A Deuterium NMR Study of some Ammonium Tetraphenylborates

Marco L. H. Gruwel and Roderick E. Wasylishen

Department of Chemistry, Dalhousie University, Halifax, Nova Scotia, Canada B3H 4J3

Z. Naturforsch. **45a,** 55–66 (1990); received August 31, 1989

Deuterium nmr has been used to study the rotational dynamics of the ammonium ion in ammonium tetraphenylborate and of the cation in a series of methylammonium tetraphenylborates. The results of variable temperature ^{2}H relaxation measurements (T_{1Z} and T_{1Q}) on the parent compound, $ND_4B(C_6H_5)_4$, lead to a low activation energy for reorientation of the ND_4^+ ion, 5.0 ± 0.5 kJ mol^{-1}, indicative of weak cation-anion interactions. Related studies of the tetramethyl-d$_{12}$ ammonium salt indicate rapid jumps of the whole cation ($\tau \ll 10^{-5}$ s) over the complete temperature range investigated, 137 to 385 K, with an activation energy of 14.1 ± 0.5 kJ mol^{-1}. Deuterium nmr lineshape studies of the methylammonium salt indicate rapid reorientation of the CD_3 and ND_3 groups about their C_3 axes; however, the motion of the C–N axis is restricted to large amplitude librations. Similar studies of the dimethylammonium salt indicate methyl group jumps at 245 K; at temperatures above 320 K the cation also undergoes two-site jumps about the C_2 axis. In the case of the trimethylammonium salt, the nmr lineshapes indicate methyl group jumps superimposed on C_3 rotations of the complete cation about the N–H bond axis over the temperature interval 185–348 K. In all the tetraphenylborate salts studied, the ^{2}H nmr lineshapes indicate substantial librational motion of the cation at room temperature.

Key words: ^{2}H nmr, rotation, ammonium derivatives, tetraphenylborates.

1. Introduction

In aqueous solution, ammonium chloride, or any methyl substituted ammonium halide, will react with sodium tetraphenylborate to yield water insoluble salts of the type: $NH_{4-n}(CH_3)_n\,B(C_6H_5)_4$ ($n = 0$ to 4). These salts are particularly interesting because of the peculiar size and shape of the large delocalized tetraphenylborate anion [1–3]. Infrared and x-ray diffraction studies of the parent compound, $ND_4B(C_6H_5)_4$, provide evidence for hydrogen bonding between the N–H bonds and the π-system of the anion phenyl rings [3]. In a more recent infrared study of ammonium tetraphenylborate, Roberts and Strauss [4] claim an extremely low barrier for rotations of the ammonium ion, approximately 20 cm^{-1} ($\simeq 0.24$ kJ mol^{-1}). The report of this low barrier has prompted us to study the ^{2}H nmr relaxation rates of the deuterated derivative, $ND_4B(C_6H_5)_4$ as a function of temperature. The nmr activation energy for reorientation of the ammonium ion obtained from our relaxation data is compared with the values reported for other ammonium salts [5–13].

In addition, we have used ^{2}H nmr to characterize the motion of the cation in methylammonium, dimethylammonium, trimethylammonium and tetramethylammonium tetraphenylborate. The latter compound is of particular interest since its structure is available from single crystal x-ray diffraction data [2] (see Figure 1). The anisotropic temperature coefficients indicate large amplitude motion of the methyl carbon atoms. The results of the present study allow us to comment on the nature of the motion responsible for the large thermal parameters.

II. Theory

For deuterium nuclei the interaction of the nuclear quadrupole moment with fluctuating electric field gradients (EFG's) is so efficient that relaxation of these spins is completely dominated by the quadrupolar mechanism [14]. The quadrupolar Hamiltonian can be expressed as a sum of products of 2$^{\text{nd}}$ rank spin and bath tensor components as given by

$$H_q = \sum_{m=-2}^{2} (-1)^m F_{-m} A_m. \quad (1)$$

After rearrangement of common terms, the bath tensor components can be expressed in Wigner rotation

---

Reprint requests to Professor R. E. Wasylishen, Department of Chemistry Dalhousie University, Halifax, Nova Scotia, Canada B3H 4J3.

0932-0784 / 90 / 0100-0055 $ 01.30/0. – Please order a reprint rather than making your own copy.

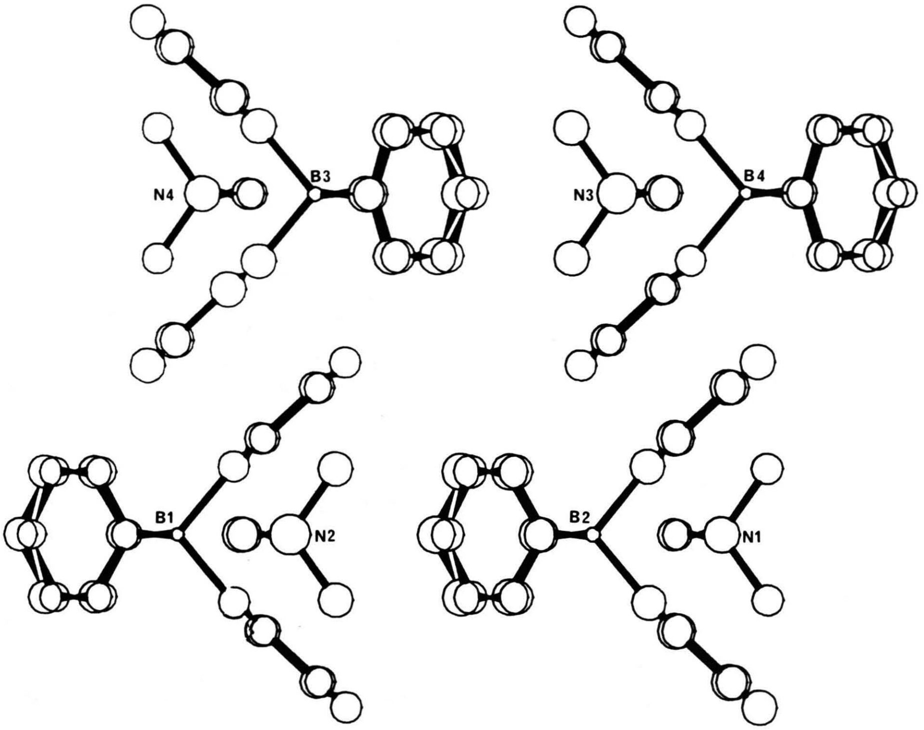

Fig. 1. Structure for tetramethylammonium tetraphenylborate (from data in [2]).

matrix elements [15, 16]

$$F_m = D^{(2)}_{m,0}(\Omega) - \eta(\sqrt{6})^{-1}\,[D^{(2)}_{m,2}(\Omega) + D^{(2)}_{m,-2}(\Omega)]. \quad (2)$$

In the discussion which follows we will assume the electric field gradient to be axially symmetric, i.e., $\eta = 0$. This is an excellent assumption for deuterium nuclei in the $C-{}^2H$ and $N-{}^2H$ bonds studied here [17, 18].

