

VIII. NUCLEAR MAGNETIC RESONANCE AND HYPERFINE STRUCTURE

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RESEARCH OBJECTIVES

1. Nuclear Magnetic Resonance

We are still concerned with the general problem of studying the structures and internal dynamics of materials by observing perturbations of the magnetic resonances of nuclei embedded in them. The direct interaction of nuclear magnetic moments in solids has given us some information about crystal structures and molecular motion in crystals. We are preparing to carry out pulsed radiofrequency experiments which will provide a more powerful tool for studying these and related effects. Most of our recent research emphasis, however, has been on the study of electronic perturbations of resonances in rapidly tumbling molecules in liquids, and particularly on the phenomenological aspects of these interactions and their interpretation. Since it has also been found that nuclear resonances in molecules can provide a good deal of information about the problem of restricted internal rotation about single bonds, we are continuing studies of the energetics of this kind of process.

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.

F. Bitter, L. C. Bradley III

A. NUCLEAR MAGNETIC RESONANCE

1. Nuclear Spin Interaction in Molecules

It is generally accepted that "high-resolution" nuclear resonance spectra of molecules, which offer a fruitful approach to studies of molecular structure, can be interpreted on the basis of the phenomenological spin Hamiltonian

$$h^{-1} \mathcal{H} = \nu_0 \sum_i (1 - \delta_i) I_{zi} + \sum_i \sum_{j>i} A_{ij} \vec{I}_i \cdot \vec{I}_j$$

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in which ν_0 is a reference Larmor frequency, δ_i is a "chemical shift" arising from field-induced electron currents, and A_{ij} is a constant describing the coupling of nuclei i and j through hyperfine interactions with their common electron distribution. When $|A_{ij}|$ is much less than $|\nu_0(\delta_i - \delta_j)|$ for all i and j , the problem can be treated by perturbation theory, and a particularly simple spectrum results, from which the A 's and δ 's can be extracted by inspection. When this is not the case, the evaluation of these parameters, which are of considerable current interest in molecular theory, may become very difficult. The customary approach has been one of repeated explicit diagonalization of \mathcal{H} by using trial parameters until a spectrum is obtained that matches the theoretical spectrum. Even with as few as three interacting spins (six independent parameters) this process may be very laborious unless the trial parameters are chosen by inspiration. We have been concerned with simplifying this procedure along two lines: (a) intelligent choice of the starting representation in order to make maximum use of existing symmetries, and (b) actual inversion of the calculation, so that the A 's and δ 's appear as the output of a calculation of which the experimental spectrum is the input. The second treatment, applied specifically to systems of three spins, but extendible in principle to larger systems, will be described in detail in an article to be submitted to the Journal of Chemical Physics. It may be broadly outlined as follows:

a. The fact that \mathcal{H} commutes with the total z angular momentum and the invariance of $\text{Tr}(\mathcal{H})$ result in a set of interval rules for spectral lines which enables the construction of the set of eigenvalues from the spectrum.

b. These same facts, together with the invariance of $\text{Tr}(\mathcal{H}^2)$ and $\text{Tr}(\mathcal{H}^3)$, make it possible to obtain from the eigenvalues a semiunique set of diagonal elements of \mathcal{H} in the representation in which the spins are independently quantized.

c. In this representation the desired A 's and δ 's are then easily obtained as definite linear combinations of the diagonal elements.

This method has been applied to a number of representative cases, with great saving in labor over the customary procedure. A number of interesting features are displayed when the problem is attacked from this point of view, among them is the fact that there may be as many as 16 independent sets of A 's and δ 's which are consistent with a given set of spectral line positions.

