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Absorption of Microwaves by Oxygen in the Millimeter Wavelength Region*†

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Pressure broadening of the absorption lines near 60 000 Mc/sec because of the oxygen molecule has been examined in pure oxygen, and in oxygen-nitrogen mixtures. The apparatus consisted of a large nonresonant cavity spectrometer, with bolometer detectors. At pressures of a few millimeters, a fairly constant $(\Delta\nu/P)$ value of 1.94±5 percent (Mc/sec) per mm Hg has been found for pure oxygen, independent of the rotational state of the molecule. To explain absorption in dry air at pressures from one-quarter to one atmosphere, a value of 0.75 for the broadening ratio of $(\Delta\nu/P)$ for O_2-N_2 to $(\Delta\nu/P)$ for O_2-O_2 accounts satisfactorily for the broadening effect of nitrogen. A theoretical analysis has been applied assuming the important molecular interactions are the London dispersion (polarizability) and exchange forces. Dipole-dipole forces are absent, and quadrupole- and magnetic-dipole effects are found to be too weak to be effective.

INTRODUCTION

ALTHOUGH many high-precision measurements have been made on the resonant frequencies of molecules in the microwave region, there are relatively few and far less exact measurements on the line shapes and intensities of microwave absorption lines. Detailed and extensive knowledge of line shapes would be valuable, however, in determining the nature of intermolecular forces. The particular case of O_2 which has been examined here is unusual in that electric dipole and certain other long-range forces which ordinarily broaden microwave transitions are absent. Furthermore, much of the absorption of millimeter waves in the atmosphere comes from transitions in O_2, and hence measurements of this spectrum are of help in understanding and calculating microwave transmission in the atmosphere.

Historically the O_2 spectrum was one of the first to be observed in the microwave region. In the electronic ground state of the oxygen molecule $(^3\Sigma_g^-)$ the electron spins pair to give a net spin of unity. The magnetic moment associated with this electronic spin can interact with the magnetic field of microwave radiation, resulting in absorption of energy.[1] The electron spin S may take on three orientations with respect to K, the angular momentum of molecular end-over-end rotation; the total angular momentum J therefore can equal $K-1$, K, or $K+1$. Transitions between these spin fine structure components of the ground state rotational levels lie in the 5 mm wavelength region. (One line occurs near 2.5 mm.) Selection rules permit resonant transitions between the $J=K$ and $J=K+1$ levels, referred to as $+$ lines; and between the $J=K$ and $J=K-1$ levels, referred to as $-$ lines. For $(O^{16})_2$, symmetry considerations restrict K to odd integers.

The Van Vleck-Weisskopf, collision-broadening, line-shape theory[2] is believed to be the most appropriate in the microwave spectral region. (For this theory to be applicable the line breadth must be caused primarily by pressure broadening.) Using this theory Van Vleck has prepared formulas for O_2 absorption[1] in which the line breadth $\Delta\nu$ appears as an undetermined parameter. This line-breadth parameter $\Delta\nu$ represents the effect of collision damping in broadening the spectral line. $\Delta\nu$, which corresponds to the molecular collision rate, usually is directly proportional to the molecular density, i.e., to the pressure P; hence the pressure normalized impact parameter $\Delta\nu/P$ is the more meaningful quantity. The theory of Anderson[3] is currently believed to be the most suitable for calculating microwave line-breadth parameters.

In the past the microwave O_2 spectrum has been examined at various pressures. At low pressures the widths of the resolved O_2 lines have been observed. At high pressures, where the wings of the individual resonances overlap greatly, the intensity caused by the envelope of the unresolved lines has been measured. Precision and accuracy generally were poor. The data often could not be easily interpreted; proposed theories and line-breadth mechanisms could not be seriously tested.

In order to obtain independent reliable information on line widths and intensities we have carefully investigated the microwave O_2 spectrum at both high and low pressures. In general, the high-pressure measurements were in accord with the low-pressure results. Mechanisms proposed as responsible for line breadth have been critically examined. Theoretical line-breadth calculations have been revised and extended: a line-width computation that corresponds closely to the experimental results is presented.

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[1] J. H. Van Vleck, Phys. Rev. **71**, 413 (1947). A summary of previous theoretical and experimental work is also given here.

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

[3] P. W. Anderson, dissertation, Harvard University, 1948; Phys. Rev. **76**, 647 (1949).

EXPERIMENTAL TECHNIQUE

The untuned cavity spectrometer was used in these experiments. This type of spectrometer is particularly suitable for line breadth and absolute intensity measurements. The microwave nonresonant cavity spectrometer was first described by Lamb,[4] and has been employed previously in the investigations of Becker and Autler[5] and Weingarten.[6]

A simplified diagram of the spectrometer is shown in Fig. 1. Microwave radiation is introduced by a suitable horn; since the wavelength is small in comparison to cavity dimensions, a large number of normal modes of oscillation can exist. The moving blades of a fan-like "mode-mixer" periodically vary the boundary conditions, insuring the presence of a large number of modes all with essentially the same degree of excitation and absorption. Under these conditions the response of randomly disposed square-law detecting elements, averaged in time and over the cavity volume, is proportional to the Q of the cavity and contents. This Q is then determined absolutely by comparison with the Q after addition of a known loss; the known loss is provided by a microwave reference window which, when opened, permits radiation egress from the cavity.[7] For each absorption determination three or four measurements are required: detector response when the cavity is evacuated, response after addition of gas, and response under at least one of these two previous conditions when, in addition, the microwave window is opened. (See Appendix A.)

In the arrangement for the O_2 measurements, 5-mm radiation is obtained from a crystal frequency doubler powdered by a 1-cm klystron. The 5-mm radiation is modulated at 20 cps by a motor-driven variable waveguide attenuator before being introduced to the cavity.

