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PHYSICS

1969

SovietRxiv

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Abstract

Full Text

UDC 541.67

PHYSICS

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THE INFLUENCE OF THE CHARACTER OF INTRAMOLECULAR ORIENTATIONAL MOTION ON MAGNETIC RELAXATION IN SOLIDS

(Presented by Academician E. K. Zavoiskii, 10 VI 1968)

Numerous works (review (^{1})) have been devoted to the study of nuclear magnetic spin-lattice relaxation in solids caused by intramolecular dipole-dipole interactions of nuclei, modulated by the rotational Brownian motion of molecules or groups of atoms. For the interpretation of experimental data it is customary to use theories ($^{2-4}$) constructed for the case of interaction of equivalent nuclei in liquids. According to these concepts, the spin-lattice relaxation time T_1 is determined by the formula

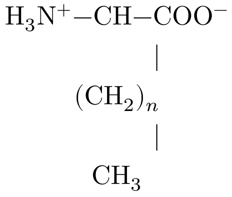
$$\frac{1}{T_1} = K\left(\frac{\gamma^4\hbar^2}{\omega_0}\right) I(I+1) \sum_j{}' r_{ij}^{-6} \times \left[\frac{\omega_0\tau_c}{1+\omega_0^2\tau_c^2} + \frac{4\omega_0\tau_c}{1+4\omega_0^2\tau_c^2}\right], \qquad (1)$$

where γ is the gyromagnetic ratio of the resonating nuclei; ω_0 is the resonance frequency; I is the nuclear spin; $\hbar$ is the reduced Planck constant; r_{ij} is the internuclear distance; K is a constant depending on the process of molecular reorientation.

Calculation of T_1 for a solid by formula (1), taking into account the fraction of nuclei responsible for relaxation, in only some cases (^{5}) gives satisfactory agreement with experiment.

Fig. 1. Dependence of the proton spin-lattice relaxation time T_1 on reciprocal temperature for glycocol (1), aminobutyric acid (2), and norleucine (3)

We have carried out a comparative study of proton relaxation caused by the rotational motion of the CH_3- and NH_3^+-groups in L, D-amino acids



$$\begin{array}{c} H_3N^+{-}CH{-}COO^- \\ | \\ (CH_2)_n \\ | \\ CH_3 \end{array}$$

(alanine, $n = 0$; aminobutyric acid, $n = 1$; norvaline, $n = 2$; norleucine, $n = 3$) and $H_3N^+{-}CH_2{-}COO^-$ (glycocol).

All samples were chemically pure crystalline powders. Measurements of T_1 were carried out by the method (^{6}) on a relaxometer for solids (^{7}). The operating frequency was 27.5 MHz. The temperature was varied from 77°K to the melting point of the sample.

All protons of the NH_3^+ group participate in hydrogen bonds with oxygen atoms of neighboring molecules. Consequently, reorientations about the C–N axis are possible only through strictly definite angles between fixed positions. Rotation of the CH_3 groups, however, is relatively free.

The plot of the temperature dependence of T_1 (Fig. 1) has, for each sample, a low-temperature minimum, caused by relaxation of all protons of the molecule through the mobile CH_3 group, and a high-temperature minimum, caused by relaxation through the mobile NH_3^+ group. The experimental values of T_1 at the minimum, $(T_1)_{\min}$, as a function of the fraction of mobile protons relative to their total number (the parameter p) are given in Fig. 2.

Values of $(T_1)_{\min}$ for isolated NH_3^+ and CH_3 groups, obtained by extrapolating the straight lines in Fig. 2 to $p = 1$, are respectively 10 and 13 msec. The theoretical values of $(T_1)_{\min}$, calculated from formula (1), are 2.85 msec for NH_3^+ groups ($r = 1.41$ Å) and 12.1 msec for CH_3 groups ($r = 1.8$ Å). Thus, there is good agreement between theory and experiment for CH_3 groups and a strong discrepancy in the case of NH_3^+ groups. Apparently, reorientations of CH_3 groups have a character analogous to the Brownian rotational motion of molecules in liquids.

Fig. 2. Values of $(T_1)_{\min}$ for the amino acids studied as a function of the parameter p (p is the ratio of the total number of protons to the number of protons in the NH_3^+ or CH_3 group). The upper experimental points correspond to relaxation of protons through CH_3, and the lower ones to relaxation through the NH_3^+ group.

In the case of NH_3^+ groups, however, only those rotations are possible that do not disturb the symmetry of the crystal lattice. Consequently, reorientations of

Fig. 2. Values of $(T_1)_{\min}$ for the amino acids studied as a function of the parameter p (p is the ratio of the total number of protons to the number of protons in the NH_3^+ or CH_3 group). The upper experimental points correspond to relaxation of protons through CH_3, and the lower ones to relaxation through the NH_3^+ group.

