A. PARAMAGNETIC RESONANCE IN OXYGEN GAS

Starting with the improved theory of the field-free energy levels and state functions of the oxygen molecule reported earlier (1), precise Zeeman effect calculations have been made to locate individual lines of the spectrum. About 40 X-band and 40 S-band transitions have been studied. For each of these, the constant term and slope of the energy level separation at the appropriate value of the external field $H_0$ (obtained previously by graphical interpolation (2)) have been calculated. From these quantities, magnetic fields for the experimental resonance frequencies 9396 Mc/sec and 2987 Mc/sec have been calculated to within a few gauss. These calculated fields have been compared with the experimental X-band results reported previously (1) and with the S-band spectrum obtained subsequently. In this S-band spectrum, 78 lines were resolved in the region between 1980 gauss and 9300 gauss. In essentially all cases, the theoretical field checked with the experimental field to within 8 gauss; most were much closer. A small systematic deviation is being investigated. With this number of lines calculated exactly, it should be possible to identify most of the remaining lines by combining the graphically estimated positions with the temperature dependence of the intensity (which gives an estimate of $K$) and with the results of the circular polarization experiments (which will discriminate between $\Delta M = \pm 1$ transitions).

With the line identification program well under way, a start has been made on line-width studies. The widths of 6 lines of the X-band spectrum have been carefully measured at 80°K and at pressures of 1 to 4 mm Hg. Although there is a small extrapolated width at zero pressure because of inhomogeneity of the magnetic field over the cavity, fitting the slope of the pressure dependence by least squares should give the correct line breadth parameter in gauss/mm Hg. This is then converted to the more meaningful frequency width by use of the slope of the energy level separation mentioned above. (The fact that Beringer and Castle (3) incorrectly made this conversion with $\nu_0/H_0$ rather than $\nu_0/dH_0$ largely accounts for their anomalous linewidth results.) The result, $\Delta \nu = 6.05 \pm .10$ Mc/mm Hg, for the lines $K = 1$, $J = 2$, $M = -1\rightarrow 0$, $0\rightarrow 1$, and $1\rightarrow 2$ indicates, as might be expected, no appreciable M dependence of the collision-broadening cross section. This result, and the results $\Delta \nu = 5.5 \pm .1$ Mc/mm for $K = 3$, $J = 4$, $M = -1\rightarrow 0$; $\Delta \nu = 5.1 \pm .1$ Mc/mm for $K = 5$, $J = 6$, $M = -1\rightarrow 0$; and $\Delta \nu = 5.1 \pm .1$ Mc/mm for $K = 9$, $J = 10$, $M = 0\rightarrow 1$ indicate a small K dependence which roughly fits the form

$$\Delta \nu = C_1 + C_2 K^{-\frac{1}{2}}$$
(V. MICROWAVE SPECTROSCOPY)

predicted by some theoretical considerations. Further linewidth studies to check this dependence, the J dependence, and the temperature dependence are planned.

M. Tinkham

References

1. Quarterly Progress Report, Research Laboratory of Electronics, M.I.T., July 15, 1953, pp. 28-29
2. Quarterly Progress Report, Research Laboratory of Electronics, M.I.T., April 15, 1953, p. 19

B. CIRCULAR POLARIZATION IN CAVITIES

In certain magnetic resonance experiments it is desirable to excite a single, circularly polarized mode in the cavity containing the sample under study. In this case, the instantaneous H vector at the sample rotates in a plane with constant magnitude rather than oscillating along a line, as in the usual linear polarization. Since the perturbative Hamiltonian can quite generally be written

\[ \mathcal{H}' = g_\rho \vec{\mathbf{H}} \cdot \mathbf{J} = g_\rho \left[ H_z J_z + \frac{1}{2} (H_+ J_- + H_- J_+) \right] \]

it is clear that such circularly polarized radiation (being either \( H_+ \) or \( H_- \), depending on the sense of the rotation) will only induce transitions between states connected by matrix elements of \( J_- \) or \( J_+ \), respectively, but not both. Thus we obtain a sharp experimental distinction between \( \Delta M = -1 \) and \( \Delta M = +1 \) transitions. This technique allows a determination of the sign of the gyromagnetic ratio of the absorber.

An immediate application in this laboratory will be in the experimental analysis of the complex spectrum of oxygen gas. In this molecule one can have absorptive transitions of either \( \Delta M = +1 \) or \( -1 \), depending on the way the electronic spin and the rotational angular momentum are coupled in the particular states involved. Thus the use of circular polarization will divide the spectrum into two groups, giving considerable aid in the analysis of the spectrum. Another prospective application is in refining measurements of the selection rules governing transitions in paramagnetic salts in which the crystalline electric field partially breaks down the angular momentum quantization.

The experimental method of providing such a polarized field is to excite the two degenerate orthogonal TE_{ll} modes in a cylindrical cavity 90° out of phase. These modes are excited through a hole precisely centered in one end to maintain the degeneracy of the cylindrical symmetry. This hole couples into the center of the side wall of a piece

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of square waveguide in which the two orthogonal $\text{TE}_{01}$ modes are equally excited. One cavity mode is excited by the transverse $H$ of one guide mode; the other is excited by the longitudinal $H$ of the other guide mode. The phase and amplitude of the two standing wave modes at the hole are independently adjusted by orthogonal shorting vanes in the end of the guide. One can readily show that the two incident waves must be phased to give linear polarization along one diagonal of the guide, whereas the reflected wave bearing the information from the cavity is linear along the other diagonal. A piece of microwave plumbing has been built to couple properly into these modes. With this apparatus, a klystron has been stabilized to the cavity with a modified Pound-Zaffarano scheme, and some preliminary tests have been made. The relative signal strengths on reversing the sense of the circular polarization indicate that a 20-db enhancement of one mode over the other is easily obtainable. A vacuum-tight model for the oxygen experiment is under construction.

M. Tinkham