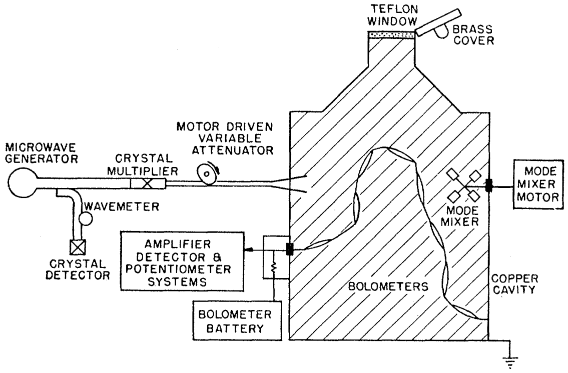

FIG. 1. Nonresonant cavity spectrometer.

TABLE I. O_2 line breadth parameter as function of rotational quantum number K ($T=300°K$).

K	Series	Experimental value	Theoretical fit
			(Mc/sec) per mm Hg
1	+	2.20±10%	2.075
1	−		2.064
3	+	2.23±10%	1.944
3	−		1.943
5	+	1.96± 5%	1.940
5	−	1.99± 5%	1.937
7	+	1.92± 5%	1.937
7	−	1.82± 5%	1.935
9	+	1.93± 5%	1.938
9	−	2.00± 5%	1.937
11	+		1.939
11	−	1.97±10%	1.938
13	+		1.940
13	−	1.86± 5%	1.940
15	+		1.941
15	−	1.99± 5%	1.941
17	+		1.942
17	−	1.82±10%	1.942
19	+		1.942
19	−	1.92±10%	1.942
21	+		1.943
21	−		1.943
23	+		1.943
23	−		1.943
25	+		1.943
25	−		1.943
27	+		1.944
27	−		1.944
29	+		1.944
29	−		1.944

The response of a chain of vacuum bolometers is fed into a high-gain, narrow-band, 20-cps amplifier, rectified, and finally measured with a conventional potentiometer arrangement or alternatively displayed on a recording potentiometer.

The microwave window is made from a Teflon disk which can be covered by a brass lid. The effective area of this window was determined by comparison with a "standard" reference window opening on the conical surface of the cavity. This window comparison was made at a wavelength of 1.35 cm, necessarily before the outer (pressure) lid of the cavity was made vacuum tight. The window calibration is presumed to be the same at the higher frequencies at which the O_2 absorption occurs and, as explained below, was corroborated by integrated intensity measurements of individual O_2 lines.

EXPERIMENTAL RESULTS

Low Pressure Observations: Resolved O_2 Lines

Observations were made on resolved O_2 lines at pressures of 2 to 10 mm Hg. (The positions of most of these resonances have been accurately determined by Burkhalter *et al.*[8]) Traces were made over the contours of several lines while the source frequency was swept mechanically. From these traces peak intensity and half-width were determined independently at various

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[4] W. E. Lamb, Jr., Phys. Rev. **70**, 308 (1946).

[5] G. E. Becker and S. H. Autler, Phys. Rev. **70**, 300 (1946).

[6] I. R. Weingarten, dissertation, Columbia University, 1948 (unpublished).

[7] The energy loss caused by passage of radiation through the window was derived by Lamb (see reference 4). The behavior of cavity and window predicted by Lamb has been verified by Becker and Autler (see reference 5) and by Weingarten (see reference 6).

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

O_2 pressures. Since the product of peak intensity and half-width (this quantity has been called integrated intensity) is calculable in terms of known constants these results furnish a check on the window calibration. The window calibration at 5 mm, as inferred from integrated intensity measurements, was equal to that at 1.35 cm within 5 percent experimental error.

The normalized impact parameter $\Delta\nu/P$ and peak intensity γ_p were found to be independent of pressure[9] over the range investigated (2–10 mm Hg). In determining line shapes over extended frequency ranges, corresponding points on four separate recorder traces had to be correlated. The assumptions had then to be made that the klystron-power level did not change between pairs of window-open, window-closed traces (see Appendix A), and that the klystron frequency sweep rate was linear between the 30-Mc/sec frequency standard marker pips. These assumptions were not always good, but numerous traces were taken to minimize the error involved. Figure 2 shows a typical resulting curve. Agreement with the Van Vleck-Weisskopf line shape is made to within experimental error.

Subsequently the window calibration was assumed valid and line breadths were inferred from measured peak intensities by using the integrated intensity relationships. Intensity contributions from the wings of adjoining lines were subtracted when necessary. The values of $\Delta\nu/P$, measured at ambient temperature, were referred to 300°K. (For this, a hard sphere model of O_2 was assumed, giving $\Delta\nu/P$ a temperature variation of $T^{-\frac{1}{2}}$.) Because of experimental difficulties, the uncertainties assigned to the $\Delta\nu/P$ values are larger than the probable errors derived on a purely statistical basis. The data are shown in Fig. 3; the recent results of Anderson, Smith, and Gordy,[10] and of Gokhale and Strandberg,[11] are also shown. In Table I as well as in Fig. 3 our data are compared with the results of a theoretical calculation (discussed later). Experimental values for the 1^- and 3^+ lines are slightly larger than the theoretical expectations; the experimental values for large K may be lower than theoretical expectations.

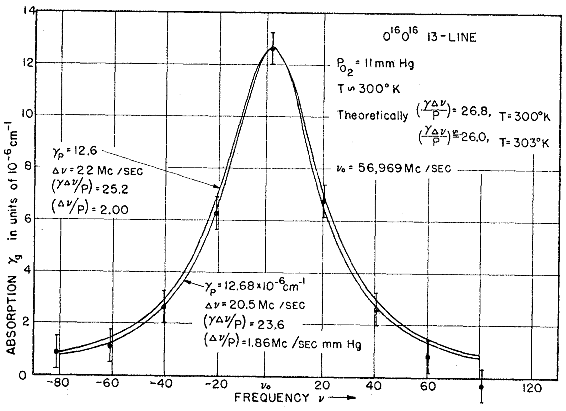

FIG. 2. Plot of the shape of the 13^- line in the absorption spectrum of $(O^{16})_2$.

