

Deuteron NMR Spectra of ND_4 Tunneling at Low Frequencies in $(\text{ND}_4)_2\text{SnBr}_6$

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Z. Naturforsch. **50a**, 373–380 (1995); received September 26, 1994

Dedicated to Professor W. Müller-Warmuth on the occasion of his 65th birthday

Deuteron NMR spectra of slowly tunneling ND_4^+ ions are analysed. Spectra are calculated as functions of the tunneling parameters which are the tunneling frequencies about the symmetry axes C_2 and C_3 of the tetrahedral ion. The structure and splittings within the ground torsional level (GTL) are obtained by fitting the spectra of $(\text{ND}_4)_2\text{SnBr}_6$. Comparison with the GTL structure obtained before for NH_4^+ in the same compound gives the isotope reduction factor of the tunneling frequency about 200.

Key words: Tunneling rotation, Ammonium ion, ^2H -NMR spectroscopy, Molecular dynamics.
PACS number 76.60

1. Introduction

NMR spectroscopy is one of the methods used to study molecular dynamics in solids. The shape of NMR spectra results from the magnetic hyperfine interactions between spins, the spectral features being related to the arrangement of spins in space and the mobility of the system.

We have considered systems of protons ($I = 1/2$) or deuterons ($I = 1$) in solid, diamagnetic nonconducting compounds. In evaluating the spectra we restrict ourselves, respectively, to dipole-dipole or quadrupole interactions. The dipole-dipole interaction of nuclear dipole moments couples all spins of a system. The quadrupole interaction of a nuclear quadrupole moment with an electric field gradient (EFG) has a single particle character. Isotope substitution, i.e. observation of both protonated and deuterated systems allows making use of the characteristic differences between these spin interactions. Rigid systems of N protons are identified by characteristic features in the NMR spectra of powder samples for $N = 2, 3$, and 4, whereas for higher N the structure is lost [1]. On the other hand any number of deuterons in a rigid system gives a single doublet spectrum, provided no differences in the EFGs exist.

A detailed study of molecular reorientations is based on their specific averaging effects on the spectra, which reflect specific transformation properties of the respective interactions. The ammonium ion in many low barrier ammonium salts exhibits quantum rotation at low temperatures, also called tunneling. As a consequence the ground torsional level (GTL) is split into sublevels labelled by irreducible representations of the tetrahedral point group T : A, E, and 3 T. One can find different degeneracies of the sublevels and different splittings between them depending on the shape of the three-dimensional barrier. The splittings vary approximately exponentially with the barrier height. Inclusion of tunneling requires formal quantum mechanical treatment of space coordinates. The symmetrised wavefunctions of a multispin molecule may be labelled with the irreducible representations of the molecular symmetry group. Except for diatomic molecules, states of different symmetry are coupled by molecular hyperfine interactions. This is of basic importance not only for spin conversion and relaxation processes, but also for the spectra. The NMR spectra of the tunneling ammonium ion may be calculated using a time-independent theory involving space and spin coordinates of protons. It was shown how the NMR spectra are useful in studying tunneling and determining the GTL structure [2]. The tunneling splittings can be determined by the proton NMR spectra only in the range: $10^0 \div 10^5$ Hz [3].

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For one dimensional rotation the torsional energy levels may be calculated from the Mathieu equation with a potential $V_n = \frac{V_0}{2}(1 - \cos n\alpha)$ [4]. In the case of the ammonium ion it may be applied only to one dimensional rotations about one of its four C_3 or three C_2 symmetry axes. In general, however, ammonium ions may experience a potential barrier of greatly varying height and symmetry and thus perform more complex motions, both in the tunneling rotation and reorientation ranges. A very thorough discussion of a tetrahedron in a cubic crystalline field may be found in the paper by King and Hornig [5]. Smith developed numerical methods of obtaining GTL structures for low-symmetry potentials (e.g. [6] and references therein). Unfortunately, his results suffer considerably from complexity and convergence problems in the calculations, as well as from the idealized form of potentials.

