

NMR Relaxation Time Simulation for Different Models of Motion in $(\text{CH}_3)_3\text{NBH}_3$

Roman Goc

Institute of Physics, A. Mickiewicz University, Umultowska 85, 61-615 Poznań, Poland

Reprint requests to R. G.; goc@amu.edu.pl

Z. Naturforsch. **58a**, 537 – 540 (2003); received July 23, 2003

Monte Carlo simulations of complex rotation of single $-\text{CH}_3$ groups, $-(\text{CH}_3)_3$ groups and $-\text{BH}_3$ groups were performed for trimethylamine borane $(\text{CH}_3)_3\text{NBH}_3$. In the course of these simulations the correlation functions for different models of rotation were determined. Knowledge of these functions and of some data extracted from NMR experiments allowed for the calculation of the longitudinal magnetic relaxation time T_1 as a function of temperature. The values of relaxation times obtained from Monte Carlo simulations are compared to experimental results published by other authors. There is a clear relation between the assumed model of rotation and the shape of the T_1 curve versus temperature.

Key words: Correlation Function; Monte Carlo; NMR, Relaxation.

1. Introduction

The trimethylamine borane $(\text{CH}_3)_3\text{NBH}_3$ has been studied experimentally [1, 2] and by numerical simulations [3, 4]. The simulations were used to calculate the van Vleck second moment for the rigid structure and for different models of rotation of the $-\text{CH}_3$, $-\text{N}(\text{CH}_3)_3$, and $-\text{BH}_3$ groups about their C_3 axis. It seems reasonable to make the next step in simulations and calculate the correlation functions for models of motion analyzed in previous papers [3, 4].

The idea of using the Monte Carlo (MC) method for calculating the correlation functions for molecular motions was first presented by Bustard [5]. Since then it has been applied by numerous researchers to analyze the influence of different types of stochastic motions on the relaxation time T_1 measured in NMR experiments. One of the latest papers on this subject [6] presents MC simulations of diffusional jumps in order to calculate correlation functions and relaxation times T_1 resulting from this motion.

A detailed description of the procedures used to simulate molecular rotations and calculate correlation functions for this rotation is presented in [7]. Application of these procedures for analyzing the dynamics of ammonium ions in ammonium bromide was published in [8].

In this paper, procedures from [7] are exploited for calculating correlation functions for complex rotations

of molecular groups $-\text{CH}_3$, $-\text{N}(\text{CH}_3)_3$, and $-\text{BH}_3$ in trimethylamine borane $(\text{CH}_3)_3\text{NBH}_3$. Correlation functions are evaluated for three different models of internal rotation, and for each model the NMR relaxation times T_1 are calculated.

2. Theoretical Principles of the Simulations

The equation defining the correlation functions for any type of stochastic motion can be written as

$$G^{(q)}(\tau) = N^{-1} \sum_{i=1}^N \sum_{m=1}^N \langle F_{im}^{(q)}(t) F_{im}^{(q)*}(t + \tau) \rangle_t \quad (1)$$

where N is the total number of spins included in calculation, $F_{im}^{(q)}(t)$ are functions of the position-vectors connecting two different particles i and m at the time t , $F_{im}^{(q)*}(t + \tau)$ complex conjugates of these functions at $t + \tau$. These functions depend on the physical phenomenon for which one wants to calculate the correlation functions. Brackets $\langle \rangle_t$ denote the time average. Equation (1) is not suitable for MC calculation, but we are dealing with ergodic systems, and the time average may be replaced by an ensemble average resulting in the following definition of correlation functions:

$$G^{(q)}(\tau) = N^{-1} \sum_{i=1}^N \sum_{m=1}^N F_{im}^{(q)}(\mathbf{r}_{im}) \sum_{k=1}^L P(\mathbf{r}_{im} | \mathbf{r}_k, \tau) \cdot F_{im}^{(q)*}(\mathbf{r}_{im} + \mathbf{r}_k). \quad (2)$$

\mathbf{r}_{im} are vectors connecting particles included in the calculation, and \mathbf{r}_k are changes of these vectors in the time τ . The summation must be carried out only over pairs of different particles, so the vectors \mathbf{r}_{im} are different from zero. $P(\mathbf{r}_{im}|\mathbf{r}_k, \tau)$ is the relative probability that two particles, initially separated by \mathbf{r}_{im} , change their separation by \mathbf{r}_k in time τ . The above definitions leave the meaning of the functions $F_{im}^{(q)}$ the same as in (1). L is the number of steps into which we divide the changes of vectors \mathbf{r}_{im} in the course of the rotation. The values of these steps are then used to calculate the probabilities of finding particles which change their position by $\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_k$.

