

## Research Article

# Using the Intramolecular Contribution to the Second Moment of NMR Line Shape to Detect Site Symmetry Breakdown in Molecular Crystals

Ferid Bashirov<sup>1</sup> and Nail Gaisin<sup>2</sup>

<sup>1</sup>Department of General Physics, Institute of Physics, Kazan Federal University, Kremlevskaya Street 18, Kazan 420111, Tatarstan Republic, Russia

<sup>2</sup>Department of Physics, Institute of Petroleum, Chemistry and Nanotechnology, Kazan Technological University, Karl Marx Street 66, Kazan 420015, Tatarstan Republic, Russia

Correspondence should be addressed to Ferid Bashirov; [fbashir@mail.ru](mailto:fbashir@mail.ru)

Received 15 September 2015; Revised 15 November 2015; Accepted 29 November 2015

Academic Editor: Guang Zhu

Copyright © 2015 F. Bashirov and N. Gaisin. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

A new approach to simulating the intramolecular contribution to the anisotropic second moment of NMR spectral lines broadened by magnetic dipole-dipole interaction of nuclei is suggested. The extended angular jump model is used by approximating the local hindered molecular motion (HMM). The theoretical result allow describing the site symmetry distortion by new experimental parameters  $q_{\alpha}$ , the dynamic weights of irreducible representations of the HMM crystallographic point symmetry group. The application of the theory to describing the intraionic second moment of the proton NMR spectral line in monocrystalline ammonium chloride proves the tetragonal distorted tetrahedral site symmetry of ammonium ions.

## 1. Introduction

The second moment of the NMR spectral line broadened due to the magnetic dipole-dipole interaction has been yielded by Van Vleck as one of the main probes of hindered molecular motion (HMM) in crystalline substances [1]. As the magnitude of the second moment depends rigorously on geometrical and physical peculiarities of nuclear motion, measuring the second moment allows one to test various models of HMM taking place in condensed matter.

At present, three principal model diversities of local HMM exist: the rotational diffusion model (RDM), the fixed angular jump model (FAJM), and the extended angular jump model (EAJM) [2, 3]. Using RDM shown to be very successful by describing HMM happened in liquids [4–7]. FAJM works sufficiently well in isotropic media of powders [8–10]. At last, the EAJM is appropriated for exploring the HMM of symmetrical molecules in any condensed molecular media: single crystals, powders, and liquids. It was fruitfully applied to discuss the broadened lines of incoherent scattering of

neutrons, dielectric and infrared absorption, Raman scattering of light, and the rates of nuclear magnetic relaxation in mono- and polycrystalline molecular media [2, 3]. This paper is devoted to expanding EAJM approach to simulate the second moment of NMR-absorption line broadened due to the magnetic dipole-dipole interaction in condensed molecular media. It is dedicated also to showing that the intramolecular part of the second moment is sensitive to symmetry breakdown effect in the HMM. As an application, we revise the experimental data of Bersohn and Gutowsky concerning the 2nd moment of the proton spectral line in the single crystal of ammonium chloride [11]. A new interpretation of the data follows the tetragonal distorted site symmetry of  $\text{NH}_4^+$  ions in  $\text{NH}_4\text{Cl}$  that firstly has been determined by the proton relaxation experiments [12].

## 2. Theory

According to Van Vleck, the contribution of identical resonant nuclei to the second moment of NMR spectral line

broadened owing to their magnetic dipole-dipole interaction with resonant and with nonresonant nuclei in a crystal lattice, can be calculated by using a well-known expression [1]:

$$M_2^{(i)} = \sum_j M_2^{(ji)} = \sum_j \frac{3}{4} \gamma_j^2 \hbar^2 I_j (I_j + 1) \frac{(3\cos^2\theta_{ji} - 1)^2}{r_{ji}^6}, \quad (1)$$

where the index  $i$  labels a target resonant nucleus of a chosen molecule and the index  $j$  other nuclei of the substance;  $\gamma_j$  and  $I_j$  are, respectively, the gyromagnetic ratio and the quantum number of the nuclei;  $\hbar$  is Planck's constant divided by  $2\pi$  and  $\theta_{ji}$  is the polar angle formed by the internuclear vector  $\mathbf{r}_{ji}$  with the induction vector of the stationary magnetic field  $\mathbf{B}_0$  determined in the laboratory reference frame (LRF).