Already a long time ago Knispel *et al.* [7] noticed that two kinds of ^2H -NMR spectra can be observed from polycrystalline deuterated ammonium compounds at helium temperatures. One possibility is a so-called Pake doublet with a 135 kHz separation of the two horns. It is observed in the presence of a high barrier, i.e. when the ND_4^+ ions are rigid. On the other hand, narrow, asymmetric spectra were obtained at the resonance frequency ν_0 of 6.1 MHz for $(\text{ND}_4)_2\text{SnCl}_6$, providing evidence for tunneling rotation. Later on theoretical low field spectra were calculated for the tunneling ND_4^+ ion [8]. Despite of difficulties in performing the measurements, low field spectra may have some applications [14].

A group theoretical approach was applied to the GTL structure of the ND_4^+ ion [9]. Expressions for GTL energy sublevels were written in terms of parameters representing tunneling frequencies about separate C_3 and C_2 symmetry axes. The tunneling parameters depend on respective planar cross-sections of a three-dimensional potential. Neither the potentials nor the tunneling splittings are known, so we treat the tunneling parameters as unknown parameters. It makes the problem of NMR spectra of tunneling ND_4^+ ions tractable. The dependence of the spectra on the splittings within the librational ground state multiplet supplies representative cases [9]. Subsequent comparison with experimental spectra allows a direct identification of the GTL, and splittings may also be deduced in some cases.

In comparison to NH_4^+ the tunneling splitting for the ND_4^+ ion is strongly reduced because of the larger moment of inertia. The isotope effect is given by the ratio of the tunneling splitting of the NH_4^+ ion to that of the ND_4^+ ion ($X = \nu_t^{\text{H}}/\nu_t^{\text{D}}$). This ratio was theoretically predicted to be in the range of $50 \div 5000$ depending on the torsional frequency of the ion [10]. Deuteron NMR spectroscopy is till now the unique method to measure the tunneling splittings for the ND_4^+ ion. Preliminarily level-crossing effects in the spin-lattice relaxation [11] and spectra [12] were used for this purpose. Recently NMR spectroscopy at strong magnetic fields was applied. Analysis of ^2H -NMR spectra of the ND_4^+ ion tunneling in a tetrahedral potential was already presented for single crystals [13] and powder samples [14]. Methods to measure tunneling frequencies in the $0.1 \text{ MHz} < \nu_t < 20 \text{ MHz}$ range were outlined for $(\text{ND}_4)_2\text{SnCl}_6$ as an example, but the methods are also applicable to other cubic compounds. These are characterised by the (A, 3 T, E) GTL structure and the tunneling frequency is defined by the A to 3 T splitting. The obtained spectra are symmetric and have two A doublets in the centre as the dominating feature. Tunneling splittings up to about 10 MHz can be derived directly by comparing the splittings of these doublets with respective ones in theoretical spectra. This method was applied with success to study a single crystal of $(\text{ND}_4)_2\text{SnCl}_6$, where $\nu_t = 7.1 \text{ MHz}$ was obtained [13], and a powder sample of $(\text{ND}_4)_2\text{TeCl}_6$ with $\nu_t = 1.5 \text{ MHz}$ [15]. Small splittings within the T levels manifold were also derived from the angular dependence of the T spectral components [16].

Most of the ammonium salts have a crystal symmetry lower than cubic. Low symmetry barriers lead to other GTL structures at low temperatures and to complex reorientations at higher temperatures [17]. There is a need for more data on tunneling frequencies and crystalline potentials. Except for a few cases accessible to high resolution neutron scattering [18], in all remaining cases the GTL structure for NH_4^+ may be obtained only from NMR spectra. NMR remains the only method in the ND_4^+ case, as the tunneling splitting is always reduced beyond the resolution of INS methods. Deuteron NMR spectra of ND_4^+ tunneling in lower than tetrahedral crystalline fields do not have clearly distinguishable symmetry species components. Nevertheless a GTL structure can be directly recognized from the shape of the deuteron spectra, however an estimation of the tunneling splittings can be achieved only by fitting the whole spec-

trum. Representative examples of both 2H -NMR single crystal and powder spectra were given for various GTL structures in [9]. The sensitivity to ν_i is illustrated and various GTL structures are identified.