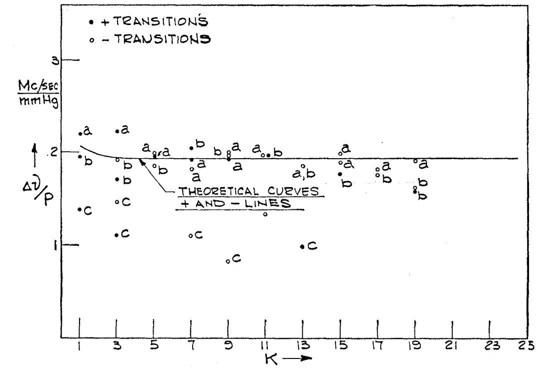

FIG. 3. Results of recent line-width measurements in the $(O^{16})_2$ spectrum. Our results are labeled "a", those of Anderson *et al.* (see reference 10) are "b", and those of Gokhale and Strandberg (see reference 11) are "c". Errors are assigned to points marked "a" as follows: ±10 percent for 1^+, 3^+, 11^-, 17^-, and 19^-; ±5 percent for the others.

The ratio of O_2-N_2 broadening to O_2 self-broadening was determined by the reduction in peak intensity of an O_2 line on addition of N_2. The broadening ratio is given by

$$\beta=\left[\frac{\gamma(O_2-O_2)}{\gamma(O_2-N_2)}-1\right]f(O_2)\Big/[1-f(O_2)],$$

where $\gamma(O_2-O_2)$ refers to the peak line intensity in pure O_2, and $\gamma(O_2-N_2)$ refers to the peak line intensity upon addition of N_2. The fraction of O_2 is denoted by $f(O_2)$. For the observed lines, β was found to be 0.90±15 percent. Anderson, Smith, and Gordy[10] report a β value of 0.79 for the 9− O_2 line. As indicated below, β can also be obtained from the high-pressure observations.

High-Pressure Observations: Envelope of O_2 Lines

O_2 absorption in dry air at ambient temperature was measured at pressures of $\frac{1}{4}$, $\frac{1}{2}$, and 1 atmosphere to determine whether high-pressure absorption could be calculated from low-pressure half-width parameters. The results are shown in Figs. 4–6. As in the case of the low-pressure data, experimental uncertainties are believed to be greater than the statistical probable errors. Two theoretical absorption curves were computed at all three pressures: one with an oxygen self-broadening impact parameter of about 1.97 Mc/sec per mm Hg and an N_2-O_2 broadening ratio β of 0.92; the other with the O_2 impact parameters listed in Table I, and β

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[9] Pressure independence of $\Delta\nu/P$ and peak intensity indicate that only pressure broadening is contributing to line breadth. Other effects such as natural line breadth, Doppler breadth, and saturation breadth can be shown to be negligible. Zeeman splitting because of the earth's magnetic field which could conceivably be significant was not observed—the iron tank enclosing the copper microwave cavity had been degaussed.

[10] Anderson, Smith, and Gordy, Phys. Rev. **87**, 561 (1952).

[11] B. V. Gokhale and M. W. P. Strandberg, Phys. Rev. **84**, 844 (1941).

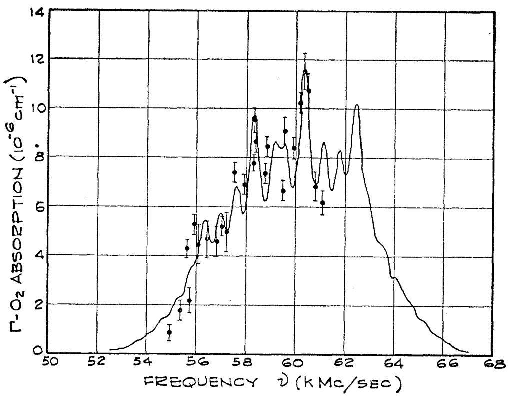

FIG. 4. Microwave absorption in dry air at $\frac{1}{4}$ atmosphere pressure and 300° Kelvin by oxygen. A theoretical plot is shown using $\beta=0.75$.

equal to 0.75. Only for the 1-atmosphere data was it really evident that the second set of parameters furnished the better fit to the experimental points. Both theoretical absorption curves are shown, together with the 1-atmosphere data, in Fig. 6. In Figs. 4 and 5, the theoretical curves are based on the second set of parameters.

The one-atmosphere data correspond to an oxygen-nitrogen broadening ratio perhaps slightly smaller than the 0.75 shown in Fig. 6. The total line width at one atmosphere pressure thus appears to be less than one would expect from the low-pressure values of $(\Delta\nu/P)$ for O_2 and the ratio β. The value 0.75 for β is just about at the 15 percent error limit ascribed to the low-pressure measurements. More accurate measurements are thus needed to determine whether this discrepancy is real. Perhaps the assumption of linear dependence of the half-widths on the pressure does not hold exactly up to one atmosphere, or perhaps the Van Vleck-Weisskopf line-shape formula is not applicable over as wide a range about the center of a line as was previously supposed.

Previous investigation of O_2 absorption at high pressures has been limited. (Early work is summarized by Van Vleck.[1]) Beringer[12] in 1944 used wave-guide techniques to measure O_2 attenuation in O_2-N_2 mixtures. His data were not sufficiently accurate to decide between the line breadth values of 0.02 and 0.05 cm^{-1}/atmos. (The conversion factor from cm^{-1}/atmos to (Mc/sec) per mm Hg is 39.5.) Beringer also found the nitrogen-oxygen broadening ratio to be about unity. Mueller's observations of microwave transmission in the atmosphere and in a wave guide (see Van Vleck, reference 1) suggested a value of 0.02 cm^{-1}/atmos. The microwave radiometer was used by Dicke *et al.*[13] to determine absorption of radiation in the 1-cm wavelength region. Dicke's data correspond to a breadth of 0.02 cm^{-1}/atmos. Lamont[14] also proposed a $\Delta\nu/P$ value of about 0.02 cm^{-1}/atmos from field attenuation measurements at 5-mm wavelengths. Later Strandberg *et al.*[15] employed a wave-guide bridge to observe O_2 absorption at millimeter wavelengths in oxygen-nitrogen mixtures at atmospheric pressures. Although the absorption found corresponded to a line breadth of 0.04 cm^{-1}/atmos, fluctuations in absorption indicated a value $\leqslant 0.02$ cm^{-1}/atmos. Strandberg also reported unusual behavior of O_2 absorption in O_2-N_2 mixtures. Nicoll and Warner[16] have examined solar absorption with a microwave radiometer at 8 mm wavelength. They have not attempted however to determine experimentally the separate contribution of O_2 and H_2O to observed attenuation.

