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Rotational tunneling in solids: Theory of neutron scattering. II.

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Tedrahedral molecules or polyatomic ions (e.g., methane or the ammonium ion) in a solid experience a rotational potential with 12 equivalent minima. The rotational-energy spectrum shows a characteristic tunneling spectrum which, since the advent of high-resolution neutron scattering techniques, is accessible to the experiment. Tunneling frequencies have since been used to determine rotational potentials with the aim to assess the rather unknown anisotropic intermolecular forces. Further information is contained in the intensity of the tunneling lines, in their polarization for different directions of the momentum transfer and in their $|Q|$ dependence. To extract this information we have undertaken a detailed study of the tunneling wave functions including their librational width and the symmetry of the spin functions. For the properly symmetrized wave functions neutron scattering matrix elements have been calculated, and line intensities have been derived. The calculation has been performed for fully protonated and fully deuterated molecules (XH_4 and XD_4). The pocket-state formalism has been used, and the influence of finite-width pocket states on the line intensities has been studied in detail. Special attention has been attributed to molecules at low-symmetry lattice sites. On the one hand, the interpretation of the experimental data is particularly difficult for low site symmetries; on the other hand, there are fewer degeneracies and consequently more transition lines. The increased experimental information can be used to determine the symmetry elements and the strength of the rotational potential. The information contained in the intensities turns out to be extremely important.

I. INTRODUCTION

A molecule or polyatomic ion experiences an angle-dependent orientational potential as it rotates in a solid. For tetrahedral molecules this potential possesses 12 equivalent minima or potential pockets. If the potential barriers between the pockets are high and if the moment of inertia of the molecule is large, the molecule sits in one of the 12 pockets and performs small angular oscillations around its equilibrium orientation. The angular oscillations are also termed librations. The librational ground-state wave function in one of the 12 potential pockets is called a pocket state. For high barriers and large moments of inertia the 12 pocket states are degenerate. For low barriers and small moments of inertia this degeneracy is lifted because of the overlap of the librational wave functions in different pockets. For tetrahedral molecules in low-symmetry crystal fields, the dominant 120° overlap matrix elements h_1, h_2, h_3, and h_4 for rotations of the molecule around the four threefold symmetry axes are all different. This is also true for the less important 180° overlap matrix elements H_x, H_y, and H_z for rotations around the three twofold symmetry axes of the molecule. Consequently the 12 states are separated into a singlet A state, three triplet T states, and a doublet E state. Several nuclear-spin states may combine with each of these levels. This considerably increases the multiplicity of the levels.[1] Specific-heat[2] and nuclear-magnetic-resonance[3] T_1 measurements provide integral information on the tunneling splitting, while neutron[4–12] and advanced NMR techniques[13–15] provide spectroscopic information and thus can yield a complete level scheme. Experiments of the latter kind have been performed on solid CH_4 (Refs. 4 and 11) and recently on all isotopic methanes[7,9] $CH_{4-n}D_n$ with $n = 1, 2, 3, 4$, furthermore on methane adsorbed on grafoil,[10] on SiH_4,[16] and on a number of NH_4^+ salts.[5,6,8,14,15] In all the examples mentioned so far, the orientational potential reflects the tetrahedral symmetry of the charge distribution in the molecule.[17] It is very nearly tetrahedral also in $CH_{4-n}D_n$ (for $n = 1, 2, 3$) which, however, are no spherical top molecules. There are 12 equivalent minima or potential pockets. Rotational tunneling with one degree of freedom is realized for CH_3 side groups[3,18–23] rotating around the bond which connects them to the rest of the molecule and for NH_3 molecules rotating around the axis of their dipole moment which often is aligned by the electrostatic field in the crystal. One-dimensional rotation in threefold symmetry with three potential pockets is conceptually much easier.[24]

The tunnel splitting may be used to obtain the tunneling levels and several authors have related the level spacing to the orientational potential which determines the rotational motion of the molecule.[25–29]

In this paper we will calculate the intensities of the different tunneling transitions in a neutron scattering experiment. The intensities are closely related to the shape of the wave functions. This is analogous to phonon intensities which yield the polarization vectors of the phonon modes.

One way to describe the wave function of a tunneling system is by means of linear combinations of pocket states.[30] The intensity is strongly influenced by the way the pocket states are combined to tunneling wave functions. These combinations are determined by the symmetry requirements under proton or deuteron exchange and by the site symmetry at the position of the XH_4 or XD_4 molecule. ($X=\mathrm{C}$ or N). For strong potentials, i.e., for small splittings, the tunneling states are strongly peaked and their detailed shape is of lesser importance for the calculation of the intensities. This is true in spite of the fact that the splitting itself depends on the shape of the wave functions in the overlap region, i.e., on the tails of the pocket states.

The expected low sensitivity of the intensities on the detailed shape of the pocket states was the starting point for an earlier calculation[30] where the pocket states have been replaced by δ functions in the minima of the potentials. It has been criticized by Ozaki, Kataoka, and Yamamoto[31] that this approximation has also been applied to the case of solid CH_4 with quite a sizable tunnel splitting which is an indication of not so narrow pocket states. In the present paper we shall go beyond the δ-function approximation by using isotropic pocket states of finite width. The width parameter for solid CH_4 will be taken from an earlier calculation.[26] It will be seen that the crude δ-function approximation provides quite a good zero-order approximation for the intensities. The main effect of the finite width of the wave functions is a reduction of the intensities with increasing momentum transfers. Such a behavior, reminiscent of the usual Debye-Waller factor, is expected. Ozaki *et al.*[31] have constructed their wave functions as linear combinations of free rotor functions[32] which have been optimized to represent the measured tunnel splitting. Their functions are better than ours in the sense that they also contain the anisotropy of each individual pocket state originating from the anharmonicities of the potential pockets. In view of the relatively good results obtained even with δ functions, it is clear that anisotropic pocket states will not change our results appreciably. Therefore we have restricted ourselves to the very simple finite width pocket states. A generalization to anisotropic states is, however, possible also within the pocket state formalism.