We have chosen $(\text{ND}_4)_2\text{SnBr}_6$ as an example for a low symmetry potential. Two phase transitions have been found in $(\text{NH}_4)_2\text{SnBr}_6$ at 157 K and 144 K [19–23]. The high temperature cubic antiferroite structure changes to a tetragonal intermediate phase and further to a monoclinic structure at low temperatures. The temperature dependence of the proton spin-lattice relaxation time T_1 was measured down to 60 K and an activation energy $E_a = 1.44$ kcal/mol was obtained in the low temperature phase [24].

Some information about the ground torsional level structure of the NH_4^+ ions has also been obtained. The relaxation time T_1 was measured for a single crystal of $(\text{NH}_4)_2\text{SnBr}_6$ at 20 K in a wide range of magnetic fields. Several level-crossing T_1 minima were found. These led to establishing of the following splittings: 4.6 MHz between T–2T levels and 31 MHz between A–T levels [25].

Nuclear spin diffusion was also measured in $(\text{NH}_4)_2\text{SnBr}_6$. Zeeman reservoirs of spin species reach a common spin temperature in a time at least two orders of magnitude shorter than T_1 [26].

II. Theoretical Principles

In the case of ^2H -NMR spectra of deuterated ammonium ions we can limit ourselves to Zeeman, tunneling, quadrupole and dipole-dipole contributions:

$$\mathcal{H} = \mathcal{H}_Z + \mathcal{H}_T + \mathcal{H}_Q + \mathcal{H}_D. \quad (1)$$

Zeeman and tunneling Hamiltonians give rise to zeroth order energies in spin and space coordinates, respectively. Quadrupole and dipole interactions, bilinear in both coordinates, are acting as perturbations.

The calculation of the NMR spectra is based in our treatment on numerical solution of the eigenvalue problem for the general Hamiltonian (1). Here we only briefly report on the treatment of tunneling and calculations of spectra; more details can be found in [9].

The ammonium ion has a form of a regular tetrahedron with four nuclear spins at the apices and a nitrogen in the center, which is taken as space-fixed. There is no evidence of any distortion. The point group T has 12 elements, which are rotations about three C_2

and four C_3 space fixed symmetry axes. Splittings within the GTL depend on the tunneling parameters and reflect both strength and symmetry of a crystalline field experienced by the ammonium ion.

A single particle wavefunction $\phi_i(\gamma)$ describes the localization probability of a particle on an apex (γ) of the tetrahedron, pointing into the direction of the C_3^i (CRF) axes. A simple product wavefunction $\phi(E) = \phi_1(a)\phi_2(b)\phi_3(c)\phi_4(d)$ describes a ground spatial configuration. Symmetry rotations change the position of the tetrahedron in space and they are equivalent to permuting $(abcd)$, $C_2^Z \phi(E) = \phi_1(b)\phi_2(a)\phi_3(d)\phi_4(c) = \phi(C_2^Z)$. By applying the various symmetry operations, we move about between indistinguishable space states, which are, however, no eigenstates of \mathcal{H} . Similarly we may define simple product spin wavefunctions $\psi_i^M = m_1(a)m_2(b)m_3(c)m_4(d)$, where $M = \sum_i m_i$.

There are 12×81 space-spin simple products. On this basis we may construct convenient linear combinations which have to be invariant under molecular symmetry rotations. A wavefunction

$$\bar{\psi}_i^M = \frac{\sqrt{3}}{6} \sum_{i=1}^{12} \phi(P_i) \psi_i^M(P_i), \quad (2)$$

has the required symmetry.

