

Semiclassical analysis of the nuclear-magnetic-resonance absorption of a tetrahedrally coordinated four-spin-1/2 system*

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A semiclassical theory of proton magnetic-resonance absorption of the NH_4^+ ion in solids is presented. In this theory, the lattice variables are treated as classical functions of time, while the nuclear spins are treated quantum mechanically. No effects of the exclusion principle are considered. Theoretical spectra are calculated in the limit of fast motion, when the NH_4^+ ion is either rotating uniformly or undergoing random reorientations about a single, fixed symmetry axis. If the ion is assumed to reorient rapidly about a single C_3 axis, a satisfactory agreement between theoretical and experimental spectra is obtained for NH_4VO_3 at 77 K. The theoretical line shape also agrees quite well with the experimental line shape of NH_4I at 4 K, if the NH_4^+ ion is considered to be rotating around a fixed C_4 axis with a single frequency equal to 1.5 times the NH_4 dipolar frequency. It is shown that this "classical" frequency, which causes satellites to appear in the absorption spectrum, is a measure of the torsional ground-state splitting of the NH_4^+ ion in the crystal field.

I. INTRODUCTION

The low-temperature NMR absorption line shape of a tetrahedrally coordinated four-proton spin group has been studied by a number of authors. Bersohn *et al.*¹ calculated the line shape for a system of four protons, the so-called four-spin- $\frac{1}{2}$ system, in an ammonium ion NH_4^+ in order to explain the proton absorption line shape in a single crystal of NH_4Cl at 77 K. Their work explained well the "rigid"-lattice proton absorption spectrum of a strongly hindered NH_4 group in which the protons are distinguishable during the characteristic time of the experiment. In an experimental study of a number of ammonium compounds, Richards *et al.*² found that in some lattices the proton line shape of the NH_4 group did not become a rigid-lattice spectrum even at 20 K. It was concluded that in these solids, thermal reorientation was still effective in narrowing the proton absorption line at this temperature. It was shown later that this interpretation is not satisfactory in all cases reported.

To explain the narrow absorption line observed in solid methane (CH_4) at 1.3 K, Tomita³ considered that the total spin of the four methane protons was a good quantum number (nuclear spin isomerism). Since the methane molecule and ammonium ion are structurally very similar, it was thought that the spin isomerism might be responsible for the relatively narrow proton absorption line observed in some ammonium salts at low temperatures. A study of the proton line shapes at 4.2 K was undertaken⁴ on several ammonium compounds to investigate the possibility of nuclear spin isomerism in the ammonium ions. It

was pointed out that the four-spin- $\frac{1}{2}$ and nuclear-spin-isomeric pictures are just two limiting cases of proton distinguishability. The four-spin- $\frac{1}{2}$ picture is valid when the protons are completely distinguishable during the characteristic time of the experiment, which is of the order of the inverse absorption linewidth ($\sim 2 \times 10^{-5}$ sec), while the concept of nuclear spin isomerism is valid when the protons are completely indistinguishable during this time. Since some of the measured absorption spectra showed distinct differences from the theoretical line shapes predicted for the spin-isomerism model, it was concluded that a theoretical study of the intermediate case of particle indistinguishability was necessary.

A great deal of attention was given to the experimental line shape of NH_4I at 4.2 K.^{5,6} This absorption spectrum showed pronounced structure in the wings which could not be explained by any theoretical model available. To explain this line shape Dunn *et al.*⁷ calculated the proton magnetic resonance line shapes of an ammonium ion undergoing quantum-mechanical tunneling through the potential barriers of different heights and symmetries. It was assumed that at 4.2 K, tunneling is appreciable only about the four threefold symmetry axes of the NH_4 tetrahedron. They chose the characteristic tunneling frequency ω_T as 8 G, and the interionic absorption line broadening as 4 G², and obtained good agreement with the experimental line shape of NH_4I . A similar calculation was performed by Watton *et al.*⁸ who based their calculation on the assumption that tunneling is possible about twofold and threefold symmetry axes simultaneously. The theoretical results compared well with the experimental line shapes at 4.2 K, when ω_T was 9.8 G

and the interionic broadening was 3.5 G^2 .

However, the experimental results obtained in this laboratory show that the proton absorption spectrum of NH_4I is independent of temperature from 1.4 to 45 K. Since the interactions of the NH_4^+ ion with the rest of the lattice become important at such high temperatures (45K) the experimental line shape should be reproducible also without using the concept of coherent tunneling. The following approach is used. The dynamic behavior of the " NH_4^+ -ion-lattice" system is approximated by assigning a certain time dependence to the orbital part of the dipolar Hamiltonian. The lattice variables are considered to be classical functions of time. At first the simplest case of the NH_4^+ ion rotating around a fixed symmetry axis is dealt with. The dipolar Hamiltonian is separated into a static part and a time-dependent part and the absorption spectrum is calculated using the time-dependent perturbation theory. Even in this simple model, good agreement between theoretical results and the experimental line shape of NH_4I is obtained if it is assumed that the NH_4^+ ion is rotating about a single C_4 axis with a frequency corresponding to 9G and that the interionic broadening is 3.2G^2 . It is clear that in this model, the frequency of the classical rotation corresponds to ω_r in the quantum-mechanical model.

At higher temperatures, more and more dynamic modes of the lattice are excited. It is then appropriate to treat the lattice variables in the dipolar Hamiltonian as random functions of time. The motionally narrowed absorption spectra are calculated in the case when the NH_4^+ ion is reorienting rapidly about a specified axis of rotation. The theoretical spectra are compared with the experimental absorption line shape of NH_4VO_3 in which the ammonium ion is strongly hindered. If in a lattice the NH_4 ion is weakly hindered, the symmetry considerations have to be introduced; i.e., the semiclassical approach becomes inappropriate.

II. FORMULATION OF THE PROBLEM

The total Hamiltonian of the system, including the rf field interaction term, is considered to be

$$\mathcal{H}(t) = \mathcal{H}_L + \mathcal{H}_Z + \mathcal{H}_D^0 + \mathcal{H}_{\text{rf}}(t). \quad (1)$$

\mathcal{H}_L is the energy operator of the lattice degrees of freedom. \mathcal{H}_Z is the Zeeman energy operator of the four-spin- $\frac{1}{2}$ system in the external dc magnetic field \vec{H}_0 and is given by

$$\mathcal{H}_Z = -\gamma \hbar \vec{H}_0 \cdot \vec{I}, \quad (2)$$

where

$$\vec{I} = \sum_{i=1}^4 \vec{I}_i$$

is the total spin operator and γ is the gyromagnetic ratio for proton. \mathcal{H}_D^0 is the time-independent (secular) part⁹ of the dipole-dipole interaction among the protons of the NH_4 group. This Hamiltonian may be written

$$\mathcal{H}_D^0 = K_D \sum_{i < j} U_{ij}^0 V_{ij}^0, \quad (3a)$$

where

$$V_{ij}^0 \equiv [I_i^0 I_j^0 - \frac{1}{4}(I_i^{+1} I_j^{-1} + I_i^{-1} I_j^{+1})], \quad (3b)$$

$$U_{ij}^0 \equiv -(\frac{16}{5}\pi)^{1/2} Y_2^0(\theta_{ij}, \phi_{ij}) = 1 - 3 \cos^2 \theta_{ij},$$

and $K_D \equiv \gamma^2 \hbar^2 / \gamma_0^3$. In the above, $Y_2^k(\theta, \phi)$ are normalized spherical harmonics, r_0 is the length of the vector \vec{r}_{ij} from the j th to the i th nucleus, and θ_{ij} and ϕ_{ij} are the polar angles specifying the direction of \vec{r}_{ij} . $\mathcal{H}_{\text{rf}}(t)$ represents the interaction between proton magnetic moments and the rf field $\vec{H}_1(t)$, applied along the x axis of the space-fixed coordinate system (x, y, z) . It has the form

$$\mathcal{H}_{\text{rf}}(t) = -\hbar \omega_1 I_x (e^{i\omega t} + e^{-i\omega t}), \quad (4)$$

where $\omega_1 = \gamma H_1$, ω is the frequency of the oscillating magnetic field, and I_x is the x component of the total spin operator.

