Microwave Magnetic Resonance Spectrum of Oxygen*

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(Received September 7, 1950)

The complex magnetic-resonance spectrum of oxygen gas is observed at 9340 Mc/sec in magnetic fields up to 9000 oersted. Some 40 lines are resolved. A partial analysis of the spectrum is made with the help of Henry's recent Zeeman theory of O_2. Other lines are identified by the temperature dependence of the relative intensities. Line widths are measured by several techniques and range from 0.6 to 4 Mc/sec/mm Hg at room temperature. The temperature and pressure dependence of the line widths are investigated.

I. INTRODUCTION

MOLECULES which have permanent magnetic moments exhibit an absorption spectrum arising from magnetic dipole transitions between Zeeman levels of a single rotational state. Such spectra have been observed by us[1,2] at three-centimeter wavelengths using the method of magnetic resonance. The present paper describes in detail our measurements with oxygen gas.

The details of the interaction of an external magnetic field with the molecular electronic orbital and spin angular momenta depend upon the internal coupling of these momenta. In Hund's case (a), where the electronic orbital momentum and spin momentum are strongly coupled to the internuclear axis and weakly coupled to the nuclear rotation, the external field effectively interacts with their resultant J; at available field intensities the magnetic level displacements are given to fair approximation by simple Zeeman theory.[3] Nitric oxide[1] exemplifies this situation. In extreme case (b) coupling where the electronic spin is very weakly coupled to the orbital and rotational momenta, an external field of low intensity breaks down the coupling and produces the Paschen-Back effect.[3] In both of these extreme situations the spectral interpretation can be made by vector-model considerations; perturbation calculations are only necessary when accurate line positions and intensities are required. Oxygen, in which the spin-rotation coupling is about 2 cm^{-1} is in neither of these simple categories for the conditions of the present experiment. Fields sufficient to separate adjacent magnetic levels by the observing frequency (0.3 cm^{-1}) break down the internal coupling to a considerable degree, but not nearly enough to produce the Paschen-Back regularities.

The ground electronic state of the oxygen molecule is $^3\Sigma$. The angular momenta in zero field approximate case (b) coupling. The rotational states are characterized by K (total angular momentum except for spin) and each K state is split into a triplet by the interaction[4] of K with S. These levels are denoted by J where $J=K$, $K\pm1$. K takes on all odd integral values, and at ordinary temperatures a large number of K states are well populated. (At room temperature the Boltzmann factor, apart from the degeneracy, for $K=17$ is about a tenth that for $K=1$.) The separation of J levels differs only slightly in the various K states; the K to $K+1$ and K to $K-1$ spacings being about 2 cm^{-1}.

On introduction of a magnetic field each K triplet splits into 3 $(2K+1)$ Zeeman levels. In view of the large number of well-populated states several hundred magnetic levels become available for magnetic resonance transitions. At very low fields the M level energy displacements follow Zeeman theory.[3] If these formulas held at fields of a few thousand oersteds, only the magnetic levels of the $K=1$ state would be separated sufficiently to be resonant at our observing frequency. However, at the field strengths employed, the internal coupling breaks down; some observable transitions for high K values are pushed to moderate fields and some of those for low K values are displaced beyond attainable field strengths.

The absence of a simple coupling scheme and the large number of levels involved makes it impossible to analyze the spectrum without the use of an accurate theory. Such a Zeeman theory for O_2 was developed by Schmid, Budó, and Zemplén.[5] Their formulas result by introducing the magnetic field interactions after computing the coupling which leads to the K triplets. These formulas are not sufficiently accurate for use here, and are particularly poor for low K values. Henry[6] has recently computed the positions and intensities of several of our lines by a more exact procedure which includes all of the perturbations at one time. Our agreement with these calculations is quite good and will be discussed in detail in Sec. II.

