strictly Lorentzian. Hence, corrections for other types of broadening may occasionally be very important, especially if the extraneous broadening does not of itself give a Lorentzian shape (such as the Gaussian contribution from Doppler broadening). The effect of Doppler smearing is important in turbulent atmospheres or in nebulae where the columns are long and large relative motions arise.

The line widths are used to calculate life times for the states being probed once line broadening due to molecular interactions only has been established.

**COLLISION THEORIES**

Anderson (8) has obtained general formulas for line widths and shifts. His expression for the shape of a pressure broadened line is

$$\alpha(\nu) = \frac{8\pi^2 N f \nu^2 \Delta \nu |\mu_{ij}|^2}{3ckT(\nu - \nu_0 + (\Delta \nu)^2)}$$  (2)

where the notation holds as in Equation (1). Note that a possible line shift in frequency has been introduced by a shift term, $\Delta \nu_0$. As in Equation (1), a second resonant term has been omitted for the case of $\Delta \nu << \nu_0$. The shape of the function in Equation (2) is identical to the Van Vleck-Weisskopf shape, when the line shift is not present.

Pressure-induced shifts in center frequencies of microwave lines may be expressed as $\Delta \nu = \alpha \Delta \nu$, where $\alpha$ is constant and $\Delta \nu$ is the half-power half-width. These shifts are very small for microwave lines, and only a few shifts have actually been observed. (9,10,11) They are typically of the order $10^{-2} \Delta \nu$. These small shifts do not affect pressure broadening studies in general unless they alter the line shape.

Anderson's expressions for the line width and frequency shift, in mixtures of two different types of molecules (denoted by subscripts 1 and 2), where the number of molecules per unit volume of each type is $N_1$ and $N_2$, respectively, may be written as

$$2\pi \Delta \nu = N_1 \nu_1 \sigma_{11} + N_2 \nu_2 \sigma_{12}$$  (3)

and

$$2\pi \Delta \nu_0 = N_1 \nu_1 \sigma_{01}'' + N_2 \nu_2 \sigma_{02}''$$  (4)
Subscript 1 applies to the molecule ("absorber") whose line is being observed, and subscript 2 applies to the other type of molecule (the "perturber") involved in the binary collisions.

The width and shift of course have contributing terms from both "self" broadening (collisions between two molecules of type 1) and "foreign-gas" broadening (collisions between a molecule of type 1 and one of type 2), as shown in the two equations above. The symbol $\sigma'$ refers to the mean relative velocity of colliding molecules, and $\sigma''$ are the real and imaginary parts of the collision cross section, respectively. ($\sigma''$ is the real part of the self-broadening cross section.) In self broadening $N_2 = 0$. Consequently, some type of weighting factor must be employed with the classical impact parameter to differentiate between the strengths of various collisions. In this fashion, the quantum effects can be introduced through the weighting factor.

We may define an interaction function $S(b)$ which carries all the information concerning the forces arising between the molecules within the region of interest. The parameter $S(b)$ represents the entire family of forces associated with the system.

The interaction between the molecules is of two forms; one in which the incident radiation is shifted in phase and the other in which the molecular structure is altered. These two interactions can be expressed in terms of "cross-section" for the processes as

$$\sigma = \sigma' + i\phi'' = \int_{-\infty}^{\infty} b S(b) \, db$$  \hspace{1cm} (5)

The problem is now reduced to finding $S(b)$, which may be difficult for some molecules.

We may expand the orders of $S(b)$ in the expansion as

$$S(b) = S_0(b) + S_1(b) + S_2(b) + \cdots$$  \hspace{1cm} (6)

one finds that $S_0(b) = 0$ (for no interaction) and the $S_1(b)$ is purely imaginary so that it contributes only to the line shift of Equation (4), and not to the half-width as determined by Equation (3).

There are two second-order terms, which are called $S_2(b)_0$ and $S_2(b)_m$; these give the intermolecular coupling of colliding molecules which contributes to the line width for intermolecular potential, $H_c(t)$, to be specified. In fact, $S_2(b)_m$ gives the diagonal elements of the coupling matrix and $S_2(b)_0$ gives the off-diagonal elements.

The interaction function $S(b)$ must be determined in the Anderson formalism to solve the phase shift and damping cross-section. Further treatment of this problem by Anderson can be found in Reference 8.