The relaxation rate of Zeeman order, R_{1Z}, and quadrupolar order, R_{1Q}, is given by [15]

$$R_{1Z} = (3/4)\,\pi^2\langle\chi^2\rangle[J_1(\omega_0) + 4J_2(2\omega_0)],$$
$$R_{1Q} = (3/4)\,\pi^2\langle\chi^2\rangle[3J_1(\omega_0)], \quad (3)$$

where the quadrupole coupling constant (QCC), $\chi = eQeq/h$, represents the product of the largest component of the EFG tensor, eq, and the nuclear quadrupole moment eQ. The spectral density $J_m(\omega)$ is the cosine transform of the bath tensor components correlation function in the laboratory frame [16]:

$$J_m(m\,\omega) = 2\int_0^\infty \mathrm{d}t\,\cos m\,\omega\,t \cdot \langle D^{(2)*}_{m,0}(\Omega(0))\,D^{(2)}_{m,0}(\Omega(t))\rangle_{\mathrm{lab}}\,. \quad (4)$$

In order to calculate the spectral densities one has to transform the EFG tensor from the molecular frame, in which the principal components are known, into the laboratory frame in which one performs the experiments. First we will discuss these transformations for the tetramethyl-d_{12} ammonium ion and secondly for the ammonium-d_4 ion.

i) The tetramethylammonium ion. Three successive transformations have to be made for this ion (Figure 2). The first transforms interaction elements from the crystal fixed axis frame to the laboratory frame. This transformation introduces the powder angles (θ, φ) [16, 19, 20],

$$\langle D^{(2)*}_{m,0}(\Omega(0))\,D^{(2)}_{m,0}(\Omega(t))\rangle_{\mathrm{lab}} \quad (5)$$
$$= \sum_{a,a'=-2}^{2} d^{(2)}_{m,a}(\theta)\,d^{(2)}_{m,a'}(\theta)\,C_{a,a'}(t)\,e^{+i(a-a')\varphi}.$$

The function $C_{a,a'}(t)$ is determined by the modulation of the crystal angles (Θ, Φ) due to the reorientation of the tetramethylammonium ion in this frame. This modulation can be written as an expansion of Wigner rotation matrix elements:

$$C_{a,a'}(t) = \sum_{b,b'=-2}^{2} \langle D^{(2)*}_{0,b}(\Omega(0))\, D^{(2)}_{0,b'}(\Omega(t))\rangle_{C_3} \cdot \langle D^{(2)*}_{a,b}(\Omega(0))\, D^{(2)}_{a',b'}(\Omega(t))\rangle_{T_d}\,. \qquad (6)$$

Here we have assumed the two reorientation processes, methyl C_3 flips and the tetrahedron (T_d) motion, to be independent of each other. The ensemble averaging over the tetrahedron motion (= whole ion motion) was approximated by an isotropic reorientation model, fast C_2 and C'_3 motions compared with the *QCC* (*vide infra*). Note that a C'_3 jump corresponds to the simultaneous jump of three methyl groups about a particular C−N axis. Also, note that two successive C'_3 jumps about different N−C axes may be equivalent to a C_2 flip. The assumption of isotropic motion greatly simplifies the calculation of the Zeeman relaxation rate [20]. The effective correlation time for this motion, τ_{T_d}, can be interpreted in terms of C'_3 and C_2 reorientational correlation times [19]. For the whole ion reorientation we thus write

$$\langle D^{(2)*}_{a,b}(\Omega(0))\, D^{(2)}_{a',b'}(\Omega(t))\rangle = (1/5)\, \delta_{a,a'}\, \delta_{b,b'}\, e^{-t/\tau_{T_d}}\,, \qquad (7)$$

where $\delta_{i,j}$ is the Kronecker delta function. The averaging due to methyl C_3 flips of the C−^{2}H bond was treated in terms of a C_3 model as described by Torchia and Szabo [20]. This results in the following correlation function:

$$C_{a,a'}(t) = \sum_{b=-2}^{2} |d^{(2)}_{0,b}(\beta)|^2\, [\delta_{b,0} + (1-\delta_{b,0})\, e^{-t/\tau_{C_3}}] \cdot (1/5)\, \delta_{a,a'}\, e^{-t/\tau_{T_d}}\,. \qquad (8)$$

The assumption of isotropic motion for the whole ion reorientation results in the selection of only diagonal elements of the methyl C_3 flip reorientation matrix. The non-diagonal terms of this matrix give rise to nonexponential relaxation [20]. These terms were overlooked by Wallach [21] but included in calculations by Edholm and Blomberg [22]. Finally we obtain for the spectral density (*m* independent):

$$J(\omega) = (2/5)\left\{(1/4)\,(3\cos^2\beta - 1)^2\, \frac{\tau_{T_d}}{1+(\omega\,\tau_{T_d})^2} + [(3/4)\sin^2 2\beta + (3/4)\sin^4\beta]\, \frac{\tau_1}{1+(\omega\,\tau_1)^2}\right\}. \qquad (9\,\mathrm{a})$$

The correlation rate $\tau_1^{-1} = \tau_{T_d}^{-1} + \tau_{C_3}^{-1}$ and τ_{C_3} equals 1/3 *k*, where *k* = jump rate for the methyl C_3 reorientation. Assuming the angle between the methyl C_3 axis and the C−^{2}H bond, β, is 109.4° (9 a) reduces to

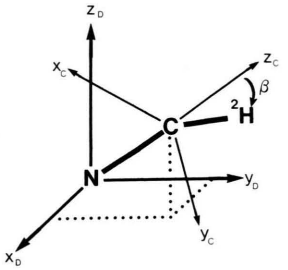

Fig. 2. Graphic representation of the tetramethylammonium ion in the two frames indicated by the labels *C*, the axes frame for the methyl group reorientation, and *D*, the axes frame for the whole ion reorientation. The Laboratory frame can have any orientation with respect to the *D* frame. The angle between the methyl-C_3 axis and the C−^{2}H bond is indicated by β.

$$J(\omega) = (2/5)\left\{(1/9)\, \frac{\tau_{T_d}}{1+(\omega\,\tau_{T_d})^2} + (8/9)\, \frac{\tau_1}{1+(\omega\,\tau_1)^2}\right\}. \qquad (9\,\mathrm{b})$$

ii) Ammonium ion. The rotational motion of the ammonium ion in ammonium tetraphenylborate can be described by the isotropic whole ion reorientation term (7) in the previous section. The resulting spectral density is given by

$$J(\omega) = (2/5)\, \frac{\tau_{T_d}}{1+(\omega\,\tau_{T_d})^2} \qquad (10)$$

and is identical to that obtained in reference [19] for fast C_2 and C_3 flips.

III. Experimental

The ^{2}H nmr experiments on tetramethylammonium tetraphenylborate and ammonium tetraphenylborate were performed at 55.42 MHz on a Nicolet 360 NB spectrometer. For tetramethylammonium tetraphenylborate a Nicolet highband probe with typical $\pi/2$ pulses of 40−50 μs was used. Ammonium tetraphenylborate was studied with a ^{2}H nmr probe of Probe Systems Inc. having typical $\pi/2$ pulses of 6−7 μs. Methylammonium, dimethylammonium and trimethylammonium tetraphenylborate were studied at 30.72 MHz on a Bruker MSL 200 using $\pi/2$ pulse lengths of 4.5 μs. The temperature in each probe was regulated to 1 K with cold N_2 gas and a heater built into the probes.

All R_{1Z} values were obtained from peak heights obtained at 12 or more different τ values in the π-τ-$\pi/2$ pulse sequence with phase cycling [23]. To observe ^{2}H nmr spectra of methylammonium, dimethylammonium and trimethylammonium tetraphenylborate, a solid echo technique was used [24] with a pulse separation of 40 μs. The Zeeman relaxation rates, R_{1Z}, in the latter tetraphenylborate salts were determined by means of an inversion recovery experiment which included a solid echo before signal detection. Quadrupolar order relaxation rates, R_{1Q}'s, were measured with the Jeener-Broekaert pulse sequence [25]. After the application of the second pulse in the Jeener-Broekaert three pulse sequence [25, 26],

$$(\pi/2)|_y - \tau_1 - (\pi/4)|_{\pm x} - \tau_2 - (\pi/4)|_x - (\mathrm{ACQ})|_{\pm x},$$

one can study the decay of the created quadrupolar order. It can be shown that the magnetization in the x-channel of the receiver after the 3 pulse sequence is [27]:

$$\langle I_x(t)\rangle = \frac{\mathrm{d}}{\mathrm{d}t} G(t')|_{t'=\tau_1} \frac{\mathrm{d}}{\mathrm{d}t'} G(t')|_{t'=t},$$

where $G(t)$ represents the free induction decay after a $\pi/2$ pulse. The maximum transfer of Zeeman into quadrupolar order occurs at a time τ_1, where the FID after a $\pi/2$ pulse shows an inflection point. The second delay in the pulse sequence, τ_2, is a variable relaxation delay. All R_{1Q} values were calculated from peak heights obtained at 10 or more different τ_2 values in the Jeener-Broekaert pulse sequence. The errors in the R_{1Z} and R_{1Q} rate measurements are estimated to be less than 5 and 10%, respectively.

