V. NUCLEAR MAGNETIC RESONANCE AND HYPERFINE STRUCTURE

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RESEARCH OBJECTIVES

1. Nuclear Magnetic Resonance

(a) Nuclear Spin Interactions in Molecules. It has become clear that high-resolution nuclear-resonance experiments can give a great deal of information relative to the geometrical and electronic structures of molecules. It is believed that all observed spectral structures can be accounted for on the basis of the Hamiltonian

$$\frac{1}{\hbar}\mathscr{H} = H \sum_i \gamma_i (1 - \delta_i) + \sum_i \sum_{j>i} J_{ij} \vec{I}_i \cdot \vec{I}_j$$

where H is the applied magnetic field, γ_i is the gyromagnetic ratio of nucleus i, $\vec{I}_i$ is its spin operator, and δ_i and J_{ij} are coupling constants characteristic of the electronic wavefunctions of the molecule. We are attempting to justify the form of this Hamiltonian in intermediate coupling cases, and to correlate the coupling constants with simple descriptions of the molecular wavefunctions. Standard radiofrequency techniques are being used, with particular attention to the magnetic field uniformity and stability which will permit resolution of lines separated by approximately 1 part in 10^8 of the total field.

(b) Molecular Motion in Solids. Large-scale motion in solids can have important effects on the macroscopic properties of substances in which they occur. This fact is particularly evident in solid-state diffusion and chain twisting in polymers such as rubber. Nuclear-resonance linewidth measurements can give rather direct information on the types of motion that are present and on their activation energies. We are applying this method to cases that are not practicably accessible by other methods, with special reference to ion and terminal group reorientation. Results which have been obtained deal with $Co(NH_3)_6^{+++}$ and MF_6^- ions and $-CH_3$ and $-CF_3$ groups in various crystal lattices.

J. S. Waugh

2. Hyperfine Structure

The purpose of this work is to learn about nuclear structure from detailed investigations of atomic energy levels. Atomic electrons actually penetrate the nucleus in the course of their orbital motion, and the position of the various possible energy levels is influenced by the electron-nuclear interaction.

The investigations of this group are concerned with changes in the energy levels produced by reorientation of the nucleus with respect to the atomic angular momentum, and with accurate comparison of energy levels of isotopes, both stable and unstable. A combination of radiofrequency or microwave and optical techniques is being used.

Previously reported investigations of the isotopes of mercury are being extended, and new work on cadmium and calcium is being undertaken.

F. Bitter

A. SOME INTERRELATIONS OF THE MAGNETIC SUBLEVELS OF HYPERFINE-STRUCTURE LINES

In the double-resonance experiment performed on natural mercury (described in previous reports), microwave resonance was established between the m-sublevels of a certain F-level belonging to one of the odd isotopes (Hg^{199} or Hg^{201}). The energy of these sublevels depends upon the following parameters:

B_z, the magnetic field

g_J, the atomic g-factor for the electronic configuration

a, the magnetic dipole interaction energy

b, the electric quadripole interaction energy (for Hg^{201} only)

and it is given by the roots of secular equations which are easily obtained from an elementary quantum-mechanical calculation (1).

The value of g_J is accurately known from measurements on the even isotopes; in establishing a resonance we accurately determine the energy difference between two such m-sublevels, so that, if we also know the magnetic field, we have a relation between the remaining constants. For Hg^{199}, one resonance suffices to obtain a; for Hg^{201}, each resonance gives a relation between a and b. Consequently, from two resonances in Hg^{201}, we can obtain both a and b.

The determination of a and b has been achieved in various ways; for example, by Kusch, Millman, and Rabi (2) on the $^2S_{1/2}$ state of Li^7. But their technique was different from ours. In their apparatus the frequency could be varied, and the field could be kept constant, so that they were able to eliminate B_z from their equations. We did not have the advantage of a variable frequency and were forced to use B_z in our calculations. Consequently, our equations take a different form.