The time-independent Schrödinger equation corresponding to Eq. (1) is

$$i\hbar \frac{\partial \psi(t)}{\partial t} = \mathcal{H}(t) \psi(t). \quad (5)$$

In the interaction picture representation

$$\psi'(t) = e^{(i/\hbar)\mathcal{H}_L t} \psi(t), \quad (6)$$

the equation for $\psi'(t)$ reads

$$i\hbar \frac{\partial \psi'(t)}{\partial t} = [\mathcal{H}_Z + \mathcal{H}_D^0(t) + \mathcal{H}_{\text{rf}}(t)] \psi'(t), \quad (7)$$

where $\mathcal{H}_D^0(t)$ is given by

$$\mathcal{H}_D^0(t) = e^{(i/\hbar)\mathcal{H}_L t} \mathcal{H}_D^0 e^{-(i/\hbar)\mathcal{H}_L t}. \quad (8)$$

At this point the following approximations are introduced:

(i) $\mathcal{H}_D^0(t)$ is considered as a classical function of time in lattice coordinates and as a quantum-mechanical operator in spin coordinates. That is $\mathcal{H}_D^0(t) = \mathcal{H}_D^0(q(t), \sigma)$, where q stands for lattice coordinates and σ for spin coordinates.

(ii) Since the evolution in time of $\psi(t)$ which is due to \mathcal{H}_L was transformed away, $\psi'(t)$ is approximated by a state vector in a 16-dimensional spin space of the four-spin- $\frac{1}{2}$ system under consideration. $\psi'(t)$ is replaced by $\psi_\sigma(t)$, where the subscript σ denotes the dependence on spin variables

only. The final form of the Schrödinger equation relevant to the present problem is

$$i\hbar \frac{\partial \psi_{\sigma}}{\partial t} = [\mathcal{H}_Z + \mathcal{H}_D^0(q(t), \sigma) + \mathcal{H}_{rf}(t)] \psi_{\sigma}. \quad (9)$$

The time dependence of \mathcal{H}_D^0 is introduced in the following way. In the body-fixed coordinate system (x', y', z') , in which the z' axis lies along either the C_2 or C_3 symmetry axis of the tetrahedron and which is rotated through the Euler angles¹⁰ α, β, γ with respect to the space-fixed coordinates (x, y, z) , U_{ij}^0 can be expressed in the form

$$U_{ij}^0 = -\frac{8\pi}{5} \sum_{m=-2}^2 Y_2^{m'}(\theta'_{ij}, 0) Y_2^{m'*}(\beta, \gamma) e^{im'\phi'_{ij}}. \quad (10)$$

The asterisk is the complex-conjugate symbol. The Euler angles α, β are identical to the polar angles ϕ, θ of the z' axis with respect to the coordinate system (x, y, z) . If the system is rotating or reorienting around the z' axis, the only quantity that is changing with time is $\phi'_{ij} = \phi'_{ij}(t)$. The word rotation is to be understood in the usual sense of classical mechanics, while reorientation means a random jumping from one orientation of the system to another with characteristic frequency of jumping. By reorientation around the C_4 axis we mean jumps by 90° around the C_2 axis, while the reorientation around the C_3 axis means 120° jumps around this axis. Consequently we can write

$$U_{ij}^0(t) = \langle U_{ij}^0 \rangle + F_{ij}(t), \quad (11)$$

where

$$\langle U_{ij}^0 \rangle = -\frac{8\pi}{5} Y_2^0(\theta'_{ij}, 0) Y_2^0(\beta, 0) \quad (12)$$

and

$$F_{ij}(t) = -\frac{8\pi}{5} \sum_{m \neq 0} Y_2^{m'}(\theta'_{ij}, 0) Y_2^{m'*}(\beta, \gamma) e^{im'\phi'_{ij}(t)}. \quad (13)$$

It should be noted that Eq. (12) is applicable when the ammonium ion rotates around C_2 or C_3 symmetry axes, or if it reorients around C_3 or C_4 axes. When the ion is undergoing jumps of 180° around a C_2 axis, the $m' = \pm 2$ terms in (13) are time independent; i.e.,

$$e^{\pm i2\phi'_{ij}(t)} = e^{\pm i2\phi'_{ij}(t)} = \text{const}$$

which adds an extra term to $\langle U_{ij}^0 \rangle$. Consequently $\langle U_{ij}^0 \rangle$ becomes

$$\langle U_{ij}^0 \rangle = -\frac{8\pi}{5} \pi [Y_2^0(\theta'_{ij}, 0) Y_2^0(\beta, 0) + 2Y_2^2(\theta'_{ij}, 0) Y_2^0(\beta, 0) \cos 2(\phi'_{ij} - \gamma)]. \quad (14)$$

Using the above results, the truncated dipolar Hamiltonian can be written

$$\mathcal{H}_D^0(t) = \langle \mathcal{H}_D^0 \rangle + V'(t), \quad (15)$$

where

$$\langle \mathcal{H}_D^0 \rangle = K_D \sum_{i,j} \langle U_{ij}^0 \rangle V_{ij}^0 \quad (16)$$

and

$$V'(t) = K_D \sum_{i,j} F_{ij}(t) V_{ij}^0. \quad (17)$$

The next step is to solve the eigenvalue equation

$$\mathcal{H}_0 | \alpha M \rangle = \hbar E(\alpha, M) | \alpha M \rangle, \quad (18)$$

where $\mathcal{H}_0 \equiv \mathcal{H}_Z + \langle \mathcal{H}_D^0 \rangle$. M is the total magnetic quantum number and α characterizes the dipolar correction to the Zeeman energy. The matrix elements $\langle \alpha M | \psi_{\sigma}(t) \rangle$ for transitions induced by the time-dependent perturbation

$$V(t) = V'(t) + \mathcal{H}_{rf}(t) \quad (19)$$

are calculated using the perturbation expansion of the time evolution operator $U(t, t_0)$,¹¹ where

$$\psi_{\sigma}(t) = U(t, t_0) \psi_{\sigma}(t_0). \quad (20)$$

Finally, the derived absorption spectra are obtained using the calculated transition probabilities per unit time for the various spectral lines.

It should be mentioned that no effects of the exclusion principle are included, even though the symmetry adapted spin states are used in Secs. III–IX. These states are used merely because of the simplifications in calculating the matrix elements. The effects of the lattice dynamics on the NMR line shape are introduced only through the prescribed time dependence of the dipole-dipole interaction.

III. EIGENFUNCTIONS AND EIGENVALUES OF THE TIME-INDEPENDENT PART \mathcal{H}_0 OF THE TOTAL HAMILTONIAN

Equation (18) can be rewritten introducing the Larmor frequency $\omega_0 = \gamma H_0$, which gives

$$E(\alpha M) = -\omega_0 M + \omega_D^0(\alpha M), \quad (21)$$

and consequently

$$\langle \mathcal{H}_D^0 \rangle | \alpha M \rangle = \hbar \omega_D^0(\alpha M) | \alpha M \rangle, \quad (22)$$

where $\hbar \omega_D^0(\alpha M)$ represents the dipolar shift of the corresponding Zeeman energy. We shall expand $| \alpha M \rangle$ in terms of the symmetry adapted spin states $| M \chi_i^R \rangle$ as given by Tomita.³ The symbol $M \chi_i^R$ represents the basis state belonging to the i th row of the R th irreducible representation of the point group T , and M is the eigenvalue of I^0 . Therefore

$$| \alpha M \rangle = \sum_{R,i} C_{R,i}^{(\alpha M)} | M \chi_i^R \rangle. \quad (23)$$

When we insert the above expansion into the Eq.