II. CONSTRUCTION OF THE WAVE FUNCTIONS

The tunneling states of different molecules in the sample do not couple.[30] The neutron scattering cross section therefore is a sum over the contributions from the individual molecules. The double differential scattering cross section of a single molecule can be written (we follow the notation of Ref. 30):

$$\frac{d^2\sigma}{d\Omega\, dE}=\frac{k'}{k}\sum_{\mu,\mu'}\sum_{\alpha,\alpha'}P_\mu P_\alpha |M|^2\delta(\omega-\omega_{\alpha\alpha'}) \ , \tag{2.1}$$

$$M=\langle\psi_{\alpha'}\mu'\vec{k}'|W|\psi_\alpha\mu\vec{k}\rangle \ . \tag{2.2}$$

This is the cross section for neutron scattering into the solid angle element $d\Omega$ around Ω and into the energy interval between E and $E+dE$. Unprimed symbols relate to quantities before scattering, primed symbols to the same quantities after scattering. $|\mu\vec{k}\rangle=|\mu\rangle\exp(i\vec{k}\cdot\vec{r})$ is a plane-wave state (wave vector $\vec{k}$) of the neutron in the spin state $|\mu\rangle$. $|\psi_\alpha\rangle$ is a tunneling state of the molecule, P_μ and P_α are the statistical weights for the states of the neutron and of the molecule, $\hbar\omega$ is the energy gained by the neutron, and $\hbar\omega_{\alpha\alpha'}$ is the energy difference between the states $|\psi_\alpha\rangle$ and $|\psi_{\alpha'}\rangle$. W is the interaction of the neutron with the four protons (or deuterons) of the molecule

$$W=\sum_{\gamma=1}^{4}A_\gamma\delta(\vec{r}-\vec{r}_\gamma) \ , \tag{2.3}$$

$$A_\gamma=A_{\mathrm{si}}+A_{\mathrm{sd}}\vec{S}\cdot\vec{I}_\gamma \ , \tag{2.4}$$

$\vec{r}$ and $\vec{S}$ are the position and spin operator of the neutron, $\vec{r}_\gamma$ and $\vec{I}_\gamma$ are the position and spin operator of one of the four protons (or deuterons) of the molecule. $A_{\mathrm{si}}=a_{\mathrm{coh}}$ is the spin-independent part of the proton (deuteron) scattering length, and $A_{\mathrm{sd}}=2[I(I+1)]^{-1/2}a_{\mathrm{inc}}$ is the spin-dependent part.

To evaluate Eq. (2.1) we need the wave functions $|\psi_\alpha\rangle$. A former treatment[30] of the problem had two shortcomings: (i) it was restricted to protonated molecules and (ii) the pocket-state wave functions have been approximated by δ peaks in the potential minima. In this paper we shall extend the treatment to deuterated molecules and we shall consider wave functions of finite width.

Equation (2.1) will first be evaluated for the case of a tetrahedral molecule in a tetrahedral field. This is the situation encountered in $(NH_4)_2SnCl_6$,[6,12] where the 120° overlap matrix elements are all equal: $h_1=h_2=h_3=h_4=h$ (note the change in notation from Ref. 30). The three T levels then are degenerate with an A-T level spacing $\Delta_{A-T}=8h$ and a TE spacing $\Delta_{T-E}=4h$. Building on this most symmetrical example we shall explicitly derive the scattering law also for trigonal site symmetry with $h_1 \neq h_2 = h_3 = h_4$ and for site symmetry 2 or $mm2$ with $h_1 = h_2 \neq h_3 = h_4$. The formalism is valid for any symmetry.

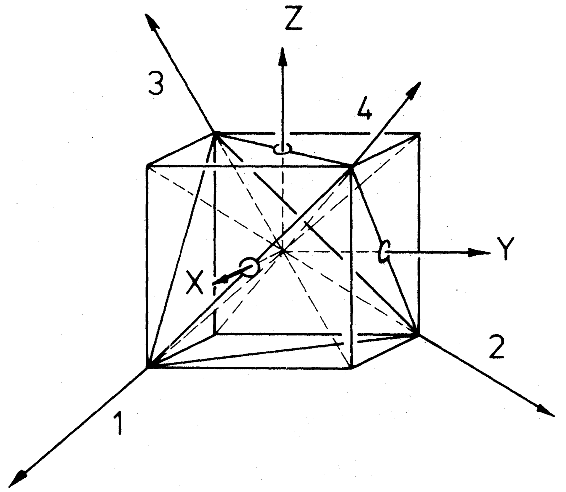

FIG. 1. Equilibrium orientation of a tetrahedron in a crystal field. In a pocket state the tetrahedron performs small angular oscillations around the equilibrium orientation. Different pocket states are obtained by even permutations of the spin states of the four protons or deuterons at the corners of the tetrahedron.

To define the pocket states we attach a coordinate system to the crystal in such a way that Fig. 1 shows one of the 12 equilibrium orientations of the molecule. The numbers 1, 2, 3, and 4 in Fig. 1 identify the four sites around a central carbon (CH_4, CD_4) or nitrogen atom (NH_4^+, ND_4^+) which may be occupied by protons (or deuterons). The individual protons (deuterons) of the molecule are not identified. The tunneling wave functions $|\psi_\alpha\rangle$ are then constructed as linear combinations

$$|\psi_\alpha\rangle = D_\alpha |\phi_\alpha\rangle \sum_{m=1}^{M} b_{\alpha m} [\chi_m\rangle \ , \tag{2.5}$$

of pocket states[30]

$$[\chi_m\rangle = [\mu_1\mu_2\mu_3\mu_4\rangle \ . \tag{2.6}$$

μ_γ (with $\gamma = 1, 2, 3$, and 4) denotes the spin state of the proton at site γ without identifying which proton it is. Following Ref. 30 the so-defined pocket state $[\chi_m\rangle$ is written with an angular bracket to distinguish it from $|\chi_m\rangle = |\mu_1\mu_2\mu_3\mu_4\rangle$ where μ_γ identifies the individual proton. The functions $[\chi_m\rangle$ are totally symmetric under a symmetry operation of the tetrahedron [corresponding to an even permutation of the four protons (deuterons)].[1] For protons μ_γ assumes the values $+\frac{1}{2}$ and $-\frac{1}{2}$. The sum in Eq. (2.5) then runs over $M=16$ terms. For deuterons μ_γ assumes the values $+1$, 0, and -1 leading to $M=81$ terms in Eq. (2.6). The rotational state function $|\phi_\alpha\rangle$ with $\alpha = A$, E, or T is introduced in order to allow for a finite librational width of the wave function. It describes the oscillations of the frame (Fig. 1) which has been used to define the symmetrized spin functions and multiplies each spin function $[\mu_1\mu_2\mu_3\mu_4\rangle$. When the rotations are described in terms of quaternions $\tau = (\tau_1\tau_2\tau_3\tau_4)$, a Gaussian function centered at the equilibrium orientation $\tau_{\text{eq}} = (0,0,0,1)$

$$\langle \tau | \phi_\alpha \rangle = \langle \tau | X_\alpha \rangle = \tilde{C}_\alpha \exp(X_\alpha \tau_4^2) \tag{2.7}$$

would be a good representation for $|\phi_\alpha\rangle$. Wave functions of the type (2.7) have been used several times in context with tunneling.[30] More sophisticated forms of the rotational part of the wave function[27] are necessary when tunneling frequencies have to be determined with high precisions. For relatively weak potentials the width parameter X_α is different for the A-, T-, and E-type wave functions.[26] This is the reason why different transitions should have a different $|Q|$ dependence as predicted by Ozaki *et al.*[31] For stronger potentials the differences between X_A, X_T, and X_E become very small and the effect disappears. $\tilde{C}_\alpha$ is a normalization constant which guarantees the normalization of $|\phi_\alpha\rangle$ on the surface of the four-dimensional unit sphere: $\oint d^4\tau |\langle \tau | X_\alpha \rangle|^2 = 1$. In the limit of small amplitudes the mean squared angular displacement $\langle \vec{\gamma}^{\,2} \rangle$ of a molecule from its equilibrium orientation τ_{eq} is found from the equation

$$\begin{aligned} \langle \vec{\gamma}^{\,2} \rangle_\alpha &= \langle \gamma_1^2 + \gamma_2^2 + \gamma_3^2 \rangle_\alpha \\ &= 12 \langle X_\alpha | \tau \rangle \tau_1^2 \langle \tau | X_\alpha \rangle \\ &= 3/X_\alpha + O(1/X_\alpha^2) \ . \end{aligned} \tag{2.8}$$

