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Proton-Magnetic-Resonance Study of the Spin-Symmetry States of Ammonium Ions in Solids*

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The proton-magnetic-resonance absorption spectra at 4.2 °K have been obtained for a number of ammonium salts. Some of these solids exhibit narrow proton spectra even at 4.2 °K. Information obtained from proton-relaxation data precludes the possibility of thermally activated molecular reorientation as the effective mechanism for line narrowing at this temperature. The results are discussed in terms of indistinguishability of the ammonium-group protons and the formation of nuclear-spin-symmetry states (spin isomerism) and are compared with the predictions of a theoretical treatment developed by Tomita. Features characteristic of spin isomerism were found in a number of spectra, but the Tomita treatment was inadequate to give quantitative agreement.

INTRODUCTION

Proton-absorption line shapes and second moments have been observed in ammonium chloride and ammonium bromide at 77 °K by Bersohn and Gutowsky.[1] Their observations compared well with those expected for a rigid lattice in which the protons of the ammonium groups are distinguishable, a so-called "four-spin-$\frac{1}{2}$" system.

However, in a study of a number of ammonium salts, Richards and Schaefer[2] found that some had not attained their rigid-lattice spectra at 20 °K. They concluded that in these salts some degree of thermal reorientation was still effective in narrowing the proton-absorption line at this temperature, an interpretation whose difficulties can well be demonstrated by the example of ammonium sulphate. To obtain quantitative agreement with the second moment of 33.3 ± 1.1 G^2 observed in this salt at 20 °K, Richards and Schaefer were forced to postulate that at this temperature two-thirds of the ammonium ions were rigid, while one-third were rapidly reorienting (a "semirigid lattice"). This is in contradiction with the known fact that there are equal numbers of each of two inequivalent ammonium ions in the structure of ammonium sulphate.

Tomita[3] interpreted the narrow proton-absorption line shape of methane at 4.2 °K in terms of the formation of nuclear-spin states of definite permutation symmetry (nuclear-spin isomerism). Since the methane molecule and ammonium ion are structurally very similar (the protons in each being tetrahedrally coordinated around the central atom of the group—carbon in the case of methane and nitrogen in the case of the ammonium ion), it was thought that the same mechanism might be responsible for the relatively narrow proton linewidths previously observed in some ammonium salts at low temperatures. For this reason, a study of the proton line shapes at 4.2 °K was undertaken on 19 ammonium salts to investigate the possibility of nuclear-spin isomerism in the ammonium ions. Also, in some cases where the information was not already available, the temperature dependence of the spin-lattice relaxation time (T_1) was studied to gain information on the motional processes present in these materials.

THEORY

The theoretical NMR absorption line shape for a four-proton system exhibiting spin isomerism has been developed by Tomita[3] and applied to the case of the methane molecule. We now apply this same treatment to the ammonium ion and summarize only the main points, since the mathematical details can be found elsewhere.[3,4] Since the interaction between spin and spatial variables is negligibly small, the total wave function (Ψ) can be written as a product of space (ψ) and spin (ϕ) parts: $\Psi = \psi\phi$. The molecule is in its vibrational and electronic ground states at low temperature. If the protons are indistinguishable, Ψ must be invariant under any real reorientation of the ion, necessitating the existence of physically real states only in the combinations $\psi(A)\phi(A)$, $\psi(E)\phi(E)$, $\psi(T)\phi(T)$ which are referred to as meta, para, and ortho states, respectively. A, E, and T label the irreducible representations of the tetrahedral group.

There are 16 nuclear-spin eigenstates of the Zeeman Hamiltonian $\mathcal{H}_z$ represented by $|m_1 m_2 m_3 m_4\rangle$, where m_i is the z component of $\vec{I}^i$ (the spin operator for proton i). m_i takes the values $\pm\frac{1}{2}$ for protons. With respect to the tetrahedral symmetry group of the NH_4^+ ion these states reduce to the members $5A + E + 3T$ corresponding to 2, 0, 1, respectively, for the total-spin quantum numbers I of the proton group.

The torsional ground state of the ammonium ion

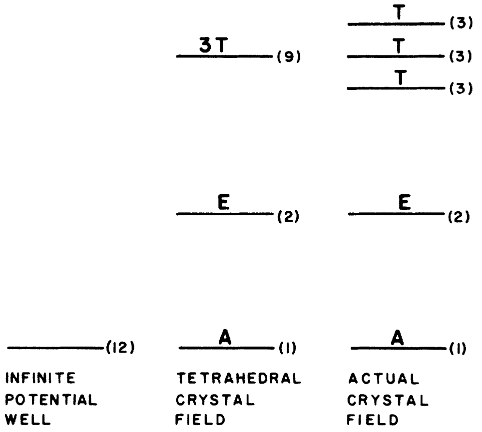

FIG. 1. In a finite crystal field the 12-fold-degenerate torsional ground state of the NH_4^+ ion splits into the levels $A+E+3T$. The degeneracy of the $3T$ levels is lifted by a crystal field with symmetry lower than tetrahedral.

in an infinite potential well is 12-fold degenerate since there are 12 equivalent orientations of the ion (corresponding to even permutations of the four protons). These also reduce, with respect to the tetrahedral symmetry group of the ammonium ion, to the members $A+E+3T$. The degeneracy among these different members is generally removed by a tunneling of the ion in a finite crystal field, but if this field has tetrahedral symmetry the three distinct T members remain degenerate (Fig. 1).

If the spatial energy levels are well separated, only spin transitions which conserve the symmetry type (A, E, or T) will be observed in first order. Thus in a first-order-perturbation calculation of the dipolar splittings, only the semidiagonal part of the matrix representation of $\mathcal{H}'_d$ (the secular proton dipole-dipole ineraction), involving matrix elements between states of the same symmetry, needs to be diagonalized.

For distinguishable protons there are no symmetry restrictions on the wave function, and so the nuclear-spin energy states are given by diagonalizing the complete matrix representation of ${}'_d$ including matrix elements between all symmetry states. This is the "four-spin-$\frac{1}{2}$" situation and has been treated previously for certain crystal orientations[1,5] although a general analytic solution, necessary for determining the theoretical powder spectrum, has not been obtained.

As Tomita has shown for the spin isomer case, the meta component of the absorption spectrum consists of a δ function at the Larmor field (H_0), while the ortho component consists of six lines symmetrically displaced from H_0 by fields of

$$h_1 = \pm C \cos \tfrac{1}{3}\Psi \ ,$$

$$h_2 = \pm C \cos \tfrac{1}{3}(\pi - \Psi) \ ,$$

$$h_3 = \pm C \cos \tfrac{1}{3}(\pi + \Psi) \ , \tag{1}$$

where $C = 1.5\ \gamma \hbar r^{-3}$ and

$$\cos\Psi\ (\theta, \phi) = 1 - \tfrac{27}{2} \sin^2 2\phi \cos^2\theta \sin^4\theta. \tag{2}$$

Here (θ, ϕ) are the spherical angular coordinates specifying the orientation of the applied field relative to the molecule.