(22) and use the orthonormality property of the basis vectors,

$$\langle M' \chi_{i'}^{R'} | M \chi_i^R \rangle = \delta_{M', M} \delta_{R', R} \delta_{i', i},$$

we obtain immediately the secular determinant which gives the values for dipolar shifts of the Zeeman energy levels

$$|\langle M \chi_{i'}^{R'} | \langle \mathcal{H}_D^0 \rangle | M \chi_i^R \rangle - \hbar \omega_D^0(\alpha M) \delta_{R', R} \delta_{i', i} | = 0. \quad (24)$$

The constants $C_{R', i}^{(\alpha M)}$ are determined from equations

$$\sum_{R', i} C_{R', i}^{(\alpha M)} [\langle M \chi_{i'}^{R'} | \langle \mathcal{H}_D^0 \rangle | M \chi_i^R \rangle - \hbar \omega_D^0(\alpha M) \delta_{R', R} \delta_{i', i}] = 0. \quad (25)$$

The matrix elements in Eqs. (24) and (25) are

$$\langle M \chi_{i'}^{R'} | \langle \mathcal{H}_D^0 \rangle | M \chi_i^R \rangle = K_D \sum_{k < j} \langle U_{kj}^0 \rangle \langle M \chi_{i'}^{R'} | V_{kj}^0 | M \chi_i^R \rangle. \quad (26)$$

IV. TRANSITION AMPLITUDES AND TRANSITION PROBABILITIES PER UNIT TIME FOR THE SYSTEM ROTATING UNIFORMLY AROUND A FIXED SYMMETRY AXIS

Suppose that at the initial time t_0 the system is in an eigenstate $|\alpha M\rangle$ of \mathcal{H}_0 . The probability for transition to eigenstate $|\alpha' M - 1\rangle$, is

$$W_{(\alpha M) \rightarrow (\alpha' M - 1)} = |\langle \alpha' M - 1 | U(t, t_0) | \alpha M \rangle|^2, \quad (27)$$

where

$$\begin{aligned} \langle \alpha' M - 1 | U(t, t_0) | \alpha M \rangle \\ = \langle \alpha' M - 1 | U^{(1)}(t, t_0) + U^{(2)}(t, t_0) + \dots | \alpha M \rangle \end{aligned} \quad (28)$$

and

$$\langle \alpha' M - 1 | U^{(1)}(T, -T) | \alpha M \rangle = \left(-\frac{i}{\hbar} \right) e^{-i\psi T} (-2\hbar\omega_1) \langle \alpha' M - 1 | I_x | \alpha M \rangle \frac{\sin\{[E(\alpha' M - 1) - E(\alpha M) - \omega]T\}}{E(\alpha' M - 1) - E(\alpha M) - \omega},$$

where ψ is equal to $E(\alpha' M - 1) + E(\alpha M)$. With more algebra¹² one arrives at the following expression for the second-order amplitude in the limit of large T :

$$\begin{aligned} \langle \alpha' M - 1 | U^{(2)}(T, -T) | \alpha M \rangle = \left(-\frac{i}{\hbar} \right) e^{-i\psi T} (-2\hbar\omega_1) \sum_{m' \neq 0} \left(-\frac{K_D}{m' \hbar \omega_r} \right) \langle \alpha' M - 1 | [I_x, V_{Dm'}] | \alpha M \rangle \\ \times \frac{\sin\{[E(\alpha' M - 1) - E(\alpha M) - \omega + m' \omega_r]T\}}{E(\alpha' M - 1) - E(\alpha M) - \omega + m' \omega_r}. \end{aligned}$$

In the course of deriving this result the following assumptions and approximations were made: (a) The part of the rf interaction which is proportional to $e^{i\omega t}$ and is responsible for the absorption of energy from the spin system was neglected; (b) $E(\alpha' M - 1) - E(\alpha M) \approx \omega_0 \gg \omega_r$; (c) $\hbar\omega_r \gg K_D$; (d) $\lim_{T \rightarrow \infty} [\sin(m' \omega_r T) / m' \omega_r] = 0$ for $m' \omega_r \neq 0$, or in other words $\sin(m' \omega_r T) / (m' \omega_r)$ is very small for $\omega_r \gg 1/T$ (conservation of energy); (e) The terms in the second-order transition amplitude which cause the absorption of the rf energy at the same frequency as the first-order transition amplitude were neglected.

By using Eqs. (27) and (28), the transition probability becomes

$$U^{(0)}(t, t_0) = \exp[-(i/\hbar)\mathcal{H}_0(t, t_0)], \quad (29)$$

$$U^{(1)}(t, t_0) = \left(-\frac{i}{\hbar} \right) \int_{t_0}^t d\tau U^{(0)}(t, \tau) V(\tau) U^{(0)}(\tau, t_0), \quad (30)$$

$$\begin{aligned} U^{(2)}(t, t_0) = \left(-\frac{i}{\hbar} \right) \int_{t_0}^t d\tau \int_{t_0}^{\tau} d\tau' U^{(0)}(t, \tau) V(\tau) U^{(0)}(\tau, \tau') \\ \times V(\tau') U^{(0)}(\tau', t_0). \end{aligned} \quad (31)$$

The interaction Hamiltonian $V(t)$ was defined in Eq. (19).

When the NH_4^+ ion rotates around the z' axis with ω_r , we have

$$\phi'_{ij}(t) = \phi_{ij}^0 + \omega_r t. \quad (32)$$

When the spherical harmonics in Eq. (13) are written explicitly (Condon-Shortley phase), Eq. (17) becomes

$$V'(t) = K_D \sum_{m' \neq 0} V_{Dm'} e^{im' \omega_r t}, \quad (33a)$$

where

$$V_{Dm'} = \sum_{i < j} A_{ij}^{m'} V_{ij}^0 \quad (33b)$$

and

$$A_{ij}^{+1} = (A_{ij}^{-1})^* = -\frac{3}{4} \sin 2\theta'_{ij} \sin 2\beta e^{i(\phi'_{ij} - \gamma)}, \quad (34a)$$

$$A_{ij}^{+2} = (A_{ij}^{-2})^* = -\frac{3}{4} \sin^2 \theta'_{ij} \sin^2 \beta e^{i2(\phi'_{ij} - \gamma)}. \quad (34b)$$

Consequently the interaction $V(t)$ becomes

$$V(t) = K_D \sum_{m' \neq 0} V_{Dm'} e^{im' \omega_r t} - \hbar\omega_1 I_x (e^{i\omega t} + e^{-i\omega t}). \quad (35)$$

The first-order transition amplitude is found, using the preceding expressions, to be

$$W_{(\alpha M) \rightarrow (\alpha' M-1)} = 4\pi\omega_1^2 \left[|\langle \alpha' M - 1 | I_x | \alpha M \rangle|^2 \delta(\Omega(\alpha M, \alpha' M - 1) - \omega) + \sum_{m' \neq 0} \left(\frac{K_D}{m' \hbar \omega_r} \right)^2 |\langle \alpha' M - 1 | [I_x, V_{Dm'}] | \alpha M \rangle|^2 \delta(\Omega(\alpha M, \alpha' M - 1) + m' \omega_r - \omega) \right] T, \quad (36)$$

where Ω is introduced as

$$\Omega(\alpha M, \alpha' M - 1) = E(\alpha' M - 1) - E(\alpha M), \quad (37)$$

which is in the neighborhood of the Larmor frequency ω_0 . The probability of transition per unit time is

$$P_{(\alpha M) \rightarrow (\alpha' M-1)} \equiv \frac{dW_{(\alpha M) \rightarrow (\alpha' M-1)}}{dt} = \frac{W_{(\alpha M) \rightarrow (\alpha' M-1)}}{T}.$$

Equation (36) predicts an absorption spectrum consisting of a central line at the Larmor frequency ω_0 , and satellites at $\omega_0 \pm \omega_r$ and $\omega_0 \pm 2\omega_r$ whose amplitudes are reduced by factors of $(K_D/\hbar\omega_r)^2$ and $(K_D/2\hbar\omega_r)^2$, respectively. As the perturbation calculation is extended to higher order, further satellites are predicted, in agreement with the classical calculation¹³ which predicts an infinite series of satellites on each side of the central peak, centered at frequencies $\omega = \omega_0 \pm m\omega_r$, where m is an integer. The intensity of the satellites becomes smaller with increasing m . For this

reason, only a finite portion of the absorption spectrum around ω_0 is observed. Therefore if $(K_D/\hbar\omega_r)^2 \ll 1$, we can write

$$P_{(\alpha M) \rightarrow (\alpha' M-1)} = 4\pi\omega_1^2 |\langle \alpha' M - 1 | I_x | \alpha M \rangle|^2 \delta(\Omega(\alpha M, \alpha' M - 1) - \omega), \quad (38)$$

which gives the familiar motionally narrowed "Gutowsky-Pake" spectrum.¹⁴

V. TRANSITION AMPLITUDES AND TRANSITION PROBABILITIES FOR SYSTEM REORIENTING RANDOMLY AROUND FIXED SYMMETRY AXIS

If $V'(t)$ is a random function of time, the ensemble average of $W_{(\alpha M) \rightarrow (\alpha' M-1)}$ denoted as $\overline{W}_{(\alpha M) \rightarrow (\alpha' M-1)}$ is observed in an experiment. It is easy to see that if the NH_4 ion undergoes random reorientations around a certain symmetry axis, $\overline{V}'(t) = 0$. Therefore

$$\overline{W}_{(\alpha M) \rightarrow (\alpha' M-1)} = 4\omega_1^2 |\langle \alpha' M - 1 | I_x | \alpha M \rangle|^2 \frac{\sin^2[\Omega(\alpha M, \alpha' M - 1) - \omega]T}{[\Omega(\alpha M, \alpha' M - 1) - \omega]} + \langle |\langle \alpha' M - 1 | U^{(2)}(T, -T) | \alpha M \rangle|^2 \rangle_{\text{av}}. \quad (39)$$