In cases where X_α is large, $\langle \tau | X_\alpha \rangle$ is a function which is sharply peaked at the equilibrium orientation. Then one may equally well use the function

$$\langle \tau | \phi_\alpha \rangle = \langle \tau | N_\alpha \rangle = C_\alpha \tau_4^{2N_\alpha} \ , \tag{2.9}$$

which for large N_α is also sharply peaked at the equilibrium orientation.[33] A similar integration as Eq. (2.9) yields

$$\langle \vec{\gamma}^{\,2} \rangle_{N_\alpha} = 3/N_\alpha + O(1/N_\alpha^2) \ . \tag{2.10}$$

In the following we shall rather use $\langle \tau | N_\alpha \rangle$ because several integrations are much easier to perform. The coefficients $b_{\alpha m}$ of Eq. (2.5) have been determined in several steps. First consider a spin state $[\chi_1\rangle = [\mu_1\mu_2\mu_3\mu_4\rangle$ together with the 11 states $[\chi_m\rangle$ which follow from even permutations of the symbols μ_1, μ_2, μ_3, and μ_4. The 12 even permutations correspond to different configurations of the spins at the four sites which are occupied by protons or deuterons. The 12 spin configurations are related to each other by rigid body rotations of the tetrahedron; they are pocket states. We combine these 12 pocket states $[\chi_m\rangle$ to linear combinations of A-, T_x-, T_y-, T_z- or E-type symmetry

$$|\eta_\alpha\rangle = D_\alpha \sum_m g_{\alpha m}[\chi_m\rangle \quad . \tag{2.11}$$

The coefficients $g_{\alpha m}$ are found in Table I. The index α identifies one of the 12 symmetry representations. D_α is a normalization constant which is different for the A, T, and E states. [$D_A = 1/\sqrt{12}(1+8b)$, $D_T = \frac{1}{2}$, and $D_E = 1/\sqrt{12}(1-4b)$ where b is the 120° overlap.] In XD_4 where each of the μ_i may assume three different values we have the following possibilities for $[\mu_1\mu_2\mu_3\mu_4\rangle$: $[\alpha\alpha\alpha\alpha\rangle$, $[\alpha\alpha\alpha\beta\rangle$, $[\alpha\alpha\beta\beta\rangle$, and $[\alpha\alpha\beta\gamma\rangle$ with $\alpha \neq \beta \neq \gamma \neq \alpha$. In XH_4 molecules with only two possible values for μ_i, the last case does not exist. From $[\alpha\alpha\alpha\alpha\rangle$ one only obtains the A-type combination $|\eta_A\rangle = [\alpha\alpha\alpha\alpha\rangle$. An inspection of Table I shows that there are no functions of T- and E-type symmetry. Similarly we generate one function each of A-, T_{x1}-, T_{y1}-, and T_{1z}-type symmetry from $[\alpha\alpha\alpha\beta\rangle$. Again the E-type combinations are absent and

$$|\eta(T_{x1})\rangle = |\eta(T_{x2})\rangle = |\eta(T_{x3})\rangle \quad .$$

For the same reason the six permutations of $[\alpha\alpha\beta\beta\rangle$ decompose into one A-, three T-, and two E-type combinations whereas $[\alpha\alpha\beta\gamma\rangle$ yields all (12) possible combinations ($=A, 3x3\,T, 2E$).

One thus obtains 81 combinations $|\eta_\alpha\rangle$ for XD_4 molecules and 16 combinations $|\eta_\alpha\rangle$ for XH_4 molecules. The symmetrized functions are eigenfunctions of the tunneling Hamiltonian H_t (in the pocket-state subset of the Hilbert space). They are also eigenfunctions of I^z. $\vec{I} = \sum_{\gamma=1}^{4} \vec{I}_\alpha$ is the operator of total nuclear spin and thus the eigenvalues of I^z are $\langle I^z\rangle = \mu_1+\mu_2+\mu_3+\mu_4$. Table I has been constructed for the case of a tetrahedral molecule at a site of tetrahedral symmetry. For lower site symmetry the decomposition into A and E states remains unchanged. The states of T symmetry, however, have to be arranged differently:

$$|\lambda(T_\sigma)\rangle = \sum_\alpha R_{\sigma\alpha}|\eta(T_\alpha)\rangle \quad . \tag{2.12}$$

The coefficients $R_{\sigma\alpha}$ are found from a diagonalization of H_t in the 3×3 subspace of T functions

$$\langle\eta(T_\alpha)|H_t|\eta(T_\beta)\rangle = E_\alpha\delta_{\alpha\beta} \quad .$$

For trigonal site symmetry ($h_1 = h_2 = h_3 \neq h_4$) and for symmetry 2 ($h_1 = h_2 \neq h_3 = h_4$) the coefficients $R_{\sigma\alpha}$ do not depend on the size of the overlap matrix-elements, they are determined by symmetry alone. For cases of lower symmetry as , e.g., m with $h_1 \neq h_2 = h_3 \neq h_4$ encountered in NH_4ClO_4,[5,30] or for no site symmetry at all with all four h_γ different, the 3×3 submatrix of H_t has to be diagonalized numerically and the $R_{\sigma\alpha}$ depend on the special values of the h_γ. We do not consider these cases of low symmetry. For tetrahedral site symmetry where all h_γ are equal: $h_1 = h_2 = h_3 = h_4 = h$, the wave functions of A-, T-, and E-type symmetry belong to the eigenvalues $E_A = 8h$, $E_T = 0$, and $E_E = -4h$ (with $h < 0$) of the tunneling Hamiltonian.

In a last step, linear combinations $|\psi_\alpha\rangle$ are formed from the $|\eta_\alpha\rangle$ which diagonalize $\vec{I}^2$. This is easily achieved as the 81×81 matrix $\langle\eta_\alpha|\vec{I}^2|\eta_{\alpha'}\rangle$ already is block diagonal, the maximum block size being 4×4.

