

Line-Breadths of the Microwave Spectrum of Oxygen*

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Line-breadth parameters for oxygen have been determined with a Zeeman modulation spectrograph for fifteen microwave transitions occurring in the 5-mm wavelength region. Measured values lie in the range 0.0319 to 0.0516 $\text{cm}^{-1}/\text{atmos}$, with a population weighted mean of 0.0475 $\text{cm}^{-1}/\text{atmos}$. Investigation of the variation of the line-breadth parameter as a function of K , the rotational angular momentum quantum number, reveals greater line-breadth for the most populated states. This leads to an interpretation of the self-broadening collision process as a mechanism involving not only the quadrupole-quadrupole and polarization interactions predicted theoretically, but also a rotational resonance interaction.

Measurements are also reported for the line-breadths of oxygen transitions broadened by the perturbing molecules ammonia, nitrous oxide, nitrogen, and argon. Collision diameters are then determined for these molecules, and the results are shown to compare favorably with results from kinetic theory and from ammonia-broadening experiments. Interpretations of these data also strengthen the rotational resonance interpretation. A line-breadth parameter is calculated for air.

I. INTRODUCTION

THE absorption of microwave energy by oxygen contained in the earth's atmosphere was predicted by Van Vleck¹ on the basis of the interaction of the magnetic moment of oxygen with the magnetic field of the electromagnetic radiation. According to Van Vleck this absorption has two forms, resonant and non-resonant, the resonant absorption being greatest at 5-mm wavelength and completely overshadowing the nonresonant absorption. Using equations derived by Schlapp,² Van Vleck predicted the presence of twenty-six absorption lines arising from levels of significant population. All but one of these lines fall in the 5-mm wavelength region, the one line occurring at 2.5-mm wavelength. The twenty-five lines are spaced by only a few hundred megacycles, a spacing so narrow that at high pressures the lines are sufficiently broadened by collisions to be overlapped. At atmospheric pressure the resonant absorption band of oxygen, centered at 5-mm wavelength, is 10^4 Mc wide.

The radiation, or natural, broadening of spectral lines and Doppler broadening are of no consequence in our experiments. In the present work only collision broadening will be considered. The intensity of the absorption band depends upon the manner in which the widths of the fine-structure lines vary with pressure. It is customary to express this variation in terms of a line-breadth parameter which is defined as the half-width, measured at half-intensity, of an absorption line at a pressure of 1 atmos, the quantity being expressed

in $\text{cm}^{-1}/\text{atmos}$. Van Vleck and Weisskopf³ have shown the possibility of a variation of the line-breadth parameter with the rotational state. Considerable research has been devoted to the determination of the line-breadth parameter for oxygen. Beringer,⁴ the first to measure this quantity, determined the intensity of the integrated absorption at high pressures, from which the parameter may be obtained. He found that pure oxygen has an absorption at the band center of 67 db/km for 1 atmos pressure. The line-breadth parameter was concluded to have a value between 0.02 and 0.05 $\text{cm}^{-1}/\text{atmos}$. Beringer's measurements also indicated an integrated absorption for air of 14 db/km at 1 atmos. Lamont⁵ determined the maximum attenuation of microwave energy in dry atmosphere to be 15.7 db/km at 5.13-mm wavelength. From these measurements it was concluded that the value of the parameter corrected from atmospheric absorption is less than 0.02 $\text{cm}^{-1}/\text{atmos}$. Strandberg, Meng, and Ingersoll⁶ have very carefully repeated Beringer's work⁴ on high pressure absorption. From measurements on pure oxygen at 80-cm Hg pressure, they have determined the line-breadth parameter to be 0.02 $\text{cm}^{-1}/\text{atmos}$.

All of these measurements were made on the integrated high pressure absorption band of oxygen and not upon resolved lines. From such data it is impossible to determine any variation of the line-breadth parameter with rotational states. The first complete resolution of the rotational oxygen absorption spectrum at low pressures was reported by Burkhalter, Anderson, Smith, and Gordy.^{7,8} Approximate measurements by them on the line-breadth parameter for three individual transi-

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¹ J. H. Van Vleck, *Phys. Rev.* **71**, 413 (1947).

² R. Schlapp, *Phys. Rev.* **51**, 343 (1937).

³ J. H. Van Vleck and V. F. Weisskopf, *Revs. Modern Phys.* **17**, 227 (1945).

⁴ R. Beringer, *Phys. Rev.* **70**, 53 (1946).

⁵ H. R. L. Lamont, *Phys. Rev.* **74**, 353 (1948).

⁶ Strandberg, Meng, and Ingersoll, *Phys. Rev.* **75**, 1524 (1949).

⁷ Burkhalter, Anderson, Smith, and Gordy, *Phys. Rev.* **77**, 152 (1950).

⁸ Burkhalter, Anderson, Smith, and Gordy, *Phys. Rev.* **79**, 651 (1950).

tions indicated a range of values from 0.02 to 0.05 $\text{cm}^{-1}/\text{atmos}$.

More complete measurements on fourteen resolved absorption lines are reported in the present paper.⁹ A more precise method of measurement is used than that for the preliminary results.⁸ The results suggest a dependence of the line-breadth parameter on rotational state. Values obtained range from 0.0319 to 0.0516 $\text{cm}^{-1}/\text{atmos}$. A rough value has also been reported by Anderson, Johnson, and Gordy for the single rotational transition occurring at 2.5-mm wavelength.¹⁰ A more precise measurement of this line by Hill and Gordy[§] yields $\Delta\nu=0.064 \text{ cm}^{-1}/\text{atmos}$ at $T=300^\circ\text{K}$ and 0.09 $\text{cm}^{-1}/\text{atmos}$ at $T=195^\circ\text{K}$.