To obtain the spectrum resulting from a powder sample a polycrystalline average must be taken of the above single-crystal spectra. The effects of neighboring molecules can be included in an approximate way as a Gaussian broadening. The final spectrum is then the superposition of the meta and ortho components weighted according to their transition probabilities in the ratio 5 : 3.[3] The same procedure may be used in the present case to obtain the proton contribution to the absorption spectrum of the ammonium ions in the solids being studied.

A calculation of the second moment of the unbroadened ortho component yields a value of M'_2 (ortho) = 39.8 G^2 for a proton-proton separation r of 1.68 Å (a typical value for an NH_4^+ ion). With a weighting of meta : ortho of 5 : 3 and since the second moment of the meta component (a δ function) is zero, the second moment of their unbroadened sum M'_2 is

$$M'_2 = \tfrac{3}{8} M'_2\ (\text{ortho}) = 14.9\ G^2$$

for this same value of r. On the basis of the preceding treatment, the total second moment M_2 for a spin-isomeric spectrum is expected to be about $15 + \sigma^2$, where σ^2 is the interionic contribution to the second moment.

This treatment was developed by Tomita for methane, so it is not as applicable for an ammonium ion since the latter is complicated by the presence of a nitrogen nucleus at the center of the proton group. The nitrogen contribution to the dipolar interaction, though smaller than that of the protons, is not entirely negligible. Although the magnetic dipole moment of the naturally abundant nitrogen isotope N^{14} is much less than that of a proton, its contribution to the dipolar interaction is nevertheless significant because the nitrogen-proton separation is less than the proton-proton separation. To take this into account, we must first modify the basis eigenstates of the Zeeman Hamiltonian ($\mathcal{H}_z$) so as to also specify the z component n of the nitrogen spin. In order to keep as close a formalism as possible to Tomita's four-proton treatment, n is written as a subscript to his previously defined basis states, the new ones being written as $| m_1 m_2 m_3 m_4 \rangle$, where n takes the values 0, ±1 for N^{14} with spin 1 (m_i is the z component of the spin $\vec{I}^i$ for proton i).

TABLE I. Matrix elements $\mathcal{H}'_{dn}$ for $n=1$ in symmetry-adapted basis. Matrix elements for $n=-1$ are the negative of these, while those for $n=0$ are all zero.

$$
\left|\begin{array}{c|c|ccc|c|cc|ccc}
a'_2 & & & & & & & & & & \\
\hline
 & a'_1 & & & & & & & & & \\
\hline
 & & e' & f' & g' & & & & & & \\
 & & f' & h' & k' & & & & & & \\
 & & g' & k' & l' & & & & & & \\
\hline
 & & & & & 0 & & & & & \\
 & & & & & & 0 & 0 & & & \\
 & & & & & & 0 & 0 & & & \\
 & & & & & & & & 0 & 0 & 0 \\
 & & & & & & & & 0 & 0 & 0 \\
 & & & & & & & & 0 & 0 & 0
\end{array}\right.
$$

where

$$
\left|\begin{array}{c} 2a'_2 \\ 4a'_1 \\ 12e' \\ 6\sqrt{2}f' \\ 2\sqrt{6}g' \\ 6h' \\ 2\sqrt{3}k' \\ 2l' \end{array}\right| = \left|\begin{array}{cccc} 1 & 1 & 1 & 1 \\ 1 & 1 & 1 & 1 \\ 5 & 5 & 5 & -3 \\ -1 & -1 & 2 & 0 \\ -1 & 1 & 0 & 0 \\ 2 & 2 & -1 & 3 \\ -1 & 1 & 0 & 0 \\ 0 & 0 & 1 & 1 \end{array}\right| \left|\begin{array}{c} B_{10} \\ B_{20} \\ B_{30} \\ B_{40} \end{array}\right|
$$

Second, we must add a nitrogen contribution, $\mathcal{H}'_{dn}$ to the dipolar Hamiltonian, where

$$\mathcal{H}'_{dn} = \sum_i B_{i0} I^i_z I^n_z \quad ,$$

$\vec{I}^i$ and $\vec{I}^n$ are the spin operators for proton i and the nitrogen nucleus, respectively, and $B_{i0} = \gamma\gamma_n \hbar^2 r_0^{-3} \times (1-3\cos^2\theta_{i0})$. γ, γ_n are the gyromagnetic ratios for the proton and nitrogen nuclei and θ_{i0} the angle the nitrogen-proton vector $\vec{r}_{ni}$ makes with $\vec{H}_0$ ($r_0 = |\vec{r}_{ni}|$). It should be noted that the "flip-flop" terms like $I^i_+ I^n_-$ have been excluded from the truncated Hamiltonian $\mathcal{H}'_{dn}$, since they do not commute with $\mathcal{H}_z$ (are nonsecular) and so do not contribute to the splitting in first order. For each n, using the same symmetry-adapted states as Tomita, the irreducible matrix representation of $\mathcal{H}'_{dn}$ can be calculated. The matrix elements for $n=1$ are given in Table I (those for $n=-1$ being just the negative of these), while those for $n=0$ are all zero.

We will define a Cartesian coordinate system fixed with respect to the ammonium ion with origin at the nitrogen nucleus and the x, y, z axes bisecting the edges of the tetrahedron formed by the four protons (Fig. 2). The protons are numbered as shown. In this reference frame $\vec{H}_0$ will be given spherical angular coordinates (θ, ϕ) in terms of which the B_{i0} can be shown to be

$$
\begin{aligned}
B_{10} &= B_0[-\sin^2\theta \sin 2\phi + \sin 2\theta (\sin\phi + \cos\phi)] \quad , \\
B_{20} &= B_0[-\sin^2\theta \sin 2\phi - \sin 2\theta (\sin\phi + \cos\phi)] \quad , \\
B_{30} &= B_0[\sin^2\theta \sin 2\phi - \sin 2\theta (\sin\phi - \cos\phi)] \quad , \\
B_{40} &= B_0[\sin^2\theta \sin 2\phi + \sin 2\theta (\sin\phi - \cos\phi)] \quad , \qquad (3)
\end{aligned}
$$

where $B_0 = \gamma\gamma_n \hbar^2 r_0^{-3}$.

The elements a'_2 and a'_1 of Table I are symmetric combinations of the B_{i0} and so are zero for all θ, ϕ. Therefore, the meta component is unaffected by the nitrogen contribution, remaining a δ function at H_0.

