Ammonium Ions Dynamics in NH_4Br – Proton NMR T_1 Measurements and Simulations

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Monte Carlo simulation of correlation functions for ammonium bromide have been carried out and the NMR relaxation times T_1 resulting from these functions were calculated. Results of simulations are compared to experimental values of T_1 measured in the temperature range 92 K to 292 K.

Key words: NMR; NH_4Br; Relaxation; Monte Carlo; Simulation.

1. Introduction

It is well established that ammonium bromide undergoes a number of phase transitions with respect to the disorder and relative orientation of the ion in the lattice [1]:

phase I (NaCl) ⇒ phase II (CsCl) ⇒ phase III (tetragonal) ⇒ phase IV (CsCl).

The p-T phase diagram [2, 3] for this compound is given in Figure 1. Generally, different models of motion of the ammonium ions are proposed for different phases, and many research papers deal with this problem.

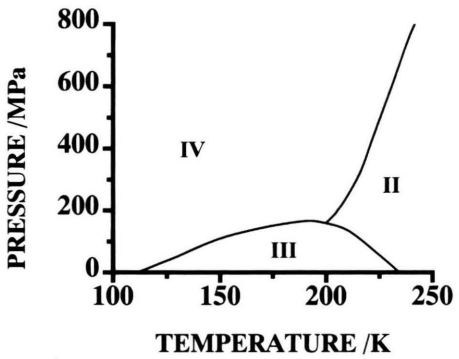

Fig. 1. The p-T phase diagram for ammonium bromide.

Numerous papers [4 - 10] were devoted to NMR T_1 relaxation time calculations for different types of anisotropic reorientations of the ammonium cation. An extensive review of ammonium ion studies by different methods can be found in [11]. The dynamics of ammonium ions in NH_4Cl was also studied in our laboratory [12], in which case a proton Van Vleck [13] second moment was calculated for different models of ammonium ion motion in a single crystal.

The main aim of this paper was to get further insight into ammonium cation reorientation in phase II and III at normal pressure. To achieve this, calculations of relaxation times T_1 were performed for different models of reorientations. Our calculations of T_1 were based on the Monte Carlo simulation of correlation functions with both intra- and interionic interactions taken into account. Inclusion of the interionic contribution in the correlation function simulation is only possible with Monte Carlo or molecular dynamics calculations. Usually only the intraionic or intramolecular contributions to the correlation function are calculated, as only this contribution can be evaluated analytically and exact calculations are possible only for very simple molecules or ions. The accuracy of the results obtained by the Monte Carlo method is limited only by the power of the computer used and by the available CPU time. Results of our Monte Carlo calculations were compared to experimental data.

2. Experimental Results

The spin-lattice relaxation times T_1 were measured as a function of temperature (92 K - 292 K) by the

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saturation method using a pulse spectrometer operating at 25 MHz. The analysis of the obtained results was performed under the assumption of isotropic reorientation (one correlation time) of the ammonium cation in the ordered phases II and III. The activation parameters calculated from the measurements in phase III are $\tau_0 = 8.3\times10^{-15}$ s and $E_a = 16.4$ kJ/mol.

A detailed analysis of the experimental data shows that the activation energies obtained from the slope of the $\ln T_1$ dependence on $1/T$ on the low and high temperature side of the minimum of T_1 differ by about 15%. This difference suggests that ammonium ion reorientations might be anisotropic with more than one correlation time [5 - 7]. As we observed only one minimum in the experimental T_1 dependence on temperature, the activation parameters describing these suggested the two types of reorientation should not differ significantly.

The correlation time evaluated from these measurements in phase II (ordered, at room temperature, and at normal pressure) $\tau = 9.12\times10^{-12}$ s and the activation energy $E_a = 13.7$ kJ/mol agrees well with analogous parameters calculated from QNS results [14] under the assumption of 90° jumps of ammonium cations about C_2 axes.

3. Relaxation Time Calculations for Ammonium Bromide

3.1. General Considerations

In order to analyse the experimental NMR relaxation times T_1 for ammonium bromide and relate their values to the dynamics of ammonium ions, Monte Carlo simulations of correlation functions were performed, and from the knowledge of these functions combined with some experimental data the relaxation times T_1 as a functions of temperature were calculated. The pioneer paper describing the application of the Monte Carlo method to simulate correlation functions was published by Bustard [15]. Some of the latest applications of this method can be found in [16 - 18].

