Simulation of the NMR Second Moment as a Function of Temperature in the Presence of Molecular Motion. Application to $(CH_3)_3NBH_3$

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The method for simulating the second moment of the NMR absorption spectrum as a function of temperature is presented. The second moment is first calculated as a function of the number of jumps of rotating molecules or their parts (like methyl groups). This number of jumps is rescaled into the frequency of internal rotation and these frequencies are recalculated into equivalent temperatures. The relation between frequency of rotation, and temperature is established on the basis of the Arrhenius relation $\nu_c = \nu_0 \exp(-E_a/RT)$. The described method is then applied to the analysis of molecular motion in trimethylamine borane $(CH_3)_3NBH_3$. The proposed method is especially useful in the case of complex structures, where combined motions are possible, because the NMR second moment is much more sensitive to the geometry of motion than the magnetic relaxation times T_1 or $T_{1\rho}$ usualy used in studies of the internal dynamics of solids.

Key words: NMR; Second Moment; Internal Rotation; Simulation.

1. Introduction

The second moment of the NMR absorption spectrum was for years exploited as the main indicator of internal motion in solids as described in monographs [1, 2]. The theoretical basis for such applications of the NMR second moment measurements were given by Van Vleck [3] and one of the first papers on the subject was published by Andrew and Eads [4]. Since then thousands of papers have been published, and the internal dynamics was analyzed for thousands of materials. After the introduction of pulse methods into NMR, the magnetic relaxation times T_1 and $T_{1\rho}$ became popular as probes for internal motions in solids. Relaxation time measurements give better insight than second moment ones, into the dynamic parameters correlation frequency ν_c and activation energy E_a. Compared to second moment studies, relaxation time studies are sensitive to the molecular motion in a much wider frequency range and therefore they now dominate in NMR studies of internal dynamics.

In spite of all advantages of relaxation studies there is one feature in the second moment measurements which is evidently superior over those. The value of the second moment strongly depends on the geometry of motion which influences it and therefore such studies permit better verification of different models of rotation. Any studies of that kind are conducted with a similar scheme: experimental results are compared to their calculated values. The calculations are performed on the basis of existing theories and must incorporate a geometrical and dynamical model of the studied motion. Agreement between measured and calculated values is a criterium for accepting the assumed model.

The work presented here describes the application of the Van Vleck formula for the simulation of the NMR second moment as a function of the frequency of the internal rotation and, consequently, as a function of temperature. The method developed here is then applied to the analysis of the internal motion in trimethylamine borane, $(CH_3)_3NBH_3$. Results of the calculations are compared to experimental data from [5, 6].

2. Second Moment Calculation – Basic Theory

The basis for all NMR second moment calculations and simulations were given by Van Vleck in his famous paper [3]. The formula for the second moment given there relates to the so-called rigid structure. In case of NMR the rigid structure does not mean *absolutely* rigid. There might be motions of molecules,

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ions or structural groups constituting the material under consideration but the frequencies of these motions must be lower then the width of the NMR absorption line (expressed in frequency units) at temperatures close to 0 K. Explanation of such a definition of the rigid structure is given below.

Let us consider the pulse NMR experiment. The recorded signal (FID) decreases to zero in time of the order of a few spin-spin relaxation times T_2. Fourier transform of the FID gives the NMR absorption spectrum, with the half width at half height

$$\delta\nu_{1/2} \cong 1/T_2. \tag{1}$$

The FID fully defines the NMR absorption spectrum and is collected during a time period of the order of T_2. Therefore, if during that time there are no jumps of molecules or their parts, the FID is recorded for the rigid structure. Therefore, if molecules rotate with the average frequency

$$\nu_\mathrm{c} < 1/T_2 \cong \delta\nu_{1/2}, \tag{2}$$

this means that, from the NMR point of view the structure is rigid.