Murphy and Boggs (12) have derived expressions for widths and shifts of spectral lines, using methods analogous to those of Anderson, in terms of the life times of initial and final ortational states of colliding molecules. Their expression for the shape of pressure broadened microwave lines is identical to Equation (2). They obtained the modified Van Vleck-Weisskopf line shape with a term for shift in resonance frequency as obtained by Anderson. If the average life times of the initial and final states of the absorbing molecule (averaged over all possible states of the colliding molecules) are $\tau_i$ and $\tau_f$, respectively, then the equations for the half-width, $\Delta \nu^3$, and frequency shift, $\Delta \nu^1$, are expressed by

$$\Delta \nu^1 = \frac{1}{\sqrt{\pi \tau_i}} + \frac{1}{\sqrt{\pi \tau_f}}$$  \hspace{1cm} (7)

$$\Delta \nu^0 = \left[ (E_f^0 - E_i^0) - (E_f^0 - E_i^0) \right] \frac{1}{\hbar}$$  \hspace{1cm} (8)

with $E_i$ and $E_f$ being the average perturbed energies of the states, and $E_i^0$ and $E_f^0$ being the unperturbed energies of the two states. The symbol $\hbar$ represents Planck's constant.

A function $\phi(J_1, J_2)$ can be defined which gives the number of transitions per unit time induced out of the $J_1$ level of the absorber by collisions with perturbing molecules in the rotational level $J_2$, and
averaging over all possible \( J_o \) levels with the aid of the Boltzmann distribution \( P_B(J_o) \). Life times of the energy states of the absorber are then given by

\[
\frac{1}{\tau_i} = \sum_j P_b(J_2) \phi(J_i, J_2)
\]  

(9)

The function \( \phi(J_i, J_o) \) is given by Equation (II-44) of Ref. 12. Equation (9) above allows us to compute the average lifetimes of any two levels \( J_i \) and \( J_f \) between which transitions may occur. Equation (7) then determines the theoretical pressure boradened half-width.

Half-widths of spectral lines calculated with the Murphy-Boggs theory are typically less than values obtained from Anderson's theory. This is because the variation of \( S_2(b) \) with the variation in impact parameter is different in the two theories. Murphy and Boggs have shown that conversion of their formulation to that of Anderson gives an equivalent curve for \( S_2(b) \) as shown in Figure 2.

EXPERIMENTAL METHODS

We have used the following experimental methods to determine the line width, line shape, center frequency shifts and effects of Stark fields.

Experimental investigations of widths of spectral lines require that the width of each line be measured as a function of pressure for a pressure range sufficiently large to allow an accurate value of the line width parameter to be determined for each line. A suitable line width spectrograph must be capable of measuring small frequency intervals (50-500KHz) accurately.

Usually, frequency measurements to within 15KHz are essential in line width studies. Center frequencies for many known rotational transitions are available from tables and do not change much with pressure. The frequency separations between individual resonances are usually great enough such that an absolute frequency determination of one part in \( 10^4 \) is sufficiently accurate to positively identify a desired transition. In structure studies resolution must be improved to about \( 1/10^8 \).

When measuring line shifts the requirements of both absolute frequency determinations and relative frequency determinations are much more restrictive. Absolute values of 1KHz in 50gHz must be maintained in order to measure frequency shifts encountered in many molecular transitions. This requirement prevents or restricts frequency shift measurements of many transitions.

A block diagram of the line width spectrograph used in this study is shown in Figure 3. This spectrograph, except for the Stark cell, has been discussed in the literature, (13) as have similar precursor spectrometers.(14,15)

For simplicity, the spectrograph is divided into five sections: (1) the radiation source (klystron) and associated supply, control, and sweep circuits; (2) the absorption cell, attenuators, etc.; (3) signal detection, amplification, and display circuitry; (4) the frequency measuring system; and (5) the vacuum and gas handling system.

Reflex klystrons manufactured by OKI, Varian, and Raytheon served as sources of microwave radiation in the spectrograph. Usually, klystrons are available which produce fundamental frequencies at the desired transition frequencies. However, some higher frequencies can only be reached by frequency doubling in crystal harmonic generators. This is a common technique, and adequate power is available at the first harmonic to enable us to multiply to a range of over 100gHz.

