Zeeman Effect and Line Breadth Studies of the Microwave Lines of Oxygen*

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Measurements made at 90°K and at 300°K on the O_2 line breadths show that the line breadth parameter, $\Delta\nu$, varies as T^{-x}, with x ranging in value from 0.76 for the 9_- line to 0.90 for the 1_- line. The type of variation of x with the rotational quantum number N indicates that both rotational resonance and quadrupole moment interactions are important factors in determining the line breadths. The Zeeman splittings observed for the 1_-, the 1_+, and the 3_- lines are in good agreement with the splitting predicted from first-order perturbation theory.

ZEEMAN EFFECT

THE Zeeman effect of the O_2 lines was first investigated by Schmidt, Budo, and Zempler[1] in the optical region, where the "microwave lines" appear as a fine structure superimposed upon the transitions of higher energy. Because of the low resolution obtainable in the optical region, their measurements were of necessity made with very high fields where the internal couplings were partly broken down. Similarly, the microwave paramagnetic resonance measurements on O_2 by Beringer and Castle[2] were made with such high fields that some decoupling of the internal momentum vectors was produced. In contrast, the present investigations were made with extremely weak fields (less than 100 gauss) at which no decoupling effects are expected.

A preliminary measurement of the Zeeman splitting of a single line (the 1_- line at 2.5-mm wavelength) reported earlier from this laboratory[3] indicated a discrepancy of about 20 percent with the weak-field Zeeman theory. The Zeeman work has been continued, and the more extensive and accurate measurements reported here are in complete agreement with theory.

The level splitting for the weak-field case is easily calculated from the vector model treatment.[3] It is given by

$$E_H = -g\beta H M_J, \tag{1}$$

where

$$g = \frac{J(J+1)+S(S+1)-N(N+1)}{J(J+1)}.$$

In the last expression N represents the quantum number for the end-over-end rotation,[4] S the electronic spin quantum number, and J the quantum number for the total angular momentum. Since for O_2 $S=1$, there are three J values for each value of N,

$$J=N+1,\quad N,\quad N-1.$$

Also,

$$M_J=J,\quad J-1,\quad J-2\cdots-J.$$

The selection rules are

$$\Delta J=\pm1,\quad \Delta N=0,\quad \text{and}\quad \Delta M_J=0,\quad \pm1.$$

Because the interaction with the microwave radiation field occurs through the magnetic dipole moment, the $\Delta M_J=\pm1$ components are observed when the externally imposed H is perpendicular to the magnetic component of the radiation, and the $\Delta M_J=0$ components when it is parallel to this field component. In our experiment we imposed the dc magnetic field by placing the wave-guide cell along the axis of a solenoid. With this arrangement both the σ and π components are observable. Nevertheless, for two of the lines investigated, the $1_+(J=2\rightarrow1)$

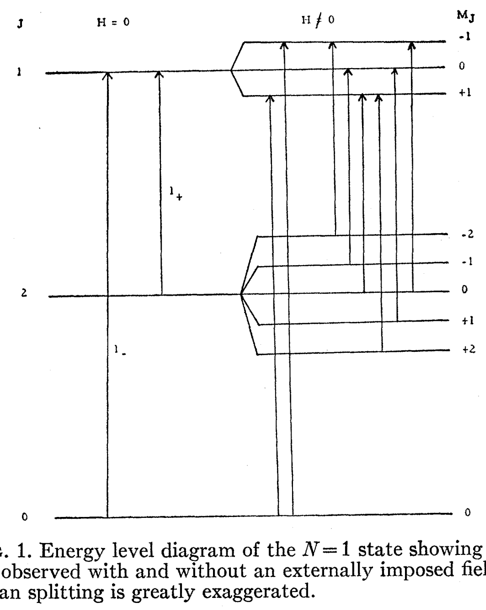

FIG. 1. Energy level diagram of the $N=1$ state showing transitions observed with and without an externally imposed field. The Zeeman splitting is greatly exaggerated.

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[1] Schmidt, Budo, and Zempler, Z. Physik **103**, 250 (1936).
[2] R. Beringer and J. G. Castle, Jr., Phys. Rev. **81**, 82 (1951).
[3] Gordy, Smith, and Trambarulo, *Microwave Spectroscopy* (John Wiley and Sons, Inc., New York, 1953), Sec. 3.2b.
[4] The symbol K has been conventionally used in the past, but because of possible confusion with symmetric-top notation [see J. H. Van Vleck, Revs. Modern Phys. **23**, 213 (1951)] we have [following Gordy, Smith, and Trambarulo, *Microwave Spectroscopy* (John Wiley and Sons, Inc., New York, 1953)] adopted the notation N as recommended by an international committee on nomenclature headed by Professor F. A. Jenkins [J. Opt. Soc. Am. **43**, 410 (1953)].

