

VIII. MAGNETIC RESONANCE

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RESEARCH OBJECTIVES

The activity of this group is centered on the study of the structure and atomic dynamics of solids and fluids through experiments on nuclear and electronic magnetism. Work is under way on six specific projects.

1. Structure of Liquid Dielectrics

Nuclear spin Hamiltonians of interest in magnetic-resonance experiments can be expressed in terms of spherical tensors of rank 2, a circumstance that arises because the nuclear moments involved are magnetic dipole and electric quadrupole. The secular interactions, which give rise to shifts and splittings of the nuclear Zeeman levels, thus have scalar parts and parts that depend on the orientation of molecules through $Y_{\ell m}(\theta, \phi)$. In ordinary liquids, rapid molecular reorientation makes the anisotropic terms unobservable, inasmuch as the average of $Y_{\ell m}$ over a spherically symmetric probability distribution vanishes. In a polar liquid subjected to an electric field, however, the probability distribution is no longer exactly spherical, and one expects to see small perturbations of the nuclear-resonance spectrum which depend on electric field intensity E and temperature T as $(E/T)^2$, and also on the local order in the liquid produced by intermolecular forces. For molecules of known properties it becomes possible to measure such averages as $\overline{Y_{20}}$ through the nuclear-resonance spectrum. This information, together with a knowledge of $\overline{Y_{10}}$ obtained from dielectric studies, is expected – for the first time – to provide detailed information about the degree and type of local order produced by molecular interaction in dielectric liquids. It is also expected that such experiments will throw light on the mechanism of electrical conduction in insulating liquids. The present state of our experiments is described in this report.

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2. Magnetic Relaxation in Gases

Nuclear relaxation in monatomic gases such as helium is exceedingly slow, a fact that has suggested the use of He^3 nuclear moments in navigational gyroscopes. We are studying the mechanisms responsible for such relaxation by performing transient magnetic-resonance experiments on gases at high pressures for which the relaxation is rapid enough to be measurable. We are even more actively studying nuclear relaxation by similar methods in simple polyatomic gases, in which there are stronger mechanisms arising from the anisotropy of the forces between colliding molecules. We are at present attempting to get a detailed picture of these forces in the simple prototype system of hydrogen deuteride gas at low temperatures. We hope, in collaboration with Professor Irwin Oppenheim, to arrive at an exact theoretical connection between nuclear relaxation times and intermolecular forces for simple systems.

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3. Transport Properties of Dense Fluids

For a long time, a great deal of theoretical attention has been devoted to the general problem of the nonequilibrium properties of liquids and dense gases. Despite the fact that diffusion, viscosity, thermal conductivity, and so forth, are among the most classical subjects of experimental physical chemistry, almost none of the work that has been

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done is of direct use in testing transport theory. This is because of the necessity of low temperatures and/or high pressures for obtaining high densities of fluids composed of single atoms or small molecules. Also, one would like experimental values of transport coefficients over wide ranges of temperature and density, since one would expect transport theories to do a better job of predicting the form of temperature and density dependences than of giving numerical values of the transport coefficients. Fortunately the experimental difficulties of the classical methods are largely obviated, in the case of diffusion, by the spin-echo technique of nuclear resonance. We have already used this method to study the temperature dependence of self-diffusion in liquid ethane over an extremely wide temperature range (see Quarterly Progress Report No. 64, pages 37-39). We have now completed and tested a system for extending the same type of measurements to high pressures. It will be used initially to study the experimentally convenient liquids CH_4 and C_2H_6 , and will then be extended to monatomic and other polyatomic liquids.

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4. Atomic Motion in Solids

Thermal relaxation of nuclei in solids typically occurs through the agency of magnetic dipole-dipole interactions, randomly modulated by the motions of nuclei with respect to one another. In general, it is assumed that the time autocorrelation function $G(\tau)$ describing the statistical fluctuation of these interactions $\mathcal{H}(t)$ is an exponential, described by a correlation time τ_c :

$$G(\tau) \equiv \overline{\langle \mathcal{H}(t) \mathcal{H}^*(t+\tau) \rangle} = \frac{\overline{|\mathcal{H}(t)|^2}}{c} \exp(-\tau/\tau_c).$$

This assumption, applied to solids whose atomic motions are thermally activated so that $\tau_c = \tau_{c0} \exp(E/kT)$, has been very successful in identifying the atomic motions that occur and determining the energetic barriers E that hinder them. An example from our recent work is described in this report.

