Line Breadths in the Microwave Magnetic Resonance Spectrum of Oxygen*

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The line-breadth parameters of a number of lines of the X-band magnetic resonance spectrum of O_2 have been measured and interpreted with the aid of a previously reported theory of the spectrum. The results are that the M-dependence of the line width is negligible, and there is only a slight decrease in width with increasing K. A typical width (half-width at half-intensity) at 300°K is 2.2 (Mc/sec)/mm Hg. At pressures up to 8 mm Hg, the line centers have been found to shift less than 2 percent of the line width. The average temperature dependence of the normalized line breadth parameter ($\Delta\nu/P$) is found to be $T^{-0.75}$. This may be compared with the theoretical $T^{-0.627}$ and the $T^{-0.85}$ found by previous workers. We find O_2-N_2 collisions to be no less effective than O_2-O_2 collisions in producing broadening.

1. INTRODUCTION

LINE breadths (half-width at half-intensity) in the millimeter microwave spectrum of oxygen have been reported by numerous investigators,[1] and Beringer and Castle[2] have given results for the magnetic resonance spectrum. The various results, however, have not been completely satisfactory. For example, there are sizable discrepancies between the results of Gokhale and Strandberg and those of other investigators of the millimeter spectrum. The results of Beringer and Castle could not be properly converted to frequency widths with the existing theory. Also, there is poor agreement between the experimental temperature dependence of the line breadth and that predicted by theory. In view of this unsatisfactory situation, line-width measurements were made as part of the comprehensive study of the microwave spectrum of the oxygen molecule which was previously reported.[3] The results of these measurements and of the re-evaluation of the measurements of Beringer and Castle are given in this paper.

In the microwave spectrum of a gas at the pressures used in these experiments one may neglect all sources of broadening except collision broadening and the instrumental broadening resulting from any inhomogeneity of the magnetic field over the cavity containing the sample. (The power level was always kept low enough to preclude any saturation broadening effects.) From kinetic theory, the normalized line-breadth parameter for collision broadening, $\Delta\nu/P$, is conveniently expressed as

$$\Delta\nu/P=2b^2/(\pi MkT)^{\frac{1}{2}}, \tag{1}$$

where $\Delta\nu$ is the half-width at half-maximum intensity, P is the pressure, T the absolute temperature, M the molecular mass, and b the "collision diameter." This normalized line breadth is independent of P for the low pressures used. However, it does depend on T, and it will, in general, also vary from line to line in the spectrum because the collision cross section πb^2 for radiation interruption will depend on the quantum state of the molecule. If the molecules acted like hard spheres, b would simply be the diameter of the sphere, and $(\Delta\nu/P)\propto T^{-\frac{1}{2}}$. Actually, the effective collision diameter is greater for slow molecules which have more time to interact during each encounter. Thus b decreases with increasing T, and the total temperature dependence is

$$\Delta\nu/P\propto T^{-n}, \tag{2}$$

where $n>\frac{1}{2}$. One may show that if the interaction potential is proportional to r^{-p}, then

$$n=\frac{1}{2}\frac{p+1}{p-1}. \tag{3}$$

Thus the exponent n is a convenient indicator of the "hardness" of the intermolecular interaction potential.

2. EXPERIMENTAL METHOD

In taking the experimental data, an X-band recording resonance spectrometer with magnetic field modulation was used. This apparatus yields a trace of the derivative of the absorption along an abscissa linear in the magnetic field. Since the modulation amplitude was always less than one-tenth of the line width, the considerations given by Andrew[4] show that the spurious increase in line width introduced by the finite modulation amplitude is less than 1 percent. This was confirmed experimentally by extrapolation. Three independent values of the line width for a Lorentz shape were deduced from each trace by measuring the separations of the points of one-half, three-quarters, and full-maximum signal. The absence of any trend in the discrepancies among these determinations confirms that the shape is indeed Lorentzian, as it should be for collision broadening. Since the deflection

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[1] Those studying the resolved spectrum include: B. V. Gokhale and M. W. P. Strandberg, Phys. Rev. **84**, 844 (1951); Anderson, Smith, and Gordy, Phys. Rev. **87**, 561 (1952); R. M. Hill and W. Gordy, Phys. Rev. **93**, 1019 (1954); J. O. Artman and J. P. Gordon, Phys. Rev. **87**, 227(A) (1952); J. O. Artman, Ph.D. thesis, Physics Department, Columbia University, 1953 (unpublished); J. O. Artman and J. P. Gordon, Phys. Rev. **96**, 1237 (1954).

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

[3] M. Tinkham and M. W. P. Strandberg, Phys. Rev. **97**, 937 and 951 (1955), referred to in the text as I and II.