A detailed description of transforming (2) into a form permitting application of MC methods is given in [7]. The final equation from this paper reads

$$G^{(q)}(\tau) = \frac{1}{N_U} \sum_{i=1}^{N_U} \sum_{m=1}^{N_T} \sum_{k=1}^L P(\theta_{im}, \varphi_{im}, r_{im} | \theta_k, \varphi_k, r_k, \tau) \cdot F_{im}^{(q)}(\theta_{im}, \varphi_{im}, r_{im}) \cdot F_{im}^{(q)*}(\theta_{im} + k\Delta\theta, \varphi_{im} + k\Delta\varphi, r_{im} + k\Delta r), \quad (3)$$

where N_U is the number of spins in the crystallographic unit cell, N_T the total number of spins taken into account in the simulation, θ_{im} , φ_{im} , and r_{im} are the spherical co-ordinates of vectors \mathbf{r}_{im} connecting spins i and m . $\Delta\theta$, $\Delta\varphi$, and Δr are the values of steps in which changes of relevant co-ordinates, in the course of motion, are determined. These steps are equal to the maximum allowed changes divided by the number of assumed steps L . For a practical calculation it is more convenient to have all values in (3) expressed in Cartesian co-ordinates x , y , z of the spins involved in the summation. This can be easily done with elementary analytical geometry, as explained in [7].

Equation (3) defines the correlation functions for single crystal material, and spatial averaging must be performed to get correlation functions for the polycrystalline sample, because such a sample was used for the NMR relaxation time T_1 measurements. This averaging must be done numerically, but this procedure, which is an elementary one, will not be described here.

The correlation functions calculated numerically were then approximated by a linear sum of three decaying exponentials, and analytical Fourier transforms

of these expressions were calculated from the equation

$$J^{(q)}(\omega) = \int_0^{\infty} G^{(q)}(\tau) e^{-i\omega\tau} d\tau. \quad (4)$$

This method of calculation allowed the determination of spectral densities $J^{(q)}(\omega)$ without restrictions arising from the limited number of discrete values of correlation functions determined by the MC calculation.

The spin-lattice relaxation time T_1 was calculated according to the well known Bloembergen-Purcell-Pound (BPP) formula

$$\frac{1}{T_1} = \frac{3}{2} \gamma^4 \hbar^2 I(I+1) \{J^{(1)}(\omega_I) + J^{(2)}(2\omega_I)\}, \quad (5)$$

where γ is the gyromagnetic ratio of the resonant nuclei, I their spin, \hbar Planck's constant divided by 2π , and ω_I the Larmor frequency of the resonant nucleus.

3. Numerical Calculations and Results

The coordinates of the atoms were taken from [3], where they were calculated on the basis of data from [9]. Details of the numerical procedures are explained in [7]. The difference between the calculation for benzene reported in [7] and for trimethylamine borane (CH₃)₃NBH₃ presented in this paper lies in the more complex rotation of the fragments of molecules in (CH₃)₃NBH₃.

Three models of motions were used for the calculations, denoted on the graphs according to the scheme

I) 3×Me+ BH_3 : only individual $-\text{CH}_3$ groups and $-\text{BH}_3$ groups rotate.

II) $\text{N}(\text{Me})_3+\text{BH}_3$: individual $-\text{CH}_3$ groups are rigid, $-(\text{NCH}_3)_3$ groups rotate, and $-\text{BH}_3$ groups rotate.

III) 3×Me+ $\text{N}(\text{Me})_3+\text{BH}_3$: superposition of I and II rotations.

Correlation functions have been calculated for a block of 1331 unit cells, arranged as a central unit cell surrounded by a five close shells of total 1330 unit cells. The numerical calculations were performed on a CRAY SV1 and on an SGI ORIGIN 3800 computer with programs written in C language by the author. The average run for the number of jumps n going from 0 to 10^5 took about 3000 minutes of the CPU.

Examples of some correlation functions obtained from the MC calculations are presented in Figs. 1 and 2. The time unit τ_d is defined, following [5], as the

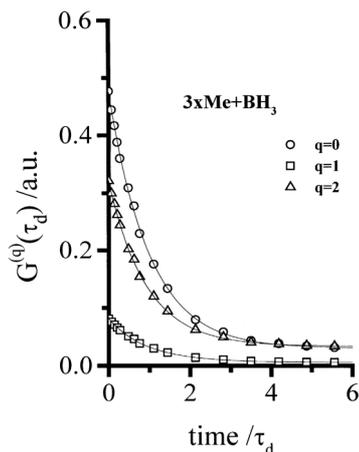


Fig. 1. Correlation functions from MC simulation for trimethylamine borane $(\text{CH}_3)_3\text{NBH}_3$ for the model I of motion. Continuous lines are the best fits to the simulated points by a linear sum of three decaying exponentials.