Beringer and Castle,¹¹ in applying the strong-field Zeeman theory developed by Henry¹² for the microwave magnetic resonance spectrum of oxygen, found values from 0.017 to 0.100 $\text{cm}^{-1}/\text{atmos}$. Their most reliable data, however, yielded values between 0.036 to 0.056 $\text{cm}^{-1}/\text{atmos}$.

The most recently published data on the 5-mm lines are those of Gokhale and Strandberg,¹³ and Artman and Gordon.¹⁴ Our results are in agreement with those of Artman and Gordon within the probable error in the two measurements. However, certain of the line widths measured by Gokhale and Strandberg lie outside the error limits estimated for the two measurements. The reason for this discrepancy is not yet known.

II. DESCRIPTION OF APPARATUS

Since the oxygen molecule does not possess a permanent electric dipole moment, sensitive techniques must be used for the detection of the transitions of oxygen. The Zeeman-modulation method used in the present work has been previously described.⁸ Figure 1 is a block diagram of the spectrometer used in the present investigation. Detection of oxygen transitions is achieved in the following manner. A 1-cm klystron supplies energy to a frequency-doubling crystal which generates

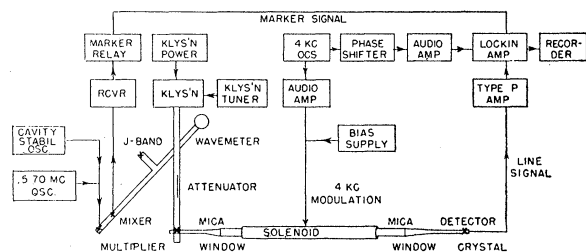


FIG. 1. Block diagram of the Zeeman modulation spectrograph.

⁹ A preliminary account has been given by Anderson, Smith, and Gordy, *Phys. Rev.* **82**, 264 (1951).

¹⁰ Anderson, Johnson, and Gordy, *Phys. Rev.* **83**, 1061 (1951).

[§] R. M. Hill and W. Gordy (to be published).

¹¹ R. Beringer and J. G. Castle, Jr., *Phys. Rev.* **81**, 82 (1951).

¹² A. F. Henry, *Phys. Rev.* **80**, 396 (1950).

¹³ B. V. Gokhale and M. W. P. Strandberg, *Phys. Rev.* **84**, 844 (1951).

¹⁴ J. O. Artman and J. P. Gordon, *Phys. Rev.* **87**, 227 (1952).

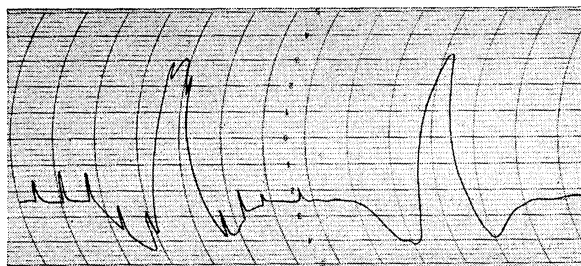


FIG. 2. An O_2 line recording with and without frequency markers.

5-mm energy for transmission through the absorption cell. The klystron is mechanically tuned with a small driving motor very slowly through the absorption frequency. The absorption line is split into its Zeeman components at a 4-kc rate under the influence of a weak sinusoidal magnetic field applied to the molecules by a solenoid surrounding the absorption cell. The detector crystal responds to a 4-kc pulsating signal which results from a shifting of the absorption frequency in and out of the klystron frequency by the alternating Zeeman field. The detected signal is amplified and passed through a lock-in amplifier (coherent detector), and the output is displayed on an Esterline-Angus recorder. The recorder drive is synchronized with the klystron-tuning drive.

Because of the symmetry of the Zeeman splitting, the detected signal would occur at twice the modulation frequency. When a lock-in amplifier is used, it is desirable to detect at the fundamental frequency of the modulation. Hence, a current of form $(1+\cos\omega t)$ is applied through the solenoid. Further, because the modulating magnetic fields are of the order of magnitude of the earth's magnetic field, it is necessary to compensate for the Zeeman broadening caused by the earth's field. This is achieved by orientation of the absorption cell and solenoid along the direction of the earth's field. A compensating current is then introduced into the solenoid. The amount of compensation has been checked experimentally on an absorption line by adjustment for minimum line-width.

So that the width of the recorded absorption lines can be measured, distance along the recorder chart is calibrated in units of frequency. This calibration is repeated for each separate recording of an absorption line. It was found possible to superimpose on the recorder-trace a lattice of several strong frequency markers spaced at 5.70-Mc intervals. Since the recording of a line is an operation requiring several minutes, the marker system must be frequency-stabilized so that the marker lattice will remain in fixed position on the line tracing. For this reason, a stable frequency is beat with the klystron frequency, and the resulting beat—detected by a communication receiver—triggers a relay which indicates the marker on the recorder chart. A cavity-stabilized, 3-cm oscillator supplies a constant frequency signal which is fed to a frequency-tripling

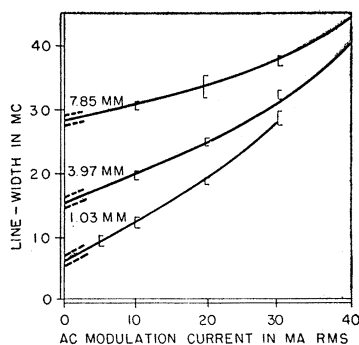


FIG. 3. Typical interpretation of recorded data ($J=18 \rightarrow 19$).

