PHYSICAL REVIEW B **77**, 212404 (2008)

Acoustical enhancement of nuclear magnetic relaxation rates in liquids

Quoc Lam Vuong, Yves Gossuin, and Pierre Gillis
Biological Physics Department, University of Mons-Hainaut, 7000 Mons, Belgium

(Received 5 November 2007; revised manuscript received 26 February 2008; published 11 June 2008)

Proton nuclear magnetic relaxation is known to depend on thermal motion. That motion can be affected if an acoustic wave runs through the sample. Nuclear magnetic relaxation was shown to be modified by acoustic waves in solids, but the phenomenon was never observed in liquids. A quantitative estimation is here obtained for liquids whose relaxation is governed by magnetic dipolar coupling, thanks to the calculation of the increment to spectral density functions due to acoustic stimulation. The result of the calculation leads to the conclusion that the effect is negligible for monochromatic excitation if the wave amplitude remains compatible with the safety requirements typical of magnetic resonance imaging.

DOI: 10.1103/PhysRevB.77.212404 PACS number(s): 76.60.−k, 76.60.Es, 43.35.+d

I. INTRODUCTION

The idea that ultrasound could influence NMR observations periodically appears in literature for a long time—an early quotation, even if not the first one, can be found in a 1952 paper.[1] Investigations were therefore carried out, with the hope to display modifications of relaxation times within liquid and solid samples under the effect of ultrasound.

The reality of that effect is established for solid samples.[1] In solids, resonant acoustic irradiation causes saturation of the nuclear magnetization, just like resonant irradiation by an rf field. Providing a qualitative explanation of that effect is rather straightforward: Phonons are excited by the presence of an acoustic wave in a crystal. Those phonons modify the populations in the spin states, and subsequently, the transitions between the spin states whose probability governs the relaxation times. The phenomenon is interpreted as a resonance between phonon energy and transitions within the crystal. A summary of experiments and theories about solids was reported by Shutilov,[2] who mainly refers to modulation by the lattice vibrations of the electric quadrupolar coupling of individual spins with the lattice.

The effects in liquids are less obvious, beyond the well known feature that acoustic waves carry on thermal energy, which could induce a very limited warming up, which in turn reduces the relaxation rates; we disregard that purely thermal effect, which is much too tenuous to be of any practical interest. Using the rigorous quantization of the interaction of a radio frequency field with the spins[3] as a model seems irrelevant. Experiments on pure liquids showed no significant modification.[4–6] Relaxation times within inhomogeneous liquids (containing Gadolinium for instance) were reported to be modified,[6–8] which awoke the interest of magnetic resonance imaging (MRI) experts: Such an effect could improve contrast in MRI.

Bowen[4] showed that a previous positive prediction by Al'tschuler[9] concerning nuclear magnetic acoustic resonance absorption in a liquid via magnetic dipole coupling was based on an erroneous extrapolation of properties that are typical of elastic lattice vibrations. Bowen's conclusion was that "the nuclear magnetic resonance acoustic transition probability must be obtained by direct calculation of the magnetic spectral density." That calculation represents the aim of our work: Providing quantitative estimations of variations of relaxation times caused by acoustic waves in pure liquids, thanks to the calculation of spectral density functions.

The resonant mechanism associated with the presence of phonons is nonpertinent in liquids. However, if an effect is expected, it could be due to molecular motions specifically induced by acoustic waves, as described by fluid kinetics and diffusion theory. We consider magnetic dipole-dipole interaction in the Redfield formalism applied to a system wherein translational motion is dominant. Rotational motion, which brings the dominating contribution to relaxation in water, is expected to be still less affected by acoustic waves.

Going back to qualitative arguments, a significant effect could perhaps be expected if two time scales coincide: on one hand, the correlation time that defines the decay of the autocorrelation function and on the other hand, the period of the acoustic wave. That is not the case for usual liquids because the motional correlation time is several orders of magnitude shorter than the acoustic period. Our conclusion confirms the previous negative predictions: The calculated supplementary contribution to relaxation rates is negligible for monochromatic progressive waves as well as for stationary waves.

II. COHERENT MOTION DUE TO ACOUSTIC WAVES

Relaxation is always caused by a time-modulated interaction between magnetic moments within the system. Here, coupling is supposed to be dipolar, while time modulation arises from translational diffusion. That modulation is perturbed by acoustic waves, because the motion induced by the acoustic flux modifies the autocorrelation function, which determines the spectral density.

