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## Recalculation of the NMR second moment for $(\text{CH}_3)_3\text{NBH}_3$

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**Abstract.** The proton second moment for the trimethylamine–borane complex— $(\text{CH}_3)_3\text{NBH}_3$ —has been measured and calculated by Reynhardt who assumed a rather complicated model of internal dynamics to achieve agreement between the measured and calculated values. In this paper the proton second moment for the same material has been calculated assuming a different and simpler model of internal dynamics taken from the deuterium NMR study of  $(\text{CD}_3)_3\text{NBH}_3$  by Penner *et al.* The agreement between experimental and calculated values of the second moment, reported in our paper, is as good as in Reynhardt's study, but the model of internal dynamics consistent with the Penner results seems to be more probable as it does not require the assumption of the existence of non-equivalent molecules or even 'non-equivalent' crystallographical unit cells.

### 1. Introduction

The second moment of the NMR absorption spectrum is a very good indicator of molecular structure and dynamics as described in monographs by Abragam (1961) and Slichter (1990). Due to Van Vleck's (1948) formula for the theoretical value of the second moment, the crystallographic and molecular structure as well as the internal dynamics of solids can be verified through NMR measurements.

The trimethylamine–borane complex has been a subject of NMR studies by Yim and Gilson (1970), Reynhardt (1986) and Penner *et al.* (1995). The measured values of the proton second moment as a function of temperature between 50 K and 360 K are shown in figure 1 of the Reynhardt (1986) paper. To calculate theoretical values of the second moment Reynhardt (1986) assumed the model of rotation which is presented in table 1 of his paper.

To simplify the description of different models of rotation for the  $(\text{CH}_3)_3\text{NBH}_3$  complex we introduce the following notation:

A—represents three individual methyl groups,

B—represents the  $(\text{CH}_3)_3\text{N}$  group with possible axis of rotation along the N–B bond,

C—represents the  $\text{BH}_3$  group,

D—represent the whole complex  $(\text{CH}_3)_3\text{NBH}_3$ .

Subscripts *rig* and *rot* denote rigid structure or rotation of the particular group of atoms. The subscript *rot* in connection with A, B and C groups denotes rotational jumps by  $120^\circ$  about the  $C_3$  axis of symmetry. As to the whole complex we consider two possible models of motion denoted as:

$D_{rot,180}$ —means rotational jumps by  $180^\circ$  about the axis perpendicular to the N–B bond and passing through the nitrogen atom,

$D_{iso}$ —means isotropic rotation about the centre of gravity of the molecule.

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For example,  $A_{rig}, B_{rig}, C_{rig}, D_{rig}$  indicates a completely rigid molecule, and  $A_{rot}, B_{rig}, C_{rot}, D_{rig}$  a molecule with individual  $\text{CH}_3$  and  $\text{BH}_3$  groups rotating but with a rigid  $(\text{CH}_3)_3\text{N}$  group, and the molecule being rigid as a whole.

To obtain an agreement between the measured and calculated second moment Reynhardt (1986) assumed that three molecules in the hexagonal unit cell reported by Geller *et al* (1951) are nonequivalent. One of these molecules differs from the other two and has a different activation energy for a specific reorientation. For simplicity we call it the Reynhardt model. In the description of this model of rotation the numbers proceeding letters A, B, C and D denote how many molecules from the unit cell have the listed groups rigid or rotating. The Reynhardt model describing the internal dynamics of  $(\text{CH}_3)_3\text{NBH}_3$  as a function of temperature is summarized in table 1.

**Table 1.** The Reynhardt model of internal dynamics for  $(\text{CH}_3)_3\text{NBH}_3$ .

(a) $T < 80$ K	$3(A_{rig}, B_{rig}, C_{rig}, D_{rig})$
(b) $120 < T < 155$ K	$2(A_{rot}, B_{rot}, C_{rot}, D_{rig}) + 1(A_{rot}, B_{rot}, C_{rig}, D_{rig})$
(c) $200 < T < 320$ K	$3(A_{rot}, B_{rot}, C_{rot}, D_{rig})$
(d) $325 < T < 360$ K	$2(A_{rot}, B_{rot}, C_{rot}, D_{rig}) + 1(A_{rot}, B_{rot}, C_{rot}, D_{iso})$

A different model of internal dynamics for the same trimethylamine–borane complex was proposed by Penner *et al* (1995) on the basis of the deuterium NMR study. This model, called later the Penner model, assumes all molecules in the unit cell to be equivalent. Having in mind that Penner measured a partially deuterated compound, the model of rotation, consistent with the evaluated activation energies for particular types of motion, is given in table 2. Rotation in the final temperature range was not considered by Penner *et al* (1995), but it is introduced in this paper and will be later denoted by G.