The Van Vleck [3] formula for second moments arising from dipole - dipole interaction can be written in the form

$$M_{2(I)}^{\mathrm{rig}} = M_{2(II)}^{\mathrm{rig}} + \sum_S M_{2(IS)}^{\mathrm{rig}}, \tag{3}$$

which reflects the fact that the second moment measured for the resonant spins I consists of a contribution arising from interactions with the resonant spins (II subscript) and from the sum of terms due to the interactions of resonant spins I with different nonresonant spins S (IS subscript). In other words, the average local magnetic field "seen" by resonant spins is the sum of magnetic fields produced by all resonant and nonresonant nuclei present in the sample. The right hand side terms of (3) are defined by

$$M_{2(II)}^{\mathrm{rig}} = N_I^{-1} C_{II} \sum_{i=1}^{N_I} \sum_{j=1}^{N_I} B_{ij}^2 \tag{3a}$$

and

$$M_{2(IS)}^{\mathrm{rig}} = N_I^{-1} C_{IS} \sum_{i=1}^{N_I} \sum_{k=1}^{N_S} B_{ik}^2 \tag{3b}$$

with

$$C_{II} = \frac{3}{4} \left(\frac{\mu_0}{4\pi}\right)^2 \gamma_I^2 \hbar^2 I(I+1), \tag{4a}$$

$$C_{IS} = \frac{3}{4} \left(\frac{\mu_0}{4\pi}\right)^2 \gamma_S^2 \hbar^2 S(S+1), \tag{4b}$$

$$B_{ij} = \frac{3\cos^2\Theta_{ij} - 1}{r_{ij}^3}, \tag{5a}$$

and

$$B_{ik} = \frac{3\cos^2\Theta_{ik} - 1}{r_{ik}^3}. \tag{5b}$$

For easier reading, all equations referring to interactions between resonant nuclei will be denoted by *number + a*, and those describing interaction of nonresonant spins with resonant ones by *number + b*). N_I is the number of resonant nuclei included in the calculation and N_S the number of nonresonant nuclei taken into account. μ_0 is the vacuum permeability, γ_I the gyromagnetic ratio of resonant nuclei, I their spin, and $\hbar = \frac{h}{2\pi}$. γ_S is the gyromagnetic ratio of nonresonant nuclei and S their spin. In all summations the indexes i and j run through resonant nuclei, and the index k through nonresonant nuclei. Θ_{ij} is the angle between the vector r_{ij} connecting the nuclei i and j and the direction of the external magnetic field. Θ_{ik} is the analogous quantity for the vector connecting resonant spins i with nonresonant ones k.

From the physical point of view, the second moment can be seen as the square of the average local magnetic field H_loc, induced by dipole dipole interaction at the position of resonant nuclei,

$$M_2 = \overline{H}_\mathrm{loc}^2. \tag{6}$$

The practical calculation of the second moment requires some modifications of (3a) and (3b). The main ones are directed towards decreasing the number of nuclei over which the summation must be performed. From (5a) and (5b) it follows that the contribution to the second moment decreases with the third power of distance between the interacting spins. Therefore the nuclei located "far enough" from the position of nucleus for which this contribution is evaluated can be neglected. The "far enough" is expressed more precisely as the length of the cut-off radius R_cut. We take one nucleus as an origin of our space and include in the calculation only those nuclei which are located within a sphere with radius R_cut. This cut-off radius is usually established during the introductory calculation.