To simplify the description of the models of ammonium ion motion the following notation is introduced: NxC_3: simultaneous reorientation about the N (= 1, 2, 3 or 4) threefold axis, MxC_2: simultaneous reorientation about M (=1, 2 or 3) twofold axis.

In all our simulations reorientations are considered as jumps of the protons belonging to the ammonium ion between neighbouring positions with minimum potential energy. Such a model is widely accepted and applied in numerous papers dealing with the description of molecular motion in ammonium compounds [5 - 7]. In case of ammonium bromide, which is the compound studied by us, there is no reason to assume non-equivalence within the given type (C_3 or C_2) of axes, and therefore we will consider always $N = 4$ and $M = 3$. The generally accepted models of reorientation of ammonium ions permit independent twofold and threefold motion, and we exploit this assumption in our simulations. Jumps by 90° about C_2 axes were excluded from our simulations because the influence of those jumps on correlation functions is nearly identical with the influence of 180° jumps. The possibility of such jumps leads to order-disorder transition, as was considered in [12], and we will introduce it to the correlation function simulation in the nearest future.

With the assumptions and notation explained above we have three states of ammonium ion reorientations: i) $3\times C_2$ jumps only, ii) $4\times C_3$ jumps only, iii) both jumps.

The term jump instead of rotation will be often used in this paper to emphasise the assumed model of motion of ammonium ions. The influence of the bromide magnetic moment on the NMR relaxation time T_1 will not be included in our simulation, but the crystal structure of NH_4Br is reflected through the lattice constant dimension determining distances between ammonium ions. Interaction of protons with nitrogen will be introduced as a coefficient C_N decreasing the value of the calculated relaxation time T_1. This coefficient will be held constant for all models of motion, the assumption being justified by the small and always the same distance between protons and nitrogen. Keeping this coefficient constant permits better comparison between relaxation times T_1 calculated for different models of motion, as those values are not influenced by eventual changes of this coefficient with the change of the model of motion.

3.2. Mathematical Framework

The basic theory concerning NMR relaxation can be found in [19], and we explain here only the general scheme of Monte Carlo simulation of correlation functions. More details of such simulations can be found in [15 - 18].

The general definition of the correlation functions for any type of stochastic motion of N particles can be written in the form

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

where $F_{im}^{(q)}(t)$ are functions of the positions of vectors connecting particles i and m evaluated at the time t. $F_{im}^{(q)*}(t+\tau)$ is the complex conjugate of these functions at the time $t+\tau$. These functions depend on the physical phenomenon for which one wants to calculate correlation functions and will be detailedly described later. The brackets $\langle \rangle_t$ denote the time average. In general, correlation functions $G^{(q)}(\tau)$ are complex functions, but in the case interesting us it is sufficient to consider their real part.

The time average defined by (1) cannot be calculated by the Monte Carlo method, but we are dealing with ergodic systems and the right hand side of (1) may be replaced by an ensemble average, resulting in

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

$\boldsymbol{r}_{im}$ are the vectors connecting particles included in calculation, and $\boldsymbol{r}_k$ are changes of these vectors in time τ. The summation must be carried only over $i \neq m$, so the vectors $\boldsymbol{r}_{im}$ have lengths different from zero. $P(\boldsymbol{r}_{im}|\boldsymbol{r}_k, \tau)$ is the relative probability that two particles initially separated by a vector $\boldsymbol{r}_{im}$, change their separation by $\boldsymbol{r}_k$ in the 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 $\boldsymbol{r}_{im}$ resulting from the motion of atoms. The values of these steps are then used to calculate probabilities of finding particles which change their position by $\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots \boldsymbol{r}_L$.

The further discussion will be restricted to NMR phenomena. In such case the functions $F_{im}^{(q)}$ are defined as follows [19]:

$$F_{im}^{(0)} = (1 - 3\cos^2\theta_{im})/r_{im}^3, \quad (2a)$$

$$F_{im}^{(1)} = \sin\theta_{im} \cos\theta_{im} \exp(-i\varphi_{im})/r_{im}^3, \quad (2b)$$

$$F_{im}^{(2)} = \sin^2\theta_{im} \exp(-2i\varphi_{im})/r_{im}^3. \quad (2c)$$

θ and φ are the spherical co-ordinates of the vectors $\boldsymbol{r}$ connecting particles which in our consideration are nuclear spins. The direction of the z axis, from which the value of θ is determined, is taken to be parallel to the external magnetic field H_0.