TABLE I. The coefficients $g_{\alpha m}$ which are used in Eq. (2.12) to construct properly symmetrized wave functions $|\eta_\alpha\rangle$ from the pocket states $[\chi_m\rangle$. α denotes the symmetry label A, T_{x1}, etc., and m enumerates the 12 pocket states.

m	Symmetry operation	Permutation	A	T_{x1}	T_{x2}	T_{x3}	T_{y1}	T_{y2}	T_{y3}	T_{zi}	T_{z2}	T_{z3}	E_1	E_2
1	E	1234	+1	+1	0	0	+1	0	0	+1	0	0	+1	+1
2	C_{2x}	4321	+1	+1	0	0	−1	0	0	−1	0	0	+1	+1
3	C_{2y}	3412	+1	−1	0	0	+1	0	0	−1	0	0	+1	+1
4	C_{2z}	2143	+1	−1	0	0	−1	0	0	+1	0	0	+1	+1
5	$C_3^-(111)$	2314	+1	0	+1	0	0	+1	0	0	+1	0	ϵ	ϵ^*
6	$C_3^+(11\bar{1})$	4132	+1	0	+1	0	0	−1	0	0	−1	0	ϵ	ϵ^*
7	$C_c^+(\bar{1}11)$	1423	+1	0	−1	0	0	+1	0	0	−1	0	ϵ	ϵ^*
8	$C_3^+(1\bar{1}1)$	3241	+1	0	−1	0	0	−1	0	0	+1	0	ϵ	ϵ^*
9	$C_3^+(111)$	3124	+1	0	0	+1	0	0	+1	0	0	+1	ϵ^*	ϵ
10	$C_3^-(1\bar{1}1)$	4213	+1	0	0	+1	0	0	−1	0	0	−1	ϵ^*	ϵ
11	$C_2^-(11\bar{1})$	2431	+1	0	0	−1	0	0	+1	0	0	−1	ϵ^*	ϵ
12	$C_3^-(\bar{1}11)$	1342	+1	0	0	−1	0	0	−1	0	0	+1	ϵ^*	ϵ

$\vec{I}^2$ does not mix functions of different symmetry and, of course, it leaves I_z diagonal.

Thus the functions $|\psi_\alpha\rangle$ simultaneously diagonalize H_t, I^z, and $\vec{I}^2$. They are the correctly symmetrized eigenfunctions which will be used for the calculation of the neutron scattering matrix elements.

Up to now we have diagonalized the Hamiltonian in the subspace spanned by the 16 (or 81) librational ground-state pocket states. The quality of the functions $|\psi_\alpha\rangle$ obtained by this procedure depends on the choice of the librational ground-state function $|\phi_\alpha\rangle$. We have used the Ritz variational principle to optimize the parameter N_α defined in Eq. (2.9). N_α has been chosen such that $\partial E_\alpha/\partial N_\alpha=0$ where $E_\alpha=\langle\psi_\alpha|H_t|\psi_\alpha\rangle$. Of course the parameter N_α assumes different values for the states of different symmetry. For CH_4 in phase II with a potential

$$V(\tau)=A^{(3)}H_{11}^{(3)}(\tau) \tag{2.13}$$

and $A^{(3)}=-35\,\hbar^2/2\theta$ the following values have been obtained: $N_A=13.53$, $N_T=14.04$, and $N_E=14.32$.

III. NEUTRON SCATTERING CROSS SECTION

The spin-independent scattering amplitude $A_{\rm si}$ in Eq. (2.5) is not an operator in spin space. It therefore only contributes to the diagonal matrix elements in Eq. (2.2) but does not contribute to the tunneling transitions. We will therefore omit contributions connected with $A_{\rm si}$ from now on. Defining

$$I_\gamma^\pm=I_\gamma^x\pm iI_\gamma^y \tag{3.1a}$$

and

$$S^\pm=S^x\pm iS^y\ , \tag{3.1b}$$

A_γ may be rewritten

$$A_\gamma=A_{\rm sd}[S^zI_\gamma^z+\tfrac{1}{2}(S^+I_\gamma^-+S^-I_\gamma^+)]\ . \tag{3.2}$$

A_γ is an operator which acts on the neutron spin and on the spin of the proton (deuteron) at position γ. We form matrix elements with respect to the neutron states $|\mu\rangle=|\alpha\rangle=$"up" and $|\mu\rangle=|\beta\rangle=$"down" before and after scattering

$$\langle\alpha|A_\gamma|\alpha\rangle=+\tfrac{1}{2}A_{\rm sd}I_\gamma^z\ , \tag{3.3a}$$

$$\langle\beta|A_\gamma|\beta\rangle=-\tfrac{1}{2}A_{\rm sd}I_\gamma^z\ , \tag{3.3b}$$

$$\langle\beta|A_\gamma|\alpha\rangle=+\tfrac{1}{2}A_{\rm sd}I_\gamma^+\ , \tag{3.3c}$$

$$\langle\alpha|A_\gamma|\beta\rangle=+\tfrac{1}{2}A_{\rm sd}I_\gamma^-\ . \tag{3.3d}$$

These matrix elements are operators which only act on the proton (deuteron) spin and on the rotational part $|\phi_\alpha\rangle$ of the wave function. The first two terms refer to the non-spin-flip scattering, the other two terms represent the spin-flip scattering. The discussion is the same for all four terms of Eq. (3.3); it is therefore sufficient to discuss one of them, say Eq. (3.3c). The matrix element (2.2) of W between the neutron plane-wave states $|\vec{k}\rangle$ and $|\vec{k}'\rangle$ becomes

$$M=\tfrac{1}{2}A_{\rm sd}\left\langle\psi_{\alpha'}\left|\sum_{\gamma=1}^{4}g_\gamma I_\gamma^+\right|\psi_\alpha\right\rangle\ , \tag{3.4}$$

where $g_\gamma=\exp(i\vec{Q}\cdot\vec{r}_\gamma)$ and $\vec{Q}=\vec{k}-\vec{k}'$. The operator in Eq. (3.4) is decomposed into its irreducible representations[7,31,32,34]

$$\sum_{\gamma=1}^{4}g_\gamma I_\gamma^+=\tfrac{1}{4}(g_AI_A^++g_{Tx}I_{Tx}^++g_{Ty}I_{Ty}^++g_{Tz}I_{Tz}^+)\ . \tag{3.5}$$

An operator P_A, P_{Tx}, P_{Ty}, and P_{Tz} follows from the operators P_γ which operate on the particles at positions γ according to

$$P_A=P_1+P_2+P_3+P_4\ , \tag{3.6a}$$

$$P_{Tx}=+P_1-P_2-P_3+P_4\ , \tag{3.6b}$$

$$P_{Ty}=-P_1+P_2-P_3+P_4\ , \tag{3.6c}$$

$$P_{Tz}=-P_1-P_2+P_3+P_4\ . \tag{3.6d}$$

This is a definition where the site 4 is distinguished. It is noteworthy that W decomposes into irreducible representations of A- and T-type symmetry, but does not contain an operator of E-type symmetry. In the product $\langle\psi_{\alpha'}|W|\psi_\alpha\rangle$ only those terms contribute which are totally symmetric (of A type). From the group multiplication table for T symmetry and the lack of E terms in W it follows that a neutron cannot induce an A to E transition. This selections rule is valid for protonated as well as for deuterated samples.[34]