The periodic structure of crystalline materials permits further limitation of the number of resonant nuclei denoted i required for ensemble averaging of contributions to the second moment. In the worse case this number is equal to the number of resonant nuclei in the crystallographic unit cell of the considered material. We denote this number by N_U. Therefore the first sums in (3a) and (3b) must be taken only over N_U nuclei, and the results must be divided also by N_U in order to get an average value over all possible positions of resonant nuclei. Denoting the number of resonant nuclei within the sphere of cut-off radius R_{cut} by N_{IR}, and the analogous number for nonresonant nuclei by N_{SR}, we can rewrite (3a) and (3b):

$$M_{2(II)}^{\mathrm{rig}} = N_U^{-1} C_{II} \sum_{i=1}^{N_U} \sum_{j=1}^{N_{IR}} B_{ij}^2, \tag{6a}$$

$$M_{2(IS)}^{\mathrm{rig}} = N_U^{-1} C_{IS} \sum_{i=1}^{N_U} \sum_{k=1}^{N_{SR}} B_{ik}^2. \tag{6b}$$

The number of terms in (6a) and (6b) are substantially reduced compared to (3a) and (3b). As we deal with double sums, this is a tremendous gain in terms of computational time. For a numerical calculation we usually take a block of unit cells with a linear dimension 3, 5, 7, 9, or 11. Such a block consists of a central unit cell surrounded by 1, 2, 3, 4, or 5 closed shells of unit cells. All numbering of nuclei starts from the central unit cell. Such an arrangement eliminates the boundary effect arising when considering nuclei from other than the central unit cell, as these peripheral nuclei have a different number of neighbours from different sites, and from this point of view are not equivalent to nuclei from the centrally located unit cell.

3. Second Moment, Influence of Motion

The internal motion of nuclei influences the second moment through averaging the local field H_{loc} which is a product of dipole dipole interaction. The necessity of averaging the dipole dipole interaction in the calculation of the second moment influenced by motion is explained very nicely in [2] p. 84.

The theory says [1] p. 451, that the second moment is invariant with respect to internal motion, but the measurements for many different materials give clear dependence of the second moment on the temperature, that is on the frequency of internal motion. The explanation of this contradiction is as follows. Any internal motion modulates the dipole dipole interaction, and this results in averaging its static part and gives rise to the side band satellite NMR absorption lines at the frequencies

$$\omega_0 \pm 2\pi\nu_{\mathrm{c}},$$

where ω_0 is the Laromor frequency for the resonance nuclei and ν_{c} is the frequency of motion. The averaging of the static part of the dipole dipole interaction narrows the central part of the absorption spectrum. The internal motion is a stochastic process, and the frequencies of motion of individual molecules are spread from zero to well above ν_{c}. This causes the spreading of the satellite lines in the same frequency range. The final result of that kind of motion is a narrow central part of the NMR spectrum and broad wings so weak that experimentally unobservable. The second moment of the central part of the NMR spectrum is smaller then the second moment for the rigid structure. If one could include the contribution from those broad wings, the experimentally evaluated second moment would not depend on the temperature, that is on the frequency of internal motion. Therefore no contradiction between theory and experiment exists. In the typical temperature dependence of the NMR second moment on temperature, that is on the frequency of internal motion, the decrease of the second moment occurs in a temperature range, the position and width of which depends on the type of the studied material. Below and above that region the second moment does not depend on the temperature, that is on the frequency of motion.

In the temperature range where changes occur, the observed line width and the measured second moment decreases with increasing frequency ν_{c} of internal motion, which in most cases follows the Arrhenius relation

$$\nu_{\mathrm{c}} = \nu_0 \exp(-E_{\mathrm{a}}/RT). \tag{7}$$

The final value of the motionaly decreased second moment depends on the geometry of the motion and, in case of single crystals, on the orientation of the sample with respect to external magnetic field. Such geometrical relations follow directly from terms defined by (5a) and (5b). These are the only terms the internal motion can influence. Therefore our further discussion of the influence of internal motion on the second moment will be focused on the discussion of calculations of the proper averages of the terms B_{ij} and B_{ik}.

The calculation of the NMR second moment M_2 in case of internal motion can be divided into two tasks.

i) Finding the value of M_2 for the limiting case when the motion is very fast, that is, when the dipole dipole interaction is averaged to its minimal value for the given type of motion.

ii) Calculating the dependence of M_2 on temperature. This requires determination of the degree of averaging of the dipole dipole interaction as a function of the frequency of the motion, and rescaling these frequencies into temperatures.