1N26 crystal mounted on a section of 1-cm wave guide. Simultaneously, a crystal-controlled 5.7-Mc signal of about 3 v rms is mixed with the 1-cm energy generated in the tripler crystal to produce in the wave-guide radiation of frequencies $30,000 \pm 5.70n$ Mc, where n is an integer. An absorption line with and without the frequency markers superimposed is shown in Fig. 2.

Examination of Fig. 2 will disclose that the shape of a recorded absorption line is not that of the anticipated line contour. This is because the method of detection employed responds to the second derivative of the line shape. A simple explanation of this type of response is given in Appendix A. Line-widths are obtained by measurement of the distance in terms of frequency between the recorded minimums shown in Fig. 2. That this is the line-width may be shown from the fact that the minimums of the second derivative of the line-shape formula correspond to the half-intensity points of the line-shape formula⁸ for very small modulations. In practice, the line-width is determined from the distance between the recorded minimums, measured in terms of the number of marker intervals. The change in frequency between markers is assumed linear. This is not necessarily true, but any error arising from this assumption is small in comparison with the greater random deviation among actual readings. Note that the interval between markers represents 11.40 Mc, since the klystron frequency is being doubled. Because line half-widths at half-intensity are desired, however, the distance between minimums must be divided by two.

III. THE MEASURING PROCEDURE

In this investigation it was desired to make two kinds of measurements: one of the self-broadening of oxygen lines, and the other of the broadening of these lines by foreign gases. In the self-broadening measurements, three kinds of information are desired: the value of the line half-width at some specified pressure, the variation of the line-width with pressure, and the variation of the line-width with K , the rotational angular momentum quantum number.

For the measurement at constant pressure, five recordings are made of the particular line for each of four

successively decreasing modulation amplitudes. The modulation currents used are always the smallest necessary to record the lines with usable amplitudes above noise. For each line there is an optimum modulation for best reproduction, and this modulation is generally employed. The most commonly used modulating fields have amplitudes of 0.51, 1.02, 2.05, 3.08, and 4.10 oersteds. The five determinations of line-width for a particular modulation are averaged, and a mean deviation from the mean is determined. The mean values are then plotted as a function of the amplitude of the applied field. A typical plot of these data is given in Fig. 3. Since it is necessary to determine the line-width with no broadening Zeeman field, the data are extrapolated to zero modulating field. The intercept is taken as the limiting line-width at the given pressure. Because of the deviation in the mean of the observed line-widths at specified pressure and modulation, the zero modulation intercept has a small range of possible values. These are taken as the extreme values of the line-width.

These measurements were performed on a single line at several pressures in order to test the variation of line-width with pressure, and the data are reproduced in Fig. 4. Linear behavior is confirmed over a one-hundredfold variation in pressure. It is to be noted that the line-width for zero pressure apparently does not vanish. This residual line-width is found to be reasonably constant for all transitions and may be attributed to inadequate compensation of the earth's field, to inhomogeneity in the earth's field in the immediate vicinity of the absorption cell, and to the presence of a finite klystron output frequency spectrum. The latter

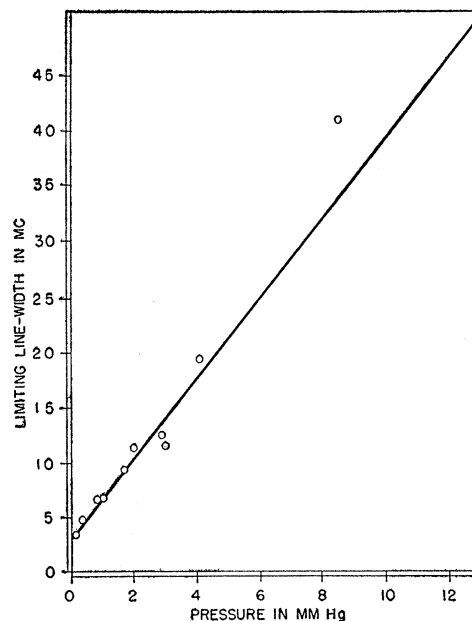


FIG. 4. Observed line-width as a function of pressure. Pure oxygen. $J=4 \rightarrow 3$.

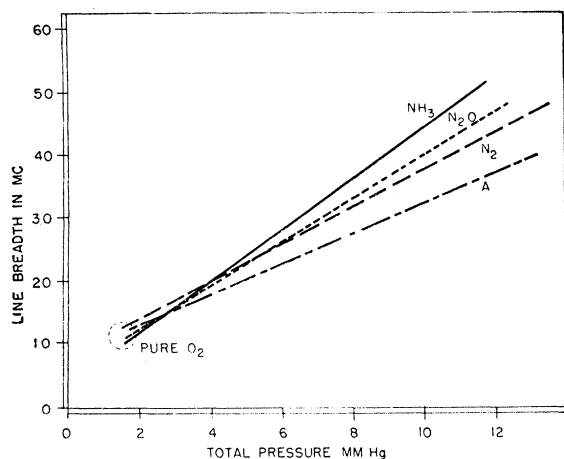


Fig. 5. The broadening of an oxygen line by various foreign gases. $J=8 \rightarrow 9$. The partial pressure of O_2 is 1.5 mm of Hg.

contribution was measured to be less than one-third of the total effect.