For convenience, we shall replace  $(3\cos^2\theta_{ji} - 1)^2$  by  $(16\pi/5)|Y_0^{(2)}(\theta_{ji})|^2 = (16\pi/5)|Y_0^{(2)}(\varphi_{ji}, \theta_{ji})|^2$ , where  $Y_0^{(2)}(\theta_{ji}) = Y_0^{(2)}(\varphi_{ji}, \theta_{ji})$  is the zeroth element of normalized spherical harmonic of the second order, the zeroth component of the unit spherical tensor of the 2nd rank, which depends on the polar angle  $\theta_{ji}$ , but it has no dependence of the azimuth angle  $\varphi_{ji}$ . Moreover, we shall rewrite (1) in terms of spherical tensor components as

$$\begin{aligned} M_2^{(ji)} &= \sum_j M_{2ji} \\ &= \sum_j \frac{12\pi}{5} \gamma_j^2 \hbar^2 r_{ji}^{-6} I_j (I_j + 1) |Y_0^{(2)}(\varphi_{ji}, \theta_{ji})|^2. \end{aligned} \quad (2)$$

By the way, the angles  $\theta_{ji}$  and  $\varphi_{ji}$  relate LRF whereas the internuclear vectors are fixed in the crystallographic reference frame (CRF). Taking into account the transformation rule of spherical tensors by a rotation to the three-dimensional Euler angles  $(\phi, \vartheta, \xi)$  from CRF to LRF given by the expression

$$Y_0^{(2)}(\varphi, \theta) = \sum_{m=-2}^2 D_{0m}^{(2)}(\phi, \vartheta, \xi) Y_m^{(2)}(\varphi', \theta'), \quad (3)$$

where  $D_{0m}^{(2)}(\phi, \vartheta, \xi)$  is an element of Wigner matrix, we can express  $M_2^{(ji)}$  in the form

$$\begin{aligned} M_2^{(ji)} &= \sum_j \frac{12\pi}{5} \gamma_j^2 \hbar^2 r_{ji}^{-6} I_j (I_j + 1) \\ &\cdot \left| \sum_{m=-2}^2 D_{0m}^{(2)}(\phi, \vartheta, \xi) Y_m^{(2)}(\varphi_{ji}, \theta_{ji}) \right|^2. \end{aligned} \quad (4)$$

Replacing  $D_{0m}^{(2)}(\phi, \vartheta, \xi) = \sqrt{(4\pi/5)} Y_m^{(2)}(\vartheta, \phi)$  allows us to reduce (4) to

$$\begin{aligned} M_2^{(ji)} &= \sum_j \frac{48\pi}{25} \gamma_j^2 \hbar^2 r_{ji}^{-6} I_j (I_j + 1) \\ &\cdot \left| \sum_{m=-2}^2 Y_m^{(2)}(\phi, \vartheta) Y_m^{(2)}(\varphi_{ji}, \theta_{ji}) \right|^2, \end{aligned} \quad (5)$$

where  $(\phi, \vartheta)$  and  $(\varphi_{ji}, \theta_{ji})$  are, respectively, the spherical angles of the vector  $\mathbf{B}_0$  and the internuclear vector  $\mathbf{r}_{ji}$ , determined with respect to CRF.

At sufficiently low temperatures, a regime of rigid lattice is valid in molecular crystals. At high temperatures ( $T > 40$  K), the direction of some internuclear vectors changes accidentally due to classical rotational displacement. Consequently, angles  $(\varphi_{ji}, \theta_{ji})$  become random functions of time. Such motion changes a spectral distribution law of NMR signals. Therefore, the simulation of a second moment for molecular substances has to be performed by accounting for intramolecular nuclei as well as intermolecular ones:

$$M_2^{(ji)} = M_2^{(\text{intra}ji)} + M_2^{(\text{inter}ji)}. \quad (6)$$

The term  $M_2^{(\text{inter}ji)}$  denoted by the label “(inter  $ji$ )” is the intermolecular part of  $M_2^{(ji)}$ . Its calculation is out of the interest of this paper.

The other term of the sum (6)  $M_2^{(\text{intra}ji)}$  labeled by “intra  $ji$ ” is the part of  $M_2^{(ji)}$  delivered by nuclei inner with respect to the given molecule. It is convenient to present  $M_2^{(\text{intra}ji)}$  in the form [5, 13, 14]

$$M_2^{(\text{intra}ji)} = \sum_{j=1}^{N-1} \frac{3}{4} \gamma_j^2 \hbar^2 I_j (I_j + 1) \int_{-\delta\nu}^{\delta\nu} J_{ji}^{(0)}(\omega) d\nu, \quad (7)$$

where  $N$  is the number of identical resonant nuclear spins in the considered molecule and

$$J_{ji}^{(0)}(\omega) = \int_{-\infty}^{+\infty} K_{ji}^{(0)}(t) \exp(i\omega t) dt \quad (8)$$

is the nonnormalized spectral density function of the auto-correlation function:

$$K_{ji}^{(0)}(t) = \langle F_{ji}^{(0)}(t) F_{ji}^{(0)*}(t + \tau) \rangle. \quad (9)$$

In its turn, the function  $F_{ji}^{(0)}(t)$  is the coordinate part of spin-spin interaction Hamiltonian of nuclei  $i$  and  $j$ , given by

$$\begin{aligned} F_{ji}^{(0)}(t) &= r_{ji}^{-3} [3\cos^2\theta_{ji}(t) - 1] \\ \text{or } F_{ji}^{(0)}(t) &= \left(\frac{16\pi}{5}\right)^{1/2} r_{ji}^{-3} Y_0^{(2)}[\theta_{ji}(t)]. \end{aligned} \quad (10)$$

The integration is prescribed within the limits of the double line width from  $-\delta\nu$  up to  $+\delta\nu$  in (7). By the way,  $\delta\nu = 1/T_2$ , where  $T_2$  is the spin-spin relaxation time,  $\omega = 2\pi\nu = \gamma_i B_0$  is the resonance angular frequency of spins  $i$ ,  $\gamma_i$  is their gyromagnetic ratio, and  $B_0$  is the module of induction vector of the static magnetic field.