The elements e' to l' are not, in general, zero, and so the ortho component is affected by the nitrogen contribution. However, for $\vec{H}_0$ along the x direction $\theta = \frac{1}{2}\pi$ and $\phi = 0$, whence, it follows from Eqs. (3) that $B_{i0} = 0$ for all i. For this field direction and the equivalent directions along the y and z axes, the nitrogen contribution is zero for the ortho component too. Therefore, the four-proton treatment discussed above applies exactly for this particular orientation. Inserting these values of θ and ϕ into Eqs. (2) and (1) we find ortho component lines at field values $h_1 = \pm 1.5\gamma\hbar r^{-3}$ with relative intensity 1, h_2, and $h_3 = \pm 0.75\gamma\hbar r^{-3}$ with relative intensity 2, plus the meta-component line at H_0 with relative intensity 10. These relative intensities preserve the over-all ratio of 5:3 for meta: ortho.

The Gaussian broadening of these lines by the appropriate interionic broadening factor σ^2 yields the spin-isomeric spectrum which should be observed for $\vec{H}_0$ in the x, y, or z directions, which correspond to the ⟨100⟩-type directions in the cubic crystals studied, e.g., NH_4Cl, $(NH_4)_2SnCl_6$.

In summary, Tomita's treatment predicts that

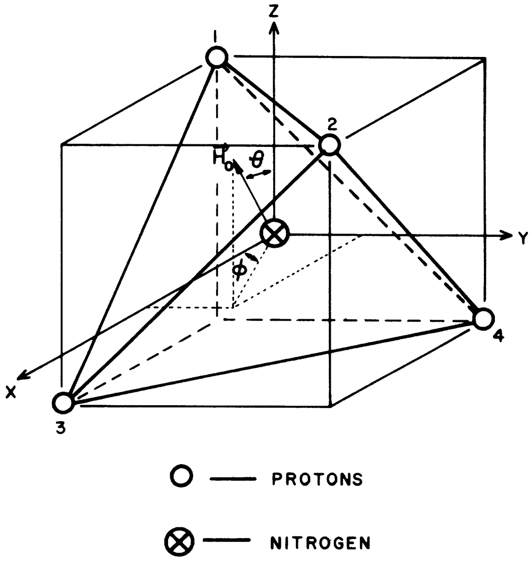

FIG. 2. NH_4^+ coordinate system. $\vec{H}_0$ has spherical angular coordinates (θ, ϕ).

a spin-isomeric spectrum will exhibit a dominant, narrow resonance (the meta component) at the Larmor frequency with some wing structure (the ortho component) giving an over-all second moment of about 16 to 20 G^2.

RESULTS AND DISCUSSION

Relaxation

Proton spin-lattice relaxation times T_1 were measured for several of the ammonium salts over various temperature ranges. The incoherent-pulse spectrometers used operated at 5.4, 19, 20.7, or 42 MHz with dead times from 20 to 6 μsec and 90°-pulse widths of a few μsec. Tektronix series 160 units were used for timing and triggering. The free-induction-decay signals were displayed on an oscilloscope and either measured directly or recorded first on film.

Of the 19 solids studied in this work T_1 data has previously been reported for NH_4Cl,[6] NH_4Br,[7] $(NH_4)_2SO_4$,[8,9] $(NH_4)_2BeF_4$,[10,11] and NH_4NO_3.[12,13] The temperature dependences of T_1 for two of the remaining solids [$(NH_4)_2Ce(NO_3)_6$ and $(NH_4)_2SeO_4$] are shown in Fig. 3. The leveling off of T_1 below about 25 °K for $(NH_4)_2Ce(NO_3)_6$ is the result of paramagnetic impurities dominating the relaxation at these temperatures. Except for a few cases [such as $(NH_4)_2U_2O_7$], the limiting effect of paramagnetic relaxation occurs at too low a temperature to interfere with the determination of the activation energy E_a.

Since the correlation time τ_c for a thermally activated reorientation follows the usual Arrhenius expression $\tau_c = \tau_c^0 e^{E_a/kT}$, the parameters pertinent to this investigation are E_a and the preexponential factor τ_c^0. These are listed, where they are known, in Table II. It should be noted that the hindering barrier to rotation is some $\frac{1}{2}$ kcal/mole larger than E_a.

The dipolar relaxation time for ionic reorientation is given by

$$\frac{1}{T_1} = C_d\left(\frac{\tau_c}{1+\omega_L^2\tau_c^2} + \frac{4\tau_c}{1+4\omega_L^2\tau_c^2}\right) ,$$

where C_d depends upon the nuclei concerned and their configuration and $\omega_L/2\pi$ is the Larmor frequency.

From this expression a minimum in T_1 occurs when $\omega_L\tau_c = 0.62$. For $(NH_4)_2SeO_4$ this minimum occurs around 198 °K at 20.7 MHz (Fig. 3), while the activation energy is 4.7 ± 0.2 kcal/mole. These lead to $\tau_c = 3.2\times10^{-14} e^{2.4\beta}$ sec for the reorientational correlation time, where $\beta = 1000/kT$. When the correlation frequency [defined as $(2\pi\tau_c)^{-1}$] becomes less than the linewidth, no motional averaging takes place and so the line broadens. The linewidth for the solids is of the order of 40 kHz and so we find for $(NH_4)_2SeO_4$ that the lattice is effectively rigid below 116 °K.

For $(NH_4)_2Ce(NO_3)_6$ the T_1 minimum occurs around 59 °K at 5.4 MHz with an activation energy of 1.6 kcal/mole (Fig. 3). Hence $\tau_c = 2.2\times10^{-14} \times e^{0.8\beta}$ sec and the lattice is effectively rigid below about 42 °K. In fact, the temperature at which T_1 reaches a minimum is lower in this solid than in any of the others studied. This fact, coupled with