If we set

Δy = energy difference between sublevels in cm^{-1}

$H = B_z g_J \mu_B$ in cm^{-1}

the value of a for Hg^{199}, as obtained from transitions in the F = 3/2 level, is

$$a = \frac{\Delta y^2 - \Delta yH}{H - \frac{3}{2}\Delta y} \qquad \text{for } m = -\frac{1}{2} \rightarrow m = -\frac{3}{2} \qquad (1)$$

and

$$a = \frac{\Delta y^2 - \Delta yH}{\frac{3}{2}\Delta y - H} \qquad \text{for } m = \frac{1}{2} \rightarrow m = \frac{3}{2}$$

For Hg^{201} we were not able to find a closed form for the expression for a and b, and had to use a computational method. (The root of a third-order equation is included in this expression.) However, from a transition in the $F = 5/2$ level ($m = 3/2 \rightarrow m = 5/2$), we obtain the following relation between a and b:

$$\frac{5}{2} a + 10b = \frac{\Delta y^2 - \Delta yH}{\frac{2}{5} H - \Delta y} \tag{2}$$

It is interesting that

$$\frac{5}{2} a + 10b$$

is exactly the splitting between the $F = 5/2$ and $F = 3/2$ levels of Hg^{201} (at zero field), as predicted by the interval rule. Furthermore, Eqs. 1 can also be transformed to give

$$\frac{3}{2} a = \pm \frac{\Delta y^2 - \Delta yH}{\frac{2}{3} H - \Delta y} \tag{3}$$

where $(3/2)a$ is, again, the exact splitting of the $F = 3/2$ and $F = 1/2$ levels of Hg^{199}.

Equations 2 and 3 are obtained from rather lengthy expressions which contain radicals, and so forth, so that the possibility of a reduction to simple forms is interesting. Moreover, the symmetry between Eqs. 2 and 3 and the fact that they are related to the zero-field splitting of the F-levels raises the suspicion that they might be consequences of a more general quantum-mechanical rule. If this is true, a knowledge of the underlying general rule should permit the formulation of closed-form results for any arbitrary combination of J and I. This will be extremely helpful, especially in cases in which our straightforward calculations present impossible algebraic difficulties.

<div align="right">A. C. Melissinos</div>

<div align="center">References</div>

1. See, for example, Th. Schmidt, Z. Physik 111, 332 (1938-39).
2. P. Kusch, S. Millman, and I. I. Rabi, Phys. Rev. 57, 765 (1940).

B. INTERMEDIATE COUPLING IN NUCLEAR RESONANCE SPECTRA

We define an intermediate coupling case as one in which, in the molecular nuclear spin Hamiltonian, $J_{ij} \sim H(\gamma_i \delta_i - \gamma_j \delta_j)$ for one or more nuclear pairs (i, j). In these cases the energy level schemes and selection rules are complicated, and lead to
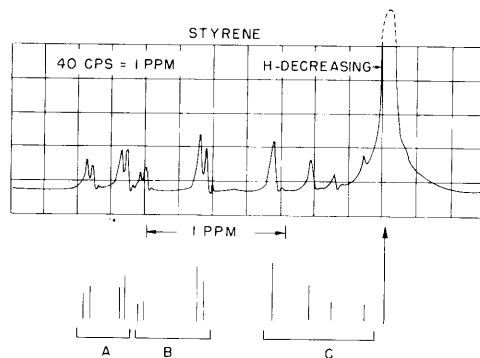
Fig. V-1. Proton resonance spectrum of styrene. Parameters used for predicting spectrum:

$$\delta_B - \delta_A = 0.55 \text{ PPM} \qquad J_{AB} = 1.6 \text{ cps}$$
$$\delta_C - \delta_A = 1.67 \text{ PPM} \qquad J_{AC} = 12 \text{ cps}$$
$$J_{BC} = 20 \text{ cps}$$

complex spectra that provide a stringent test of the Hamiltonian. We have attempted to find consistent sets of J's and δ's from which observed spectra can be calculated, with the sort of success illustrated in Fig. V-1, which applies to the three-spin ethylenic system of styrene. The intense line on the right is attributable to the protons ignored in this calculation. Five adjustable parameters are able to reproduce 12 line positions and 12 intensities within experimental error.

These calculations are now being extended to more complex systems, with some attention to the information obtainable from incompletely resolved spectra.

J. S. Waugh

C. THE FREE ELECTRON MODEL FOR CHEMICAL SHIFTS

The problem of calculating δ's (chemical shifts) and J's (spin-spin interaction constants) from molecular theory is a very difficult one. In the comparatively simple case of aromatic molecules, we have extended a suggestion of Pople (1) to calculate chemical shifts on the basis of a free electron model. The chemical shifts are regarded as being caused by the magnetic fields arising from precession of the π electron systems of these molecules in the applied field. A complete description of this work will appear soon (2).

J. S. Waugh

References

1. J. A. Pople, J. Chem. Phys. 24, 1111 (1956).
2. J. S. Waugh and R. W. Fessenden, J. Am. Chem. Soc. (in press).