Observation of CH_3 Tunneling Manifold by Level-Crossing NMR

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Rotational tunneling spectra of strongly hindered CH_3 torsional oscillator pairs which do not interact among themselves are reported. These results are obtained by applying the Zeeman-tunneling level matching method in the proton spin rotating frame. Two noninteracting CH_3 particle manifolds explain the observed CH_3 multiquantum transitions driven by intramolecular and/or intermolecular dipole-dipole interactions to first or second order. Level matching resonances indicating that two methyl groups simultaneously undergo a symmetry breaking transition are observed. The dependencies of level-crossing transitions on Zeeman-tunneling mixing time and tilt angle are reported.

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We are reporting a renewal of an experiment with which tunneling spectra of atomic groups such as CH_3 or NH_4 can be obtained with improved resolution and excellent signal. The experiment is a Zeeman-tunneling level matching in which mixing times are set long enough for the density matrix to nearly attain its diagonal form. Unlike the established NMR methods, the reported technique, which detects population equalization at level-matching resonances, gives the ground state manifold spectrum with resolution beyond the nuclear spin dipolar linewidth.

It has been generally agreed that the ideal model system for studies of quantum coherence is the methyl group CH_3 embedded in a rigid lattice [1]. This model is favored for its simplicity and for the extraordinary number of diverse environments in which the CH_3 group is found. The reported results on a few model compounds are well understood since they conform to the single particle in an effective potential model. However, most interesting are observations of spectra with features which have not been seen before.

Since the strongly hindered model methyl oscillators with small tunneling splittings (of 10 kHz to 1 MHz) generally remain in a coherent state to rather high temperatures, a lot of emphasis was placed on developing detection methods for such small tunneling splittings. The first NMR observation of a tunneling "wing" of a proton free induction decay [2] was followed by a level matching NMR in the rotating frame [3,4]. A year later the time evolution of nuclear magnetization to semiequilibrium in a spin rotating frame (SPOTS) was Fourier transformed to give tunneling satellites [5]. After this, a high to low field cycling NMR, combined with low frequency irradiation, was introduced. The ensuing spectrum showed well defined tunneling satellites [6]. In addition, high-field level-crossing techniques have been developed to study the tunneling above the MHz range [7,8].

The rotating-frame level-crossing experiment [3] begins by transferring the nuclear spin Zeeman polarization at a high magnetic field of ~1 T into the proton spin rotating frame of a low magnetic field of ~1 mT. In this sudden change of the magnetic field which the spins experience, the large proton equilibrium magnetization is oriented along a small field generated in a coil by an rf pulse (spin locking). In equilibrium at a high field, the proton spin magnetization is $M_0 = C\mathrm{H}_0/T_L$, where C is the Curie constant, $\mathrm{H}_0 \sim 1$ T, and the lattice temperatures T_L is about 10 K. Once this high-field magnetization is locked in the rotating frame of $\mathrm{H}_1 \simeq 1$ mT, the ensuing Zeeman spin temperature T_S becomes ~10 mK. Colloquially, nuclear spins in their rotating frame become cold. This transfer of polarization from high static field to low rotating-frame field is achieved in ~1 μs, while typically the equilibrium of spins and lattice is established in a few seconds. This allows many manipulations to be carried out while the spins are essentially isolated from the lattice.

The method employs a three rf pulse sequence $A_x(\theta) - B_y(\tau) - \mathrm{delay}(t) - C_y(\tau)$, where the subscripts indicate the phase. The sequence is shown as an inset in Fig. 1. The spin rotation by the rf pulse A is usually selected to be 90°. The rf field amplitudes, H_1, of pulses B and C are the same. Their durations, which are also equal, are varied between 100 μs and 100 ms, and the delay t between B and C pulses is usually set so that $10T_2 \approx t \ll T_{1\rho} \sim T_{1t}$. Here T_2 and $T_{1\rho}$ are the spin-spin relaxation time in the laboratory frame and the spin-lattice relaxation time in the rotating frame, respectively, and T_{1t} is the spin conversion time (tunneling relaxation time). If the large Zeeman polarization in the B pulse rotating frame is partially lost while the pulse B is "on," by implication, the discrete energy states of the methyl group may have taken on some of this polarization. If so, some polarization could be "returned" to the Zeeman system during the pulse C. For this reason, pulse C is established suddenly at a time when the nuclear spin coherence in the x-y plane is already phased out, to ensure that any signal after the pulse C is turned off can be due only to the polarization exchange between the CH_3 tunneling states and Zeeman states established by the rf field of the pulse C.