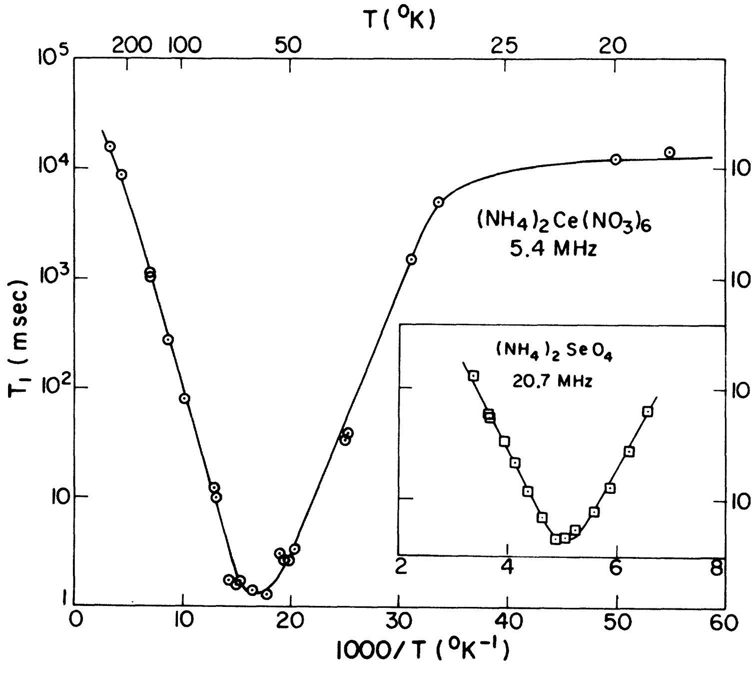

FIG. 3. Proton T_1 vs inverse temperature for powdered $(NH_4)_2SeO_4$ and $(NH_4)_2Ce(NO_3)_6$.

its very low activation energy, would also make the "rigid-lattice" temperature in this solid lower than in the others. Indeed, taking a hypothetical case where the T_1 minimum occurs at 50 °K (for a frequency of 20 MHz), with an activation energy of 1 kcal/mole (both quantities lower than those of any of the solids studied) the same calculation shows the lattice would be rigid below about 30 °K. It is clear from this that thermally activated molecular reorientation is effectively frozen out at 4.2 °K and so cannot be responsible, in any of the solids studied, for any line narrowing observed at this temperature.

Absorption

Proton-absorption derivative spectra at 4.2 °K were recorded for powdered samples of all 19 ammonium salts using a conventional Pound-Knight-Watkins cw spectrometer operating at approximately 40 MHz. The absorption spectra obtained from these by integration are shown in Figs. 4–6. Such gross features as second moments (M_2) and peak-to-peak linewidths (δ) at 4.2 °K are listed in Table II. In the cases of NH_4Cl and $(NH_4)_2SnCl_6$ single-crystal-absorption derivative spectra were also obtained in an identical manner, with the applied field being varied in the (001) plane from along the [100] to along the [110] crystal directions. Those for NH_4Cl have been reported previously[1] and those for $(NH_4)_2SnCl_6$ are shown in Fig. 7.

At 4.2 °K, T_1 was too long in most cases to be measured by pulse techniques, and so it was measured by observing the saturation-decay rate of the absorption signal on switching suddenly into resonance. Values between 10 and 600 sec were obtained in most cases. Since T_2 in these solids is ~10 μsec and the rf field was measured to be < 0.25 mG, the saturation factor ($\gamma^2 H_1^2 T_1 T_2$) was in the range 0.3–0.05 or lower. Saturation effects were thus deemed small to negligible.

The spectra obtained fall into three general categories:

1. Wide Spectra

NH_4Cl (Fig. 4) is a typical member of this category, the others being the other two ammonium

TABLE II. Parameters extracted for the 19 salts studied.[f]

Material	Source	Crystal class	τ_c^0 (10^{-14} sec)	E_a (kcal/mole)	T_1 at 4.2 °K (sec)	M_2—low temperature (G^2)	δ at 4.2 °K (G)
NH_4Cl	MCB(A)[a]	cubic	$4.4^{(6)}$	$4.7^{(6)}$	220	49.5 ± 0.5^{f}	23.1 ± 0.4
NH_4Br	MCB(R)[a]	cubic	$1.83^{(7)}$	$4.00 \pm 0.16^{(7)}$		48.0 ± 0.5^{f}	23.2 ± 0.8
NH_4F	B[b]	hex.				53 ± 2	22 ± 1
$(NH_4)_2SeO_4$	A[c]	monoc.	3.2	4.7 ± 0.2	13	$50.6 \pm 1.2^{(2)}$	22.7 ± 0.8
$(NH_4)_2U_2O_7$	A[c]					25 ± 1	2.9 ± 0.1
$(NH_4)_2Cr_2O_7$	F[d]	monoc.	0.78	2.0 ± 0.2	600	$7.59 \pm 0.35^{(2)}$	2.9 ± 0.2
$(NH_4)_2S_2O_8$	F(ACS)[d]	monoc.	16.1	1.7 ± 0.2	380	19.0 ± 0.5	2.9 ± 0.1
NH_4SnCl_3	A[c]			1.2 ± 0.3	10	9.6 ± 0.5	2.1 ± 0.1
$(NH_4)_2SnCl_6$	A[c]	cubic	36.6	1.2 ± 0.2	40	5.4 ± 0.5	1.80 ± 0.05
$(NH_4)_2PtI_6$		cubic				10 ± 1	1.9 ± 0.1
$(NH_4)_2Ce(NO_3)_6$	A[c]	monoc.	2.2	1.6 ± 0.2	160	3.0 ± 0.2	1.5 ± 0.1
NH_4GaCl_4	A[c]					28 ± 1	3.0 ± 0.4
$(NH_4)_2SO_4$	F(PS)[d]	rhomb.	$7.0^{(8)}$ 8.0	$3.9^{(8,9)}$ 2.7	> 1000	$33.3 \pm 1.1^{(2)}$	4.6 ± 0.2
$(NH_4)_2SeO_3$	A[c]					38 ± 1	22.2 ± 0.8
$(NH_4)_2TeO_4$	A[c]				13	26 ± 1	5.1 ± 0.4
$(NH_4)_2BeF_4$	A[c]	rhomb.	$3.0^{(11)}$ 3.0	4.3 ± 0.7 2.4 ± 0.2 $^{(10,11)}$		25 ± 1	6.8 ± 0.4
$(NH_4)_2S_2O_3$	F(P)[d]	monoc.	7.5 2.9	1.7 ± 0.2 2.8 ± 0.2	520	26 ± 1	3.3 ± 0.2
NH_4NO_3	BDH[e]	rhomb.	$29.6^{(13)}$	$2.4 \pm 0.2^{(12)}$	660	$50.0 \pm 1.3^{(2)}$	7.7 ± 0.2
NH_4VO_3	A[c]		0.8	1.9 ± 0.2	140	$21.6 \pm 0.8^{(2)}$	11.2 ± 0.2

[a] Matheson, Coleman and Bell (R, reagent grade) (A, reagent ACS).

[b] Baker Chemical Co., Baker (analyzed reagent grade).

[c] Alpha Inorganics (reagent grade).

[d] Fisher Scientific Co. (ACS, certified ACS) (PS, primary standard) (P, purified).

[e] British Drug Houses (analytical reagent grade).

[f] H. S. Gutowsky, G. E. Pake, and R. Bersohn, J. Chem. Phys. 22, 643 (1954).