Figure 2: Fig. 2. Values of $(T_1)_{\min}$ for the amino acids studied as a function of the parameter p (p is the ratio of the total number of protons to the number of protons in the NH_3^+ or CH_3 group). The upper experimental points correspond to relaxation of protons through CH_3, and the lower ones to relaxation through the NH_3^+ group.

NH_3^+ groups have the character of random rotational jumps between equivalent positions in the crystal lattice, and theories (2–4) cannot be applied in this case.

An attempt to solve this problem was made by one of the authors in work (8), where, on the basis of a consideration of random rotational jumps of molecules (groups of atoms) in a crystal lattice (9), T_1 is calculated.

In the general case of the magnetic dipole-dipole interaction of several nonequivalent nuclei with different spins I_i and I_j in one and the same molecule, the following expression was obtained for the probability

$$W^{M_i,\,M_j}_{M_i+n,\,M_j+m}$$

of the relaxation transition $M_i, M_j \to M_i{+}n, M_j{+}m$ between stationary Zeeman energy levels:

$$W^{M_i,\,M_j}_{M_i+n,\,M_j+m} = \frac{2}{\hbar^2} \sum_j{}' P_{ij}^2 \left| (V_{nm})^{M_i,\,M_j}_{M_i+n,\,M_j+m} \right|^2 \times$$

$$\times \left| \sum_l P^{(2)}_{kl}(\cos\beta) e^{-il\alpha} Y^l_2(\theta_{ij}, \varphi_{ij}) \right|^2 \frac{\tau_c^{-1}(1-\cos k\chi) + T^{-1}_{mj}}{\left[\tau_c^{-1}(1-\cos k\chi) + T^{-1}_{mj}\right]^2 + (n\omega_i + m\omega_j)^2}, \tag{2}$$

where $P_{ij} = \sqrt{6\pi/5}\,\gamma_i\gamma_j\hbar^2 r_{ij}^{-3}$; r_{ij} is the radius vector joining nuclei i and j in the molecule; $\left|(V_{nm})^{M_i,\,M_j}_{M_i+n,\,M_j+m}\right|^2$ is the average of the square of the spin part of the matrix element over all possible values of the quantum number M_j; $P^{(2)}_{kl}(\cos\beta)$ are normalized associated Legendre functions, $k =$

$= (n+m)$; β characterizes the direction of the reorientation axis; $Y^l_2(\theta'_{ij}, \varphi'_{ij})$ are spherical functions of the second order, which in the molecular coordinate system ξ, η, ζ are constant numbers, and they are easily found if the orientation of the axes ξ, η, ζ and the positions of nuclei i and j in the molecule are known; τ_c is the mean time between two successive rotations; χ is the minimum angle of rotation ($\chi = 2\pi/n_\chi$, where n_χ is the number of equivalent positions) allowed by the symmetry of the molecule (or of the unit cell); T_{mj} is the characteristic time of change of the spin of nucleus j. In the case of equivalent nuclei, when $I_i = I_j$ and $\omega_i = \omega_j$, T_{mj}^{-1} in (2) must be set equal to zero.

For three equivalent nuclei equidistant from the reorientation axis, in the polycrystalline state of the substance at $n_\chi = 3$, i.e., when $\chi = 120°$, using (2), we obtain the formula for the spin-lattice relaxation time:

$$\frac{1}{T_1} = \frac{3}{4\pi}\frac{\gamma^4\hbar^2}{r^6}\left[\frac{\tau_c}{1 + {}^4\!/_9\,\omega_0^2\tau_c^2} + \frac{\tau_c}{1 + {}^{16}\!/_9\,\omega_0^2\tau_c^2}\right]. \tag{3}$$

According to (3), the minimum of T_1 will be observed when the condition $\omega_0\tau_c = 1.2$ is fulfilled.

The value of $(T_1)_{\min}$ for NH_3^+, calculated from formula (3), is equal to 9.9 msec, which agrees well with experiment.

The experimental values of the activation energy of the rotational motion of NH_3^+ groups, calculated from formulas (1) and (3), coincide and are, for glycocoll, 8.3 kcal/mole. This value agrees well with the activation energy for breaking two hydrogen bonds, equal to 10.5 kcal/mole, obtained from X-ray structural data [10], and 6.1 kcal/mole from NMR broad-line data [11].

Thus, in the series of racemic amino acids studied by us, NMR relaxation in the low-temperature region is due to Brownian rotation of CH_3 groups, and in the high-temperature region to random reorientations of NH_3^+ groups between fixed positions in the crystalline lattice.

The study of nuclear spin-lattice relaxation in solid crystalline bodies and the interpretation of experimental data on the basis of formula (2) make it possible to obtain information on the structure of the substance, the dynamics of motion, and the interactions of molecules in the crystalline lattice.

The authors express their gratitude to A. I. Rivkind for the proposed topic of the experimental study and for his constant interest in the work.

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Received
6 VII 1968

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