In the limit of large T , the first-order term of Eq. (39) is identical to that of Eq. (36). The typical term for the second-order transition probability per unit time has the form

$$\kappa = 4\omega_1^2 \frac{K_D^2}{\hbar^2} \sum_{i,j} \left| \sum_{\alpha''} \frac{\langle \alpha' M - 1 | V_{ij}^0 | \alpha'' M - 1 \rangle \langle \alpha'' M - 1 | I_x | \alpha M \rangle}{[\Omega(\alpha M, \alpha'' M - 1) - \omega]} \right|^2 G_{ij}(0) \frac{\tau_c}{1 + [\Omega(\alpha M, \alpha' M - 1) - \omega]^2 \tau_c^2}, \quad (40)$$

where the autocorrelation function of the random function F_{ij} , see Eq. (23), is defined as

$$G_{ij}(\tau) = (F_{ij}(\tau) F_{ij}^*(0))_{\text{av}} = G_{ij}(0) e^{-|\tau|/\tau_c}$$

and τ_c is the so-called correlation time. Its effect is to generate sidebands or wings at $\omega \neq \Omega(\alpha M, \alpha' M - 1)$, whose relative intensity is given approximately by

$$\frac{1}{\pi} \frac{K_D^2}{\hbar^2 (\Delta\omega)^2} \left(\frac{\tau_c}{1 + (\Delta\omega)^2 \tau_c^2} \right), \quad (41)$$

where

$$\Delta\omega = \Omega(\alpha M, \alpha' M - 1) - \omega \approx \Omega(\alpha M, \alpha'' M - 1) - \omega.$$

This approximation breaks down when $\hbar\Delta\omega$ is of the order of K_D or smaller. On the other hand, the expression (41) becomes negligible when $\Delta\omega \gg 1/\tau_c$. Therefore, the absorption spectrum

consists of a strong central peak primarily due to the first-order transitions plus weaker "wings" generated by the second-order transitions extending out to the frequencies of the order of $\omega_0 \pm 1/\tau_c$.

VI. NUCLEAR-MAGNETIC-RESONANCE ABSORPTION SPECTRUM IN THE LIMIT OF FAST MOTION

It has been shown in previous sections that the satellites cannot be observed if $(K_D/\hbar\omega_r)^2 \ll 1$. Similarly, in the case of random motion, the intensity of the wings in the limit of fast motion $\Delta\omega_{\text{RL}}\tau_c \ll 1$, becomes negligible. Here $\Delta\omega_{\text{RL}}$ is the rigid-lattice value of the linewidth of the proton absorption spectrum. In the limit of fast motion only the first-order term in the expression for the transition probability per unit time needs to be considered; i.e.,

$$P_{(\alpha M) \rightarrow (\alpha' M-1)} \propto |\langle \alpha' M - 1 | I_x | \alpha M \rangle|^2, \quad (42)$$

where

$$I_x = \sum_{i=1}^4 I_{xi}.$$

The formula for the transition probability per unit time assumes that the system was with certainty in state $|\alpha M\rangle$ before scattering with the rf field occurred. If the spin system is in thermal equilibrium with the lattice, all energy eigenstates will be occupied to some extent. In this case the right-hand side of the Eq. (42) should be multiplied by the appropriate Boltzmann factor. However, since $\hbar\omega_0/kT \approx 10^{-5}$ in the field of 10^4 G at room temperature, the Boltzmann factors are approximately 1 over the whole temperature range of the experiment. The quantities in Eq. (42) were evaluated¹⁵ using $|\alpha M\rangle$ in the symmetry adapted basis.

For a powder sample the calculated spectrum is an isotropic average over all orientations of H_0 . The dimensionless off-field parameter h is defined as

$$h = \frac{H_0 - \omega/\gamma}{\gamma\hbar/r_0^3}, \quad (43)$$

where H_0 is the applied field and ω is 2π times the rf frequency used in the experiment. If the center of the l th component line occurs at $h_l = h_l(\beta, \gamma)$, then the probability of finding the absorption line between h and $h + \Delta h$ in a powder sample is

$$W_l(h)\Delta h = \frac{1}{4\pi} \int_R \int P_l(\beta, \gamma) d(\cos\beta) d\gamma. \quad (44)$$

The integration is performed over the region R where

$$h \leq h_l(\beta, \gamma) \leq h + \Delta h$$

and $P_l(\beta, \gamma)$ is the intensity of the l th component line. Inverting the solution for $h_l(\beta, \gamma)$ to give $\gamma = g_l(\beta, h)$, the following result is obtained:

$$W_l(h) = \frac{1}{4\pi} \int_R \frac{\partial g_l(\beta, h)}{\partial h} P_l(\beta, g_l(\beta, h)) d(\cos\beta), \quad (45)$$

where $\partial g_l/\partial h$ is the Jacobian of the mapping $(\beta, \gamma) \rightarrow (\beta, h)$. If $h_l = h_l(\beta)$ and $P_l = P_l(\beta)$, Eq. (45) reduces to the familiar Pake's spectrum¹⁶

$$W_l(h) = P_l(\beta) \frac{d(\cos\beta)}{dh}. \quad (46)$$

Whenever the Pake formula was not applicable, a numerical solution of Eq. (45) was used.

The resulting powder spectra for the three motions of the NH_4 ion are given by

$$W(h) = \sum_i W_i(h) \quad (47)$$

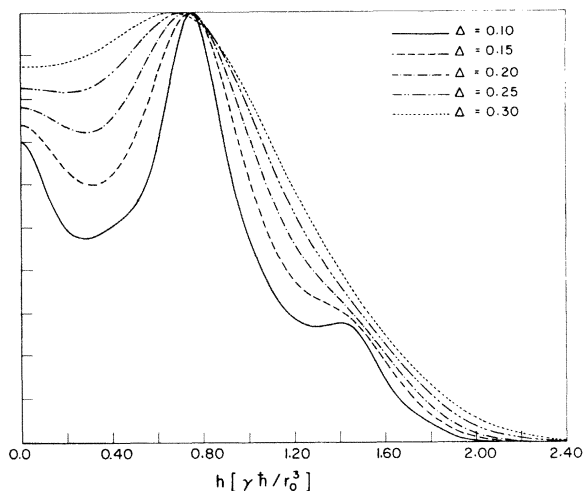


FIG. 1. Proton magnetic resonance absorption spectrum of the NH_4^+ ion undergoing rapid C_2 reorientations. The broadening parameter is in units of $\gamma\hbar/r_0^3$.

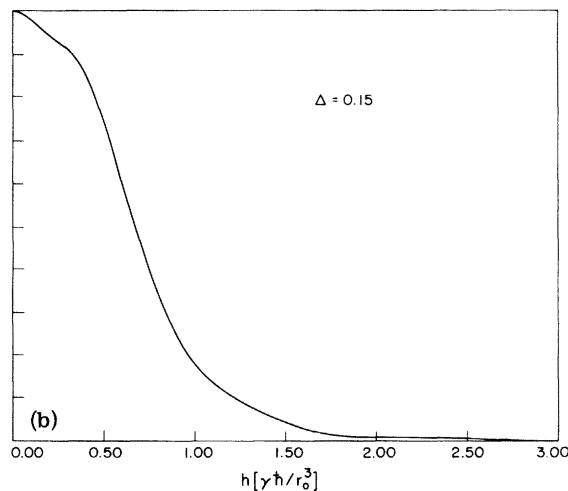
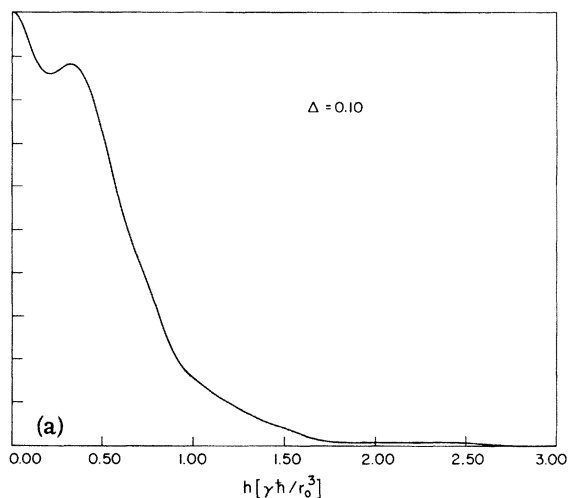


FIG. 2. Proton magnetic resonance absorption spectrum of the NH_4^+ ion undergoing rapid C_3 reorientations.