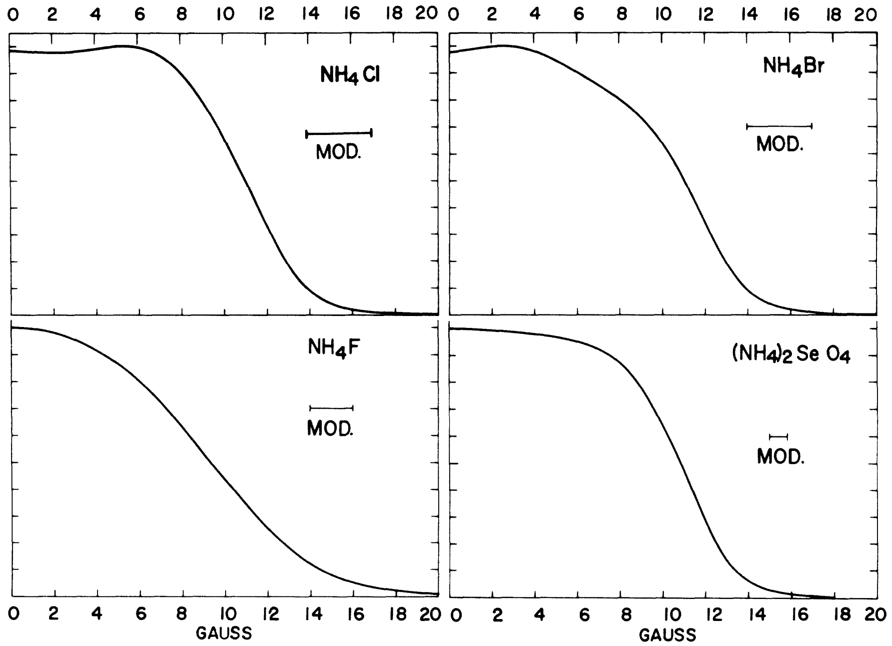

FIG. 4. Wide proton-absorption spectra. Obtained by numerical integration of experimental derivative spectra.

halides NH_4Br and NH_4F, and the selenate $(NH_4)_2SeO_4$. Their spectra (Fig. 4) have no dominant central component and all are broad with large second moments comparable to the "rigid-lattice" value. None of these solids exhibit the spin-isomeric line shape.

The single-crystal derivative spectra of NH_4Cl obtained at 4.2 °K for the [100] and [110] field directions are identical to those obtained for this solid at 77 °K by Bersohn and Gutowsky.[1] They found good agreement between their experimental line shapes (especially the [100]) and those predicted for a "four-spin-$\frac{1}{2}$" system in which the entire matrix representation of $\mathcal{H}_d'$ is diagonalized (protons are distinguishable—no symmetry restrictions on the wave function). The poorer agreement obtained by them for the [110] direction was attributed to the use of the same interionic broadening factor for each skeletal line. This criticism, however, applies equally to both orientations. A more probable explanation lies in the fact that the nitrogen contribution, which they neglected, though zero for the [100] is nonzero for the [110] field direction.

The strong similarity of all powder spectra in this group to that of NH_4Cl suggests that they are all of the "four-spin-$\frac{1}{2}$" type in which the ion is held rigidly enough by the crystal field for tunneling of the ammonium ion to be negligible and hence for the protons to be distinguishable. This interpretation is consistent with the high activation energies for rotation (≥ 4 kcal/mole) in these solids.

2. *Narrow Spectra*

All of the spectra (Fig. 5) in this group are narrow with second moments much less than the rigid-lattice value, and all exhibit an extremely narrow central component and some degree of structure in the wings at about 4 or 5 G from the center of the resonance. The division between categories 2 and 3 is somewhat arbitrary, and $(NH_4)_2U_2O_7$ and NH_4GaCl_4 might have been placed in 3 on the basis of their second moments alone. They have been placed in 2 because of their strong central components. The dashed curves in Fig. 5 are the theoretical spin-isomer line shapes, using Tomita's theory, which most closely fit the central components of the observed spectra, using an intraionic proton-proton separation of 1.68 Å—a typical value for these solids. For the case of $(NH_4)_2SnCl_6$, a typical member of this group, the best fit was achieved with a σ^2 of 1 G^2. The other members of this category and the σ^2 necessary to achieve a fit with the central component are $(NH_4)_2U_2O_7$, with a σ^2 of 4 G^2; $(NH_4)_2CrO_7$, $(NH_4)_2S_2O_8$, and NH_4SnCl_3, all with a σ^2 of 2 G^2; $(NH_4)_2PtI_6$, $(NH_4)_2Ce(NO_3)_6$, and NH_4GaCl_4, with a σ^2 of 1 G^2. Although the central components of these spectra can be reproduced quite well by a spin-isomeric line shape, the wing structure clearly cannot. Tomita's treatment predicts pronounced wing structure at about 9 G from the center of the resonance compared with that observed at only 4 or 5 G and a second moment of 16 to 20 G^2 compared to several observed values of 10 G^2 or less.

An attempt to explain these extremely low second moments could be made by assuming that the splittings of the spatial levels in such low crystal fields ($E_a \leq 2$ kcal/mole) are so large that the Boltzmann factor becomes important at 4.2 °K. This has been suggested for $(NH_4)_2Ce(NO_3)_6$.[14] Such a splitting would increase the population of the lower *A* states at the expense of the higher *T* ones, thereby increasing the ratio of meta : ortho from 5 : 3 and hence decreasing the second moment (since the second moment of the meta component is only the interionic broadening σ^2). Although this would decrease the amount of wing structure associated with the ortho component, it would still occur at the same position in the spectrum, about 9 G from H_0. This would still be in conflict with the observed wing structure at about 4 or 5 G from H_0.

In Fig. 8 is shown the observed spectrum for a single crystal of $(NH_4)_2SnCl_6$ for the [100] field direction (integrated from the derivative in Fig. 7) along with the theoretical spin-isomer spectrum for this same orientation. This orientation is particularly easy to interpret because of the complete absence of any nitrogen contribution. It can be seen that the theoretical structure predicted at about 9 G is completely absent, while only a semblance of that at about 5 G remains.

We can conclude that the spin-isomeric spectrum of Tomita is exhibited by none of the solids in this category, but that their protons, nevertheless, cannot be regarded as distinguishable, as can those in category 1. The presence of a central meta component is obvious, and its independence of crystal orientation is apparent from Fig. 7. (This is to be compared with the "four-spin-$\frac{1}{2}$" spectrum of NH_4Cl in which no such component was observed.) However, the ortho component, which is responsible for the wing structure, is much narrower (spread around H_0 much less) than the theoretical ortho isomer component predicted by Tomita.