In general, where correlations exist between the motions of neighboring nuclei or where the motion is complex in character, the assumption that a single correlation time exists is certainly not correct. The nuclear relaxation time is still a measure of the correlation function, being directly related to its Fourier transform evaluated at the experimental resonance frequency. We are beginning a series of studies of relaxation in various solids with the object of mapping out the correlation function experimentally and finding out what sorts of departures from exponential behavior do occur typically. Such work requires observing the relaxation of nuclear magnetization toward equilibrium in an applied magnetic field whose strength is variable from a few to many thousand oersteds. The usual procedure is to polarize the sample in a strong field and then reduce the field quickly to the desired value. After a time, the field is restored to a large value and the remaining magnetization is measured by means of a free-induction decay or an adiabatic fast passage. Alternatively, the desired low magnetic fields can be obtained in the rotating frame by means of Solomon's "spin-locking" procedure.

J. S. Waugh

5. Electron-Spin Resonance

A good deal of interest exists in the properties of magnetically dilute solutions of transition metal ions in diamagnetic crystals, partly because of the applications of such systems to optical masers. We are carrying out some optical and X-band electron spin-resonance studies on the d^4 ion Cr^{+2} in CaF_2 and SrF_2 single crystals. The object of this work is to obtain an analysis of the Jahn-Teller effect through its influence on the

F^{19} hyperfine interaction at low temperatures. We are also carrying on some electron spin-resonance work on solutions of rare-earth metals in liquid ammonia in the hope of throwing some further light on the structure of these peculiar conducting liquids (see this report).

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6. Mössbauer Effect

Isomer shifts and quadrupole splittings in recoilless gamma-ray spectra are known to be related to the electronic structure of solids, but the theoretical interpretation of these quantities ab initio is very difficult. We have done some preliminary studies of a number of solid monosubstituted ferrocyanides having a range of tetragonal crystal field strengths in an attempt to establish semiempirical criteria for the discussion of chemical bonding. This work is now dormant, but results obtained thus far are partially discussed in a paper that has been submitted to Applied Optics.

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STATUS OF CURRENT PROJECTS

1. NUCLEAR MAGNETIC RESONANCE OF POLAR LIQUIDS IN ELECTRIC FIELDS

Detection of the small effects of dipolar interactions and anisotropy of chemical shift on the nuclear magnetic resonance (NMR) spectrum of a liquid subject to an electric field requires the greatest possible spectral resolution. In sample cells of most practical designs the applied magnetic field is made inhomogeneous by the presence of the cell structure and the sample itself, both of which have magnetic susceptibilities different from that of the surrounding air. Small currents flowing in the sample also produce inhomogeneous magnetic fields of their own. After much experimentation, we seem to have solved the first of these problems by constructing long cylindrical cells containing the sample liquid in a long cavity of rectangular cross section. The cell body is cast from an epoxy resin that has been doped with rouge until its volume diamagnetic susceptibility matches that of the sample. The electrodes are sufficiently thin that they do not appreciably distort the magnetic field. As far as the magnetostatic problem is concerned, the sample cell can then be treated as an infinite homogeneous cylinder, inside which the field is uniform. We have also tried long concentric glass cells in which the sample and electric field appear in a thin annulus. The glass is coated with a chemically inert semiconducting film (courtesy of Dr. D. W. Rice of the Corning Glass Company). Such a cell avoids, in principle, both sources of field inhomogeneity mentioned above. But it must be rapidly spun about its cylinder axis in order to average out the line broadening that arises because the relative directions of the electric and magnetic fields are different in different parts of the cell. This averaging reduces the observable effects of the electric field on the NMR spectrum by a factor of four. This, together with the complications inherent in making the necessary electrical connection to a rotating cell, have resulted in our preference for the, perhaps less elegant, parallel-plate geometry.

