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FINAL TECHNICAL REPORT NO. FTR-1

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OPACITY OF THE ATMOSPHERE AT MILLIMETER WAVELENGTHS

**UARI REPORT NO I**

1 JANUARY 1962

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UNIVERSITY OF ALABAMA RESEARCH INSTITUTE  
HUNTSVILLE, ALABAMA



OPACITY OF THE ATMOSPHERE AT MILLIMETER WAVELENGTHS

1 January 1962

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Interim Director

University of Alabama Research Institute  
Huntsville, Alabama



## ABSTRACT

The theory of absorption by molecular oxygen in the wavelength region between 1 and 10 millimeters is summarized, and experimental methods of measuring atmospheric absorption are discussed. It is concluded that the agreement between experiment and theory is in general satisfactory.

Short-period fluctuations in atmospheric absorption, possibly correlated with variations in the earth's magnetic field or other external factors, have been suspected. The probable effects of time-varying external fields, Zeeman splitting, and statistical orientations of the oxygen molecule in the magnetic field are analyzed. None of these factors appear to explain the suspected variations.

A limited experimental program is included in the study.



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## 1. INTRODUCTION

The millimeter wavelength portion of the electromagnetic spectrum occupies a transition region between the microwave atmospheric window, where attenuation is relatively small, and the long infrared opaque region, where there is essentially no transmission. Such transition regions can often provide fundamental knowledge of the properties of the absorbing medium.

The potentialities of experiments in the millimeter wavelengths are being realized with the development of new techniques for transmitting and handling them. For example, already under consideration are activities in development of small, light-weight systems, in the design of reasonably secure communication systems, and in the study of the atmosphere (of other planets as well as of the earth), by means of transmission into or through the atmosphere either from above or from below.

The theories which predict the propagation of electromagnetic waves through the various constituents of the atmosphere have been able to account reasonably well for the frequencies of the observed maxima of absorption. However, the quantitative predictions of the theory in the wings of the lines have been less successful. The pertinent experiments in this range of frequencies (from 30 KMcps to 300 KMcps) have been quite limited in number and in frequency coverage. Furthermore, a correlation between theory and experiment is difficult because of the constantly varying atmospheric conditions along the path, plus an incomplete knowledge of the composition of the upper atmosphere.



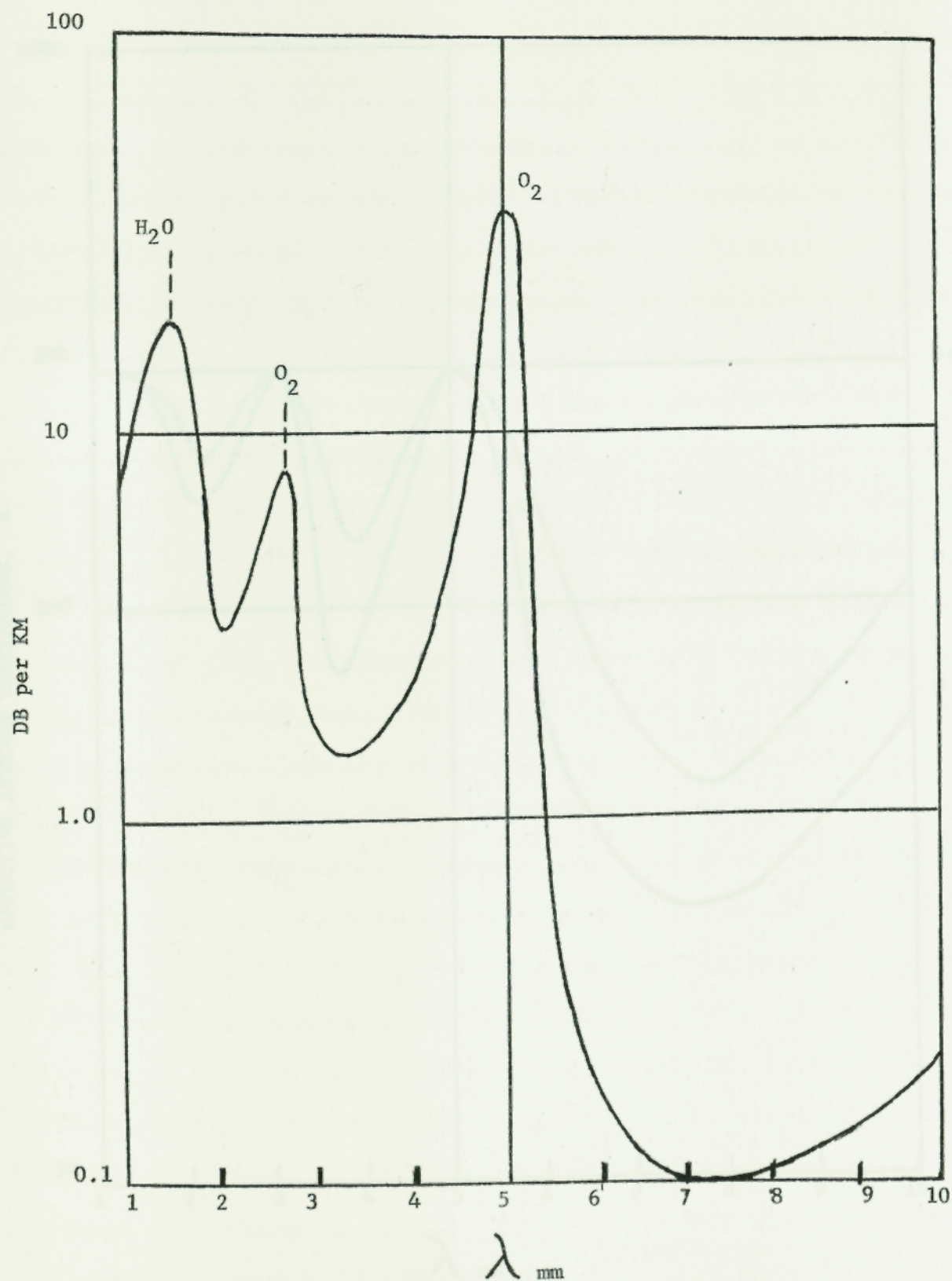


Fig. 1. Approximate attenuation in sea-level atmosphere.

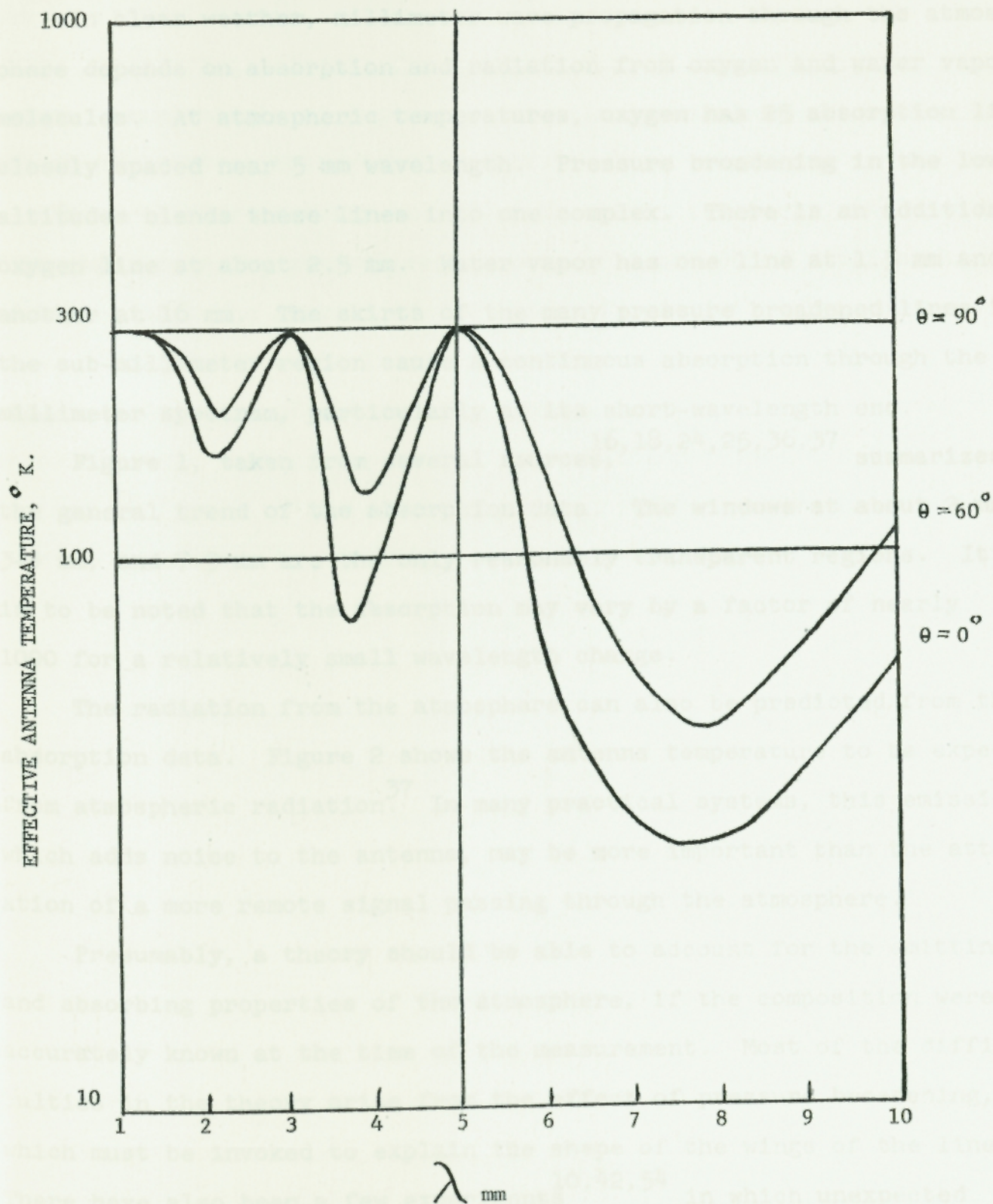


Fig. 2. Emission from the atmosphere. Ground-based antenna. Angle  $\theta$  is the zenith angle.



In clear weather, millimeter wave propagation through the atmosphere depends on absorption and radiation from oxygen and water vapor molecules. At atmospheric temperatures, oxygen has 25 absorption lines closely spaced near 5 mm wavelength. Pressure broadening in the lower altitudes blends these lines into one complex. There is an additional oxygen line at about 2.5 mm. Water vapor has one line at 1.3 mm and another at 16 mm. The skirts of the many pressure broadened lines in the sub-millimeter region cause a continuous absorption through the millimeter spectrum, particularly at its short-wavelength end.

Figure 1, taken from several sources,<sup>16,18,24,25,36,37</sup> summarizes the general trend of the absorption data. The windows at about 2 mm, 3-4 mm, and 7-9 mm are the only reasonably transparent regions. It is to be noted that the absorption may vary by a factor of nearly 1000 for a relatively small wavelength change.