One obvious mechanism for narrowing the ortho component is provided by the crystal field sym-

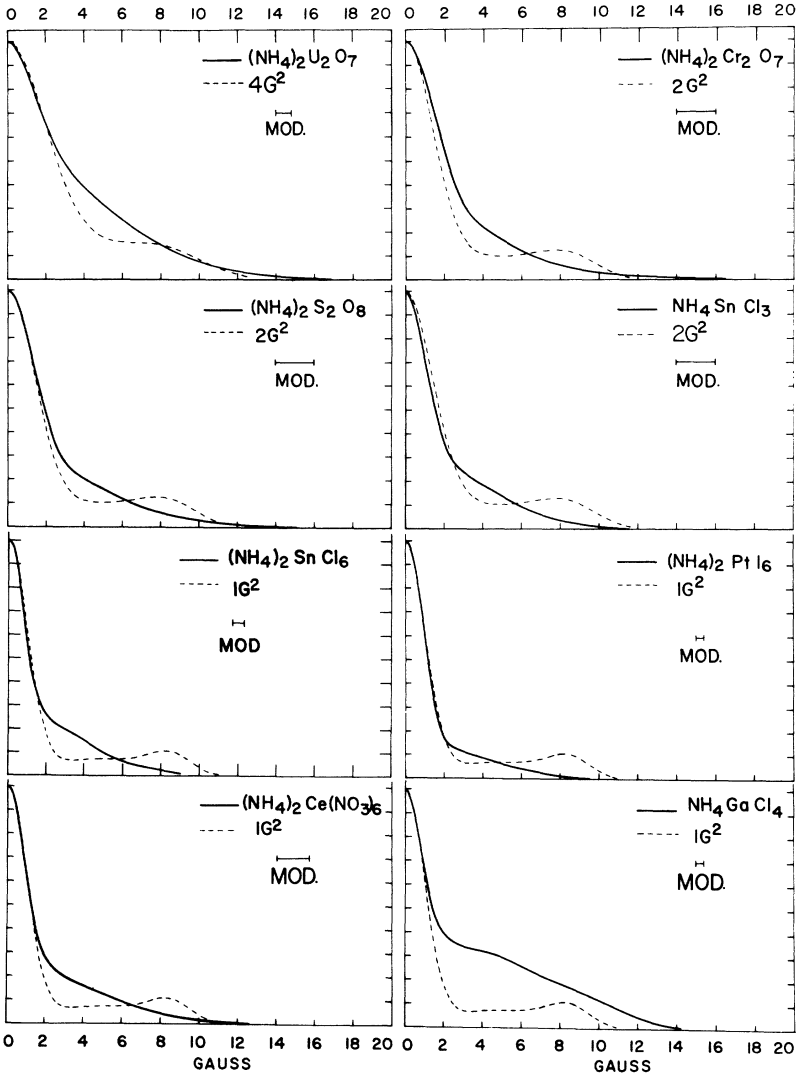

FIG. 5. Narrow proton-absorption spectra. Obtained by numerical integration of experimental derivative spectra. Dashed curves are theoretical spin isomeric line shapes, the value of σ^2 used being indicated for each.

metry. As was mentioned before, if the ammonium ion is situated in a tetrahedral environment [as in $(NH_4)_2SnCl_6$], the $3T$ spatial levels are degenerate, resulting in a certain line shape for the ortho component. However, if the environment of the ion has lower than tetrahedral symmetry, the degeneracy of the $3T$ levels will be removed and certain components of the ortho spectrum will be displaced by an amount equal to this splitting of the levels. If this splitting is much greater than the linewidth, these components will be pushed far out into the wings and be unobserved, leading to a reduction of the observed ortho component. On the other hand, if this splitting is only of the order of the linewidth, these components, while pushed out towards the wings, are still observed, thus broadening somewhat the ortho component. The latter is probably the situation in, for example, $(NH_4)_2Cr_2O_7$. It is clear in any case that Tomita's theory, in its failure to consider explicitly the spatial states, is inadequate to explain this ortho component.

The extreme narrowness of the meta components of most of the solids in this group should be noted. An exact calculation of the expected intermolecular broadening cannot be carried out since the crystal structure of most of these materials is not known. However, an estimation can be made, for example, in the case of $(NH_4)_2SnCl_6$ since although the proton positions are not known accurately, the rest of the structure is.[15] Making the approximation that the protons are all situated at the centers of their appropriate ions, the intermolecular second-moment contribution out to third-nearest neighbors is 0.7 G^2. This is quite consistent with the observed broadening of the meta component of 1 G^2 which will also contain the field inhomogeneity and modulation broadenings. It should be noted that if there is any ordering of the spin-symmetry types among the ions, this intermolecular broadening may be reduced, since an E-type ($I = 0$) ion will contribute no broadening,

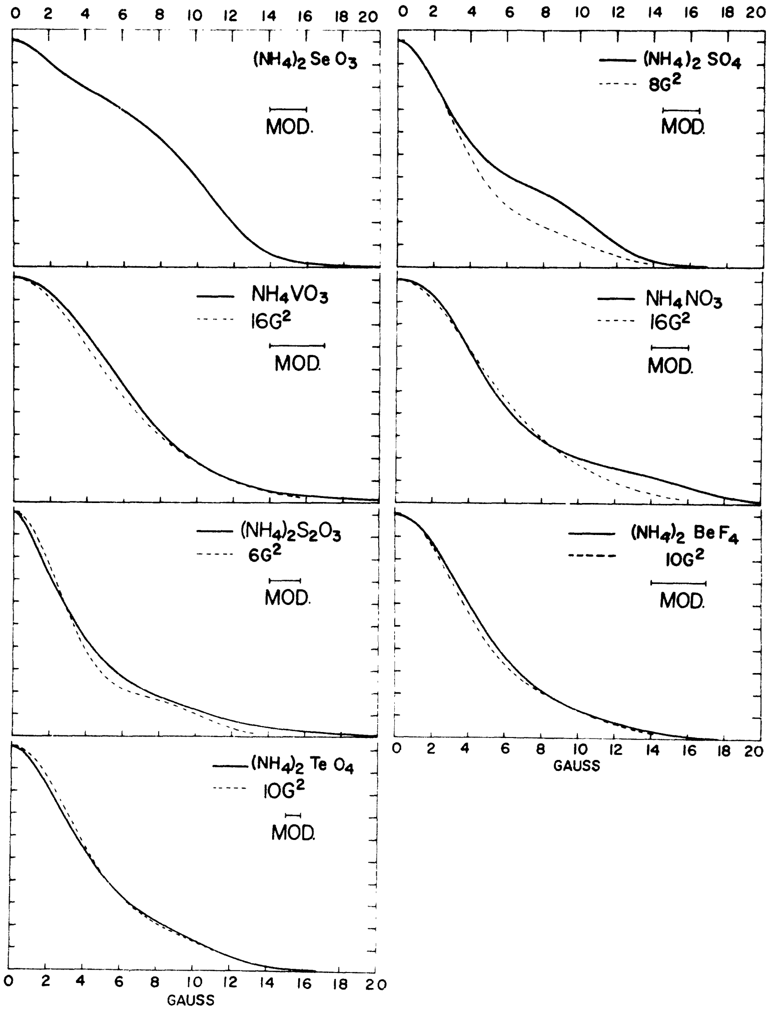

FIG. 6. Broad Gaussian proton-absorption spectra. Obtained by numerical integration of experimental derivative spectra. Dashed curves are theoretical spin isomeric line shapes, the value of σ^2 used being indicated for each.