Henry's calculations are very laborious and have been carried out in detail for only the magnetic levels of the $K=1$ and $K=3$ states. They serve to identify only a few of the observed lines. A partial identification of other lines was made by observing the spectrum at

* Assisted by the ONR.
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[1] R. Beringer and J. G. Castle, Jr., Phys. Rev. **78**, 581 (1950) and Phys. Rev. **76**, 868 (1949) for the gas NO.
[2] R. Beringer and J. G. Castle, Jr., Phys. Rev. **75**, 1963 (1949) for O_2 and J. G. Castle, Jr. and R. Beringer, Phys. Rev. **80**, 114 (1950) for NO_2.
[3] G. Herzberg, *Molecular Spectra and Molecular Structure* (Prentice-Hall, Inc., New York, 1939).
[4] See R. Schlapp, Phys. Rev. **51**, 342 (1937), Phys. Rev. **39**, 806 (1932) for a precise theory of the O_2 states in zero external field.
[5] Schmid, Budó, and Zemplén, Z. Physik **103**, 250 (1936).
[6] A. Henry, Phys. Rev. **80**, 396 (1950).

room and at liquid air temperatures. Comparison of intensities permits an estimation of the Boltzmann factor and hence of the K values of the unidentified lines. These measurements will be discussed in Sec. III.

The main experimental procedures employed in most of the present studies have been described.[1] A microwave signal is transmitted through a gas-filled resonant cavity and received with a bolometer. A dc magnetic field is adjusted until the quantum frequency of an allowed transition between magnetic sublevels coincides with the observing frequency. The microwave magnetic field induces transitions and is partially absorbed. A small ac magnetic field modulates the absorption and the microwave power to the bolometer. The modulation is detected by the bolometer and is amplified, usually at the fundamental of the modulation frequency, in which case the output signal *vs* H is essentially the first derivative of the absorption line. The amplified signal is detected in a phase-coherent mixer and used to deflect a long-period galvanometer. The galvanometer readings trace the first derivative of the absorption line contour as the dc magnetic field is varied.

Several minor changes in the apparatus and experimental procedures were made in the course of the present experiments. One of these, detection at the second harmonic of the modulation frequency, is discussed in Sec. IV. Another change is the use of a direct-coupled triode preamplifier. When preceded by a well-shielded input transformer this amplifier had a measured noise voltage at 30 cycle/sec of only twice the Johnson noise of the 400-ohm signal source. Under ideal conditions, the preamplifier improved our minimum detectable signal by a factor ten or more over that described,[1] but this factor was not always realized because of the increased noise contribution from the microwave oscillator. This noise was particularly troublesome when the stabilized oscillator was tightly coupled to the gas-filled cavity and when that cavity had an unusually high Q.

II. OBSERVATIONS AND ANALYSIS BY THEORY

In all of the experiments the observing frequency was 0.31 cm^{-1} (9340 to 9360 Mc/sec); the magnetic field intensities ranged from 3000 to 9000 oersteds. In this range of field intensities about 40 lines are observed at room temperature. A typical spectrum is shown in Fig. 1. The line contours are essentially the first derivatives of the absorption coefficients *vs* H except for distortions produced by finite modulation.[7] The room temperature measurements employed a TM_{011} mode cylindrical cavity with H parallel to the axis of the cavity.

Table I lists the lines observed in Fig. 1 and other runs, their relative intensities,[8] and resonance field values for an observing frequency of 9340 Mc/sec. The lines are labeled with Arabic numbers for purpose of reference. Table I also lists the calculated resonance field values from Henry's work,[6] the K, J, $M \rightarrow M-1$ values for each, and the calculated relative intensities. It is seen that the agreement with theory is generally satisfactory.

The absolute strength of the absorption can be computed in terms of observed quantities by the formulas of reference 1. Expressed as an absorption Q of the transition, the computed strength at resonance is

$$\frac{1}{Q_A}=\frac{2fN\nu\pi\mathfrak{M}^2\mu_0^2}{(2J+1)kT\Delta\nu}$$

for an O_2 line observed in a TM_{011} cavity at frequency ν. Here f is the fraction of all molecules which are in the