With the operator (3.5) transition matrix elements between the spin part of the wave functions which have been constructed in Sec. II are calculated. Truly elastic transitions ($A\leftrightarrow A$, $E_a\leftrightarrow E_b$, $T_x\leftrightarrow T_x$, etc.), are induced by the A component of the operator, inelastic transitions ($A\leftrightarrow T$ and $T\leftrightarrow E$) as well as elastic transitions which for reduced symmetry would become inelastic as, e.g., $T_x\leftrightarrow T_y$ are related to the T component of the interaction operator. The matrix elements thus contain factors of the type $G_{AA}=\langle\phi_A|g_A|\phi_A\rangle$, $G_{TT}=\langle\phi_{Tx}|g_{Ty}|\phi_{Tz}\rangle$, $G_{TE}=\langle\phi_{Tx}|g_{Tx}|\phi_E\rangle$, etc. Here $|\phi_A\rangle$, $|\phi_{Tx}\rangle$, $|\phi_E\rangle$, etc., represents the rotational part of the wave function. In an earlier treatment $|\phi_A\rangle$, $|\phi_{Tx}\rangle$, $|\phi_E\rangle$ all have been approximated by sums of δ functions, then $G_\gamma=g_\gamma$ and G_{AA}, G_{TT}, etc., become sums of exponentials. In this paper we will evaluate G_γ with the rotational wave function $\langle\tau|N_\alpha\rangle$ defined in Eq. (2.9). The actual calculation is postponed to Sec. IV.

When all the matrix elements between the 16

TABLE II. XH_4: Intensities for transitions between the groups of states with symmetry α and α' where $\alpha, \alpha' = A, T_x, T_y, T_z$, or E. The following abbreviations have been used: $a^2 = |G_A|^2$, $b_x^2 = |G_{Tx}|^2$, $b_y^2 = |G_{Ty}|^2$, and $b_z^2 = |G_{Tz}|^2$. Here G_α is composed from $G_\gamma = \langle \exp(i\vec{Q}\cdot\vec{R}_\gamma)\rangle$ with $\gamma = 1, 2, 3, 4$ according to Eqs. (3.6). A common factor $\sigma_{\text{inc}}/864$ has been extracted from Tables II and III.

	A	T_x	T_y	T_z	E
A	$135a^2$	$45b_x^2$	$45b_y^2$	$45b_z^2$	0
T_x	$45b_x^2$	$27a^2$	$27b_z^2$	$27b_y^2$	$36b_x^2$
T_y	$45b_y^2$	$26b_z^2$	$27a^2$	$27b_x^2$	$36b_y^2$
T_z	$45b_z^2$	$27b_y^2$	$27b_x^2$	$27a^2$	$36b_z^2$
E	0	$36b_x^2$	$36b_y^2$	$36b_z^2$	0

states for CH_4 or NH_4^+ and all the matrix elements between the 81 states for CD_4 have been calculated these elements are squared and inserted into Eq. (2.1). The tunnel splitting usually is very small. (A few μeV corresponding to roughly 0.1 K). For usual measuring temperatures ($T \gtrsim 4$ K) all the statistical weights P_α are equal ($P_\alpha = \frac{1}{16}$ for CH_4, NH_4^+ and $P_\alpha = \frac{1}{81}$ for CD_4). Small tunnel splittings are related with small energy transfers and therefore also the modulus of the momentum of the neutron is practically unchanged: $k \approx k'$ and $k'/k \approx 1$. With the help of Eq. (3.3) the sum over μ and μ' is performed. We do not sum over α and α' but rather group all the states of A-, T_x-, T_y-, T_z-, and E-type symmetry to obtain the intensities in the different elastic and inelastic lines. The results are given in Tables II and III for protonated and deuterated samples.

The $\vec{Q}$ dependence of all the strictly elastic lines is contained in the factor a^2. As the three T states are degenerate, all the inelastic and the elastic lines which would be inelastic in reduced symmetry have a common factor $b_x^2 + b_y^2 + b_z^2$ which determines their $\vec{Q}$ dependence. The former treatment with δ-type wave functions lead to the following powder average:

$$a^2 = 4[1 + 3j_0(QR)]$$

and

$$b_x^2 = b_y^2 = b_z^2 = 12[1 - j_0(QR)] \ ,$$

where R is the proton-carbon distance. An inspection of Tables II and III shows, that for δ-shaped wave functions the total cross section is $4\sigma_{\text{inc}}$ for all values of Q. In this limit one also finds from Tables II and III that the intensity ratio of the outer $(A \leftrightarrow T)$ to the inner $(T \leftrightarrow E)$ transition is $\frac{5}{4}$ for the protonated samples and $\frac{5}{6}$ for the deuterated samples. It should be noted that these results have been derived for temperatures which are high in comparison with the tunnel splitting ($k_B T >> \Delta_{A-T}$ and Δ_{T-E}). For low temperatures only the A state is populated and for long neutron wavelengths the total scattering cross section[35] of the protons in CH_4 increases to $8\sigma_{\text{inc}}$.

In light methane temperatures around 1 K are low enough for an observation[36] of the effect. A recent successful experiment on ammonium perchlorate[37]

TABLE III. XD_4: The same as Table II for deuterated molecules. Both tables have been constructed for tetrahedral symmetry and temperatures which are high in comparison with the tunnel splitting.

	A	T_x	T_y	T_z	E
A	$70a^2$	$30b_x^2$	$30b_y^2$	$30b_z^2$	0
T_x	$30b_x^2$	$42a^2$	$42b_z^2$	$42b_y^2$	$36b_x^2$
T_y	$30b_y^2$	$42b_z^2$	$42a^2$	$42b_x^2$	$36b_y^2$
T_z	$30b_z^2$	$42b_y^2$	$42b_x^2$	$42a^2$	$36b_z^2$
E	0	$36b_x^2$	$36b_y^2$	$36b_z^2$	$20a^2$

with a tunnel splitting of ~10 μeV was performed at much lower temperatures (down to 70 mk). For $X\mathrm{D}_4$ molecules the total incoherent scattering cross section increases from $4\sigma_{\mathrm{inc}}$ to $7\sigma_{\mathrm{inc}}$ when the temperature is lowered to values where only the A state is populated. For CD_4 this would again correspond to measuring temperatures below 100 mk.