The radiation from the atmosphere can also be predicted from the absorption data. Figure 2 shows the antenna temperature to be expected from atmospheric radiation.<sup>37</sup> In many practical systems, this emission, which adds noise to the antenna, may be more important than the attenuation of a more remote signal passing through the atmosphere.

Presumably, a theory should be able to account for the emitting and absorbing properties of the atmosphere, if the composition were accurately known at the time of the measurement. Most of the difficulties in the theory arise from the effect of pressure broadening, which must be invoked to explain the shape of the wings of the lines. There have also been a few experiments<sup>10,42,54</sup> in which unexpected variations in absorption are suspected. Such fluctuations, if real, would provide valuable checks on the theory. It seems, on the whole,



that a critical survey of the state of the theoretical analyses, especially considering possible fluctuations due to external factors, is needed. Particularly of importance are the assumptions which have been made in the various theoretical models.

This report represents an effort to survey critically the theory of absorption in the general region between 1 and 10 mm wavelength, and to estimate the success of the theory in predicting the measured values. Primary emphasis is given to clear-weather absorption by oxygen, since the same type of theory also applies to water vapor. The main reason for this choice lies in the fact that experiment and theory are far more difficult to compare in the case of water vapor, because of the wide variations in humidity.



## 2. MEASURED VALUES OF ATMOSPHERIC ABSORPTION

2.1 General Methods. Experiments to determine the absorption in the atmosphere fall into three general classes. First, there is the laboratory measurement, over a short path, of the attenuation between a laboratory transmitter and laboratory receiver.<sup>2,6,23</sup> This method has the advantage of affording the ability to control the conditions in the absorbing path at will. However, in order to obtain sufficient absorption to be measurable at frequencies in the wings of the lines, the gas is usually at a rather high pressure. Measurements of this type, while affording the same electrical path length, do not always reproduce the conditions in the earth's atmosphere, especially as concerns pressure broadening.

A second method, which has been used quite successfully to obtain absorption data at longer path lengths, measures the attenuation over some kilometers between a ground-based transmitter and a ground-based receiver. Such experiments<sup>40,41,42</sup> give the absorption at atmospheric pressure, but do not take into account the vertical variations in the atmospheric conditions. Furthermore, these experiments often suffer from an incomplete knowledge of the atmospheric conditions over the path of propagation.

The third method measures the absorption in the atmosphere of some naturally occurring radiation which is in or beyond the atmosphere. For instance, the sun is often used as the source for this type of experiment.<sup>19,29,31,34,53</sup> It has the advantage of measuring through the entire atmospheric layer around the earth. It must, however, assume that the source of the radiation is itself constant with time and of known spectral distribution. A variation of this method measures the



thermal emission from the atmosphere itself as a function of zenith angle. A series of such measurements for different zenith angles can also furnish a value of the atmospheric absorption.<sup>1,13</sup> It must be assumed that the atmospheric conditions do not change during a run.

In order to compare these methods, and to compare them with theory, some knowledge of the structure of the atmosphere is required. The third method yields the total attenuation in a column of atmosphere rather than the attenuation per unit length. If the equivalent sea-level height of the actual column of atmosphere (approximately 20 KM) can be inferred by means of some model of the atmosphere, then the third method may yield indirectly the attenuation per unit length. Although this comparison would seem to be of doubtful validity, it is encouraging that the values as given by the three methods usually agree fairly well, and sometimes surprisingly well.

2.2 Absorption Coefficient. Consider thermal radiation from a source at temperature  $t_s$ , passing through a thin absorbing layer  $dz$  thick at temperature  $t_a$  with power absorption coefficient  $\gamma$ . The power absorbed in this layer is  $\gamma k t_s dz$ , where  $k$  is the Boltzmann constant. The thermal radiation from this layer is  $\gamma k t_a dz$ . The effective temperature measured by an antenna at the bottom of this layer is to be found.

Let the antenna position be at  $z=0$ . The effective temperature at  $z=0$  is that due to (1) the external radiation attenuated by the absorbing layer, plus (2) the radiation emitted by the various levels, itself attenuated by the lower levels. Let the first of these be  $t_1$  and the second  $t_2$ . Let the height of the medium be  $h$ . Then,

$$dt_1 = \gamma t_1 dz$$

$$t_1 = t_s e^{\int_h^0 \gamma dz}$$

(2-1)



The antenna temperature  $t_2$  due to radiation from a layer  $dz$  high at a height  $z'$  at temperature  $t_a$  is given by

$$dt_2 = -\tau t_a \left( \exp \int_{z'}^0 \tau dz \right) dz' \quad (2-2)$$

$$t_2 = - \int_h^0 \tau t_a \left( \exp \int_{z'}^0 \tau dz \right) dz'$$

If the path makes an angle  $\theta$  with the vertical, and if it is assumed that the atmosphere is horizontally stratified, we have

$$dz_v = (\cos \theta) dz \quad (2-3)$$

where  $dz_v$  is measured vertically and  $dz$  along the path. Therefore,

$$t_\theta = t_s e^{\int_h^0 \tau \sec \theta dz_v} + \int_h^0 -\tau t_a \sec \theta \cdot e^{\int_{z'}^0 \tau \sec \theta dz_v} dz' \quad (2-4)$$

The quantity  $-\int_h^0 \tau dz_v$  is called the zenith opacity  $\tau_0$ , or sometimes the total vertical attenuation (TVA). Consequently,

$$t_\theta = t_s e^{-\tau_0 \sec \theta} + \int_h^0 -\tau t_a \sec \theta \cdot e^{\int_{z'}^0 \tau \sec \theta dz_v} dz' \quad (2-5)$$

The absorbing atmosphere is mainly that at the lower levels. If the temperature of this layer is assumed isothermal at the temperature  $t_a$ , and if  $\tau$  is constant in this layer, we can write:

$$t_\theta = t_s e^{-\tau_0 \sec \theta} + t_a \int_h^0 (-\tau \sec \theta) e^{\tau \sec \theta z_v'} dz_v' \quad (2-6)$$

$$t_\theta = t_s e^{-\tau_0 \sec \theta} + t_a \left( 1 - e^{-\tau_0 \sec \theta} \right)$$



The assumptions made in deriving this equation have been shown to be reasonable by means of various experiments in which  $t_e$  was measured as a function of the zenith angle  $\theta$ . Equation (2-6) is the basis of extensive measurements<sup>13,31,53</sup> of the total vertical attenuation in the earth's atmosphere. From a knowledge of the atmospheric profile, the equivalent sea-level depth of the atmosphere can be fairly well predicted, and thus the attenuation per unit length of path at sea level is inferred.

2.3 Experiments in the 100-300 KMcps Region. As the techniques of radiometry advance, more data can be expected in the range around the window near 2 mm wavelength.<sup>44</sup> Little is known about this portion of the spectrum, and even relatively crude data would be welcome. During the summer of 1961, a laboratory evaluation of the feasibility of using multiplier-mixer super-heterodyne radiometers in the frequency range from 100 KMcps to 200 KMcps was made under this contract in the U. S. Army Rocket and Guided Missile Research and Development Operations facility.

The initial tests were made with equipment and components that were already present in the lab. During the summer, other components were constructed for use in later tests.

The two initial tests were made with a 4 millimeter klystron local oscillator and a 4 millimeter to 2 millimeter multiplier with appropriate crystals. No 2 millimeter noise source was available; an 8 millimeter and a 3 centimeter noise source were available. The noise power from these noise sources was radiated from an open wave guide end. A 2 millimeter horn was placed in line with the radiating guide end to intercept the noise. Chopping was accomplished in the 8 millimeter case by



mechanically inserting a resistive load into the 8 millimeter waveguide, and in the 3 centimeter case by means of a ferrite switch operated in the 3 centimeter waveguide. The usual amplification and detection followed the multiplication and mixing. Results were negative in both cases. It is difficult to assess the meaning of these results, since no knowledge of the 2 millimeter noise power output of the 8 millimeter and 3 centimeter noise sources was obtainable.

The second test employed the same 4 millimeter klystron with an 8 millimeter to 4 millimeter multiplier and the same 8 millimeter noise source and chopper as in the initial tests. The chopped output of the 8 millimeter noise source was multiplied and mixed with the output of the 4 millimeter local oscillator. A radiometer capable of detecting temperature changes of a few hundred degrees resulted.

During the carrying out of these tests, mechanical choppers to operate in 4 millimeter and 2 millimeter guide were being constructed. Following the completion of the 4 millimeter chopper, a test was made with an 8 millimeter local oscillator and an 8 millimeter to 4 millimeter multiplier. The radiated noise output of the 8 millimeter noise source was intercepted by a 4 millimeter horn, chopped in the 4 millimeter waveguide, and mixed with the multiplied 8 millimeter local oscillator signal. A working radiometer having a sensitivity of a few hundred degrees Kelvin was achieved.

The final test utilized a 4 millimeter local oscillator, a 4 millimeter to 2 millimeter multiplier, and 8 millimeter and 3 centimeter noise sources. The radiated noise output was intercepted by a 2 millimeter horn and chopped in the 2 millimeter waveguide. The results were negative. No detectable signal output was measured.



More extended tests on this radiometer are needed in order to measure the three unknowns which made these tests undefinitive. No knowledge of the noise temperature of the 8 millimeter noise source at 2 millimeters is available. A noise source operating in smaller waveguide would be very desirable. This higher frequency noise source or a 2 millimeter oscillator would also allow tests to determine the efficiency of the 2 millimeter chopper to be made. Additionally, further work should be done to gain knowledge of the conversion efficiency of the crystals at these frequencies and to find better crystals.

Because of the above state-of-the-art limitations, no useful data on atmospheric attenuation was acquired in these tests.



### 3. THEORY OF ABSORPTION

3.1 Pressure Broadening. The first theory of pressure broadening was proposed by Lorentz<sup>27</sup> in 1906. Lorentz treated resonant absorption while Debye<sup>11</sup> treated nonresonant absorption. It was expected that the Debye theory was merely a special case of the Lorentz theory; however, this is not the case, and for many years a single integrated theory was lacking. The need for a more complete theory was met by J.H. Van Vleck and V.F. Weisskopf<sup>51</sup> in 1945. They made a modification in the assumptions of Lorentz and derived an equation for absorption which encompassed both the theories of Lorentz and Debye. The line breadth parameter,  $\Delta\nu$ , was left as an undetermined constant in their equation. The more recent theoretical work which has been done on collision broadening has been directed toward deriving explicit expressions for  $\Delta\nu$ . In 1946, H.M. Foley<sup>17</sup> used the Fourier expression for the intensity distribution in a pressure broadened line to obtain a formula for the line breadth and the line shift of a spectral line. He made the adiabatic collision approximation. Anderson<sup>3</sup> developed a generalized theory of pressure broadening which differed from previous theories by taking into account transitions among quantum states caused by collisions. His basic assumption was that the colliding molecules could be treated as point dipoles which followed definite paths. Mizushima<sup>32</sup> deduced the Fourier integral formula with the adiabatic assumption and applied the theory to ammonia and molecular oxygen. Baranger<sup>5</sup> later proposed a theory which treats the colliding molecules quantum mechanically and allows for inelastic collisions, degeneracy, and overlapping lines.