3.3. Details of Simulation for NH_4Br

To calculate the correlation functions defined by (2) we generate co-ordinates of all protons from ammonium groups within a block of 1331 unit cells ($11 \times 11 \times 11$), and then jumps of protons are simulated by means of proper permutation of their positions as described in [12]. The functions $F_{im}^{(q)}(\boldsymbol{r}_{im})$ and $F_{im}^{(q)*}(\boldsymbol{r}_{im} + \boldsymbol{r}_k)$ are calculated with values of the complex conjugate taken after the ammonium ions have performed a defined number of jumps, then the required probabilities $P(\boldsymbol{r}_{im}|\boldsymbol{r}_k, \tau)$ are evaluated and the finally correlation functions $G^{(q)}(\tau)$ are calculated. The structural data required for these simulations were taken from [20]. The calculations were performed for the structural parameters determined at atmospheric pressure, that is for a lattice constant $a = 0.406$ nm. The details required for the numerical calculation of correlation functions defined by (2) are quite cumbersome. They are described in [18] and will not be repeated here. The Monte Carlo method does not include time in a direct form but, following the original idea introduced by Bustard [15], the time is measured in units τ_d defined as follows: τ_d is a time interval during which on average each molecule considered in the calculation performs one jump.

The time unit defined in such a way is very close to the correlation time τ_c defined for the purpose of describing the stochastic motion influencing NMR phenomena [19]. In the case of ammonium bromide, the model of possible motions is simple enough to assume

$$\tau_d = \tau_c,$$

and the correlation time τ_c will be taken from our experimental studies. From the above explanation it follows that τ_d has nothing to do with the speed of the computer used in the simulation. All time intervals are converted into a number of jumps performed by ammonium ions, and the real time necessary to simulate these jumps on the computer is not relevant for our calculations.

The sampling rate during the evaluation of the correlation function, that is the increase in time delay

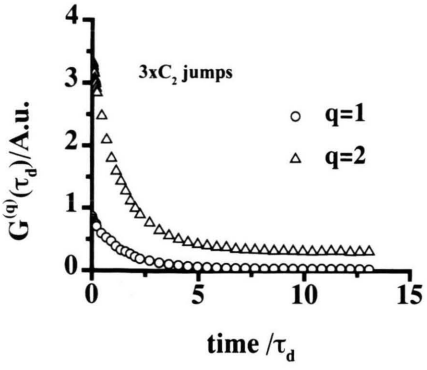

Fig. 2. Correlation functions simulated for ammonium bromide with jumps about three twofold axes.

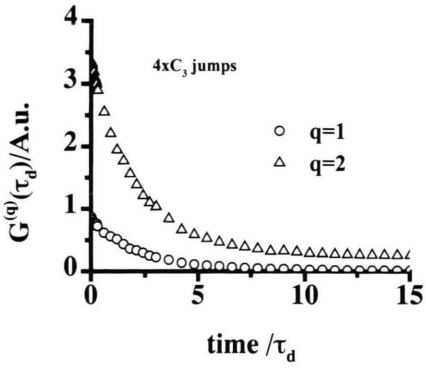

Fig. 3. Correlation functions simulated for ammonium bromide with jumps about four threefold axes.

between calculating subsequent values of $G^{(q)}$, determines the details of spectral density functions

$$J^{(q)}(\omega) = \int_{-\infty}^{\infty} G^{(q)}(\tau) e^{-i\omega\tau} \mathrm{d}\tau \tag{3}$$

used in the T_1 calculation. To get a high frequency information, a high sampling rate is required, but low frequency information may be obtained only from values of correlation functions for long values of time τ, that is for a large number of jumps performed between calculating $F_{im}^{(q)}$ and $F_{im}^{(q)*}$. A compromise is necessary because a calculation with a high sampling rate and for long times would be unreasonably long and costly. We therefore performed the calculation with a high sampling rate for times τ close to zero and decreased the rate for longer times. One hase to remember that the time τ is measured in units τ_d that is, in other words, in the number of jumps which molecules performed between calculating $F_{im}^{(q)}$ and $F_{im}^{(q)*}$.