We may define four expectation values of the tunneling Hamiltonian related to rotations about four C_3^i axes:

$$\Delta(i) = \langle \phi(P_n) \psi_i^M(P_j) | \mathcal{H}_T | \phi(P_m) \psi_k^M(P_k) \rangle, \quad (3)$$

where $P_m = C_3^i P_n$ and $P_k = C_3^i P_j$, and three rotations about C_2^a axes:

$$\Pi(\alpha) = \langle \phi(P_n) \psi_i^M(P_j) | \mathcal{H}_T | \phi(P_m) \psi_k^M(P_k) \rangle, \quad (4)$$

where $P_m = C_2^a P_n$ and $P_k = C_2^a P_j$.

The tunneling Hamiltonian describes a degree of overlap between ND_4^+ wavefunctions of neighbouring pocket states. With regard to \mathcal{H}_T we assume here only that it gives an expectation value between states related by a feasible rotation of the ammonium ion. Tunneling parameters (3) and (4) will be adjusted in order to fit experimental spectra.

At high magnetic fields only the secular part of the quadrupole Hamiltonian is relevant. It may be written as

$$\begin{aligned} \mathcal{H}_Q^i &= h \nu_Q Q_{20} V_{20} \\ &= \frac{h C_Q}{8} [3 I_Z^i I_Z^i + I(I+1)] (3 \cos^2 \Theta_i - 1), \quad (5) \end{aligned}$$

where Θ_i is the angle between the symmetry axis of the axially symmetric EFG tensor and \mathbf{B}_0 , and C_Q is the quadrupole coupling constant.

The Hamiltonian (5) is diagonal in the simple product representation and the spectrum may be calculated directly. It would represent a sum of spectra of four noninteracting, motionless deuterons.

The secular part of the dipole-dipole interaction

$$\bar{\mathcal{H}}_D = \sum_{i,j} \frac{\mu_0}{16\pi} \gamma_D^2 \hbar r_{i,j}^{-3} [I_Z^i I_Z^j - \frac{1}{4}(I_+^i I_-^j + I_-^i I_+^j)] (3 \cos^2 \Theta_{ij} - 1), \quad (6)$$

where Θ_{ij} is the angle between \mathbf{r}_{ij} and \mathbf{B}_0 , fills the diagonal submatrices of the general Hamiltonian with offdiagonal terms. The contribution of the Hamiltonian (6) to the eigenenergies of the system is relatively small.

Peculiarities of the quadrupole Hamiltonian, explaining features observed in the spectra, may be followed conveniently when it is written in a symmetry adapted form:

$$\begin{aligned} \bar{\mathcal{H}}_Q &= \sum_{i=1}^4 \bar{\mathcal{H}}_Q^i = \frac{1}{4} \sum_{G=A, T_X, T_Y, T_Z} B_G^0 S_G^0 \\ &= \frac{1}{4} \sum_G \left(\sum_{i=1}^4 a_G^i Q_{20}^i \right) \left(\sum_{i=1}^4 a_G^i V_{20}^i \right), \end{aligned} \quad (7)$$

where

$$\begin{pmatrix} a_A^i \\ a_{T_X}^i \\ a_{T_Y}^i \\ a_{T_Z}^i \end{pmatrix} = \begin{pmatrix} 1 & 1 & 1 & 1 \\ 1 & -1 & 1 & -1 \\ -1 & 1 & 1 & -1 \\ 1 & 1 & -1 & -1 \end{pmatrix}. \quad (8)$$

We may express V_{20}^i in a suitable common molecular reference frame (MRF) and observe that $\sum_i V_{20}^i = 0$ due to the tetrahedral symmetry. Therefore not only E, but also A terms are not present in (4) and the respective levels are not shifted by the quadrupole interaction in first order.