The tetraphenylborate compounds were prepared by reaction of sodium tetraphenylborate and the appropriate deuterated amine hydrochloride in aqueous solution. Sodium tetraphenylborate (99 + % pure) and dimethyl-d_6 amine-HCl were purchased from Aldrich Chemical Company Inc. Methyl-d_3 amine-HCl, tetramethyl-d_{12} amine-HCl and D_2O were obtained from MSD Isotopes.

IV. Results and Discussion

i) Tetramethyl-d_{12} Ammonium Tetraphenylborate

Recently Ratcliffe and Ripmeester [17] used ^{2}H nmr to investigate the reorientation processes involving the tetramethylammonium cation in a series of solid salts. The main conclusion of this study was that on heating the samples from low temperature, the onset of methyl C_3 rotations frequently occurs after the onset of whole ion reorientation. They found that the activation energy for methyl group rotation is generally larger than 17 kJ mol^{-1} in tetramethylammonium salts and that lower activation energies indicate the presence of other reorientation processes. Our ^{2}H T_{1Z} results for tetramethylammonium tetraphenylborate are summarized in Figure 3. In the temperature region of 137–385 K we obtained an apparent activation energy of 14.1 ± 0.5 kJ mol^{-1}. Because this value of E_a is somewhat smaller than the barrier that one would expect for methyl group rotation, we assume it corresponds to a barrier for overall reorientation of the cation. The ^{2}H nmr lineshape was isotropic over the complete temperature range investigated, 137–385 K, and exhibited a linewidth of only 2 kHz at the lowest temperature. The implication is that even

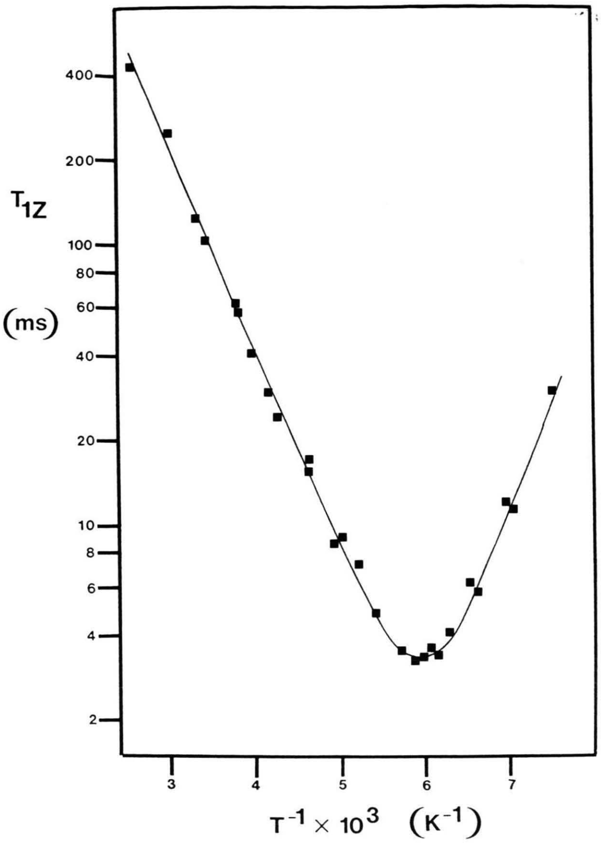

Fig. 3. Deuterium Zeeman relaxation times for the tetramethylammonium ion in tetramethyl-d_{12} ammonium tetraphenylborate as a function of reciprocal temperature.

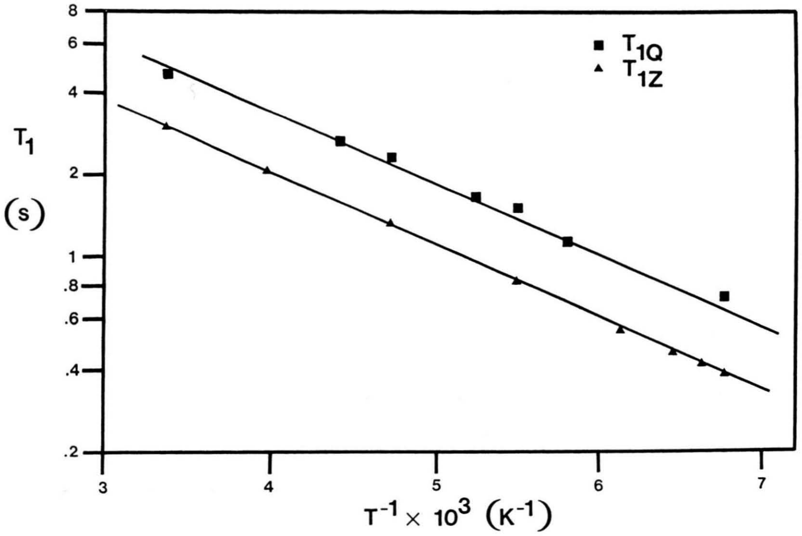

Fig. 4. Deuterium Zeeman (T_{1Z}) and quadrupolar (T_{1Q}) relaxation times for the ammonium ion in ammonium-d$_4$ tetraphenylborate as a function of reciprocal temperature.

at 137 K, $\tau_{T_d} \ll \chi^{-1}$ (6×10^{-6} s); note that only rapid tetrahedral jumps about any two of the four equivalent C_3' axes of the whole ion are necessary to average the quadrupolar splitting to zero (alternatively jumps about the three equivalent C_2 axes or numerous combinations of C_2 and C_3' jumps will result in an isotropic lineshape).

It is of interest to briefly discuss the $T_{1,\min}$, 3.6 ± 0.2 ms, observed in Figure 3. If one assumes that the motion of the $(CD_3)_4N$ ion is best described by slow methyl group jumps superimposed on rapid tetrahedral jumps of the whole ion, i.e., $\tau_{C_3} \gg \tau_{T_d}$ the Zeeman relaxation rate can be expressed as

$$R_{1Z} = (3/10)\,\pi^2 \langle \chi^2 \rangle \cdot \left\{ \frac{\tau_{T_d}}{1+(\omega_0 \tau_{T_d})^2} + 4\,\frac{\tau_{T_d}}{1+4(\omega_0 \tau_{T_d})^2} \right\}. \tag{11}$$

The Lorentzian sum at the right hand side of (11) has a maximum at $\omega_0 \tau = 0.6158$. From this we calculate a ^{2}H QCC of 151 ± 5 kHz. This value is lower than the values obtained from line shapes at 69–77 K by Ratcliffe and Ripmeester [17], which are typically 168 kHz, for various tetramethylammonium salts. Assuming $\tau_{C_3} = \tau_{T_d}$, substitution of $T_{1,\min}$ and $J(\omega)$ (9) into (3) results in a slightly larger value of χ, 152.7 kHz. If one makes the unreasonable assumption that methyl group rotations are much faster than whole ion rotations, i.e., $\tau_{C_3} \lesssim 10^{-2} \tau_{T_d}$, then $\chi \simeq 160$ kHz. The low value that one obtains for χ from the $T_{1,\min}$ probably results from the fact that librational motions are not considered in deriving the relaxation expressions. This type of motion can cause additional averaging of the ^{2}H QCC and adds to the spectral density [28]. The relatively weak electrostatic interactions between the large tetramethylammonium and tetraphenylborate ions are expected to result in a shallow reorientation potential in which rapid librational motions are possible. This hypothesis is supported by the large thermal ellipsoids observed in the x-ray study of $(CH_3)_4N\,B(C_6H_5)_4$ (see Fig. 2 in [2]).