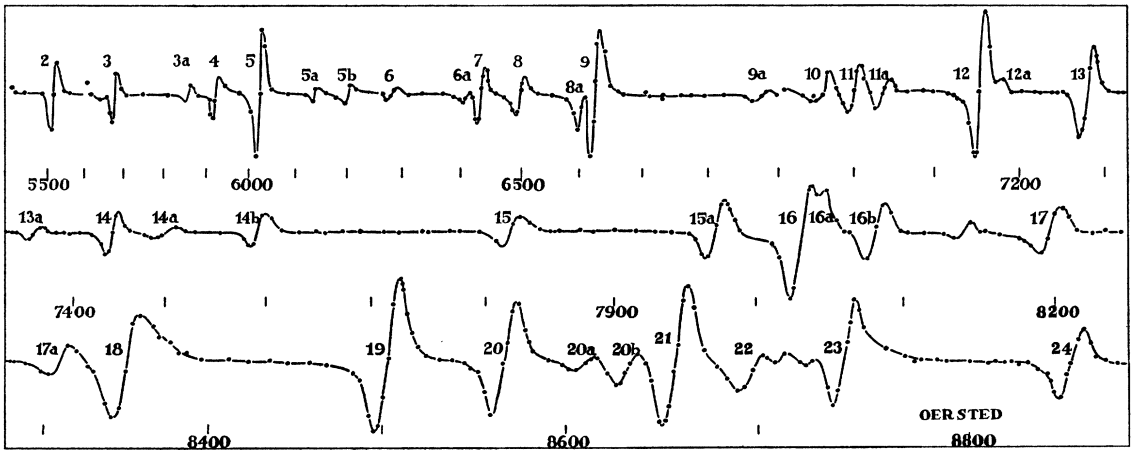

FIG. 1. Magnetic resonance spectrum of O_2 at 300°K. Fixed observing frequency is 9360 Mc/sec, O_2 pressure 4.0 mm Hg, modulation amplitude 8.5 oersted. The ordinate in each of the three traces is the galvanometer position. Lines are numbered to correspond to the text.

[7] These distortions are discussed in reference 1 on p. 584.

[8] The *relative intensity* is here defined as a number proportional to the transition matrix element squared times the population factor of the rotational state involved. It is thus independent of the line width and comes directly from theory. In terms of the observed signal strength: intensity $\propto$ (signal strength)$\Delta\nu$.

TABLE I. Magnetic resonance absorption lines in oxygen at 9340 Mc/sec.

Line No.	Observed Resonance field (oersted)	Observed relative intensity at 300°K	Calculated resonance field (oersted)	Calculated relative intensity at 300°K	Quantum numbers $K, J, M \rightarrow M-1$	Relative $\Delta\nu$
1	4100	—			——	——
2	5527	0.48	5524	0.53	$1, 1, 0 \rightarrow -1$	0.89
3	5659	0.52				1.4
3a	5845	0.24				1.5
4	5925	0.30				0.78
5	6014	Taken as 1.00	6023	1.00	$1, 2, 2 \rightarrow 1$	Taken as 1.00
5a	6138	0.09				0.9
5b	6190	0.12				0.8
6	6280	0.11				1.2
6a	6406	0.14				1.2
7	6437	0.35				0.82
8	6497	0.36				1.2
8a	6600	0.26				0.6
9	6620	1.1	6634	1.50	$1, 2, 1 \rightarrow 0$	0.99
9a	6884	0.10				1.3
10	6965	0.39				1.1
11	7000	0.29				0.70
11a	7037	0.26				1.1
12	7149	0.92	7170	1.00	$1, 2, 0 \rightarrow -1$	0.97
12a	7172	0.08				0.6
13	7284	0.39				0.69
13a	7357	0.16				1.3
14	7445	0.22	7448	0.62	$3, 2, 0 \rightarrow -1$	0.74
14a	7496	0.20				1.8
14b	7585	0.15				0.6
15	7814	0.19				0.82
15a	7962	0.29				0.7
16	8025	0.68				0.76
16a	8038	0.07				0.5
16b	8076	0.25				0.6
17	8196	0.23				0.67
17a	8310	0.11				0.51
18	8352	0.76				0.9
19	8500	0.83	8529	1.24	$3, 4, 0 \rightarrow -1$	0.70
20	8563	0.48				0.57
20a	8607	0.07				0.5
20b	8626	0.09				0.3
21	8657	0.58				0.55
22	8690	0.18				0.55
23	8745	0.48				0.60
24	8857	0.25				0.48

relevant J state, N the number of molecules per cm^3, $\mathfrak{M}^2$ the square of the matrix element of the transition, μ_0 the Bohr magneton, and $\Delta\nu$ half of the line width at half maximum intensity. To sufficient approximation

$$f=\frac{(2J+1)e^{-BK(K+1)hc/kT}}{\sum_K \sum_J (2J+1)e^{-BK(K+1)hc/kT}},$$

where $B=1.44$ cm^{-1}. Formulas for the square of the matrix element are given in reference 6. For line No. 2, $K=1$, $J=1$, the M values are 0, -1, and $\mathfrak{M}^2=\frac{1}{2}$. Other constants are $f=0.014$ for $T=300$°K, $N=3.2\times10^{16}$, and $\Delta\nu=1.9$ Mc/sec at 1 mm Hg, giving $Q_A=2.2\times10^8$. The observed signal at optimum modulation referred to the bolometer terminals is 1.0×10^{-6} volt for line No. 2 at 300°K. This corresponds to an observed $Q_A=7.2\times10^8$. The disagreement is probably outside of experimental errors in the measured signal strength, apparatus gain, and line width determinations. Other lines also give signal strengths smaller, by a factor three to five, than those calculated from theory.[6]