Examples of correlation functions simulated under the described assumptions for ammonium bromide are given in Fig. 2 and Figure 3. Presented are results of simulation of functions defined by (2) for $q = 1$ and $q = 2$, as only those two functions determine the longtitudial relaxation time T_1 measured in an NMR experiment. The amplitude of $G^{(q)}$ is considered as given in arbitrary units because the coefficient C_K representing the coupling of the proton with the nitrogen nucleus will be introduced in the process of relaxation time calculation. The value of this coefficient was chosen to get an agreement between simulated and experimental values of T_1 at the temperature where they experience the minimum (the relaxation rate is the fastest). Once C_K was determined, it was kept constant for all calculations. Therefore the value of this coefficient does not influence the dependence of relaxation times on the model of motion, and the analyses of such dependence was one of the main reasons to undertake these simulations.

The calculations were performed on a Cray T3E 900 supercomputer, and the CPU time required to obtain one set of correlation functions (together with functions for $q = 0$) was about 1100 minutes. The obtained discrete values of the correlation function were approximated by two exponential decays represented by the general equation

$$G^{(q)}(\tau) = A_1^{(q)} \exp(-\tau/\tau_{d_1}^{(q)}) + A_2^{(q)} \exp(-\tau/\tau_{d_2}^{(q)}). \tag{4}$$

The time constants τ_{c_1} and τ_{c_2} were then introduced according to the relations

$$\tau_{c_1}^{(q)} = \tau_{d_1}^{(q)} \tau_c, \quad \tau_{c_2}^{(q)} = \tau_{d_2}^{(q)} \tau_c$$

with the correlation time τ_c defined by the Arrhenius relation

$$\tau_c = \tau_0 \exp(-E_a/RT).$$

Please note that there is only one experimental correlation time τ_c.

Values of preexponential factor τ_0 and activation energy E_a were calculated from our experimental results. This procedure allows the use of the analytical expression for the Fourier transform of correlation functions and simplifies the calculation of relaxation times as a function of the temperature. The spectral

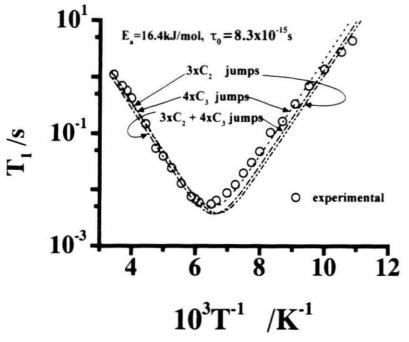

Fig. 4. Relaxation times T_1 calculated for ammonium bromide for different models of rotations. All calculations with activation energy E_a = 16.4 kJ/mol and $\tau_0 = 8.3\times10^{-15}$ s.

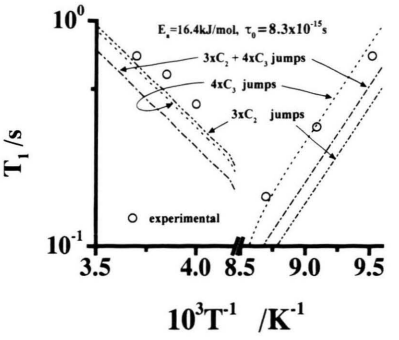

Fig. 5. Two fragments of Fig. 4 drawn with different scale to give better insight into the dependence of T_1 on the model of motion. Calculations with activation energy E_a = 16.4 kJ/mol and $\tau_0 = 8.3\times10^{-15}$ s.

densities defined by (3) of the correlation functions given by (4) are

$$J^{(q)}(\omega) = C_K \sum_{i=1}^{1} \frac{2\tau_{c_i}^{(q)}}{1 + \left(\omega\tau_{c_i}^{(q)}\right)^2}. \tag{5}$$

Please note that C_K does not have the q index as it is the same for all correlation functions as well as for all types of motions assumed for the simulation.

