

## V. MICROWAVE SPECTROSCOPY

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Three projects have been terminated and theses submitted to the Department of Physics as a result of the work of this group. The abstracts of these theses are presented below. For full details, consult the theses themselves or the technical reports based upon them. (D. W. Posener's thesis has already been published as Technical Report No. 255.) The essential results will also be published later in technical journals.

### A. MICROWAVE SPECTRUM OF THE WATER MOLECULE

A centrifugal distortion theory applicable to the water molecule and its isotopic modifications has been rederived, apparently eliminating typographical and analytical errors now present in the literature. Using infrared data with this theory, rotational constants and distortion parameters have been calculated for the molecules  $H_2O$ ,  $D_2O$ , and HDO, and the resulting theoretical transition frequencies compared with those observed in the microwave region.

Theoretically calculated parameters have also been used to obtain Q-branch frequencies in HDO. While the frequencies computed directly are considerably different from those observed, a simple method is available for relating the two sets with very good accuracy. Analysis of the method leads to the inference that the theoretical distortion corrections are very nearly the true ones, and that reasonable agreement (by which we mean the best available by convenient methods of computation) with experiment can be obtained by a simple (and small) variation of the effective moments alone. The resulting parameters also account satisfactorily for the known  $|\Delta J| = 1$  transition in HDO, whose frequencies are still better explained by a further small change in the theoretical effective moments, together with a rather large variation of another distortion constant. The detailed discussion of the procedure used indicates that the consistency of the results is good.

For this type of molecule, centrifugal distortion effects are so large that approximate methods of calculation have only a limited usefulness; the validity of the Hillger-Strandberg-Kivelson-Wilson approximation for the calculation of Q-branch frequencies in HDO is discussed in detail.

The results for HDO give the following effective reciprocal moments of inertia:

$$\begin{aligned}a &= 7.0396 \pm 0.0005 \times 10^5 \text{ Mc/sec} \\b &= 2.7360 \pm 0.0005 \times 10^5 \text{ Mc/sec} \\c &= 1.9186 \pm 0.0005 \times 10^5 \text{ Mc/sec}\end{aligned}$$

with  $\kappa = -0.6841 \pm 0.0002$

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New Transitions observed in the microwave spectra of D<sub>2</sub>O and HDO are:

D <sub>2</sub> O	2 <sub>20</sub> → 3 <sub>13</sub>	10,919.39 ± 0.05 Mc/sec
HDO	8 <sub>45</sub> → 8 <sub>44</sub>	24,844.77 ± 0.05 Mc/sec
HDO	10 <sub>56</sub> → 10 <sub>55</sub>	8836.95 ± 0.1 Mc/sec
HDO	11 <sub>57</sub> → 11 <sub>56</sub>	22,581.1 ± 0.2 Mc/sec

A line previously reported, at 26,880.38 ± 0.05 Mc/sec, is identified as the 6<sub>24</sub> → 7<sub>17</sub> transition of HDO.

D. W. Posener

### B. ZEEMAN EFFECT IN ROTATIONAL SPECTRA OF <sup>1</sup>Σ MOLECULES

The study of the interaction of a rotating <sup>1</sup>Σ molecule with an external magnetic field has been extended to include asymmetric rotors. Two general classes of molecules have been considered: those molecules in which there is no nuclear quadrupole interaction and those in which a nuclear quadrupole interaction exists. In the former case, only the interaction of the rotational molecular magnetic moment has to be considered, while in the latter, the effect of a nuclear magnetic moment must be included. The matrix elements of the molecular magnetic moment are known and are functions of a molecular gyromagnetic tensor which in the most general case is nondiagonal. These matrix elements had been given in the JKM representation, but application of the Wang symmetrizing transformation effects considerable simplification, transforming these elements to a form much more suited to calculation. From the form of the transformed matrix it can be shown that the first-order Zeeman effect depends only on the diagonal terms of the gyromagnetic tensor. Consequently, only three parameters are required to specify the first-order perturbation completely. Furthermore, since the transformation properties of the gyromagnetic tensor are known, it is possible to obtain the gyromagnetic tensors of isotopic species of the molecule if the complete gyromagnetic tensor for one molecule is known. The three isotopic modifications of the water molecule, H<sub>2</sub>O, HDO, and D<sub>2</sub>O, were chosen to verify the theory. In H<sub>2</sub>O, the principal axes of the gyromagnetic tensor coincide with the principal inertial axis, and consequently the tensor is diagonal. Since rotational constants for all three molecules are known, it is possible to transform the g-tensor of H<sub>2</sub>O to that of either HDO or D<sub>2</sub>O. Thus, only three constants are needed to determine completely the first-order Zeeman effect in the rotational spectra of all three molecules. The necessary constants are determined from experimental measurements, and the g-tensors of the three molecules are given.