ii) Ammonium-d$_4$ Tetraphenylborate

The crystal structure of this compound shows that the ammonium ions can rotate in a cage with site symmetry D_{2d} and have only small distortions from T_d symmetry [3]. The IR study by Westerhaus et al. [3] indicated a relatively large amount of rotational freedom for the ammonium ion. This is strengthened by our ^{2}H relaxation results, presented in Figure 4. These observations allow us to use an isotropic reorientation model, due to fast C_3 and C_2 flips, for the interpretation of the relaxation rates. The data in Fig. 4 are clearly in the extreme narrowing limit; $\omega_0 \tau_{T_d} \ll 1$. Thus the Zeeman and quadrupolar relaxation rates are

$$R_{1Z} = (3/2)\,\pi^2 \langle \chi^2 \rangle\, \tau_{T_d}, \tag{12a}$$

$$R_{1Q} = (9/10)\,\pi^2 \langle \chi^2 \rangle\, \tau_{T_d}. \tag{12b}$$

For this model the theory predicts a temperature independent ratio of $R_{1Z}/R_{1Q} = 5/3$. This is, within experi-

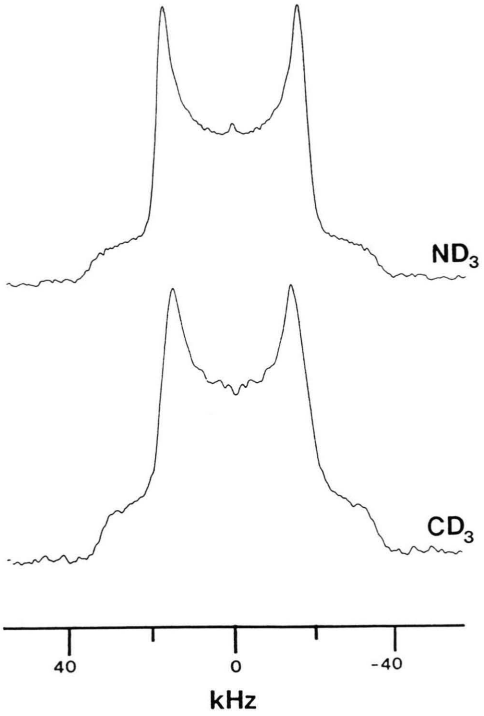

Fig. 5. Quadrupolar echo spectra of specifically deuterated methylammonium tetraphenylborate at 298 K.

Table 1. Activation energies for reorientation of ammonium ions in salts with monovalent anions from ^{2}H nmr relaxation data.

Ammonium Salt	E_a	Phase or Temp. Range	Ref.
ND_4Cl	19.7 kJ mol^{-1}	CsCl	[7]
ND_4Br	15.1	CsCl	[8]
ND_4I	3.2, 3.5	cubic	[9, 10]
	10.9, 12.5	tetragonal	[9, 10]
ND_4NCS	17.1	monoclinic	[11]
ND_4NO_3	10.7	tetragonal $T < 200$	[12]
$ND_4B(C_6H_5)_4$	5.0	tetragonal	this study
ND_4ClO_4	4.0	orthorhombic	[13]

mental error, what we observe. We conclude that over the temperature range of 148–298 K, the spectral density of the motion can indeed be described by one effective correlation time τ_{T_d}. The activation energy for this process is 5.0 ± 0.5 kJ mol^{-1}. The activation energy for ammonium ion reorientation in several other salts where the anion has unit charge is given in Table 1. The low value of E_a for $ND_4B(C_6H_5)_4$ is consistent with the observations of Westerhaus et al. [3], who interpreted their results in terms of weak ammonium ion-phenyl ring interactions, but it is more than one order of magnitude larger than the rotational barrier reported by Roberts and Strauss [4].

iii) Methylammonium Tetraphenylborate

Both the ND_3CH_3 and NH_3CD_3 derivatives were studied at 298 K. The ^{2}H nmr powder spectra of both compounds (Fig. 5) indicate non-isotropic averaging of the ^{2}H EFG. For a deuterium nucleus in a stationary X–D bond the frequency separation between the two allowed nmr transitions is given by

$$\Delta\nu = (3/4)\sqrt{\langle\chi^2\rangle}(3\cos^2\theta - 1), \qquad (13)$$

where θ is the angle between the largest principal component of the EFG tensor (along the X–D bond) and the applied static magnetic field B_0. In a powder sample, averaging over the powder angles results in a characteristic Pake doublet with a peak-to-peak splitting of $(3/4)\sqrt{\langle\chi^2\rangle}$. Any motion of the X–D bond about a rotation axis with threefold or higher symmetry will modulate the frequency separation given by (13). If the angle between the X–D bond and the rotation axis is β, the quadrupolar splitting is reduced by a factor $P_2(\cos\beta)$, where P_2 is the second order Legendre polynomial [29], i.e., $(3\cos^2\beta - 1)/2$. The overall lineshape of the powder spectrum is not influenced by motion provided the time scale of the motion is much smaller than χ^{-1}, however the breadth of the spectrum is reduced when such motion is present. For rapid C_3 jumps or diffusion of three equivalent deuterium nuclei in an XD_3 group about a stationary C_3 axis, (13) predicts a Pake doublet with splitting $(3/4)\chi(1/3)$, assuming tetrahedral geometry. Note that the asymmetry parameter for the motionally averaged lineshape is zero even if the static lineshape has $\eta \simeq 0.1$ for each of the equivalent deuterium nuclei [30, 31]. For the $CD_3NH_3^+$ ion we assume $\chi = 168$ kHz, $\eta = 0.06$ (the values obtained in several tetramethylammonium salts [17]); therefore one would expect a splitting of 42 kHz. This anticipated splitting is close to the value of 41.6 kHz measured in $CD_3NH_3ClO_4$ [32] at 100 K. The observed splitting in $CD_3NH_3B(C_6H_5)_4$ of 29.1 kHz at 298 K and 34.2 kHz at 158 K implies substantial librational motion of the methyl group in addition to jumps or rotations about a C_3 axis. The ^{2}H nmr lineshape of the CD_3NH_3 moiety (see Fig. 5) is clearly asymmetric. We attribute this asymmetry to large angle librations of the CD_3 group [33–35]. Spectral asymmetry in ^2H nmr lineshapes of rotating $-XD_3$ groups can also arise from non-equivalence in the static χ values for each of the ^2H nuclei [34–36]. Although such asymmetry has been observed for CD_3 and ND_3 groups in the presence of highly polar groups it is not expected to be important in the tetraphenylborate salts.

The ^2H nuclear quadrupolar coupling constant for the ND_3 group in $CH_3ND_3B(C_6H_5)_4$ is unavailable. Because the ND_3 group can participate in hydrogen bonding, the value of χ is expected to be quite dependent on the nature of the anion-cation interactions. In methylammonium perchlorate, where anion-cation interactions are relatively weak, Jurga and Spiess observed a ^2H quadrupolar splitting of 42 kHz at approximately 100 K, implying $\chi(ND_3) \simeq 168$ kHz [32]. Assuming a similar value for $\chi(ND_3)$ in the tetraphenylborate salt, the data in Table 2 lead one to conclude that the librational motions of the ND_3 group are somewhat more restricted than those of the CD_3 group. This conclusion is also supported by the lack of asymmetry observed in the ^2H spectrum of $CH_3ND_3B(C_6H_5)_4$ (Figure 5).