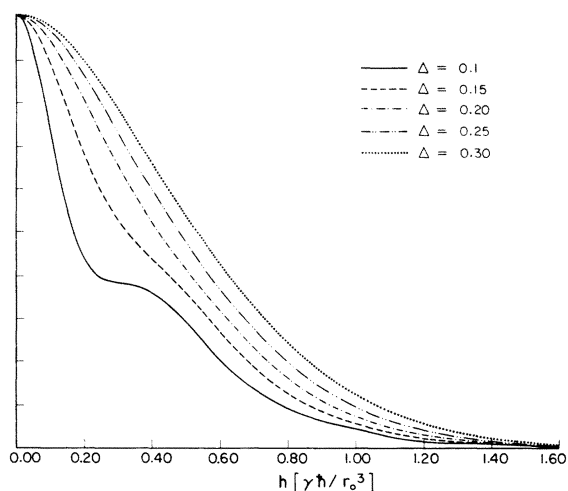


FIG. 3. Proton magnetic resonance absorption spectrum of the NH_4^+ ion undergoing rapid C_4 reorientations.

The number of terms is determined by the number of possible lines in Eq. (42). The effect of interionic broadening is introduced by convoluting $W(h)$ with a Gaussian function

$$S(h-h') = N e^{-(h-h')^2/2\Delta^2}, \quad (48)$$

where N is a normalization factor, and Δ is an adjustable parameter measuring the strength of the interionic dipole-dipole interaction. The final line shapes are given by

$$F(h) = \int_{-\infty}^{\infty} W(h') S(h-h') dh'. \quad (49)$$

$F(h)$ has been plotted for various values of the broadening parameter Δ in Figs. 1–3 for C_2 , C_3 , and C_4 motions.

The second moments of these spectra are

$$M_2 = M_2' + (\gamma\hbar/r_0^3)\Delta^2, \quad (50)$$

where M_2' is the intraionic contribution to M_2 and Δ is the interionic broadening parameter. Introducing $K_M = \gamma^2\hbar^2/r_0^6$, the values of M_2' for rapid C_2 , C_3 , and C_4 motions, respectively, are $\frac{27}{40}$, $\frac{27}{80}$, and $\frac{9}{40}$ in K_M units. In G^2 the second moments become 24, 12, and 8, respectively.

VII. ABSORPTION LINE SHAPE WITH SATELLITES FOR THE FOUR-SPIN TETRAHEDRON ROTATING UNIFORMLY ABOUT A SPECIFIED SYMMETRY AXIS

In order to calculate the shape of a satellite, only the following quantities need to be considered:

$$A_{(\alpha M) \rightarrow (\alpha' M-1)}^{(m')} = |\langle \alpha' M - 1 | [I_x, V_{Dm'}] | \alpha M \rangle|^2, \quad (51)$$

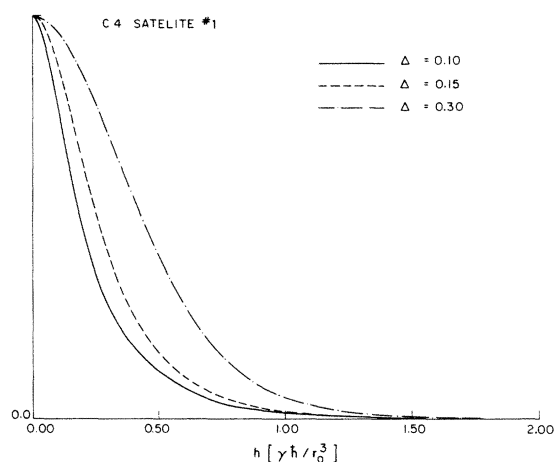


FIG. 4. Line shape of the satellite No. 1 in the case of the NH_4^+ ion rotating about a single C_4 axis.

where V_{Dm} is defined in Eq. (33). A satellite will be called satellite No. 1 if it is generated by the V_{D1} term of $V'(t)$ and satellite No. 2 if it is generated by V_{D2} . The calculation, while lengthy, is analogous to that of Sec. VI. The broadened line shapes of the satellites pertaining to uniform rotation about the C_4 axes are given in Figs. 4 and 5.

Finally, to obtain the complete line shape the results of Sec. VI and the above are combined. Each satellite is weighted by its relative intensity $(K_D/m\hbar\omega_r)^2$. The resulting spectra for C_3 rotation are shown in Fig. 6 for two values of the broadening parameter Δ . The corresponding spectra for C_4 rotation are shown in Fig. 7. The parameter $d = \hbar\omega_r/K_D$ was taken to be $\frac{3}{2}$ to give optimal agreement with the experimental spectrum of powdered NH_4I . It should be noted that this choice of parameter is not consistent with assumption (c) in Sec. IV.

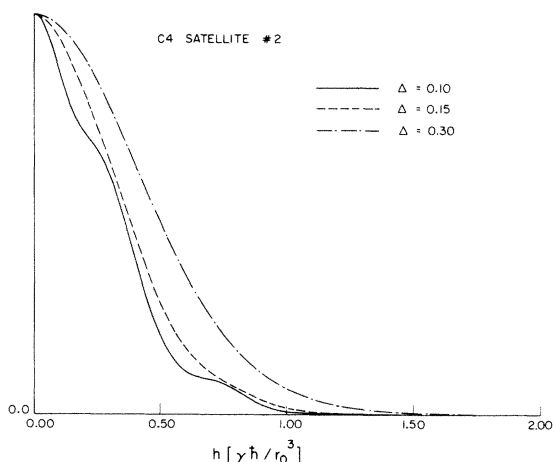


FIG. 5. Line shape of the satellite No. 2 in the case of the NH_4^+ ion rotating about a single C_4 axis.

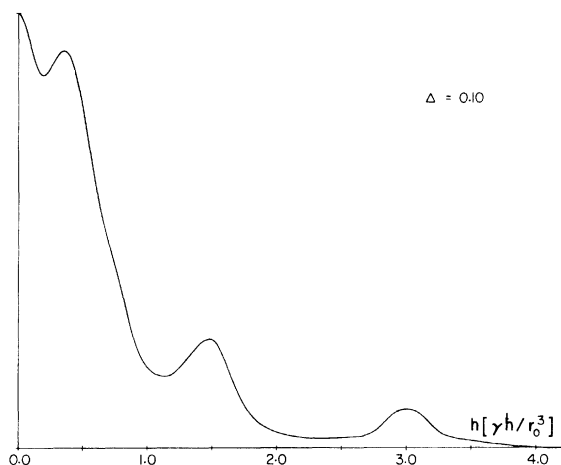


FIG. 6. Proton magnetic resonance absorption spectrum of the NH_4^+ ion rotating around a single C_3 axis, $\hbar\omega_r$ is $\frac{3}{2}K_D$.

VIII. COMPARISON OF THEORETICAL AND EXPERIMENTAL SPECTRA

A. Spectra in fast-motion limit

It was established by analysis of proton spin-relaxation data¹⁷ that at 77 K, the NH_4^+ ion in NH_4VO_3 can be considered (for the purpose of the proton linewidth) to be reorienting around a single C_3 symmetry axis. The C_2 reorientations are effectively "frozen"; i.e., $\tau_{C_2} \sim 1$ sec while $\tau_{C_3} \sim 2 \times 10^{-7}$ sec. For this reason, NH_4VO_3 represents at 77K a model system for the $\langle \mathcal{H}_D^0 \rangle_{C_3}$ case. The calculated and experimental proton absorption spectra are shown in Figs. 2 and 8, respectively. If the proton-proton distance is taken to be 1.68 Å, the

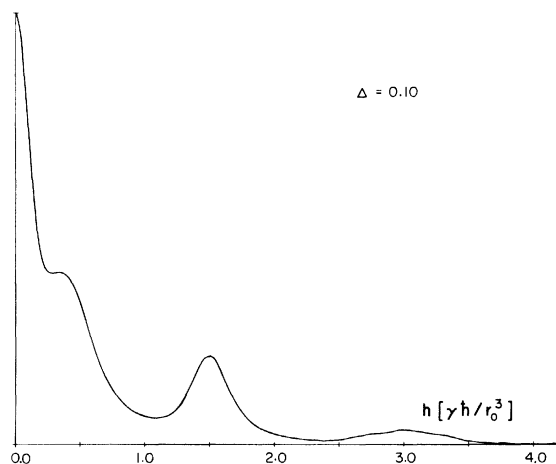


FIG. 7. Proton magnetic resonance absorption spectrum of the NH_4^+ ion rotating around a single C_4 axis, $\hbar\omega_r$ is $\frac{3}{2}K_D$.