The remaining question concerns the quantitative importance of that modification. Our approach is an extension of the standard derivation of relaxation rates in liquids:[10] A hydrodynamic description of the elementary motions within the liquid is used to determine the spin autocorrelation function, whose Fourier transform is the spectral density needed to obtain the relaxation rates. That standard derivation assumes unrestricted diffusion for the water molecules motion, which was corrected later, with the proper volume of the molecules being considered as forbidden.[11] However, that correction essentially concerns the high frequency asymptotic regime, when the spectral density goes to zero, so that the investigated increment to the relaxation rates itself goes to zero.

The acoustic wave adds a supplementary contribution to the flux governing Fick's law; that flux then reads

$$\vec{j}(\vec{r},t) = -D\vec{\nabla}n(\vec{r},t) + n(\vec{r},t)\,\delta\vec{v}(\vec{r},t), \qquad (1)$$

where D is the diffusion coefficient, $n(\vec{r},t)$ is the number of interacting spins per volume unit, and $\delta\vec{v}(\vec{r},t)$ is the local velocity resulting from the local pressure oscillation. We neglect the D dependence on temperature and pressure, which is known to be negligible for the sound wave amplitudes we are considering.[12]

Incorporating that acoustic flux in the continuity equation modifies in turn the diffusion equation, which becomes

$$\frac{\partial n}{\partial t} = D\Delta n - \delta\vec{v}\,.\,\vec{\nabla}n - n(\vec{\nabla}\,\delta\vec{v}), \qquad (2)$$

where we specify, respectively, for a progressive plane wave and for a stationary wave,

$$\delta\vec{v} = -A\,\sin(\vec{k}\vec{r} - \omega t + \Phi), \qquad (3)$$

$$\delta\vec{v} = -A\,\cos(\vec{k}\vec{r} + \Phi_1)\sin(\omega t + \Phi_2). \qquad (4)$$

For an acoustic wave with a 10 W/cm^2 power, A is on the order of 0.01 m/s. In Eqs. (3) and (4), the change in velocity due to the acoustic stimulation is linear in A; the first correction in A^3 being neglected.

The last term in Eq. (2) is negligible in our case: $\delta\vec{v}$ depends on the position through $\vec{k}\vec{r}$, which is almost constant along the distance run during the correlation time. The z coordinate may thus be substituted by its initial value z_0. We therefore write, if $n = n_1(x)n_2(y)n_3(z)$ and if we assume the propagation of the sound wave directed along the z axis, which is defined by the direction of the static magnetic field,

$$\frac{\partial n_3(z,t)}{\partial t} = D\frac{\partial^2 n_3(z,t)}{\partial z^2} - \delta v_z \frac{\partial n_3(z,t)}{\partial z}. \qquad (5)$$

Equation (5) can easily be solved,

$$n_3(z,t;z_0,0) = \frac{1}{\sqrt{4\pi Dt}}e^{-[z - z_0 + h(t) - h(0)]^2/(4Dt)}, \qquad (6)$$

where $h(t) = (A/\omega)\cos(kz_0 - \omega t + \Phi)$ for a running wave and $h(t) = (A/\omega)\cos(kz_0 + \Phi_1)\cos(\omega t + \Phi_2)$ for a stationary wave. The phase Φ was introduced in order to account for the initial time in Eqs. (5) and (6), which is not the time when the sound wave was turned on.

$P(\vec{R},t+\tau;\vec{R}_0,t)$, which is the conditional probability that the two interacting spins are distant from $\vec{R}$ at time $(t+\tau)$, knowing they were distant from $\vec{R}_0$ at time t, may be deduced from Eq. (6),

$$P(\vec{R},t+\tau;\vec{R}_0,t) = \frac{\displaystyle\int\int n(\vec{r}_1,t+\tau;\vec{r}_{01},t)\,n(\vec{r}_1 - \vec{R},t+\tau;\vec{r}_{01} - \vec{R}_0,t)\,d\vec{r}_1 d\vec{r}_{01}}{\displaystyle\int\int\int n(\vec{r}_1,t+\tau;\vec{r}_{01},t)\,n(\vec{r}_1 - \vec{R},t+\tau;\vec{r}_{01} - \vec{R}_0,t)\,d\vec{r}_1 d\vec{r}_{01} d\vec{R}}. \qquad (7)$$