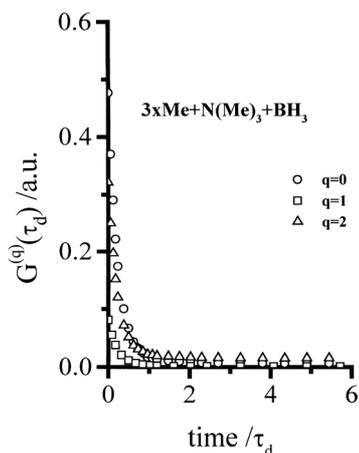


Fig. 2. Correlation functions from a MC simulation for trimethylamine borane $(\text{CH}_3)_3\text{NBH}_3$ for the model III of motion. To avoid congestion of points and lines, the fits to the points by decaying exponentials are not shown.

average time required for performing one jump by each molecule within the block of unit cells considered in the calculation. This means that correlation functions are calculated only once as a function of the number of jumps of individual rotating groups. The temperature scale is introduced by relating τ_d to correlation time τ_c taken from the Arrhenius relation.

More details concerning the time scale in the MC calculations of correlation functions can be found in [7]. The same problem of recalculating the num-

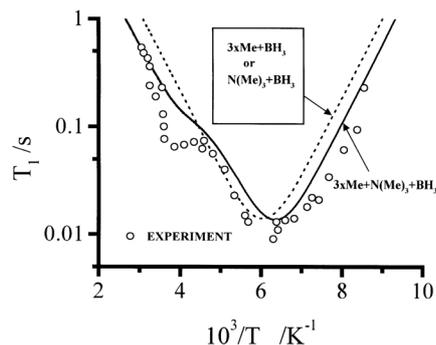


Fig. 3. NMR relaxation times T_1 of trimethylamine borane $(\text{CH}_3)_3\text{NBH}_3$, calculated for three models of motion as described in Part 3 of this paper.

ber of jumps as a function of temperature is described in details in [3] in connection with the second moment calculation as a function of temperature for the same compound – trimethylamine borane. After applying the analytical and numerical procedures described in [7], the relaxation time T_1 as a function of temperature was obtained for the three models of rotation mentioned above. It is depicted in Fig. 3 together with experimental data taken from [1]. As the correlation functions were expressed in arbitrary units, the relaxation times T_1 had to be normalized to the experimental values. This was done by setting the calculated T_1 value at the minimum, to the experimental value at this temperature. Therefore, without calculating absolute values of T_1 , we got the shape of the temperature dependence of the NMR relaxation time and used this shape to analyze models of rotation for the studied compound. In fact, this shape is more informative than absolute values of T_1 , which are usually measured with about 10% uncertainty, and they are often strongly influenced by impurities in the sample.

4. Discussion

The experimental values of relaxation time T_1 show a clearly pronounced “valley” in the vicinity of $1000/T = 4$, that is at about 250 K. The T_1 values simulated for models of rotation denoted as I and II in Part 3 of this paper do not show an anomaly in the whole temperature range. There is a small “valley” in the T_1 values simulated for the most complex model of motion, denoted as III in this paper.

The weakness of this anomaly results, in our opinion, from the simplicity of the model of motion used for the calculations presented here. The

same activation energies and correlation times were assumed for rotation of individual $-\text{CH}_3$ groups, for $-\text{N}(\text{CH}_3)_3$ groups, and for $-\text{BH}_3$ groups. Such a simplification allows for a rapid testing of the applicability of the MC simulation of correlation functions for the complex motion in this molecule.

The development of an algorithm allowing different dynamical parameters for every axis of rotation in a molecule is in progress. A computer program based

on more realistic models of motion for the simulation of correlation times should be ready soon. With such a program we should obtain the values of simulated relaxation times much more closely resembling the anomaly in the experimental values.

Acknowledgement

All numerical calculations were performed in Poznan Computing and Networking Center; <http://www.man.poznan.pl/pcss/public/>

- [1] E. C. Reynhardt, J. Phys. C: Solid State Phys. **19**, 1823 (1986).
- [2] G.H. Penner, B. Zhao, and K.R. Jeffrey. Z. Naturforsch. **50a**, 81 (1995).
- [3] R. Goc, Z. Naturforsch. **57a**, 29 (2002).
- [4] R. Goc, J. Phys: Cond. Matter **11**, 2977 (1999).
- [5] L. D. Bustard, Phys. Rev. B, **22**, 1 (1980).
- [6] X. Luo and C. A. Sholl, J. Phys: Cond. Matter **15**, 937 (2003).
- [7] R. Goc, Z. Naturforsch. **54a**, 358 (1999).
- [8] R. Goc, J. Wasicki, and S. Lewicki, Z. Naturforsch. **54a**, 689 (1999).
- [9] J. R. Doring, Y. S. Li, and J. D. Odom, J. Mol. Struct. **16**, 443 (1973).