The outcome of calculus by using (7)–(10) depends on the physical model of molecular motion. According to the goal of the present study, we shall apply EAJM approach [2, 3] as the model of HMM, within the framework of which an analytical expression of the normalized spectral density

function (SDF)  $J_0^{(2)}(\omega)$  of zero component of the 2nd rank tensor  $Y_0^{(2)}[\phi(t), \vartheta(t)]$  can be written for a single crystal by

$$\begin{aligned} J_0^{(2)}(\omega) &= J_0^{(2)}(q_\alpha, \phi, \vartheta, \omega) \\ &= \frac{5}{2\pi} \sum_{\alpha} \sum_{l=0}^2 \frac{q_\alpha \tau_\alpha}{1 + (\omega \tau_\alpha)^2} a_{\alpha l 0}(\phi) \cos^{2l} \vartheta. \end{aligned} \quad (11)$$

In agreement with the EAJM approach, polar angle  $\theta_{ji}$  of the internuclear vector  $\mathbf{r}_{ji}$  does not present explicitly in (11). Instead, there are two spherical angles  $\phi$  and  $\vartheta$ , which fix the orientation of main axis of the crystallographic reference frame in the laboratory one. Index  $\alpha$  labels irreducible representations (IR)  $\Gamma_\alpha$  of the molecule motion point symmetry group  $G$  and  $l$  labels an intermediate summation.

Taking into consideration (11), nonnormalized SDF takes the form

$$\begin{aligned} J_0^{(ji)}(\omega) &= J_0^{(ji)}(q_\alpha, \phi, \vartheta, \omega) = \frac{16\pi}{5} r_{ji}^{-6} J_0^{(2)}(q_\alpha, \phi, \vartheta, \omega) \\ &= 8r_{ji}^{-6} \sum_{\alpha} \sum_{l=0}^2 \frac{q_\alpha \tau_\alpha}{1 + (\omega \tau_\alpha)^2} a_{\alpha l 0}(\phi) \cos^{2l} \vartheta. \end{aligned} \quad (12)$$

The rated expressions of the factors  $a_{\alpha l 0}(\phi)$  are tabulated explicitly as a function of azimuth angle  $\phi$  for all crystallographic point symmetry groups of pure rotation in [2, 3]. The quantities  $q_\alpha$  are the adjustable parameters of the theory called the dynamic weights of IR  $\Gamma_\alpha$ . They characterize the symmetry distortion and have to be experimentally determined. Parameter  $\tau_\alpha$  is a correlation time adapted to IR  $\Gamma_\alpha$  that relates the expression:

$$\tau_\alpha = \left( 1 - \chi_{\alpha E}^{-1} \sum_i p_i \chi_{\alpha i} \right)^{-1} \tau, \quad (13)$$

where  $\chi_{\alpha i}$  and  $\chi_{\alpha E}$  are the characters of  $i$ th and identical classes, respectively,  $p_i$  are probabilities of fundamental acts of the motion appropriate to  $i$ th class of the group  $G$ , and  $\tau$  is a mean time between two consequent steps of motion. The time  $\tau$  is ordered to Arrhenius low:

$$\tau = \tau_0 \exp\left(\frac{E_a}{RT}\right), \quad (14)$$

where  $E_a$  is the height of activation energy barrier averaged on the HMM motion symmetry group and  $\tau_0$  is a mean time between two sequential attempts to overlap the barrier.

By substituting (12) in (7), we shall obtain

$$\begin{aligned} M_2^{(\text{intra}ji)} &= \sum_{j=1}^{N-1} 6\gamma_j^2 \hbar^2 r_{ji}^{-6} I_j (I_j + 1) \\ &\cdot \int_{-\delta\nu}^{\delta\nu} \sum_{\alpha} \sum_{l=0}^2 \frac{q_\alpha \tau_\alpha}{1 + (2\pi\nu\tau_\alpha)^2} a_{\alpha l 0}(\phi) \cos^{2l} \vartheta d\nu. \end{aligned} \quad (15)$$