J. S. Waugh

2. Hindered Internal Rotation

In sufficiently unsymmetrical molecules it is, in general, possible to observe in the high-resolution nuclear resonance spectrum, characteristic complexities that are related to hindrance of rotation about a single bond (1). We have made careful measurements of the temperature dependence of the spectrum in two cases, and we have interpreted them on the basis of a simple model to obtain the energy difference between two adjacent

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potential minima. In $\text{CH}_2\text{Br}-\text{CF}_2\text{Br}$, ΔE is found to be 0 ± 400 cal/mole, as compared with a result of approximately 700 cal/mole from an equally simple treatment based on the infrared spectrum (2). In $\text{CHClBr}-\text{CF}_2\text{Br}$, which has not been studied by any other method, we find that ΔE is 2200 ± 700 cal/mole. A more sophisticated treatment awaits a firmer understanding of the variation of spin-spin coupling constants A_{ij} with internal configuration.

R. W. Fessenden, J. S. Waugh

References

1. J. S. Waugh, Nuclear resonance spectra of hindered internal rotors, Quarterly Progress Report, Research Laboratory of Electronics, M.I.T., Oct. 15, 1957, p.22.
2. R. E. Kagarise, Rotational isomerism in 1,2-dibromo-2,2-difluorethane, J. Chem. Phys. 24, 1264L (1956).

B. HYPERFINE STRUCTURE OF RADIO THALLIUM

The caption of Fig. VII-2 in Quarterly Progress Report No. 51, page 52, should have read: "From left to right: the first, third, and sixth lines are Tl^{199} ; we tentatively assign the second, fifth, and seventh lines to natural thallium, and the fourth line to Tl^{200} ."

R. J. Hull, H. H. Stroke

C. THE g-FACTOR OF THE $5s\ 5p\ ^3P_1$ LEVEL OF CADMIUM

The g-factor of the $5s\ 5p\ ^3P_1$ level of cadmium has been determined by comparing the magnetic field at which Δm_J transitions induced by a 50-mc oscillating magnetic field occurred in cadmium with the magnetic field at which the same transitions occurred in mercury, for which the g-factor of the $6s\ 6p\ ^3P_1$ level is known. The magnetic fields were compared by measuring the currents in the Helmholtz coils which produced them. The result is $g = 1.4975 \pm 10$. The value predicted by theory (1) is $g = 1.4986 \pm 6$.

R. F. Lacey

References

1. R. F. Lacey, The relation between the g-factors and the lifetimes of excited states of two-electron atoms, Quarterly Progress Report No. 51, Research Laboratory of Electronics, M.I.T., Oct. 15, 1958, p. 53.

D. HEAVY ABSORPTION OF A SPECTRAL LINE

We shall calculate the transmission of light from a single Doppler-broadened spectral line passing through a gas with a Doppler-broadened absorption resonance in

the limit of small transmission.

The relative transmission, ϕ , can be expressed (1) as an integral:

$$\phi(\mu, \beta, y) = \left(\frac{\beta}{\pi}\right)^{1/2} \int_{-\infty}^{\infty} \exp\left[-\mu e^{-x^2} + \beta(x+y)^2\right] dx \quad (1)$$

The following symbols will be used:

[1] = the incident line

[2] = the absorbing line

T = absolute temperature

M = gram molecular weight

ν_1 = center frequency of line [1]

n = density of molecules in the absorbing gas

ℓ = path length of light in the gas

σ_0 = cross section for absorption of the center of absorption resonance

$$x = \left(\frac{\nu - \nu_2}{\nu_2}\right) \left(\frac{M_2 C^2}{2RT_2}\right)^{1/2}$$

$$y = \left(\frac{\nu_1 - \nu_2}{\nu_2}\right) \left(\frac{M_2 C^2}{2RT_2}\right)^{1/2}$$

$$\beta = \frac{T_2}{T_1} \frac{M_1}{M_2} \frac{\nu_2}{\nu_1}$$

$$\mu = \sigma_0 n \ell$$

The term $\mu \exp(-x^2)$ is the Gaussian-shaped absorption coefficient; the factor $\exp[-\mu \exp(-x^2)]$ represents the transmission of the gas as a function of frequency. The second factor, $\exp[-\beta(x+y)^2]$, represents the Gaussian frequency distribution of the incident light. The factor β measures the difference in widths of the two Gaussian lines, and y measures the difference in their center frequencies. This frequency difference could have two causes. First, the incident line could arise from one pure isotope, and the absorbing line from another at a slightly different frequency. Second, small frequency changes can be produced either on the light source or on the absorber by means of magnetic fields.