When experimental uncertainties are considered, these previous results for the center of the atmospheric O_2 absorption are not inconsistent with our $\Delta\nu/P$ value of 1.94 (Mc/sec) per mm Hg (0.049 cm^{-1}/atmos) and our nitrogen-oxygen broadening ratio value of 0.75.

THEORY

In the microwave spectral region the impact type of pressure-broadening theory is generally applicable.[17] The impacts may be described semiclassically as follows: The molecules are essentially isolated from each other; occasional molecular encounters cause perturbations in the energy levels of a radiating molecule; hence, during the encounter or "collision" the frequency of the radiator is modified. If subsequently radiation continues without loss of energy a phase change,

$$2\pi \sum_{\text{collision}} \Delta\nu\Delta t \quad \text{or equivalently} \quad \sum_{\text{collision}} \Delta E\Delta t/\hbar,$$

has been introduced, ΔE is the change in energy level separation caused by the perturbation. The change of phase in such *adiabatic* encounters is equivalent to the

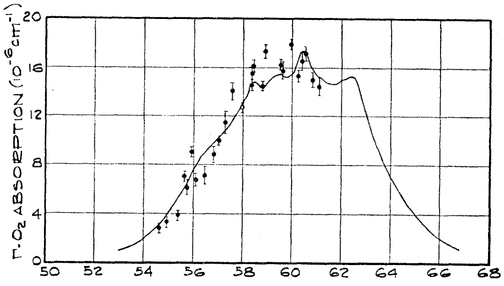

FIG. 5. Microwave absorption in dry air at $\frac{1}{2}$ atmosphere pressure and 300° Kelvin by oxygen. A theoretical plot is shown $\beta=0.75$.

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[12] R. Beringer, Phys. Rev. **70**, 53 (1946).

[13] Dicke, Beringer, Kyhl, and Vane, Phys. Rev. **70**, 340 (1946).

[14] H. R. Lamont, Phys. Rev. **74**, 353 (1948); Proc. Phys. Soc. (London) **61**, 562 (1948).

[15] Strandberg, Meng, and Ingersoll, Phys. Rev. **75**, 1524 (1949).

[16] G. R. Nicoll and F. L. Warner, Telecommunications Research Establishment Memorandum 471, July 1951 (unpublished).

[17] C. H. Townes and A. L. Schawlow, *Microwave Spectroscopy* (McGraw-Hill Book Company, Inc., New York, to be published). A general discussion of microwave line breadth is included.

introduction of new frequencies, and therefore contributes to line broadening.

Collisions in which the radiator makes a transition are called by Townes[17] *diabatic* collisions; here the behavior of the radiator after collision is unrelated to its prior condition. By definition, a collision can be said to occur when the change in phase in a molecular encounter is at least one radian. But in the microwave spectral region the interaction energy necessary to produce such a phase change can be shown to be more than sufficient to cause a transition, i.e., in the microwave spectral region almost all molecular encounters result in diabatic collisions. Any microwave pressure-broadening theory must take into account these diabatic collisions. In the particular case of O_2 the collision diameter is so small that they are especially important.

The impact pressure-broadening theory of Anderson[3] appears to be the most appropriate for use in the microwave spectral region. This formulation differs from most others in that the effects of diabatic as well as adiabatic collisions are taken into account. Anderson derives line-shape formulas similar to those of Van Vleck-Weisskopf and in addition obtains general expressions for line breadth.

Various interactions have been proposed to account for O_2 and O_2-N_2 broadening.[3,8,10,18,19] In principle the change in phase including the sum of *all* the interactions should be evaluated. (This point often has not been clearly stated in the literature.) A more feasible procedure is first to estimate the quantitative importance of these interactions by comparing the phase changes caused by each interaction acting alone, and then to perform a line breadth calculation considering only the important effects. Fortunately in the case of O_2 only two types of interactions are significant; a fairly rigorous calculation can then be made on the basis of just these two effects.

Analogously to the gas-kinetic collision rate formula, the pressure-normalized microwave line breadth parameter $(\Delta\nu/P)_{ij}$ can be written

$$\left(\frac{\Delta\nu}{P}\right)_{ij}=\frac{n_j}{P}\frac{v_i}{\sqrt{2}}b_{ij}^2\left[\frac{1+M_i/M_j}{2}\right]^{\frac{1}{2}},$$

where n_j/P is the pressure-normalized molecular density, v_i is the average molecular velocity, M_i, M_j are the molecular masses, and b_{ij} represents the effective microwave collision diameter. The experimental data presented indicate that both O_2-O_2 and O_2-N_2 collision diameters are fairly independent of the rotational quantum number K of the radiating molecule and that O_2-N_2 broadening is less than O_2-O_2 broadening. The O_2-O_2 line breadth [$\sim$1.95 (Mc/sec) per mm Hg] corresponds to a $b(O_2-O_2)$ value of 4.40A, while for $\beta=0.90$ the O_2-N_2 breadth corresponds to a $b(O_2-N_2)$ of 4.24A [or to a $b(O_2-N_2)$ of 3.88A for $\beta=0.75$]. From viscosity data[20] the collision diameters are $b(O_2-O_2)=3.60$A, $b(O_2-N_2)=3.38$A. Hence it is likely that O_2-O_2 and O_2-N_2 interactions are much the same and caused by forces of rather short range.