In order to determine the nature of the CD_3 and ND_3 rotations in the methylammonium tetraphenylborates we have measured Zeeman relaxation rates at 158 K and 295 K (Table 2). Since $R_{1Z}(\theta = 0°) > R_{1Z}(\theta = 90°)$ and $\omega_0 \tau \ll 1$, the data indicate a dominance of C_3 jumps as opposed to diffusion about a C_3 axis [20, 30]. The measurement of $R_{1Z}(\theta = 90°)$ is complicated because both the $\theta = 35.3°$ and $\theta = 90°$ orientations contribute to the 90° discontinuity in the Pake doublet. In the case of diffusion, the rate of spin-lattice relaxation of the powder pattern is independent of orientation [20].

Finally it is important to recognize the time-scale for C_3 jumps of the methylammonium cation. The T_{1Z} values are 4.40 s and 6.58 s, respectively, for the ND_3 and CD_3 groups at 298 K, implying τ values in the ps time scale. Also, if $\chi(ND_3) \simeq \chi(CD_3)$ then $\tau_{CD_3} < \tau_{ND_3}$; that is the methyl groups have a slightly shorter correlation time than the ND_3 groups which are probably involved in weak hydrogen bonding with the aromatic rings of the anions. Regardless of the assumptions regarding the magnitude of χ, it is clear that the frequency of C_3 jumps for the ND_3 and CD_3 groups are similar and on the ps time-scale. Also, the activation energies for ND_3 and CD_3 groups are equal within experimental error, 4.1 ± 0.5 kJ mol^{-1} and 4.2 ± 0.5 kJ mol^{-1}, respectively. These low activation energies measured for the methylammonium cation in methylammonium tetraphenylborate are comparable to those reported for C_3 reorientation in methylammonium perchlorate, 3.6 kJ mol^{-1} (ND_3 group) and 4.3 kJ mol^{-1} (CD_3 group) [32]. Small E_a values for NH_3 and CH_3 reorientation were also derived from ^1H nmr [37]. Typically much larger E_a values have been reported for NH_3 and CH_3 rotations in simple methylammonium salts, see e.g., [38–40].

Table 2. Relaxation rates and doublet splittings for the methylammonium ion in methylammonium tetraphenylborate.

T(K)	$^2H_3NCH_3$ R_{1Z} (s^{-1})		$H_3NC^2H_3$ R_{1Z} (s^{-1})	
	$\theta = 90°$	$\theta = 0°$	$\theta = 90°$	$\theta = 0°$
295	0.227	0.282	0.152	0.222
158	0.962	1.282	0.685	0.926

T(K)	Splitting (kHz)	T(K)	Splitting (kHz)
295	32.6 ± 0.5	295	29.1 ± 0.5
260	33.9	–	–
228	35.1	230	31.2
189	36.0	189	32.9
158	36.9	158	34.2

iv) Dimethylammonium Tetraphenylborate

Deuterium nmr spectra of dimethylammonium-d_2 tetraphenylborate, $(CH_3)_2ND_2B(C_6H_5)_4$, at 145 K and 325 K are shown in Figure 6. The low temperature spectrum represents that of a static $N-{}^2H$ bond and could be simulated with $\chi = 170 \pm 5$ kHz. The extra intensity observed in the centre of the spectrum may result from partial saturation because of the short recycle time used in acquiring the spectrum. The spectrum obtained at 325 K indicates rapid two site exchange between sites separated by an angle of $2\beta = 103° \pm 1°$ (*vide infra*). That is, the dimethylammonium cation undergoes jumps about a C_2 axis which bisects the H–N–H bond angle.

Deuterium nmr spectra of the methyl deuterium labelled dimethylammonium tetraphenylborate, $(CD_3)_2NH_2B(C_6H_5)_4$ are shown in Figure 7. At 245 K the quadrupolar splitting is 37 ± 0.5 kHz, consistent with rapid methyl C_3 jumps. The high temperature spectrum at 320 K indicates the presence of

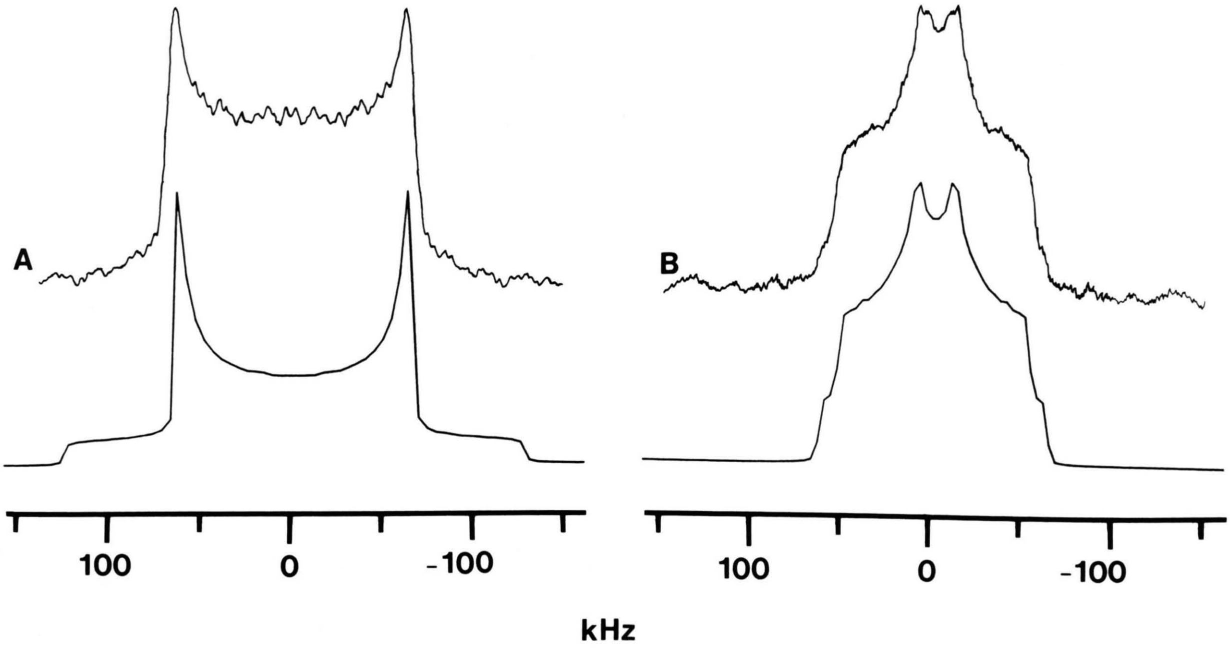

Fig. 6. Deuterium line shapes of dimethylammonium-d$_2$ cations in $(CH_3)_2ND_2B(C_6H_5)_4$ at 145 K (A) and 325 K (B). Both spectra were simulated with a QCC of 170 kHz, and $\eta = 0$. Spectrum B was simulated assuming fast C_2 jumps with a jump angle, 2β, of 103°.

rapid C_2 jumps in addition to the methyl group C_3 jumps.

