

Selective determination of anisotropic magnetic interactions from high-resolution NMR spectra of powdered samples

M. A. Alla, E. I. Kundla, and E. T. Lippmaa

Cybernetics Institute, Estonian Academy of Sciences

(Submitted 26 December 1977)

Pis'ma Zh. Eksp. Teor. Fiz. **27**, No. 4, 208–211 (20 February 1978)

It is shown that in the case of rapid synchronous rotation of a system in the spin and spatial coordinates it is possible to reconstruct selectively the influence of the anisotropic interactions on the high-resolution NMR spectra of rare nuclei in solids.

PACS numbers: 76.60.Cq, 75.30.Gw

Rapid rotation of powdered samples at the magic angle ($\theta = \arccos 1/\sqrt{3}$) to the direction of the constant magnetic field H_0 , together with the suppression of the spin-spin interactions between observable rare nuclei $S(^{13}\text{C}, ^{29}\text{Si}, \dots)$ and other abundant nuclei $I(^1\text{H}, ^{19}\text{F}, \dots)$, makes it possible to register individual NMR signals from non-equivalent rare nuclei with a relative line width of the order of 10^{-6} .^[1,2] Just as in liquids, the spectrum is determined here by the isotropic mean values of the tensor interactions, while the anisotropy components are fully averaged out.

The proposed experiment for the determination of the principal values of the tensor of a certain interaction of a considered spin S with the surrounding can be divided into three stages: 1) An appreciable transverse magnetization of the rare spins is produced. 2) During a time interval τ , the spin system is subjected to the action of pulsed and stationary high-frequency (HF) magnetic fields in such a way that a change, synchronous with the mechanical rotation, is produced in the spin coordinates of the Hamiltonian. During this time the evolution of the system is determined by a certain anisotropic interaction chosen by the experimenter. 3) The free-precession signal of the rare nuclei is registered under the conditions of high resolution. The NMR spectrum obtained by Fourier transformation depends, naturally, on the state of the system at the instant of the termination of the second stage. The dependence of the line intensities on τ is subjected to an additional Fourier transformation, and the obtained line shape is used to determine the principal values of the tensor of the interaction chosen in stage 2).

The behavior of the spin system during the time of the second stage is described by the kinetic equation

$$\dot{\rho}_V = -iL(\tilde{H})\rho_V, \quad (1)$$

which is obtained from the Liouville equation

$$\dot{\rho} = -iL(H)\rho, \quad L(H)Q = [H, Q], \quad (2)$$

with the aid of the transformations

$$\begin{aligned}
 R^{\pm 1} &= \exp(\pm i\omega_1 t \sum_i I_{zi} \pm i\omega_2 t S_z), \\
 T^{\pm 1} &= \exp(\pm i\theta^I \sum_i I_{yi} \pm i\theta^S S_y), \\
 V^{\pm 1} &= \exp(\pm ih_{eff}^I t \sum_i I_{zi} \pm ih_{eff}^S t S_z)
 \end{aligned} \tag{3}$$

in accordance with

$$Q_V = V^{-1} T^+ R^{-1} Q R^+ T^{-1} V^+ \tag{4}$$

The deviations $\Delta^{I,S} = \omega^{I,S} - \omega_{1,2}$ of the HF fields from the Larmor frequency $\omega^{I,S}$ and $\gamma_{I,S} H^{I,S}$ of the intensities of the HF fields determine in (3) the effective magnetic field in the rotating system of coordinates for both spins

$$h_{eff} = [\Delta^2 + (\gamma H)^2]^{1/2}, \quad \cos \theta = \Delta / h_{eff} \tag{5}$$

When determining the state of the spin system at the instant of termination of the second stage, the solution of Eq. (1) was assumed to be

$$\rho_V = \{ \exp[-it'L(H_{eff})] \} \rho_{0V} \tag{6}$$

where H_{eff} is the value of \bar{H} averaged either over the interval between the pulses (pulsed HF field^[2]) or over the entire second stage (stationary HF field^[3]). During the time of short HF pulses, all the internal interactions are neglected.

A summary of the results is contained in Table I, which indicates the presence (+) or absence (-) of nonzero mean values of the anisotropic components of the electron screening (H_c), and of the scalar (H_J) and dipole-dipole (H_d) interactions in different variants of experiments with pulsed (first two variants) or stationary (next

TABLE I.

Experimental conditions		H_c^S	H_J^{IS}	H_d^{IS}	H_d^{II}
$ h_{eff} \gg \omega_r$	$\Delta^I = 0, \quad (\pi)_k^S$	+	-	-	+
	$\cos^2 \theta^I = 1/3, \quad (\pi)_k^S$	+	+	+	-
$\Delta^I = 0$	$h_{eff}^S = k\omega_r$	+	-	-	-
	$h_{eff}^S = h_{eff}^I$	-	+	-	-
	$h_{eff}^S \pm h_{eff}^I = k\omega_r$	-	-	+	-
	$h_{eff}^I = 1/2 \omega_r$	-	-	-	+