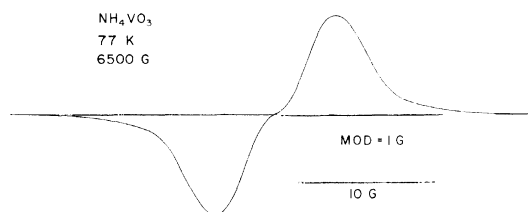


FIG. 8. Experimental proton magnetic resonance absorption spectrum (derivative) of the polycrystalline NH_4VO_3 at 77 K.

constant $\gamma\hbar/r_0^3$ assumes the value of 5.9 G. The calculated linewidth is then 7.6 ± 0.3 G, while the experimental linewidth is 8.8 ± 0.6 G. It should be noted that the small discrepancy between the two may be due to an incorrect estimate of the proton-proton distance. When the two line shapes in Figs. 2 and 8 are compared, one may estimate the inter-ionic broadening parameter Δ as 0.23 ± 0.02 . Accordingly, the second moment becomes $(M_2)_{C_3} = (M_2')_{C_3} + (5.9\Delta)^2 = 13.8 \pm 0.4 \text{ G}^2$, in good agreement with the experimental $15 \pm 1 \text{ G}^2$. In conclusion, in this solid in which the C_2 reorientations are hindered strongly ($E_{a2} = 2550$ K), and the C_3 reorientations are hindered moderately ($E_{a3} = 950$ K), the agreement between the semiclassical theory and the experimental result is satisfactory. We were unable to find any solid in which NH_4^+ ion reorients rapidly about a single C_2 or C_4 axis, for the purpose of testing the $\langle \mathcal{H}_D^0 \rangle_{C_2}$ and $\langle \mathcal{H}_D^0 \rangle_{C_4}$ cases.

B. Spectra in which satellites are observed

This group includes NH_4I and $(\text{NH}_4)_2\text{SO}_4$. In both lattices, the NH_4^+ ion reorientations are moderately hindered, and both display satellites in their proton magnetic resonance absorption spectra, Figs. 9–12. In NH_4I the NH_4^+ ion experiences a

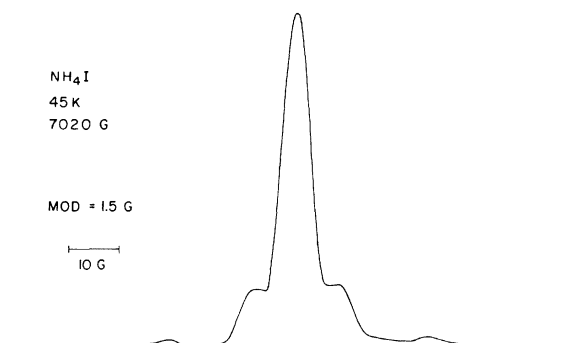


FIG. 9. Experimental proton magnetic resonance absorption spectrum of polycrystalline NH_4I at 45 K (twenty recordings).

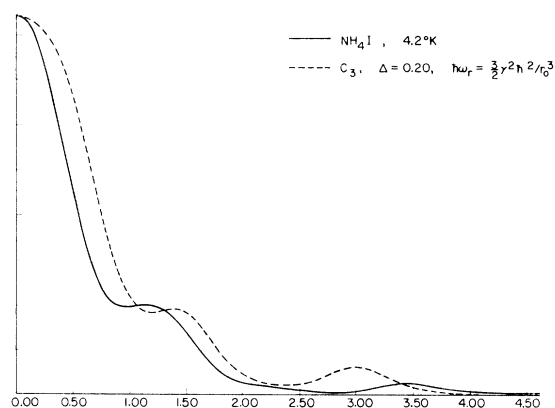


FIG. 10. Proton magnetic resonance absorption spectrum of NH_4I at 4.2 K and 35 MHz (solid curve) is compared to the calculated absorption spectrum (dashed curve) for the NH_4 tetrahedron rotating about a single C_3 axis.

tetrahedral crystal field of moderate strength ($E_a = 1200 \text{ K}$).¹⁸ It was found that the proton absorption spectrum is independent of temperature in the range from 1.4 to 45 K. The spectrum at 4 K is unaffected by a change in the Larmor frequency from 35 to 3 MHz. In ammonium sulfate, which has a hexagonal crystal field, there are two nonequivalent NH_4^+ lattice sites.¹⁹ In one site, the NH_4 reorientations are strongly hindered ($E_a^{\text{I}} = 1950 \text{ K}$), and in the other, moderately hindered ($E_a^{\text{II}} = 1350 \text{ K}$). It is easy to extrapolate that in $(\text{NH}_4)_2\text{SO}_4$ the satellites belong to the type-II ion, which represents one-half of all NH_4 ions.

Since the proton line shape of NH_4I remains practically unchanged to 45 K, it was thought that

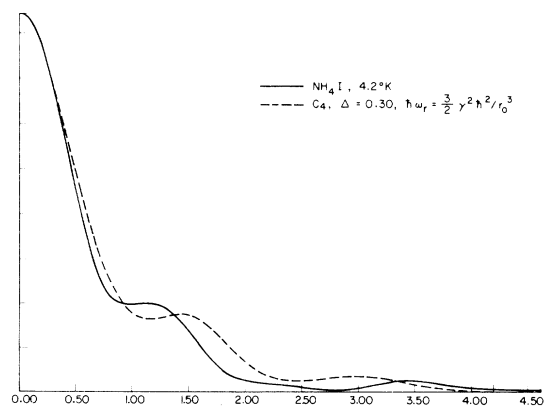


FIG. 11. Proton magnetic resonance absorption spectrum of NH_4I at 4.2 K and 35 MHz (solid curve) is compared to the calculated absorption spectrum (dashed curve) for the NH_4 tetrahedron rotating about a single C_4 axis.

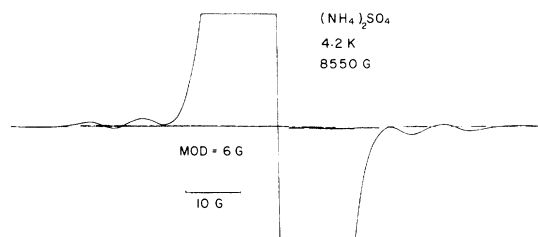


FIG. 12. Experimental proton magnetic resonance absorption spectrum (derivative) of polycrystalline $(\text{NH}_4)_2\text{SO}_4$ at 4.2 K.

a "classical" rotation could account for the satellites. Both the single C_3 axis rotation as well as the single C_4 axis rotation, including the first two satellites, were evaluated with $\hbar\omega_r = \frac{3}{2}K_D$ and compared with the experiment, Figs. 10 and 11. The agreement is quite good in both cases, although it is better for the case of the classical rotations around a single C_4 axis. The frequency of classical rotation is $3.8 \times 10^4 \text{ sec}^{-1}$, which corresponds to 9 G.