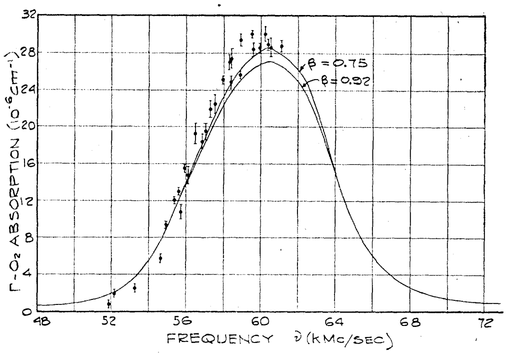

FIG. 6. Microwave absorption in dry air at 1 atmosphere pressure and 300° Kelvin by oxygen.

Since $(O^{16})_2$ has no electric dipole moment, the longer-range Van der Waals interactions, usually found to account for microwave line breadth, do not occur. Oxygen interactions that should be examined include magnetic dipole, molecular electric quadrupole, London dispersion, and exchange.

Oxygen molecular magnetic-dipole interaction is readily shown to contribute insignificantly toward line breadth—the collision diameter caused solely by this effect (estimated by determining the distance of closest approach at which the change in phase is one radian) is only 0.238A. This interaction is of course not present in O_2-N_2 collisions.

Oxygen broadening caused by molecular electric quadrupole interaction alone has been calculated by Mizushima[18] using the methods of adiabatic collision theory.[21] From the more appropriate semidiabatic approach of Anderson the O_2-O_2 collision diameter caused by quadrupole interactions is estimated (in the same fashion as in the previous case) to be less than 1.71A. Although the nitrogen molecular quadrupole is at least three times as large as that of oxygen,[22] O_2-N_2 as well as O_2-O_2 molecular quadrupole broadening is probably quite small.

Anderson[3] has made a calculation for O_2 broadening caused by London dispersion forces.[23] This type of force may be described as an interaction between the fluctuating dipole moment of one molecule, associated with

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[18] M. Mizushima, Phys. Rev. **83**, 94 (1941); **84**, 363 (1951).

[19] Anderson, Smith, and Gordy, Phys. Rev. **82**, 264 (1951).

[20] E. H. Kennard, *Kinetic Theory of Gases* (McGraw-Hill Book Company, Inc., New York, 1932), p. 149.

[21] In Appendix B the distinction between the adiabatic and Anderson pressure-broadening theories is made clear. For the case of O_2 the results of these two theories are compared in some detail.

[22] R. R. Howard and W. V. Smith, Phys. Rev. **79**, 128 (1950); W. V. Smith and R. Howard, Phys. Rev. **79**, 132 (1950).

[23] Anderson's final formulas for London dispersion force broadening were found to be in error and have been corrected.

the motion of its electrons, and the dipole moment which it induces in a second molecule. (The description "dispersion forces" derives from the appearance in the interaction formula of energy terms characteristic of the optical dispersion wavelength. Alternatively, since the molecular polarizabilities also appear in the formula, these forces have been called "polarizibility forces.") Precise calculations show that dispersion forces do contribute significantly toward observed O_2-O_2 line widths but yield a breadth of 1.27 (Mc/sec) per mm Hg, far too small. Similar results are obtained for O_2-N_2 interaction.

The exchange repulsion between two molecules arises from the interaction of their electronic wave functions. Examination shows that exchange interaction contributes substantially toward oxygen line breadth. Since exchange and polarization are by far the largest contributors to broadening, the line breadth resulting from the combination of these forces alone will be calculated.[24]

The polarizability interaction is specified in terms of parameters known from optical measurements. The exchange interaction is much more difficult to treat theoretically. Although a reasoned assumption as to the form of this interaction can be made, the exchange oxygen parameters in general are not known. Some information can be gleaned from O_2 gas-kinetic collision diameter data; exchange parameters for other substances have been determined from the study of the structure of solids and from the investigation of repulsive forces between molecules in gases. Oxygen exchange parameters were selected that appeared plausible in view of these data and which resulted in calculated exchange-polarizability line widths agreeing closely with observed values.

The exchange interaction[25] is taken to be of the form

$$H_{\text{exchange}}=\frac{3}{3+\epsilon}\frac{4}{\pi}kTe^{-[(r-b_{kT})/a]}[1+\epsilon\cos^2\Theta],$$

in which the parameters are defined as: a = exchange force range, b_{kt} = gas-kinetic collision diameter, ϵ = measure of geometric anisotropy of O_2, Θ = angle between figure axis of radiator and the radiator-perturber distance r, k = Boltzmann constant, and T = temperature in °K. From the data on page 149 of Kennard's book,[20] b_{kT} for O_2 is 3.60A at 300°K. Epsilon is estimated by Miller (verbal communication and reference 26) to be 0.85 with an uncertainty of no more than 15 percent. With these parameters fixed, $a(O_2-O_2)$ was chosen to be 0.420A in matching theoretical polarizability-exchange widths to observed line breadths.

To fit alkali halide energies and lattice constants in solids, Born and Mayer[27] chose an a of 0.345A (this and other early work is summarized by Seitz[28]). Rittner,[29] in a recent paper investigating repulsive forces in alkali halide molecules, selected the smaller value 0.31A. Since the interionic diameters of alkali halide molecules are less than those of the corresponding crystals, Rittner[29] suggested that a rough proportionality exists between interaction range a and intermolecular diameter b.

Repulsive forces between rare gas molecules have been considered theoretically by Slater,[25] who obtained a range of 0.217A for He. Bleick and Mayer[30] calculated a range of 0.209A and a collision diameter of 2.058A for Ne. Kunimine[31] determined a to be 0.272A for argon. Since the oxygen molecule is larger than the alkali halide molecules and the rare gas atoms, the selection of 0.420A for $a(O_2-O_2)$ does not appear unreasonable. In these references the exponential dependence of the exchange interaction on r is shown to correspond roughly to $1/r^{10}$ or $1/r^{11}$. The power of r is approximated by the ratio of the gas-kinetic collision diameter b to the intermolecular force range a:

$$H_{\text{exchange}}\propto e^{-r/a}\approx A/r^n;\quad n\approx b_{kT}/a.$$

For a b_{kT} value of 3.60A and an a value of 0.420A, $n\approx 8.6$, which is reasonably close to 10.