The integration in Eq. (7) can be achieved almost completely, neglecting the edge effects; more precisely, the spatial inhomogeneity arising from the presence of the sound wave is cancelled by the integration over z_1. Equation (7) reduces to the following one, after some straightforward calculations:

$$P(\vec{R},t+\tau;\vec{R}_0,t) = (8\pi D\tau)^{-3/2}e^{-[(X - X_0)^2 + (Y - Y_0)^2]/(8D\tau)} \times \frac{\displaystyle\int dz_{01}e^{-(Z - Z_0 + \Delta z)^2/(8D\tau)}}{\displaystyle\int dz_{01}}, \qquad (8)$$

where the new position variable Δz is due to the acoustic wave,

$$(\text{progressive wave}) \quad \Delta z = (4A/\omega)\sin(kZ_0/2)\sin(\omega\tau/2) \times\cos(kz_{01} - kZ_0/2 + \Phi - \omega\tau/2), \qquad (9)$$

$$(\text{stationary wave}) \quad \Delta z = (4A/\omega)\sin(kZ_0/2)\sin(\omega\tau/2) \times\sin(kz_{01} - kZ_0/2 + \Phi_1) \times\sin(\omega\tau/2 + \Phi_2). \qquad (10)$$

The only remaining spatial integration concerns one "free" variable (z_{01}). We are now able to estimate the autocorrelation function, which is defined as[10]

$$G^{mm'}(t,\tau) = \frac{8\pi}{15}\sqrt{s_m s_{m'}}N\int\int \frac{Y_2^m(\Omega_0)^* Y_2^{m'}(\Omega)}{R_0^3 R^3} \times P(\vec{R},t+\tau;\vec{R}_0,t)\,d^3\vec{R}_0 d^3\vec{R}, \qquad (11)$$

where $s_m = 4m^2 - 9m + 6$, $Y_l^m(\Omega)$ is a spherical harmonic function, and N is the mean number of interacting spins per volume unit and where the singularity in $R = 0$ is avoided by the introduction of a closest approach distance (d).

Spatial isotropy implies that $G^{mm'}$ is diagonal. The symmetry is reduced by the presence of an acoustic plane wave, but remains cylindrical, which is enough to maintain the diagonality of the autocorrelation function. Usually, that autocorrelation function does not depend on t, because of invariance with respect to a time translation. That property is no longer obvious in the presence of an acoustic wave. Precisely, the t dependence of the autocorrelation function [Eq. (11)] is "hidden" in the phases Φ characterizing Δz. However, the effective interaction governing relaxation does not last longer than the time the two interacting spins spend near each other, i.e., a time on the order of d^2/D, and that time is much shorter than the sound period.

The displacement due to the acoustic wave, Δz in Eq. (8), may be handled as a small perturbation, allowing for a power expansion. The first order contribution is null, because of the integration over z_{01}, which only appears in a single sinusoidal function; for short waves, its integration over the available space amounts to going over several cycles of the trigonometric function. If this is not true because of a possible long wavelength, the slope of the magnetization decay could then be phase-dependent. The decay could slightly oscillate around its value without sound, at the frequency of the sound wave, but it must be noted that the period of the sound wave is much shorter anyway than the relaxation times we are discussing. It is thus necessary to average over Φ or Φ_2, in order to obtain a measurable relaxation time, and the invariance with respect to a time translation is then restored. At first order, averaging over the phase also leads to a vanishing increment to the relaxation rate. We therefore evaluate the effect of the sound wave at second order in A.

III. ACOUSTIC INCREMENT OF RELAXATION RATES

We obtain for a progressive wave, after defining the diffusion time $\tau_D = d^2/D$,

$$\Delta G^{mm'}_{(S)}(\tau) = \delta_{mm'}\frac{8s_m}{45d^3}N\left(\frac{A}{\omega d}\right)^2 \sin^2(\omega\tau/2)\left(\frac{\tau_D}{\tau}\right)^2\int_0^\infty\left[f_m(u) - \frac{3\sqrt{\pi\tau}}{\tau_D}(J_{3/2}(u))^2\right]e^{-2u^2\tau/\tau_D}du, \tag{12}$$

where $J_l(u)$ is a Bessel function of order l and where

$$f_m(u) = \left(\frac{11-2m^2}{7}\right)(u\cos u - 3\sin u)(u\cos u - \sin u)/u^4 + \left(\frac{m^2-4}{5}\right)(\sin u/u)^2 + \frac{3(m^2-9)}{35} \times[5u\cos u + (u^2-5)\sin u]^2/u^6.$$

Considering a stationary wave only multiplies the rhs of Eq. (12) by a factor of $\sin^2(\omega t/2+\Phi_2)$.