The theory concerning pressure broadening has reached a high level of sophistication. The experimental techniques for measuring absorption



and line breadth parameters have also been improved greatly.<sup>2,43</sup> When Van Vleck wrote his papers<sup>48,49</sup> concerning absorption by molecular oxygen and uncondensed water vapor, the individual lines in the oxygen absorption line at 5 mm had not been resolved. The line breadth was assumed to be the same for all the lines, and it was found by first measuring the absorption and then choosing a value of  $\Delta\nu$  which would best fit the experimental data. Van Vleck concluded that  $\Delta\nu$  was  $0.02 \text{ cm}^{-1}$ . In general, the agreement of theory with experiment for oxygen and water vapor was very good except in the wings of the water vapor absorption line at 1.35 cm, where the residual absorption was four times as great as predicted by the theory. This discrepancy could be explained if the line breadth parameters of the absorption lines in the short millimeter and near infrared regions were different from their values at 1.35 cm. An effect of this nature has been found in the spectrum of oxygen by Anderson, Smith, and Gordy<sup>4</sup>. They measured fifteen transitions in the 5 mm region and found line breadth parameters ranging from  $0.0319$  to  $0.0516 \text{ cm}^{-1}/\text{atmos}$ , with a population weighted mean of  $0.0475 \text{ cm}^{-1}/\text{atmos}$ .

3.2 Theory of Van Vleck and Weisskopf. There are two limiting cases of collisions which may be delineated. These are weak and strong collisions. A strong collision may be defined to be one in which the impact is so great that the orientation of the molecule after the collision is independent of the orientation before the collision. The additional assumption is usually made that the collision is adiabatic. This means that the collision takes place over an interval of time which is short compared with the period of oscillation of the impressed field. Under these assumptions, the molecules may be regarded as distributed in accordance with the Maxwell-Boltzmann law after collision,



and the orientation of the particles will depend on the instantaneous value of the field after collision. On the other extreme, a collision is said to be weak when the collision has very little effect in changing the orientation of the molecule, so that an appreciable change in orientation can be obtained only as the result of a large number of impacts.

We will use the strong collision model, which is generally considered the more reasonable for absorption in gases.

Consider a harmonic oscillator with angular frequency  $\omega_0$ , charge  $e$ , and mass  $m$ , in an incident electromagnetic wave of angular frequency  $\omega$ . If  $E \cos \omega t$  is the electric field, the equation of the oscillator is

$$m(\ddot{x} + \omega_0^2 x) = eE \cos \omega t \quad (3-1)$$

where  $x$  is the displacement in the direction of  $E$ . The general solution of this equation is

$$x = R \left[ \frac{eE e^{i\omega t}}{m(\omega_0^2 - \omega^2)} + C_1 e^{i\omega_0 t} + C_2 e^{-i\omega_0 t} \right] \quad (3-2)$$

The constants  $C_1$  and  $C_2$  are determined by the values of  $x$  and  $\dot{x}$  immediately after the last collision of the oscillator. Lorentz assumed that positive and negative values of  $x$  and  $\dot{x}$  were equally probable and that on the average  $x = \dot{x} = 0$  immediately after collision. Van Vleck and Weisskopf<sup>51</sup> assume that the values of  $x$  and  $\dot{x}$  are not randomly distributed, but instead are distributed according to the Boltzmann distribution law for a Hamiltonian function

$$H(t) = \frac{p^2}{2m} + \frac{1}{2} m(\omega_0 x)^2 - exE \cos \omega t \quad (3-3)$$



If we let the time of last collision be at  $t = t_0$ , then

$$\bar{x}(t_0) = \frac{\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} x e^{-H(t_0)/kT} dx dp}{\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-H(t_0)/kT} dx dp} \quad (3-4)$$

$$\bar{\dot{x}}(t_0) = \frac{\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \frac{p}{m} e^{-H(t_0)/kT} dx dp}{\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-H(t_0)/kT} dx dp} = 0 \quad (3-5)$$

If we evaluate the integrals in Eq. (3-4), we find that

$$\bar{x}(t_0) = R \left[ \frac{e}{m \omega^2} E e^{i \omega t_0} \right] \quad (3-6)$$

We now assume that  $x(t_0) = \bar{x}(t_0)$  and  $\dot{x}(t_0) = \bar{\dot{x}}(t_0)$ . The constants  $C_1$  and  $C_2$  may now be found. If we let  $t = t_0 + \theta$ , we have

$$x = R \left[ \frac{e E e^{i \omega t}}{m(\omega_0^2 - \omega^2)} \right] \left[ 1 - \frac{e^{i(\omega_0 - \omega)\theta}}{2} \left( \frac{\omega}{\omega_0} + \frac{\omega^2}{\omega_0^2} \right) + \frac{e^{-i(\omega_0 + \omega)\theta}}{2} \left( \frac{\omega}{\omega_0} - \frac{\omega^2}{\omega_0^2} \right) \right] \quad (3-7)$$

We must now remember that the oscillator undergoes many collisions over a period of time. If the collisions occur at random with a mean interval  $\tau$ , then the probability that the last collision experienced before  $t$  was in the interval between  $t - \theta - d\theta$  and  $t - \theta$  is  $\frac{1}{\tau} e^{-\theta/\tau} d\theta$ . In order to average over the times of last collision we must multiply Eq. (3-7) by  $\frac{1}{\tau} e^{-\theta/\tau}$  and integrate over  $\theta$  from 0 to  $\infty$ .

The result is

$$x = R \left\{ \frac{e E e^{i \omega t}}{m(\omega_0^2 - \omega^2)} \left[ 1 - \frac{1}{2} \frac{\omega}{\omega_0} \left( 1 + \frac{\omega}{\omega_0} \right) \frac{1/\tau}{\frac{1}{\tau} - i(\omega_0 - \omega)} + \frac{1}{2} \frac{\omega}{\omega_0} \left( 1 - \frac{\omega}{\omega_0} \right) \frac{1/\tau}{\frac{1}{\tau} + i(\omega_0 + \omega)} \right] \right\} \quad (3-8)$$



Now that we have found  $x$ , we calculate the absorption coefficient.  $x$  may be written in the form  $x = R[e E c^{1/2} (x' - i x'')]$ . The absorption coefficient  $\gamma$  is defined to be the average amount of work done on the assembly of oscillators by the wave divided by the average energy flux in the wave. In symbols

$$\gamma = N \frac{\langle e E \dot{x} \rangle}{c \langle E^2 \rangle / 4\pi} = \frac{4\pi}{c} \frac{\langle E \frac{dP}{dt} \rangle}{\langle E^2 \rangle}$$

or  $\gamma = 4\pi N e x'' \omega / c$  where  $N$  is the number of oscillators per unit volume.  $x''$  is easily found from Eq. (3-8), and  $\gamma$  then becomes

$$\gamma = \frac{2\pi N e^2}{m c} \left( \frac{\omega}{\omega_0} \right)^2 \left[ \frac{\frac{1}{\tau}}{\frac{1}{\tau^2} + (\omega - \omega_0)^2} + \frac{\frac{1}{\tau}}{\frac{1}{\tau^2} + (\omega + \omega_0)^2} \right] \quad (3-9)$$

All of the calculations so far have been classical, but these results can be generalized to the quantum mechanical case by means of the correspondence principle. Each transition between stationary states can be identified with an equivalent classical oscillator. From the results given by Heitler<sup>21</sup> we replace  $e^2/m$  by  $8\pi^2 \nu_{ij} |\mu_{ij}|^2 / 3h$  and we replace  $\omega_0$  by  $2\pi \nu_{ij}$ . Because of the symmetry in Maxwell's equations in  $E$  and  $H$ , the moment matrix element  $\mu_{ij}$  may be either electric or magnetic. After the molecules have been distributed over the various possible states according to the Boltzmann law and the sum is taken over the various possible transitions, we find that

$$\gamma = \frac{8\pi^3 \nu N}{3 h c} \cdot \frac{\sum_{ij} |\mu_{ij}|^2 f(\nu_{ij}, \nu) e^{-W_{ij}/KT}}{\sum_j e^{-W_j/KT}} \quad (3-10)$$

where we have used  $\omega = 2\pi \nu$ . Then  $f(\nu_{ij}, \nu)$  is given by

$$f(\nu_{ij}, \nu) = \frac{1}{\pi} \frac{\nu}{\nu_{ij}} \left[ \frac{\Delta \nu}{(\nu_{ij} - \nu)^2 + (\Delta \nu)^2} + \frac{\Delta \nu}{(\nu_{ij} + \nu)^2 + (\Delta \nu)^2} \right] \quad (3-11)$$



where  $\Delta V = \frac{1}{2\pi\gamma}$ .

In a physical situation, there is never a single frequency in a wave, but rather a range of frequencies. In order to see if the presence of other frequencies will have an appreciable effect on the absorption, we replace the field  $E \cos \omega t$  by  $E_1 \cos \omega_1 t + E_2 \cos \omega_2 t$ . The equation of motion then becomes

$$m(\ddot{x} + \omega_0^2 x) = e E_1 \cos \omega_1 t + E_2 \cos \omega_2 t \quad (3-12)$$

The Hamiltonian function of the system is now given by

$$H(t) = \frac{p^2}{2m} + \frac{1}{2} m(\omega_0 x)^2 - e x (E_1 \cos \omega_1 t + E_2 \cos \omega_2 t) \quad (3-13)$$

If we assume that the oscillators are distributed according to a Hamiltonian of this form, and if we find  $x$  in the same manner as before, then we can again calculate  $\gamma$  if we know  $x$ . In the previous calculation of  $\gamma$  we assumed that the time averages were taken over an infinite period of time. We now assume that the time average is taken over a time  $T$ ; this introduces some terms which are in general small in comparison with the  $\gamma$  given by Eq. (3-9) and which vanish as  $T \rightarrow \infty$ .

