

## V. MICROWAVE SPECTROSCOPY

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### A. ZEEMAN EFFECT

For a symmetric top molecule, lines resulting from transitions between levels of nonzero K exhibit a first-order Stark effect. Hence, if a magnetic field is applied, a given Stark component will not be split but will only shift in frequency, since the M degeneracy is completely removed. Consequently, simultaneous Stark-Zeeman measurements on a symmetric top molecule afford a means of determining the sign as well as the magnitude of a nuclear or a molecular magnetic moment. Measurements made on the  $J = 2 - 3$ ,  $K = 1$ ,  $F = 3/2 - 3/2$  line of methyl iodide,  $\text{CH}_3\text{I}$ , show that the nuclear magnetic moment of  $\text{I}^{127}$  is positive, in agreement with sign determinations made by other means.

Experimental and theoretical work is continuing on the Zeeman effect for asymmetric molecules.

B. F. Burke

### B. PARAMAGNETIC RESONANCE EXPERIMENTS

The study of paramagnetic resonance absorption by  $\text{Mn}^{++}$  ions in solution, which was reported in the Quarterly Progress Report, July 15, 1951, has been continued. The apparatus used (Fig. V-1) is essentially that previously described except that a Pound stabilized oscillator has been introduced as a microwave source. The work has been directed toward determining the basic structure of the spectrum and investigating how the widths of the lines are modified by ionic concentrations and by the temperature.

#### Basic Structure

The energy level structure of the ground state of the  $\text{Mn}^{++}$  ion in solution is given by the solutions of the Hamiltonian  $H = g\beta \vec{H} \cdot \vec{S} + A \vec{I} \cdot \vec{S}$  where  $g$  is the electron  $g$  factor,  $\beta$  is the Bohr magneton, and  $A$  expresses the degree of interaction between the nuclear and electronic spin moments. If energy differences between successive levels for which  $\Delta M = \pm 1$  are converted to magnetic fields by the relation  $h\nu = \text{energy difference}$ , one obtains

$$H = \frac{h\nu}{g\beta} - Am - \frac{A^2}{2H_0} \left[ \frac{35}{4} + m(2M - 1) - m^2 \right]$$

as the positions of the maxima of the absorption lines. The first term gives the

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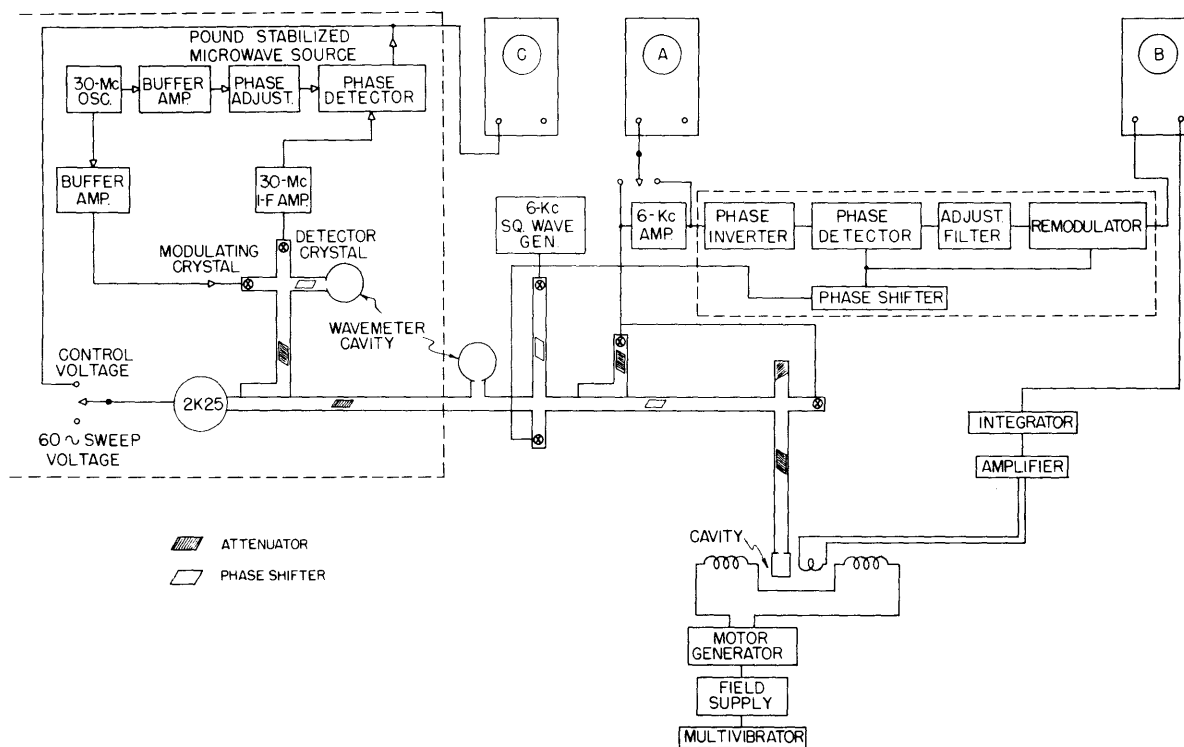