The derivation of Eq. (12) is based on well known properties of spherical harmonic functions, as shown in the Appendix.

The relaxation rates may be written as[10]

$$1/T_1 = \frac{3}{2}\gamma^4\hbar^2 I(I+1)(\mu_0/4\pi)^2[J^{(1)}(\omega_0) + J^{(2)}(2\omega_0)], \tag{13a}$$

$$1/T_{1\rho} = \frac{3}{8}\gamma^4\hbar^2 I(I+1)(\mu_0/4\pi)^2[J^{(2)}(2\omega_0) + 10J^{(1)}(\omega_0) + J^{(0)}(2\omega_1)], \tag{13b}$$

$$1/T_2 = \frac{3}{8}\gamma^4\hbar^2 I(I+1)(\mu_0/4\pi)^2[J^{(2)}(2\omega_0) + 10J^{(1)}(\omega_0) + J^{(0)}(0)], \tag{13c}$$

where γ is the nuclear gyromagnetic ratio, $\hbar$ is Planck's constant, I is the nuclear spin, and ω_0 and ω_1 are the nuclear spin Larmor frequencies in the static field and in the rf field, respectively. The spectral densities $J^{(m)}(\omega)$ are the Fourier transforms of the autocorrelation functions defined in Eq. (11) and specified in Eq. (12).

The increment to the spectral density function assignable to the acoustic wave then reads

$$\Delta J^{(m)}_S(\omega_I) = \left(\frac{A}{\omega d}\right)^2\frac{4s_m N\tau_D}{15d^3}M_m(\omega\tau_D,\omega_I\tau_D), \tag{14}$$

$$M_m(\eta,\mu) = \int_0^\infty du\left\{\frac{\eta f_m(u)}{3}\left[2\tan^{-1}\Omega - \frac{\log(1+\Omega^2)}{\Omega}\right] - \frac{(\sin u - u\cos u)^2}{u^4}\log(1+\Omega^2)\right\}, \tag{15}$$

where $\Omega = \eta/(2u^2 + i\mu)$.

Spectral densities are decreasing functions of the Larmor frequency. Their value at null frequency, which is given by $M_m(\eta,0)$, provides therefore an upper bound for the investigated increment. Furthermore, we also know that $\eta = \omega\tau_D \ll 1$: Even for an acoustic wave with a 100 MHz frequency, η is on the order of 10^{-3} for water molecules.

The dependence of $M_m(\eta,0)$ on η may be analytically deduced from Eq. (15) by dividing the integration domain over u in Eq. (15) in two parts, respectively corresponding to $\Omega > 1[u < (\eta/2)^{1/2}]$ and to $\Omega < 1[u > (\eta/2)^{1/2}]$. Knowing that $f_m(0) = (m^2-2)/21$, and that both functions go asymptotically to zero as $1/u^2$, it can be shown that $M_m(\eta,0) = [C_m\eta^{3/2} + O(\eta^2)]$. A numerical computation of the integral allows estimating constant C_m,

$$M_m(\eta,0) = 0.012(0.65m^2 + 0.05m - 3.7)\eta^{3/2}. \tag{16}$$

We are now able to put a boundary on the spectral density increment,

$$\Delta J^{(m)}(\omega_I) < 4s_m N(A/d)^2\tau_D^3(\omega\tau_D)^{-1/2}C_m/(15d^3),$$

which results in a relative increment for $m=0$,

$$\Delta J^{(0)}(0)/J^{(0)}(0) < 0.05(15/4\pi)[\tau_D/(d/A)]^2(\omega\tau_D)^{-1/2}. \tag{17}$$

It can easily be checked that the squared factor $\tau_D/(d/A)$ (i.e., the ratio between the time needed to diffuse a distance d and the time for the acoustic flux to run the same distance d) is on the order of 10^{-3}, while $\eta = \omega\tau_D$ is always larger than 10^{-3}. The relative increment is thus smaller than 10^{-5}. Considering a stationary wave only brings a slight modification:

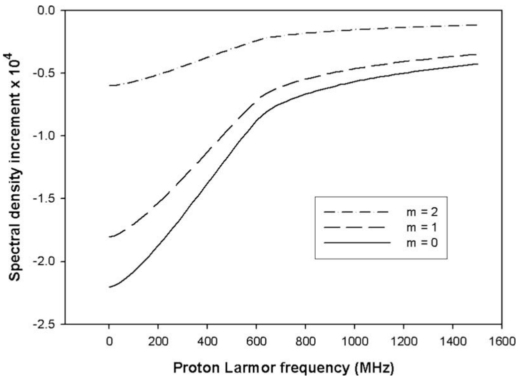

FIG. 1. Spectral density dimensionless increment due to acoustic stimulation (sound wave power: 10 W/cm^2), as given by $M_m(\omega\tau_D,\omega\tau_D)$ defined in Eq. (14), with $\tau_D=3\times10^{-11}$ s ($D=3\times10^{-9}$ m^2/s and $d=3\times10^{-9}$ m), for an acoustic frequency of 10 MHz ($\omega\tau_D=0.00188$).

the result given by the rhs of Eq. (14) is divided by 2, as the result of averaging over Φ_2. The upper bound becomes still smaller for long waves: the factor $\sin(kZ_0/2)$ [Eqs. (9) and (10)] could then be approximated by $kZ_0/2$, which introduces in the upper bound a factor of $k^2Z_0^2/4$ instead of 1 in our estimation.

Spectral densities were numerically obtained from Eq. (14), as functions of the Larmor frequency. The solutions are shown in Fig. 1.

IV. CONCLUSION

Proton nuclear magnetic relaxation rates are potentially influenced by the presence of an acoustic flux within a liquid. Our calculation shows that no observable effect is expected for acoustic waves whose amplitude remains small enough to avoid cavitation. That negative conclusion agrees with previous experiments on $CHCl_3$ and $CHBr_3$,[7] and is confirmed by recent new attempts at the University of Valenciennes (France) to measure relaxation rate modifications under acoustic excitation in pure water and in aqueous gels.[13]

That result is a confirmation of intuitive expectations. Relaxation is indeed governed by the interactions between spins determining the autocorrelation function. Now, autocorrelation functions go to zero after the correlation time, i.e., the diffusion time in our case. As a consequence, the range of the interactions that have to be taken into account is itself very short. More precisely, the diffusion time is much shorter than the sound wave period, and the effective interaction range is much smaller than the sound wavelength. Relaxation thus occurs within a region that is affected as a whole by the acoustic flux, which only adds a constant velocity to the interacting spins. One can then define a virtual local and instantaneous relaxation rate, which is automatically averaged by spatial integration. For small wavelengths, that spatial integration also results in a time averaging, while the time averaging has to be explicitly performed for long wavelengths, through its dependence with the initial phase of the sound wave. Considering the respective contributions from an expansion with respect to the wave amplitude, the first correction corresponds to the second order term, which remains much too small to be observed.

The limitation of the wave amplitude is needed if cavitation is to be avoided. That phenomenon is indeed out of the scope of our work, although it is known to likely happen and to modify proton relaxation rates in liquids, but any quantitative prediction for that modification is missing, without mentioning possible damaging effects on patients submitted to MRI.

Larger effects on relaxation rates could be expected if the correlation time governing relaxation is on the same order of magnitude as the sound period, as one can guess from Eq. (17). That condition is obviously not fulfilled for the frequencies considered here. We thus consider our result as an upper bound, indicating that the frequency range usually associated with ultrasound waves does not lead to observable effects. An overlap between the acoustic periods and the correlation times could be provoked by a lengthening of the correlation times characterizing the relaxation mechanisms, by instance if larger magnetized particles (namely, superparamagnetic particles) are suspended in the sample. However, such particles are MRI contrast agents, which are devoted at increasing relaxation rates, with a much larger effect than the rate enhancement expected from submitting the sample to ultrasound waves.

ACKNOWLEDGMENTS

The authors are very grateful to Robert N. Muller and Jacques Reisse, who strongly encouraged them to address a problem they followed for a long time.