The result for  $\gamma$  is

$$\gamma = \gamma_0 + \frac{4\pi N e^2 (1 - \cos^2 \omega_1 T)}{m c (\omega_0^2 - \omega_1^2) T} \left[ 1 - \frac{\omega_1^2 (\omega_0 + \omega_1)}{(2\omega_0^2) [1 + T^2 (\omega_0 - \omega_1)^2]} + \frac{\omega_1}{\omega_0^2} \frac{\omega_0 - \omega_1}{[1 + T^2 (\omega_0 + \omega_1)^2]} \right] \quad (3-14)$$

$$+ \frac{4\pi N e^2 E_2 \omega_2}{m c E_1 (\omega_0^2 - \omega_2^2)} \left[ \frac{1 - \cos(\omega_1 - \omega_2) T}{(\omega_1 - \omega_2) T} - \frac{1 - \cos(\omega_1 + \omega_2) T}{(\omega_1 + \omega_2) T} \right]$$

$$\times \left[ 1 - \frac{1}{2} \frac{\omega_2 (\omega_0 + \omega_2)}{\omega_0^2 [1 + T^2 (\omega_0 - \omega_2)^2]} + \frac{1}{2} \frac{\omega_2}{\omega_0^2} \frac{\omega_0 - \omega_2}{[1 + T^2 (\omega_0 + \omega_2)^2]} \right]$$



$$+ \frac{2\pi N e^2 E_2 \omega_2^2}{m c E_1 \omega_0^2} \left[ \frac{\sin(\omega_1 + \omega_2)T}{(\omega_1 + \omega_2)T} + \frac{\sin(\omega_1 - \omega_2)T}{(\omega_1 - \omega_2)T} \right]$$

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$$\times \left[ \frac{1/T}{1/T^2 + (\omega_0 - \omega_2)^2} + \frac{1/T}{1/T^2 + (\omega_0 + \omega_2)^2} \right]$$

where  $\mathcal{T}_0$  is given by Eq. (3-9). A comparison of the other terms with  $\mathcal{T}_0$  shows that in general  $\mathcal{T}_0$  is much larger than the other terms.

However, it is possible for the third term to become large if  $E_2 \gg E_1$  and  $\omega_0 \approx \omega_2$  (Eq. (3-14) is not valid when  $\omega_0 = \omega_2$  of course). This effect is similar to the Luxemburg effect. It is, however, unlikely that the additional terms will contribute anything to ordinary atmospheric absorption. The second term in Eq. (3-14) would also be retained in Eq. (3-9) if the transient terms were kept in Eq. (3-9). It is clear that Eq. (3-14) reduces to Eq. (3-9) as  $T \rightarrow \infty$ .

It has been assumed throughout that the change in phase of the field during collision is small. If the frequency of the wave is high enough so that the phase changes appreciably during a collision, then the collisions are ineffective in creating thermal equilibrium, and the correct analysis of the absorption is that given by Lorentz. In the microwave region the frequency is low enough so that the Van Vleck-Weisskopf theory holds.

We have also assumed that there is a single relaxation time  $\mathcal{T}$  for all the molecules. It is possible that one could separate the molecules into different classes with different values of  $\mathcal{T}$ . In this event the final formulas must be integrated over a range of values of  $\mathcal{T}$ . A spread in the values of  $\mathcal{T}$  will lead to more absorption in the wings of a line than one would expect from the absorption in the



center of the line. This is true since the absorption in the center is proportional to  $\tau$  avg and the absorption in the wings is proportional to  $\frac{1}{\tau}$  avg.

3.3 Fourier Integral Theory. Many of the most recent theories of pressure broadening are based on the Fourier integral theory, which was first developed by Weisskopf in 1933<sup>52</sup>. The derivation of the Fourier integral which will be presented here is similar to that given by Mizushima<sup>32</sup>.

We consider the simultaneous collision of three or more molecules to be negligible. This assumption will be valid if the pressure is not too high. We can consider the Hamiltonian of the system to have three parts,

$$H = H_{\alpha} + H_{\beta} + H_{\alpha\beta} \quad (3-15)$$

where  $H_{\alpha}$  and  $H_{\beta}$  are the Hamiltonians of the isolated molecules  $\alpha$  and  $\beta$ , respectively, and  $H_{\alpha\beta}$  is the intermolecular potential between the two molecules. In the event that the radiation field interacts with molecule  $\alpha$ , we must add  $H_r$  to the Hamiltonian where

$$H_r = F\mu e^{-i\omega t} \quad (3-16)$$

and  $\mu$  is the dipole moment of the molecule,  $\omega$  is the angular frequency of the field, and  $F$  is the amplitude of the field. We will also consider the simultaneous optical transition of two molecules to be negligible, so that we do not have to add the Hamiltonian which gives the interaction of the field with molecule  $\beta$ .

We take the functions which make  $H_{\alpha}$  and  $H_{\beta}$  diagonal as our basis. Let the total wave functions be expanded as

$$\Psi = \sum_i a_i^* \psi_i \quad (3-17)$$



where the star indicates the fact that we are considering a Schrödinger representation. We then have

$$\sum_i a_i^* H \psi_i = i\hbar \sum_i \left( \psi_i \frac{\partial a_i^*}{\partial t} + a_i^* \frac{\partial \psi_i}{\partial t} \right) \quad (3-18)$$

We must include the term  $\partial \psi_i / \partial t$  because of the relative motion of the molecules. If we multiply Eq. (3-18) by  $\psi_j^*$  and integrate or sum over all the variables we find that

$$i\hbar \frac{\partial a_i^*}{\partial t} = \sum_j \left( H - i\hbar \frac{\partial}{\partial t} \right)_{ji} a_j^* \quad (3-19)$$

In everything that follows we will make the adiabatic assumption.

This means that we neglect the effect of motion of the molecule, or that we neglect  $i\hbar \frac{\partial}{\partial t}$  in comparison with  $H$ . The result is

$$i\hbar \frac{\partial a_i^*}{\partial t} = (E_j + v_j) a_i^* + \sum_j (H_{\alpha\beta}'' + H_r) a_j^* \quad (3-20)$$

where  $E_j$  is the energy of the isolated molecule in state  $j$ ,  $v_j$  is the diagonal part of  $H_{\alpha\beta}$ , and  $H_{\alpha\beta}''$  is the remaining part of  $H_{\alpha\beta}$ .

We now change to a Heisenberg representation

$$a_i^* = a_i \exp \left\{ -\frac{i}{\hbar} \left( E_i t + \int_0^t v_i dt \right) \right\} \quad (3-21)$$

If we neglect all of the  $a_i$  except  $a_i$ , which we assume to be unity,

Eq. (3-20) becomes

$$\begin{aligned} & \left[ i\hbar \frac{\partial a_i}{\partial t} + a_i (E_i + v_i) \right] \exp \left[ -\frac{i}{\hbar} \left( E_i t + \int_0^t v_i dt \right) \right] \\ &= (E_j + v_j) a_j \exp \left[ -\frac{i}{\hbar} \left( E_i t + \int_0^t v_i dt \right) \right] + \\ &+ (H_{\alpha\beta}'' + H_r)_{ji} \exp \left[ -\frac{i}{\hbar} \left( E_i t + \int_0^t v_i dt \right) \right] \end{aligned} \quad (3-22)$$

or

$$i\hbar \frac{\partial a_i}{\partial t} = (H_{\alpha\beta}'' + H_r)_{ji} \exp \left\{ \frac{i}{\hbar} \left[ (E_j - E_i) t + \int_0^t (v_j - v_i) dt \right] \right\}$$



If we now neglect  $H''_{\beta}$ , we may integrate Eq. (3-22) to find

$$i\hbar a_j = \mu_{ji} F \int_{-\infty}^{\infty} \exp\left[\frac{i}{\hbar} \left\{ (E_j - E_i)t + \int_0^t (V_j - V_i) dt - i\omega t \right\}\right] dt \quad (3-23)$$

Hence the transition probability from state  $i$  to state  $j$  is given by

$$|\mu_{ji}|^2 F^2 \int_{-\infty}^{\infty} \exp\left[\frac{i}{\hbar} \left\{ (E_j - E_i)t + \int_0^t (V_j - V_i) dt - i\omega t \right\}\right] dt \quad (3-24)$$

3.4 Line Breadth and Line Shift. Eq. (3-24) is the Fourier integral formula. By means of this result, we can derive expressions for the line breadth  $\Delta\nu$  and the line shift  $\Delta\nu'$  due to pressure broadening.

If we ignore the numerical factors in Eq. (3-24), we may write

$$I(\omega) = \left| \int_{-\infty}^{\infty} \exp\left[i(\omega_{if} - \omega)t + i n_{if}(t)\right] dt \right|^2 \quad (3-25)$$

where  $I(\omega)$  is the intensity distribution,  $i$  is the initial state and  $f$  is the final state,  $\omega_{if} = \frac{1}{\hbar} (E_f - E_i)$ , and

$$n_{if}(t) = \frac{1}{\hbar} \int_0^t (V_f - V_i) dt = \frac{1}{\hbar} \int_0^t [\langle f | H_{\alpha\beta} | f \rangle - \langle i | H_{\alpha\beta} | i \rangle] dt \quad (3-26)$$

$$I(\omega) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} dt_1 dt_2 e^{i(\omega_{if} - \omega)(t_1 - t_2)} e^{i[n_{if}(t_1) - n_{if}(t_2)]} \quad (3-25)'$$

Let  $t_1 - t_2 = \tau$  and  $t_2 = t$ . Then Eq. (3-25') becomes

$$I(\omega) = \int_{-\infty}^{\infty} d\tau e^{i(\omega_{if} - \omega)\tau} \phi(\tau) \quad (3-27)$$

$$\phi(\tau) = \int_{-\infty}^{\infty} dt e^{i[n_{if}(t+\tau) - n_{if}(t)]} \quad (3-28)$$

We now make the assumption that the times of collisions are short compared with the time between them. This means that we may write

$$n_{if}(t+\tau) - n_{if}(t) = \sum_{\text{collisions}} m_c \quad (3-29)$$

from  $t$  to  $t+\tau$



where  $\eta_c$  are the phase shifts due to the various collisions occurring in the interval between  $t$  and  $t+\tau$ . We may write  $\eta_c$  as

$$\eta_c = \int_{\text{collision}} dt \left[ \langle i | H_{\alpha\beta} | i \rangle - \langle f | H_{\alpha\beta} | f \rangle \right] \quad (3-30)$$

The types of collisions may be divided into classes which will depend on the paths followed by the molecules. Corresponding to each element of cross section  $d\sigma_k$ , there will be a definite phase-shift  $\eta_k$ .

The probability that a collision in  $d\sigma_k$  occurs in a time  $d\tau$  is given by

$$P d\sigma_k = n v d\tau d\sigma_k \quad (3-31)$$

where  $n$  is the number of molecules per unit volume and  $v$  is their average velocity (it is always justifiable in collision broadening problems to assume that all molecules have the average velocity  $v$ ).