Fig. V-1

Apparatus for paramagnetic resonance experiments.

position of the line if no hyperfine structure (hfs) were present. The second term would split this into six equally-spaced hfs lines, symmetrically located about  $H_0 = h\nu/g\beta$ . The third term, which is quite small, has two principal effects. The term in  $m^2$  introduces a nonuniform spacing of the hfs lines, whereas the term in  $(2M - 1)$  causes a slight separation of the absorption lines arising from the various electronic spin transitions. Since these are not resolved, and since the sum of the  $(2M - 1)$  values weighted with the intensities of the transitions is zero, the  $(2M - 1)$  term causes no shift, but only a slightly increased line width, especially in the lines for which  $m = \pm 5/2$ . Using as a reference a small sample of an organic radical (diphenyl-trinitro-phenyl-hydrazyl), which gives a very narrow absorption line with well-known  $g$  factor, the positions of the 6 lines were measured. The results fit the theoretical form with  $g = 2.001 \pm 0.001$  and  $A = 94.9$  gauss. This  $g$  value lies within experimental error of that of the free electron and also of the values obtained by others for ions in various solids. The  $A$  value differs markedly from the 68 gauss obtained by England and Schneider (1) for the  $Mn^{++}$  ions present as activators in a ZnS phosphor, and from the approximately 100 gauss obtained by Bleaney and Ingram (2) for dilute single crystals of two manganese salts. In this case the configurational interaction which makes the hfs possible is the

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promotion of a 3s electron to the 4s state. Our results indicate that the strength of this interaction depends upon the environment of the ion more strongly than anticipated. It would be interesting to see if this A value can be controlled by varying the solvent or the ionic concentration.

### Line Width

The line width has been interpreted in terms of electric and magnetic perturbations produced on the absorbing ion by its ionic neighbors and by the sheath of water molecules surrounding it. These perturbations broaden the energy levels in two general ways: by causing small randomly distributed shifts in the positions of

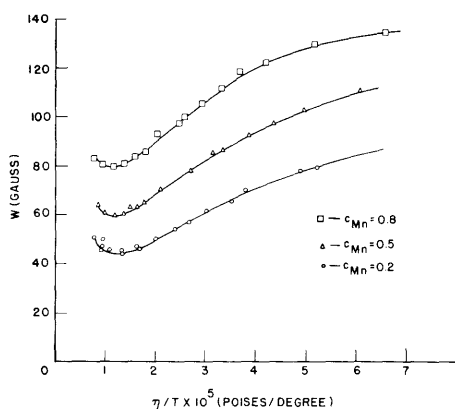


Fig. V-2

W as a function of  $\eta/T$ , with  $c_{an} = 1$ ;  
(anion is  $Cl_2^-$ ).

the levels and by shortening the lifetimes by inducing transitions. To get a quantitative dependence on temperature, the random Brownian motion is decomposed into a noise spectrum (3). The intensity of the spectrum depends upon frequency by the factor  $\tau_c / (1 + \omega^2 \tau_c^2)$ , where  $\tau_c$  is the correlation time of the motion. The first general mechanism is produced by electric and magnetic fields with frequency components  $\omega$  small compared to the frequency width of the line, that is, by fields which do not average out over the lifetime of the states. Thus the noise factor reduces approximately to  $\tau_c$  for values of small  $\omega$ , and this contribution to line width increases with  $\tau_c$ . The second mechanism acts through components near the Larmor frequency. With X-band frequencies, this makes  $\omega\tau > 1$ , causing this contribution to depend approximately on  $1/\tau_c$ . Since  $\tau_c$  is proportional to  $\eta/T$ , where  $\eta$  is the viscosity, it turns out that the line width W for a given sample should be approximately expressible in the form

$$W = \frac{A}{\frac{\eta}{T}} + B \sqrt{W \frac{\eta}{T}} .$$

The coefficients A and B depend upon the nature and concentration of the ions in solution, and may be approximated fairly well by linear combinations of the concentrations. The experimental results do fit such curves as well as expected, in view of the number of approximations involved. The principal approximation in the simplified theory is replacing  $\tan^{-1} 2\tau_c/\tau$  by  $2\tau_c/\tau$ , which eliminates the observed leveling off at large  $\tau_c$ . Figure V-2 shows the experimental results for a series in which the total ionic

