N. N. Korst, V. A. Savel'ev, N. D. Sokolov

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Abstract

Full Text

N. N. Korst, V. A. Savel' ev, N. D. Sokolov

Allowance for Averaging over the Ground Vibrational State in Calculating the Second Moment of a Nuclear Magnetic Resonance Signal

(Presented by Academician V. N. Kondrat' ev, May 14, 1962)

It is known that the Van Vleck formula (^{1}) for the second moment of the proton nuclear magnetic resonance (NMR) signal makes it possible to calculate the distances between hydrogen atoms in a solid, and also to draw conclusions about their mobility. In this way one can solve, in particular, the interesting question of the presence or absence in ice of collective proton transfers along hydrogen bonds. In (^{2}) the second moment $\langle\Delta\omega^2\rangle$ of the proton signal of ice was calculated; for a model of immobile protons the authors found $\langle\Delta\omega^2\rangle = 25$ gauss^2, while in the presence of proton transfers it was 20% smaller. Experimentally, however, it was found (^{3}) that at $T = 90^\circ$K, $\langle\Delta\omega^2\rangle = 36.7 \pm 1.7$ gauss^2. To explain such an unexpectedly high value of the second moment, the author of (^{3}) assumed that the valence angle HOH of a water molecule in an ice crystal is not tetrahedral, as shown by neutron-diffraction data, but is only $102 \pm 2^\circ$, which is less even than for a free water molecule (104.5°).

In reality, the reason for the discrepancy between the experimental and theoretical values of the second moment lies in the fact that the Van Vleck formula does not take into account the uncertainty in the position of the protons in the ground vibrational state, associated with the zero-point energy of the atoms.

If the internal motion has a frequency considerably greater than the NMR line width, then taking this uncertainty into account amounts to substituting into the Van Vleck formula for the second moment

$$\langle\Delta\omega^2\rangle = \frac{\mathrm{Sp}\{[\mathscr{H}, S_x]^2\}}{\mathrm{Sp}[S_x^2]} \tag{1}$$

(where $\mathscr{H}$ is the secular part of the spin Hamiltonian, and S_x is the projection of the total spin of the system on the x-axis) the quantity $\mathscr{H}$ averaged over the given motion (^{4}-^{7}). In practice this means that, instead of directly substituting into the expression $(3\cos^2\theta_{ij} - 1)/R_{ij}^3$, which enters the Van Vleck formula (θ_{ij} is the angle between the direction of the external magnetic field and the radius vector R_{ij} connecting the i-th and j-th protons), the equilibrium values θ_{ij} and R_{ij}, it should first be averaged over the ground vibrational state. Taking this averaging into account makes it possible, in principle, to explain the experimental value of the second moment of ice without assuming a change in the equilibrium value of the valence angle HOH.

Taking into account contributions only from the nearest pairs of protons, the expression for the second moment of a single crystal of ice can be written in the form

$$\langle \Delta\omega^2 \rangle = \frac{3}{4} g^4 \beta^4 \hbar^{-2} I(I+1) \left[\frac{3\cos^2\theta - 1}{R^3} \right]^2 . \tag{2}$$

In order to average the expression in square brackets, we expand it in a series in powers of the deviations from the equilibrium values of the natural coordinates $\Delta r_1, \Delta r_2$ (the amplitudes of the valence vibrations of the OH bonds) and $\Delta\Phi$ (the ampli-

there deformation vibrations) and restrict ourselves to terms quadratic in Δr_1 and Δr_2 and fourth-order terms in $\Delta\Phi$. Then for a polycrystal (after averaging over all possible mutual orientations of the vectors **R** and **H**) we find