Let  $f(t, \tau)$  be the integrand in Eq. (3-28).

$$f(t, \tau) = \exp \left[ i \{ \eta_{if}(t+\tau) - \eta_{if}(t) \} \right] \quad (3-32)$$

If a collision of type  $k$  occurs in a time  $d\tau$  after  $\tau$ , then

$$f(t, \tau+d\tau) = \exp \left[ i \{ \eta_{if}(t+\tau+d\tau) - \eta_{if}(t+\tau) + \eta_{if}(t+\tau) - \eta_{if}(t) \} \right]$$

or using Eq. (3-29), we have

$$f(t, \tau+d\tau) - f(t, \tau) = [\exp(i\eta_k) - 1] f(t, \tau) \quad (3-33)$$

If we now take the integral (this is equivalent to averaging over  $\tau$ ) we obtain

$$d\phi(t) = \phi(\tau+d\tau) - \phi(\tau) = \langle (\exp i\eta_k - 1) f(t, \tau) \rangle \quad (3-34)$$

where  $\langle \rangle$  denotes the average over  $\tau$ .



This is the point at which the impact theory assumption must be made. We assume that the time  $d\tau$  is short compared to the interval between collisions (so that it contains one collision at most), and we assume that  $d\tau$  is long in comparison with the duration of a collision. The latter assumption must be made so there will be no correlation between what happens in the interval  $d\tau$  and what happens in the preceding or following times.

Under these conditions, we can take the averages in Eq. (3-34) separately. We obtain

$$d\varphi(\tau) = \langle \exp(i\eta) - 1 \rangle_{av} = d(\tau) \left[ n v d\tau \int d\sigma_k [\exp(i\eta) - 1] \right] \quad (3-35)$$

We then have  $\varphi(\tau) = e^{-n v \sigma \tau}$  (3-36)

where

$$\sigma = \int d\sigma (1 - e^{i\eta}) = \sigma_R + i \sigma_I \quad (3-37)$$

If we use this result in Eq. (3-27), we get#

$$I(\omega) = 2R \int_0^\infty d\tau \exp \left[ i(\omega_{if} - \omega + n v \sigma_I) \tau - n v \sigma_R \tau \right] \quad (3-38)$$

or

$$I(\omega) = \frac{2 \Delta \nu}{[\nu - \nu_{if} - \Delta \nu]^2 + (\Delta \nu')^2}$$

where

$$\nu = \frac{\omega}{2\pi}, \quad \nu_{if} = \frac{\omega_{if}}{2\pi}, \quad n v \sigma_I = 2\pi (\Delta \nu')$$

and

$n v \sigma_R = 2\pi (\Delta \nu)$ . Thus the half-width is given by

$$\Delta \nu = \frac{n v}{2\pi} \int d\sigma (1 - \cos \eta) \quad (3-39)$$

#This step is explained in Eq. (3-48) and (3-49).



and the shift by

$$\Delta T' = \frac{m\pi}{2\pi} \int dT (\sin n) \quad (3-40)$$

We also have from gas kinetic theory

$$m\pi dT = 8\pi \left( \frac{m}{2KT} \right)^{3/2} \exp\left(-\frac{mV^2}{2KT}\right) V^3 dV \rho d\rho G M \quad (3-41)$$

where  $m$  is the reduced mass,  $V$  is the relative velocity,  $\rho$  is the impact parameter, and  $G$  is the probability of the molecule being in a rotational state.  $V$  and  $\rho$  are integrated from 0 to  $\infty$ , and  $G$  is summed over all states.

3.5 Overlapping Lines in Pressure Broadening. The absorption spectrum is obtained by summing Eq. (3-38) over  $i$  and  $f$  after the appropriate constant factor has been included in Eq. (3-38).

More general expressions for the line breadth have been given by Anderson<sup>3</sup> and Baranger<sup>5</sup>. Since Baranger's work is an extension of the work done by Anderson, we will discuss the work of Baranger. His theory takes into account inelastic collisions, degeneracy, and overlapping lines. The paths of the perturbers will be assumed to be classical, so that their interaction is a definite function of time. The justification for this treatment lies in the fact that when the velocity of a molecule is determined to a good accuracy, the positions may also be known to a few Angstrom units for all except the lightest molecules. The ranges of the interactions which are important in line broadening are many times this distance. In a later paper Baranger removes this difficulty by treating the perturbing molecules by quantum mechanics. We will not consider this latter paper, since it seems to be a good approximation to assume classical paths for the case of absorption by unionized gases.



We now consider the problem of overlapping lines in pressure broadening. This work includes Anderson's case of a single isolated line as a special case. The impact approximation is again made. This consists in assuming that the average collision is weak, but it does not exclude the possibility of a few strong collisions. We again assume that the average time between the strong collisions is much longer than the duration of the collision, and also that the molecules move independently of each other.

Let  $P(\omega)d\omega$  be the power emitted or absorbed in the frequency interval  $d\omega$  about  $\omega$ . Then we have<sup>15</sup>

$$P(\omega)d\omega = \frac{4\omega^4 n_+}{3c^3} I(\omega)d\omega \quad (3-42)$$

$$I(\omega) = (2\pi T)^{-1} \left| \int_0^T dt e^{i\omega t} \langle \psi_f(t) | \underline{d} | \psi_i(t) \rangle \right|^2 \quad (3-43)$$

$|\psi_i(t)\rangle$  is the initial state and  $\langle \psi_f(t)|$  is the final state in the Schrödinger picture. Positive  $\omega$ 's correspond to emission, negative  $\omega$ 's to absorption.  $n_+$  is the number of photons per quantum state after the emission or before the absorption, i. e., whichever state of the radiation field has the larger number of photons.

$\underline{d}$  is the dipole moment of the molecule and the absolute square in Eq. (3-43) also involves a summation over the three components of  $\underline{d}$ .

$\underline{d}$  is time independent in the Schrödinger representation.  $T$  is a very long time, which will be taken to be infinite in the limit. Eq. (3-43) has already been summed over all angles and polarizations of the light. From now on  $I(\omega)$  will be referred to spectrum or line shape in the case of an individual line. The true line shape will also include the factor  $4\omega^4 n_+ / 3c^3$ .



where the asterisk means complex conjugate. We then find  $\Phi(s)$  only for  $s > 0$  and use Eq. (3-48) for  $s < 0$ . Thus,

$$I(\omega) = \pi^{-1} R \int_0^{\infty} e^{i\omega s} \Phi(s) ds \quad (3-49)$$

The expression for  $\Phi(s)$  can be modified by introducing the Schrödinger time evolution operator,  $T(s)$ , which transforms a state at time 0 into a state at time  $s$ .

$$T(s) |\psi(0)\rangle = |\psi(s)\rangle \quad (3-50)$$

$T(s)$  is a unitary operator. We can now obtain  $\Phi(s)$  in the form of a trace. We have

$$\begin{aligned} \Phi(s) &= \sum_{i,f} P_i \left[ \langle \psi_i(0) | \underline{d} | \psi_f(0) \rangle \langle \psi_f(0) | T^*(s) \underline{d} T(s) | \psi_i(0) \rangle \right]_{av} \\ &= \sum_{i,f,g} P_i \left[ \langle \psi_i(0) | \underline{d} | \psi_f(0) \rangle \langle \psi_f(0) | T^*(s) | \psi_g(0) \rangle \langle \psi_g(0) | \underline{d} T(s) | \psi_i(0) \rangle \right]_{av} \\ \text{or} \quad &= \sum_{i,g} P_i \left[ \langle \psi_i(0) | \underline{d} T^*(s) | \psi_g(0) \rangle \langle \psi_g(0) | \underline{d} T(s) | \psi_i(0) \rangle \right]_{av} \\ \Phi(s) &= \text{Tr} \left[ \underline{d} T^*(s) \cdot \underline{d} T(s) \rho \right] \quad (3-51) \end{aligned}$$

We have written  $\underline{d} T^*(s)$  for the matrix whose elements are  $\langle \psi_i(0) | \underline{d} T^*(s) | \psi_f(0) \rangle$  and  $\underline{d} T(s) \rho$  for the matrix whose elements are  $\langle \psi_i(0) | \underline{d} T(s) \rho | \psi_f(0) \rangle$ .

**3.6 One-State Case.** We will now consider the case where the interaction of the perturbers with the lower state of the atom can be neglected. This case often arises in practice since the atom is more tightly bound and less easily polarized in its lower state. We will consider the case where the lower state is the final state (emission).

The problem is to compute  $\Phi(s)$ . Using the assumption above, we must sum over all initial states in Eq. (3-47), but not over all final states. We will find it necessary to be concerned only with



final states of energy  $E_f$ . We introduce a degeneracy index  $\alpha$ . Then,

$$\begin{aligned}\Phi(s) &= \sum_{i,\alpha} \left[ \langle \psi_i | \underline{d} T^*(s) | \psi_{f,\alpha} \rangle \langle \psi_{f,\alpha} | \underline{d} T(s) | \psi_i \rangle \right] \cdot P_i \\ &= \sum_{i,\alpha} \left[ \langle \psi_i | \underline{d} | \psi_{f,\alpha} \rangle e^{i E_f s / \hbar} \langle \psi_{f,\alpha} | \underline{d} T(s) | \psi_i \rangle \right] \cdot P_i\end{aligned}$$

We can take the energy of the final state to be zero; that is,

$$\Phi(s) = \sum_i \left[ \langle \psi_i | \left\{ \sum_{\alpha} \underline{d} | \psi_{f,\alpha} \rangle \langle \psi_{f,\alpha} | \underline{d} \right\} T(s) | \psi_i \rangle \right] \cdot P_i$$

If we define the Hermitian operator  $\underline{D}$  by

$$\underline{D} = \sum_{\alpha} \underline{d} | \psi_{f,\alpha} \rangle \langle \psi_{f,\alpha} | \underline{d} \quad (3-52)$$

then

$$\Phi(s) = \text{Tr} [\underline{D} T_{AV}(s) \rho] \quad (3-53)$$

We must now evaluate the average of  $T(s)$ .

$T(s)$  satisfies the Schrödinger equation

$$i \hbar \frac{dT}{ds} = [H_0 + V_T(s)] T(s) \quad (3-54)$$

where  $H_0$  is the unperturbed Hamiltonian, and  $V_T(t)$  is the interaction Hamiltonian. Another evolution operator  $U(s)$  may be defined by

$$T(s) = e^{-i H_0 s / \hbar} U(s) \quad (3-55)$$

$U(s)$  is then given by

$$U(s) = \mathcal{I} \exp \left[ -\frac{i}{\hbar} \int_0^s V_T'(t) dt \right] \quad (3-56)$$

where

$$V_T'(t) = e^{i H_0 t / \hbar} V_T(t) e^{-i H_0 t / \hbar} \quad (3-57)$$



$\mathcal{T}$  is the time ordering operator which makes operators act in the order prescribed by the time in their argument, with time increasing from right to left. Eq. (3-57) may be easily verified by showing that Eq. (3-55) satisfies Eq. (3-54) with this form for  $U(s)$ .