The identifications of the observed spectral lines using Henry's calculations were in most cases unambiguous on the basis of the resonance field alone. When this was not the case, use was also made of the theoretical relative intensities. Finally, the change in line intensity with temperature was used to confirm the assignments and to make K value assignments for lines not computed by Henry. This procedure will be discussed in Sec. III.

III. OBSERVATIONS AND ANALYSIS BY TEMPERATURE CHANGE

The relative populations of the various rotational states of O_2 can be changed markedly by a change from room temperature to that of liquid air. These population changes are observed as changes in the relative signal strengths[9] of the various lines, and allow the rotational

[9] The signal strength is defined as being proportional to the output galvanometer deflection at optimum modulation and hence proportional to $1/Q_A$. In terms of our definition of intensity: signal strength $\propto$ (intensity)/$\Delta\nu$.

states of the lines to be identified thereby. The procedure is as follows.

The observed signal strength is proportional to $1/Q_A$. For a given gas pressure and temperature, various lines have signal strengths proportional to $\mathfrak{M}^2 f/(2J+1)\Delta\nu$. Experimental evidence shows that $\Delta\nu$ scales with temperature by approximately the same factor for all of the lines, and that $\Delta\nu$ is proportional to the pressure at constant temperature. Since f depends to a good approximation only on K and the temperature, a comparison of sets of relative signal strengths at two known temperatures serves to assign K values. The observed signal strengths and results of such an analysis are given in Table II. It is seen that the K values obtained in this way are in good agreement with those deduced in Table I by correlation with Henry's calculations.

The observations at liquid air temperature required certain apparatus modifications. A circular TE_{111} mode cavity, contained in a Dewar vessel, was used to detect resonance. The cavity was oriented with its axis vertical; two vertical wave guides of thin walled brass supported the cavity from above and carried the microwave power to and from the cavity through circular holes in its top plate. The wave-guide electric fields were parallel to the dc magnetic field of the electromagnet. In this configuration, unlike that for the TM_{011} cavity, the microwave magnetic field in the cavity has components both parallel and perpendicular to the dc magnetic field. Only the perpendicular components contribute to the observed spectrum.

The signal-to-noise ratio was greater for the low temperature observations than for those at room temperature. Lowering the temperature increases the cavity Q, increases the difference in population of adjacent M levels, and decreases the partition function, combining to increase the signal strength for low K lines. In practice, these gains are partially offset by the

TABLE II. Assignment of K values by temperature dependence of the signal strength.

Line No.	Relative signal strength $T=300°K$	$T=78°K$	Assigned K
1	—	0.06	—
2	0.54	0.54	1
3	0.38	0.34	3
3a	0.16	<0.03	⩾9
4	0.39	0.30	3
5	1.0	1.0	1
5a	0.10	<0.05	⩾5
5b	0.14	<0.03	⩾9
6	0.09	0.09	1
6a	0.12	0.05	7
7	0.43	0.23	5
8	0.30	0.12	7
8a	0.44	<0.04	⩾9
9	1.1	1.1	1
9a	0.08	0.06	3 or 5
10	0.30	0.03	9 or 11
11	0.41	0.05	9 or 11
11a	0.24	0.03	9 or 11
12	0.95	0.95	1
12a	0.14	<0.04	⩾7
13	0.57	0.19	7
13a	0.12	0.05	5 or 7
14	0.30	⩾0.21	3 or 5
14a	0.11	<0.03	⩾7
14b	0.25	<0.01	⩾5
15	0.23	0.12	5
15a	0.41	<0.03	⩾11
16	0.89	0.50	5
16a	0.14	<0.07	⩾11
16b	0.41	<0.03	⩾11
17	0.35	0.12	7
17a	0.22	—	—
18	0.85	0.23	7 or 9
19	1.2	0.80	3 or 5
20	0.85	0.17	9
20a	0.14	<0.03	⩾9
20b	0.30	0.03	9 or 11
21	1.0	0.40	7
22	0.33	0.07	9
23	0.80	0.24	7
24	0.52	<0.03	⩾11