Matrix elements are developed for the more complicated case of a molecule in which nuclear quadrupole coupling exists, and the simplified case of a molecule in which interactions between rotational energy levels are negligible is treated. Experimental data

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obtained from Zeeman observations of the spectrum of vinyl chloride are compared with the theory, and approximate values for the gyromagnetic tensor are deduced.

Finally, the nuclear magnetic moment of two radioactive nuclei,  $\text{Se}^{79}$  and  $\text{S}^{35}$ , were measured by observing the Zeeman effect in the rotational spectra of the linear molecules  $\text{OCSe}^{79}$  and  $\text{OCS}^{35}$ .

The results were:

$$\mu(\text{S}^{35}) = 1.00 \pm 0.04 \text{ nm} \quad \mu(\text{Se}^{79}) = -1.015 \pm 0.025 \text{ nm}$$

B. F. Burke

## C. MICROWAVE ABSORPTION OF GASES AND VAPORS AT HIGH TEMPERATURES

A simple high-temperature microwave spectrograph capable of working up to  $900^\circ\text{C}$  is described. Details of temperature control and cell design are given. Six lines in the absorption spectrum of  $\text{KCl}$  vapor were measured. Analysis of these lines for  $\text{K}^{39}\text{Cl}^{35}$  gives  $B_e = 3856.10 \pm 0.40 \text{ Mc/sec}$  and  $\alpha_e = 23.64 \pm 0.10 \text{ Mc/sec}$ , which confirms previous microwave measurements. For  $\text{K}^{39}\text{Cl}^{37}$ , values of  $B_e = 3746.07 \pm 0.60 \text{ Mc/sec}$  and  $\alpha_e = 22.05 \pm 0.75 \text{ Mc/sec}$  were found in substantial agreement with the results of molecular beam measurements. A value of isotopic mass ratio of  $\text{Cl}^{37}$  to  $\text{Cl}^{35}$  was obtained in agreement with mass spectrographic data. The Stark effect in  $\text{K}^{39}\text{Cl}^{35}$  was studied and a value for the dipole moment of  $10.1 \pm 0.2$  Debye units was derived. This is somewhat lower than the molecular beam result of  $10.61 \pm 0.01$  Debye units.

One line was observed in  $\text{K}^{39}\text{Br}^{79}$  at the frequency predicted by molecular beam data.

The Stark effect of the  $J = 1 \rightarrow 2$  line in  $\text{NaCl}$  was measured. A value of  $8.5 \pm 0.4$  Debye units was obtained for the dipole moment.

Line-width measurements were made for pressures that are self-broadening in ammonia at several temperatures from room temperature to  $400^\circ\text{C}$ . A  $T^{-1}$  law of variation of line breadth with temperature was confirmed. This is in agreement with recent theories of ammonia pressure broadening.

P. A. Tate

## D. PARAMAGNETIC RESONANCE IN OXYGEN GAS

The installation and adjustment of the new magnet mentioned in a previous report (1) have made available magnetic fields of sufficient strength and homogeneity to allow study of the magnetic resonance spectrum at  $9400 \text{ Mc/sec}$ . Using the flip-coil feedback control system that we have developed, and driving the control helipot with a geared-down synchronous motor, we have swept from 0 to  $11,000$  gauss over a period of approximately 3 hours. Such runs have been made at  $80^\circ\text{K}$ , with an oxygen pressure of  $1.4 \text{ mm Hg}$  in the cavity, and at several higher pressures at room temperature. A total of 109 lines has been observed, most of them well above noise. The superior sensitivity of

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our technique to that of Beringer and Castle (2) is indicated by the fact that they reported only 41 lines. Forty of our lines are at lower fields than that of the lowest "allowed" transition, whereas they found only one in this region. By carrying the search up to 11,000 gauss, we have found that the densely spaced spectrum cuts off at about 9200 gauss, with isolated lines at 9545 and 10,590 gauss. This is in good agreement with the preliminary calculations reported in the Quarterly Progress Report, April 15, 1953.