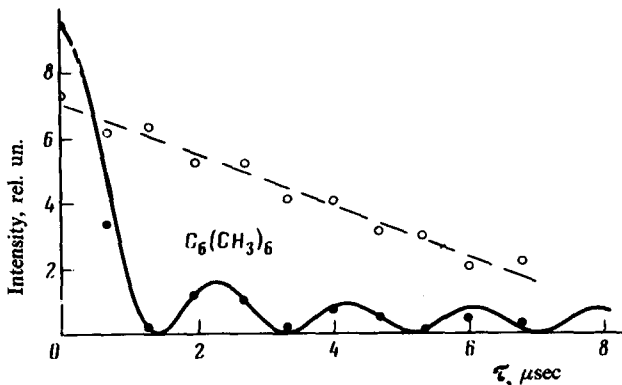


FIG. 1. Dependence of the intensity of the lines of ^{13}C in the high-resolution spectrum of hexamethylbenzene on the duration of the pulsed excitation of the ^{13}C nuclei.

four variants) action on the spins S . The symbol $(\pi)_k^{\frac{1}{2}}$ signifies that π pulses are applied to the spins S every k ($k=1$ and 2) quarter-period of revolution.

In the theoretical analysis we assumed a high frequency of mechanical rotation compared with the internal interactions. If the spin-spin coupling between the I and S is suppressed, or if the coupling between equal spins I is weak, then the interactions acquire a static character and the requirement of ultrahigh speed rotation can be relaxed. In the case of the first experiment of the table, the frequency of rotation should greatly exceed only the linewidth in the high-resolution spectrum.

To verify the foregoing arguments experimentally, we measured the anisotropy of the chemical shift in solid hexamethylbenzene at $H_0 = 10$ kG. The transverse magnetization of the ^{13}C system (S) was produced by transfer of polarization from the protons

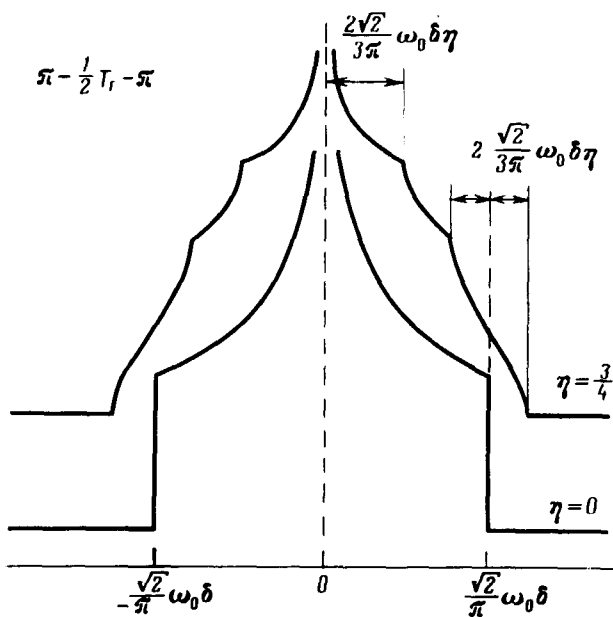


FIG. 2. Theoretical line shape in the double-Fourier-transformation spectrum used for selective reconstruction of the influence of the anisotropy of the electron screening.

(I) in the rotating coordinate system at an HF field intensity 20 kG. During the second stage of the experiment, strong π pulses were applied on the ^{13}C nuclei every half-cycle of the rotation (1.5 kHz). The dependence of the intensity of the lines from the methyl and from the ring carbon nuclei on the duration τ of the second stage is shown in Fig. 1. The solid line corresponds to the theoretical damping of the signals from aromatic carbon nuclei at a chemical-shift anisotropy $\delta=113$ m.f. (112 m.f. in⁽⁴⁾) and is in satisfactory agreement with the experimental points. The damping of the line from the methyl group is due mainly to inhomogeneity of the field H_0 .

As already stated, the second Fourier transformation of the damping curve makes it possible to determine directly from the shape of the obtained line the anisotropy and symmetry parameters (δ and η) of the electron screening of the nuclei. The lower curve of Fig. 2 corresponds to the theoretical damping curve of Fig. 1 and can be expressed in terms of elliptic integrals of the first kind $F(\pi/2, k)$

$$I(\omega) = \frac{1}{\omega^S \delta \sqrt{1 + \sqrt{1 - (a\omega)^2}}} F\left(\frac{\pi}{2}; \sqrt{\frac{2\sqrt{1 - (a\omega)^2}}{1 + \sqrt{1 - (a\omega)^2}}}\right), \quad (7)$$

$$a = \pi/\sqrt{2} \omega^S \delta.$$

The upper curve represents the line shape in the case of an asymmetrical screening tensor.

¹J. Schaefer and E. O. Stejskal, J. Am. Chem. Soc. **98**, 1031 (1976).

²E. Lippmaa, M. Alla, and T. Tuherm, Magnetic Resonance and Related Phenomena, Proc. Twenty-ninth Congress Ampere, ed. by H. Brunner, K. H. Hausser and D. Schweitzer, Heidelberg-Geneva, 1976, p. 113.

³E. Kundla, Izv. Akad. Nauk Est. SSR Ser. Fiz.-Mat. (in press).

⁴J. S. Waugh, M. G. Gibby, and S. Kaplan, Magnetic Resonance and Related Phenomena, Proc. Seventeenth Congress Ampere, ed. by V. Hovi, North-Holland, 1973, p. 11.