The klystron control unit (Figure 3) is designed so that the focus, anode (beam), and reflector potentials may be conveniently adjusted. The control unit has special provision for applying source modulation and oscilloscope sweep voltages to the klystron repeller in order to gain time varying signals which can be amplified and analyzed to determine each resonance shape and center frequency.

Sine wave modulation was used in this investigation as this enables the differentiation of the resonance profiles. It has been found that resolution is improved by using second derivatives instead of first.
Line shape distortion introduced by standing waves is also reduced, as previously observed by Netterfield et al. (6)

Naturally, distortion of the line shape due to electronic factors can lead to errors in line width and shift measurements. A possible source of distortion results from the nature of klystron power modes. If a spectral line is observed at a frequency where the power mode has appreciable curvature, the power variations detected as being due to the resonance are superimposed on a nonlinear baseline; this causes the absorption line (and all derivative profiles) to depart from the true shape.

This problem can usually be overcome by adjusting the focus, beam, and reflector potentials so that the power mode peaks near the center frequency of the observed line. Klystron power modes are generally essentially flat over a reasonably wide frequency range (about 2MHz) near the center of the mode, so distortion due to curvature is minimal there.

The kind of cell to be chosen for absorption studies is determined by the nature of fields to be applied to the molecules. We have chosen a parallel plate wave guide which can be used for both Stark field application and source modulation. The cell design is shown in Figure 4. The cell design enables application of several kinds of signals to the molecules. The parallel plate arrangement allows application of d.c. fields which will both change the molecular dipole alignment and alter the line shape in accordance with the Stark components in the spectra. Also ports exist for introduction of laser radiation and additional microwave radiation into the molecular system.

The cell length chosen was only 1.8 m because of high capacitance arising when plate widths are made sufficiently wide to reduce fringing effects at the edges of the cell plates. The use of wide propagation plates (.1 m) required a glass cylinder for vacuum enclosure that had a very large volume. This large volume requires longer pumping times to purge the cell between runs, but this is a minor inconvenience.

To admit source radiation to the cylindrical cell, provision had to be made to convert the rectangular TE10 mode microwave radiation from the klystron to the dominant mode of the absorption cell. A reverse process was necessary at the detector end because most of the crystal detector mounts available were made of rectangular guide. These mode conversions were effected by using tapered feed-horns fashioned to gradually change from rectangular to parallel plate propagation over a length of .30 m.

A 30-db coupler diverts a small fraction of the klystron source power to a crystal mixer, for use in the frequency-measuring system.

Power absorptions due to microwave transitions in a gaseous molecular sample are often less than 1/106 of the off-resonance power level in the absorption cell, and it is these small power absorptions that must be measured to obtain line widths. Therefore, signal detection and amplification is a critical stage in the experimental process. The maximum sensitivity of a spectrograph is limited by the noise that appears during absorption, detection, and amplification, so the performance characteristics of the equipment used for this purpose are very important.

Shorted-input equivalent noise generated in the pre-amplifier was measured to be less than 0.6 V, which was about as large a value as could be tolerated when crystal currents were below a few A.

The detected signal was amplified in the pre-amplifier, and sent to a PAR Model 122 phase-sensitive detector. The "lock-in" was also tuned to 34kHz, and was referenced to the square wave output from the same Heathkit EUW 27 audio generator that produces the sine wave source modulation as well.

Visual display of the phase detector output signal is provided by using the Tektronix 502A dual-trace oscilloscope which also generates the klystron sweep voltage. The phase detector signal can be sent to one pen of a dual-channel Rikadenki B-261 strip chart recorder for a permanent record of the data. The second chart pen is used to display frequency markers. A typical recorder display of the first derivative
profile of a spectral line in methyl cyanide is given in Figure 5.

Signals may be obtained at any level of derivative desired with the choice dictated by what portion of the line is to be observed for study.

Detection at the first harmonic of a sine wave modulation signal yields a crystal signal which is proportional to the second derivative of the absorption profile, $\alpha (2\nu)$. The appearance of the first derivative can be seen to occur because the slowly-swept klystron output is "chopped" by a high-frequency modulation which essentially samples the instantaneous slope of the power output curve at the rate of the chopper frequency. The higher derivatives of the absorption curve arise because the absorption profile is nonlinear.(6)

There are several reasons for experimentally observing derivatives of the line instead of the absorption profile. First, modulating the klystron output frequency permits the use of high-gain a.c. amplification. Second, baseline noise would make location of the precise half-power points very difficult in observing the line profile. Third, distortion due to standing waves is reduced by using higher derivatives.(6) Finally, the frequency resolution of the lines was found to be improved by observing second derivatives. Turning points in the derivatives could be observed to less than 15kHz.