Second order corrections

$$\delta E_k^G = \sum_{G'} \sum_l |\langle \Psi_{Gk}^M | \bar{\mathcal{H}}_Q | \Psi_{G'l}^M \rangle|^2 / (E_k^G - E_l^{G'}). \quad (9)$$

exhibit a hyperbolic dependence on the tunneling frequency $-\hbar \nu_t = (E_k^G - E_l^{G'})$, whereas expectation values in the numerator differ from zero only for (A, T), (T, E) and (T_u, T_w) pairs of (G, G') symmetry subscripts, provided the T levels are nondegenerate. These cause a fine, tunneling dependent structure of the spectra.

Many GTL structures to be considered exhibit various degrees of degeneracy and an adequate perturbation theory approach would be required. Application of numerical methods gives accurate solutions in every case. Numerous representative examples were given elsewhere [9], where all interested may also find a more detailed discussion of the calculations of the tunneling ND_4^+ spectra.

III. Experimental Results

Ammonium hexabromostannate was prepared by mixing concentrated solutions of ammonium bromide and tin(IV) bromide in 47% hydrobromic acid. A pale yellow precipitate was obtained. Deuteration was performed by solving the precipitate twice in heavy water containing DBr. The deuteration level was estimated to be 99.6%.

A Bruker MSL-300 pulsed NMR spectrometer was used together with a Thor superconducting magnet for measurements of the deuteron spectra at 38 MHz. A homemade immersion cryostat was employed to cool a two-cylinder NMR probehead. The temperature was changed by controlled heating of the inner cylinder containing the sample.

Several hundreds of FID signals following a short ($\sim 1 \mu\text{s}$), small angle pulse were accumulated and spectra had been obtained after the Fourier transform using a standard FFT procedure.

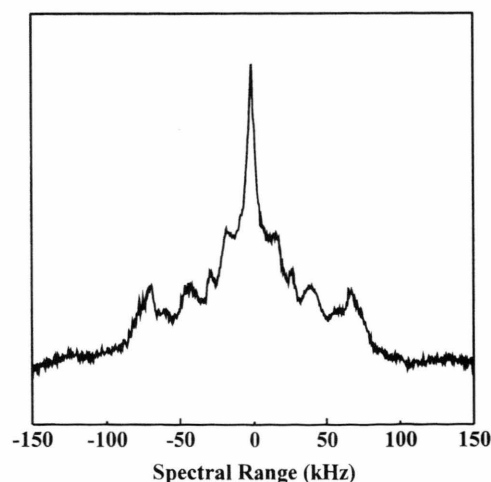


Fig. 1. ^2H -NMR powder spectrum of $(\text{ND}_4)_2\text{SnBr}_6$ measured at 38 MHz and 4.2 K.

The spectrum obtained from a powder sample of $(\text{ND}_4)_2\text{SnBr}_6$ at helium temperature, after a waiting time of 5 hours, is shown in Figure 1. It shows features characteristic of slow tunneling of ammonium ions. It falls in the category of slightly deformed tetrahedral field, as its shape can be compared with those in Figs. 7b and 8b of [9].

Up to about 30 K no changes in the spectra were observed. The spectra at higher temperatures are shown in Figure 2. A decreasing amplitude of the innermost doublet is observed and it finally disappears at 34 K. Subsequently other doublets also undergo motional narrowing and the central narrow component grows up. At about 45 K the fast reorientation limit has been reached.

IV. Fitting Procedure

We calculated series of spectra changing step by step the tunneling parameters Δ and π and looked for a shape fitting the experimentally observed spectrum at 4.2 K. The computer program described in [9] has been used.

We begin with the tetrahedral field case and assume that all Δ parameters are equal. Although the GTL structure of ammonium ions in $(\text{NH}_4)_2\text{SnBr}_6$ is not exactly (A-3T-E) [25], the splittings within the T manifold are expected to be relatively small in the deuterated compound, so we may find a spectrum quite similar to the A-3T-E case. Some spectra representing such a tetrahedral potential are given in Figure 3. Some similarity can be recognized in the spectrum of Fig. 3b and the experimental one. We now fix three Δ parameters at the respective value and increase the fourth one. It represents a slight trigonal distortion of the threedimensional potential. The corresponding spectra are shown in Figure 4. Whereas the central doublets do not change very much the outer parts evolve in the wrong direction. The separations of the three central doublets appear to be quite close to the experimental values. Now in order to amplify the outer parts of the spectrum we decrease all parameters step by step while keeping their difference as in the case of Figure 4a. As a satisfactory result we