To reduce the dipolar line broadening the dipolar Hamiltonian can be manipulated by tilting the magnetic field in the rotating frame. This effective field $\mathbf{H}_e$ is a vector sum of the rf rotating field $\mathbf{H}_1 = \mathrm{H}_1\hat{\mathbf{y}}$ and the

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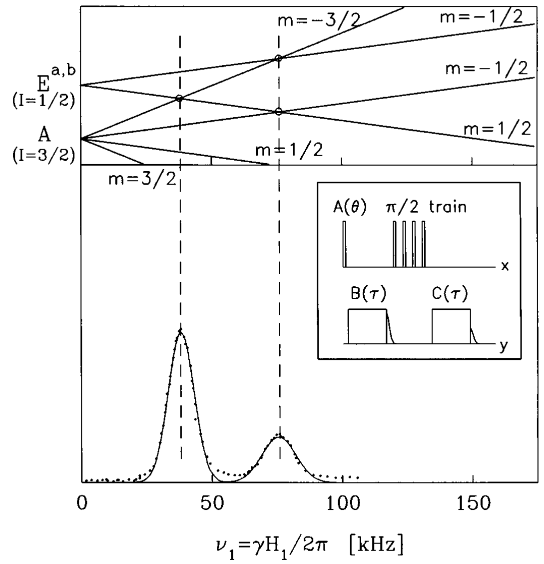

FIG. 1. The energy ground state manifold in a progressively larger magnetic field of a single CH_3 group in an effective hindering potential of threefold symmetry and, below, the Zeeman-tunneling level-crossing spectrum of methylmalonic acid at 30 K with rf irradiation of 100 μs. The solid line is the fit with two Gaussians. Pulse sequence used for the normal and tilted rotating frame experiments is shown as an inset. The pulses on the upper line have rf phase x, on the lower line, phase y. The sequence $A_x(\pi/2)$-$B_y(\tau)$ alone is the spin-locking sequence. In the tilted frame version, pulse A is tilting the magnetization by a desired angle θ (e.g., 54.7°), and pulses B and C are off resonant by h such that $\cot\text{an}\theta = h/H_1$. The 90° pulse train destroys any remaining magnetization along the z axis as well as the dipolar order.

so-called off resonance field $\mathbf{h} = 2\pi(\nu_0 - \nu)/\gamma\hat{\mathbf{z}}$, where ν_0 is the Larmor frequency, ν the actual frequency which is slightly different from the resonant frequency ν_0, and γ is the proton spin gyromagnetic ratio, while $\hat{\mathbf{y}}$ and $\hat{\mathbf{z}}$ are unit vectors along the y and z axes, respectively. The field $\mathbf{H}_e$ could be tilted at θ with respect to the main field $\mathbf{H}_0$. The best appear to be the level-crossing spectra in the $\theta = 80°$ tilted frame, while spectra at the tilt angle of $\theta = 54.7°$ are most narrow. The effect of the 54.7° tilt (magic angle) is striking, since the leading term of the dipolar interaction vanishes, because $3\cos^2\theta - 1$ becomes zero.

The search for unknown Zeeman-tunneling states matching conditions where polarization transfer would occur is conducted with pulses B and C of equal rf field amplitudes. We usually begin with $H_1 = 0.1$ mT and proceed in 0.01 to 0.05 mT increments, up to 5 mT. If the B and C rotating frames are tilted, for each new rf field $\mathbf{H}_1$ the off field h has to be adjusted to maintain the tilt angle constant at all H_1.

The first experiment was performed with methylmalonic acid. With mixing time of only 100 μs a level-crossing peak is observed at $\nu_1 = \frac{1}{2}\nu_t$ and another at $\nu_1 = \nu_t$, in excellent accord with the CH_3 single-particle ground state multiplet (Fig. 1). Under the polarization equilibration at $\nu_1 = \frac{1}{2}\nu_t$ and $\nu_1 = \nu_t$ the magnetic quantum numbers change by $|\Delta M| = 2$ and $|\Delta M| = 1$, respectively. From the positions of the polarization transfer maxima the tunneling frequency of the methylmalonic acid is estimated to be 76 ± 1 kHz, in agreement with the published value [9].