$V_T'(t)$  is a sum of interactions due to the different perturbers. If  $V_i'(t)$  is the interaction due to the  $i^{\text{th}}$  perturber, we may write

$$U(s) = \mathcal{T} \exp\left[-\frac{i}{\hbar} \int_0^s V_1'(t) dt\right] \times \dots \times \exp\left[-\frac{i}{\hbar} \int_0^s V_N'(t) dt\right] \quad (3-58)$$

and

$$U_{\text{av}}(s) = \mathcal{T} \left[ \left\{ \exp\left(-i \int_0^s V'(t) dt\right) \right\}^N \right] \quad (3-59)$$

$N$  is the total number of perturbers.

Eq. (3-59) is very complicated because of the presence of the time ordering operator, which causes a hopeless entanglement of the operators. We must now make the impact assumption which states that two strong collisions never occur simultaneously. In this case, the collisions take place one after the other, and there is no question about the order in which to write the operators in Eq. (3-59). Notice that no restriction is made on the weak collisions. It is possible that several weak collisions can occur simultaneously or at the same time as a strong collision. The justifications for treating the problem this way are discussed by Baranger<sup>5</sup>.

Using this assumption, we can compute  $U_{\text{av}}(s)$  by first computing an expression relating to a single perturber

$$\left[ \mathcal{T} \exp\left(-\frac{i}{\hbar} \int_0^s V'(t) dt\right) \right]_{\text{av}} \quad (3-60)$$



and then raising it to the  $N^{+h}$  power while treating the collisions in chronological order. We will take  $S$  to be much longer than the time of a strong collision. Because the average collision is weak, it will take many collisions to produce a  $U_{av}(s)$  appreciably different from unity. In the great majority of cases, the bracket in Eq. (3-60) is unity because the perturber will not often make any collisions in the interval considered. The probability of a collision occurring in this interval is of the order of  $N^{-1}$ , and the probability of two collisions occurring is of the order of  $N^{-2}$ . Let  $d\nu$  be the frequency of a particular type of collision when all the perturbers are present; then the frequency with a single perturber is  $N^{-1}d\nu$ , and the probability of such a collision occurring in time  $dt$  is  $N^{-1}d\nu dt$ . Let  $S$  be a unitary matrix, for a collision occurring at time zero, given by

$$S = \mathcal{I} \exp \left[ -\frac{i}{\hbar} \int_{-\infty}^{\infty} V'(t) dt \right] \quad (3-61)$$

If a collision occurs at time  $\tau$  between 0 and  $S$ , then Eq. (3-60) is given by

$$e^{iH_0\tau/\hbar} S e^{-iH_0\tau/\hbar} \quad (3-62)$$

since the state at time  $\tau$  is  $e^{-iH_0\tau/\hbar}$  times what it was at time zero.

The deviation from unity in Eq. (3-60) due to a particular type of collision occurring in the time interval  $d\tau$  at time  $\tau$  is

$$N^{-1} d\nu dt \left( e^{iH_0\tau/\hbar} S e^{-iH_0\tau/\hbar} - 1 \right) \quad (3-63)$$

Eq. (3-60) is found by treating all types of collisions between 0 and  $S$ ; it is given by

$$1 + N^{-1} \int_0^S dt e^{iH_0 t/\hbar} \left[ \int (S-1) d\nu \right] e^{-iH_0 t/\hbar} \quad (3-64)$$



If we let

$$H = -i\hbar \int (1-s) d\nu \quad (3-65)$$

and

$$H'(t) = e^{iH_0 t/\hbar} H e^{-iH_0 t/\hbar} \quad (3-66)$$

then Eq. (3-64) may be written as

$$1 - iN^{-1}\hbar^{-1} \int_0^s H'(t) dt \quad (3-67)$$

Now, since  $N$  is a very large number, the result of raising Eq. (3-67) to the  $N^{th}$  power (which gives  $U_{av}(s)$ ) is easily verified to be given by

$$U_{av}(s) = \mathcal{I} \exp \left[ -\frac{i}{\hbar} \int_0^s H'(t) dt \right] \quad (3-68)$$

to a good approximation. Then  $T_{av}(s)$  is given by Eq. (3-55) as

$$T_{av}(s) = e^{-iH_0 s/\hbar} \mathcal{I} \exp \left[ -\frac{i}{\hbar} \int_0^s H'(t) dt \right]$$

or

$$T_{av}(s) = \exp \left[ -\frac{i}{\hbar} (H_0 + H) s \right] \quad (3-69)$$

The last equation is verified since the derivatives of the two expressions in Eq. (3-69) are the same. The expressions are equal because  $H$  is a constant.

The main result of Baranger's study is that when the impact approximation is valid, it is possible to replace the fluctuating, time-dependent interaction between the molecule and the perturbers by a constant effective interaction  $H$ . From Eq. (3-65) we see that  $H$  is not



Hermitian, and hence the energy levels will have an imaginary part, which will result in a line-breadth for the spectrum. In order to compute  $\mathcal{H}$  we must know  $S$ , which is the usual collision matrix. The calculation of  $S$  may be very difficult, but it is a standard problem in time-dependent quantum mechanics. Anderson<sup>3</sup> has developed an approximate method for calculating  $S$ .

3.7 Line Shape for the One-State Case. Now that we have found  $T_{av}(s)$ , we can find the line shape for the one-state case. Under the validity conditions, which will be stated later, the density matrix  $\rho$  varies much too slowly to affect the shape of individual lines, and we may consider it to be constant for a single line or a group of a few lines which overlap.

The line shape is obtained from Eq. (3-49). The integral will be performed in the operator form, and we will assume that the imaginary parts of the eigenvalues of  $H_0 + \mathcal{H}$  are of the right sign to make the integral converge at infinity. Baranger states that this is the case, but he gives no proof of this statement. Since  $\rho$  is a constant for the lines under consideration, we have

$$\pi \rho^{-1} I(\omega) = \mathcal{R} \text{Tr} \left[ \underline{\mathcal{D}} \int_0^\infty e^{i\omega s} e^{-\frac{i}{\hbar} (H_0 + \mathcal{H}) s} ds \right]$$

or

$$\pi \rho^{-1} I(\omega) = -\mathcal{J} \text{Tr} \left[ \underline{\mathcal{D}} \left( \omega - \frac{H_0}{\hbar} - \frac{\mathcal{H}}{\hbar} \right)^{-1} \right] \quad (3-70)$$

We must now evaluate Eq. (3-70) in terms of the eigenvalues of  $H_0 + \mathcal{H}$ .

Let the eigenstates of  $H_0 + \mathcal{H}$  be  $|\phi_i\rangle$  and the eigenvalues

$\hbar(\omega_i - i\omega_i')$   $\omega_i' > 0$ . Then,

$$(H_0 + \mathcal{H}) |\phi_i\rangle = \hbar(\omega_i - i\omega_i') |\phi_i\rangle \quad (3-71)$$



Now since  $H_0 + \mathcal{H}$  is not Hermitian, the states  $|\phi_i\rangle$  are not mutually orthogonal, but we can find another set of functions,  $\langle \chi_j |$ , such that

$$\langle \chi_j | \phi_i \rangle = \delta_{ij} \quad (3-72)$$

It follows that

$$\sum_i |\phi_i\rangle \langle \chi_i| = 1 \quad (3-73)$$

It is then possible to write Eq. (3-70) as

$$\pi \rho^{-1} I(\omega) = \sum_i \left[ \frac{\omega_i'}{(\omega - \omega_i)^2 + \omega_i'^2} R \langle \chi_i | \mathcal{D} | \phi_i \rangle - \frac{\omega - \omega_i}{(\omega - \omega_i)^2 + \omega_i'^2} \Im \langle \chi_i | \mathcal{D} | \phi_i \rangle \right] \quad (3-74)$$

From Eq. (3-74), we see that the shape of a group of spectral lines is a sum of lines which have a Lorentz line shape plus a sum of terms which do not have a Lorentz shape. For large  $\omega$ , the latter terms are all proportional to  $\omega^{-1}$ . Since  $\mathcal{D}$  is a Hermitian operator, it follows that  $\Im \text{Tr}(\mathcal{D}) = 0$ , and hence the contribution of these terms away from the resonances is very small. The latter terms are important only in the region where the lines overlap.

Anderson's results can be easily obtained from this theory. We will only consider the nondegenerate case (Anderson also treats the degenerate case). Let  $|\psi_i\rangle$  and  $E_i$  be the eigenstates and eigenvalues of  $H_0$ . We calculate the eigenvalues of  $H_0 + \mathcal{H}$  by first-order perturbation theory. This means that this method will be valid only when  $\mathcal{H}$  is small compared to the energy level spacing of  $H_0$ . Thus, the theory is restricted to non-overlapping lines. We have

$$E_i + \langle \psi_i | \mathcal{H} | \psi_i \rangle = \hbar(\omega_i - i\omega_i') \quad (3-75)$$



and we use  $\langle \psi_i |$  and  $|\psi_i \rangle$  instead of  $\langle \chi_i |$  and  $|\varphi_i \rangle$ . Then the second term of Eq. (3-74) vanishes, since a diagonal matrix element of  $\mathcal{D}$  is real, and we get

$$\pi \rho^{-1} \mathcal{I}(\omega) = \sum_i \frac{\omega_i'}{(\omega - \frac{E_i}{\hbar} - d_i)^2 + \omega_i'^2} \langle \psi_i | \mathcal{D} | \psi_i \rangle \quad (3-76)$$

where

$$d_i = \frac{1}{\hbar} R \langle \psi_i | H | \psi_i \rangle, \quad \omega_i' = \frac{1}{\hbar} \mathcal{J} \langle \psi_i | H | \psi_i \rangle \quad (3-77)$$

If we write the diagonal elements of  $S$  as  $\langle \psi_i | S | \psi_i \rangle = \alpha_i e^{-i\varphi_i}$

then (using Eq. (3-65),

$$d_i = R \langle \psi_i | -i \int (1-S) d\tau | \psi_i \rangle = R \int -i (1 - \alpha_i e^{-i\varphi_i}) d\tau$$

or

$$d_i = \int \alpha_i \sin \varphi_i d\tau \quad (3-78)$$

In similar fashion,

$$\omega_i' = \int (1 - \alpha_i \cos \varphi_i) d\tau \quad (3-79)$$

For the case of inelastic collisions,  $\alpha_i$  is one, and Eq. (3-78) and (3-79) are the same as Eq. (3-39) and (3-40).

A discussion of the validity conditions is presented in some detail by Baranger; these conditions will be merely stated here. If  $\tau$  is the duration of typical impact,  $\omega_i'$  the width of the level, and  $d_i$  the level shift, then the impact approximation is valid when

$$\omega_i' \ll \tau^{-1} \quad d_i \ll \tau^{-1} \quad (3-80)$$



We have restricted ourselves to dealing with the one-state case. The results for the two-state case, where both the initial and the final state interact appreciably with the perturbers, are analogous to the results already derived.