In general, data are taken for three pressures: 1, 4, and 8 mm Hg. The slope of a straight line through a plot of limiting line-width as a function of pressure is taken as the line-width for 1 mm Hg pressure. This method of interpreting the data averages the three observed values and eliminates the residual width. From the maximum and minimum slopes of lines drawn through the elongated points, the deviations in line-widths are determined.

The second point under investigation is the effect of various concentrations of foreign gases on the width of oxygen absorption lines. The experimental procedure is first to measure the limiting line-width of pure oxygen at a pressure of about 1.5 mm Hg. The pressure is then increased by the addition of the foreign gas. Four increments in pressure, each of about 2.5-mm Hg, are used. This allows determination of the line-widths of mixtures of gases at fixed oxygen partial pressure and variable total pressure. Typical data are plotted in Fig. 5.

IV. THE SELF-BROADENING OF OXYGEN

Anderson¹⁵ has given an elegant quantum-mechanical treatment for collision broadening in the microwave region. His treatment is based on an impact theory, as contrasted to a statistical approach. The basic assumption is that colliding molecules follow straight line paths. Collisions are classified as either strong or weak. In the strong collision the perturbation of a molecule is sufficiently great to induce a transition and thus to interrupt the absorption. Accordingly, a given state life-time results in an uncertainty in the energy of the level. The values of life-time are statistically distributed, and, similar to the classical Lorentz broadening theory, result in a line-breadth for the absorption.

¹⁵ P. W. Anderson, Phys. Rev. **76**, 647 (1949).

Weak collisions do not cause transitions and are known as adiabatic collisions. The initial and the final energy level for the transition are each temporarily perturbed slightly, not necessarily equally. This results in a net shift in the absorption frequency. The energy level perturbations may be considered as arising from Stark or Zeeman effects on the absorbing molecule caused by a perturbing field associated with the colliding molecule.

Since oxygen does not have a permanent electric dipole, the usual types of electrical interactions of importance for collision effects, namely, dipole-dipole and dipole-quadrupole interactions, cannot be considered as responsible for the observed broadening. Distinct possibilities do exist, however, for induced dipole interactions as well as for quadrupole-quadrupole electrical interactions. Such magnetic interactions as dipole-dipole, dipole-quadrupole, and induced polar interactions are of little importance. In the broadening formula given by Anderson,¹⁵ the line-breadth is proportional to the square of the dipole moment. A comparison of ammonia with oxygen gives the ratio of the squares of their respective electric and magnetic dipole moments as 7800, so that ammonia lines might be expected to be broader by this factor. Experimentally, ammonia lines have been found only about 16 times broader than oxygen lines. Thus, magnetic dipole-dipole interactions contribute an insignificant amount to the observed broadening.

Electrostatic interactions may account for the observed width of oxygen absorption lines, however. Two types of interaction have been postulated: quadrupole-quadrupole and polarizability interactions. Smith and Howard¹⁶ have shown the possible existence of a small quadrupole moment for oxygen. Mizushima¹⁷ has calculated on the basis of a modified impact theory, the line-breadth caused by quadrupole-quadrupole interactions. This has the form, for high K values,

$$\Delta\nu/c = 1.33 \times 10^{15} Q(1/K \pm 3/8K^2)^{\frac{1}{2}},$$

where Q is the quadrupole moment, the + sign applies to transitions $J=K+1 \rightarrow K$, and the - sign to transitions $J=K-1 \rightarrow K$. For high K values this becomes approximately

$$\Delta\nu/c = \text{const} K^{-\frac{1}{2}}. \quad (1)$$

Although experimental evidence shows the measured line-width to vary, for high K , approximately according to this formula, the value required for the quadrupole moment of oxygen is several times too large as compared with the upper limit, $Q < 0.09 \times 10^{-16}$ cm², set by Smith and Howard¹⁶ from measurements on the broadening of ammonia lines by oxygen. The effects of polarizability interactions have been calculated by Anderson,¹⁸ and these lead to values for the line-width

¹⁶ W. V. Smith and R. R. Howard, Phys. Rev. **79**, 132 (1950).

¹⁷ M. Mizushima, Phys. Rev. **83**, 94 (1951); **84**, 362 (1951).

¹⁸ P. W. Anderson, Ph.D. thesis, Harvard University (1949).

from 0.025 cm⁻¹/atmos for $K=3$ to 0.014 cm⁻¹/atmos for $K=21$. The form of both types of interactions is approximately the same, and their sum is still too small to explain the observed line-breadths.

The experimental data on self-broadening obtained in this investigation are listed in Table I. The experimental observations have a mean deviation of about 10 percent. Our experimental values for the line-widths are generally higher than those predicted from early high pressure observations⁴⁻⁶ but are reasonably close to those values measured recently.^{8,11,14} The most interesting feature is the variation of the line-breadth with K . The largest values of the line-breadth occur in the region of the maximum predicted by the Boltzmann distribution for oxygen at room temperature. The interpretation of this observation is based upon rotational resonance. This type of interaction is common in the infrared region, but it is not generally observed at microwave frequencies because a relatively small fraction of the total number of molecules are thermally distributed in the sufficiently low-lying rotational states which give rise to microwave transitions. Ammonia and oxygen, because of the unusual origins of their spectra, have many rotational levels lying in a frequency range allowing microwave transitions. The microwave spectrum of ammonia originates in the inversion of the ammonia molecule and is not due to rotation. The microwave spectrum of oxygen arises from a spin reorientation and again is not related to the rotational state of the molecule. Anderson¹⁵ has considered rotational resonance effects in his theoretical calculations on the self-broadening of ammonia lines.