As this spectrum is the direct result of the transfer of polarization between the Zeeman and tunneling levels (during the pulse B) and back (during the pulse C), the magnetization following pulses B and C should depend on the duration τ of these pulses when population equilibration (mixing) occurs. Therefore, the time during which a level-crossing signal reaches its extremum can be measured by increasing the equilibration (or mixing) time τ until the signal following B is minimum and the signal following C is maximum. For methylmalonic acid the mixing times of maximum intensities at $\nu_1 = 38$ and 76 kHz were found to be ~1.5 and ~5 ms, respectively. It follows that in Fig. 1 the full intensities of the two level-crossing peaks have not been reached yet since the equilibration was allowed to run only 100 μs.

When the mixing time is increased to 10 ms, to establish full intensities of the two level-crossing peaks and for weaker transitions to bring about a measurable polarization transfer, a spectrum with six peaks turns out (Fig. 2). To account for these, the two-particle states AA, AE, and EE, with spins of 3, 2, and 1, respectively, are invoked [10,11]. It should be noted that three or more (noninteracting) CH_3 multiplets, e.g., AAA, AAE, and so on, have the same level-crossing spectrum as in Fig. 2 with additional level-matching resonances. However, since only two-particle level-matching resonances were observed, the two-particle manifold is employed as the simplest model for discussing the observed level-crossing spectra. The level crossings at $\nu_e = \frac{2}{3}\nu_t$ and $\nu_e = 2\nu_t$ demonstrate that two tunneling CH_3 groups undergo a simultaneous symmetry breaking transition which is induced by the intermethyl dipolar interaction. The transition at $\nu_e = \frac{1}{4}\nu_t$ is a four quanta ($|\Delta M| = 4$) event, and the transitions at $\nu_e = \frac{2}{3}\nu_t$ and $\nu_e = \frac{1}{3}\nu_t$ are three quanta ($|\Delta M| = 3$) events.

Since the dipolar interaction which couples the experimentally matched (degenerate) levels is a tensor operator of rank 2, it gives rise to matrix elements between energy states whose magnetic quantum numbers differ by 0, ±1, or ±2. Thus the $|\Delta M| = 3$ and $|\Delta M| = 4$ transitions are forbidden in first order. However, these second-order transitions bring about polarization transfer if orders of magnitude longer mixing times are allowed. To illustrate this, spectra of hexane with various mixing times τ in the normal rotating frame ($\theta = 90°$) are shown in Fig. 3. Here the second-order transition peaks at $\nu_1 = \frac{1}{4}\nu_t$ (71 kHz) and $\nu_1 = \frac{1}{3}\nu_t$ (97 kHz) do not show up until the mixing time becomes 1 ms. In 1 ms the $\frac{1}{2}\nu_t$ peak is nearly at its maximum. As the mixing time is increasing, the $|\Delta M| = 3$ (at $\nu_1 = \frac{1}{3}\nu_t$) and $|\Delta M| = 4$ (at $\nu_1 = \frac{1}{4}\nu_t$) transitions continue to grow while the $\nu_1 = \frac{1}{2}\nu_t$ peak remains of constant intensity.