$$\begin{aligned} \langle \Delta\omega^2 \rangle = \frac{3}{5} g^4 \beta^4 \hbar^{-2} R^{-6} I(I+1) \Bigg\{ 1 &+ \frac{6\,\overline{(\Delta r_1)^2}}{\left[2r_0 \sin\frac{\Phi_0}{2}\right]^2} + \frac{6\,\overline{(\Delta r_2)^2}}{\left[2r_0 \sin\frac{\Phi_0}{2}\right]^2} \\ &+ \frac{10\,\overline{\Delta r_1 \Delta r_2}}{\left[2r_0 \sin\frac{\Phi_0}{2}\right]^2} + \frac{9}{4}\,\overline{(\Delta\Phi)^2} + \frac{87}{32}\,\overline{[(\Delta\Phi)^2]^2} \Bigg\} , \end{aligned} \tag{3}$$

where $R = [2r_0 \sin\Phi_0/2]$ is the distance between two protons; r_0 is the equilibrium value of the O–H bond length; Φ_0 is the equilibrium value of the HOH valence angle.

Let us now express Δr_1, Δr_2, and $\Delta\Phi$ in terms of the normal coordinates Q_i and use the relation $\overline{Q_i^2} = \hbar/2m_i\omega_i$, where m_i is the corresponding reduced mass and ω_i is the frequency of the normal vibration. For ice the frequencies are equal to (8): $\omega_1 = 3090$ cm^{-1}, $\omega_2 = 1595$ cm^{-1}, $\omega_3 = 3180$ cm^{-1}. As calculation by formula (3) shows, the main contribution (70% of the total correction) to the correction to the second moment of ice is made by the term with $\overline{(\Delta\Phi)^2}$*. The librational vibrations of H_2O, which somewhat reduce the second moment, are taken into account in an analogous way. As a result, for the second moment of polycrystalline ice, taking into account the contribution from distant protons (about 1 gauss^2 (2,3)), we obtain the value

$$\langle \Delta\omega^2 \rangle = 0.80\,\gamma^4 \hbar^2 R^{-6} \{1 + 0.21\} = 31.1 \text{ gauss}^2 .$$

Further improvement, apparently, may be achieved by taking hydrogen bonds into account.

As was indicated above, collective transitions of protons along hydrogen bonds should reduce the value of the second moment of ice by 20%. It follows from the calculation presented that such transitions at $T = 90^\circ$ K are unlikely, since otherwise the experimental value of the second moment should not have exceeded ~ 29 gauss^2.

An analogous calculation was carried out by us for polyethylene and 1,2-dichloroethane. The second moments of the proton NMR signal of the CH_2 groups of these compounds were measured in works $^{(9,10)}$, and it turned out that, as for ice, the theoretical values calculated without taking account of averaging over the ground vibrational state are approximately 30% smaller than the experimental ones. To explain this discrepancy, the authors $^{(9,10)}$ proposed that in these compounds the H—C—H valence angle is smaller than the tetrahedral angle and is 103°. However, calculations of the second moment by formula (3) for the CH_2 group give satisfactory agreement with experiment for the tetrahedral value of the angle. The results of the calculations are given in Table 1. In the calculation it was assumed $^{(8)}$:

$$\omega_1 = 2853 \text{ cm}^{-1}, \quad \omega_2 = 1450 \text{ cm}^{-1}, \quad \omega_3 = 2908 \text{ cm}^{-1};$$

the contribution of distant protons was taken into account in accordance with $^{(9,10)}$.

Table 1

Values of the second moment (in gauss^2)

Compound	Calc., rigid lattice	Calc. by formula (3)	Expt.
Polyethylene	25.3	32.8	34.8
1,2-Dichloroethane	12.6	17.6	18.2

It is quite possible that corresponding corrections should be introduced into a number of other calculations published in the literature of interatomic distances by

NMR data if, in these calculations, no averaging over the ground vibrational state was performed.

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P. N. Lebedev Physical Institute
Academy of Sciences of the USSR

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* According to our estimate, the contribution of terms of the form $[(\Delta r)^2]^2$, $\Delta r_1 \Delta r_2 (\Delta\Phi)^2$, $\overline{(\Delta r)^2\,(\Delta\Phi)^2}$ amounts to about 1% of the total correction.

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Note: Figure translations are in progress. See original paper for figures.