The temperature variation of gas-kinetic collision diameters can be expressed by the relation $(b_{kT})_T=(b_{kT})_{T_0}(T_0/T)^m$. It can be shown that m is approximated by a/b. For O_2-O_2 collisions, m is 0.155, (see Kennard, reference 20, p. 149) in reasonable agreement with 0.117, the ratio of $a(O_2-O_2)$ (0.420A) to $b(O_2-O_2)$ (3.60A).[32]

Only a rough estimate can be made of the exchange parameters for O_2-N_2 collisions. The O_2-N_2 diffusion diameter is 3.38A at 300°K (see Kennard, reference 20, p. 201). Following the suggestion of Rittner[29] $a(O_2-N_2)$ can be estimated from the relation

$$a(O_2-O_2)/b_{kT}(O_2-O_2)\sim a(O_2-N_2)/b_{kT}(O_2-N_2)$$

to be 0.394A.

For these O_2-O_2 exchange-polarizability collision parameters, the impact parameter,[33]

$$\Delta\nu/P=(n\nu/P\sqrt{2})(b_{\text{eff}}^2)$$

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[24] Contribution of the so-called resonance interactions to oxygen line breadth is negligible. These effects are discussed in Appendix C.

[25] J. C. Slater, Phys. Rev. **32**, 349 (1928).

[26] Miller, Townes, and Kotani, Phys. Rev. **90**, 542 (1953).

[27] M. Born and J. E. Mayer, Z. Physik **75**, 1 (1932).

[28] F. Seitz, *The Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1945).

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is found from

$$b_{\mathrm{eff}}^2=b^2+(fg_\pm)\left[\frac{1.071\times10^5}{b^8}+12.94e^{-2(b-3.60)/a}\right.$$

$$\times a^2b^2\left(1+\frac{a}{b}+\frac{a^2}{2b^2}\right)+\frac{9.419\times10^3a^{\frac{3}{2}}}{b^{7/2}}$$

$$\times e^{-(b-3.60)/a}\left\{1-\frac{7}{2}\frac{a}{b}+\frac{7\cdot9}{4}\left(\frac{a}{b}\right)^2\right.$$

$$\left.\left.-\frac{7\cdot9\cdot11}{8}\left(\frac{a}{b}\right)^3+\frac{7\cdot9\cdot11\cdot13}{16}\left(\frac{a}{b}\right)^4\cdots\right\}\right],$$

where a and b are in A, $a=0.420$, and b is determined from the relations:

$$\tfrac{1}{2}\eta^2(b)=1,$$

$$\eta(b)=\left[\frac{9.258}{b^5}\times10^2+5.087(ab)^{\frac{1}{2}}e^{-(b-3.60)/a}\right](fg_\pm)^{\frac{1}{2}}.$$

Also

$$f=\frac{K(K+1)}{(2K-1)(2K+3)},$$

$$g_+=1-\left[1-\frac{3}{K(K+1)}\right]\frac{(2K+5)(2K+4)(2K)(2K-1)}{[(2K+1)(2K+3)]^{\frac{3}{2}}(2K+2)^2}\quad(+\text{lines}),$$

$$g_-=1-\left[1-\frac{3}{K(K+1)}\right]\frac{(4K^2-9)(4K^2-4)}{(4K^2-1)^{\frac{3}{2}}(2K)^2}\quad(-\text{lines}).$$

The $fg_\pm$ functions are substantially *independent* of K (see Appendix B). The results of this $\Delta\nu/P$ calculation are displayed in Fig. 2 and tabulated in Table I.

By performing a similar analysis β, the ratio $[(\Delta\nu/P)$ for $O_2-N_2]/[(\Delta\nu/P)$ for $O_2-O_2]$, is found to be 0.88.

SUMMARY

The spin reorientation spectrum of O_2 in the millimeter wavelength region has been investigated both at high and low pressures with the untuned cavity spectrometer.

The resolved O_2 lines observed at low pressures corresponded to values of the rotational quantum number K extending from 1 to 19. The line breadth parameters were found to be fairly independent of the value of K, averaging to 1.94 (Mc/sec) per mm Hg. For several lines both the peak intensity γ_p and the line breadth parameter $\Delta\nu/P$ were independently determined. The product $\gamma_p(\Delta\nu/P)$ was found to agree to ±5 percent with theoretical values which are expressed in terms of known physical constants. Beta, the ratio of the O_2-N_2 broadening parameter to the O_2 self-broadening parameter, was determined by observations on a number of individual lines to be 0.90 ± 15 percent.

Applicability of various proposed theories to oxygen broadening has been examined in detail. The line breadth can be most reasonably interpreted as resulting from Van der Waals interactions of the London dispersion and exchange types. Although the dispersion interaction constants are known from optical measurements there are no direct determinations of the exchange parameters. The choice of exchange parameters agrees qualitatively, however, with what is known about the properties of oxygen and other molecules. The line breadths computed by following the general formulation of P. W. Anderson match most of the observed values within experimental error.

The absorption of O_2 in dry air was measured at pressures of $\frac{1}{4}$, $\frac{1}{2}$, and 1 atmos. At these pressures, absorption is caused by the addition of the many overlapping individual lines. A good fit to the experimental data was obtained by simply adding the contributions from the various lines, using the Van Vleck-Weisskopf line shape formula with an oxygen self-broadening parameter value of 1.94 (Mc/sec) per mm Hg and an oxygen-nitrogen broadening ratio β of 0.75. This value of β is somewhat more accurate than the low-pressure value, and is the appropriate parameter for use in calculating line breadths at pressures near one atmosphere; the data obtained are useful in predicting atmospheric absorption of oxygen under various conditions.

Absorption on the far wings of the oxygen lines may perhaps be lower than that expected from extrapolation from the central region.