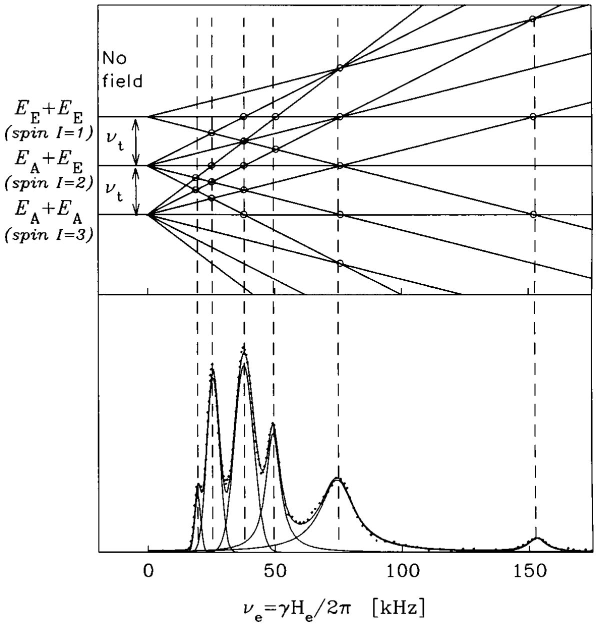

FIG. 2. The energy level diagram of two nominally noninteracting methyl groups with level crossings at $\nu_e = n\nu_t$ for $n = \frac{1}{5}, \frac{1}{4}, \frac{1}{3}, \frac{1}{2}, \frac{2}{3}$, 1, and 2. At the bottom is the tunneling spectrum at 30 K of methylmalonic acid obtained in the rotating frame tilted by $\theta = 54.7°$. The duration τ of pulses B and C was 100 ms. Note that the level crossing at $\nu_e = \frac{1}{5}\nu_t$ is not observed. The symbols on the ordinate refer to the product states of two noninteracting tunneling CH_2 groups: $|A\rangle|A\rangle$, $|A\rangle|E\rangle$, and $|E\rangle E\rangle$. When their energies are added the lowest is $E_A + E_A$, next is $E_A + E_E$, followed by $E_E + E_E$. In this picture these states are separated by ν_t. Since the spins of the two noninteracting CH_3 groups add up, the total spin of the $|A\rangle|A\rangle$ state is 3, of the $|A\rangle|E\rangle$ states is 2, and of the $|E\rangle|E\rangle$ states is 1.

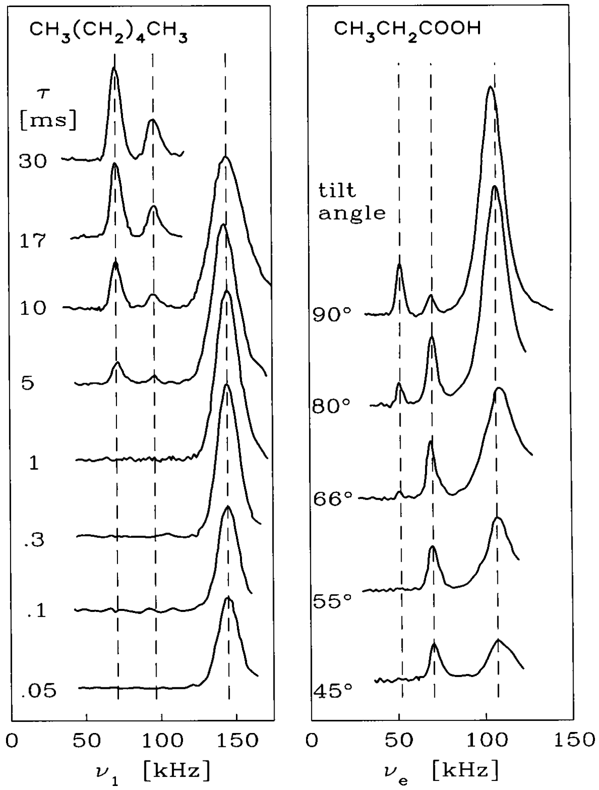

FIG. 3. Spectra of hexane at 30 K with different mixing times τ are shown at the left side. The normal rotating frame with $\theta = 90°$ was employed. Spectra of propionic acid with different tilt angles θ are at the right side. The mixing time τ and the temperature were 10 ms and 30 K, respectively. The vertical lines represent level crossings (from left to right) at $\frac{1}{4}\nu_t$, $\frac{1}{3}\nu_t$, and $\frac{1}{2}\nu_t$.

It is well known that the dipolar Hamiltonian term which connects energy states with magnetic quantum numbers differing by ± 1 is proportional to $\sin\theta \cos\theta$, while the term responsible for the $|\Delta M| = 2$ transitions is proportional to $\sin^2\theta$. Consequently, in the normal rotating frame, where $\cos\theta = 0$, odd transitions are not allowed. The same argument can be extended to higher order transitions. Spectra of propionic acid in Fig. 3 illustrate the θ dependence of the intensities of level-crossing lines. As the effective field tilts away from the x-y plane the even quantum number peaks at $\nu_e = \frac{1}{4}\nu_t$ (52 kHz) and $\nu_e = \frac{1}{2}\nu_t$ (107 kHz) begin to decrease, while the odd quantum number transition line at $\nu_e = \frac{1}{3}\nu_t$ (71 kHz) begins to increase. Here it should be noted that our rf coil may not be exactly perpendicular to the main field H_0; this enables odd transitions $\nu_1 = \frac{1}{3}\nu_t$ at $\theta = 90°$ (Fig. 3)

Level-crossing spectra of methyl rotators in four lattices, with high hindrance for rotation and, subsequently, low tunneling splittings, are presented in Fig. 4. The materials are methylmalonic acid, dimethyl sulfide, propionic acid, and hexane. The mixing times were all 10 ms, during which the level-crossing peaks brought about by second-order processes grew substantially. The four two-methyl states spectra indicate that CH_3 groups in all these solids are noninteracting.