APPENDIX

Expanding Eq. (8) in powers of A/ω, we get at second order

$$P(\vec{R},t+\tau;\vec{R}_0,t) = (8\pi D\tau)^{-3/2}e^{-|\vec{R}-\vec{R}_0|^2/8D\tau} \times\left\{1+\frac{A^2}{\omega^2 D\tau}\left[\frac{(Z-Z_0)^2}{4D\tau}-1\right] \times\sin^2\frac{kZ_0}{2}\sin^2\frac{\omega\tau}{2}\right\},$$

where the zero order is the result without any acoustic wave, while the second term is associated with the sound wave correction. Inserting this expression in Eq. (11), a correction term appears in the autocorrelation function

$$\Delta G^m(\tau) = \frac{2A^2}{15\omega^2\sqrt{\pi}(2D\tau)^{5/2}}s_m N\sin^2\frac{\omega\tau}{2}\int\int\frac{Y_2^m(\Omega_0)^* Y_2^{m'}(\Omega)}{R_0^3R^3} \times\left(\frac{(Z-Z_0)^2}{4D\tau}-1\right)e^{-|\vec{R}-\vec{R}_0|^2/8D\tau}d^3\vec{R}_0 d^3\vec{R}, \tag{A1}$$

where the factor $\sin^2(kZ0)$, which is time independent and smaller than 1, has been omitted, which means that Eq. (A1) must be considered as yielding an upper bound for the spectral densities.

Equation (A1) can be transformed thanks to the following properties:

(i)

$$e^{-\frac{|\vec{R}-\vec{R}_0|^2}{8Dt}} = (8\pi Dt)^{3/2}\int_{R^3}\frac{e^{-2Dt\rho^2}}{\rho} \times \sum_{\substack{\ell_1 m_1\\ \ell_2 m_2}}\left(\frac{1}{r_0 r}\right)^{1/2} i^{\ell_1}(-i)^{\ell_2} Y_{\ell_1}^{m_1}(\Omega)^* Y_{\ell_1}^{m_1}(\Omega') Y_{\ell_2}^{m_2}(\Omega_0) \times Y_{\ell_2}^{m_2}(\Omega')^* J_{\ell_1+\frac{1}{2}}(\rho R) J_{\ell_2+\frac{1}{2}}(\rho R_0) d\vec{\rho},$$

where Ω and Ω_0 are the solid angles corresponding to vectors $\vec{R}$ and $\vec{R}_0$, Ω' corresponds to $\vec{\rho}$, and $J_l(x)$ is the Bessel function of order l.

(ii) For half order Bessel functions, $J_{n+3/2}(x)/x^{n+1/2} = -d/dx[J_{n+1/2}(x)/x^{n+1/2}]$.

(iii) Integrating over the solid angles can be performed thanks to the fact that $Z=(4\pi/3)^{1/2} R Y_1^0(\Omega)$ and $Z_0=(4\pi/3)^{1/2} R_0 Y_1^0(\Omega_0)$, and that spherical harmonics are orthonormal functions.

(iv) Clebsch–Gordan coefficients allow writing

$$Y_{\ell_1}^{m_1}(\Omega) Y_{\ell_2}^{m_2}(\Omega) = \sum_{\ell,m}\sqrt{\frac{(2\ell_1+1)(2\ell_2+1)}{4\pi(2\ell+1)}} C_{\ell_1,\ell_2;0,0}^{\ell;0} C_{\ell_1,\ell_2;m_1,m_2}^{\ell;m} Y_\ell^m(\Omega).$$

The integrations on the radial variables R and R_0 are performed by using property (ii). Equation (12) is finally obtained by setting $u=\rho d$.

---

[1] A. Kastler, Experientia **8**, 1 (1952).

[2] V. A. Shutilov, Sov. Phys. Acoust. **8**, 383 (1963).

[3] J. Jeener and F. Henin J. Chem. Phys. **116**, 8036 (2002).

[4] L. O. Bowen, Br. J. Appl. Phys. **15**, 1451 (1964).

[5] L. O. Bowen, Proc. Phys. Soc. Jpn. **87**, 717 (1966).

[6] J. Homer and S. U. Patel, J. Chem. Soc., Faraday Trans. **86**, 215 (1990).

[7] A. Kassner, R. Bannerman, and R. A. Lerski, Phys. Medica **11**, 47 (1995).

[8] J. Homer, P. McKneown, W. R. McWhinnie, S. U. Patel, and G. J. Tilstone, J. Chem. Soc., Faraday Trans. **87**, 2253 (1991).

[9] S. A. Al'tschuler, Sov. Phys. JETP **1**, 29 (1955).

[10] A. Abragam, *The Principles of Nuclear Magnetism* (Clarendon, Oxford, 1961).

[11] Y. Ayant, E. Belorizky, J. Alizon, and J. Gallice, J. Phys. (Paris) **36**, 991 (1975).

[12] V. V. Kisel'nik, N. G. Malyuk, A. N. Toryanik, and V. M. Toryanik, J. Struct. Chem. **14**, 911 (1974).

[13] J.-J. Fabre (private communication).