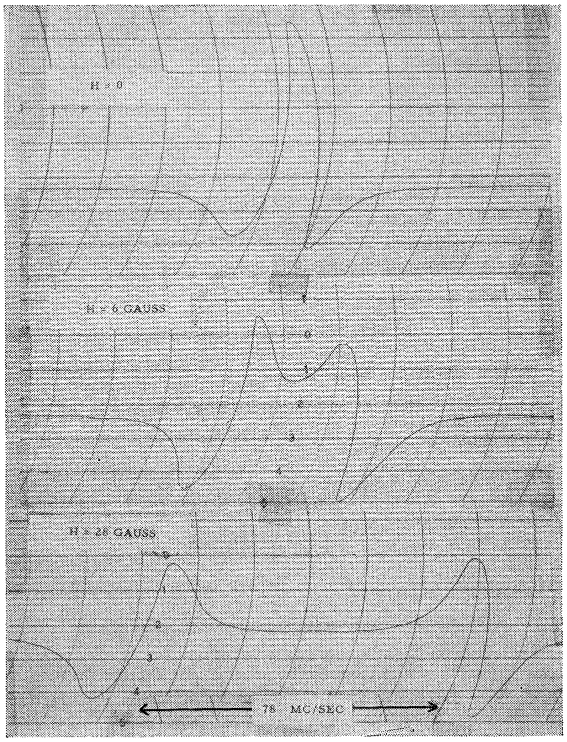

FIG. 2. Recording of the 1_+ line ($J=2\rightarrow1$) with and without magnetic fields.

and 1_-($J=0\rightarrow1$), no displacement of the $\Delta M_J=0$ component is produced by the field, and with the detection system employed which depends upon modulation by an ac magnetic field these undisplaced components are not detected. Furthermore, only two $\Delta M_J=\pm1$ components are observed for both the 1_+ and 1_- lines. The reasons for this simplicity will be apparent from an examination of the energy level diagram of Fig. 1. Although there are six $\Delta M_J=\pm1$ components for the $J=2\rightarrow1$ line, two sets are triply degenerate, and, hence, there are only two distinguishable components. Like those of the 1_- line these are displaced equally on either side of the unsplit zero-field line and likewise have the same splitting for a given field as those of the 1_- line.

Figure 2 shows the 1_+ line both with and without the application of the dc field. The method of detection employs small amplitude Zeeman modulation and is the same as that previously described.[5] With this method of detection the graph of the unsplit (zero dc field) line represents the second derivative of the actual line contour, whereas that for the individual Zeeman components represents the first derivative of their line contour. For the 3_- line ($J=2\rightarrow3$) there are many components which were incompletely resolved with the low fields employed in our experiments. The outer components were sufficiently separated, however, for measurement. These gave results in good agreement with theory.

Table I gives a comparison of the experimentally measured quantity $2\Delta\nu/H$ for the different lines with the values calculated with Eq. 1. Here $2\Delta\nu$ represents the separation of the observed doublets of the 1_- and 1_+ lines and of the outer Zeeman components of the 3_- line. The theoretical values lie well within the limits of error of the experimental ones. Since the $J=0$ state is not split by an external field, it is possible to evaluate the g factor for the $J=1$, $N=1$ state from the measured splitting of the $J=0\rightarrow1$ line. The result is 0.99 ± 0.01, in agreement with the theoretical value of 1.00. With the observed g factor of the $J=1$ level thus determined, the g factor for the $J=2$, $N=1$ state can then be obtained from the splitting of the $2\rightarrow1$ line. It is 1.00 ± 0.01 as compared with the theoretical value of 1.00.

TABLE I. O_2 Zeeman splitting.[a]

Line	$2\Delta\nu/H$ in (Mc/sec)/gauss Observed	Calculated
1_-	2.78 ± 0.02	2.80
1_+	2.80 ± 0.02	2.80
3_-	5.14 ± 0.04	5.12

[a] The splitting, $2\Delta\nu$, represents the separation of the observed doublet for the 1_- and 1_+ lines and the separation of the two outermost components for the 3_- line.