Performing just prescribed integration, we shall finally get the second moment expression specified by intramolecular

action of spins  $j$  to spin  $i$  for a given single crystal in an analytical form:

$$\begin{aligned} M_2^{(\text{intra}ji)} &= \sum_{j=1}^{N-1} \frac{6}{\pi} \gamma_j^2 \hbar^2 r_{ji}^{-6} I_j (I_j + 1) \\ &\cdot \sum_{\alpha} \sum_{l=0}^2 q_\alpha a_{\alpha l 0}(\phi) \cos^{2l} \vartheta \arctg(2\pi \cdot \delta\nu \cdot \tau_\alpha). \end{aligned} \quad (16)$$

For a powder, averaging (16) over the angles  $\phi$  ( $0 \leq \phi \leq 2\pi$ ) and  $\vartheta$  ( $0 \leq \vartheta \leq \pi$ ) reduces it to

$$\begin{aligned} M_2^{(\text{intra}jipow)} &= \sum_j \frac{6}{5\pi} \gamma_j^2 \hbar^2 r_{ji}^{-6} I_j (I_j + 1) \sum_{\alpha} q_\alpha \arctg(2\pi \cdot \delta\nu \cdot \tau_\alpha). \end{aligned} \quad (17)$$

In a regime of the fast thermal molecular motion, the inequality  $2\pi \cdot \delta\nu \cdot \tau_\alpha \ll 1$  is valid that follows the equality  $\arctg(2\pi \cdot \delta\nu \cdot \tau_\alpha) = 0$ . In this case the dipole-dipole contribution to the second moment disappears; that is,  $M_2^{(\text{intra}ji)} = 0$ , and so-called phenomenon of ‘‘spectral line narrowing’’ or ‘‘bandwidth narrowing’’ is observed.

It should be noted that in case the molecular motion is frozen, the alternative inequality  $2\pi \cdot \delta\nu \cdot \tau_\alpha \gg 1$  followed by  $\arctg(2\pi \cdot \delta\nu \cdot \tau_\alpha) = \pi/2$  is valid. Furthermore, taking into consideration that the dynamic weights of irreducible representations are normalized to unity, namely,  $\sum_{\alpha} q_\alpha = 1$ , (17) reduces down to a permanent value:

$$M_2^{(\text{intra}jipow)} = \sum_j \frac{3}{5} \gamma_j^2 \hbar^2 r_{ji}^{-6} I_j (I_j + 1) \quad (18)$$

presented earlier by Abragam and L6sche [15, 16]. For monocrystalline samples, (16) reduces to an expression maintaining the angular dependence in the second moment:

$$\begin{aligned} M_2^{(\text{intra}ji)} &= \sum_j 3\gamma_j^2 \hbar^2 r_{ji}^{-6} I_j (I_j + 1) \sum_{\alpha} \sum_{l=0}^2 q_\alpha a_{\alpha l 0}(\phi) \cos^{2l} \vartheta. \end{aligned} \quad (19)$$

It is noted that in the case of not resonant nuclear spins contribute to the 2nd moment, (19) has to be corrected by the factor  $4/9$  [17]. Labelling not resonant nuclear spins by the index  $j'$ , this contribution will be expressed in the regime of slow molecular motion as

$$\begin{aligned} M_2^{(\text{intra}j'i)} &= \sum_{j'} \frac{4}{3} \gamma_{j'}^2 \hbar^2 r_{j'i}^{-6} I_{j'} (I_{j'} + 1) \\ &\cdot \sum_{\alpha} \sum_{l=0}^2 q_\alpha a_{\alpha l 0}(\phi) \cos^{2l} \vartheta. \end{aligned} \quad (20)$$

### 3. Application to Monocrystalline Ammonium Chloride

Ammonium chloride  $\text{NH}_4\text{Cl}$ , being one of the most studied substances, is frequently used as a touchstone of the validity

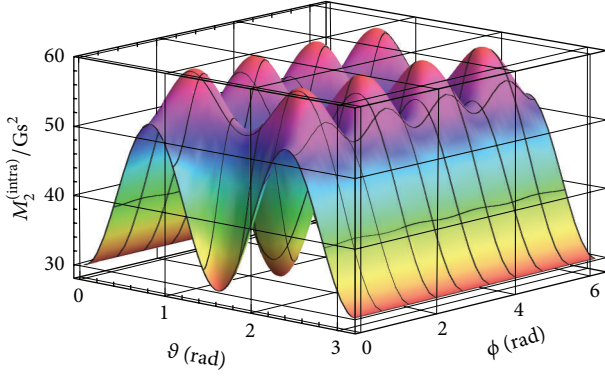


FIGURE 1: The angular dependence of intraionic contribution to the proton NMR spectral line second moment in ammonium chloride single crystal drawn according to (26) for a slow motion regime of  $\text{NH}_4^+$  cation (the numerical parameters used in (26) are  $q_1 = 0.254$ ,  $q_2 = 0.757$ ,  $0 \leq \phi \leq 2\pi$ , and  $0 \leq \vartheta \leq \pi$ ).