From the $T = 320$ K spectrum of the dimethyl-d$_6$ ammonium cations, the C–N–C bond angle can be estimated. To interpret this spectrum, the C_3 flip averaged largest principal component of the ^{2}H EFG tensor will be assumed to coincide with the z-axis of the coordinate system shown in Figure 8. As EFG tensor components transform as 2$^{\text{nd}}$ rank spherical harmonics, it is most convenient to define the y-axis of the jump averaged frame ($= y^J$) perpendicular to the C–N–C plane. The jump angle 2β thus coincides with the C–N–C bond angle. It can be shown that the relation between the flip averaged and "static" components of the EFG tensor are given by [34, 41, 42] (see Fig. 8):

$$\begin{aligned} V^J_{xx} &= V_{zz}\sin^2\beta + V_{xx}\cos^2\beta, \\ V^J_{yy} &= V_{yy}, \\ V^J_{zz} &= V_{zz}\cos^2\beta + V_{xx}\sin^2\beta. \end{aligned} \tag{14}$$

The simulation in Fig. 7 was performed with $2\beta = 118.4° \pm 0.5°$. Details of the simulation are given in the legend of Figure 7. All spectra were simulated without a finite pulse correction. Similar values, 116.8° and 119.0°, were obtained for the C–N–C bond angles in the dimethylammonium tin and tellurium hexachloride salts, respectively from ^{2}H nmr [43]. The C–N–C bond angle in $[(CH_3)_2NH_2]_2SnCl_6$ from ^{2}H nmr [43] is in excellent agreement with the value determined from x-ray diffraction, 116.9° ± 0.5° [44].

The ^{2}H nmr lineshapes of $(CD_3)_2NH_2B(C_6H_5)_4$ between 250 K and 300 K (see Figs. 7c and d) are unusual in that they appear to result from the superposition of two different lineshapes: one from cations in which the methyl groups perform rapid C_3 jumps (i.e., the 245 K spectrum) and the other from cations where both the methyl groups rotate and the cation itself rapidly jumps about a C_2 axis (i.e., the 320 K spectrum). The implication is that there is a temperature dependent distribution of sites where the cation is rigid except for methyl C_3 flips and where the cation performs rapid C_2 flips in addition to methyl C_3 flips. The spectra in this temperature range could not be simulated assuming C_2 flips at rates comparable to χ^{-1} [30, 41]. This behaviour of the dimethylammonium cation contrasts with that recently observed in the tin and tellurium hexachloride salts, where Ikeda

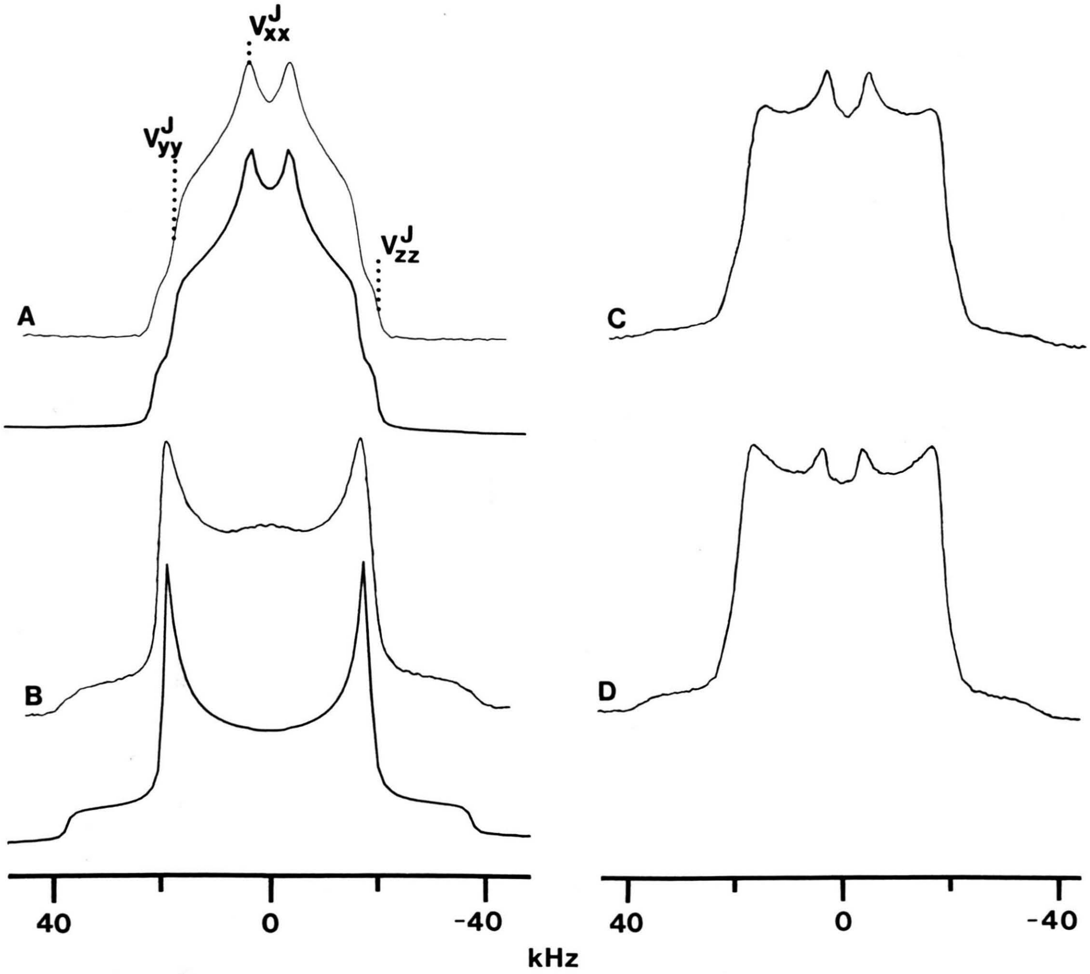

Fig. 7. Deuterium quadrupolar echo spectra of dimethyl-d_6 ammonium tetraphenylborate at 320 K (A), 245 K (B), 275 K (C) and 270 K (D). Spectrum A was simulated with a QCC of 45.8 kHz, a jump angle $2\beta = 118.4°$ and a fast exchange between the sites. Spectrum B was simulated with a QCC of 50.0 kHz. In (A) the principal components V^J_{ii} in the jump averaged frame are indicated. Both simulations were performed with $\eta = 0$.

et al. [41] clearly observed spectra due to $(CD_3)_2NH_2$ cations performing C_2 flips at rates comparable to χ^{-1} (the intermediate exchange regime).

The ^2H Zeeman spin-lattice relaxation times of the dimethyl-d_6 ammonium ions between 298 and 355 K are shown in Figure 9. The relaxation times were measured on the V_{xx} discontinuity (see Figure 7). No abrupt change in T_1 was observed in this temperature range, suggesting that a phase transition is unlikely. Between 215 and 245 K the ^2H Zeeman spin-lattice relaxation times showed an activation energy of 9.4 ± 2.0 kJ mol^{-1}. This value compares well with the energy barrier for methyl group C_3 jumps of 13 kJ mol^{-1} observed in dimethylammonium nitrate [45].

v) Trimethylammonium Tetraphenylborate

Both the trimethyl-d_9 ammonium $(CD_3)_3NH$, and the trimethylammonium-d_1, $(CH_3)_3ND$, cations were studied by ^2H nmr. The deuterium resonance of the $(CH_3)_3ND$ ion showed a doublet splitting of 112 kHz at 294 K. This value is close to 124 kHz expected for a static N$-^2$H bond. The difference in these values indicates small angle wobbling of the N$-^2$H bond [30]. This is consistent with x-ray crystallographic

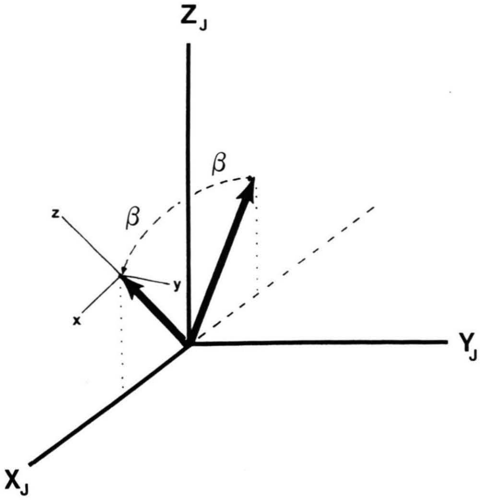

Fig. 8. Representation of the two site exchange process using two different coordinate frames. The J-superscripted axes refer to the jump frame and the second frame is used as a reference for the methyl C_3 flip averaged frame.