[4] E. R. Andrew, Phys. Rev. **91**, 425 (1953).

is stationary at the maximum signal points, the accuracy with which their separation may be determined is rather limited in the presence of noise. Thus, the other two determinations were given the dominant weight when the best experimental value was chosen for each chart. Each piece of raw data is the average of these best widths from two charts of the given line at the same temperature and pressure.

The data obtained in this way were fitted to a dependence of the form

$$\Delta H = (\Delta H)_0 + (\Delta H/P)P \qquad (4)$$

by least squares. Since $(\Delta H)_0$ is the result of field inhomogeneity over the cavity, its value should increase smoothly as one considers lines at increasing fields. On this basis a smoothed set of $(\Delta H)_0$ values was chosen, and from them a new fit for the $\Delta H/P$ values was made. This procedure allows us to obtain some of the advantages of the data on *all* lines in fitting *each* line.

Two completely independent sets of data were taken and fitted in this way. They were made with different cavities and different pole pieces. In each set, data were taken at three to ten different pressures at each temperature. The adjustment procedure described is supported by the fact that the largest adjustments were of opposite sign for the two sets and tended to bring the data toward a common result. Thus we are assured that our procedure only averages out random errors and does not eliminate any actual effect.

3. RESULTS

The results of our measurements are given in Table I. The conversion to frequency widths made use of the computed $d\nu/dH$ factors quoted in II. The indicated errors are estimated limits of error based on the errors of the individual least-squares fittings and on the differences between the results obtained with the two sets of data.

For comparison, let us also consider the results of Beringer and Castle.[2] As far as the transitions were identified in reference 2 (half only to K value), they were correctly assigned except for line 17. However, the calculations of II allow total identification to be made and the proper $d\nu/dH$ factors calculated to convert widths in gauss to widths in megacycles per second. Values for the line widths of reference 2 corrected by a factor of $(H/\nu)(d\nu/dH)$ are also tabulated in Table II.[5] The temperature-dependence exponent, n, is indicated in the last column. To simplify direct comparison with our data, their 85°K data have been converted to 78°K by using an average T-dependence.

TABLE I. Line-breadth data. ($\Delta\nu/P$ is in (Mc/sec)/mm Hg.)

K	J	M	$\Delta\nu/P$ O_2 at 300°K	$\Delta\nu/P$ O_2 at 78°K	$\Delta\nu/P$ Air at 78°K	$\Delta\nu(\text{air})/\Delta\nu(O_2)$	n
1	1	$-1\to0$	2.35±0.10	6.13±0.3	6.13±0.3	1.00±0.06	0.71±0.04
1	2	$1\to2$	2.20±0.10	6.00±0.2	6.02±0.3	1.00±0.06	0.74±0.04
1	2	$0\to1$		5.92±0.3			
1	2	$-1\to0$	2.23±0.14	6.20±0.1	6.21±0.2	1.00±0.04	0.76±0.06
3	2	$0\to-1$		5.93±0.3	6.63±0.3	1.12±0.08	
3	4	$-1\to0$	2.00±0.10	5.70±0.3	6.12±0.3	1.07±0.06	0.78±0.06
5	4	$0\to-1$		6.0 ±0.5			
5	6	$-1\to0$		5.5 ±0.3			

TABLE II. Line-breadth data of Beringer and Castle re-evaluated by our work.

B and C[a] line number	K	J	M	Corrected $\Delta\nu/P$ 300°K	85°K	78°K	n
2	1	1	$-1\to0$	2.24	6.52	6.98	0.85
5	1	2	$1\to2$	2.49	6.98	7.47	0.82
9	1	2	$0\to1$		6.21	6.65	
12	1	2	$-1\to0$	2.08	6.38	6.84	0.89
14	3	2	$0\to-1$		5.83	6.24	
19	3	4	$-1\to0$		6.62	7.09	
3	3	$2\to4$	$0\to1$		6.97	7.47	
4	3	$4\to2$	$-2\to-1$	2.42	7.41	7.94	0.89
17	5	4	$0\to-1$		6.83	7.31	
16	5	$4\to6$	$0\to1$		7.02	7.52	
7	5	$6\to4$	$-2\to-1$	2.18	6.16	6.60	0.825
11	9	$8\to10$	$2\to3$		6.57	7.04	

[a] See reference 2.

