VIII. MAGNETIC RESONANCE

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RESEARCH OBJECTIVES

The work of this group continues to be centered on the study of structure and atomic dynamics of solids and fluids through experiments on nuclear and electronic magnetism. Particular attention is given to intermolecular forces and the mechanisms through which they are reflected in nuclear magnetic relaxation. The following specific projects are under way at the present time.

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. The present state of our experiments is described in this report.

J. D. Macomber, E. T. Stone

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. Basically these forces lead to rotational transitions of various kinds and the nuclear relaxation times reflect the cross sections for such inelastic collision. Transitions between different initial and final rotational states reflect themselves differently in the nuclear relaxation time according to the nature of the coupling between the nuclei and the molecular framework. Such couplings may include the angle-dependent dipolar coupling between nuclei, the spin-rotational interaction, anisotropy of the chemical shielding, etc. Each of these has its own characteristic dependence on temperature, magnetic field, and isotopic substitution. By varying such parameters we are attempting to sort out the role played by different rotational states and thereby to get a clearer understanding of the nature of the intermolecular forces involved.

J. H. Rugheimer, J. W. Riehl

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 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 has been used initially to complete the earlier investigation of liquid C_2H_6 and will now be turned to the study of simpler liquids.

C. G. Wade

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:

$$G(\tau) \equiv \overline{\left\langle \mathcal{H}(t)\, \mathcal{H}^{*}(t+\tau) \right\rangle} = \overline{\left| \mathcal{H}(t) \right|^{2}}\, \exp(-\tau/t_c).$$

This assumption, applied to solids whose atomic motions are thermally activated so that $\tau_c = \tau_{co}\, \exp(E/kT)$, 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.

R. Newmark, A. Leonardi

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.

D. S. Thompson

A. STATUS OF CURRENT PROJECTS

1. NUCLEAR MAGNETIC RESONANCE OF POLAR LIQUIDS IN ELECTRIC FIELDS

Our attempts to observe the quadratic electric field effect in liquid CH_3NO_2 and other substances has so far not been entirely successful. We are now attempting to observe the quadrupole splitting of the deuterium resonance in heavy chloroform and other substances, which is induced by the alignment of the molecule in an electric field. These splittings are expected to be an order of magnitude larger than the dipolar splittings which we have heretofore been looking for.

While this experiment is being set up we have been working on two associated theoretical problems. One has to do with the sideband phenomena which are produced when the electric field is modulated (see Quarterly Progress Report No. 72, pages 61-63; No. 75, pages 37-38). The other has to do with the manner in which intermolecular forces and local order in the liquid are reflected in the results of the electric field experiment as opposed to experiments in which the static dielectric constant is measured. A result of Kirkwood's theory[1] of dielectrics can be expressed for the case of pure orientation polarization by

$$\left\langle \cos \theta_i \right\rangle_E = \frac{1}{3} \frac{\mu E}{kT} \left\{ 1 + (N-1) \left\langle \cos \gamma_{ij} \right\rangle_o \right\}. \tag{1}$$

The quantity on the left is essentially what is experimentally measured when the dielectric constant is determined in an electric field E, θ_i being the direction of the i'th dipole with respect to the electric field. The average on the right is over the equilibrium distribution of the liquid in the absence of a field, γ_{ij} being the angle between dipoles i and j. In the NMR electric field experiment one measures the alignment rather than the polarization of the liquid, which turns out to be expressible in a form analogous to Kirkwood's result above, as

$$\left\langle P_2(\cos \theta_i) \right\rangle_E = \frac{1}{15} \left(\frac{\mu E}{kT} \right)^2 \left\{ 1 + (N-1) \left[\left\langle P_2(\cos \gamma_{ij}) \right\rangle_o - \frac{N-6}{2} \left\langle \cos \gamma_{ij} \right\rangle_o \right.\right.$$

$$\left.\left. + \frac{3(N-2)}{2} \left\langle \cos \gamma_{ij} \cos \gamma_{ik} \right\rangle_o \right] \right\} \tag{2}$$

This expression exhibits the fact that, regardless of the type of intermolecular forces present, the NMR electric field effect is quadratic in (E/T). Also it displays the types of intermolecular correlations that can contribute. In the limit of vanishing intermolecular forces both of these results correspond to Debye's theory for dilute gases. When intermolecular forces are important the local order they produce is reflected quite differently in the results of the two experiments. A detailed discussion of this work, together with calculations based on equation (2) above, will be submitted for publication in the near future.

J. M. Deutch, J. D. Macomber, E. T. Stone

References

1. J. G. Kirkwood, J. Chem. Phys. 7, 911 (1939).

2. SELF-DIFFUSION IN LIQUID ETHANE

The work of Gaven[1] on diffusion in ethane between the triple point and the critical point has been extended to pressures above 2000 atmospheres. In order to determine the dependence of diffusion constant on density, approximate measurements were also made of the equation of state, taking the density at a given pressure as proportional to the amplitude of the observed free induction decay. Gaven had found that his results on the temperature dependence of diffusion could be fitted satisfactorily into the framework of the free volume theory of liquids, either with or without an intrinsic dependence of T on $T^{1/2}$. Our new results on the density dependence show that these simple theories are in fact untenable, as might have been expected. A description of this work will appear in the author's doctoral thesis and also be submitted for publication.

C. G. Wade

References

1. J. V. Gaven, Jr., Spin-Echo Studies of Diffusion in Liquids, Ph. D. Thesis, Department of Chemistry, M. I. T., November 1961.