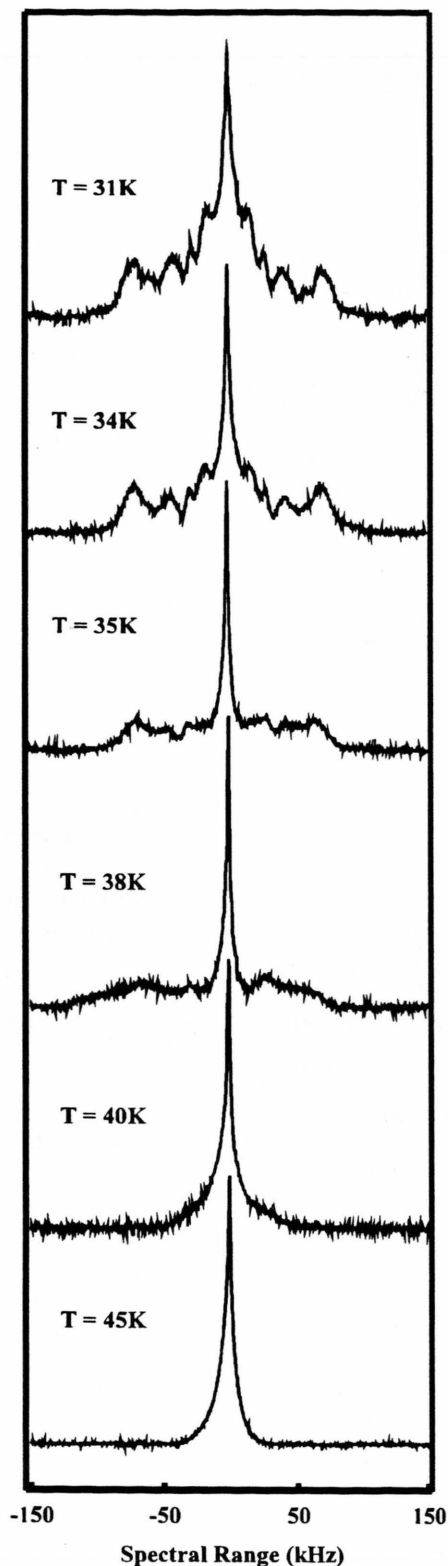


Fig. 2. ^2H -NMR spectra of $(\text{ND}_4)_2\text{SnBr}_6$ measured at 38 MHz and different temperatures in the motional narrowing range.

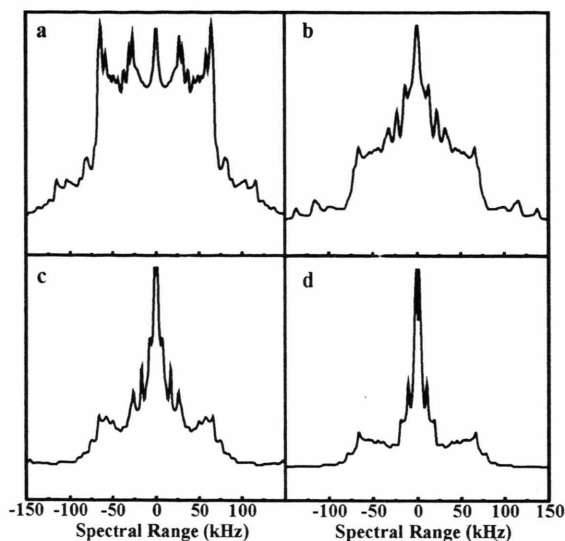


Fig. 3. ^2H -NMR spectra of ND_4^+ ions tunneling in a tetrahedral potential calculated for increasing tunneling parameters: a) $\Delta = \Delta(4) = 10$ kHz, b) $\Delta = \Delta(4) = 20$ kHz, c) $\Delta = \Delta(4) = 30$ kHz, d) $\Delta = \Delta(4) = 50$ kHz.