The first problem has been solved by different methods [4, 5, 7] all of them being more or less approximate. A numerical solution to this problem for benzene and ammonium chloride was presented in [8, 9] and a general case was described in [10]. The numerical calculations have an accuracy determined only by the accuracy of the structural data for the studied material, and have many advantages over the method applied previously. The second task is more complicated, and its solution will be presented in this paper. It is based on a Monte Carlo simulation and can be applied to any material with known crystal structure and x, y, z co-ordinates for all nuclei included in the simulation.

4. Second Moment Dependence on the Temperature

The dependence of the second moment on temperature is found in three steps:

i) simulating the second moment as a function of individual jumps of molecules,

ii) recalculating the number of jumps into frequency of motion,

iii) combining *i)* and *ii)* to assign temperature to each number of jumps.

The basic formulae for our consideration will be those developed in [10]. In case of internal motion in a solid the nuclei take few different positions allowed by the symmetry of the studied material. As an example we will analyse the hydrogen nuclei (protons) in a methyl group. In this case the motion is a rotation about the C_3 axis of symmetry. In solids this rotation is considered as jumps by 120 degrees between three equivalent positions. The time of a jump itself is assumed to be negligibly small, and the average time of residing in the allowed position is called the correlation time and denoted by τ_c. The frequency of motion, called correlation frequency, is defined as

$$\nu_c = 1/(2\pi\tau_c). \tag{8}$$

The formula for the second moment when internal motion occurs may be written in the form

$$M_{2(I)}^{\text{rot}} = M_{2(II)}^{\text{rot}} + \sum_S M_{2(IS)}^{\text{rot}}, \tag{9}$$

$$M_{2(II)}^{\text{rot}} = N_U^{-1} C_{II} \sum_{i=1}^{N_U} \sum_{j=1}^{N_{IR}} \langle B_{ij} \rangle^2 , \tag{9a}$$

$$M_{2(IS)}^{\text{rot}} = N_U^{-1} C_{IS} \sum_{i=1}^{N_U} \sum_{k=1}^{N_{SR}} \langle B_{ik} \rangle^2 , \tag{9b}$$

where the brackets $\langle\ \rangle$ denote averaging with respect to internal motion.

We start with calculating these average values as functions of the number of individual jumps n, that is with step *i)* listed at the beginning of this chapter. Since the terms B_{ij} and B_{ik} are identical from the algebraic point of view, we perform such averaging for both of them according to the formula

$$\langle B_{i\alpha} \rangle_n = \frac{1}{n} \sum_{l=1}^{n} \frac{3\cos^2 \Theta_{i\alpha l} - 1}{r_{i\alpha l}^3} \quad \text{with } \alpha = j, k. \tag{10}$$

The symbol $\langle\ \rangle_n$ denotes averaging over n positions of nuclei during the time of the experiment, where the "time of the experiment" is the time of recording the FID. We will name it the time of averaging t_a, because the average value of the dipole dipole interaction is the result of spins taking n positions during that time. This time of averaging is of the order of the spin-spin relaxation time T_2 and is approximately equal to the inverse of the NMR absorption line width $\delta\nu_{1/2}$ for the rigid structure. Therefore the correlation frequency ν_c used to characterise the frequency of the internal motion will be defined by the relation

$$\nu_c = n_c/(2\pi t_a), \tag{11}$$

where

$$n_c = n/N_{\text{ax}}, \tag{12}$$

and

$$t_\text{a} = 1/\delta\nu_{1/2}. \tag{13}$$

N_ax is the total number of axis of rotations (or of rotating groups) in the block of unit cells considered in the calculation. Therefore n_c is the average number of jumps per rotating group. For $n_\text{c} = 1$ and $t_\text{a} = \tau_\text{c}$, (11) is exactly the definition given by (8).