Finally, the relaxation time can be written as

$$\frac{1}{T_1} = C_T\{J^{(1)}(\omega_I) + J^{(2)}(2\omega_I)\} \tag{6}$$

with

$$C_T = \frac{3}{2}\left(\frac{\mu_0}{4\pi}\right)^2 \gamma^4\hbar^2 I(I+1), \tag{6a}$$

where μ_0 is the vacuum permeability, γ 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. The C_T coefficient evaluated for protons is (in SI units) 6.408 $\times$ 10^{-49} s^{-2}. C_K = 16 was chosen, as this value gives the best agreement between the experimental and simulated value of T_1 at their minimum. Calculations of spectral densities and relaxation times T_1 were performed on a PC computer with a Pentium II processor operating at 333 MHz, and the CPU time required for them was negligible.

The aim of our simulation was to get an idea about the influence of different models of ammonium ion motion on the NMR relaxation times T_1. The obtained results are visualised in Figs. 4, 5, and 6, with Figs. 5 and 6 presenting the zoomed parts of Figure 4.

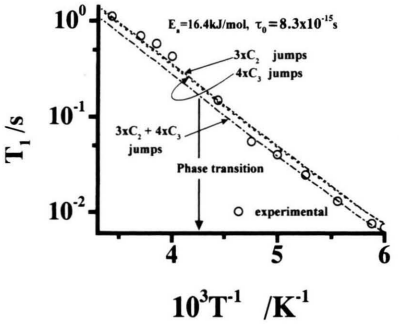

Fig. 6. The high temperature part of Fig. 4, drawn with different scale to give better insight into the region of temperature where the phase transition occurs. Calculations with activation energy E_a =16.4 kJ/mol and $\tau_0 = 8.3\times10^{-15}$ s.

The final calculation of relaxation times were performed with one value of the activation energy E_a = 16.4 kJ/mol and one value of the preexponential factor $\tau_0 = 8.3\times10^{-15}$ s in order to minimise the influence of these parameters on the T_1 dependence in models of motion.

4. Conclusions

The Fig. 4 is not very convenient for analysis due to the congestion of points and lines, but Figs. 5 and 6 allow to summarise our conclusions as to the influence of different types of motions on the relaxation NMR time and permit a comparison between experimental and simulated relaxation times. Those conclusions are presented in Table 1.

At the phase transition temperature, depicted in Fig. 6 with an arrow, there is an evident change of the model of motion which best fits the experimental data.

Table 1. Relations between the model of motion and the longtitudal relaxation rate of protons in ammonium bromide.

10^3T^{-1}	Most effective model of motion	Less effective model of motion	Best agreement with experiment	See Fig.
< 4.0	$3\times C_2 + 4\times C_3$	$3\times C_2$, $4\times C_3$	$3\times C_2$	4, 5 and 6
4.5 - 6.0	$3\times C_2 + 4\times C_3$	$3\times C_2$	$3\times C_2 + 4\times C_3$	4 and 6
> 7.0	$3\times C_2$	$4\times C_3$	$4\times C_3$	4 and 5

In disordered phase II ($10^3T^{-1} < 4.5$) with ammonium ions randomly distributed between two equivalent positions, the best agreement with experimental results is given by the model of motion with jumps about only one type of axis with no significant difference between the C_2 and C_3 axis.

In the ordered phase III, but above the temperature corresponding to the minimum of T_1 ($4.5 < 10^3T^{-1} < 6.5$), the simulation with combined $3\times C_2 + 4\times C_3$ jumps best fits the experimental data, cf. Figure 6. At low temperatures ($10^3T^{-1} > 7.0$) the best agreement with experiment is obtained for jumps about C_3 axis only. It is worth to notice that in this temperature region there is the greatest difference between the effect of $3\times C_2$ and $4\times C_3$ jumps on the NMR relaxation time. The combined motion $3\times C_2 + 4\times C_3$ is more effective than $4\times C_3$ jumps alone but less effective than the $3\times C_2$ jumps.

All the simulations presented in this paper were performed for ammonium bromide at normal pressure, which corresponds to the lattice constant a = 0.406 nm.

The ammonium bromide seems not to be a very suitable compound for verifying the models of jumps through the relaxation times simulation because the high symmetry of the ammonium ion suggests that differences in relaxation times due to the different models of motion may be small, and this is really the case in our simulations. Nevetherless we came to some conclusions that simulations of this type are helpful in analysing the experimental data concerning NMR relaxation times.

Acknowledgement

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