IV. FINITE-AMPLITUDE WAVE FUNCTIONS

The problem which remains to be solved is the determination of the expectation value of $g_\gamma = \exp(i\vec{\mathrm{Q}}\cdot\vec{\mathrm{R}}_\gamma)$ in a pocket state (2.9). This is the task for transitions without a change of symmetry, for transitions with a change of symmetry $(\alpha \rightarrow \alpha')$ the matrix elements

$$\begin{aligned} G_{\gamma,\alpha\alpha'} &= \langle \exp(i\vec{\mathrm{Q}}\cdot\vec{\mathrm{R}}_\gamma)\rangle_{\alpha\alpha'} \\ &= \langle N_\alpha|\tau\rangle \exp(i\vec{\mathrm{Q}}\cdot\vec{\mathrm{R}}_\gamma)\langle\tau|N_{\alpha'}\rangle \end{aligned} \tag{4.1}$$

have to be calculated. From Eq. (4.1) we than form the matrix elements of the irreducible representations of the neutron scattering operator (3.5). For shorthand we define

$$\begin{aligned} (b^2)_{\alpha\alpha'} &= (b_x^2 + b_y^2 + b_z^2)_{\alpha\alpha'} \\ &= |G_{Tx,\alpha\alpha'}|^2 + |G_{Ty,\alpha\alpha'}|^2 + |G_{Tz,\alpha\alpha'}|^2 \ , \end{aligned} \tag{4.2a}$$

and

$$(a^2)_{\alpha\alpha'} = |G_{A,\alpha\alpha'}|^2 \ . \tag{4.2b}$$

To calculate Eq. (4.1) a primed coordinate system (x',y',z') is defined which is fixed in the molecule. Then Eq. (4.1) is evaluated for a unit vector $\vec{\mathrm{R}}'$ which rotates with the molecule and which is parallel to the z' axis:

$$\vec{\mathrm{R}}' = (x',y',z') = (0,0,1) \ .$$

Its components in the crystal fixed coordinate system are obtained from

$$\vec{\mathrm{R}} = \underline{D}^1\vec{\mathrm{R}}' \ ,$$

where[38]

$$\underline{D} = \begin{bmatrix} \tau_1^2-\tau_2^2-\tau_3^2+\tau_4^2 & 2(\tau_1\tau_2+\tau_3\tau_4) & 2(\tau_1\tau_3-\tau_2\tau_4) \\ 2(\tau_1\tau_2-\tau_3\tau_4) & -\tau_1^2+\tau_2^2-\tau_3^2+\tau_4^2 & 2(\tau_2\tau_3+\tau_1\tau_4) \\ 2(\tau_1\tau_3+\tau_2\tau_4) & 2(\tau_2\tau_3-\tau_1\tau_4) & -\tau_1^2-\tau_2^2+\tau_3^2+\tau_4^2 \end{bmatrix} \ . \tag{4.3}$$

The coordinates in the space fixed frame are

$$x = 2(\tau_1\tau_3-\tau_2\tau_4), \quad y = 2(\tau_2\tau_3+\tau_1\tau_4), \quad z = -\tau_1^2-\tau_2^2+\tau_3^2+\tau_4^2 \ . \tag{4.4}$$

We define

$$\delta = z - 1 = -2(\tau_1^2+\tau_2^2) \ , \tag{4.5}$$

where use has been made of the relation $\sum_{i=1}^4 \tau_i^2 = 1$. Equation (4.1) is expanded for small values of x, y, and δ up to fourth order:

$$\begin{aligned} \langle \exp(i\vec{\mathrm{Q}}\cdot\vec{\mathrm{R}})\rangle &= \exp(iQ_3)\langle \exp(iQ_1x + iQ_2y + iQ_3\delta)\rangle \\ &= \exp(iQ_3)[\,1 + iQ_3\langle\delta\rangle - \tfrac{1}{2}(Q_1^2+Q_2^2)\langle x^2\rangle - \tfrac{1}{2}Q_3^2\langle\delta^2\rangle - \tfrac{1}{6}iQ_3^3\langle\delta^3\rangle - \tfrac{1}{2}iQ_3(Q_1^2+Q_2^2)\langle x^2\delta\rangle \\ &\quad + \tfrac{1}{24}(Q_1^4+Q_2^4)\langle x^4\rangle + \tfrac{1}{24}Q_3^4\langle\delta^4\rangle + \tfrac{1}{4}Q_1^2Q_2^2\langle x^2y^2\rangle + \tfrac{1}{4}Q_3^2(Q_1^2+Q_2^2)\langle x^2\delta^2\rangle + \cdots\,] \ . \end{aligned} \tag{4.6}$$

Expectation values of odd powers of x or y vanish and have been omitted from Eq. (4.6); symmetries like $\langle x^2\rangle = \langle y^2\rangle$ have been exploited. When x, y, and δ from Eqs. (4.4) and (4.5) are inserted into Eq. (4.6) all the expectation values are sums of terms of the form

$$\langle \tau_1^{N_1}\tau_2^{N_2}\tau_3^{N_3}\tau_4^{N_4}\rangle = (N_1,N_2,N_3,N_4)/(0,0,0,0) \ , \tag{4.7}$$

where

$$(N_1,N_2,N_3,N_4) = \oint d^4\tau\, \tau_1^{N_1}\tau_2^{N_2}\tau_3^{N_3}\tau_4^{N_4+4N} \ , \tag{4.8}$$

with

$$4N = 2N_\alpha + 2N_{\alpha'} \ .$$

The denominator in Eq. (4.7) originates from the normalization constant C_α in Eq. (2.9). The integrals on the surface of the four-dimensional unit sphere are easily performed.[27] If one of the N_i is odd, the integral is zero. If all N_1 are even, the result is

$$(N_1,N_2,N_3,N_4)=\frac{(N_1-1)!!(N_2-1)!!(N_3-1)!!(4N+N_4-1)!!}{2^{M+2N}(M+2N+1)!}2\pi^2\ , \tag{4.9}$$

with

$$M=(N_1+N_2+N_3+N_4)/2\ .$$

It is seen that $\langle \tau_1^{N_1}\tau_2^{N_2}\tau_3^{N_3}\tau_4^{N_4}\rangle$ is of order $(1/N)^{(N_1+N_2+N_3)/2}$. In a calculation up to order $(1/N)^2$ all terms with $N_1+N_2+N_3>4$ may be dropped. x and y are of first order in τ_1, τ_2, and τ_3. Therefore the expansion (4.6) contains all terms in the order $(1/N)^2$. The terms $\langle x^2\delta^2\rangle$ and $\langle \delta^4\rangle$ are of order $(1/N)^3$ and $(1/N)^4$. They will be dropped, too. The remaining integrals in Eq. (4.6) are evaluated and terms of different order in $(1/N)$ are collected. To go beyond the special choice of the primed coordinate system with its z' axis parallel to the vector $\vec{R}'$, we furthermore replace Q_3 by $\vec{Q}\cdot\vec{R}'$ and $Q_1^2+Q_2^2$ by $(\vec{Q}\times\vec{R}')^2$. The result is

$$\begin{aligned}\langle e^{i\vec{Q}\cdot\vec{R}}\rangle = e^{i\vec{Q}\cdot\vec{R}'}\Bigg[1&+\frac{1}{N}\left(\frac{-Q^2R'^2}{2}+\frac{(\vec{Q}\cdot\vec{R}')^2}{2}-i\vec{Q}\cdot\vec{R}'\right)\\ &+\frac{1}{N^2}(Q^2R'^2-2(\vec{Q}\cdot\vec{R}')^2+\tfrac{1}{8}[Q^2R'^2-(\vec{Q}\cdot\vec{R}')^2]^2+i\vec{Q}\cdot\vec{R}'[1+Q^2R'^2-(\vec{Q}\cdot\vec{R}')^2])\Bigg]\ .\end{aligned} \tag{4.10}$$