Evaluating (10) for different numbers of jumps n and inserting the results into (9a) and (9b) gives the second moment as function of n:

$$M_2(n) = f_1(n) \tag{14}$$

Applying (11), (12) and (13) we can get M_2 as function of the frequency of motion

$$M_2(\nu_\text{c}) = f_2(\nu_\text{c}). \tag{15}$$

This is step *ii)* of our procedure. The functions f_1 and f_2 are in numerical form as a consequence of the numerical averaging of (10).

To compare directly the calculated second moment with experimental values, $M_2(\nu_\text{c})$ must be recalculated into the temperature dependence. This can be done on the basic of the Arrhenius relation (7), leading to

$$M_2(T) = f_3(T) \tag{16}$$

with f_3 in numerical form as the (14) and (15). Recalculation of the number of jumps per axis n_c into temperature is based on the equation

$$T(n_\text{c}) = \frac{E_\text{a}}{R(\ln\nu_0 - \ln n_\text{c} - \ln\gamma_I - 0.5\cdot\ln M_{2\text{rig}})} \tag{17}$$

obtained from combining (2), (11), (12) and (13) with the assumption that

$$M_{2\text{rig}} \approx (\delta\nu_{1/2\text{rig}}/\gamma_I)^2. \tag{18}$$

Knowledge of the preexponential factor ν_0 and the activation energy E_a for the analyzed type of motion is required. The start up values of these parameters may be taken from the analysis of the relaxation times studies, or simply guessed. Then some kind of fitting procedure must be performed. Calculations are repeated with different values of these parameters, and values giving $M_2(T)$ closest to the experimental data are taken as the results.

Table 1. Relative co-ordinates of atoms in trimethylamine borane $(CH_3)_3NBH_3$.

Atom	x/a	y/b	z/c
N	0.2995	0.0363	–0.0363
C	0.3617	–0.1824	0.0944
H	0.1985	–0.2878	0.1074
H	0.4270	–0.1261	0.2690
H	0.4992	–0.2724	–0.0101
C	0.5130	0.1867	–0.0607
H	0.6443	0.0814	–0.1587
H	0.5725	0.2286	0.1200
H	0.4582	0.3457	–0.1588
C	0.2104	–0.0273	–0.2747
H	0.0530	–0.1387	–0.2473
H	0.3542	–0.1237	–0.3639
H	0.1674	0.1402	–0.3642
B	0.0964	0.1799	0.1073
H	0.1832	0.2237	0.2962
H	0.0576	0.3524	–0.0103
H	–0.0680	0.0461	0.1184

5. Calculations for Trimethylamine Borane $(CH_3)_3NBH_3$

On the basis of [11] and with the assumption of a cubic lattice with $a = 0.57$ nm and one molecule per unit cell, the relative x/a, y/b, and z/c co-ordinates of atoms were generated. They are given in Table 1. Parameters of the crystal structure were established on the basis of the best agreement between the calculated and measured second moment for the rigid structure. The assumption of a cubic lattice is a little arbitrary, but this does not influence substantially the final value of the second moment. This is because the intramolecular contribution to the second moment for the rigid structure is $28.4\times10^{-8}\text{T}^2$ and the intermolecular ones is $6.2\times10^{-8}\text{T}^2$. So 80% of the second moment is due to dipole dipole interaction within the molecule.

Following the procedure described in Part 2 of this paper, we generate the x, y, z co-ordinates for a block of unit cells $3\times3\times3$. This gives the central unit cell surrounded by a closed shell of 26 unit cells. The size of the block was determined as optimal from the point of view of accuracy and CPU time required. All hydrogen, nitrogen and boron nuclei within this block were included in the summation.