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The above-mentioned sorts of spurious line broadening, as well as other forms of interference, always occur to some degree when a strong electric field is applied to a liquid whose steady-state NMR spectrum is being examined. Rather than trying to disentangle the desired shifts and splittings from these adventitious effects by direct examination of changes in the NMR line shape, we are now employing a sideband technique. Instead of a constant electric field, we apply an audiofrequency alternating field, $E_0 \cos \omega_e t$. Its effects are conveniently described with reference to the proton resonance of CH_3NO_2 , on which much of our work has been done. In the alternating field the resonance, previously a single line, splits into a triplet of intensity ratio 1:2:1 and spacing $3D_{\text{HH}}$. At the same time, sideband resonances appear at $\pm 2\omega_e$ from the main resonance. These resonances have the form of doublets of spacing $6D_{\text{HH}}$. Their amplitudes contain a component oscillating at the frequency $2\omega_e$ with intensity proportional to a product of Bessel functions: $J_0(k) J_1(k)$, where the modulation index k is given by $k = \text{const.} \times E_0^2/\omega_e$. These sidebands are not present at all unless the desired electric-field splitting exists, and their intensities, suitably measured with a lock-in detector operating at the frequency $2\omega_e$, measure D_{HH} . Calibration is conveniently made by comparison with a magnetic field modulation sideband of like frequency. In order to increase the time during which the weak signals can be integrated, it is convenient to lock the spectrometer into resonance by means of still another magnetic sideband, after the fashion of Freeman and Anderson.¹ The equipment for accomplishing this rather involved situation has now been built and successfully tested, although refinement still continues.

A preliminary account of this work was given at the Eighth Yugoslav Summer School of Physics, in Hercegnovi, September 1-7, 1963, and will be published in the Proceedings of this conference.

The polarization of a liquid by an electric field introduces into the spin Hamiltonian, among other things, a dipolar interaction for each pair of nuclei:

$$\mathcal{H}_d^{(ij)} = D_{ij}(I_i \cdot I_j - 3I_{zi}I_{zj}),$$

where

$$D_{ij} = \frac{\gamma_i \gamma_j \hbar^2}{r_{ij}^3} \langle P_2(\cos \theta_{ij}) \rangle.$$

Here, θ_{ij} is the orientation of the internuclear vector r_{ij} with respect to the magnetic field H . The average with respect to θ_{ij} is related to the averaging of the molecular dipole moment μ in the electric field E (described by an angle ψ) as follows:

$$\langle P_2(\cos \theta_{ij}) \rangle = \langle P_2(\cos \psi) \rangle P_2(\cos \alpha) P_2(\cos \beta_{ij}),$$

where a is the angle between \underline{E} and \underline{H} , and β_{ij} is that between $\underline{\mu}$ and \underline{r}_{ij} . Observation of dipolar splittings in the NMR spectrum of a molecule of known structure thus permits a determination of $\langle P_2(\cos \psi) \rangle$. Both this quantity and $\langle \cos \psi \rangle$, which for highly polar liquids is approximately obtainable from the dielectric constant ϵ :

$$\langle \cos \psi \rangle \approx \frac{(\epsilon-1) E}{4\pi\mu} \left(\frac{V}{N} \right),$$

are characteristic of the angular distribution of molecules in the electric field. For a fluid without intermolecular forces, this distribution is proportional to $\exp(\mu E \cos \psi / kT)$, and leads to

$$\langle \cos \psi \rangle = \frac{1}{3} \left(\frac{\mu E}{kT} \right); \quad \langle P_2(\cos \psi) \rangle = \frac{1}{15} \left(\frac{\mu E}{kT} \right)^2.$$

In dense fluids, in which intermolecular forces are important, either of these may be made consistent with experiment if E is replaced by an "effective field" F that is imagined to represent the effects of neighboring molecules. For this concept to be physically meaningful, the same value of F must be used in both of the above-mentioned averages, and leads to the requirement

$$\eta \equiv \langle P_2(\cos \psi) \rangle / \langle \cos \psi \rangle^2 = \frac{3}{5}.$$

The combination of the electric-field NMR experiment and measurements of dielectric constant thus provide a measure of the extent to which specific intermolecular forces cause the distribution function to depart from a basically independent-particle form describable by an effective field. Such departures may in fact be very large: The results obtained by Buckingham and McLauchlan² on the molecule p-nitrotoluene, together with the dielectric constant (estimated to be 20.5 ± 0.5 at the temperature of their NMR experiment), give $\eta \approx 4$.