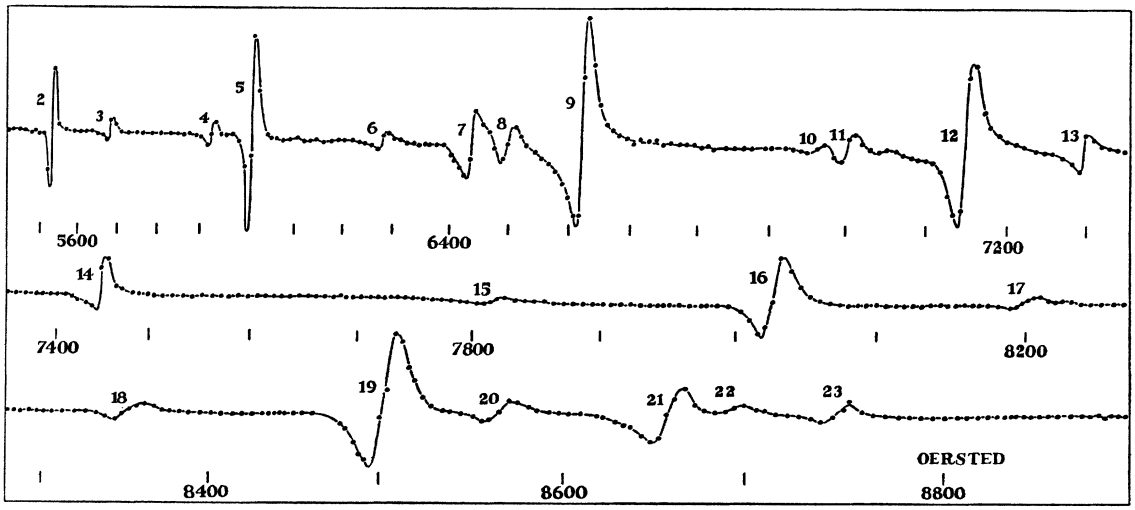

FIG. 2. Magnetic resonance spectrum of O_2 at 85°K. Fixed observing frequency is 9340 Mc/sec, O_2 pressure 3.6 mm Hg, modulation amplitude 4.2 oersted. Ordinates are galvanometer position. Lines are numbered to correspond to the text.

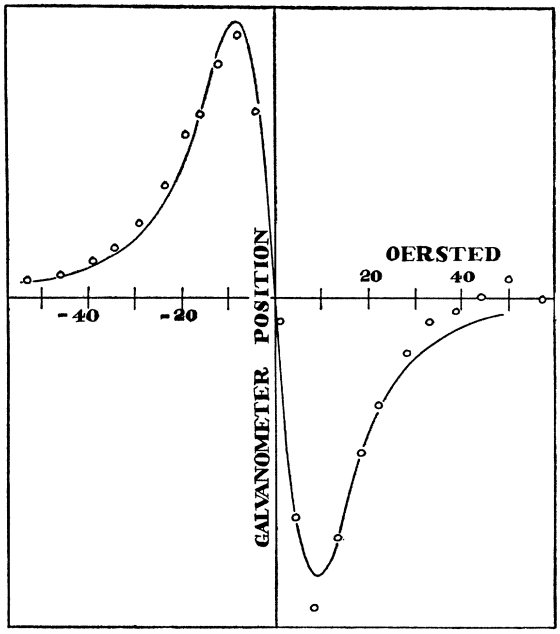

FIG. 3. First harmonic signal of a line at small modulation amplitude. The solid line is the first derivative of a Lorentz line shape with $\Delta H=14$ oersteds. Points are observed galvanometer positions for line No. 5 at 300°K and 10.1 mm Hg pressure. The ΔH value is not arbitrary but is taken from the measurements of Table III. The modulation amplitude is 3.8 oersteds in the figure.

increased 30-cycle/sec noise of our stabilized oscillators when working into the higher Q cavity. Figure 2 shows a spectrum taken with this apparatus at liquid air temperature. The pronounced changes in relative signal strength referred to above are apparent on comparison of Figs. 1 and 2.