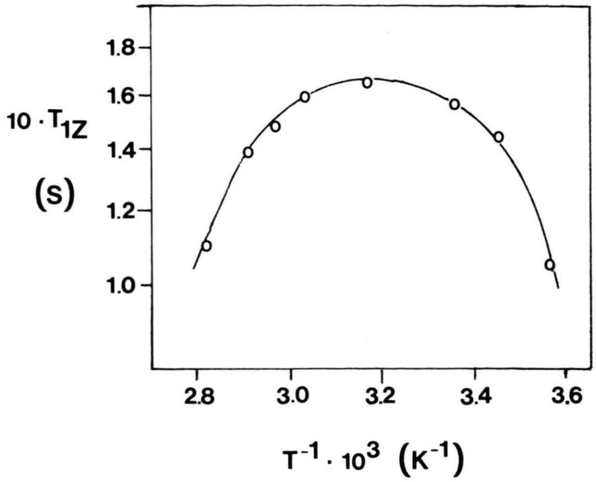

Fig. 9. Deuterium Zeeman spin-lattice relaxation times (T_{1Z}) as a function of reciprocal temperature for the dimethyl-d_6 ammonium cation in $(CD_3)_2NH_2B(C_6H_5)_4$.

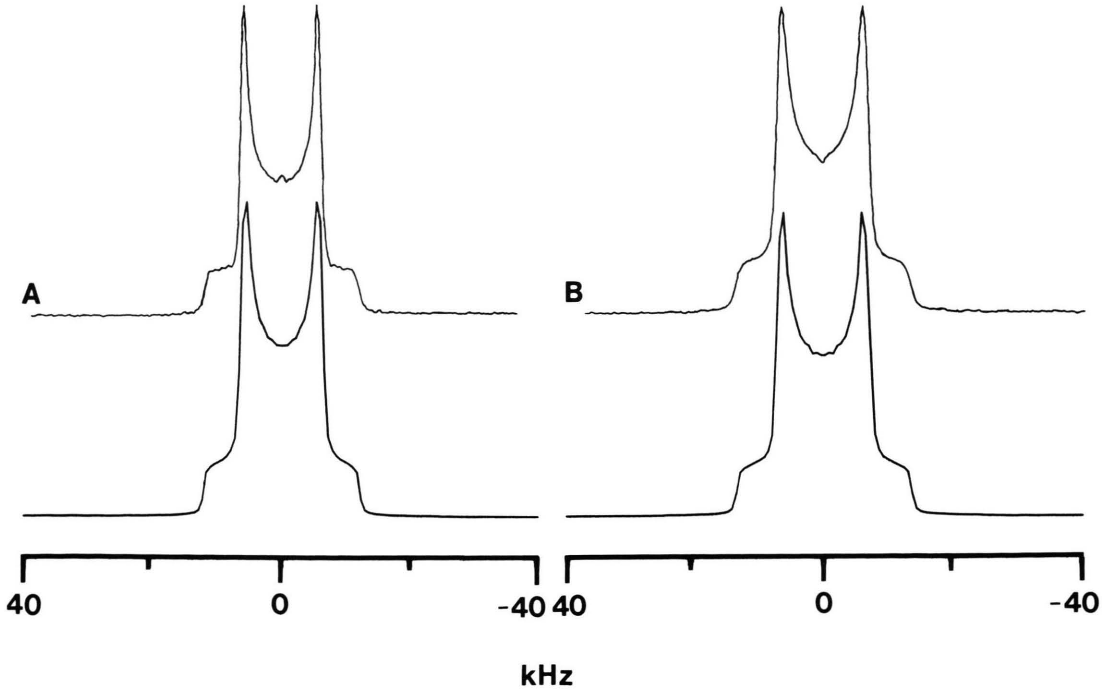

Fig. 10. Deuterium line shapes of trimethyl-d_9 ammonium tetraphenylborate at 296 K (A) and 185 K (B). The simulations of both spectra used fast C_3 and C_3' flips resulting in a motionally averaged QCC of 17.3 kHz and 19.5 kHz for A and B respectively, with $\eta = 0$. In addition, a two site exchange motion was included with flip angles of $12 \pm 1°$ and $13 \pm 1°$ for A and B, respectively.

results which show rather large thermal ellipsoids on the carbon atoms compared with values normally encountered [46]. The vibrationally averaged QCC amounts to 150 ± 5 kHz [16]. This value is close to that obtained for the $C-{}^2H$ bond in the tetramethyl-d_{12} ammonium ion in part *i.*

The ^2H line shape of the trimethyl-d_9 ammonium ion is shown in Fig. 10 at 296 and 185 K. At both temperatures the EFG is motionally averaged due to a superposition of fast methyl C_3 and cation C'_3 motions. The spectra could, however, only be simulated assuming small-angle two-site exchange in addition to the C_3 and C'_3 motions. This motion can account for the observed spectral asymmetry of $\eta = 0.07 \pm 0.01$ at both temperatures. The presence of this additional motion was also observed in x-ray data as mentioned above. Details of the spectral simulations are given in the legend of Figure 10. Using the values of the V_{yy} EFG components (see Fig. 7), values of the QCC of the $C-{}^2H$ bond can be obtained since V_{yy} is not affected by the two site exchange. Assuming fast C_3 and C'_3 flips, a QCC of 156 ± 5 and 175 ± 6 kHz is obtained from the 296 and 185 K ^2H spectra, respectively. The QCC obtained from the 185 K ^2H spectrum is in good agreement with values reported for $C-{}^2H$ bonds in other molecules [16, 17]. The assumption of fast C_3 and C'_3 flips is justified since Zeeman spin-lattice relaxation experiments indicate that $\omega_0 \tau \ll 1$. Also, no change in ^2H lineshape at 185 K was observed upon changing the quadrupolar echo delay from 40 µs to 140 µs. Between 296 and 348 K the relaxation data indicate that the overall molecular reorientation occurs with an activation energy of $20.1 \pm 2.0\ \mathrm{kJ\ mol^{-1}}$. This value agrees well with activation barriers obtained for the C'_3 motion of trimethylammonium ions in $[(CH_3)_3ND]_2MX_6$ (M = Pt, Sn, Te and X = Cl, Br) [47].

Conclusion

In this study we have demonstrated the utility of ^2H nmr lineshape and relaxation measurements in characterizing the dynamic disorder in ammonium tetraphenylborate and a series of methylammonium tetraphenylborates. In the parent compound, $ND_4B(C_6H_5)_4$, the nmr data indicate that the ammonium ion reorientates rapidly in a symmetric potential in which cation-anion interactions are relatively weak. However, the activation energy for reorientation of the ammonium ion determined in this study, $5.0\ \mathrm{kJ\ mol^{-1}}$, is substantially greater than the rotational barrier reported in a recent infrared study [4]. The tetramethylammonium ion also undergoes rapid overall reorientation in the cavity formed by the phenyl rings of the tetraphenylborate anion. The ^2H $T_{1Z,\min}$ determined in the latter compound is slightly longer than anticipated. It is suggested that this discrepancy arises because the librational motions of the cation are neglected in the relaxation model.