A qualitative, quantum-mechanical description of the collision broadening process is useful. The total time-dependent Hamiltonian for the molecule $H(t)$ can be expressed as

$$H(t) = H_0 + H_1(t) + \dots,$$

where H_0 is the Hamiltonian for no collisions, and $H_1(t)$ is the collision perturbation Hamiltonian. If H_0 is diagonalized, then $H_1(t)$ will have both diagonal and off-diagonal elements. If one neglects higher order terms, the perturbing matrix $H_1(t)$ can then be used to explain the nature of the collision. The diagonal elements of H_1 each give the probability of perturbation to the energy level with which each is associated. Thus, the diagonal elements refer to the case of weak collisions. Since H_1 refers to only one molecule undergoing collision, the values of H_1 for all collisions must be averaged over the collisions to determine the distribution of the absorption frequencies causing the line broadening. The off-diagonal elements of $H_1(t)$ give the transition probabilities for strong collisions and so account for the collision-induced transitions. Experimental observations have led to the belief that weak collisions are of little consequence in the microwave region.¹⁶ In terms of the perturbation Hamiltonian,

this means that diagonal elements may be considered nonexistent.

Because significant perturbation Hamiltonian matrix elements are completely off-diagonal, these elements may be expressed in the form $\langle K_f, J_f | H_1(t) | K_i, J_i \rangle$, where $K_f, J_f, K_i,$ and J_i are the rotational and total angular momentum quantum numbers, respectively, in the final and initial states. Since $H_1(t)$ is believed to be due to at least two causes, polarization and quadrupole interactions, considered jointly, and rotational resonance interactions, it is desirable to let

$$H_1(t) = H_1'(t) + H_1''(t), \quad (2)$$

where $H_1'(t)$ refers to polarization and quadrupole interactions and $H_1''(t)$, to rotational resonance interaction. The matrix elements for H_1 may then be expressed as

$$\begin{aligned} \langle K, J = K | H_1'(t) | K, J = K \pm 1 \rangle \\ + \langle K \pm 2, J_f | H_1''(t) | K, J_i \rangle. \end{aligned}$$

The justification for this particular form is that, first, for quadrupole and polarizability interactions, $\Delta K = 0$ for $H_1'(t)$, and, second, that $\Delta K = \pm 1, 2, 3, 4, \dots$ for $H_1''(t)$ for rotational resonance. However, $\Delta K = \pm 1, 3, \dots$ are impossible transitions since alternate rotational levels are missing, so that only $\Delta K = \pm 2, 4, \dots$ are possible. Since quadrupole and polarizability interactions both depend upon a $\cos^2\theta$ variation, where θ is the angle between the intermolecular distance r and the internuclear axis of the molecule undergoing perturbation, the rotational resonance matrix elements for these interactions will allow transitions $\Delta K = \pm 2$. Higher transitions are not ruled out, however, and the case $\Delta K = \pm 4$ may arise from two separate transitions. For example, for the transition $K \rightarrow K + 2$ there exists the possibility of a simultaneous transition $K + 4 \rightarrow K + 2$,¹⁹ if the energy difference arising from the latter

TABLE I. Experimentally determined O₂ line-widths ($T = 300^\circ\text{K}$).

K	Series	Mc/mm	(cm ⁻¹ /atmos)
1	+	1.96	0.0496
3	+	1.71	0.0434
3	-	1.92	0.0485
5	-	1.86	0.0472
7	+	2.05	0.0516
9	-	1.97	0.0499
11	+	1.97	0.0499
13	-	1.87	0.0476
15	+	1.77	0.0448
17	-	1.76	0.0445
19	+	1.58	0.0399
19	-	1.62	0.0411
21	-	1.26	0.0319
23	+	1.26	0.0319
23	-	1.49	0.0378

The various measurements show a maximum deviation from the given values of about ± 20 percent; however, the mean deviation is about ± 10 percent. In other words, these data are certainly reliable to within ± 20 percent, although they should not be considered any more accurate than ± 10 percent.

¹⁹ P. W. Anderson, private communication.

transition is less than that of the former. In general, however, transitions of higher order than $\Delta K = \pm 2$ will not be of significance and are here neglected.

The first part of the H_1 matrix element in Eq. (2) is related to the probability of a polarizability or quadrupole interaction-induced transition. Its contribution to $\Delta\nu$ has already been calculated and is expressed in Eq. (1). In an evaluation of the second term, caused by rotational resonance interaction, the matrix may be considered as having two terms, one for transitions to higher rotational states, and the other for transitions to lower states. When each term is evaluated to yield a transition probability, it might be expected that this probability will be proportional to the population of the rotational state with which resonance occurs. It appears reasonable that the rotational resonance probability for transitions $K \rightarrow K \pm 2$ should then be of the order,

$$C[f(K-2) + f(K+2)],$$

where $f(K)$ is the fractional number of molecules in the rotational state K . This term has been added to Eq. (1) to give an expression of the form,

$$\Delta\nu/c = C_1 + C_2 K^{-3} + C_3 [f(K-2) + f(K+2)]. \quad (3)$$

This equation then includes the three most likely interactions affecting oxygen: self-broadening quadrupole-quadrupole, polarizability, and rotational resonance interactions. Equation (3) has been empirically fitted to the experimental data given in Table I. The solid curve in Fig. 6 is based on Eq. (3), where $C_1 = 0.033$, $C_2 = 0.010$, and $C_3 = 0.050 \text{ cm}^{-1}/\text{atmos}$.