IV. LINE WIDTHS

A considerable part of our effort was concerned with line width measurements. Even the earliest work showed that all of the lines did not have the same width, and it was hoped to find some regularities of possible theoretical interest. Such regularities could also possibly account for the anomalous shape of the unresolved 2 cm^{-1} gas absorption band in O_2, where a single $\Delta\nu$-assignment for lines of different J and K seemed unable to fit observations throughout the band.[10,11] Recently the Duke University group[12] have reported line widths for three resolved lines of the 2 cm^{-1} spectrum, and find them to decrease with increasing K.

The method of obtaining line widths using large modulation amplitudes has been described.[1] One measures the signal contours using modulations of various magnitudes. Assuming a Lorentz-Van Vleck-Weisskopf line shape, the line contours are computed, and graphs of certain parameters of the contours *vs* modulation allow the line widths to be evaluated by extrapolation.

Recent apparatus modifications permit two other methods to be used. Increases in signal-to-noise ratio. largely due to the low noise preamplifier, permit line contours to be observed for low modulations where distortions are negligible. Figure 3 shows such a contour for line No. 5. The solid line is the first derivative of a Lorentz line shape, and is seen to fit the data satisfactorily.

Another method of line width measurement uses the second harmonic signals of the modulated absorption line. Whereas the fundamental frequency signal is most useful for determining the resonance field of a line, since the slope of the contour is greatest at resonance, the second harmonic signals allow more precise line width determinations, their contours having steepest slope near the half-intensity points of the line.

The procedure for deducing the line width from the measurements of modulation-broadened second harmonic contours is similar to that for the fundamental frequency method. One assumes a Lorentz line shape given by

$$\Delta H^2/[(H-H_0)^2+\Delta H^2].$$

The second harmonic signals are then proportional to the Fourier coefficient

$$B_2=\frac{1}{\pi}\int_{-\pi}^{\pi}\frac{\cos 2\omega t\, d(\omega t)}{[(H_1/\Delta H)+(H_m/\Delta H)-(H_m/\Delta H)(1+\cos\omega t)]^2+1},$$

where $H_1=H-H_0+H_m\cos\omega t$. B_2 as a function[13] of H_1 is the observed line contour at frequency 2ω for a

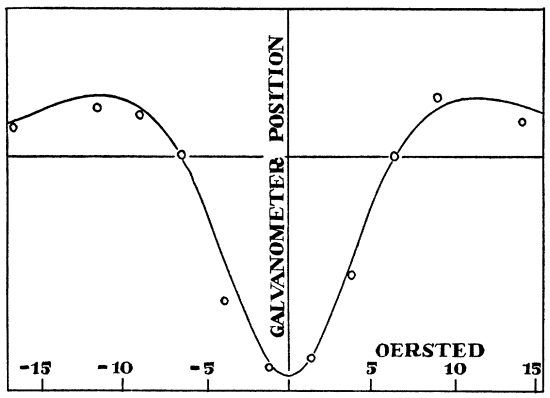

FIG. 4. Second harmonic signal contour of line No. 19. The solid line is the function B_2 plotted for the modulation amplitude used ($H_m=2.9$ oersteds) and a line width, $\Delta H=10.7$ oersteds. The circles are the observed galvanometer positions for an O_2 pressure 2.6 mm Hg at 78°K. The modulation distortion is quite small for the contour shown.

[10] J. H. Van Vleck, Phys. Rev. **71**, 413 (1947).
[11] R. Beringer, Phys. Rev. **70**, 53 (1946); H. R. L. Lamont, Phys. Rev. **74**, 353 (1948); Strandberg, Meng, and Ingersoll, Phys. Rev. **75**, 1524 (1949).
[12] Burkhalter, Anderson, Smith, and Gordy, Phys. Rev. **77**, 152 (1950); Phys. Rev. **79**, 224 (1950); and Phys. Rev. **79**, 651 (1950).
[13] Similar integrals are evaluated by W. D. Hershberger, J. Appl. Phys. **19**, 411 (1948).

modulation amplitude H_m at frequency ω. A typical observed contour is shown in Fig. 4. Figure 5 shows the dependence of the intercept (points where $B_2=0$) separation with modulation amplitude as computed from the B_2 coefficients; it is used to determine ΔH from measurements of H_m and the intercept separation.

Our best line width measurements were made with the second harmonic method. Contours such as Fig. 4 were plotted, and the intercept separations found. These were extrapolated to zero modulation using Fig. 5 to determine ΔH.

