

Also, from the relation

$$\Delta U/\Delta V = TdP/dT - P \quad (3)$$

and Eq. (1) it can be seen that ΔU is zero at 1.44°K and that the internal energy of the liquid is less than that of the solid below this temperature.

The melting pressure data also point to another interesting result. Since any reasonable extrapolation of the data gives a positive melting pressure at absolute zero, it appears likely that He³, like He⁴, does not have a triple point and that the liquid is the stable condensed phase at absolute zero.

¹ W. H. Keesom, *Communs. Physical Lab. Univ. Leiden No. 184b* (1926); *Helium* (Elsevier, Amsterdam, 1942), p. 180.

² Abraham, Weinstock, and Osborne, *Phys. Rev.* **80**, 366 (1950).

³ C. A. Swenson, *Phys. Rev.* **79**, 626 (1950).

Line Breadths of the Fine Structure of the Microwave Spectrum of Oxygen*

ROY S. ANDERSON,† WILLIAM V. SMITH, AND WALTER GORDY
Department of Physics, Duke University, Durham, North Carolina
(Received March 5, 1951)

IN a previous paper¹ we have reported on preliminary measurements of the widths of three fine structure lines of oxygen. These lines arise from reorientations of the oxygen electron spin vector $S(=1)$ with respect to the rotational angular momentum vector K , which is constant for the microwave transitions observed. It has since been possible to extend the determinations of the line-width parameter to include fourteen lines over the range of significant population.

The apparatus for detection of the lines is essentially that cited earlier.¹ To make the measurements more precise, a lattice of frequency markers of 5.70 megacycles spacing has been superimposed on the recorder trace. This superposition results in an individually calibrated recorder trace for each record made. With the detecting system used, the shape of the recorder tracing of an absorption line represents the second derivative of the line contour. Thus, it is easily demonstrated that the distance between the negative minima of the recorder trace is the full width ($2\Delta\nu$) of the line measured at half intensity.

Measurements on each of the lines have been made for at least three different pressures in the range 0.1 to 10 mm Hg. As in the earlier work, measurements at a constant pressure were made for successively decreasing modulations. Each time the measured widths were extrapolated to obtain the width for zero modulation. Since the modulating fields employed were of the order of the earth's field, it was necessary to orient the absorption cell along the earth's field and apply a dc current of proper direction and magnitude to prevent significant broadening of the lines by the earth's field. Corrections have been made, however, for broadening the lines by inhomogeneity of the magnetic field surrounding the

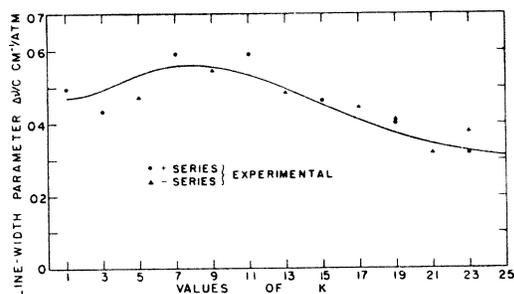


FIG. 1. Comparison of theoretical formula with experimental data. The solid curve is the plot of Eq. (2). The points represent measured values of the line-width parameter. The + series refers to transitions $J=K+1 \rightarrow K$ and the - series refers to transitions $J=K-1 \rightarrow K$.

cell. The observed line width parameter $\Delta\nu/c$ expressed in cm^{-1} per atmosphere is plotted in Fig. 1 together with a theoretical curve discussed subsequently. The data are in agreement with the single $K=11$ line reported by Gokhale and Strandberg,² and are of the same magnitude as the line widths observed by Beringer and Castle³ for $\Delta J=0$, $\Delta K=0$, $\Delta M=\pm 1$ transitions occurring in the 3-cm region at high magnetic fields.