For the less symmetrical methyl-substituted ammonium tetraphenylborates the ^2H nmr data lead to the following conclusions:

1. Between 158 K and 295 K the CD_3 and ND_3 groups of the monomethylammonium salt undergo rapid C_3 jumps about the C–N axis; however, motion of the symmetry axis is restricted to large amplitude librations.
2. Between 215 K and 245 K the methyl groups of the dimethylammonium salt undergo rapid C_3 jumps about their respective C–N axes. Above 320 K the complete cation also executes rapid C_2 jumps about its C_2 axis. Further studies using other physical techniques will be required to establish the detailed behaviour of the dimethylammonium salt between 250 K and 300 K.
3. In the trimethylammonium salt, the complete cation jumps about the N–H axis over the entire temperature range investigated (185 K–348 K). In addition, the methyl group jumps about their C_3 axes and the N–H axis undergoes large amplitude librations.

Acknowledgements

We would like to thank Professor K. R. Jeffrey, Professor O. Knop, and members of the x-ray diffraction and nmr groups at Dalhousie for helpful discussions, Professor R. G. Griffin, Professor R. J. Wittebort, and Dr. R. Weber for providing us with copies of the deuterium lineshape simulation program described in reference [30], and William P. Power for adapting the program to our computer system. Also, we wish to thank Professor C. A. McDowell for a preprint of [43], and Deanna Cosman and Colleen Slaunwhite for their assistance in preparing this manuscript. Finally, we are grateful to NSERC of Canada for financial support.

[1] S. Arnott and S. C. Abrahams, Acta Crystallogr. **11,** 449 (1958).
[2] K. Hoffmann and E. Weiss, J. Organometal. Chem. **67,** 221 (1974).
[3] W. J. Westerhaus, O. Knop, and M. Falk, Can. J. Chem. **58,** 1355 (1980).
[4] M. P. Roberts and H. L. Strauss, J. Phys. Chem. **91,** 4241 (1987).
[5] D. A. Johnson, J. Chem. Soc. Dalton Trans. 445 (1988).
[6] N. G. Parsonage and L. A. K. Staveley, Disorder in Crystals, Clarendon, Oxford 1978.
[7] D. E. Woessner and B. S. Snowden, J. Phys. Chem. **71,** 952 (1967).
[8] D. E. Woessner and B. S. Snowden, J. Chem. Phys. **47,** 2361 (1967).
[9] A. R. Sharp and M. M. Pintar, J. Chem. Phys. **53,** 2428 (1970).
[10] L. Niemelä and E. Ylinen, Annls. Acad. Sci. Fenn., Ser. A **VI,** 307 (1969).
[11] M. L. H. Gruwel, G. Facey, and R. E. Wasylishen, J. Chem. Phys. **85,** 6240 (1986).
[12] L. Niemelä and T. Lohikainen, Phys. Kondens. Mater. **6,** 376 (1967).
[13] T. J. Bastow, R. J. C. Brown, and S. L. Segel, J. Chem. Phys. **89,** 1203 (1988).
[14] A. Abragam, The Principles of Nuclear Magnetism Oxford University Press, Oxford 1961.
[15] See for instance (i) J. H. Davis, Biochim. and Biophys. Acta **737,** 117 (1983), (ii) H. W. Spiess, J. Chem. Phys. **72,** 6755 (1980) and (iii) J. P. Jacobsen, H. K. Bildsøe, and K. Schaumberg, J. Magn. Reson. **23,** 153 (1976).
[16] R. J. Wittebort and A. Szabo, J. Chem. Phys. **69,** 1722 (1978).
[17] C. I. Ratcliffe and J. A. Ripmeester, Can. J. Chem. **64,** 1348 (1986) and references therein.
[18] M. J. Hunt and A. L. MacKay, J. Magn. Reson. **15,** 402 (1974).
[19] J. C. Pratt, A. Watton, and H. E. Petch, J. Chem. Phys. **73,** 2542 (1980).
[20] D. A. Torchia and A. Szabo, J. Magn. Reson. **49,** 107 (1982).
[21] D. Wallach, J. Chem. Phys. **47,** 5258 (1967).
[22] O. Edholm and C. Blomberg, Chem. Phys. **42,** 449 (1979).
[23] R. Freeman, S. P. Kempsell, and M. H. Levitt, J. Magn. Reson. **38,** 453 (1980).
[24] J. H. Davis, K. R. Jeffrey, M. Bloom, M. I. Valic, and T. P. Higgs, Chem. Phys. Lett. **42,** 390 (1976).
[25] J. Jeener and P. Broekaert, Phys. Rev. **157,** 232 (1967).
[26] K. R. Jeffrey, Bull. Magn. Reson. **3,** 69 (1980).
[27] A. Abragam and M. Goldman, Nuclear Magnetism, Order and Disorder, Oxford University Press, Oxford 1982.
[28] E. R. Henry and A. Szabo, J. Chem. Phys. **82,** 4753 (1985).
[29] H. Margenau and G. M. Murphy "The Mathematical Principles of Physics and Chemistry", 2nd ed., D. van Nostrand Comp. Inc., Princeton, N. J., 1967.
[30] R. J. Wittebort, E. T. Olejniczak and R. G. Griffin, J. Chem. Phys. **86,** 5411 (1987).
[31] D. A. Torchia and A. Szabo, J. Magn. Reson. **64,** 135 (1985).
[32] S. Jurga and H. W. Spiess, Z. Naturforsch. **40a,** 602 (1985).
[33] A. Kintanar, T. M. Alam, W.-C. Huang, D. C. Schindele, D. E. Wemmer, and G. Drobny, J. Amer. Chem. Soc. **110,** 6367 (1988).
[34] R. G. Barnes in "Advances in Nuclear Quadrupole Resonance", edited by J. A. S. Smith, Vol. 1, p. 335, Pergamon, New York 1974.
[35] Y. Hiyama, S. Roy, K. Guo, L. Butler, and D. A. Torchia, J. Amer. Chem. Soc. **109,** 2525 (1987).
[36] M. A. Jackisch, W. L. Jarrett, K. Guo, F. R. Fronczek and L. G. Butler, J. Amer. Chem. Soc. **110,** 343 (1988).
[37] H. Ishida, R. Ikeda, and D. Nakamura, Bull. Chem. Soc. Japan **60,** 467 (1987).
[38] H. Ishida, R. Ikeda, and D. Nakamura, Bull. Chem. Soc. Japan **55,** 3116 (1982).
[39] H. Ishida, R. Ikeda, and D. Nakamura, Bull. Chem. Soc. Japan **59,** 915 (1986).
[40] H. Ishida, R. Ikeda, and D. Nakamura, J. Phys. Chem. **86,** 1003 (1982).
[41] M. G. Taylor, E. C. Kelusky, I. C. P. Smith, H. L. Casal, and D. G. Cameron, J. Chem. Phys. **78,** 5108 (1982).
[42] (a) C. M. Gall, T. A. Cross, J. A. DiVerdi, and S. J. Opella, Proc. Natl. Acad. Sci., USA **79,** 101 (1982). – (b) G. C. Leo, L. A. Colnago, K. G. Valentine, and S. J. Opella, Biochem. **26,** 854 (1987).
[43] R. Ikeda, A. Kubo, and C. A. McDowell, to be published.
[44] (a) O. Knop, T. S. Cameron, M. A. James, and M. Falk, Can. J. Chem. **61,** 1620 (1983). – (b) M. H. Ben Ghozlen, A. Daoud, and J. W. Bats, Acta Cryst. **B37,** 1415 (1981).
[45] H. Ishida, R. Ikeda, and D. Nakamura, Ber. Bunsenges. Phys. Chem. **90,** 598 (1986).
[46] O. Knop, S. Roe, A. Linden, and T. S. Cameron, private communication.
[47] R. Ikeda, R. Kadel, A. Weiss, N. Ishida, and D. Nakamura, Ber. Bunsenges. Phys. Chem. **86,** 685 (1982).