

## V. NUCLEAR MAGNETIC RESONANCE AND HYPERFINE STRUCTURE

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### A. MOLECULAR MOTION IN SOLIDS

We are continuing the study of hindered internal rotation in crystallographically isomorphous series of ionic crystals, in order to elucidate the forces acting among ions at their equilibrium distances. Experimental work has been completed on the series  $M_2SiF_6$ ,  $M = K, Rb, Cs, Tl$ . Linewidth measurements at several temperatures interpreted by means of correlation time calculations give the following results:

Substance	Log Barrier Height (Kcal/mole)	Log $\nu_0$ (sec <sup>-1</sup> )
$K_2SiF_6$	1.7	6.1
$Rb_2SiF_6$	15.1	13.2
$Cs_2SiF_6$	17.6	15.4
$Tl_2SiF_6$	11.6	14.0

The frequency factors  $\nu_0$  are less reliable than the barrier heights because of the lengths of the extrapolations that are necessary to obtain them. With one exception, however, they are of the same order of magnitude, as expected. The exception, which occurs in  $K_2SiF_6$ , suggests that the room-temperature crystal-structure information (1) on which the calculations were based is incorrect at the temperature of the linewidth transition (approximately 120°K). Accordingly, cooling and warming curves were obtained and two transitions were found: a strong one, probably of the first order, at about +1°C, and a weaker one at about -20°C.

The measured barriers for the other salts were compared with the results of calculations based on a simple model:

1. The coulomb "barrier" (actually a valley) was calculated on the IBM 650 computer, by performing lattice sums over a set of point charges of appropriate magnitudes. The difference in energy was computed between the equilibrium lattice and a lattice in which a single  $SiF_6$  ion is rotated to the top of the barrier.

2. A Van der Waals barrier was calculated in a similar fashion, but by hand, with the use of rare gas potentials from scattering experiments (2). This barrier calculation comes out an order of magnitude too large, as is to be expected because of the polarization of the F-electron distribution that occurs in Si-F bond formation. But the potentials

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will be useful for comparing the lattice forces in these salts with those in similar salts (e.g.,  $\text{MPF}_6$ ) that are still being studied.

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### References

1. J. A. Ketelaar, Z. Krist. 92, 155 (1935).
2. I. Amdur and E. A. Mason, J. Chem. Phys. 25, 632 (1956).

### B. UNEQUAL POPULATIONS OF CLOSELY SPACED ENERGY LEVELS IN ATOMS EXCITED BY ELECTRON IMPACT

If atoms are excited by unidirectional electrons, angular momentum considerations show that certain closely spaced energy levels can be expected to be unequally populated (1, 2, 3, 4). A research program has been started which has as its purpose the study of this effect and its utilization as a new method in radiofrequency spectroscopy.

For the first experiment, we decided to determine the inequalities in the populations of the magnetic sublevels of the metastable  $6^3P_2$  state in mercury, when this state is excited by electron impact.

Electrons are used to excite the  $6^3P_2$  state in mercury vapor. Then the absorption of the vapor for  $\lambda = 5461\text{\AA}$  light is measured. This serves two purposes. The first is that it serves to determine the degree of excitation of the  $6^3P_2$  state in the mercury vapor. The second is that by shining light that is polarized with either its electric vector parallel to or perpendicular to the direction of the electrons, the relative populations of the magnetic sublevels of the  $6^3P_2$  state (neglecting the effects of nuclear spin) can be determined. If all five sublevels are equally populated, the absorption of both kinds of light should be the same. However, if the  $m_J = \pm 2$  sublevels are less populated than the others, as theory seems to indicate, then the absorption of the "perpendicular" light should be less than that of the "parallel" light. This was verified by the results of the following experiment.

In order to determine whether or not this inequality exists, a planar diode constructed for the purpose of exciting large numbers of mercury atoms was put into operation. An oxide-coated cathode approximately 2.5 cm in diameter, with a distance of 1.65 cm between the cathode and anode, was used. This enabled us to obtain a large current of electrons the majority of which travel perpendicularly to the electrodes, when the gas pressure is such that the electron mean free path is greater than the inter-electrode distance, but the ionization is sufficient to ensure that the current is not space-charge limited.