From Eq. (4.10) we calculate the matrix element (4.1)

$$G_\gamma=\langle g_\gamma\rangle=\langle e^{i\vec{Q}\cdot\vec{R}_\gamma}\rangle \tag{4.11}$$

by inserting the coordinates $\vec{R}_{\gamma'}$ of the four protons or deuterons of the molecule into the right-hand side of Eq. (4.10). The width parameter N is $N=N_{\alpha\alpha'}=(N_\alpha+N_{\alpha'})/2$ for a transition between states of symmetry α and α'. This is evident from Eqs. (4.1) and (4.8). The inelastic transitions from A to T and from T to E levels contain a factor $(b^2)_{AT}$ and $(b^2)_{TE}$, respectively (see Tables II and III). From the values of N_A, N_T, and N_E given at the end of Sec. II one obtains $N_{AT}=13.785$ and $N_{TE}=14.18$ in the case of CH_4. From Eqs. (3.6) and (4.11) we find

$$\begin{aligned}(b^2)_{\alpha\alpha'}&=(|G_{Tx}|^2+|G_{Ty}|^2+|G_{Tz}|^2)_{\alpha\alpha'}\\ &=\left(3\sum_{\gamma=1}^{4}|G_\gamma|^2-\sum_{\substack{\gamma,\gamma'=1\\ \gamma'\neq\gamma}}^{4}(G_\gamma G_{\gamma'}^*+G_\gamma^*G_{\gamma'})\right)_{\alpha\alpha'}\ .\end{aligned} \tag{4.12}$$

Expression (4.12) has been evaluated for three different directions of the momentum transfer $\vec{Q}$ relative to the equilibrium orientation of the molecule. The result is shown in Fig. 2. The angular average of $(b^2)_{\alpha\alpha'}$ over all directions of $\vec{Q}$ is shown in Fig. 3 where also the zero-order[30] and first-order approximation in $1/N$ to Eq. (4.10) is given. For Figs. 2 and 3 we have used the average value $N_{\alpha\alpha'}=14$. We have also evaluated the angular averages of $(b^2)_{\alpha\alpha'}$ for $N_{A-T}=13.785$ and for $N_{TE}=14.18$, but there is almost no difference. For $QR=2$, e.g., we find $(b^2)_{AT}/(b^2)_{TE}=0.999$. From all the examples where tunneling spectra of XH_4 or XD_4 molecules have been determined by inelastic neutron scattering[4–12] or by NMR methods[13–16,19,20] CH_4 is the one with the largest tunnel splitting and consequently there is no example with broader wave functions or smaller values of N. In Figs. 2 and 3 we have evaluated Eq. (4.10) for $N=14$, its value for CH_4. For CD_4 or $(NH_4)_2SnCl_6$ the appropriate value is $N=20$ which means that the corrections of order $1/N$ and $1/N^2$ are even smaller or that the series expansion in terms of $1/N$ is valid to even larger values of QR.

The intensity ratio of the outer to the inner transition $R=I(A-T)/I(T-E)$ recently has been deter-

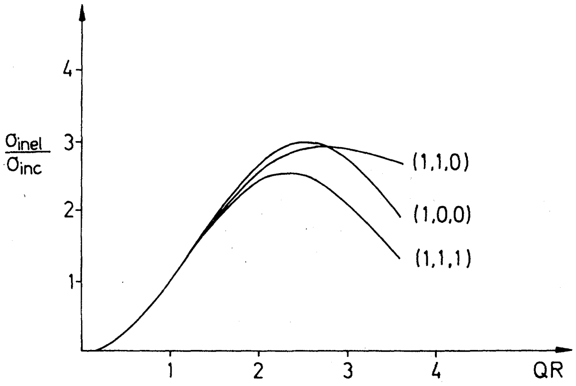

FIG. 2. Inelastic scattering cross section of a XH_4 molecule for different directions of $\vec{Q}$ as a function of the modulus of Q. The direction of $\vec{Q}$ is defined relative to the equilibrium orientation of the molecule in the coordinate frame of Fig. 1. To obtain $\sigma_{\rm inel}$ the intensities of all transition lines which are in elastic in low symmetries have been added. The lines are based on Eq. (4.10) with inclusion of the terms of order $1/N$ and $1/N^2$. For the drawing $N=14$.

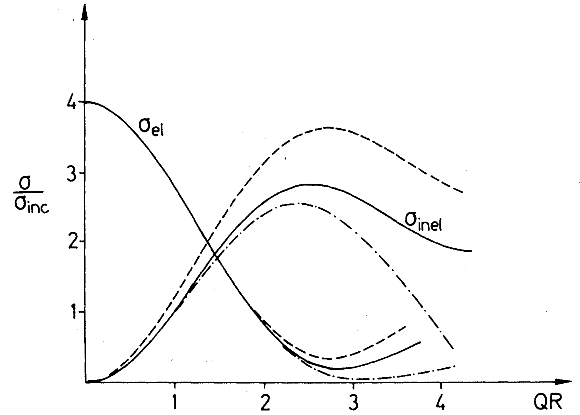

FIG. 3. Powder average of the strictly elastic and the inelastic scattering cross section. The different lines correspond to different approximations in Eq. (4.10). Dashed line: only the term of order 1 in the wavy bracket has been used. This is the δ-function approximation of Ref. 30. Dash-dotted line: the terms of order $1/N$ are included. Solid line: contains all terms of order $1/N^2$.

mined rather precisely[39]: $R = 1.40 \pm 0.05$. For the δ-function approximation of Ref. 30 the value is 1.25, as has been remarked in Sec. III. With the width parameters N_A, N_T, and N_E for CH_4 it is seen that the effective width parameter $\frac{1}{2}(N_\alpha + N_{\alpha'})$ is smaller for the T-E transition than for the A-T transition. The corresponding correction to the value $R = 1.25$ thus is negative. It is only of the order of a tenth of a percent but its tendency is to worsen the agreement with experiment.

In this respect the calculation of Ozaki *et al.*[31] which yields $R = 1.3$ seems to fit the experiment better. The reason for this better agreement might be that the wave functions of Ozaki *et al.* are anisotropic within the potential pockets and that this anisotropy is different for states of different symmetry.