**Table 2.** The Penner model of internal dynamics for  $(\text{CD}_3)_3\text{NBH}_3$ .

(I) $T < 80$ K	$A_{rig}, B_{rig}, C_{rig}, D_{rig}$
(II) $120 < T < 155$ K	$A_{rig}, B_{rot}, C_{rot}, D_{rig}$
(III) $200 < T < 320$ K	$A_{rot}, B_{rot}, C_{rot}, D_{rig}$
Extension to Penner model	
(IV) $325 < T < 360$ K	$A_{rot}, B_{rot}, C_{rot}, D_{rot,180}$

In this description of the assumed rotation there is no need to use numbers representing the amount of molecules with rigid or rotating groups of atoms as all molecules are equivalent, and denoted groups either are rigid or rotate in all molecules. A comparison of these two models of the internal dynamics of the trimethylamine–borane complex can be summarized as follows:

Reynhardt	Penner
(a) equivalent to	(I)
(b) different from	(II)
(c) different from	(III)
(d) not considered by Penner <i>et al</i>	(1995)

The model of molecular dynamics proposed by Penner *et al* (1995) seems to be more natural because it does not assume that molecules in the compound are non-equivalent. Such an assumption does not seem very probable if one takes into account that the crystal structure

reported by Geller *et al* (1951) is also consistent with a rhombohedral unit cell with one molecule per unit cell. In such a case it would be rather difficult to think about 'nonequivalent' unit cells. In favour of the Penner model speaks also the fact that the deuterium NMR is more sensitive to the motion of atoms compared to proton NMR study and one could expect that conclusions regarding internal dynamics drawn from deuterium experiments might be more reliable than those drawn from proton NMR measurements. The Penner *et al* (1995) deuterium measurements do not cover the temperatures above 233 K therefore no conclusions are drawn in their paper as to the eventual tumbling of the whole  $\text{N}(\text{CD}_3)_3\text{BH}_3$  complex.

In order to obtain an additional indicator as to which of these models of rotation is more probable, the calculation of the proton second moment for the  $(\text{CH}_3)_3\text{NBH}_3$  complex has been performed assuming the Penner model of rotation extended to rotation of the whole molecule above 325 K. The results of the second moment calculation reported in this paper show that within experimental error both models give a good agreement of the calculated proton second moment with the measured values, but we insist that the Penner model seems to be more realistic because it does not include the assumption of non-equivalency of molecules which seems to be not very well justified.

## 2. Second moment calculation—general approach

Van Vleck's (1948) formula for the NMR second moment in case of internal rotation of molecules or groups of atoms can be written in the form

$$M_{2(I)}^{rot} = M_{2(II)}^{rot} + \sum_S M_{2(IS)}^{rot} \quad (1)$$

where

$$M_{2(II)}^{rot} = N_U^{-1} C_{II} \left\{ \sum_{i=1}^{N_U} \left( \sum_{j=1}^{N_U} \langle B_{ij} \rangle_n^2 + \sum_{j=N_U+1}^{N_I} \langle B_{ij} \rangle_n^2 \right) \right\} \quad (2)$$

and

$$M_{2(IS)}^{rot} = N_U^{-1} C_{IS} \left\{ \sum_{i=1}^{N_U} \left( \sum_{k=1}^{N_{US}} \langle B_{ik} \rangle_n^2 + \sum_{j=N_U+1}^{N_S} \langle B_{ik} \rangle_n^2 \right) \right\} \quad (3)$$

with

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

$$C_{IS} = \frac{1}{3} \left( \frac{\mu_0}{4\pi} \right) \gamma_I^2 \hbar^2 S(S+1) \quad (3a)$$

$$\langle B_{ij} \rangle_n = \frac{1}{n} \sum_{l=1}^n \frac{3 \cos^2 \Theta_{ijl} - 1}{r_{ijl}^3} \quad (2b)$$

and

$$\langle B_{ik} \rangle_n = \frac{1}{n} \sum_{l=1}^n \frac{3 \cos^2 \Theta_{ikl} - 1}{r_{ikl}^3}. \quad (3b)$$

$\mu_0$  is the vacuum permeability,  $\gamma_I$  the gyromagnetic ratio of resonant nuclei,  $I$  their spin and  $\hbar = h/2\pi$  where  $h$  is the Planck constant.  $S$  denotes the spin of the nonresonant nuclei included in the calculation and  $\gamma_S$  their gyromagnetic ratio. The other symbols used in the above equations are explained below.

- $N_U$  is the number of resonant nuclei in one crystallographic unit cell,  
 $N_{US}$  the number of nonresonant nuclei in one crystallographic unit cell,  
 $\Theta_{ijl}$  the angle between the  $r_{ijl}$  vector connecting nuclei  $i$  and  $j$  in position  $l$  and the direction of the external magnetic field,  
 $\Theta_{ikl}$  the analogous angle for nuclei denoted  $i$  and  $k$  in position  $l$ ,  
 $n$  the number of positions taken by nuclei in course of rotation.