Helmholtz coils around the tube provide a magnetic field in the direction of the

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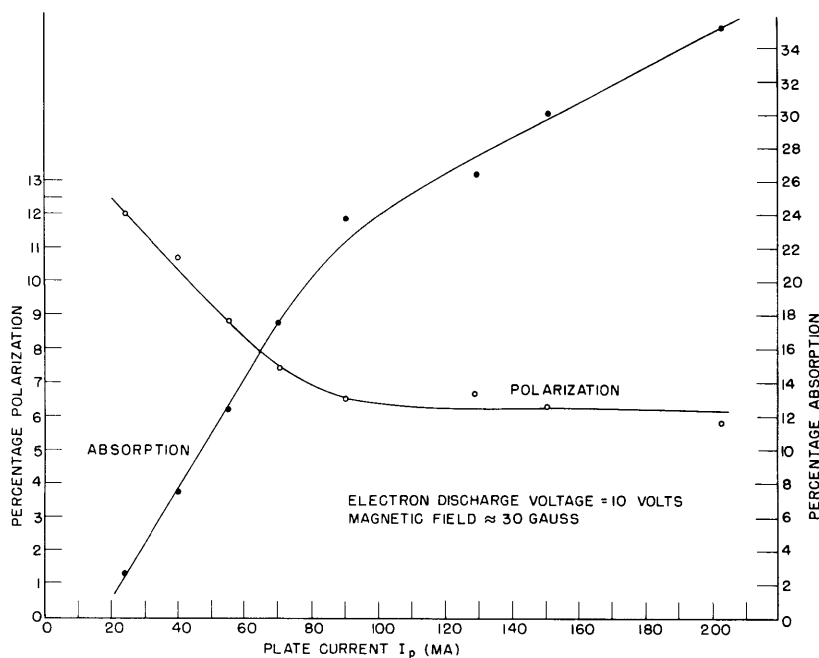


Fig. V-1. Polarization and absorption against plate current.

electron beam. Although the effect of a magnetic field is not entirely understood, we have found that a magnetic field does increase the polarization effects.

The curve of Fig. V-1 shows the variation of the percentage of polarization as a function of the plate current in the directed electron discharge. Measurements were made by means of a rotating polaroid and a narrow-band amplifier. Natural mercury was used in the light source and in the discharge. The percentage of polarization is defined as

$$P = \frac{I_{\parallel} - I_{\perp}}{I_{\parallel} + I_{\perp}} \times 100$$

where  $I_{\parallel}$  is the intensity of the "parallel" polarized light absorbed and  $I_{\perp}$  is the intensity of the "perpendicular" polarized light absorbed. Another curve shows the over-all absorption of the  $\lambda = 5461 \text{ \AA}$  radiation as a function of plate current.

Further experiments are planned, including the measurement of the hyperfine-structure separations in the metastable  $6^3P_2$  states of  $\text{Hg}^{197}$  and  $\text{Hg}^{201}$ .

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References

1. H. W. B. Skinner, Proc. Roy. Soc. (London) A112, 642 (1926).
2. H. W. B. Skinner and E. T. S. Appleyard, Proc. Roy. Soc. (London) A117, 224 (1928).
3. H. G. Dehmelt, Phys. Rev. 103, 1125 (1956).
4. W. E. Lamb, Phys. Rev. 105, 559 (1957).

C. MAGNETIC DIPOLE MOMENT AND ISOTOPE SHIFT OF RADIOACTIVE Hg<sup>197</sup>

A double-resonance experiment combined with magnetic scanning was successfully performed on Hg<sup>197</sup>. The radioactive mercury was produced by bombarding pure gold in the M. I. T. cyclotron for 12 hours and was then sealed into an evacuated quartz cell. The activity of the sample was only 5 milliroentgens/hour at a distance of 20 cm; it is possible, however, to prepare cells that contain five or ten times as much radioactive mercury.

Hg<sup>197</sup> has a spin  $I = 1/2$ , and thus only two transitions in the  $F = 3/2$  level of the  $^3P_1$  excited state are to be expected. Both were observed – but with small signal-to-noise ratios (see Fig. V-2).

a.  $m = -1/2 \rightarrow -3/2$

at a microwave frequency  $f_{\text{Hg}} = 3053.4 \text{ mc}$

and a magnetic field of proton frequency  $f_p = 8858 \pm 6 \text{ kc}$

b.  $m = 1/2 \rightarrow 3/2$

at a microwave frequency  $f_{\text{Hg}} = 3053.4 \text{ mc}$

and a magnetic field of proton frequency  $f_p = 10,149 \pm 4 \text{ kc}$

For a microwave frequency of 3053.4 mc, the corresponding resonances of Hg<sup>199</sup> (which also has a spin  $I = 1/2$ ) occur at  $f_p = 8844.2 \pm 1 \text{ kc}$  and  $f_p = 10,198.3 \pm 2 \text{ kc}$ .