Overall, the detection and amplification system was found to be sensitive enough to measure microwave lines with absorption coefficients as small as $10^{-7}$ cm$^{-1}$.

The small frequency intervals that must be determined in line width studies can be conveniently measured by producing "frequency markers" of known frequency separation on the same chart that records the derivative of the line shape. Half power points could be established by this scale but for line shift determinations it was necessary to determine absolute frequencies as well as relative frequencies.

The markers are generated in the standard way by mixing part of the source radiation (extracted with the 30-db coupler) with microwave radiation from General Radio Models 1112A and 1112B frequency standards. In addition an interpolation signal generator, Tektronix Model 191, is used to span any frequency intervals not near the "comb" of frequencies generated from the General Radio Standards.

Sum and difference frequencies are obtained by crystal-mixing the various signals; the difference frequencies for the above configuration are in the radio frequency range, and are detected with a Wells-Gardner Model BC-348Q radio receiver. The receiver is typically tuned to receive 250kHz difference frequencies. By tuning the frequency standard signals so that one of its harmonics is approximately equal in frequency to the transition frequency of the line being observed, two frequency markers appear at intervals of 250kHz. The total separation of 500kHz between these markers can then be used as a basis for measuring frequency separations between derivatives peaks.

Evacuation of the absorption cell was performed by a vacuum system consisting of a LN$_2$ cold-trapped Van Waters and Rogers HV-1 oil-vapor diffusion pump connected to a Welch Duo-seal Model 1405 forepump. Pressure measurements made with a calibrated McLeod gauge indicated that the system was capable of an ultimate vacuum at room temperature of $10^{-7}$ mm of Hg. A McLeod gauge was used for pressure measurements initially. A bellows driven pressure gauge is under development for future use in pressure measurements.(23)

Gases were admitted into the cell when desired from a series of "dosing" reservoirs mounted on a dosing manifold. A diagram of the dosing and manifold system is given in Figure 6.

**DESIGN OF THE EXPERIMENT**

The experiments were conducted in the following manner.

Line width parameters were determined by admitting samples of gas into the cell and allowing a suitable time for equilibration of pressures and transient effects in the system. Measurements were then made on widths and shifts of the resonance component of interest. Once a family of pressures and widths and a family of pressures...
and center frequencies were obtained, the two parameters $\Delta \omega$ and $\Delta \nu$ can be obtained for the specific transition. It is, of course, necessary that all line widths be corrected for the non-pressure effects before line width parameters are obtained. Likewise, any effects upon the resonance centroid which are non-pressure must be compensated for before a true value of $\Delta \nu$ is known. Once true line width parameters and center frequency shifts are deduced they can be compared to theory and both collisional forces which interrupt radiation and collisional forces which produce only phase shifts in the molecule's energy levels can be analyzed.

These results can then be used to study the nature of the environment of the molecular gas whether it be in a binary mixture of gases in the laboratory, in interstellar nebulae or in the atmosphere of a planetary body.

REFERENCES

1. See, for example, Abstracts of the Austin Symposium on Gas Phase Molecular Structure held biennially at Austin, TX by Chemistry Department and directed by J.E. Boggs for recent activity in structure studies and Abstracts of annual Symposium on Molecular Spectroscopy, Columbus, Ohio, for other applications of microwave studies to chemistry.


FIGURE 1. Profiles of a Lorentzian line and its first two derivatives. (A) Lorentzian line shape, (B) First derivative, (C) Second derivative.
FIGURE 2. Graph of $S(b)$ versus $b$ for two impact theories summarized in this paper. (A) Anderson theory, (B) Murphy-Boggs theory, (C) G. Buffa et al ref. 11.
FIGURE 3. Block diagram of the line width spectrograph.
FIGURE 4. Parallel plate wave guide design for use in this investigation.
FIGURE 5. Chart recorder trace of the three hfs spectral components in the (0→1) rotational transition of methyl cyanide.
FIGURE 6. Diagram of the pressure measuring and gas handling apparatus used in this investigation.