THE EFFECT OF ORIENTATION OF THE MOLECULES OF A LIQUID IN AN ELECTRIC FIELD ON NUCLEAR MAGNETIC RESONANCE

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The splitting of the lines of nuclear magnetic resonance in an electric field is evaluated in the case of a nucleus possessing a quadrupole moment and making up the molecules of a liquid or gas. Splitting (or broadening) in the case of nonlinear molecules possessing a constant electric dipole moment is due to their partial orientation in an electric field. The magnitude of the splitting is strongly dependent upon the properties of the nucleus and the molecule, and is of the order of several kilocycles per second in an intermediate case for a field of 10^5 V/cm.

No quadrupole splitting of the nuclear magnetic resonance spectrum is observed in liquids and gases, for the potential is spherically symmetrical in the laboratory system of coordinates, owing to the rapid random rotation of the molecules, and consequently there is no quadrupole interaction. If the (nonlinear) molecules containing the nuclei have quadrupole moment, and have a nonvanishing constant dipole moment, then they become partially oriented in an external electric field. In this case it is possible in principle to observe quadrupole splitting of the spectrum, or at least the line broadening if the splitting is smaller than the line width. We present below an estimate of the magnitude of the indicated effect.

Quadrupole interaction is determined by the Hamiltonian (see [1])

$$\mathcal{H}_Q = \frac{1}{6} \sum_{m=-2}^{2} Q^m (\nabla E)_m. \qquad (1)$$

The tensors Q^m and $(\nabla E)_m$ have components

$$Q^0 = \frac{2 \cdot 3eQ}{2I(2I-1)} [3\hat{I}_z^2 - I(I+1)],$$

$$Q^{\pm 1} = \frac{3eQ}{2I(2I-1)}(\hat{I}_z\hat{I}_\pm + \hat{I}_\pm\hat{I}_z), \qquad Q^{\pm 2} = \frac{3eQ}{2I(2I-1)}\hat{I}_\pm^2:$$

$$(\nabla E)_0 = \tfrac{1}{2}\partial^2\varphi/\partial z^2, \qquad (\nabla E)_{\pm 1} = \partial^2\varphi/\partial x\,\partial z \mp i\partial^2\varphi/\partial y\,\partial z,$$

$$(\nabla E)_{\pm 2} = \tfrac{1}{2}(\partial^2\varphi/\partial x^2 - \partial^2\varphi/\partial y^2 \mp 2i\partial^2\varphi/\partial x\,\partial y), \qquad (2)$$

where x, y, z are the coordinates in the laboratory system.

Let ψ, ϑ, and φ be the Euler angles of a coordinate frame x', y', z' which is rigidly fixed in the molecule, with the z' axis directed along the dipole moment. Since

$$x_i = \sum_j a_{ij}x_j', \qquad x_i' = \sum_j a_{ji}x_j$$

$$(x_1 = x; \quad x_2 = y; \quad x_3 = z; \quad x_1' = x'; \quad x_2' = y'; \quad x_3' = z'),$$

where a_{ij} are the direction cosines of the angles of the axes of both systems, which depend on the Euler angles, the gradient of the field in the laboratory system is expressed in terms of the gradient of the field in the system fixed in the molecule by the formulas

$$\frac{\partial^2\varphi}{\partial x_i\,\partial x_j} = \sum_{k,m} \frac{\partial^2\varphi}{\partial x_k'\,\partial x_m'} a_{ik}a_{jm}. \qquad (3)$$

Upon rotation of the molecule the angles ψ, ϑ, and φ vary with the time. The probability that the dipole moment is directed in a solid angle $\vartheta - \vartheta + d\vartheta$, $\psi - \psi + d\psi$ and that the angle of the molecule's own rotation lies between φ and $\varphi + d\varphi$ is

$$dW \approx C \exp\left[-\frac{pE\cos\vartheta}{kT}\right] \frac{\sin\vartheta}{2} d\vartheta \frac{d\psi}{2\pi} \frac{d\varphi}{2\pi}$$

$$\approx \left[1 - \frac{pE\cos\vartheta}{kT} + \frac{1}{2}\left(\frac{pE}{kT}\right)^2\left(\cos^2\vartheta - \frac{1}{3}\right)\right]$$

$$\times \frac{\sin\vartheta}{2} d\vartheta \frac{d\psi}{2\pi} \frac{d\varphi}{2\pi}. \qquad (4)$$

Calculation of the average values of the products $a_{ik}a_{jm}$ with the aid of (4) yields from (3), accurate to terms of order $(pE/kT)^2$,

$$-\frac{\partial^2\varphi}{\partial x^2} = -\frac{\partial^2\varphi}{\partial y^2} = \frac{1}{2}\frac{\partial^2\varphi}{\partial z^2}$$

$$= \frac{1}{30}\left(\frac{pE}{kT}\right)^2 \frac{\partial^2\varphi}{\partial z'^2} = \frac{eq}{15}\left(\frac{pE}{kT}\right)^2 = a,$$

and all the cross derivatives are equal to zero. Thus, the averaged field is actually symmetrical, with a symmetry axis directed along the electric field, while the matrix elements $\mathcal{H}_Q$ are

$$(m \mid \mathcal{H}_Q \mid m') = \frac{3eQ \cdot}{2I(2I-1)} \frac{a}{6} [3m^2 - I(I+1)] \delta_{mm'}.$$

If the electric field is directed parallel to the magnetic field H, then the single resonant line of frequency γH is replaced by several lines

$$\omega_m = \gamma H + \frac{3eQ}{2I(2I-1)} \frac{a}{2\hbar} |2m+1|, \qquad m < J.$$

The splitting of the frequencies $\delta\omega = \omega_{m+1} - \omega_m$ is

$$\delta\omega = \frac{3eQ}{2I(2I-1)} \frac{a}{\hbar} = \frac{e^2qQ}{2\hbar} \left(\frac{pE}{kT}\right)^2 \frac{1}{2I(2I-1)}.$$

According to data given, for example, in [2] we have in order of magnitude p = 10^{-18} cgs esu, and e^2qQ ranges from 10^3 to 1 Mc. If we specify p = 6×10^{-18}, e^2qQ = 40 Mc, and I = $\frac{3}{2}$, then for room temperature (T = 300°K) and a field E = 100 kV/cm we obtain $\delta\omega$ = 3 kc.

The line width in the case of quadrupole relaxation due to rotation can be estimated from the formula (see [3])

$$\Delta\omega = \frac{4}{5} \pi^2 (e^2qQ/\hbar)^2 \tau_c, \tag{5}$$

where τ_c is the correlation time, with an order of magnitude 10^{-11} sec. Numerical calculation yields $\Delta\omega$ = 12 kc.

Thus, in strong electric fields one can observe splitting or at least broadening of the nuclear magnetic resonance lines, due to the static quadrupole interaction occurring upon orientation of the molecules.

The line width is proportional to the square of the parameter of the quadrupole interaction, while the splitting is proportional to its first degree. Therefore, if only the line width is determined by the quadrupole relaxation as a consequence of the thermal rotation of the molecule [formula (5)], the conditions for the observation are better for molecules with smaller values of e^2qQ.

[1] L. D. Landau and E. M. Lifshitz, Quantum Mechanics, Pergamon, 1958.

[2] C. H. Townes and A. L. Schawlow, Microwave Spectroscopy, McGraw-Hill, N.Y., 1955.

[3] I. Masuda, J. Phys. Soc. Japan 11, 670 (1956).

Translated by J. G. Adashko
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