In the evaluation of ϕ , we first consider the special case, $y = 0$. Then

$$\phi(\mu, \beta) = 2 \left(\frac{\beta}{\pi}\right)^{1/2} \int_0^{\infty} \exp\left[-\mu e^{-x^2} - \beta x^2\right] dx \quad (2)$$

The integrand has a maximum at

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$$\left(\log \frac{\mu}{\beta}\right)^{1/2} = a \quad (3)$$

Let

$$x^2 = a^2 + z$$

Then

$$\phi = \left(\frac{\beta}{\mu}\right)^\beta \left(\frac{\beta}{\pi}\right)^{1/2} \int_{-a^2}^{\infty} \frac{\exp[-\beta e^{-z} - \beta z] dz}{(a^2 + z)^{1/2}} \quad (4)$$

since $\mu \exp(-a^2) = \beta$, and $\exp(-\beta a^2) = (\beta/\mu)^\beta$.

The term $\exp[-\beta e^{-z} - \beta z]$ has a maximum for $z = 0$, and falls off rapidly to zero for $|\beta z| > 1$. Then, if $a^2 \gg 1/\beta$, or if $\log[(\mu/\beta)^\beta] \gg 1$, we have

$$\phi \approx \left(\frac{\beta}{\pi}\right)^{1/2} \left(\frac{\beta}{\mu}\right)^\beta \frac{1}{a} \int_{-a^2}^{\infty} \exp[-\beta e^{-z} - \beta z] dz \quad (5)$$

Let

$$\psi(\beta) = \int_{-a^2}^{\infty} \exp[-\beta e^{-z} - \beta z] dz \quad (6)$$

and

$$\beta e^{-z} = w$$

Then

$$\psi(\beta) = \frac{1}{\beta^\beta} \int_0^\mu e^{-w} w^{\beta-1} dw \quad (7)$$

If $\mu \gg 1$, then

$$\psi(\beta) \approx \frac{1}{\beta^\beta} \int_0^\infty e^{-w} w^{\beta-1} dw = \frac{\Gamma(\beta)}{\beta^\beta}$$

So that, finally, we obtain

$$\phi(\mu, \beta) \approx \frac{\Gamma(\beta)}{\mu^\beta} \left(\frac{\beta}{\pi \log \frac{\mu}{\beta}}\right)^{1/2} \quad \text{for } \frac{\mu^\beta}{\beta} \gg e \quad (8)$$

For the special case, $\beta = 1$ — that is, when the incident and absorbing lines have the

same Doppler widths – Eq. 8 reduces to

$$\phi(\mu) \approx \frac{1}{\mu(\pi \log \mu)^{1/2}} \quad (9)$$

which, for large μ , is essentially the same as the result of Chapman (2).

We shall now consider the general case, $y \neq 0$. Let

$$\phi(\mu, \beta, y) = \phi_1(\mu, \beta, y) + \phi_2(\mu, \beta, y) \quad (10)$$

and then

$$\begin{aligned} \phi_1 &= \left(\frac{\beta}{\pi}\right)^{1/2} \int_{-\infty}^0 \exp -\left[\mu e^{-x^2} + \beta(x+y)^2\right] dx \\ \phi_2 &= \left(\frac{\beta}{\pi}\right)^{1/2} \int_0^{\infty} \exp -\left[\mu e^{-x^2} + \beta(x+y)^2\right] dx \end{aligned} \quad (11)$$