The functions $f(K)$ have been determined from the expression for the fractional population of a thermal Boltzmann distribution of rotational states,

$$f(K) = \frac{(2K+1) \exp[-B_0 K(K+1)hc/kT]}{\sum \sum_{JK} (2J+1) \exp[-B_0 K(K+1)hc/kT]},$$

where $B_0 = 1.44 \text{ cm}^{-1}$ oxygen, $T = 298^\circ\text{K}$, $K = 1, 3, 5, \dots$ and $J = K \pm 1$. The mean line-breadth parameter, obtained by weighting according to population, is $0.0475 \text{ cm}^{-1}/\text{atmos}$.

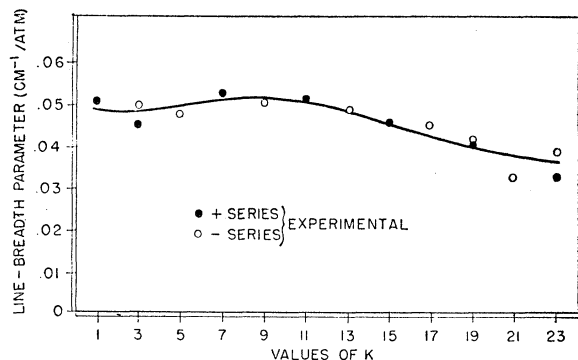


FIG. 6. O_2 line-breadth parameters as a function of K .

The K -independent term C_1 is here evaluated experimentally and includes contributions from short-range interactions of all types. It is comprised partly of the polarizability interactions. However, Anderson's polarizability calculations account for only 0.014 in this term. The large remainder is attributed to short-range interactions of other types.

From Eq. (3) C_2 is seen to contain the effect of all of the quadrupole and part of the polarizability interactions. If it is assumed that C_2 contains as much as three-fourths quadrupole interaction, substitution of $3C_2/4$ into Mizushima's expression for quadrupole interaction, Eq. (1), gives $Q \cong 0.06 \times 10^{-16} \text{ cm}^2$, which is in good agreement with the upper limit $Q < 0.09 \times 10^{-16} \text{ cm}^2$ determined by Smith and Howard.¹⁶

Definite proof for the hypothesis of rotational resonance as presented here can only be determined from experimental observation of the shift of the peak values of $\Delta\nu/c$ to lower K values as temperature is decreased or to higher K values with an increase in temperature. This investigation is currently being made in this laboratory.

V. THE BROADENING OF OXYGEN LINES BY FOREIGN GASES

An investigation of line broadening by foreign gases is of value in the determination of the nature of line broadening processes. Interpretations of observations on lines broadened by foreign gases are based upon the kinetic theory. For pure oxygen the line-breadth is given by²⁰

$$2\Delta\nu_0 = \sqrt{2} n_0 \bar{v}_0 b_0^2 \text{ sec}^{-1},$$

where $\Delta\nu_0$ is the half-intensity half-width of the line, n_0 is the molecular density, \bar{v}_0 is the mean molecular speed, and b_0 is the microwave collision diameter of oxygen. In the case of foreign broadening the appropriate expression is²⁰

$$2\Delta\nu_{0f} = \sqrt{2} n_0 \bar{v}_0 b_0^2 + n_f (\bar{v}_0^2 + \bar{v}_f^2)^{1/2} b_{0f}^2 \text{ sec}^{-1}, \quad (4)$$

where $\Delta\nu_{0f}$ is the half-intensity half-width of the foreign broadening line, n_f is the molecular density of the foreign gas, \bar{v}_f is the mean molecular speed of the foreign gas, and b_{0f} is the collision diameter for mixed collisions. The mean molecular speed is determined from the formula,

$$\bar{v} = 2(2R_m T / \pi M)^{1/2} \text{ cm sec}^{-1},$$

where R_m and M are the molar gas constant ($R_m = 8.32 \times 10^7 \text{ cgs}$) and the molecular weight, respectively. Equation (4) may be represented as a linear variation of pressure by

$$\Delta\nu_{0f} = p_0 \Delta\nu_0 + p_f \Delta\nu_f \text{ sec}^{-1}, \quad (5)$$

where p_0 is the partial pressure of oxygen, p_f is the partial pressure of foreign gas, and $\Delta\nu_0$ and $\Delta\nu_f$ are the half-intensity half-widths at unit pressure of the self-

²⁰ R. Howard and W. V. Smith, Phys. Rev. **79**, 128 (1950).

broadened line and of the foreign-broadened line, respectively.

The results obtained from observations on the collision broadening of oxygen lines by ammonia, nitrous oxide, nitrogen, and argon are summarized in Table II. The data are based on measurements of the broadening of the $J=8 \rightarrow 9$ transition in oxygen. The error in these data is approximately 10 percent, the same as that for self-broadening. Collision diameters obtained in this investigation are compared with those obtained from the kinetic theory and with those by other investigators for the same perturbing molecules acting on ammonia.

The perturbing gases represent, in the order of their listing in Table II, large electric moment, small electric dipole moment, quadrupole moment, and electrical inactivity. Collision diameters obtained by this method show excellent agreement with results from the kinetic theory and with measurements based on the collision broadening of ammonia lines. This agreement provides evidence of the accuracy of the method of measurement described herein.