Before making final calculations to check exact positions of individual lines, it has been deemed necessary to clear up some discrepancies in the theory of the field-free spectrum since this is involved as a starting point for the Zeeman-effect calculation. These discrepancies from the Schlapp formula due to neglect of centrifugal distortion have been treated by Mizushima (3) and by Miller (4) but not in a completely satisfactory manner. We have treated this problem by introducing into the Hamiltonian the vibrational energy terms and the dependence of the constants on internuclear distance, reducing to an effective Hamiltonian for the ground state by Van Vleck's perturbation method, and diagonalizing the reduced problem. The results fit the entire spectrum quite well, and the fitting evaluates the first-order change of the spin-spin coupling parameter  $\lambda$  about its value  $\lambda_0$  at the equilibrium internuclear distance  $R_0$  as

$$\lambda = \lambda_0 \left( 1 + 0.290 \frac{\Delta R}{R_0} \right)$$

This evaluation provides another piece of information about the dependence of the electronic wave function on the internuclear distance.

M. Tinkham

### References

1. Quarterly Progress Report, Research Laboratory of Electronics, M.I.T. Jan. 15, 1953, p. 16
2. R. Beringer, J. G. Castle, Jr.: Phys. Rev. 81, 82, 1951
3. M. Mizushima: private communication
4. S. L. Miller, C. H. Townes, Phys. Rev. 90, 537, 1953

### E. A MICROWAVE ABSORPTION SPECTROSCOPE OF HIGH SENSITIVITY

In a spectroscope of the type described by Hughes and Wilson (1) the microwave power is sent through a waveguide containing the gas under investigation. A septum fixed in the center of the guide (see Fig. V-1) permits application of a square-wave

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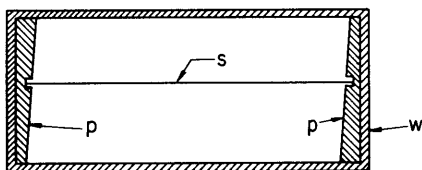


Fig. V-1

Waveguide  $w$  with Stark septum  $s$  and polystyrene supporting strips  $p$ .

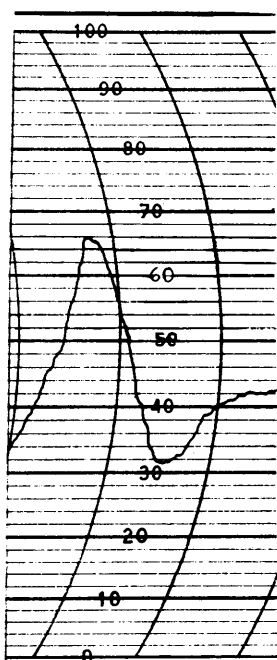


Fig. V-2

$F_i = 3/2$ ,  $F_f = 1/2$  - component of the quadrupole-split  $J = 1 \rightarrow J = 2$  transition of  $\text{OCS}^{33}$ ,  $\alpha = 7.2 \times 10^{-9}$ .

electric field in the waveguide so that the absorption appears, because of the Stark effect, as an amplitude modulation of the microwave power. With a 20-ft waveguide, a Stark modulation frequency of 6 kc/sec, and a detection system of 0.003 cps bandwidth, such a spectroscope can be expected to show a line of absorption strength of  $\alpha = 7 \times 10^{-9}$  neper/cm with a signal-to-noise ratio of 12 to 1.

However, an obstacle against realization of this sensitivity has been the fact that the 6 kc/sec square wave has set up mechanical vibrations of the septum and its supporting strips (see Fig. V-1). This difficulty has been overcome by gluing the septum to the strips and the strips to the guide walls by means of a wax. Ordinary glue could not be used because its solvent made impossible the evacuation of the guide.

Figure V-2 shows a diagram of the  $F_i = 3/2$ ,  $F_f = 1/2$ -component of the quadrupole-split  $J = 1 \rightarrow J = 2$  transition of  $\text{OCS}^{33}$ , with  $\alpha = 7.2 \times 10^{-9}$ . A line with  $\alpha = 1 \times 10^{-9}$  should still appear two times above noise. A Stark modulation frequency of 85 kc/sec is expected to give a still higher sensitivity and also to broaden the spectral line by about 120 kc/sec.

M. Peter

References

1. R. H. Hughes, E. B. Wilson, Jr.: Phys. Rev. 81, 562L, 1947
2. S. Gechwind: High Resolution Microwave Spectroscopy, Annals of the New York Academy of Sciences 55, 755, 1952