First, consider ϕ_2 . The maximum, a_2 , of the integrand must be determined from the following equation:

$$a_2 = + \left(\log \frac{\mu a_2}{\beta(a_2 + y)} \right)^{1/2} \quad (12)$$

If Eq. 12 is solved by iteration, it converges very rapidly. Let $x^2 = a_2^2 + z$. Then, we have

$$\phi_2 = \frac{1}{2} \left(\frac{\beta}{\pi}\right)^{1/2} \int_{-a_2^2}^{\infty} \frac{\exp -\left[\mu \exp(-a_2^2) e^{-z} + \beta(a_2^2 + z + 2y(a_2^2 + z)^{1/2} + y^2)\right] dz}{(a_2^2 + z)^{1/2}} \quad (13)$$

Consider the numerator of the integrand in the vicinity of $z = 0$. Here we can expand as follows:

$$\left(a_2^2 + z\right)^{1/2} = a_2 \left(1 + \frac{z}{a_2^2}\right)^{1/2} \approx a_2 + \frac{z}{2a_2} - \frac{z^2}{8a_2^3} \quad (14)$$

For $z \ll a_2^2$, the numerator becomes

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$$\begin{aligned} & \exp - \left[\beta \frac{(a_2 + y)}{a_2} e^{-z} + \beta \left(a_2^2 + z + 2a_2 z + \frac{yz}{a_2} + y^2 \right) \right] \\ & = \exp - \left[\beta(a_2 + y)^2 + \beta \left(\frac{a_2 + y}{a_2} \right) e^{-z} + \beta \left(\frac{a_2 + y}{a_2} \right) z \right] \end{aligned} \quad (15)$$

If we let

$$\beta \frac{a_2 + y}{a_2} = \rho_2$$

the numerator in the vicinity of $z = 0$ becomes

$$\exp \left[-\beta(a_2 + y)^2 \right] \exp \left[-\rho_2 e^{-z} - \rho_2 z \right]$$

As this function falls off rapidly to zero for $|z| > 1/\rho_2$, it can be used as a good approximation to the numerator of the integrand, provided that

$$\left| \frac{\beta y}{4\rho_2^2 a_2^3} \right| \ll 1$$

which comes from the third term in Eq. 14.

As before, if $\rho_2 a_2^2 \gg 1$, the denominator of the integrand becomes a_2 . Thus, ϕ_2 becomes

$$\phi_2 \approx \left(\frac{\beta}{\pi} \right)^{1/2} \frac{\exp \left[-\beta(a_2 + y)^2 \right]}{2a_2} \int_{-a_2}^{\infty} \exp \left[-\left(\rho_2 e^{-z} + \rho_2 z \right) \right] dz \quad (16)$$

As before, if $\exp \left(a_2^2 \right) \gg 1$, the integral in Eq. 15 becomes approximately

$$\frac{\Gamma(\rho_2)}{\left(\rho_2 \right)}$$

and then, we have

$$\phi_2(\mu, \beta, y) \approx \left(\frac{\beta}{\pi} \right)^{1/2} \frac{\exp \left[-\beta(a_2 + y)^2 \right] \Gamma(\rho_2)}{2a_2 \left(\rho_2 \right)} \quad (17)$$

It will be noticed that $\phi_1(\mu, \beta, y) = \phi_2(\mu, \beta, -y)$. so that we obtain directly

$$\phi_1(\mu, \beta, y) \approx \left(\frac{\beta}{\pi}\right)^{1/2} \frac{\exp[-\beta(a_1 - y)^2] \Gamma(\rho_1)}{2a_1 \binom{\rho_1}{\rho_1}} \quad (18)$$

in which

$$a_1 = + \left(\log \frac{\mu a_1}{\beta(a_1 - y)} \right)^{1/2} \quad (19)$$

$$\rho_1 = \beta \frac{a_1 - y}{a_1}$$

Equation 17 is valid if

$$\left. \begin{array}{l} \left| \frac{\beta y}{4\rho_1^2 a_1^3} \right| \ll 1 \\ \left| \rho_1 a_1^2 \right| \gg 1 \\ \exp(a_1^2) \gg 1 \end{array} \right\} \quad (20)$$

The relative transmission ϕ is, then,

$$\phi = \phi_1 + \phi_2 \quad (21)$$

R. H. Kohler

References

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