of various theories on the structure and physical properties of crystals. It is an ionic crystal, at which ammonium ions exhibit random reorientation and consequently they have no orientation ordering. Unit cell of  $\text{NH}_4\text{Cl}$  is a body-centered cube of type CsCl. At the center of a cubic cell, a tetrahedron of ammonium cation is placed and its corners are occupied by anions of chlorine. The lattice parameter is  $r_{\text{Cl-Cl}} = r_{\text{N-N}} = (3.844 \pm 0.024) \cdot 10^{-10}$  m, four nearest protons are placed in the vicinity of a nitrogen nucleus at the distance  $r_{\text{N-H}} = (1.038 \pm 0.04) \cdot 10^{-10}$  m, and the neighboring protons are spaced from each other to  $r_{\text{H-H}} = (1.695 \pm 0.04) \cdot 10^{-10}$  m [18].

Below 242.9 K, the crystal is in its ordered phase. The random local motion of ammonium ions does not change the ordered structure of the crystal. It means that the reorientation symmetry group of any ammonium ion vector is the point symmetry group of tetrahedron T.

There are two equilibrium dispositions of  $\text{NH}_4^+$  tetrahedrons with equal probability in the disordered phase observed at temperatures  $T \geq 242.9$  K. Hence, any physical quantity obeys the point symmetry group of the octahedron O in the disordered phase of  $\text{NH}_4\text{Cl}$ .

It was found that both the shape of spectral line [11] and the relaxation times [12] are anisotropic and show temperature dependence in the single crystal of  $\text{NH}_4\text{Cl}$ . To discuss the continuous wave data the quantum mechanical technique was applied [11]. The relaxation data were discussed in the framework of EAJM approach taken as the model of classical HMM of  $\text{NH}_4^+$  cation [12].

To examine the site symmetry of the ion  $\text{NH}_4^+$  in the regime of its slow motion by using the second moment of the proton NMR spectral line in  $\text{NH}_4\text{Cl}$ , we have to deal with two contributions:  $M_2^{(\text{intraHH})}$  and  $M_2^{(\text{intraNH})}$ . The first contribution is induced by interaction of an arbitrary chosen proton with other three protons of a chosen cation (19) and the second contribution—with inner nitrogen nucleus (20).

By using  $I_j = I_{\text{H}} = 1/2$  as the value of proton spin,  $(N - 1) = 3$  as the number of adjacent protons,  $\gamma_j = \gamma_{\text{H}}$ , and

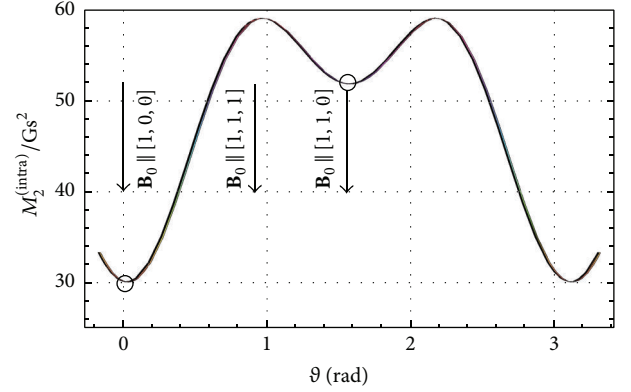


FIGURE 2: Angular dependence of the intraionic contribution to the proton NMR spectral line second moment in ammonium chloride single crystal drawn according to (26) for a slow motion regime of  $\text{NH}_4^+$  cation:  $\phi = \pi/4$  and  $-\pi/8 \leq \vartheta \leq 9\pi/8$ . The experimental values  $M_2^{(\text{intra,exp})}[1, 0, 0] = 29.9 \text{ Gs}^2$  ( $\phi = \pi/4$ ,  $\vartheta = 0$ ) and  $M_2^{(\text{intra,exp})}[1, 1, 0] = 52 \text{ Gs}^2$  ( $\phi = \pi/4$ ,  $\vartheta = \pi/2$ ) [11] used by calculating the dynamic weights  $q_1 = 0.254$  and  $q_2 = 0.757$  are fitted by open circles in the graph.

$r_{ji} = r_{\text{HH}}$ , we shall get from (19) the rated expression of  $M_2^{(\text{intraHH})}$  as

$$M_2^{(\text{intraHH})} = \frac{27}{4} \gamma_{\text{H}}^2 \hbar^2 r_{(\text{HH})}^{-6} \sum_{\alpha=1,2} \left( \sum_{l=0}^2 q_{\alpha} a_{\alpha l 0}(\phi) \cos^{2l} \vartheta \right). \quad (21)$$

Substituting  $I_{j'} = 1$ ,  $\gamma_{j'} = \gamma_{\text{N}}$ , and  $r_{j'i} = r_{\text{NH}}$  in (20) follows the rated expression of  $M_2^{(\text{intraNH})}$ :

$$M_2^{(\text{intraNH})} = \frac{8}{3} \gamma_{\text{N}}^2 \hbar^2 r_{(\text{NH})}^{-6} \sum_{\alpha=1,2} \left( \sum_{l=0}^2 q_{\alpha} a_{\alpha l 0}(\phi) \cos^{2l} \vartheta \right). \quad (22)$$