Since oxygen lacks an electric dipole moment, interactions between molecules must take place through the mechanism of shorter range forces such as quadrupole ($V \sim 1/r^5$), polarizability ($V \sim 1/r^6$), or still shorter range nonelectric forces. The magnetic dipole interaction is sufficiently small that it can be neglected despite its long range ($V \sim 1/r^3$). Anderson⁴ and Mizushima⁵ have investigated, respectively, polarizability and quadrupole interactions for $\Delta K=0$. Both interactions yield line widths that decrease fairly rapidly with increasing K , the quadrupole line width decreasing as K^{-1} for high K ,⁶ while the polarizability line width decreases somewhat more rapidly for low K , and attains a constant plateau for K greater than 15. The still shorter range nonelectric forces may be expected to be essentially independent of K , so that a combination of all three interactions (for $\Delta K=0$) may be expected to yield a line shape of the approximate form,

$$\Delta\nu_{\Delta K=0} = C_1 + C_2 K^{-1}. \quad (1)$$

The observed variation in $\Delta\nu$ with K shows an unmistakable peak about $K=7$. Since $K=7-9$ corresponds to the peak of the thermal population for room temperature, this suggests that resonance interactions contribute an important fraction of the line widths for these states. Both polarizability and quadrupole interactions have an angular $\cos^2\theta$ variation, where θ is the angle between the intermolecular distance r and the asymmetry axis of the molecule. This angular variation gives large matrix elements for $K \rightarrow K+2$ transitions. Since only odd K values are permitted for oxygen (spin $O^{16}=0$; $^3\Sigma^-$ ground state), the population of ($K \pm 2$) states near the thermal maximum is particularly high with 28 percent of all molecules in $K=7$ or $K=11$ states. These facts suggest that the total line width should be of the form

$$\Delta\nu_{\text{tot}} = C_1 + C_2 K^{-1} + C_3 [f(K-2) + f(K+2)], \quad (2)$$

where $f(K)$ is the fractional population of the K th rotational state, and the resonance interaction has been assumed independent of K to a first approximation. Figure 1 is a plot of Eq. (2) for $C_1=0.027$, $C_2=0.012$, and $C_3=0.090 \text{ cm}^{-1}$ per atmosphere. The fit is seen to be satisfactory. The best fit of the data yields a fairly low value of C_3 , which, moreover, includes part of the polarizability interaction along with the quadrupole interactions. Mizushima's expression for the quadrupole interaction alone is

$$\Delta\nu \text{ cm}^{-1}/\text{atmos} = 2.24 \times 10^{16} Q K^{-1}, \quad (3)$$

where Q is defined (as in Smith and Howard⁷) as the average Q of the rotating oxygen molecule (\equiv Margenau's Θ/ϵ).⁸ Arbitrarily assigning $3/4$ of C_3 to a quadrupole interaction gives a value of $Q=0.04 \times 10^{-16} \text{ cm}^2$ for oxygen. This value is in agreement with the upper limit of $Q \leq 0.09 \times 10^{-16} \text{ cm}^2$ deduced from the broadening of ammonia by oxygen.⁷

We wish to thank Professor Mizushima for sending us a pre-publication copy of his paper. We have also benefited from correspondence with Dr. P. W. Anderson.

* Research supported and sponsored by the Geophysical Research Directorate of the Air Force Cambridge Research Laboratories. It is published for technical information only and does not represent recommendations or conclusions of the sponsoring agency.

† The material in this paper is a part of the author's thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Duke University.

¹ Burkhalter, Anderson, Smith, and Gordy, *Phys. Rev.* **79**, 651 (1950).

² B. V. Gokhale and M. W. G. Strandberg, *Phys. Rev.* **82**, 327 (1951).

³ R. Beringer and J. G. Castle, Jr., *Phys. Rev.* **81**, 82 (1951).

⁴ P. W. Anderson, Harvard Ph.D. thesis (1949).

⁵ M. Mizushima, privately communicated.

⁶ Small differences between the $J=K+1 \rightarrow K$ and $J=K-1 \rightarrow K$ interactions have been neglected, since the observed difference is within the experimental scatter of the data.

⁷ W. V. Smith and R. Howard, *Phys. Rev.* **79**, 132 (1949).

⁸ H. Margenau, *Revs. Modern Phys.* **11**, 1 (1939).