The structure of the molecule suggests the possibility of the following types of rotation:

A_rot: rotation of individual methyl groups about N-C bonds,

B_rot: rotation of the $(CH_3)_3N$ group about the N-B bond with rigid individual methyl group,

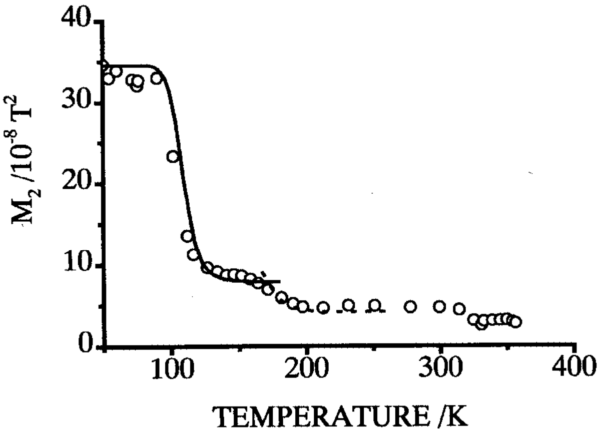

Fig. 1. Temperature dependence of the experimental and simulated values of the NMR second moment for trimethylamine borane $(CH_3)_3NBH_3$. Detailed explanations in text.

C_{rot}: rotation of BH_3 group about N-B bond.

Combination of all these types of rotation are possible. The only question is in which order they are activated when increasing the temperature from 0 to about 360 K, the highest temperature at which the M_2 measurements were performed. According to the analysis published in [6], this order is C_{rot}, B_{rot}, A_{rot}. It is obvious that during the heating of the sample, rotation activated at higher temperature is superimposed on those activated at lower temperatures. Such superposition will be expressed by a "+" sign. For example, B_{rot} + A_{rot} denotes rotation of individual methyl groups superimposed on already existing rotation of $(CH_3)_3N$ groups.

All rotating groups have C_3 symmetry. Therefore a single jump will be a rotation by 120 deg. Only the initial and final positions are important, as the time of rotation between these positions is neglected in accordance with the previously described model of rotation generally accepted in NMR studies. The method of rotating any group of atoms about a given axis by any angle is described in [10]. The final values for the calculated second moment must be averaged for the polycrystal sample, as the experiment [5] was performed with powdered material. Details of very efficient spatial averaging for the second moment calculation can be found in [12].

Results of the calculation are given in Figure 1. The circles are the experimental data taken from [5]. The solid line was drawn through the second moment values simulated for the structure with C_{rot} + B_{rot} and activation parameters for both types of rotation ν_0 = $1.1\times10^{13}s^{-1}$ and E_a = 17.0 kJ/mol. The dotted line passes trough M_2 values simulated for the structure with additional A_{rot} superimposed on already very fast C_{rot} + B_{rot}. The activation parameters for A_{rot} are $\nu_0 = 9.9\times10^{13}s^{-1}$ and E_a = 26.0 kJ/mol. These results agree well with the model of rotation and activation parameters published in [6]. The second moment values for the limiting cases, the offset of a given type of rotation and very fast rotation, are the same as the results of other calculations [13] and are in good agreement with data in [5]. Tumbling suggested in [5] at temperatures above 330 K was not simulated in this paper. This could be easily done with the described procedure, but the CPU time required for such a simulation would be too long, making costs too high. This was also the reason for not extending the calculation above 270 K.

The numerical calculation were performed on a CRAY SV1 (1.2 GFLOPS per processor) supercomputer. The average run for the number of jumps n going from 0 to 10^5 took about 1000 minutes of the CPU.

6. Conclusions

The method of simulating values of the NMR second moment as a function of temperature presented in this paper allows very detailed analysis of the dynamics and geometry of internal motion. The method is very general and very accurate. It requires knowledge of the crystal structure and atom co-ordinates of the studied material, these data being usually easily available. The simulations can be performed in a reasonable time on a medium class supercomputer or even on a modern PC with a Pentium processor running at about 1 GHz.

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