MEASUREMENT OF MOLECULAR ROTATION BY N^{14} NUCLEAR QUADRUPOLE RESONANCE RELAXATION TIMES

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Nuclear magnetic resonance has been used extensively to study motional processes such as diffusion and molecular rotation in solids.[1] In all this work the effect actually studied is the modulation of the dipolar interaction between nuclear moments by the dynamic process. On the other hand, the study of quadrupolar relaxation processes has tended to concentrate on the interaction with lattice vibrations. Recently Woessner and Gutowsky[2] and Tokuhiro[3] have published detailed investigations of spin-lattice relaxation in the pure quadrupole resonance of Cl in several molecules. In a number of cases very rapid exponential changes in T_1 were observed which were explained by these authors in a rather complicated way. It has occured to us that a much simpler geometrical effect of molecular rotations might be important. We were rather surprised when we could not find this effect discussed anywhere in the literature, though similar effects on the linewidth were apparently investigated by Ayant.[4]

A rotating molecule in a solid usually has a number of discrete positions with relatively high potential barriers between them. As a result, the rotational correlation time (τ) is essentially the residence time of the molecule in a definite potential minimum, whereas the transition between minima is very rapid. As a rule, the local field gradients at the nucleus will have different orientations in space for the different positions of the molecule. The nuclear wave function remains unchanged during the jump, whereas the quadrupolar Hamiltonian changes.[4] Clearly this is a very effective mechanism for exchanging energy between the nuclear spin and the lattice. In fact, for reasonably large rotational angles one expects T_1 to be of the order of the rotational correlation time (τ). To illustrate this effect we have measured the spin-lattice relaxation time in the pure quadrupole resonance of N^{14} in hexamethylene tetramine.[5] This is a particularly simple case because the field gradients have cylindrical symmetry and N^{14} has spin 1. Using standard techniques, it can be shown that the polarization of the nuclear spin at a given position in space (i.e., with a definite orientation of the field gradient) is given by

$$\frac{d(P^{\nu}-P_0)}{dt}=\sum_{\nu'}\left[\frac{1-3\cos^2\theta_{\nu\nu'}}{2\tau}(P^{\nu}-P^{\nu'})-\frac{3(1-\cos^2\theta_{\nu\nu'})}{2\tau}(P^{\nu}-P_0)\right], \tag{1}$$

where

$$P^{\nu}=n_1^{\nu}+n_{-1}^{\nu}-2n_0^{\nu}=\langle 3I_z^2-I^2\rangle_{\nu}. \tag{2}$$

n_m^{ν} is the population of the state $|m\rangle_{\nu}$ for nuclei at site ν, and $\theta_{\nu\nu'}$ is the angle between the principal (z) axes of the field gradients at ν and ν', respectively. It should be noted that the states $|m\rangle_{\nu}$ are defined as eigenstates of the Hamiltonian at that site (i.e., with respect to a local axis of quantization). The summation in (1) is over all the alternative sites (ν') from which a nucleus can jump to ν.

The first term on the right-hand side of (1) is obviously a "cross-relaxation" term, whereas the second one represents proper spin-lattice relaxation.

Hexamethylenetetramine is a tetrahedral molecule with N^{14} nuclei at the apexes. There are four possible positions for the N^{14} nuclei in a given molecule. Introducing the tetrahedral angles in Eq. (1), one gets

$$\frac{d(P^{\nu}-P_0)}{dt}=\frac{1}{3\tau}\sum_{\nu'}(P^{\nu}-P^{\nu'})-\frac{4}{\tau}(P^{\nu}-P_0). \tag{3}$$

In our experiment we applied repeated "90°" pulses at 3.3-3.4 Mc/sec to a powdered sample. We measured the steady-state amplitude of the free precession signals after the pulses as a function of the pulse repetition rate. We found this technique for measuring T_1 more convenient than the two pulse methods previously used mainly because the repetition of the signals increases experimental accuracy.

The explicit expression for the signal amplitude as a function of the repetition rate involves rather complex integrals. It is, however, a universal function of the ratio t/τ between the pulse separation t and the correlation time τ. The actual interpretation of experimental results is therefore not difficult.

In our measurements we covered the temperature range 77-327°K. It was found that molecular rotations dominate the relaxation time above 250°K.[6] In Fig. 1 we show a plot of $\ln\tau$ computed from our results using Eq. (3) as a function of $1/T$. One finds $1/\tau = \nu_0 e^{-\Delta E/kT}$, where $\nu_0 = 7.6\times 10^{12}$ and $\Delta E = 15.6$ kcal/mole. This should be compared with the results of Smith[7] from proton magnetic resonance. He found $\nu_0 = 7.5\times 10^{14}$ and $\Delta E = 18.7$ kcal. In fact, the two results are fairly close over the whole temperature range covered in both experiments (see Fig. 1). The agreement is, however, much better near the linewidth transitions (340-380°K), so that our results are probably more accurate.

We believe this is the first time nuclear quadrupole resonance has been used to measure the rate of motional processes in solids. The technique is, in fact, rather simple and seems to have many advantages as compared to standard nuclear magnetic resonance methods. It should be applicable to many other systems.

A more detailed account of the theory and experimental techniques will be published later.

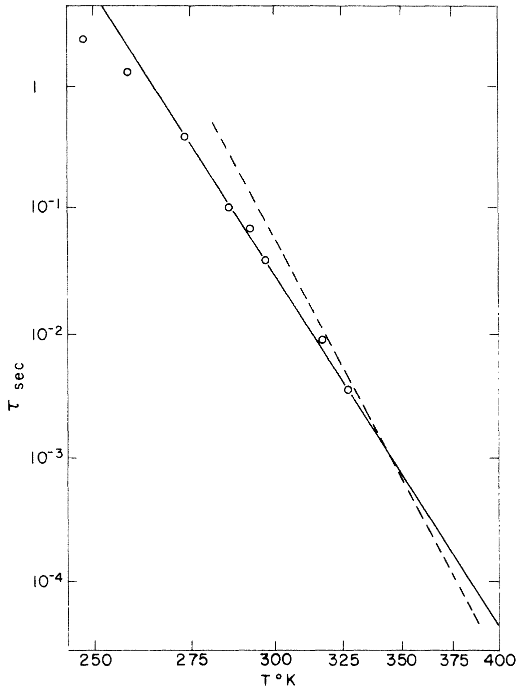

FIG. 1. Plot of the correlation time for rotations of a hexamethylene tetramine molecule (τ) versus temperature. τ was computed from N^{14} pure quadrupole relaxation times using Eq. (3). The dashed line represents the results of Smith.[7]

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[1] A. Abragam, The Principles of Nuclear Magnetism (Clarendon Press, Oxford, England, 1961), Chap. X.

[2] D. E. Woessner and H. S. Gutowsky, J. Chem. Phys. 39, 440 (1963).

[3] T. Tokuhiro, J. Chem. Phys. 41, 438 (1964).

[4] Y. Ayant, thesis, 1955 (unpublished), referred to in reference 1, Chap. X, Sec. VI Bb.

[5] G. D. Watkins and R. V. Pound, Phys. Rev. 85, 1062 (1951).

[6] At lower temperatures T_1 is dominated by vibrational processes and has approximately a T^2 temperature dependence.

[7] G. W. Smith, J. Chem. Phys. 36, 3081 (1962).