A magic frame spectrum at 10 K of acetyl acetone (2,4-pentanedione, $CH_3COCH_2COCH_3$) is shown in Fig. 5. This material is known to have low hindering potential of threefold symmetry. With INS and NMR methods [12], two A to E tunneling splittings were arrived at: ~10 GHz and a few hundred MHz. The level crossing peaks in Fig. 5 demonstrate the existence of yet another single-particle-like tunneling splitting (120 ± 2 kHz) characteristic of a strong hindering threefold potential. The small $|\Delta M| = 3$ level-crossing peak at ~40 kHz, where $\nu_e = \frac{1}{3}\nu_t$, is also seen, but none at $\nu_e = \frac{2}{3}\nu_t$. We have no explanation for the broad level-crossing base from which the level-crossing peaks stand out.

For a pair of noninteracting methyl groups having a Zeeman and rotational Hamiltonian $\hat{H}_Z + \hat{H}_R$ and a much smaller dipolar interaction $\hat{H}_\mathrm{d}$, consisting of an intramethyl group part $\hat{H}_d^{\mathrm{intra}}$ and an intergroup part $\hat{H}_d^{\mathrm{inter}}$, the 2^6 zeroth-order eigenstates are denoted by $|\Gamma M\rangle$. Here Γ indicates the symmetry and M is the magnetic quantum number. These symmetry-adapted wave functions $|\Gamma M\rangle$ which satisfy the Pauli principle are products of a spatial part $|\Gamma\rangle$ and a spin part $|M\rangle$.

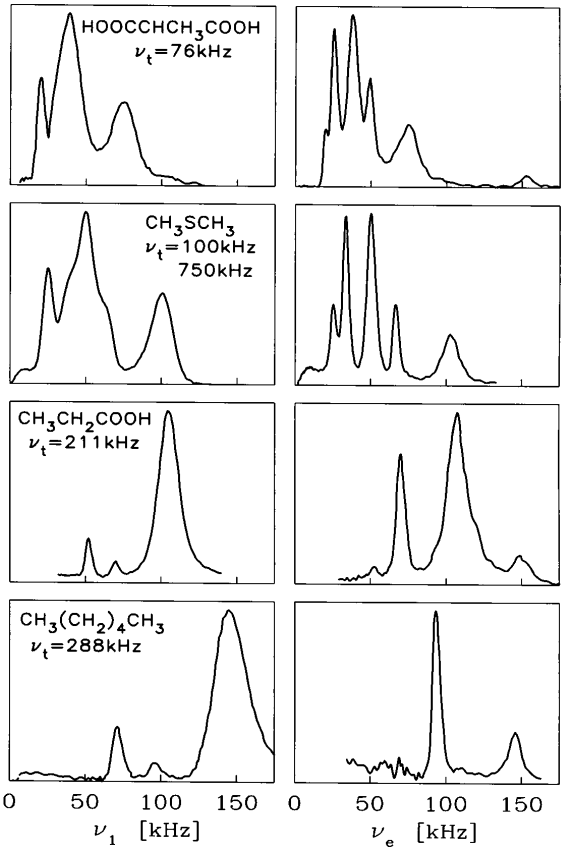

FIG. 4. Spectra at 30 K with mixing times of 10 ms are shown (from top to bottom) for methylmalonic acid, dimethyl sulfide, propionic acid, and hexane. In the left column are spectra in the rotating frame with $\theta = 90°$, and in the right column are the spectra in the magic frame, $\theta = 54.7°$.

The first-order Zeeman-tunneling transition rate is proportional to

$$|\langle \Gamma' M' | \hat{H}_d^{\Gamma''} | \Gamma M \rangle|^2,$$

where $\Gamma' = \Gamma'' \times \Gamma$, $M' = M \pm 1$ or $M \pm 2$, and $\hat{H}_d^{\Gamma''}$ is the symmetry-adapted dipolar Hamiltonian. In first order, $\hat{H}_d^{\rm intra}$ and $\hat{H}_d^{\rm inter}$ induce, respectively, the single-particle and two-particle transitions between those energy levels whose magnetic quantum numbers differ by $|\Delta M| = 1, 2$. For example, a transition between the zeroth-order Zeeman-tunneling states, $|(E^aE^a)_{\rm space}(E^bE^b)_{m=-1}\rangle$ and $|(AA)_{\rm space}(AA)_{m=-2}\rangle$, is induced at $\nu_e = 2\nu_t$ by the intermethyl group dipole-dipole interaction $\hat{H}_d^{\rm inter}$. This transition line is weaker by $(R_0/R_{ij})^6$, where R_0 and R_{ij} are the intragroup and intergroup proton-proton distances, than the first-order single symmetry breaking transition which is driven by $\hat{H}_d^{\rm intra}$. The factor depends on lattice geometry and may have a value anywhere between ~ 0.5 and $\sim 10^{-2}$.