Thus we can safely conclude that resonance b is not attributable to Hg<sup>199</sup> (or any stable isotope of mercury). For resonance a, there might be some doubt as to whether or not it is caused by Hg<sup>199</sup>. However, the scanning data clearly indicate that this is impossible, since for a scanning field of 2650 gauss, at which the Hg<sup>199</sup> resonance attains its maximum value, the observed resonance vanishes.

The magnetic dipole-interaction energy of Hg<sup>197</sup> can be obtained from the data of either resonance a or resonance b. If we use a, we obtain

$$a_{197} = 510.3 \pm 8 \times 10^{-3} \text{ cm}^{-1}$$

If we use b, we obtain

$$a_{197} = 514.8 \pm 4 \times 10^{-3} \text{ cm}^{-1}$$

If we take

$$a_{197} = 514 \pm 4$$

and

$$a_{199} = 491.5 \pm .5$$

we obtain (barring hfs anomalies), for the ratio of the moments,

$$\frac{\mu_{197}}{\mu_{199}} = 1.046 \pm .01$$

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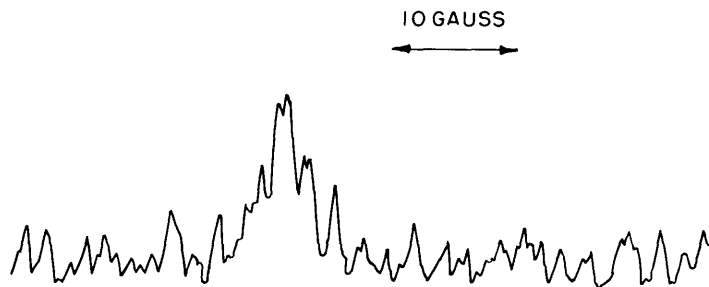


Fig. V-2. Signal obtained, 36 hours after bombardment, from the  $F=3/2, m=-1/2 \rightarrow m=-3/2$  transition of  $\text{Hg}^{197}$ .

which is in very good agreement with previous magneto-optical investigations (1).

Very strong signals were obtained from resonances in the even isotopes, especially from  $\text{Hg}^{198}$ . A larger amount of  $\text{Hg}^{196}$  than of  $\text{Hg}^{200}$  is contained in the cell; but these data have not yet been processed.

For the position of the Zeeman sublevels of  $\text{Hg}^{197}$  relative to the  $\text{Hg}^{198}$  level, we obtain:

Zeeman sublevel of $\text{Hg}^{197}$	Field	Position relative to $\text{Hg}^{198}$	
		gauss	$\text{cm}^{-1}$
$F=3/2, m=-1/2$	2080 gauss	$4340 \pm 200$	$298 \times 10^{-3}$
$F=3/2, m=1/2$	2700 gauss	$5980 \pm 200$	$413 \times 10^{-3}$

From these two sets of data we compute the zero-field position of the hfs components to be  $340 \pm 10 \times 10^{-3} \text{ cm}^{-1}$  and  $348 \pm 10 \times 10^{-3} \text{ cm}^{-1}$ , respectively. We conclude that the center of gravity of  $\text{Hg}^{197}$  is found to be  $87 \pm 10 \times 10^{-3} \text{ cm}^{-1}$  from  $\text{Hg}^{198}$ .

We believe that it will be possible to extend these measurements to the isomeric state of  $\text{Hg}^{197}$  (which has a spin of  $13/2$ ), as well as to other radioactive isotopes of mercury.

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References

1. F. Bitter, S. P. Davis, B. Richter, and J. E. R. Young, Optical studies of radioactive mercury, Phys. Rev. 96, 1531 (1954).

D. USE OF ANALYTIC WAVE FUNCTIONS IN THE DETERMINATION OF NUCLEAR MOMENTS; APPLICATION TO THE QUADRIPOLE MOMENT OF  $\text{B}^{11}$

The purpose of this study, which arose from a suggestion of Professor Morse, was to investigate the possibility of using analytic wave functions (1, 2) for the interpretation

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of hfs data. Such wave functions exist for the first 10 elements (3); we decided to work with boron. The hyperfine structure of the ground-state doublet  $^2P$  of  $B^{11}$  has been measured in a radiofrequency experiment by G. Wessel (4); the magnetic dipole moment is also known from nuclear resonance (5).