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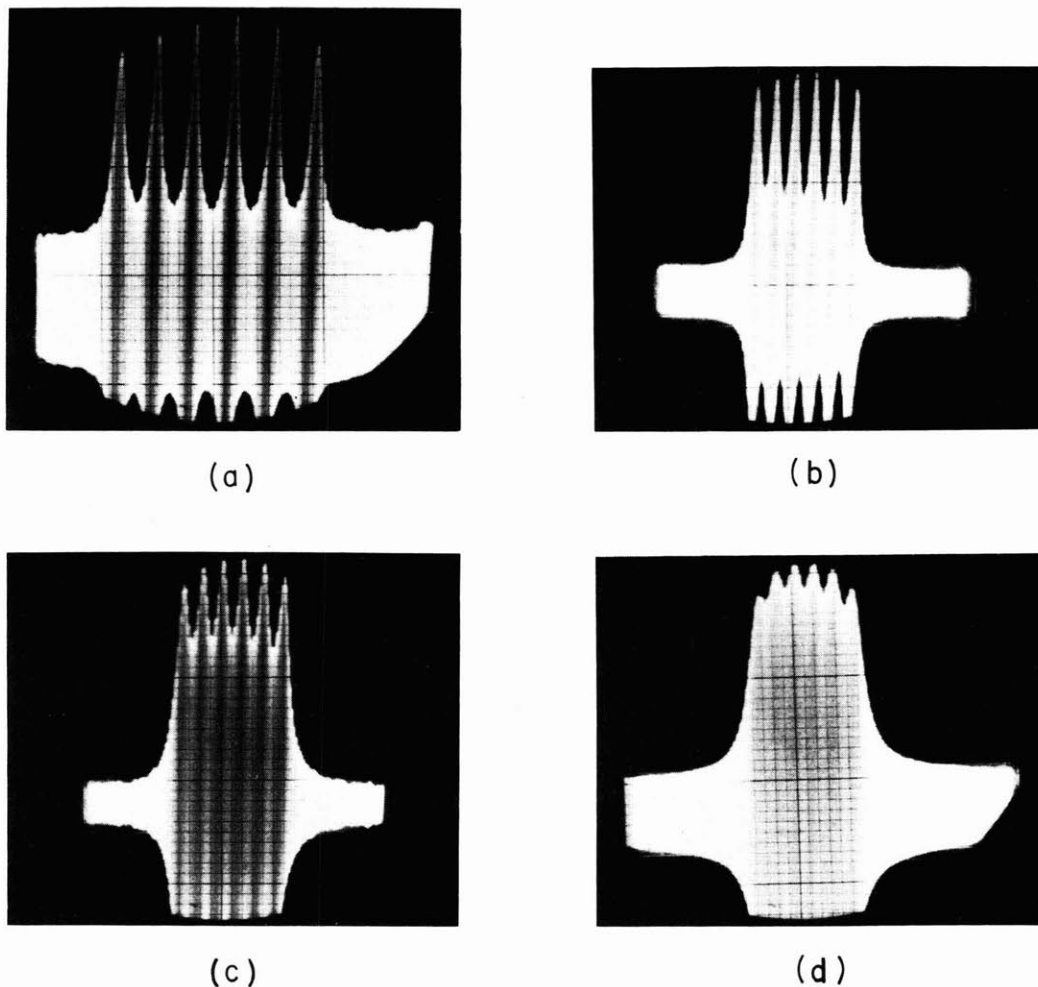


Fig. V-3

Absorption patterns (a) with 0.15 molar  $\text{MnCl}_2$  solution at  $80^\circ\text{C}$ ; (b) with 0.15 molar  $\text{MnCl}_2$  solution at room temperature; (c) with 0.15 molar  $\text{MnSO}_4$  solution at room temperature; (d) with 0.8 molar  $\text{MnCl}_2$  solution at room temperature.

concentration was held constant by substituting  $\text{CaCl}_2$  for  $\text{MnCl}_2$  when the  $\text{Mn}^{++}$  ion concentration was altered. The observed rise at low  $\eta/T$  is the result of the term in A, and the rise at high  $\eta/T$  is due to the term in B.

Other measurements were made at room temperature to test the dependence of  $W$  on ionic concentration. It was found that  $W$  is very nearly a linear function of  $\text{Mn}^{++}$  ion concentration, and also of total ionic concentration, when a solution of a nonmagnetic salt is added. To test the effect of the various anions, line widths were measured with

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0.15 molar solutions of  $\text{MnCl}_2$ ,  $\text{MnBr}_2$ ,  $\text{Mn}(\text{NO}_3)_2$ ,  $\text{Mn}(\text{C}_2\text{H}_3\text{O}_2)_2$ , and  $\text{MnSO}_4$ . The first three were all 43 gauss, within experimental error. The acetate was 60 gauss and the sulfate was 64 gauss. These results can be interpreted in terms of the effect of ionic size on  $\tau_c$  and the effect of ionic charge on the magnitude of the perturbation. Figure V-3 shows the effects of temperature, of the nature of the anion, and of the  $\text{Mn}^{++}$  ion concentration on the absorption pattern.

A detailed presentation of this work is available in "A Study of Paramagnetic Resonance Absorption in Liquids", master's thesis submitted to the Physics Department by the author in August, 1951. Work is now progressing on increasing the sensitivity of the apparatus to allow study of more dilute solutions, and of ions which give broad and therefore weak absorption patterns.

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### References

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