Using the table data,  $\gamma_{\text{H}} = 26753 \text{ s}^{-1} \text{Gs}^{-1}$ ,  $\gamma_{\text{N}} = 1933.3 \text{ s}^{-1} \text{Gs}^{-1}$ , and  $\hbar = 1.0544 \cdot 10^{-27} \text{ erg}\cdot\text{s}$  [16]; experimental values,  $r_{\text{NH}} = 1.038 \cdot 10^{-8} \text{ cm}$  and  $r_{\text{HH}} = 1.695 \cdot 10^{-8} \text{ cm}$  [18]; and the theoretical expressions of the factors  $a_{\alpha l 0}(\phi)$ ,  $a_{100}(\phi) = (1/8)(1 + 3\cos^2 2\phi)$ ,  $a_{110}(\phi) = -(3/4)(1 + \cos^2 2\phi)$ ,  $a_{120}(\phi) = (3/8)(3 + \cos^2 2\phi)$ ,  $a_{200}(\phi) = (1/4)(1 - \cos^2 2\phi)$ ,  $a_{210}(\phi) = (1/2)(1 + \cos^2 2\phi)$ , and  $a_{200}(\phi) = -(1/4)(3 + \cos^2 2\phi)$  [2, 3] in (21) and (22) allows us to obtain the rated explicit expressions of  $M_2^{(\text{intraHH})}$  and  $M_2^{(\text{intraNH})}$  as

$$M_2^{(\text{intraHH})}(q_1, q_2, \vartheta, \phi) = 28.3107 \cdot \Omega(q_1, q_2, \vartheta, \phi), \quad (23)$$

$$M_2^{(\text{intraNH})}(q_1, q_2, \vartheta, \phi) = 1.1074 \cdot \Omega(q_1, q_2, \vartheta, \phi), \quad (24)$$

where  $\Omega(q_1, q_2, \vartheta, \phi)$ , the function of the dynamic weights  $q_1$  and  $q_2$  and the angles  $\phi$  and  $\vartheta$ , is equal to

$$\Omega(q_1, q_2, \vartheta, \phi) = \{q_1 [(1 + 3\cos^2 2\phi) - 6(1 + \cos^2 2\phi) \cos^2 \vartheta + 3(3 + \cos^2 2\phi) \cos^4 \vartheta]$$

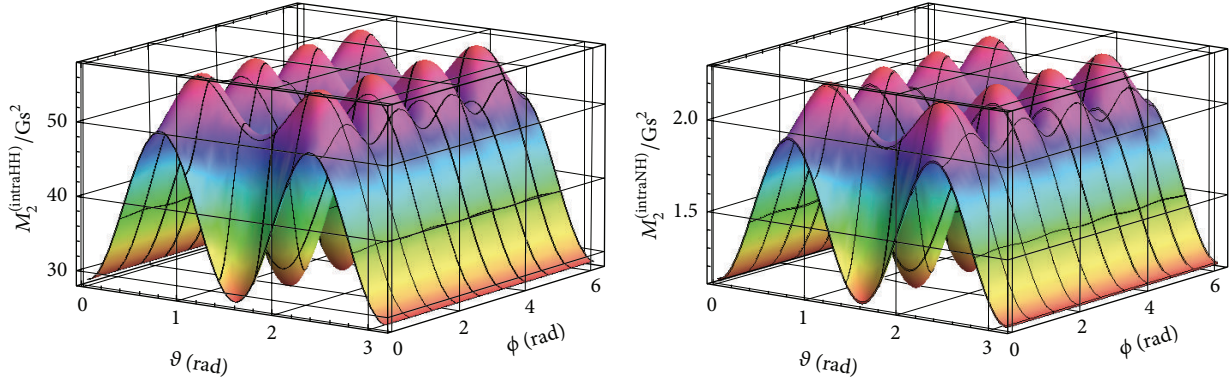


FIGURE 3: Surface-plot graphs of  $M_2^{(\text{intraHH})}$  and  $M_2^{(\text{intraNH})}$ , the intraionic contributions to the proton NMR spectral line second moment in ammonium chloride single crystal for a slow motion regime of  $\text{NH}_4^+$  cation drawn according to expressions (23) and (24) and  $q_1 = 0.254$  and  $q_2 = 0.757$ .

$$+ 2q_2 \left[ (1 - \cos^2 2\phi) + 2(1 + \cos^2 2\phi) \cos^2 \vartheta - (3 + \cos^2 2\phi) \cos^4 \vartheta \right]. \quad (25)$$

By summing (23) and (24) we get the expression of full intraionic part  $M_2^{(\text{intra})}$ , which preserves the same dependence  $\Omega(q_1, q_2, \vartheta, \phi)$  of the variables  $q_1, q_2, \phi$ , and  $\vartheta$ :

$$M_2^{(\text{intra})}(q_1, q_2, \vartheta, \phi) = 29.4181 \cdot \Omega(q_1, q_2, \vartheta, \phi). \quad (26)$$

The theoretical dependence of  $M_2^{(\text{intra})}$ , the intraionic contribution to the second moment of proton NMR spectral line in monocrystalline ammonium chloride, prescribed by (26) allows us to calculate the numerical values of dynamic weights  $q_1$  and  $q_2$  by using experimental values of  $M_2^{(\text{intra})}$ .