C. Extremely narrowed spectra

In NH_4SnCl_3 and $(\text{NH}_4)_2\text{SnCl}_6$ the NH_4 reorientations are weakly hindered, $E_a \sim 600 \text{ K}$. To as-

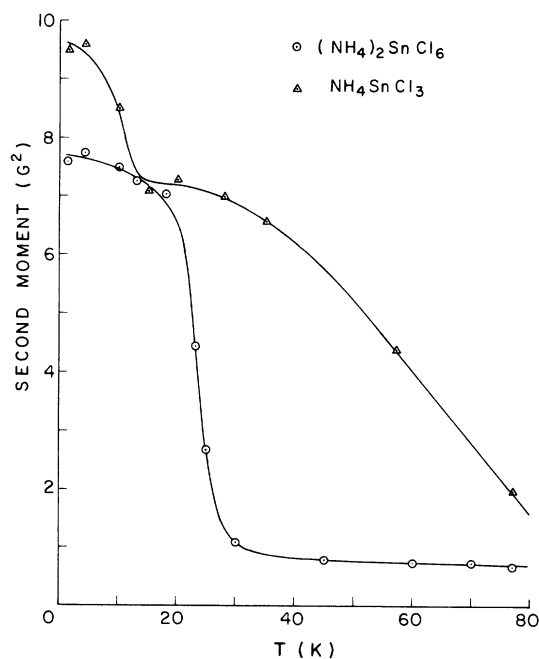


FIG. 13. Temperature dependence of the second moment of the proton magnetic resonance absorption spectrum of polycrystalline NH_4SnCl_3 and $(\text{NH}_4)_2\text{SnCl}_6$. The line shapes of these two materials are almost identical at 15 K (see Ref. 4c).

certain whether the C_3 or C_4 reorientation is responsible for narrowing the absorption line, the second moment of the proton line was measured as a function of temperature from 80 to 1.4 K, Fig. 13. It is observed in NH_4SnCl_3 that M_2 reaches a plateau value of about 7 G^2 in the temperature interval between 15 and 25 K. This observation does not suggest a single C_3 axis reorientation for which $(M_2)_{C_3} > 12 \text{ G}^2$, nor a single C_4 axis reorientation for which $(M_2)_{C_4} > 8 \text{ G}^2$. In addition, the experimental linewidth^{4c} of 2.2 G is much smaller than any calculated value. A similar discussion applies to $(\text{NH}_4)_2\text{SnCl}_6$. Therefore it is concluded that symmetry effects must be considered in order to explain the extreme narrowing of these absorption lines.

IX. DISCUSSION

From the measured temperature dependence of the spin-lattice relaxation time in NH_4I ,¹⁸ it was possible to conclude that the thermally activated random reorientations of the NH_4^+ ion are effectively frozen out at $\sim_{55} \text{ K}$. Therefore, they cannot be responsible for the deviations of the observed NH_4I proton absorption spectrum, Fig. 9, from the line shape expected for a so-called "rigid lattice."¹ Calculations based on tunneling of the NH_4^+ ion^{7,8} accounted to some extent for the experimental spectrum of NH_4I at 4 K. In these calculations, it was assumed that each NH_4^+ ion in the crystal moves independently of its neighbors in a crystal field of definite symmetry, which removes partially the degeneracy of the ground state. The energy eigenfunctions were classified according to the irreducible representations of the group T , taking into account also the effects of the exclusion principle. However, it was pointed out⁷ that for a complete theory, one must also take into account the dynamical behavior of the NH_4^+ ion.

In the present calculation, the motion of the ions is represented by a specific time dependence of the lattice variables in the dipolar Hamiltonian. In addition, the effects of the exclusion principle are ignored, a simplification which seems to be reasonable, as long as $\hbar\omega_r$ is comparable to the dipolar coupling constant K_D , a condition which is certainly fulfilled in NH_4I . In other words, Tomita's truncation of the secular part of the dipole-dipole interaction does not apply in this approximation, because the shifted absorption lines are within the observable region of the NMR absorption spectrum. The spectrum of NH_4I was reproduced quite well by assuming that the NH_4^+ tetrahedron is rotating with a classical frequency $\omega_r = 1.5K_D/\hbar$ around a specified C_3 or C_4 axis. It will now be demonstrated that this "classical" fre-

quency can be identified with the tunneling frequency of the NH_4^+ ion.

In an infinite crystal field, the ground state of the NH_4^+ ion is represented by a set of 12 real rotational wave functions, $\psi_R(0)$, where 0 stands for a symmetry element of the point group T . This set is derived by the application of twelve symmetry operations P_0 on the initial state ψ_R ,

$$\psi_R(0) = P_0\psi_R,$$

and can be reduced with respect to the symmetry point group to the irreducible members $A + E + 3F$. In a crystal field of tetrahedral symmetry, the fully degenerate ground state manifold splits into three states, Fig. 14(c). According to Nagamiya,²⁰ the energy eigenvalues in this crystal field are given by

$$\begin{aligned} E_R(A) &= a + 3b + 8c, \\ E_R(F) &= a - b, \\ E_R(E) &= a + 3b - 4c. \end{aligned} \quad (52)$$

In the above equations, it was assumed that the overlap integral

$$\langle \psi_R(0) | \psi_R(0') \rangle \ll 1 \quad \text{for } 0 \neq 0',$$

and it was therefore neglected. The energies a , b , and c are as follows:

$$\begin{aligned} a &= \langle \psi_R(E) | \mathcal{H}_R | \psi_R(E) \rangle, \\ b &= \langle \psi_R(C_2) | \mathcal{H}_R | \psi_R(E) \rangle, \\ c &= \langle \psi_R(C_3) | \mathcal{H}_R | \psi_R(E) \rangle = \langle \psi_R(C_3^2) | \mathcal{H}_R | \psi_R(E) \rangle. \end{aligned} \quad (53)$$

E, C_2, C_3, C_3^2 are the symmetry elements of the point group T .

If it is further assumed that the crystal field is such that at the lowest temperature, the tunneling is appreciable only around the four C_3 symmetry axes, then $b \ll a, c$. Thus, neglecting b in Eq. (52), we obtain

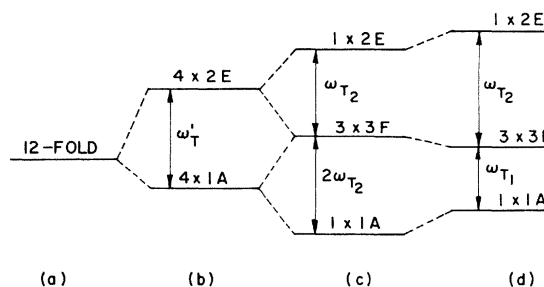


FIG. 14. (a) Infinite crystal field; (b) trigonal distortion or tunneling around a single C_3 axis; (c) tetrahedral field, tunneling around C_3 axes only; (d) tetrahedral field.

$$\begin{aligned}
E_R(A) &= a + 8c, \\
E_R(F) &= a, \\
E_R(E) &= a - 4c.
\end{aligned} \tag{54}$$

This case, illustrated in Fig. 14(c), gives rise to the very simple relation

$$\hbar\omega_{T1} = 2\hbar\omega_{T2} = -8c.$$

To restrict the motion even more, we assume that the tunneling is possible around a single C_3 axis only. Under this condition the twelvefold degenerate ground state splits into $4E + 4A$ in a manner identical to the CH_3 case.²¹ The energy eigenvalues are then given by

$$E_R(A) = a' + 2c', \quad E_R(E) = a' - c',$$

where a' and c' are in general different from a and c , Eqs. (53). This level scheme is illustrated in Fig. 14(b).

Let us consider the case of the single C_3 axis in more detail. A particular member of the rotational manifold for the infinite crystal potential is denoted by $\psi_R(1,2,3,4) \equiv \psi_1$, where the numbers 1–4 refer to the proton positions. If the NH_4 tetrahedron is rotated by $\pm\frac{2}{3}\pi$ around the C_3 axis passing through the proton four, two other wave functions belonging to the twelvefold degenerate set are $\psi_R(2,3,1,4) \equiv \psi_2$ and $\psi_R(3,1,2,4) \equiv \psi_3$. For the purpose of this discussion only these three states will be considered.