Comparison of the self-broadened collision diameter for oxygen with that determined from ammonia broadening,^{16,20-24} shows a general increase in the self-broadened collision diameter over that from the kinetic theory and the ammonia broadening measurement. This observation provides further justification for the assumption of an interaction other than that arising from quadrupoles or polarizability in the self-broadening of oxygen. Nitrogen, which has a quadrupole moment considerably larger than that estimated for oxygen, should show a rather large collision diameter from mixtures with oxygen. For oxygen-nitrogen mixtures, however, the collision diameter is very close to the kinetic theory measurement. The inference is then that nonresonant quadrupole-quadrupole collisions are relatively ineffective in broadening spectral lines. Further, polarizability interactions do not seem to cause unusual broadening since the collision diameter for argon, which does not have a quadrupole moment, is also in agreement with kinetic theory measurements. Thus, the greater collision diameter for oxygen from self-broadening as compared with that from the kinetic theory, seems to result from an interaction of greater magnitude than that of the nonresonant terms for quadrupoles or polarizability. A rotational resonance interaction again seems a reasonable interpretation.

A final determination which should be made is that of the line-breadth parameter for air. This information is valuable, for example, in studies of the propagation of microwave energy through the earth's atmosphere. The calculation is based upon a relation similar to

²¹ R. M. Hill and W. V. Smith, *Phys. Rev.* **82**, 451 (1951).

²² J. Weber, *Phys. Rev.* **83**, 1058 (1951).

²³ Potter, Bushkovitch, and Rouse, *Phys. Rev.* **83**, 987 (1951).

²⁴ B. Bleaney and R. P. Penrose, *Proc. Phys. Soc. (London)* **60**, 540 (1948).

TABLE II. Collision diameters of perturbing molecules.

Colliding molecule	Electric dipole moment ($\times 10^{18}$)	Electric quadrupole moment ($\times 10^{19}$)	O ₂ broadening	Collision diameters (Å)				
				Kinetic theory	NH ₃ broadening (3,3 line)			
O ₂	0	<0.09 ^a	4.35 ^b	3.61 ^f	4.85 ^h	3.86 ⁱ	4.31 ^j	4.18 ^k
NH ₃	1.44 ^a		4.30	4.02 ^f	13.8 ^h		13.9 ^j	13.8 ^k
N ₂ O	0.249 ^b	0.59 ^d	4.37	4.35 ^g			7.32 ^d	11.2 ^j
N ₂	0	0.27 ^c	3.79	3.68 ^f	6.4 ^h	5.54 ⁱ		
A	0	0	3.57	3.63 ^f	4.6 ^h	3.73 ⁱ		

^a A. Van Itterbeek and K. de Clippelier, *Physica* **14**, 349 (1948).

^b P. Debye, *Polar Molecules* (Dover Publications, New York, 1929), p. 40.

^c W. V. Smith and R. Howard, *Phys. Rev.* **79**, 134 (1950).

^d See reference 21.

^e This is the maximum observed value at $K=9$. The smallest observed value is 3.55 Å for $K=23$.

^f E. H. Kennard, *Kinetic Theory of Gases* (McGraw-Hill Book Company, Inc., New York, 1938), p. 149.

^g L. Loeb, *Kinetic Theory of Gases* (McGraw-Hill Book Company, Inc., New York, 1934), p. 651.

^h See reference 24.

ⁱ R. R. Howard and W. V. Smith, *Phys. Rev.* **79**, 131 (1950).

^j See reference 23.

^k See reference 22.

Eq. (5), namely,

$$\Delta\nu_{\text{air}} = \Delta\nu_{\text{O}}P_{\text{O}} + \Delta\nu_{\text{N}}P_{\text{N}} + \Delta\nu_{\text{A}}P_{\text{A}}$$

The composition of air is taken to be²⁵ N₂, 78.03 percent; O₂, 20.99 percent; A, 0.94 percent, representing 99.96 percent of the total constituency of the earth's atmosphere. If the calculation is made on the basis of 1 mm total pressure, and if the data obtained from the $J=8 \rightarrow 9$ oxygen transition are used,

$$\begin{aligned} \Delta\nu_{\text{air}} &= 1.97 \times 0.21 + 1.52 \times 0.78 + 1.24 \times 0.0094 \\ &= 1.60 \text{ Mc/mm Hg} \end{aligned}$$

or

$$(\Delta\nu/c)_{\text{air}} = 0.041 \text{ cm}^{-1}/\text{atmos.}$$

It should be noted that the figure obtained here for the line-breadth parameter of oxygen in air holds only for the transition given. In the general case of any transition it may be said that the parameter for air is approximately 82 percent that for pure oxygen.

Direct measurements on the lines of pure air at low pressures are now in progress in this laboratory.

We should like to thank Mr. Robert M. Hill for checking some of the measurements.

APPENDIX A

For simplicity the $J=0 \rightarrow 1$ transition is considered. This line will split into three Zeeman components under the influence of a magnetic field. Assume that a square-pulse magnetic field is applied to the molecules, so that for one-half period the line is degenerate and for the other half, it is split. Let $I(\nu)$ be the intensity of the unmodulated line at some frequency ν , and $\delta\nu$, the frequency splitting in the presence of the field. Subscripts 0, +, and - signify, respectively, the nonexistent, higher, and lower frequency shifts of the Zeeman components. The intensity of each component is given by a Taylor expansion:

$$I_+(\nu) = \frac{1}{3}[I(\nu) + (\partial I/\partial\nu)(-\delta\nu) + \frac{1}{2}(\partial^2 I/\partial\nu^2)(-\delta\nu)^2 + \dots],$$

$$I_0(\nu) = \frac{1}{3}I(\nu),$$

$$I_-(\nu) = \frac{1}{3}[I(\nu) + (\partial I/\partial\nu)(\delta\nu) + \frac{1}{2}(\partial^2 I/\partial\nu^2)(\delta\nu)^2 + \dots].$$

²⁵ C. D. Hodgman, editor, *Handbook of Chemistry and Physics* (Chemical Rubber Publishing Company, Cleveland).