The indexes  $i$  and  $j$  denote resonant nuclei while  $k$  denote nonresonant nuclei included in the calculation. Expressions defined by equations (2b) and (3b) must be calculated simultaneously for each group of atoms moving as a whole unit, because they describe the local magnetic field averaged by internal rotation of molecules or groups of atoms. This rotation means simultaneous movement of resonant and nonresonant nuclei with the moving molecule or group of atoms.

The detailed explanation of the above equations, together with some details of how to write a computer program performing calculations based on these equations, can be found in a paper by Goc (1998).

### 3. Details of calculation for $\text{N}(\text{CH}_3)_3\text{BH}_3$

The detailed crystal structure for the trimethylamine–borane complex has not been reported, therefore we took the structural parameters of the molecule from During *et al* (1973) as Reynhardt (1986) did and we assumed a cubic unit cell having  $a = 0.57$  nm with one molecule per unit cell. This is not exactly the structure reported by Geller *et al* (1951), but very close to it. The difference in rigid values of the second moment between the Reynhardt calculation (structure based on Geller *et al* (1951) data) and those in this paper is less than 0.03%, which should justify our simplification of the structure. Second moment calculations were performed for the block of 125 unit cells, which means one central unit cell surrounded by the double closed shell of unit cells. It is important to notice that calculation of the second moment averaged by different types of internal rotation is ‘nearly exact’, as described by Goc (1998). The term ‘nearly exact’ means that rotation of groups of atoms is simulated in all molecules from 125 unit cells and the averaged dipole–dipole interaction is calculated by the Monte Carlo method with all molecules included in the calculation. The results of calculations are summarized and compared to the Reynhardt (1986) calculations in table 3.

**Table 3.** Experimental (Reynhardt 1986) and calculated proton second moment values. Reorientation models denoted R (for Reynhardt) and P (for Penner) are described in table 1 and table 2 in the introduction. The model denoted G is explained under point IV) in table 2. All second moment values are in  $10^{-8}$  T<sup>2</sup> which is equal to G<sup>2</sup>—the units used in the Reynhardt (1986) paper.

Temperature range	Reorientation model	$M_{2calc.}$	$M_{2exp.}$
$T < 80$ K	R (a)	34.7	$33 \pm 1$
	P (I)	34.7	
$120 < T < 155$ K	R (b)	8.62	$8.3 \pm 0.5$
	P (II)	8.28	
$200 < T < 320$ K	R (c)	4.06	$44.6 \pm 0.3$
	P (III)	4.24	
$325 < T < 360$ K	R (d)	3.18	$3.0 \pm 0.3$
	G	3.70	

#### 4. Discussion and conclusion

The results of the second moment calculation for the  $(\text{CH}_3)_3\text{NBH}_3$  complex presented in this paper and based on the Penner *et al* (1995) model of internal dynamics are in good agreement with the Reynhardt (1986) experimental results as well as with his calculations, but we are confident that the model of internal dynamics described in table 2 is more probable than the model introduced by Reynhardt (1986) and described in table 1. Both models lead to equally satisfactory agreement between measured and calculated values of the second moment in the temperature region below 320 K. In the high temperature region, above 325 K, this agreement is slightly better for the Reynhardt (1986) model of rotation, but this model with non-equivalent molecules, being not well justified, seems to be less probable than the model proposed by Penner *et al* (1995).

The model of internal dynamics used for second moment calculation presented in this paper may be seen as more reliable than the one proposed by Reynhardt (1986) also for the reason of more precise calculations on which our model is based. Simulation of internal dynamics was carried out for 125 unit cells, that is for 125  $(\text{CH}_3)_3\text{NBH}_3$  complexes, each of them undergoing independent rotation. The values of internuclear distances  $r$  and angles  $\theta$  used in equations (2) and (3), which are averaged by these rotations, are calculated exactly for all nuclei in the rotating groups within the whole  $5 \times 5 \times 5$  block of unit cells. Such a procedure of calculation together with conclusions from the Penner *et al* (1995) paper speaks in favour of the model of internal dynamics presented in this paper.

The small uncertainty as to the crystal structure of the  $(\text{CH}_3)_3\text{NBH}_3$  complex does not pose a serious danger for the calculation because the main contribution (more than 80%) to the second moment is due to the dipole–dipole interactions within one  $(\text{CH}_3)_3\text{NBH}_3$  complex and the structure of the complex itself given by During *et al* (1973) is known with much higher accuracy than the crystal structure. The intermolecular contribution to the second moment becomes more important for the case of great freedom of rotation of molecules because the intramolecular contribution is then minimized. For this situation—the highest temperature—the lack of exact crystallographic data has the largest impact on calculation and it is reflected in our results as the relatively largest disagreement between theoretical and experimental values of the second moment.

The aim of this paper was to confirm the simplest possible model of internal dynamics, a model which is in accordance with the experimental results of Penner *et al* (1995). More complicated models of rotation of particular groups of atoms could be analysed, but this would require the crystal structure of the complex to be refined and all atomic positions given.

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