The mean value of the second moment at low temperature ( $-195^\circ\text{C}$ ) that is in the ordered phase has been determined for direction of the induction vector of the external static magnetic field chosen along the fourfold symmetry axis in the unit cell of  $\text{NH}_4\text{Cl}$  ( $\mathbf{B}_0 \parallel [1, 0, 0]$ ) equal to  $36.5 \text{ Gs}^2$  and along the twofold symmetry axis ( $\mathbf{B}_0 \parallel [1, 1, 0]$ )— $54.6 \text{ Gs}^2$  [11]. The respective high temperature values were equal to  $6.6 \text{ Gs}^2$  and  $2.6 \text{ Gs}^2$ . Because of the fact that the intraionic part of the second moment decreases down to zero at high temperatures, we suggest that the respective values of the second moment consist of the interionic parts only. Taking into account just presented point of view about the experimental second moments we can assume that the difference between low and high temperature values of the total second moment can be considered as the pure intraionic parts for low temperature second moments. Performing the appropriate calculations, we get the experimental values of the intraionic second moments  $M_2^{(\text{intra,exp})}$  equal to  $29.9 \text{ Gs}^2$  and  $52 \text{ Gs}^2$  for directions of magnetic field induction  $\mathbf{B}_0 \parallel [1, 0, 0]$  and  $\mathbf{B}_0 \parallel [1, 1, 0]$ , respectively.

By substituting in (26) firstly  $M_2^{(\text{intra,exp})} = 29.9 \text{ Gs}^2$ ,  $\phi = \pi/4$ , and  $\vartheta = 0$  and then  $M_2^{(\text{intra,exp})} = 52 \text{ Gs}^2$ ,  $\phi = \pi/4$ , and  $\vartheta = \pi/2$ , we get the experimental values of dynamic

weights  $q_1$  and  $q_2$ :  $q_1 = 0.254$  and  $q_2 = 0.757$ . These values of dynamic weights of two-dimensional and three-dimensional irreducible representations for tetrahedron point symmetry group of ammonium ion motion in the ordered phase of  $\text{NH}_4\text{Cl}$  are in good agreement with our data  $q_1 = 0.25$  and  $q_2 = 0.73$  derived from proton NMR relaxation experiments earlier [12]. It results in the tetragonal distorted tetrahedral site symmetry of ammonium ions in the ordered phase of  $\text{NH}_4\text{Cl}$ . It is noted that no anisotropy is predicted neither for the intraionic second moment nor for the spin-lattice relaxation rates in the ideal cubic symmetry position. In this case,  $q_1$  and  $q_2$  take respective values equal to 0.4 and 0.6.

A surface-plot graph of the intraionic contribution  $M_2^{(\text{intra})}$  to the proton NMR second moment in ammonium chloride single crystal for a slow motion regime of  $\text{NH}_4^+$  cation is shown as a function of spherical angles  $\phi$  and  $\vartheta$  of the crystal orientation in the static magnetic field for the experimental values of dynamic weights  $q_1 = 0.254$  and  $q_2 = 0.757$  in Figure 1. In Figure 2, the graph of  $M_2^{(\text{intra})}$  is shown for  $\phi = \pi/4$  as a function of the polar angle  $\vartheta$ , which forms the induction vector  $\mathbf{B}_0$  of the static magnetic field with respect to the direction  $[1, 0, 0]$  of the unit cell main axis. Here, one can see the values of  $M_2^{(\text{intra})}$  for three main orientations of the external magnetic field in the unit cell of the  $\text{NH}_4\text{Cl}$  crystal:  $\mathbf{B}_0 \parallel [1, 0, 0]$ ,  $\mathbf{B}_0 \parallel [1, 1, 1]$ , and  $\mathbf{B}_0 \parallel [1, 1, 0]$ .

Estimation of comparative contributions of the hydrogen spins versus nitrogen one to the intraionic 2nd moment is represented as interesting. The graphs of those drawn according to formulas (23) and (24) and accounting for  $q_1 = 0.254$  and  $q_2 = 0.757$  are shown in Figure 3. It is noted that they are spacelike in relation  $M_2^{(\text{intraHH})}/M_2^{(\text{intraNH})} = 28,3107/1,1074 = 25,565$ .