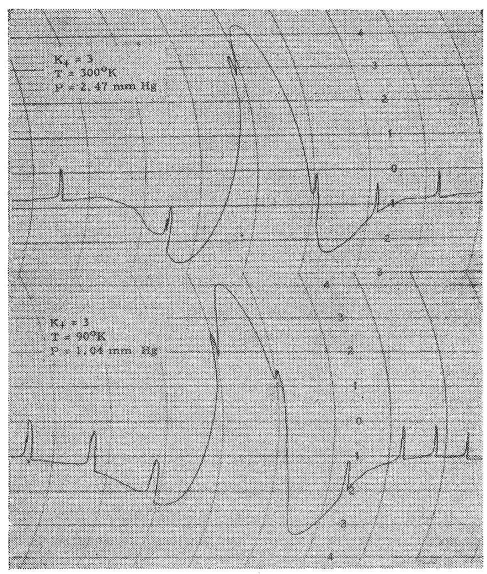

FIG. 3. Recording of the 3_+ line at room and at liquid air temperatures. Pressures are adjusted to give approximately equal line widths at the two temperatures. Small pips represent frequency markers.

[5] Burkhalter, Anderson, Smith, and Gordy, Phys. Rev. **79**, 651 (1950); Anderson, Smith, and Gordy, Phys. Rev. **87**, 561 (1952).

TEMPERATURE DEPENDENCE OF THE LINE BREADTH

The line breadth parameters for individual lines of the O_2 microwave spectrum have now been measured by three groups of investigators. Those measured by Anderson, Smith, and Gordy[5] and by Artmann and Gordon[6] are in good agreement, except that the former observers detected a decrease in the line breadth parameter with increasing N after the maximum of the Boltzmann distribution. This effect was attributed to the influence of rotational resonance on the line widths. One of the purposes of the present investigation is to gain additional information regarding the rotational resonance effect by shifting the Boltzmann maximum through cooling the sample. Another purpose is to obtain information about the other factors which significantly influence the line breadths.

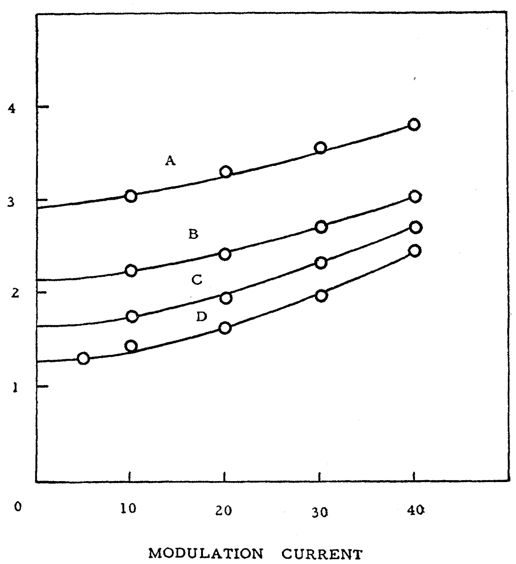

FIG. 4. Plot of measured widths for the 9_- line *versus* ac modulation current in ma. The pressures are, in mm of Hg, 2.62 for Curve A, 1.53 for Curve B, 0.84 for Curve C, and 0.45 for Curve D.

Figure 3 shows a line at both liquid air and at room temperature with the relative pressures adjusted to give approximately equal widths. To a first approximation, the observed shapes are second derivatives of the true line contours.[5] This approximation becomes better as the modulation amplitude is decreased. With the superimposed lattice of markers, the separation of the two minima was measured for several values of the modulating field, the lowest value being the lowest for which a usable line strength was obtainable. The mean value of $\Delta\nu$ for three runs at each modulation was plotted against the amplitude of the modulating field, and the best curve through these points was extrapolated to zero modulation, as shown in Fig. 4. This was done at four pressures. The "zero-field" values were then

[6] J. O. Artmann and J. P. Gordon, Phys. Rev. **87**, 227 (1952).

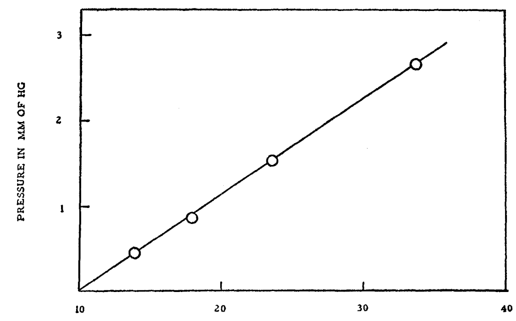

FIG. 5. Plot of zero-field line width, $2\Delta\nu$, *versus* pressure for the 9_- line. The slope yields $\Delta\nu=4.55$ (Mc/sec) per (mm of Hg).

plotted against pressure, and the best straight line was drawn through the point. Figure 5 shows this plot for the 9_- line. The residual line breadth for zero pressure is due primarily to the broadening from the earth's magnetic field. The slope of the curve, however, is directly proportional to the line breadth parameter.