3.8 Atmospheric Absorption by the Oxygen Molecule. The oxygen molecule has a  $^3\Sigma$  ground state and a magnetic dipole moment of two Bohr magnetons. The rotation of the oxygen molecule about its center of mass interacts with the permanent magnetic moment to form what is called a "rho-type triplet". The rotational quantum number exclusive of the spin will be denoted by  $K$ .  $K$  will be added vectorially to the spin  $S$  to form a total rotational quantum number  $J$ , which can assume the values  $K + 1$ ,  $K$ , and  $K - 1$ . Since the resultant spin of each oxygen atom is  $1/2$  and the spin function is symmetric in the ground state, the Pauli exclusion principle will allow  $K$  to take on only odd values. The microwave resonances are due to the decomposition of the states with the same  $K$  but different  $J$ . The components  $J = K-1$  and  $J = K + 1$  are of lower energy than the state  $J = K$ , and they almost coincide. The energy difference between  $J = K$  and  $J = K-1$  or  $K + 1$  is dependent on  $K$ , but it is nearly the same (about  $1/2$  cm) with the one exception which gives rise to a resonance at  $1/4$  cm.

The energy levels in the oxygen molecule were measured experimentally by Dieke and Babcock<sup>14</sup>, and a theoretical formula for the energy levels was given by Schlapp<sup>39</sup>, who based his results on previous work done by himself<sup>38</sup> and Hill and Van Vleck<sup>22</sup>. The levels calculated by Schlapp and the levels measured by Dieke and Babcock agree very closely. The absorption at  $0.25$  cm was not measured by Dieke and Babcock, but it was predicted by the theoretical formula of Schlapp. In his calculation of the absorption, Van Vleck chose to use the spectroscopic rather than



theoretical values of the intervals, in order to be in as close agreement as possible with experiment.

The equations which Van Vleck used are those given by Eq. (3-10) and (3-11) with the factor  $10^6 \log_{10} e$  inserted in order to express the absorption in decibels per kilometer. He then assumed various values for the line breadth  $\Delta\nu$  and proceeded to calculate the absorption for the different  $\Delta\nu$ 's. The calculated absorption and the experimentally measured absorption were then compared in order to determine the correct value for  $\Delta\nu$ . At this time, there was no theoretical means of computing  $\Delta\nu$ . The microwave measurements of Beringer<sup>6</sup> showed conclusively that  $\Delta\nu$  had the upper and lower bounds of 0.05 and 0.02  $\text{cm}^{-1}$ . By comparison with the work of other experimenters,<sup>13,33</sup> Van Vleck concluded that 0.02  $\text{cm}^{-1}$  was the most probable value for  $\Delta\nu$ .

The formulas which were used by Van Vleck in calculating the absorption will now be given. We start from

$$\gamma = 10^6 \log_{10} e \frac{8\pi^3 \nu N}{3hc} \cdot \frac{\sum_{ij} |\mu_{ij}|^2 f(\nu_{ij}, \nu) \exp(-E_j/kT)}{\sum_j \exp(-E_j/kT)} \quad (3-10')$$

$$f(\nu_{ij}, \nu) = \frac{\nu}{\pi \nu_{ij}} \left[ \frac{\Delta\nu}{(\nu_{ij} - \nu)^2 + (\Delta\nu)^2} + \frac{\Delta\nu}{(\nu_{ij} + \nu)^2 + (\Delta\nu)^2} \right] \quad (3-11)$$

Since  $\nu_{ji} = -\nu_{ij}$ , we have  $f(\nu_{ij}, \nu) = -f(\nu_{ji}, \nu)$ , and the contribution of a particular term in Eq. (3-10') is positive or negative depending on the energies of the  $i^{\text{th}}$  and  $j^{\text{th}}$  states. In order to make all of the terms in Eq. (3-10') positive, we may make the approximation

$$\nu_{ij} e^{-E_j/kT} + \nu_{ji} e^{-E_i/kT} = \frac{h \nu_{ij}^2}{2kT} \left( e^{-E_j/kT} + e^{-E_i/kT} \right) \quad (3-81)$$



which is good if  $|\gamma_{ij}| = \frac{E_j - E_i}{h} \ll \frac{kT}{h}$ . The absorption coefficient is then given by

$$\gamma = 10^6 \log_{10} e \frac{8\pi^3 \nu N}{6 c k T} \frac{\sum_i |\mu_{ij}|^2 \gamma_{ij} f(\gamma_{ij}, \nu) e^{-E_i/kT}}{\sum_i \exp(-E_i/kT)} \quad (3-82)$$

In any application to oxygen, the indices  $i$  and  $j$  really refer to the three quantum numbers  $J, K, M$ . For the transitions with which we are concerned  $J = K + 1, K$ , or  $K - 1$ . The energy does not depend on  $M$ , and only slightly on  $J$ . We can say that  $E_i$  is a function only of  $K$  in the Boltzmann factors. If  $\nu_{K+}$  is the frequency associated with the transition from the level  $J = K + 1$  to  $J = K$ , and  $\nu_{K-}$  with  $J = K - 1$  to  $J = K$ , then we may write Eq. (3-82) as

$$\gamma = 10^6 \log_{10} e \frac{4\pi^3 \nu N}{3 c k T} \sum_K \left[ (2\nu_{K+} f(\nu_{K+}, \nu) |\mu_{K+}|^2 + 2\nu_{K-} f(\nu_{K-}, \nu) |\mu_{K-}|^2 + F(\nu) |\mu_{K0}|^2 e^{-E_K/kT} \right] \cdot \left[ \sum_K 3(2K+1) e^{-E_K/kT} \right]^{-1} \quad (3-83)$$

with

$$F(\nu) = \lim_{\gamma_{ij} \rightarrow 0} \gamma_{ij} f(\gamma_{ij}, \nu) = \frac{2\nu d\nu}{\pi[\nu^2 + (\Delta\nu)^2]} \quad (3-84)$$

and<sup>49</sup>

$$|\mu_{K+}|^2 = \frac{4\beta^2 K(2K+3)}{K+1}, \quad |\mu_{K-}|^2 = \frac{4\beta^2 (K+1)(2K-1)}{K}, \quad (3-85)$$

$$|\mu_{K0}|^2 = \frac{8\beta^2 (K+K+1)(2K+1)}{K(K+1)}$$

where  $\beta$  is the Bohr magneton.

The first and second members of Eq. (3-83) represent the resonant absorption of oxygen while the third member represents the non-resonant absorption. The latter term is a result of the fact that the matrix for the magnetic moment of the oxygen molecule has diagonal elements. This



part of the absorption is due to the presence of lines whose resonance frequency is zero. The mechanism for absorption for these lines is shown by Van Vleck to be similar to that in Debye's model of absorption and dispersion of radiation by a molecule due to the statistical redistribution of these molecules by collisions.

The  $E_k$  in the Boltzmann factors may be approximated by  $Bk(k+1)$ <sup>26</sup> with  $B = 1.44 \text{ cm}^{-1}$ . A simple expression for the absorption is then easily found for the wings of the lines. If  $T = 293^\circ$ , and the pressure is 76 cm, then

$$\gamma = 0.34 \frac{\nu^2}{c^2} \left[ \frac{\Delta\nu/c}{(2 - \frac{\nu}{c})^2 + (\frac{\Delta\nu}{c})^2} + \frac{\Delta\nu/c}{(2 + \frac{\nu}{c})^2 + (\frac{\Delta\nu}{c})^2} + \frac{\Delta\nu/c}{(\frac{\nu}{c})^2 + (\frac{\Delta\nu}{c})^2} \right]$$

if  $\frac{\nu}{c} > 4.5$  or  $< 1.5 \text{ cm}^{-1}$ .

Van Vleck cautions that it should not be surprising if the detailed shape of the absorption curve is somewhat different from the shape his formulas predict, because he assumed the collisions were of infinitesimal duration. The fact that these formulas do not give the correct line shape in the case of overlapping lines is shown by Eq. (3-74), where some terms are present which do not have a Lorentz shape. The oxygen resonance at 5 mm does consist of a group of overlapping lines, since there are 25 important lines in this region with a minimum breadth of 600 mc/sec. The width of the entire resonant region is about  $10^4$  mc/sec.

3.9 Calculation of  $\Delta\nu$  for Molecular Oxygen.  $\Delta\nu$  may be calculated by using Eq. (3-30), (3-39), and (3-41). If we let  $\Delta P$  be defined by

$$\Delta P = \hbar \left[ \langle i | H_{\lambda\beta} | i \rangle - \langle f | H_{\lambda\beta} | f \rangle \right] \quad (3-87)$$

then

$$n = \int \frac{\Delta P}{\hbar} d\tau \quad (3-30').$$



The most easily handled cases are those where  $\Delta P$  is of the form

$$\Delta P = \hbar \frac{\Delta \mu}{R^n} \quad (3-88)$$

If we also assume that the path of the molecule is straight, then  $\eta$  is given by<sup>32</sup>

$$\eta = \int_{-\infty}^{\infty} \frac{\Delta \mu}{(\rho^2 + v^2 t^2)^{n/2}} dt = \frac{\Delta \mu}{v \rho^{n-1}} \frac{\pi^{1/2} \Gamma(n-1)}{[\Gamma(n/2)]^2} \quad (3-89)$$

and  $\Delta \gamma$  by<sup>32</sup>

$$\Delta \gamma = \left[ \frac{\pi^{1/2} \Gamma(n-1)}{2} \right] \left( \frac{KT}{2m} \right)^{\frac{n-3}{2n-2}} \Gamma\left(\frac{2n-3}{n-1}\right) \Gamma\left(\frac{n-3}{n-1}\right) \times \left[ \frac{\Gamma(n-1)}{[\Gamma(n/2)]^2} \right]^2 \left[ \sin \pi \frac{n-3}{2n-2} \right] < |\Delta \mu|^{2/n-1} > N \quad (3-90)$$

where  $m$  is the reduced mass.

By means of the formulas above, we may calculate the line breadth of oxygen, if we assume the interaction of the oxygen molecules to be given by a particular value of  $\eta$ . Since oxygen has a permanent dipole moment, one might think that the dominant interaction between molecules is of the magnetic dipole-dipole variety; however, this interaction is found to be too small to give the correct line-breadth for oxygen.

Mizushima<sup>32</sup> calculated the line-breadth by assuming that there is an electric quadrupole-quadrupole interaction between oxygen molecules.

This calculation will now be given.

In the oxygen molecule, the total angular momentum  $J$  is the sum of the spin angular momentum  $S$  and the rotational angular momentum  $K$ .

In the ground state of the oxygen molecule  $S = 1$  and there are three states  $J = K + 1, K, K-1$  corresponding to each  $K$  except for  $K = 0, 1$ .