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APPENDIX A. MEASUREMENT OF ABSOLUTE MICROWAVE ABSORPTION WITH THE NON-RESONANT CAVITY SPECTROMETER

If the response of the detectors in the cavity is proportional to the cavity Q, the inverse of the detector response is proportional to the cavity losses which are additive.

$$1/A_1^0=K_1\alpha_{\mathrm{tank}},$$

and

$$1/A_2^0=K_2(\alpha_{\mathrm{tank}}+\alpha_{\mathrm{window}}),$$

where A_1^0 is the detector response in the empty cavity with the microwave window *closed*, A_2^0 is the detector response in the empty cavity with the window *open*. K_1 and K_2 represent unknown proportionality factors. If the microwave generator is supplying energy at the *same* rate during both window-open and window-closed measurements, $K_1=K_2=K$ and

$$\alpha_{\mathrm{tank}}=[A_2^0/(A_1^0-A_2^0)]\alpha_{\mathrm{window}}.$$

Similarly if A_1^g, A_2^g denote window-closed, window-open detector readings when additional gas absorption α_{gas} is present,

$$\alpha_{\mathrm{tank}}+\alpha_{\mathrm{gas}}=\left(\frac{A_2^g}{A_1^g-A_2^g}\right)\alpha_{\mathrm{window}}.$$

Hence,

$$\alpha_{\mathrm{gas}}=\alpha_{\mathrm{window}}\left[\left(\frac{A_2^g}{A_1^g-A_2^g}\right)-\left(\frac{A_2^0}{A_1^0-A_2^0}\right)\right].$$

If the detector input when the cavity is evacuated is the same as when it is empty (which was not demanded in the analysis above) then three measurements suffice. For instance, from A_1^0, A_2^0, A_1^g:

$$\alpha_{\mathrm{gas}}=\alpha_{\mathrm{window}}\left[\left(\frac{A_2^0}{A_1^0-A_2^0}\right)-\left(\frac{A_1^0}{A_1^g}-1\right)\right].$$

APPENDIX B. COMPARISON OF ADIABATIC AND SEMIDIABATIC PRESSURE-BROADENING THEORIES

The more appropriate semidiabatic theory used by Anderson[3] gives not only different numerical results from those of the adiabatic theory, but also a different dependence of the line-width parameter on K.

The adiabatic theory, used by Mizushima[18] in a calculation for O_2, gives the rms phase shift α as $\langle(\eta_i-\eta_f)^2\rangle_{\mathrm{Av}}^{\frac{1}{2}}$, η_i and η_f referring to the phase shifts of the initial and final levels of the radiating molecule. If η_i equals η_f, then α vanishes. Anderson in calculating the rms phase shift considers neither $\langle(\eta_i-\eta_f)^2\rangle_{\mathrm{Av}}$ as in adiabatic analysis, nor $\langle\eta_i^2+\eta_f^2\rangle_{\mathrm{Av}}$ corresponding to the pure adiabatic case, but a quantity between these two extremes. This semidiabatic phase shift is roughly approximated by $\eta_{\mathrm{rms}}^2=\langle\eta_i^2-\eta_i\eta_f+\eta_f^2\rangle_{\mathrm{Av}}$. When η_i equals η_f, η_{rms} is not zero.

In the case of oxygen, the strong interactions are of the form $f(r)\cos^2\theta$. For this type of interaction $\eta_i\cong\eta_f$, so that while the adiabatic theory gives rms phase shifts varying inversely as K, the rms phase shifts of the diabatic or semidiabatic theories are essentially independent of K.[34] Since the K variation of the phase shift and hence $\Delta\nu/P$ depends on the method of averaging $\cos^2\theta$, these results are quite general for all oxygen Van der Waals interactions.

For example, for broadening caused solely by quadrupole interaction, the adiabatic theory gives

$$\frac{\Delta\nu}{P}=\frac{N_0}{P}\frac{1}{T}\left[\frac{9}{10}\frac{Q^2}{\hbar}\frac{1}{K}\right]^{\frac{1}{2}}1.41\left[\frac{kT}{\pi m(O_2)}\right]^{\frac{1}{4}};$$

$$\frac{N_0}{P}=0.9660\times10^{19}\frac{\mathrm{deg\ K}}{\mathrm{cm^3\ mm\ Hg}}.$$

(Several algebraic and arithmetical errors made by Mizushima have been corrected.)

The semidiabatic theory gives

$$\frac{\Delta\nu}{P}=\frac{N_0}{P}\frac{1}{T}\left[\frac{\sqrt{21}}{20}\frac{Q^2}{\hbar}\right]^{\frac{1}{2}}1.30\left[\frac{kT}{\pi m(O_2)}\right]^{\frac{1}{4}}.$$

From O_2 broadening of the NH_3 inversion line Howard and Smith[22] have set an upper bound of 0.09×10^{-16} cm^2 to Q.

Numerically,

$$\left(\frac{\Delta\nu}{P}\right)_{\mathrm{adiabatic}}<\frac{0.720}{K^{\frac{1}{2}}}\frac{\mathrm{Mc/sec}}{\mathrm{mm\ Hg}},$$

and

$$\left(\frac{\Delta\nu}{P}\right)_{\mathrm{semidiabatic}}<0.335\frac{\mathrm{Mc/sec}}{\mathrm{mm\ Hg}}.$$

APPENDIX C. RESONANCE INTERACTIONS CAUSED BY POLARIZABILITY AND EXCHANGE FORCES

Oxygen collisions generally are accompanied by transitions between the spin multiplets of a given K rotational level. In addition, rotational level transitions are possible. The most probable of these K transitions are the resonance interactions in which a K transition of the radiator is accompanied by a K transition of the perturber between the same two levels in the opposite sense, the total energy of the radiator-perturber system being preserved. These resonance collisions necessarily can occur in only a small fraction of the total number of collisions. For this small fraction of collisions the rms phase shift would be calculated from the expression:

$$\eta_{\mathrm{rms}}^2=(\eta_{\mathrm{pol}}+\eta_{\mathrm{exch}})_{\mathrm{rms}}^2+(\eta_{\mathrm{res\ pol}}+\eta_{\mathrm{res\ exch}})_{\mathrm{rms}}^2.$$

From an analysis by P. W. Anderson (private communication), the additional polarizability resonance contribution to phase shift has been estimated to be 0.02 of the usual effect. The exchange contribution to the phase shift is modified in a similar manner. Upon computation of the collision diameters, resonance is found to be unobservable for O_2-O_2 broadening. Resonance does not occur of course for O_2-N_2 broadening.