The results obtained are listed in Table II. The lines for N greater than 9 were so weak at liquid air temperatures that reliable measurements on them could not be obtained. Our results for room temperature are in good agreement with the earlier results of Anderson, Smith, and Gordy,[5] and the average line breadths of all the lines measured 1.95 (Mc/sec)/(mm of Hg) is in good agreement with the average obtained by Artmann and Gordon,[6] 1.94 (Mc/sec)/(mm of Hg). Furthermore, the variation of the line breadth parameter with temperature tends to confirm the contribution of rotational resonance to the line breadth noted by Anderson, Smith, and Gordy. The latter effect is revealed by the comparison of the line breadth ratios at liquid air with those at room temperature (Table II). This ratio increases consistently from the $K=9$ to the $K=5$ line. The $N=3$ and $N=5$ states are near the Boltzmann maximum at the temperature of liquid air, whereas at room temperature the Boltzmann maximum occurs near $N=11$.

The exponents of the temperature-dependence relation, $\Delta\nu/P=CT^{-x}$, given in Table II offer some insight into the broadening mechanism. Mizushima's theory[7] of oxygen broadening, based on a quadrupole-quadrupole interaction only, predicts that $\Delta\nu/P$ should be

TABLE II. O_2 line breadth data.

Line	$\Delta\nu$ in (Mc/sec) per (mm of Hg) $T=300°K$	$T=90°K$	$\frac{(\Delta\nu)_{T=90}}{(\Delta\nu)_{T=300}}$	x $(\Delta\nu=CT^{-x})$
1_-	1.97	5.80	2.94	0.90
1_+		5.63		
3_+	2.07	5.77	2.80	0.85
5_+	1.80	5.22	2.90	0.90
7_{-1}	2.01	5.52	2.74	0.84
9_-	1.94	4.55	2.35	0.76

[7] M. Mizushima, Phys. Rev. **83**, 94 (1951).

proportional to $T^{-\frac{3}{2}}$. The interactions considered by Anderson,[8] polarizability and rotational resonance, show a T^{-1} behavior. The statistical theory of Margenau[9] is density, but not velocity, dependent and should exhibit a T^{-1} behavior also. Thus, the values found show that much of the broadening is due to the quadrupole interaction. The results of Beringer and Castle[10] for strong-field Zeeman transitions, in agreement with the present work, show temperature dependences between $T^{-\frac{3}{2}}$ and T^{-1}. From the knowledge at hand it seems that the quadrupole-quadrupole and the rotational resonance interactions are both important mechanisms in the broadening of oxygen absorption spectra.

[8] P. W. Anderson, Phys. Rev. **76**, 647 (1949); **80**, 511 (1950).
[9] H. Margenau, Phys. Rev. **76**, 121 (1949).
[10] R. Beringer and J. G. Castle, Jr., Phys. Rev. **81**, 82 (951).

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Some Observations of Double- and Triple-Quantum Transitions*

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Data are presented which show that it is possible to observe transitions for which $\Delta J=0$, $\Delta m_J=\pm 2$ or ± 3 in a molecule characterized by a total angular J. It is also possible to observe transitions for which $\Delta F=0$, $\Delta m_F=\pm 2$ or ± 3 in an atom characterized by a total angular momentum F. In each case the process occurs by the absorption or stimulated emission of two or three equienergetic quanta.

CERTAIN experiments, to be described elsewhere, require the measurement of the frequencies of the lines resulting from the transitions $\Delta J=0$, $\Delta m_J=\pm 1$ in the ground, $^3\Sigma$, state of the O_2 molecule for several values of K, the rotational angular momentum. At low values of the magnetic field, all lines for a particular J value coincide, but at magnetic fields sufficiently high to require terms, quadratic in the field, for the representation of the energy levels, $2J$ lines may be expected to appear for each J value.

The observation of the indicated spectrum presents considerable difficulty. A molecular beam of O_2, issuing from a source of 77°K was detected on a Pirani gauge, and the total deflection of an indicating galvanometer was small. In addition, even at 77°K, a significant number of rotational levels is occupied and the population of each state is small. For example, the total population for $K=1$ is about 15 percent and the population of each J, m_J state is about 1.7 percent. Thus 3.3 percent of the particles in the beam may be involved in a particular transition. However, as Torrey[1] points out, the velocity distribution of the molecules has the effect of permitting a maximum of 0.766 of the particles to undergo a transition and the maximum effect which would appear is then about 2.6 percent of the refocused beam. It is to be noted that the effect to be observed as a consequence of a transition will generally be less than indicated as a consequence of an imperfect adjustment of the rf amplitude which induces the transitions and a limited deflecting power of the apparatus in which the transitions are observed.