The magnitude of ΔH depends, among other things, on the field value at which it is observed. Not ΔH, but $\Delta\nu$, the frequency width of the line, is the fundamental quantity in line broadening theory, and the two are related by

$$\Delta\nu=\Delta H\cdot\nu/H,$$

where ν is the fixed observing frequency and H the resonance field of the line. Thus at high fields the lines are intrinsically wider in field strength units. In the discussion which follows the line widths are reduced to $\Delta\nu$-units using the above formula.

The line width measurements were designed to discover the dependence of $\Delta\nu$ on temperature, pressure, and the quantum numbers. Figure 6 shows the observed pressure dependence of a line at 300°K. As might be expected, ΔH, and so $\Delta\nu$, is proportional to pressure for low pressures. Because of overlapping in the spectrum, we were not able to carry out these measurements at pressures greater than a few cm of Hg.

The temperature dependence of $\Delta\nu$ was studied by measuring the line widths of a selected group of strong, isolated lines at room and liquid air temperatures using the second harmonic technique. Table III gives the result of these measurements. It is seen that the line widths at constant pressure increase by an approximately constant factor of 3 for a decrease in temperature

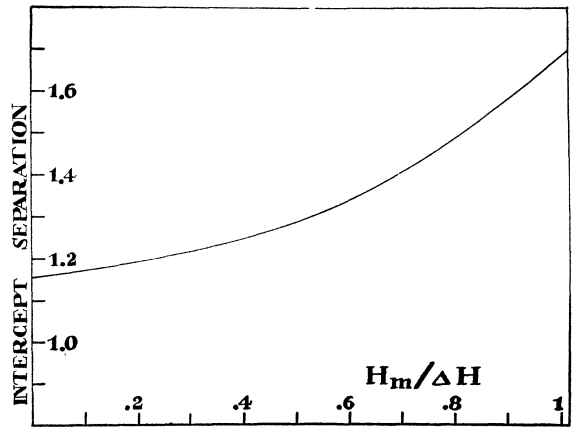

FIG. 5. Curve used to determine ΔH from measurement of the second harmonic line contour. The ordinate is the distance in ΔH units between the intercepts (zero signal points) of the function B_2. These intercept points are the most easily determined parameters of a line broadened by modulation.

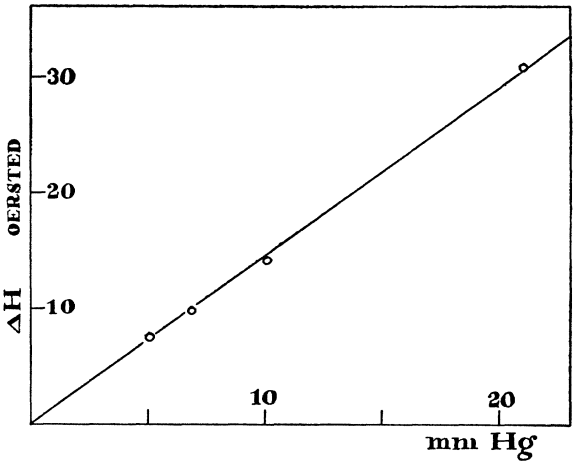

FIG. 6. Variation of width of line No. 5 with pressure at 300°K. ΔH values were determined using the measured intercept separations of second harmonic signal contours.

from 300°K to 85°K. Less precise line-width values were also taken from observed spectra such as Figs. 1 and 2. These are included in Table I in relative units which can be converted to absolute units by use of Table III.

From Table III we may take 2.0 Mc/mm Hg as an average $\Delta\nu$ for $K=1$ lines at 300°K. Converting this to one atmosphere pressure at the same temperature gives 0.051 cm^{-1}. This may be compared with the recent measurement[12] 0.053 cm^{-1} for the width of a $K=3$ line in the 2 cm^{-1} O_2 absorption spectrum and with the value 0.02 cm^{-1} to 0.05 cm^{-1} used to fit the unresolved[11] 2 cm^{-1} spectrum.

Table III and Table I do not show any regular dependence of $\Delta\nu$ with K alone. The spread in $\Delta\nu$ values for various lines from the same K state is as great as the total observed spread. Presumably this is due to a rather strong dependence of $\Delta\nu$ on M as well as the other quantum numbers. There is some evidence in Table I that the minimum $\Delta\nu$ for a given K decreases with increasing K. However, a different and incomplete sample of M values is observed for each K state.