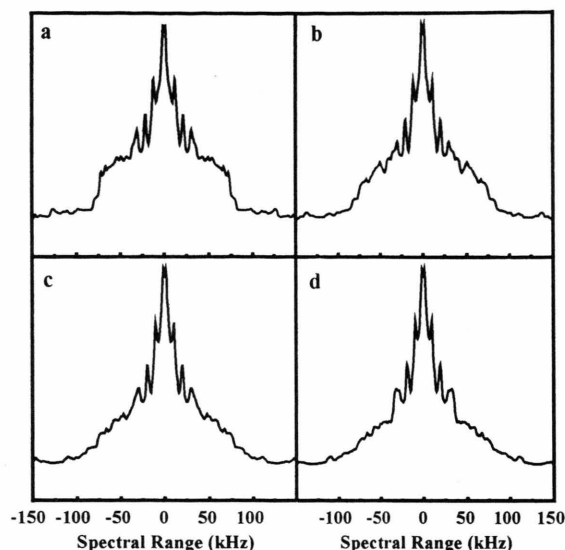


Fig. 4. ^2H -NMR spectra of ND_4^+ calculated for increasing trigonal distortion of the potential and the following tunneling parameters: a) $\Delta = 20$ kHz, $\Delta(4) = 25$ kHz, b) $\Delta = 20$ kHz, $\Delta(4) = 30$ kHz, c) $\Delta = 20$ kHz, $\Delta(4) = 35$ kHz, d) $\Delta = 20$ kHz, $\Delta(4) = 40$ kHz.

consider the one of Figure 5a. Finally we introduce the tunneling parameter π , which has to be kept low, but introduces some changes in the shape of spectra (Figure 5b–d).

We have in this case the following relations between the tunneling parameters and tunneling splittings:

$$\begin{aligned} E_T - E_A &= -8\Delta - 4\pi, \\ E_{2T} - E_A &= -3\Delta(4) - 5\Delta - 4\pi, \\ E_E - E_A &= -3\Delta(4) - 9\Delta. \end{aligned} \quad (10)$$

As the final result we obtained the following parameters: $\Delta(4) = 20$ kHz, $\Delta = \Delta(1) = \Delta(2) = \Delta(3) = 13$ kHz, $\pi = \pi_x = \pi_y = \pi_z = 1$ kHz. These lead to the spectrum in Fig. 6 and the GTL structure and splittings in Figure 7. Comparing the tunneling splittings for protonated and deuterated compounds we obtain the isotope reduction factors $X = 219$ for the T levels splitting and $X = 287$ for the A–T tunneling splitting.

The quality of fits is judged basically by eye, however adjusting the position of separate peaks in the spectrum is the first and most discriminating step. The spectra show a different sensitivity to the tunneling parameters Δ and π . With increasing tunneling splitting some spectral components are shifted away from