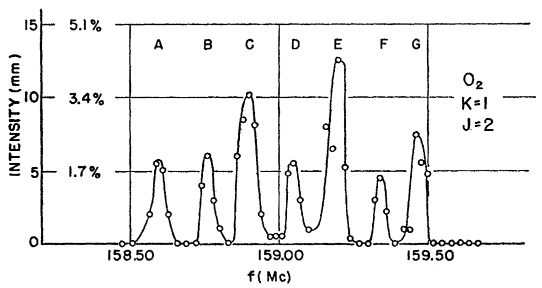


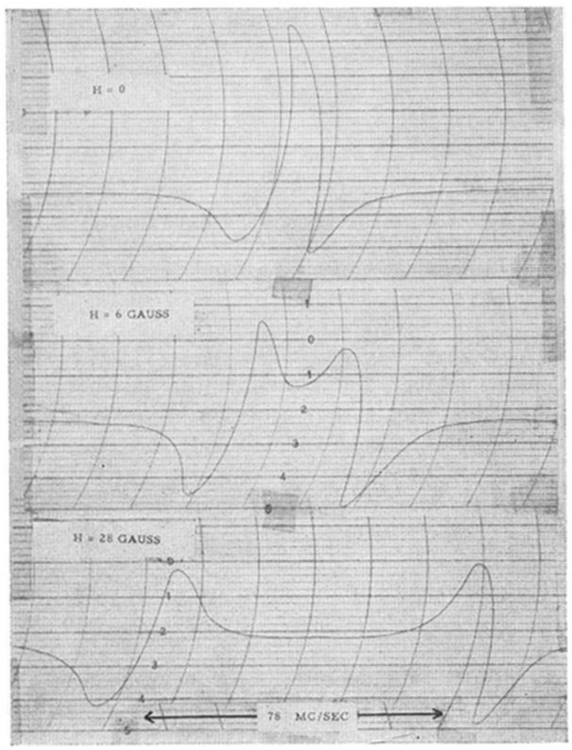
Fig. 1. The spectrum resulting from the transitions $\Delta J=0$, $\Delta m_J=\pm 1$ in the $^3\Sigma$ state of O_2 and for $K=1$, $J=2$ at a field of about 113 gauss. The intensity of the lines is given both as a fraction of the total beam and in absolute magnitude as measured on the apparatus.

In Fig. 1 is shown the spectrum resulting from the transitions which are nominally characterized by $\Delta m_J=\pm 1$ in the state $K=1$, $J=2$. It is at once seen that seven lines appear instead of the four predicted. Five of the lines (A, B, D, F, G) have an intensity of the order of that predicted for a single line, while two of the lines (C, E) have an intensity far greater than that predicted, beyond the range of experimental uncertainty.

We ascribe the observed spectrum to three processes: (1) the absorption or emission of a single quantum to give a transition for which $\Delta m_J=\pm 1$ (the lines A and G are produced by this process exclusively); (2) the absorption or emission of two equienergetic quanta to give a transition for which $\Delta m_J=\pm 2$ (the lines B, D, and F arise from this process); (3) the absorption or emission of three equienergetic quanta to give a transition for which $\Delta m_J=\pm 3$. The lines C and E result from

* This research has been supported in part by the U. S. Office of Naval Research.

[1] H. C. Torrey, Phys. Rev. **59**, 293 (1941).



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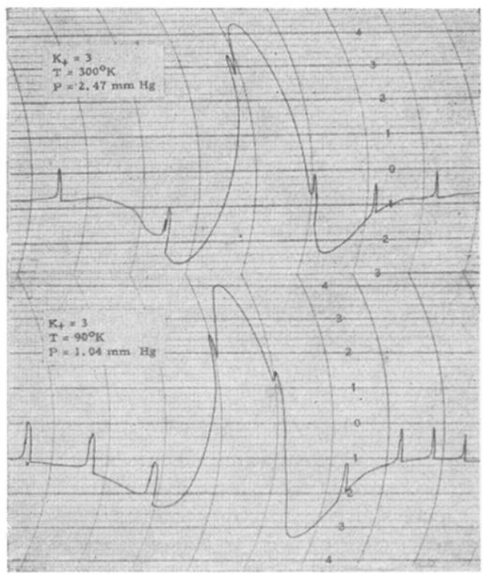

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