TABLE III. Line widths of strong, isolated lines determined by second harmonic method.

Line No.	Lorentz half-width in Mc/sec at 1 mm Hg $T=300$°K	$T=85$°K	Probable K
2	1.93	5.62	1
3	—	8.65	3
4	1.66	5.08	3
5	2.22	6.23	1
7	1.82	5.14	5
9	—	6.17	1
11	—	4.36	>9
12	2.04	6.27	1
13	1.44	4.50	7
14	—	4.13	3
16	—	4.75	5
17	—	4.42	7
19	—	4.33	3

No completely satisfactory theory of the observed line widths has been available to us. However, some tentative discussion may be of interest.

The most outstanding generalizations from the measurements of the O_2 lines are the relatively small $\Delta\nu$ values and their apparent dependence on all of the quantum numbers. The small line width results from the lack of strong forces such as exist between molecules having electric dipole moments. If we compare the O_2 widths with that expected from pure collision-broadening using kinetic theory constants, the small width is made evident. From the measured viscosity[14] at 15°C, $\Delta\nu=0.028$ cm^{-1}/atmos.$=1.1$ Mc/mm Hg, which is about half the average of the measured values of Table III. Microwave collision cross sections for polar molecules exceed the simple kinetic theory values by much larger factors.[15]

The exchange forces which contribute the greater part of the interactions in kinetic theory processes have not been calculated explicitly or applied in theories of microwave pressure broadening. One would expect them to be relatively insensitive to the rotational quantum numbers, and one would expect these forces to provide a relatively constant background contribution to all of the widths. Roughly then, half of the observed width does not arise from specific forces which can be treated with the present theories of pressure broadening.

The remaining contributions to $\Delta\nu$, and presumably those which carry the strong quantum number dependence, may be (a) electric quadrupole interactions, (b) van der Waals forces, or (c) magnetic dipole forces.

It is easily shown that (c) is small compared with (a) and (b) above.

An unpublished manuscript of M. Mizushima[16] proposes that electric quadrupole forces can account for the observed widths in the 2 cm^{-1} spectrum of O_2 and for their K dependence. We agree that these forces do make an important contribution. On modifying the Mizushima theory to the case of the present spectrum we find that the electric quadrupole moment required is of reasonable magnitude.[17] However, the predicted dependence on rotational and magnetic quantum numbers is not exhibited by the measured values.

Margenau has made a preliminary investigation of the possible role of van der Waals forces (i.e., $1/r^6$ forces) in the present spectrum. It appears that this line-width contribution will be about as large as that of the quadrupole forces. The calculated dependence of these forces on the quantum numbers is generally similar to that for the quadrupole forces. Thus no improvement in the quantum number dependence of $\Delta\nu$ is achieved.

There are two well known limiting cases for the temperature dependence of $\Delta\nu$. In pure impact theories $\Delta\nu$ is proportional to the collision frequency and thus to $T^{-\frac{1}{2}}$ for constant pressure. Microwave observations do not follow this law.[15] In pure statistical theories $\Delta\nu$ is proportional to the density of molecules and thus to T^{-1} at constant pressure. The present observations (Table III) lie between these extreme cases, the observed $\Delta\nu$ ratio at constant pressure being 3.0 for a temperature ratio of 3.5. The Mizushima model, a modified impact theory, predicts that $\Delta\nu \propto T^{-\frac{3}{2}}$ at constant pressure. With this law the $\Delta\nu$ ratio for the conditions of Table III would be 2.6. Thus the observations lie midway between a T^{-1} and a $T^{-\frac{3}{2}}$ dependence.

The authors are indebted to Professor Henry Margenau for many discussions of the pressure broadening aspects of this study and for the use of his unpublished calculations. The authors also wish to thank Dr. A. F. Henry for his interest and help in connection with the Zeeman theory of the spectrum.

[14] E. H. Kennard, *Kinetic Theory of Gases* (McGraw-Hill Book Company, Inc., New York, 1938).

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

[16] This manuscript was kindly loaned to us by Professor Margenau.

[17] Say 2×10^{-26} esu depending on the state chosen. This is not much larger than Ramsey's value for H_2 [Phys. Rev. **78**, 221 (1950)] but several times that deduced by Smith and Howard (reference 15).