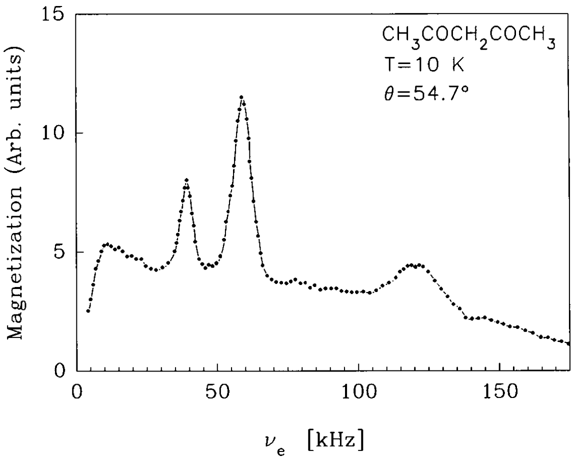

FIG. 5. Shown is the signal following pulse C of acetyl acetone at 10 K in the tilted rotating frame ($\theta = 54.7°$) with mixing time of 10 ms.

Without going into detail, all even quanta transitions depend on $\sin^2\theta$ and the odd ones on $\sin\theta \cos\theta$. This dependence can be explored by tilting the rotating frame. In addition, the $\frac{1}{4}\nu_t$, $\frac{1}{3}\nu_t$, $\frac{2}{3}\nu_t$, and $2\nu_t$ transitions are driven by $\hat{H}_d^{\rm inter}$ as well as $\hat{H}_d^{\rm intra}$, while the $\frac{1}{2}\nu_t$ and ν_t transitions are by $\hat{H}_d^{\rm intra}$ only. The population equilibration is fastest if coupling is first-order intramolecular ($\frac{1}{2}\nu_t$ and ν_t). Next come first order intermolecular processes ($2\nu_t$). Slowest are second-order intermolecular processes ($\frac{1}{4}\nu_t$, $\frac{1}{3}\nu_t$, and $\frac{2}{3}\nu_t$). This is in good accord with observations. However, if enough mixing time is allowed at each level matching, all corresponding populations are equalized yet not all peaks have the same amplitude. In such a situations, the signal depends entirely on the magnetization change which a particular population equalization brings about. For example, a weak coupling may bring about a large magnetization change ($\frac{2}{3}\nu_t$) while a strong coupling may result in a smaller magnetization change (ν_t). A calculation of the transition rates and magnetization changes, together with experimental details, will be published elsewhere.

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[1] W. Press, *Single-Particle Rotations in Molecular Crystals*, Springer Tracts in Modern Physics, Vol. 92 (Springer, New York, 1981).
[2] C. S. Johnson Jr. and C. Mottley, Chem. Phys. Lett. **22**, 430 (1973).
[3] R. S. Hallsworth, D. W. Nicoll, J. Peternelj, and M. M. Pintar, Phys. Rev. Lett. **39**, 1493 (1977).
[4] A. Z. Damyanovich, Ph.D. Thesis, University of Waterloo 1993 (unpublished).
[5] D. W. Nicoll and M. M. Pintar, Phys. Rev. Lett. **41**, 1496 (1978).
[6] S. Clough, A. J. Horsewill, P. J. McDonald, and F. O. Zelaya, Phys. Rev. Lett. **55**, 1794 (1985).
[7] P. van Hecke and G. Janssens, Phys. Rev. B **17**, 2124 (1978).
[8] G. Vandemaele, P. Coppens, and L. Van Gerven, Phys. Rev. Lett. **56**, 1202 (1986).
[9] M. J. Barlow, S. Clough, P. A. Debenham, and A. J. Horesewill, J. Phys. Condens. Matter **4**, 4165 (1992).
[10] A. Häusler and A. Hüller, Z. Phys. B **59**, 177 (1985).
[11] G. Voll, Physica (Amsterdam) **202B**, 239 (1994).
[12] A. J. Horsewill, A. M. Alsanoosi, and C. J. Carlile, J. Phys. C **20**, L869 (1987).