The detector crystal responds to the difference in the incident power (or intensity) with and without the magnetic field. The crystal signal is then proportional to

$$\begin{aligned} & [I_+(\nu) + I_0(\nu) + I_-(\nu)] - I(\nu) \\ &= \frac{1}{3} [I(\nu) - (\partial I / \partial \nu) \delta \nu + \frac{1}{2} (\partial^2 I / \partial \nu^2) \delta \nu^2 + \dots] + \frac{1}{3} I(\nu) \\ & \quad + \frac{1}{3} [I(\nu) + (\partial I / \partial \nu) \delta \nu + \frac{1}{2} (\partial^2 I / \partial \nu^2) \delta \nu^2 + \dots] - I(\nu) \\ &= \frac{1}{3} (\partial^2 I / \partial \nu^2) \delta \nu^2 + \text{higher even degree terms.} \end{aligned}$$

Because relatively low modulating fields are used, $\delta \nu^2 \gg \delta \nu^4$. Hence, terms involving fourth and higher degrees may be neglected.

Also, $\delta \nu$ is a constant for any one line. Thus, the detector responds to a signal that is proportional to $\partial^2 I / \partial \nu^2$.

The argument is good, even for the $(1 + \cos \omega t)$ type modulation used, as contrasted with the ideal square pulse of the derivation. Since the actual applied field remains within 15 percent of its maximum and minimum values for half the period of modulation, it reasonably approximates the ideal square-pulse field. The more complex Zeeman splitting resulting from higher rotational states will yield more terms in this derivation, but the net effect will be the same as that developed for the simplest case.

The Spin-Wave Theory of Antiferromagnetics

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The spin-wave theory of antiferromagnets, recently studied by Anderson for the absolute zero of temperature, is examined here for finite temperatures to derive the thermodynamic properties of antiferromagnets at low temperatures. Somewhat differently from Anderson's semiclassical treatment, the present theory has used the formulation devised by Holstein and Primakoff, upon which the thermodynamic quantities are derived quantum-statistically. The parallel susceptibility is shown to be proportional to T^2 , while the perpendicular susceptibility is independent of the temperature in the first approximation but decreases with increase in temperature if calculated in the second approximation. A tentative discussion is given of the nature of the divergences which arise in the simple formulation of spin-wave treatments in the absence of any kind of anisotropy.

INTRODUCTION

RECENTLY Anderson¹ has presented an approximate quantum theory of antiferromagnets on the basis of the semiclassical spin-wave theory first introduced by Kramers and Heller.² He examined very carefully the zero-point energy terms and showed that the spin-wave theory can be used to give pretty good approximations to the ground states of antiferromagnets. His result lies between the limits predicted by his variation method,³ and moreover, it is very close to the rigorous value in the case of a one-dimensional chain of spins equal to one-half, which was treated by Hulthén⁴ and by Bethe.⁵

As a matter of fact, the spin-wave theory of antiferromagnets is far more complicated and probably poorer as an approximate method than that of ferromagnets. Unfortunately the spin-wave theories are still far from satisfactory in both cases, because we know very little about the limitations of the method, which necessarily introduces great simplifications to bring the problem into the tractable form of independent spin-wave oscillators.

In spite of this situation, the writer wishes here to

present a statistical-thermodynamical theory of antiferromagnets based on the Hulthén-Anderson spin-wave theory. The reason is, in the first place, that the spin-wave theory is at present the only approach we can use to attack the problem at low temperatures, and secondly that Anderson's success suggests that the low-lying energy levels may be reasonably approximated by this method. Approximations for higher temperatures can be treated by several methods. Van Vleck's theory of antiferromagnetism⁶ is one of them and should be regarded as the standard theory. Refinements of this theory have been tried by Li⁷ using the Bethe-Peierls-Weiss method and also by the present author, Obata, and Ohno.⁸

The treatment to be presented here is of course to be regarded as a starting point from which we should proceed to more rigorous theories. Also it should be emphasized that such improvements will be achieved more easily by handling the density matrices directly, rather than the Hamiltonian, to yield the separate energy levels. We hope the present theory will be improved in the future by taking account of the higher terms in the Hamiltonian, which are omitted in the simple theory but are very important to establish any satisfactory theory. In the last section of this paper we shall consider, by first-order perturbation theory, some of the effects due to these higher terms together with

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¹ P. W. Anderson, *Phys. Rev.* **86**, 694 (1952).

² G. Heller and H. A. Kramers, *Proc. Roy. Acad. Sci. Amsterdam* **37**, 378 (1934).

³ P. W. Anderson, *Phys. Rev.* **83**, 1260 (1951).

⁴ L. Hulthén, *Arkiv. Mat. Astron. Fysik* **26A**, 1 (1938).

⁵ H. A. Bethe, *Z. Physik* **21**, 205 (1931).

⁶ J. H. Van Vleck, *J. Chem. Phys.* **9**, 85 (1941).

⁷ Yin-Yuan Li, *Phys. Rev.* **84**, 721 (1951).

⁸ Kubo, Obata, and Ohno (unpublished).