Allowing now for the tunneling around a chosen C_3 axis, the set ψ_1, ψ_2, ψ_3 will split into one A state and $2E$ states. The corresponding eigenfunctions are²²

$$\begin{aligned}
\psi_R(A) &= N_R(\psi_1 + \psi_2 + \psi_3), \\
\psi_R(E_1) &= N_R(\psi_1 + \epsilon\psi_2 + \epsilon^*\psi_3), \\
\psi_R(E_2) &= N_R(\psi_1 + \epsilon^*\psi_2 + \epsilon\psi_3),
\end{aligned} \tag{56}$$

and the energy eigenvalues are given by Eqs. (55). N_R is the appropriate normalization factor and $\epsilon = e^{i2\pi/3}$. An arbitrary state within this three-dimensional subspace describing the NH_4^+ ion tunneling around this single C_3 axis can be written, neglecting normalization,

$$\begin{aligned}
\psi(t) &= C_1 e^{-(i/\hbar)E_R(A)t} \psi_R(A) + C_2 e^{-(i/\hbar)E_R(E)t} \psi_R(E_1) \\
&+ C_3 e^{-(i/\hbar)E_R(E)t} \psi_R(E_2),
\end{aligned} \tag{57}$$

where the C_i 's are arbitrary complex numbers. Introducing $\hbar\omega_T \equiv E_R(E) - E_R(A)$, Eq. (57) becomes in terms of $\psi_1, \psi_2,$ and ψ_3 .

$$\begin{aligned}
\psi(t) &= e^{-(i/\hbar)[E_R(A) + E_R(E)]t/2} \\
&\times \{ [C_1 e^{+i\omega_T t/2} + (C_2 + C_3) e^{-i\omega_T t/2}] \psi_1 \\
&+ [C_1 e^{+i\omega_T t/2} + (\epsilon C_2 + \epsilon^* C_3) e^{-i\omega_T t/2}] \psi_2 \\
&+ [C_1 e^{+i\omega_T t/2} + (\epsilon^* C_2 + \epsilon C_3) e^{-i\omega_T t/2}] \psi_3 \}.
\end{aligned} \tag{58}$$

If we denote the initial condition

$$\psi(t=0) = \psi_s,$$

where $s=1,2,3$, then the expression (58) simplifies to

$$\begin{aligned}
\psi(t)_s &= e^{-(i/\hbar)[E_R(A) + E_R(E)]t} \\
&\times \sum_{r=1}^3 \left[\frac{1}{3} e^{+i\omega_T t/2} + (\delta_{r,s} - \frac{1}{3}) e^{-i\omega_T t/2} \right] \psi_r,
\end{aligned} \tag{59}$$

where s in $\psi(t)_s$ characterizes the initial condition. If the measurement of the orientation of the NH_4^+ ion is performed at the time τ , then the probability $p_{r,s}(\tau)$ that the NH_4^+ is found in the state with definite orientation ψ_r is

$$p_{r,s}(\tau) = |\langle \psi_r | \psi(\tau)_s \rangle|^2. \tag{60}$$

Assuming a small overlap; i.e., $|\langle \psi_r | \psi_{r'} \rangle| \ll 1$, where $r \neq r'$, Eqs. (59) and (60) give

$$p_{r,s}(\tau) = \delta_{r,s} \left(\frac{1}{3} + \frac{2}{3} \cos \omega_T \tau \right) + \frac{2}{9} (1 - \cos \omega_T \tau). \tag{61}$$

From Eq. (13), it follows that the classical correlation function $G(v) = F_{ij} F_{ij}^*(\tau)$ corresponding to (61) is proportional to

$$G(\tau) \propto \sum_{r,s} P_{r,s}(\tau) e^{im'\phi_r} e^{im''\phi_s}, \tag{62}$$

where $m', m'' = \pm 1, \pm 2$ and $\phi_r, \phi_s = 0, \pm\frac{2}{3}\pi$ or $\frac{3}{2}\pi, \frac{3}{2}\pi \pm \frac{2}{3}\pi$. In any case

$$G(\tau) \propto A + B \cos \omega_T \tau, \tag{63}$$

where A and B are constants. Neglecting the constant term A , the Fourier transform of $G(\tau)$ is

$$J(\omega) \propto \delta(\omega + \omega_T) + \delta(\omega - \omega_T), \tag{64}$$

where $\delta(x)$ is the Dirac δ function. With this spectrum, the transition probability per unit time, Eq. (40) becomes proportional to

$$\begin{aligned}
\kappa &= 4\omega_1^2 (K_D/\hbar\omega_T)^2 [\delta(\Omega(\alpha M, \alpha' M - 1) - \omega + \omega_T) \\
&+ \delta(\Omega(\alpha M, \alpha' M - 1) - \omega - \omega_T)].
\end{aligned} \tag{65}$$

Comparing this result with the Eq. (36) we observe that it is identical with the terms having $m' = \pm 1$ in the second part of Eq. (36), provided we choose $\omega_r = \omega_T$. Therefore, the frequency of rotation ω_r used in the semiclassical calculation of the absorption spectrum is to be interpreted as the tunneling frequency of the NH_4^+ ion. It should be noted that

classical rotation also generates satellites at $\omega_0 \pm 2\omega_r$. This is due to the terms $e^{\pm i2\phi}$, where ϕ varies continuously as $\phi = \omega_r t$, which appear in the expression for $F_{ij}(t)$, Eq. (13).

The analogy is even closer if we consider the tunneling of the NH_4^+ ion around a single fourfold axis. We choose a four-dimensional subspace $\psi_1 = \psi_R(E)$, $\psi_2 = \psi_R(C_4)$, $\psi_3 = \psi_R(C_4^2)$, and $\psi_4 = \psi_R(C_4^3)$ of the 24-fold degenerate ground state in an infinite potential. Introducing

$$d = \langle \psi_R(E) | \mathcal{H}_R | \psi_R(E) \rangle, \quad (66)$$

$$e = \langle \psi_R(E) | \mathcal{H}_R | \psi_R(C_4) \rangle = \langle \psi_R(E) | \mathcal{H}_R | \psi_R(C_4^3) \rangle,$$

and assuming that

$$\langle \psi_R(E) | \mathcal{H}_R | \psi_R(C_2) \rangle = \langle \psi_R(E) | \mathcal{H}_R | \psi_R(C_4^2) \rangle \ll d, e, \quad (67)$$

we then have to solve the following secular equation:

$$\begin{vmatrix} d-E & e & 0 & e \\ e & d-E & e & 0 \\ 0 & e & d-E & e \\ e & 0 & e & d-E \end{vmatrix} = 0, \quad (68)$$

which yields

$$\begin{aligned} E_R(A) &= d - 2e, \\ E_R(B) &= d + 2e, \\ E_R(E) &= d. \end{aligned} \quad (69)$$

It was assumed again that $\langle \psi_R(0) | \psi_R(0') \rangle \ll 1$ for $0 \neq 0'$. A , E , and B are the irreducible representations of the point group C_4 .¹⁵ The level scheme is shown in Fig. 15(b). This corresponds closely to the semiclassical situation with ω_r and $2\omega_r$ appearing in the time-dependent part of the dipole-dipole interaction.

The expression (61) is correct only for tunneling of the NH_4^+ ion in a static potential; that is, we are assuming a lattice with exactly defined posi-

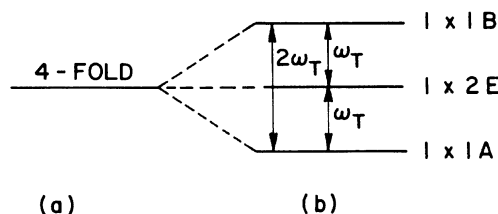


FIG. 15. (a) Infinite crystal field; (b) tunneling around a single C_4 axis.

tion and zero momentum. In a real lattice this coherent tunneling motion will be interrupted by collision processes, and consequently the expression $P_{r,s}(\tau)$ should be modified; i.e., the tunneling frequency ω_T is broadened into a frequency band

$$\omega_T - \Delta < \omega_T' < \omega_T + \Delta.$$

On the basis of the preceding discussion, it is not surprising that the line shape of NH_4I can be reasonably approximated by assuming that the NH_4^+ ion rotates with a certain classical frequency about a specified axis, since this frequency is a measure of the tunneling frequency (or frequencies) ω_T .

It may be concluded that strongly to moderately hindered NH_4^+ ions display proton spectra in solids which can be adequately described by the semiclassical theory. A single C_3 axis reorientation of the NH_4^+ ion was observed in solid NH_4VO_3 . The theoretical spectrum and the observed spectrum agree well. Single C_4 axis and single C_2 axis spectra were also calculated, but no lattice is known to us in which these excitations of the NH_4^+ ion occur. In some solids in which the NH_4 ion was moderately hindered, satellites appear in the proton absorption spectrum. This was observed in NH_4I and $(\text{NH}_4)_2\text{SO}_4$. A semiclassical theory is still adequate in this case, if the tunneling splitting is represented by a classical rotation. The absorption line shape was calculated for NH_4I , and it was observed to agree quite well with the experiment.

*Research supported by the National Research Council of Canada.

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