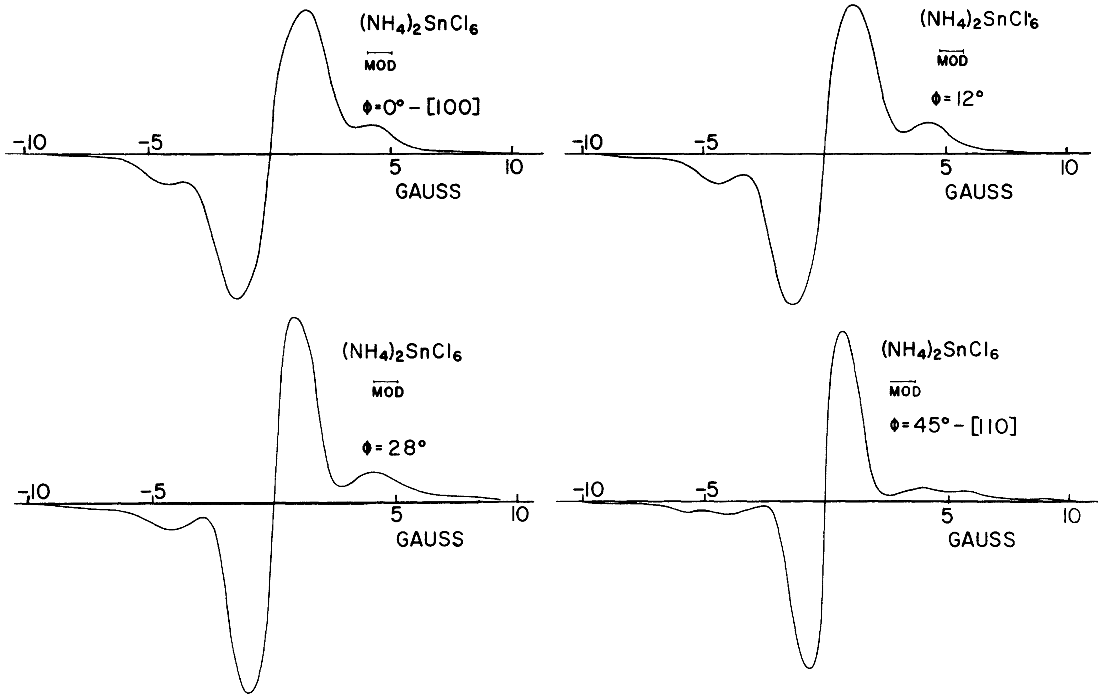

FIG. 7. Proton-absorption derivative spectra for a single crystal of $(NH_4)_2SnCl_6$. $\vec{H}_0$ is in the (001) plane and makes an angle ϕ to the [100] direction.

while a T-type ($I=1$) will contribute only two-thirds of the broadening from distinguishable protons on the same ion. Assuming that the distances between the ammonium groups in the other materials in this category are about the same or only a little smaller than in $(NH_4)_2SnCl_6$, one can account satisfactorily for the broadening of the meta component.

3. Broad Gaussian

The members of this group are characterized by spectra (Fig. 6) with a broad ($\sigma^2 \geq 6$ G^2) central component with either broadening or structure in the wings. The theoretical spin-isomer spectrum best fitting the observed spectrum for $(NH_4)_2SO_4$ is for a σ^2 of 8 G^2. However, the interionic interaction necessary to produce such a large σ^2 could no longer be considered a small perturbation, and its inclusion as a simple Gaussian broadening would be invalid. Using the proton positions given by Schlemper and Hamilton,[16] an interionic second moment of about 5 G^2 was calculated for proton-proton distances of up to 20 Å, making 8 G^2 an unrealistically high value for σ^2. Also, the amount of wing structure resolvable with this amount of broadening would be minimal, whereas that observed is quite pronounced. There are, however, two inequivalent ammonium ions in this solid,[16] the rotation of one being strongly hindered ($E_a = 3.9$ kcal/mole), the other more weakly hindered ($E_a = 2.7$ kcal/mole). Each ion may be exhibiting different types of absorption spectra, that observed being their superposition. To account for the larger second moment (33.3 G^2) of this solid, one of these would have to be the "four-spin-$\frac{1}{2}$" spectral type discussed in category 1 with a second moment around 50 G^2. If the other spectral type were spin isomeric conforming with Tomita's model with a second moment of 23 G^2 (15 G^2 for

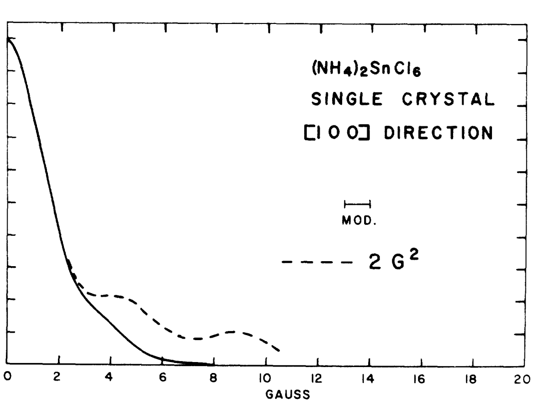

FIG. 8. Proton-absorption spectrum for $\vec{H}_0$ along [100] direction in a single crystal of $(NH_4)_2SnCl_6$. Dashed curve is theoretical spin isomeric line shape for this crystal orientation, the value of σ^2 used being indicated.

the isolated group plus an 8 G^2 broadening), the observed spectrum would have a second moment of 37 G^2 (the average of the two) which is only 10% higher than that observed. If, on the other hand, the second spectral type had been spin isomeric of the type observed in category 2, with a second moment $\lesssim 10$ G^2, the observed second moment would have been $\lesssim 30 G^2$, which is only 10% lower than that observed.