#### 4. Conclusion

The presented approach of simulating the intramolecular contribution to the second moment of NMR spectral line allows one to perform an accurate analysis of dynamics and geometry of internal motion. It requires using the extended angular jump model by approximating the

hindered molecular motion, knowledge of structure data for the studied crystal, and point symmetry property of the molecule motion as well as that of its surroundings, inclusively. Alternatively, by examining the anisotropic behavior of the second moment, this theory allows one to obtain the precise structure knowledge.

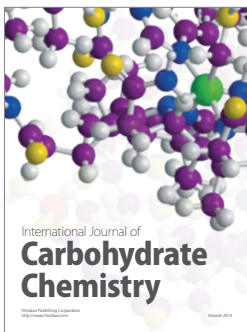
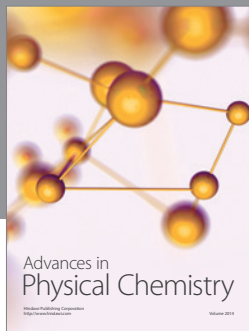
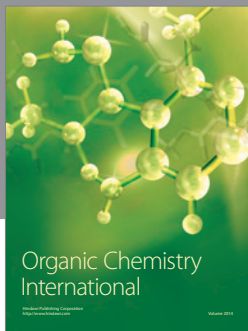
halides," *The Journal of Chemical Physics*, vol. 22, no. 4, pp. 643–650, 1954.

## Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

## References

- [1] J. H. Van Vleck, "The dipolar broadening of magnetic resonance lines in crystals," *Physical Review*, vol. 74, no. 9, pp. 1168–1183, 1948.
- [2] F. Bashirov and N. Gaisin, "The theory of hindered molecular motion and its application to spectroscopic studies," *Crystallography Reviews*, vol. 16, no. 1, pp. 3–87, 2010.
- [3] F. Bashirov, *Spectroscopic Techniques and Hindered Molecular Motion*, CRC Press, New York, NY, USA, 2012.
- [4] P. Debye, *Polar Molecules*, Reinhold, New York, NY, USA, 1929.
- [5] N. Bloembergen, E. M. Purcell, and R. V. Pound, "Relaxation effects in nuclear magnetic resonance absorption," *Physical Review*, vol. 73, no. 7, pp. 679–712, 1948.
- [6] K. A. Valiev and E. N. Ivanov, "Rotational Brownian motion," *Uspekhi Fizicheskikh Nauk*, vol. 109, pp. 31–64, 1973, English Translation: *Physics-Uspekhi*, vol. 16, pp. 1–16, 1973.
- [7] G. Williams, "Time-correlation functions and molecular motion," *Chemical Society Reviews*, vol. 7, no. 1, pp. 89–131, 1978.
- [8] N. Bloembergen, "Spin relaxation processes in a two-proton system," *Physical Review*, vol. 104, pp. 1542–1547, 1956.
- [9] R. I. Hilt and P. S. Hubbard, "Nuclear magnetic relaxation of three spin system undergoing hindered rotations," *Physical Review A*, vol. 134, pp. 392–398, 1964.
- [10] P. Rigny, "Réorientations dans les cristaux moléculaires et fonctions de corrélation," *Physica*, vol. 59, no. 4, pp. 707–721, 1972.
- [11] R. Bersohn and H. S. Gutowsky, "Proton magnetic resonance in an ammonium chloride single crystal," *The Journal of Chemical Physics*, vol. 22, no. 4, pp. 651–658, 1954.
- [12] F. I. Bashirov, "Proton spin-lattice relaxation in monocrystalline ammonium chloride," *Journal of Magnetic Resonance A*, vol. 122, no. 1, pp. 1–8, 1996.
- [13] J. G. Powles and H. S. Gutowsky, "Proton magnetic resonance of the CH<sub>3</sub> group. III. Reorientation mechanism in solids," *The Journal of Chemical Physics*, vol. 23, no. 9, pp. 1692–1699, 1955.
- [14] R. Goc, "Simulation of the NMR second moment as a function of temperature in the presence of molecular motion. Application to (CH<sub>3</sub>)<sub>3</sub>NBH<sub>3</sub>," *Zeitschrift für Naturforschung*, vol. 57, no. 1-2, pp. 29–35, 2002.
- [15] A. Abragam, *The Principles of Nuclear Magnetism*, Oxford University Press, Oxford, UK, 1961.
- [16] A. Lösche, *Kerninduktion*, Veb Deutscher Verlag der Wissenschaften, Berlin, Germany, 1962.
- [17] Ch. P. Slichter, *Principles of Magnetic Resonance*, Harper and Row, New York, NY, USA, 1965.
- [18] H. S. Gutowsky, G. E. Pake, and R. Bersohn, "Structural investigations by means of nuclear magnetism. III. Ammonium



**Hindawi**

Submit your manuscripts at  
<http://www.hindawi.com>