4. DISCUSSION

First, let us compare our results with those of reference 2. Our correction has greatly reduced the scatter of these results. However, the agreement with our data is still rather poor. At 300°K, our results agree in the mean but have a mean deviation of roughly ±8 percent. At 78°K our means differ by 14 percent, but the mean deviation about that is only ±5 percent. This difference in behavior at the two temperatures is such that our values of the exponents n are in the vicinity of 0.75, whereas their values are near 0.85. It seems clear that a systematic error is present. One possible source of error is in the measurement of the temperature, particularly of the low temperature. We measured the low temperature with a thermocouple soldered to the cavity wall. This thermocouple was calibrated at the boiling points of N_2 and O_2, as well as at the ice point, and temperatures could be read to a fraction of a degree. It was found that this temperature was always within a degree of 78°K with the liquid N_2 which we used. The data of Beringer and Castle are quoted at 85°K though liquid air was used.[6] The varying composition as the air boils away will cause an error since cavity temperatures are not directly measured.[6] However, even if we presumed that their temperature was as low as 78°K, their line width would still exceed ours. Perhaps a more promising explanation lies in the residual width $(\Delta H)_0$ at zero pressure. No particular effort was made to take field homogeneity into account in the work reported in reference 2.[6] Figure 6 of that paper would indicate the

[5] That the assumption of a linear ν to H relationship implied by the use of ν/H as a conversion factor may introduce large errors was acknowledged by Beringer in Ann. N. Y. Acad. Sci. **55**, 818 (1952).

[6] R. Beringer (private communication).

correction is negligible for 300°K measurements, in agreement with our deduction. The fact that they used a different cavity at low temperatures and at room temperatures would make the observed differential effect possible, especially for measurements at 2 or 3 mm Hg pressure used in reference 2 in the line breadth studies.[6] Since in our work, the same cavity and positioning were used for both temperatures, and since the residual width was carefully handled, it would appear that our data should be reliable.

Considering only our data on O_2 self-broadening, there seems to be a trend toward lower line widths with increasing rotational quantum number K. However, the decrease in signal strength with increasing K has precluded carrying this far enough to establish whether it levels off or continues to drop slowly. In any case, the variation with K is slight. Three transitions with $K=1$, $J=2$ were studied in an attempt to find any M-dependence of the line width. Since the widths of these three lines all agree within the experimental error, we conclude that the dependence on M is negligible, as expected. It should also be remarked that the magnitudes of our line widths are in general agreement with those found for the same value of K by Anderson *et al.*; by Hill and Gordy; and by Artman.

The lines observed in this spectrum each come from a single transition, rather than from a sum of transitions of degenerate M states as in field-free spectroscopy. It was of interest to see if there were any of the pressure shifts that are allowed in phase-shift theories of broadening. Measurements of the positions of line centers over a range of pressures up to 8 mm Hg indicate that any such shifts must be less than two percent of the line width.

We find that the exponent n in the temperature dependence increases slightly with both J and K, but the differences are all within the limits of error. The mean value of n, 0.75, should be compared with the average of 0.87 found by Beringer and Castle and the average of 0.85 found by Hill and Gordy in the 5-mm spectrum.

The theoretical position on line widths in the microwave spectrum of O_2 has been carefully reviewed by Artman using Anderson's[7] semidiabatic method. He finds that the magnetic dipole-dipole interaction, which would give $n=1$, is completely negligible in magnitude. The electric quadrupole-quadrupole interaction, which is the next longest range interaction available, would give $n=0.75$, but again the magnitude would seem to be an order of magnitude too small to account for the entire line width. He finds that a combination of polarizability and exchange interactions dominate. This short range interaction gives $n=0.627$, rather near the hard sphere value of 0.5. In view of these theoretical expectations, our lower value of n is definitely more understandable than the old values. Our data are also in reasonable agreement with Artman's prediction of a line width independent of K except for a slight drop from $K=1$ to $K>1$.

Finally, let us consider the data on the ratio of air-broadening to self-broadening at 78°K presented in Table I. We find that for the three different $K=1$ transitions the ratio is 1.00 ± 0.06; for the two $K=3$ transitions the ratio is 1.10 ± 0.10. These results are rather surprising in view of the fact that both Anderson *et al.* and Artman found N_2 only about 85 percent as effective a broadening agent as O_2. Of course, since both of these investigations were at room temperature and were of the millimeter spectrum, which involves somewhat different states, a direct comparison may not be significant.

5. CONCLUSIONS

On the basis of our data we conclude that the line width is independent of M and decreases slightly with increasing K. We find the average temperature dependence exponent n to be 0.75. This is nearer the theoretically expected value of 0.627 than the previous values of roughly 0.85. The line centers shift less than 2 percent of the line width for pressures up to 8 mm Hg. Finally, we find O_2-N_2 collisions to be no less effective than O_2-O_2 collisions in producing broadening.

[7] P. W. Anderson, Phys. Rev. **76**, 647 (1949).