The observed spectra of $(NH_4)_2BeF_4$ and $(NH_4)_2TeO_4$ are approximated very closely by Tomita's spin-isomeric spectrum with a σ^2 of $10 G^2$. The second moments of $25 \pm 1 G^2$ and $26 \pm 1 G^2$, respectively, are consistent with that predicted (15 G^2 for the intraprotonic group plus the 10-G^2 broadening factor) with a meta : ortho ratio of 5 : 3. However, not only is 10 G^2 impossibly large for σ^2, but, in $(NH_4)_2BeF_4$ at least, as in $(NH_4)_2SO_4$, there are two inequivalent ammonium ions. It is possible that here again there may be two components in the spectrum, the narrower one being broadened sufficiently by the interionic second moment that in combination with the "four-spin-$\frac{1}{2}$" component gives an apparent agreement with the theoretical spin-isomeric prediction.

The spectra of NH_4NO_3 and NH_4VO_3 can only be approximated by a spin-isomeric spectrum with a σ^2 of at least 16 G^2, which is again far too large a value to be realized in these salts. In addition, such a broadening would obliterate all wing structure, whereas in fact the NH_4NO_3 spectrum in particular exhibits quite pronounced wing structure. It is to be expected that the superposition of the broad "four-spin-$\frac{1}{2}$" component on the narrower spin-isomeric component would tend to give the latter the appearance of being broadened more than it actually is. The fact that the theoretical spin-isomeric spectrum requires a σ^2 of 16 G^2 to approximate the observed spectrum does not mean the spin-isomeric component of the observed spectrum has an intermolecular broadening of 16 G^2.

CONCLUDING REMARKS

The splitting of the torsional ground state in a finite crystal field is brought about by the overlap of the torsional oscillator wave functions between equilibrium positions of the ion. This overlap also governs the distinguishability of the protons in that if the overlap is small, the splitting is small and the protons are distinguishable for a long time, i.e., the time for the ion to tunnel from one equilibrium position to another is long. In fact, we can say that the protons are distinguishable for a time of the order of the inverse of the splitting frequency. The characteristic time t_c for an absorption experiment is the inverse of the natural linewidth in Hz (i.e., of the order of the spin-spin relaxation time T_2). If the spatial splitting is less than this natural linewidth, the protons are distinguishable over the time interval t_c and the rigid-lattice "four-spin-$\frac{1}{2}$" spectrum is observed. However, if the spatial splitting is greater than the natural linewidth, the protons are indistinguishable over the time interval t_c and certain transitions observed in the "four-spin-$\frac{1}{2}$" spectrum are shifted out into the wings and become lost in the noise thus producing a reduced second moment.

The results of this study clearly indicate that in highly hindered ammonium ions, characterized by activation energies for reorientation of ≥ 4 kcal/mole, the protons can be regarded as distinguishable at 4.2 °K. However, in the less strongly hindered ions with activation energies $\lesssim 2$ kcal/mole, the protons are indistinguishable over a time interval comparable with t_c and effects of wave-function symmetry become important. These manifest themselves by the presence of a meta component in the absorption spectra of these salts. However, the distinct differences between the observed ortho component and that predicted for spin isomerism by Tomita strongly suggest that the initial decoupling of the spin and space eigenfunctions employed by him and the subsequent independent diagonalization of the spin state representation of the dipolar Hamiltonian are not justified in these cases. A future attempt to describe this mechanism should involve an initial coupling of spin and space eigenfunctions to form physically real states, followed by diagonalization of the matrix representative of the dipolar Hamiltonian in this spin-space basis. An approach along these lines is presently being pursued.

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Ab Initio Calculations on $KNiF_3$: Ligand-Field Effects

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Restricted Hartree-Fock molecular-orbital calculations have been carried out for various states of the cluster NiF_6^{4-} "*in vacuo*" and in a surrounding of several sets of point charges representing the perovskite lattice $KNiF_3$. All electrons were included. A "double-ζ" basis set of contracted Gaussian orbitals has been used. The calculations were performed with the computer program IBMOL IV. The Hartree-Fock approximation gives a reasonable description of the covalency effects and the spectral properties of $KNiF_3$. The calculated hyperfine-field parameters f_s and f_σ and the $10Dq$ value are about 10–25% smaller than the experimental values. Similar deviations were found for the spectral transition energies. It is argued that magnitude and sign of the crystal field splitting in this compound can be understood in terms of the well-known ionic electrostatic model provided the Born repulsion is properly taken into account.

I. INTRODUCTION

In recent years $KNiF_3$ has served as a test case for studying covalency effects in transition-metal salts. Various theoretical studies have been carried out, the results of which include predictions of the electron-spin densities at the fluorine nuclei, the cubic-crystal-field-splitting parameter, and the reduction of the Racah parameters in the crystal with respect to the free-ion values. These previous studies can be subdivided into three groups: crystal field calculations, first-order approaches to the calculation of covalency effects, and many-electron self-consistent-field (SCF) calculations.

Crystal field theory,[1] when treated as a semiempirical theory with the crystal-field-splitting parameter $10Dq$ as an adjustable parameter, has been highly successful in fitting experimental data. As a fundamental theory for the behavior of transition-metal ions in crystalline fields, however, crystal field theory fails in predicting the experimental $10Dq$ value. The inadequacy of the crystal field theory has extensively been discussed in the literature[2] and will not be repeated here.

The second group of calculations[3–8] may be characterized by the fact that although the theoretical framework is exact, the working expressions that are finally used are highly simplified. We classify these calculations therefore as first-order approaches. For a review of this type of calculation we refer to an article of Owen and Thornley.[9] The calculations are all applied to a cluster consisting of a Ni^{2+} ion, surrounded by six F^- ions, assuming that the potential of the remainder of the crystal in the region of the cluster is sufficiently constant to justify this approach. Furthermore, they have in common that only the $3d$ electrons on the Ni^{2+} ion and the $2s$ and $2p$ electrons on the F^- ions are considered explicitly. Although this second group of calculations clearly points to the relative importance of covalency in ionic crystals, they suffer from making severe approximations, such as the use of an "ionic" Hamiltonian, the employment of a basis set of unperturbed free-ion wave functions, the neglect or approximation of many multicenter integrals, the neglect of higher-order terms in the overlap and covalency parameters, and the limitation introduced by using an effective core potential instead of the core electrons explicitly.

In the third group of calculations on $KNiF_3$, which we shall discuss in somewhat more detail the NiF_6^{4-} cluster, is treated as a many-electron system and efforts are made to eliminate the deficiencies summarized above as much as possible.

Unrestricted Hartree-Fock (HF) calculations were carried out by Ellis *et al.*[10] on NiF_6^{4-} and on a triatomic cluster $NiFNi^{3+}$. They used a mixed one-center Slater-type-orbital (STO) basis centered on the central site, containing functions to describe the distributions of the central-site electrons as