The absolute value sign on this result reflects the possibility that certain rather special types of local ordering in the liquid might lead to a negative value for $P_2(\cos \psi)$. Such a situation (considered very unlikely in this case) would require a reversal of the argument by which the above-mentioned authors have determined the absolute sign of the indirect spin-spin coupling constant J_{ij} .

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References

1. R. Freeman and W. A. Anderson, J. Chem. Phys. 37, 85; 2053 (1962).
2. A. D. Buckingham and K. A. McLauchlan, J. Chem. Soc., p. 144, May 1963.

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2. NUCLEAR RELAXATION IN XENON TETRAFLUORIDE

The spin-lattice relaxation time T_1 of the F^{19} nuclei in polycrystalline XeF_4 has been measured between approximately 77°K and 400°K. (See Fig. VIII-1.) At low

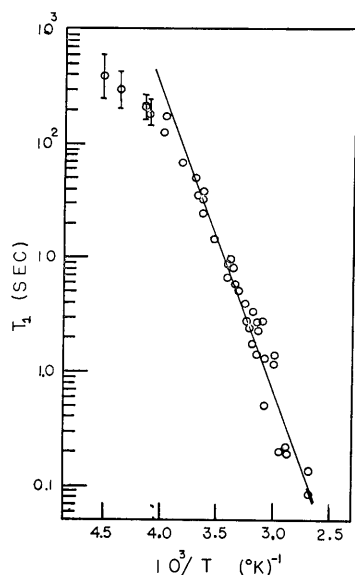


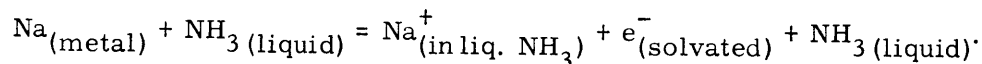
Fig. VIII-1. Spin-lattice relaxation of F^{19} in crystalline XeF_4 . The relaxation time, T_1 , is plotted on a logarithmic scale against the reciprocal of the absolute temperature. Measurements were made at 30 mc. The straight line is drawn for an activation energy for molecular motion of 12.0 kcal/mole.

temperatures T_1 is roughly constant at approximately 10^3 sec, but at higher temperatures it drops proportionally to $\exp(E/RT)$. The activation energy is 12.0 ± 1.5 kcal/mole. The molecular motion responsible for relaxation is evidently an activated reorientation of XeF_4 molecules in situ. These results are consistent with a previously reported line-width transition in the neighborhood of 250°K. Details have been submitted for publication to the Journal of Chemical Physics.

C. G. Wade

3. ELECTRON-SPIN RESONANCE OF METAL-AMMONIA SOLUTIONS

The well-known blue solutions of alkali metals in liquid ammonia exhibit a single sharp paramagnetic resonance absorption. This single resonance has been attributed to "solvated free electrons" formed, for example, in the reaction:



There has been considerable speculation concerning the degree to which the metal ions and the "solvated electrons" are associated. Knight Shifts of the Na^{23} resonance indicate an appreciable spin density of "solvated electrons" at the sodium nucleus in

sodium-ammonia solutions. This has led to a model that considers the electrons to be very closely associated with the sodium ions in solution — forming "expanded atoms." Indeed, concentrated solutions of metals in liquid ammonia have a metallic luster, and are very metallic in their electrical properties.

We have prepared and measured the paramagnetic resonance spectra of solutions of Europium metal in liquid ammonia. It was predicted that this rare-earth metal-ammonia system, which is qualitatively similar to alkali metal-ammonia systems, might further elucidate the electronic structure of metal-ammonia solutions, in that the Europium cations as well as the "solvated free electrons" might be expected to exhibit paramagnetic resonance absorption. This has been found to be the case.

Work is now in progress to measure the line shapes and linewidths of these paramagnetic resonance spectra of Eu-NH_3 as a function of concentration and temperature. Future work will include study of the absorption spectra of these solutions from the near infrared to the ultraviolet.

Recent experiments indicate that Eu metal may also dissolve in very pure tetrahydrofuran and dimethoxyethane, thereby giving blue solutions. It may also be possible to study metal-ammonia solutions of other rare-earth metals.

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