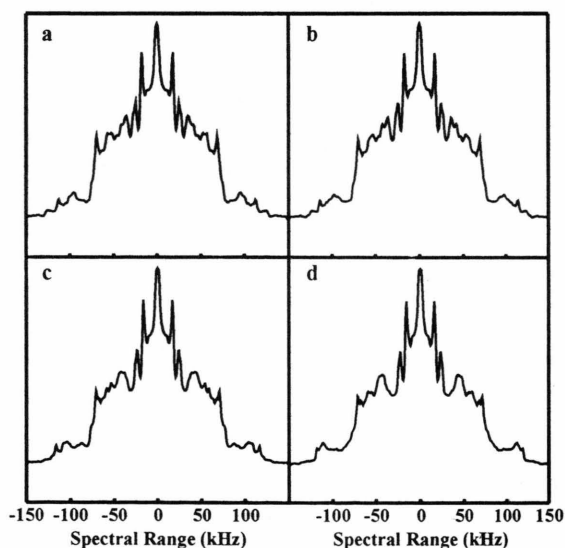


Fig. 5. ^2H -NMR spectra of ND_4^+ calculated for the following tunneling parameters: a) $\Delta = 15$ kHz, $\Delta(4) = 20$ kHz, b) $\Delta = 15$ kHz, $\Delta(4) = 20$ kHz, $\pi = 1$ kHz, c) $\Delta = 15$ kHz, $\Delta(4) = 20$ kHz, $\pi = 3$ kHz, d) $\Delta = 15$ kHz, $\Delta(4) = 20$ kHz, $\pi = 5$ kHz.

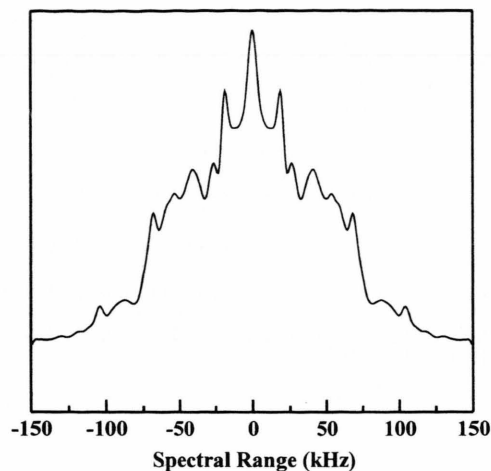


Fig. 6. Calculated ^2H -NMR spectrum of tunneling ND_4^+ ions representing the best-fit to the experimental spectrum of Figure 1. Tunneling parameters $\Delta = 13$ kHz, $\Delta(4) = 20$ kHz, $\pi = 1$ kHz had been used.

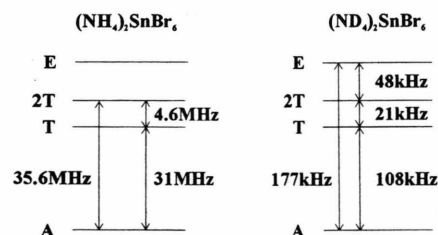


Fig. 7. Comparison of the GTL schemes of NH_4^+ and ND_4^+ in ammonium hexabromostannate.

the frequency range in which we see the spectra. It puts the upper limit of obtainable tunneling splittings to about 200 kHz. Larger A–T tunneling splittings may be obtained using a different procedure [13, 14]. It concerns analysis of separations within a multiplet in the center of the spectra.

V. Conclusions

Tunneling frequencies depend approximately exponentially on the height of the barrier, however also the slope in the overlap region plays a role. The tunneling parameters Δ and Π reflect the shape of a cross-section through the three-dimensional potential in a plane perpendicular to the axis. We may introduce representative GTL structures into our calculations by varying the tunneling parameters, the value of at most four of which may be found in this way.

The isotope substitution by deuteration doubles the moment of inertia of the ammonium ion, thus leading to a significant, barrier dependent reduction of the tunneling frequency. It was so far assumed that all splittings within a GTL structure are reduced by the same isotope factor $X = v_t^H/v_t^D$. That may not be generally true. The (A–T) and (T–T) tunneling splittings may be reduced by significantly different isotope factors, as already indicated in [16].

One naturally expects structural conclusions to be drawn based on the obtained GTL structure. It was found, however, that the shape of a barrier is not usually consistent with the point symmetry of the crystal. Ammonium ions, both protonated and deuterated may exhibit different GTL structures in salts belonging to the same crystallographic class. Possible differences increase with decreasing activation energy. Only in a few cases a clear correspondence was observed [13]. This indicates that we may expect from an analysis of ^2H -NMR spectra information only about the local symmetry of a barrier.

Acknowledgements

This project was generously financed by the State Committee for Scientific Research (Poland) grant no. 203649101. We are grateful to Dr. A. Birczyński, who participated in measurements and contributed to the discussions over all those years.

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