By approximating the operators which appear in the actual formulas (6), we obtain, for the interaction energies, in  $\text{cm}^{-1}$  (not for s-electrons):

$$\delta = 5.84298 \left( \ell + \frac{1}{2} \right) Z_i H_r(\ell, Z_i) \left\langle \frac{1}{r^3} \right\rangle \quad (1)$$

$$a_j = \frac{9.540673}{c} \times 10^7 \frac{\ell(\ell+1)}{j(j+1)} \left( \frac{\mu_I}{\mu_N} \frac{1}{I} \right) F_r(j, Z_i) \left\langle \frac{1}{r^3} \right\rangle \quad (2)$$

$$b = \frac{2.349859}{c} \times 10^8 \frac{2j-1}{2j+2} Q R_r(k, Z_i) \left\langle \frac{1}{r^3} \right\rangle \quad (3)$$

Equation 3 is valid only under the assumption that the wave function for the state is separable into radial and angular parts. All energies are given in  $\text{cm}^{-1}$ ; and  $H_r$ ,  $F_r$ , and  $R_r$  are relativistic corrections tabulated in reference 7. If a second-order perturbation calculation is made (configuration interaction), the simplified formulas (Eqs. 1, 2, and 3) will not be valid. However, Sternheimer (8, 9, 10, 11) has recently calculated and given multiplicative correction factors for these formulas, which take into account terms that arise from higher-order perturbation calculations (polarization effects). Similar work by Schwartz (12) is not in agreement with Sternheimer's results.

For computing  $\left\langle 1/r^3 \right\rangle$ , the wave functions for the valence electron(s) can be used, if they are known, or it can be obtained from one of the interactions if  $Z_i$  or the moments are known. For  $B^{11}$ , except for the analytic wave function which we wanted to check, the following information was available:

(a) A numerical wave function obtained from a double-configuration approximation of the self-consistent field equations without exchange (13). There was also an older calculation of a Hartree wave function (14).

(b) The value of  $\left\langle 1/r^3 \right\rangle$  obtained from a numerical integration of the Dirac equation (12).

(c) The accurate value of the fine structure  $15.3 \pm .2 \text{ cm}^{-1}$  (ref. 12), and the magnetic moment  $\mu_I/\mu_N = 2.6851$  (ref. 15).

Parameters for the analytic wave function of the  $(1s)^2(2s)^22p$  state of boron had been given by Tubis (3); however, because of the sensitivity of  $\left\langle 1/r^3 \right\rangle$  to the value of  $\mu c$ , the minimization was repeated (Morse and Yilmaz' tables (2) were used to the ninth significant figure of the energy), and the following parameters were obtained:

$$a = 3.60$$

$$b = 3.25$$

$$c = 0.928$$

$$\mu = 1.30404$$

$$W = 49.00878$$

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The wave function is a single determinant formed from the one-electron wave functions:

$$(1s) \quad u_1 = \sqrt{\frac{\mu^3 a^3}{\pi}} e^{-\mu ar}$$

$$(2s) \quad u_2 = \sqrt{\frac{\mu^3}{3\pi N(a, b)}} [\mu r e^{-\mu r} - 3A(a, b) e^{-\mu br}]$$

$$(2p) \quad u_3 = \sqrt{\frac{\mu^3 c^3}{\pi}} \mu c r e^{-\mu cr} P_1(\cos \theta)$$

These wave functions were used for an accurate evaluation of  $Z_i$  (5). The agreement of the experimental value of the fine structure,  $15.3 \pm .2 \text{ cm}^{-1}$ , with the calculated value,  $16.10 \pm .47 \text{ cm}^{-1}$  is good. The following values of  $\langle 1/r^3 \rangle$  (in units of  $a_0^3$ ) were obtained:

a. from the fine structure	0.5619
b. from a numerical integration of the self-consistent field equation	0.5908
c. from the integration of the Dirac equation	0.51122
d. from the analytic wave function	0.59073
e. from the hfs magnetic interaction and the magnetic moment	0.8051

From consideration of these results and, mainly, from the agreement of a, b, and d, we conclude that the best value for  $\langle 1/r^3 \rangle$  is  $0.590 \pm .030$ , and that the disagreement in e results because the simple relation (Eq. 2) is not good enough for the calculation of the magnetic interaction energy, which requires a second-order perturbation treatment. Such a calculation (16) for the gallium isotopes  $(4s)^2 4p$  revealed a discrepancy of 23 per cent in the magnetic interaction of the  $j = 3/2$  level. Strangely, though, in  $B^{11}$  the ratio

$$\frac{a_{1/2}}{F_r(1/2)} \bigg/ \frac{a_{3/2}}{F_r(3/2)} = \frac{365.87}{73.332} = 4.9892 \pm .02$$

is very close to  $j_2(j_2+1)/j_1(j_1+1) = 5$ , which furnishes a strong argument against the mixing of higher configurations.