If  $\Theta_{K,M}$  is the ordinary rotational wave function of a linear molecule with quantum numbers  $K, M$ , and  $\sigma_m$  is the spin wave function with magnetic



quantum number  $m$ , then the wave functions of these three states are given by<sup>9</sup> (pp. 78)

$$\begin{pmatrix} \psi_{k+1,m} \\ \psi_{k,m} \\ \psi_{k-1,m} \end{pmatrix} = \begin{pmatrix} \left[ \frac{(k+m)(k+m+1)}{2(2k+1)(k+1)} \right]^{1/2} & \left[ \frac{(k-m+1)(k+m+1)}{(2k+1)(k+1)} \right]^{1/2} & \left[ \frac{(k-m)(k-m+1)}{2(2k+1)(k+1)} \right]^{1/2} \\ \left[ \frac{(k+m)(k-m+1)}{2k(k+1)} \right]^{1/2} & \frac{m}{[k(k+1)]^{1/2}} & \left[ \frac{(k-m)(k+m+1)}{2k(k+1)} \right]^{1/2} \\ \left[ \frac{(k-m)(k-m+1)}{2k(2k+1)} \right]^{1/2} & \left[ \frac{(k-m)(k+m)}{k(2k+1)} \right]^{1/2} & \left[ \frac{(k+m+1)(k+m)}{2k(k+1)} \right]^{1/2} \end{pmatrix}$$

$$\times \begin{pmatrix} \oplus_{k,m-1} & \sigma_1 \\ \oplus_{k,m} & \sigma_0 \\ \oplus_{k,m+1} & \sigma_{-1} \end{pmatrix}$$

(3-91)

The diagonal element of the quadrupole interaction between two molecules has been found by Margenau<sup>28</sup> to be

$$\int \psi_{k,m}(1) \psi_{k',m'}(2) V_{12} d\tau_1 d\tau_2 = \frac{6Q^2}{R^5} \left[ \frac{k(k+1)-3m^2}{(2k+3)(2k-1)} \right] \left[ \frac{k'(k'+1)-3m'^2}{(2k'+3)(2k'-1)} \right] \quad (3-92)$$

where  $Q$  is the quadrupole moment, 1 refers to the first molecule, 2 to the second molecule, and  $V_{12}$  is the interaction Hamiltonian of the molecules, which is assumed to be an electric quadrupole-quadrupole interaction. Since Eq. (3-92) is suitably factored, it can be calculated separately for each molecule.



By means of the wave functions given by Eq. (3-91) and the results of Eq. (3-92), we can calculate the diagonal element of the quadrupole interaction between two oxygen molecules. Mizushima found the following factors to come from each molecule.

$$K[(K+1)(K+2) - 3M^2] / [(2K+1)(K+1)(K+3)], \quad J = K+1 \quad (3-93)$$

$$[K(K+1) - 3M^2][1(K+1) - 3] / [K(K+1)(2K+3)(2K-1)], \quad J = K \quad (3-94)$$

and

$$(K+1)[K(K-1) - 3M^2] / [K(2K+1)(2K-1)], \quad J = K-1 \quad (3-95)$$

Since the interaction as given by Eq. (3-92) is proportional to  $R^{-5}$ , we must use  $m = 5$  in Eq. (3-90). The result is

$$\Delta\nu = \frac{2}{\sqrt{3}} \Gamma\left(\frac{7}{4}\right) \left(\frac{kT}{M}\right)^{1/4} \langle |\Delta\mu|^{1/2} \rangle N \quad (3-96)$$

where  $M$  is the real mass of the oxygen molecule. In order to find the line breadth, the average value of the square root of the potential difference must be found. Mizushima assumed that only one of the colliding molecules undergoes a transition and that the average value of  $K$  for the perturbing molecule is large, so that Eq. (3-93), (3-94), and (3-95) may all be replaced by

$$(K^2 - 3M^2) / 4K^2 \quad (3-97)$$

for the perturbing molecule. The procedure adopted by Mizushima is to take the square root of Eq. (3-97) and average over all of the values



of  $M$ . This gives the average factor for the perturbing molecule. The line breadth for a particular transition is then found by using the difference of two of the expressions Eq. (3-93), (3-94), and (3-95) for the factor due to the perturbed molecule. Mizushima gives the average of the square root of Eq. (3-97) to be

$$\left(\frac{1}{2K}\right)^2 \int_0^K |K^2 - 3M^2|^{1/2} dM = 0.254 \quad (3-98)$$

It seems that there is an error here, and the correct result must be

$$\frac{\int_{-K}^K \frac{|K^2 - 3M^2|^{1/2}}{2K} dM}{\int_{-K}^K dM} = \frac{1}{2K} \int_0^K |K^2 - 3M^2|^{1/2} dM = 0.411 \quad (3-99)$$

Then  $\Delta\nu$  is given by

$$\begin{aligned} \Delta\nu &= \frac{2}{\sqrt{3}} \Gamma\left(\frac{7}{4}\right) \left(\frac{KT}{M}\right)^{1/4} 6^{1/2} Q(0.411) \hbar^{-1/2} \langle |A| \rangle N \\ &= (0.411)^{3/2} 2 \Gamma\left(\frac{7}{4}\right) \left(\frac{KT}{M}\right)^{1/4} Q \hbar^{-1/2} \langle |A| \rangle N \end{aligned} \quad (3-100)$$

where

$$\begin{aligned} A &= \text{Eq. (3-93)} - \text{Eq. (3-94)} && \text{for } K + 1 \rightarrow K \\ A &= \text{Eq. (3-95)} - \text{Eq. (3-94)} && \text{for } K - 1 \rightarrow K \end{aligned} \quad (3-101)$$

If there is an external magnetic field, the results of Mizushima can be modified slightly. In order to average over  $M$ , we now multiply the square root of Eq. (3-97) by the proper Boltzmann factor and then



take the average. Thus Eq. (3-99) should now be replaced by

$$\frac{\int_{-K}^K \frac{|K^2 - 3M^2|^{1/2}}{2K} e^{\alpha \frac{M}{K}} dM}{\int_{-K}^K e^{\alpha \frac{M}{K}} dM} \quad (3-102)$$

where  $\alpha = \frac{\mu H}{KT}$ . If  $\alpha$  is small then  $e^{\alpha \frac{M}{K}}$  may be expanded in a rapidly converging series. The terms of the first order in  $\alpha$  vanish, so that Eq. (3-102) is given by

$$0.411 + 0.015 \alpha^2 + o(\alpha^4) \quad (3-103)$$

correct to the third order in  $\alpha$ . A similar correction for the presence of the field must also be made in computing  $\langle |A| \rangle$ .

Mizushima concluded that the value of  $Q$  required by his equations to explain the observed line breadth of oxygen was of a plausible order. Some support to the supposition that the line-breadth is due at least partly to the quadrupole-quadrupole interaction is found in the temperature dependence of  $\Delta\nu$ . From Eq. (3-96) we see that  $\Delta\nu$  should be proportional to  $T^{-3/4}$  at constant pressure. Beringer and Castle's<sup>7</sup> experimental data at 300° K and 85° K show a temperature dependence midway between  $T^{-1}$  and  $T^{-3/4}$  dependence. The experimentally measured temperature dependence of  $\Delta\nu$  is  $\Delta\nu \propto T^{-0.85}$ .



#### 4. CONCLUSIONS

The absorption of microwave radiation by molecular oxygen is a well understood phenomenon. The agreement between absorption predicted by the Van Vleck theory and the observed values in the laboratory is in general very good. The application to the earth's atmosphere is less certain. A study of absorption by oxygen has been made by M.L. Meeks<sup>30</sup>. By means of a computer program, he calculated the absorption predicted by the Van Vleck theory in the range from 3.7 to 7.5 mm wavelength. The results of his calculations agreed well with experimental observations of atmospheric attenuation in this range by Whitehurst, Copeland, and Mitchell<sup>53</sup> at 6 mm, and by Coates<sup>8</sup> at 4.3 mm. The formidable task of a comparable program to extend over the entire millimeter wavelength region and to include the correlation between theory and experiment, has not yet been attempted anywhere.

We have made attempts to explain certain suspected variations in absorption with variations in the earth's magnetic field or other external factors. Three different approaches were tried: (1) examination of the effect of a time-varying external field on absorption, (2) investigation of Zeeman splitting as a possible factor in absorption, and (3) study of effects attributable to the statistical orientation of the oxygen molecule in a magnetic field.

The effect of a time dependent external field is given by Eq. (3-14). We see from this equation that the absorption may be affected noticeably if  $E_2 \gg E_1$  and  $\omega_0 \approx \omega_2$ . If the Fourier component of the earth's field during a magnetic storm, at a frequency close to the oxygen resonance at 5 mm, is large compared to the magnetic field of the incoming



radiation, then it seems possible that the absorption coefficient may be momentarily affected. We have been unable to check this possibility numerically.

The Zeeman effect for fields of the order of the earth's magnetic field is important only if the pressure is much less than atmospheric pressure. An analysis of the Zeeman effect is given by Hill and Gordy.<sup>23</sup> We have concluded that since the great bulk of the oxygen in the atmosphere is at relatively high pressure, and since the magnetic field changes only by about one per cent during a magnetic storm, the Zeeman effect probably can not produce appreciable variations in the absorption during a magnetic storm.

The effect of statistical orientation of the oxygen molecule on absorption was examined in conjunction with Mizushima's theory of broadening. We assume that the broadening is due to an electric quadrupole-quadrupole interaction. It is shown by Eq. (3-103) that  $\Delta\nu$  has a quadratic dependence on  $\frac{\mu H}{KT}$  if  $\frac{\mu H}{KT} \gg 1$ . For the case of molecular oxygen in a magnetic field of the order of the earth's field, this extra term is negligible at atmospheric temperatures.

A magnetic field could also affect absorption by changing Eq. (3-83). It was assumed there that  $E_K = B K(K+1) = E_J$  was a function only of  $K$ . In a magnetic field, we would have  $E_J = E_K + \frac{\mu H}{KT} \frac{M}{\sqrt{K(K+1)}}$ , so that there will be a sum over  $K$  and  $M$  in Eq. (3-83). This correction is quite small for atmospheric absorption.

Ziauddin<sup>54</sup> attributed the variations in absorption with changes in the earth's magnetic field to abnormal increases in the electron density, collision frequency, or both, at heights below about 95 KM in the atmosphere. The results of this study have indicated no mechanism



by which variations in the earth's magnetic field of the magnitude to be expected might affect absorption of microwave radiation by molecular oxygen to a noticeable extent.

It must be concluded that all attempts to explain the suspected variations in absorption by oxygen in terms of external factors which might affect the theory have failed. A further search may become useful if future observations can definitely establish that such fluctuations do exist.

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