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[34] The matrix elements of $\cos^2\theta$, which are to be suitably averaged when determining the rms phase shift, are:

$$\langle\cos^2\theta\rangle_{J=K,M}=\frac{2K^2+2K-1-2M^2}{(2K+3)(2K-1)}-\frac{2[K^2+K-3M^2]}{K(K+1)(2K+3)(2K-1)},$$

$$\langle\cos^2\theta\rangle_{J=K+1,M}=\frac{2K^2+2K-1-2M^2}{(2K+3)(2K-1)}-\frac{2[K^2+K-4KM^2-M^2]}{(2K+1)(K+1)(2K+3)(2K-1)},$$

$$\langle\cos^2\theta\rangle_{J=K-1,M}=\frac{2K^2+2K-1-2M^2}{(2K+3)(2K-1)}-\frac{2[K^2+K+4KM^2+3M^2]}{K(2K+1)(2K+3)(2K-1)}.$$

APPENDIX D. TEMPERATURE DEPENDENCE OF LINE WIDTHS

The pressure normalized impact parameter is expressed as: $\Delta\nu/P=(nv/P\sqrt{2})b_{\text{eff}}^2$. In the classical kinetic gas theory model b is independent of temperature. Since $n/P\propto T^{-1}$, $v\propto T^{\frac{1}{2}}$, it follows that $\Delta\nu/P\propto T^{-\frac{1}{2}}$. From the more sophisticated line-breadth theories $b\propto T^{-1/2(n-1)}$, therefore $\Delta\nu/P\propto T^{-(n+1)/2(n-1)}$, for $n\rightarrow\infty$, $\Delta\nu/P\propto T^{-\frac{1}{2}}$. The temperature dependence of polarizability-exchange line breadths is found to be $\Delta\nu/P\propto T^{-0.63}$. This corresponds to an interaction varying as $1/r^8$ or $1/r^9$, which is not unexpected since $H_{\text{pol}}\propto 1/r^6$, $H_{\text{exch}}\propto 1/r^9$. The agreement between this theoretical value and several recent measurements[35,36] which yielded results near $T^{-0.9}$ is not too good.

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Diffusion Parameters of Thermal Neutrons in Water

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A method is described for the determination of neutron diffusion parameters by measurements of the decay of thermal neutrons in a finite moderator with a pulsed-neutron source and a time analyzer. In the theory for the method one takes into account the "diffusion cooling" effect, which decreases the temperature of thermal neutrons below the temperature of the moderator. Measurements are reported on a cylindrical geometry, involving between 1 and 4 liters of distilled water. Analysis of the result yields a value of 0.333 ±0.003 barns for the neutron-proton capture cross section, in good agreement with other measurements, and $(36\,340\pm750)[1-(0.20\pm0.04)\kappa_0^2]$ cm²/sec for the diffusion constant of thermal neutrons in water. The term involving the "buckling" κ_0^2 of the geometry is due to the diffusion cooling effect. The value of the diffusion constant for $\kappa_0^2=0$ leads to a value for the diffusion length in excellent agreement with the result of other measurements. The diffusion cooling effect is larger by a factor of 3.5 than the theoretical value, calculated for the model of a monatomic gas.

ONE of us[1] had previously suggested a detailed study, using a pulsed neutron source, of the decay rate of the neutron flux from a moderator as a means of determining the mean life for absorption, the diffusion constant, and the related diffusion length for neutrons in the moderator. The present article reports the result of such measurements on distilled water in a cylindrical geometry.

THEORY

When the diffusion theory approximation is used the decay of the thermal neutron flux from a finite homogeneous moderator can be described as the exponential decay of a number of modes, each corresponding to a different neutron distribution in the moderator. Each of these modes vanishes on the extrapolated boundary of the moderator, which lies at the extrapolation distance $0.71l_t$ outside the true boundary. The transport mean free path of the neutrons is l_t.

For the decay constant of the νth mode we obtain, using the diffusion theory,

$$\lambda_\nu=\lambda_a+D\kappa_\nu^2, \tag{1}$$

where λ_a is the absorption probability per unit time (the inverse of the mean life for absorption θ). In a moderator containing n_i nuclei of type "i" per cm³ with the absorption cross section σ_{ai}, the absorption probability λ_a is $\Sigma n_i\sigma_{ai}v$ and since, as is mostly the case, σ_{ai} varies as $1/v$, it follows that λ_a is independent of the velocity of the neutrons.

In Eq. (1) κ_ν^2 is the geometric buckling coefficient for the geometry in the νth mode. In the cylindrical geometry used in the present investigation we have for the buckling coefficient of the lowest, fundamental, mode:

$$\kappa_0^2=(2.405/R')^2+(\pi/H')^2, \tag{2}$$

where R' and H' are the extrapolated radius and height of the cylinder.

D in Eq. (1) is the diffusion constant of the neutrons in the moderator, which is proportional to the transport mean free path and the velocity of the neutrons. D will thus depend on the "temperature" T_n of the neutrons and is related to the diffusion constant D_0 at a standard temperature T_0 by the formula:

$$D=D_0[1+\beta(T_n-T_0)-\gamma(T_n-T_0)^2]. \tag{3}$$

It is usually assumed that thermal neutrons have a Maxwellian velocity distribution of the moderator temperature T_0, irrespective of the size of the moderating geometry. In reference 1 it was shown, however, that diffusion cooling will decrease the temperature T_n of thermal neutrons below the temperature T_0 of the moderator. The temperature difference increases in

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