Evidently, we have been unable to bring the magnetic moment and hyperfine structure of  $B^{11}$  into agreement. However, we conclude that the analytic wave functions can be used for the evaluation of hfs data. In particular, if they are used for the determination of  $Z_i$ , a reliable value for  $\langle 1/r^3 \rangle$  can be obtained from the fine structure, which is independent of configuration interaction. (This might not be absolutely true for the

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lighter elements.) This value can then be used for the evaluation of the quadrupole moment. We shall use this method to obtain a new value for the quadrupole moment of  $B^{11}$ .

By using, for the average of  $\langle 1/r^3 \rangle$  over the valence electron, the value  $0.590 \pm .03$ , and Sternheimer's (9) correction for boron,  $C = 1 / \left(1 - \frac{R'}{1.5}\right) = 1.124$ , we obtain from Wessel's (4) data ( $b = 2.695 \pm .016$  mc),

$$Q = [0.043 \pm .003] \times 10^{-24} \text{ cm}^2$$

We believe that this value is better than the value given by Wessel ( $Q = 0.0355 \pm .0002$ ); he used the magnetic hyperfine structure to evaluate  $\langle 1/r^3 \rangle$ . From pure quadrupole resonance in  $B(\text{CH}_3)_3$  and  $B(\text{C}_2\text{H}_5)_3$ , Dehmelt (17) obtained for boron

$$eQ\phi_{zz}/h = 4.95 \text{ mc}$$

$$Q_{B^{10}}/Q_{B^{11}} = 2.084 \pm .002$$

Using  $\phi_{zz} = 1.44 \times 10^{15}$  in cgs units (and including the Sternheimer correction  $C = 1.124$ ), he gave for  $B^{11}$ ,  $Q = 0.053 \times 10^{-24} \text{ cm}^2$ . However, this value is certainly larger than the true  $Q$ , since the value of  $\phi_{zz}$  that he used (18) corresponds to  $\langle 1/r^3 \rangle = 0.55$ ; this is less than the actual value of  $\langle 1/r^3 \rangle$ , according to our calculations.

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### References

1. P. M. Morse, L. A. Young, and Eva S. Haurwitz, *Phys. Rev.* **48**, 948 (1935).
2. P. M. Morse and H. Yilmaz, *Tables for the Variational Determination of Atomic Wave Functions* (The Technology Press, M.I.T., and John Wiley and Sons, Inc., New York, 1956).
3. A. Tubis, *Phys. Rev.* **102**, 1049 (1954).
4. G. Wessel, *Phys. Rev.* **92**, 1581 (1953).
5. L. Schiff, *Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1949), p. 276.
6. H. Casimir, *On the Interaction Between Atomic Nuclei and Electrons* (Teyler's Tweede Genootschap, Haarlem, 1936).
7. H. Kofermann, *Kermomente*, Akad. Verlagsgesell. M.B.H., Leipzig, 1955, p. 430.
8. R. M. Sternheimer, *Phys. Rev.* **84**, 244 (1951).
9. *Ibid.*, *Phys. Rev.* **86**, 316 (1952).
10. *Ibid.*, *Phys. Rev.* **95**, 736 (1954).
11. *Ibid.*, *Phys. Rev.* **105**, 173 (1957).
12. C. Schwartz, *Phys. Rev.* **105**, 173 (1957).
13. G. K. Tsunaitis and A. P. Iutsis, *Soviet Physics JETP* **1**, 358 (1955).
14. F. W. Brown, J. H. Bartlett, Jr., and C. G. Dunn, *Phys. Rev.* **44**, 296 (1933).
15. W. Gordy, H. Ring, and A. B. Burg, *Phys. Rev.* **78**, 512 (1950).
16. G. F. Koster, *Phys. Rev.* **86**, 148 (1952).
17. H. G. Dehmelt, *Z. Physik* **133**, 528 (1952).
18. *Ibid.*, *Z. Physik* **134**, 642 (1953).