Up to now we have concentrated our attention on sites with tetrahedral symmetry. The intensity of the inelastic transitions A-T and T-E then is $b_x^2 + b_y^2 + b_z^2$. The summation over the three terms b_x^2, b_y^2, and b_z^2 largely removes the strong $\vec{Q}$ dependence of the individual terms. The intensity of each single term exhibits an angular modulation by a factor 2 for a fixed value $QR = 2$. The angular modulation of the sum, i.e., of the inelastic intensities in T_d symmetry amounts to 15% only. Two conditions should be fulfilled in a measurement of the angular modulation. (1) Obviously the inelastic transition of a substance with low site symmetry should be taken. A possible example is NH_4ClO_4, another one CH_4 on grafoil will be mentioned hereafter. (2) The modulation gets more pronounced for large momentum transfers. Here the new backscattering spectrometer of the ILL in Grenoble should provide the necessary basis.

V. SITE SYMMETRIES LOWER THAN T_d

Angular modulations of the type just described have already been observed for oriented samples of CH_4 adsorbed on grafoil.[10] The methane molecule on the grafoil surface feels a trigonal potential with the threefold symmetry axis normal to the carbon layers. The vectors $\vec{n}$ normal to the carbon planes have a preferred orientation whereas there is complete disorder concerning rotations of the planes themselves around $\vec{n}$. Consequently the scattering intensity has to be averaged over the distribution indicated above.

The calculation can be based on the δ-function approximation of Ref. 30. There the case of trigonal symmetry has been discussed extensively (for NH_4ClO_4 with an effective trigonal symmetry—the small T-state splitting[40] of 0.15 μeV was not known when Ref. 30 was written). Use can be made of Table VIII of Ref. 30 when the unique axis (the threefold symmetry axis of the potential) is chosen along the 4 axis of Fig. 1. The expression

$$G_\gamma G_\xi^* + G_\gamma^* G_\xi = 2\cos[\vec{Q}\cdot(\vec{r}_\gamma - \vec{r}_\xi)]$$

has to be averaged for rotations around the surface normal $\vec{n}$ which is parallel to the 4 axis. The results of the averaging process which depend on the direction of $\vec{Q}$ have been compiled in Table IV for $\vec{Q}$ parallel and perpendicular to $\vec{n}$. Adding up all contributions from Table VIII of Ref. 30 one obtains the intensities of all the transition lines. The result compares favorably with the inelastic line intensities observed by Smalley and Thomas.[33] There is full agreement with respect to the polarization of the scattering intensities for $\vec{Q}$ parallel and perpendicular to $\vec{n}$. Also the relative intensities within the single spectra are well represented by the results of Table IV.

The following is a general discussion of tunneling states and transition matrix elements in reduced symmetry. As long as we deal with tetrahedral molecules, only the T states are affected by a reduced site symmetry. In tetrahedral symmetry the T states are denoted by $|\psi(T_{\alpha j})\rangle$ where $\alpha = 1, 2$, and 3 for functions of T_x, T_y, and T_z symmetry, respectively. The index $j = 1, 2, \ldots, K$ denotes the different trip-

TABLE IV. CH_4 on grafoil. Average of $\cos[\vec{Q}\cdot(\vec{r}_\gamma - \vec{r}_\xi)]$ for rotations of the substrate around an axis normal to the carbon layers. The momentum transfer is parallel or normal to the layers.

	$\gamma = \xi$	$\gamma \neq \xi, \gamma$ and $\xi \neq 4$	$\gamma \neq \xi, \gamma$ or $\xi = 4$
$\vec{Q} = Q_\parallel \vec{p}$	1	$J_0(\sqrt{8/3}\,Q_\parallel R)$	$J_0(\sqrt{8/9}\,Q_\parallel R)$
$\vec{Q} = Q_\perp \vec{n}$	1	1	$\cos(4Q_\perp R/3)$

lets ($K=3$ for CH_4 and $K=18$ for CD_4) of T symmetry which can be formed from the spin functions. For tetrahedral site symmetry the T states are degenerate; i.e., the tunneling Hamiltonian H_t^c at a tetrahedral site in the T subspace is proportional to the unit matrix; it is thus diagonal in any representation and we have used the resulting freedom to construct convenient wave functions $|\psi(T_{\alpha j})\rangle$ according to a scheme similar to the one applied for operators in Eq. (3.6). The degeneracy is removed for reduced symmetry and transitions which are elastic for tetrahedral symmetry become inelastic.

This means that the functions $|\psi(T_{\alpha j})\rangle$ do not diagonalize the tunneling Hamiltonian H_t for general (noncubic) site symmetry

$$\langle\psi(T_{\alpha j})|H_t|\psi(T_{\beta j})\rangle=(H_t)_{\alpha\beta}\ . \tag{5.1}$$

The matrix elements $(H_t)_{\alpha\beta}$ only depend on the overlap of the angular wave function which is the same for all T states and hence $(H_t)_{\alpha\beta}$ does not depend on j. The matrix R which diagonalizes H_t defines the new eigenvectors $|\lambda(T_{\sigma j})\rangle$ for reduced site symmetry (and the corresponding energies $E_{T\sigma}$)

$$|\lambda(T_{\sigma j})\rangle=\sum_{\alpha}R_{\sigma\alpha}|\psi(T_{\alpha j})\rangle\ . \tag{5.2}$$

Concerning the spin functions this means that the tetrahedral states $|\eta(T_{\alpha j})\rangle$ transform to new states $|\lambda(T_{\sigma j})\rangle$ which are adapted to the new symmetry. For the calculation of transition matrix elements it is convenient to group the states according to symmetry

$$|\eta(\mu)\rangle=|\eta(T_{\alpha j})\rangle \tag{5.3}$$

with

$$\mu=K(\alpha-1)+j\ .$$

Equation (5.2) now reads

$$|\lambda\rangle=R|\psi\rangle\ , \tag{5.4}$$

where $|\psi\rangle$ and $|\lambda\rangle$ are vectors of dimension $d=3K$ ($d=9$ for CH_4, $d=54$ for CD_4) and R is the supermatrix

$$R=\begin{vmatrix} R_{11}E & R_{12}E & R_{13}E\\ R_{21}E & R_{22}E & R_{23}E\\ R_{31}E & R_{32}E & R_{33}E \end{vmatrix}\ . \tag{5.5}$$

Here $R_{\sigma\alpha}$ are the elements of the 3×3 transformation matrix R of Eq. (5.2) and E is the unit matrix of dimension K.

TABLE V. Elements of the diagonal matrices A, X, Y, and Z [Eq. (5.7)] for XH_4; $c=\frac{1}{2}$.

i	1	2	3
A_{ii}	$-c$	0	c
X_{ii}	c	0	$-c$
Y_{ii}	c	0	$-c$
Z_{ii}	c	0	$-c$

The matrix R transforms functions $|\psi\rangle$ into new functions $|\lambda\rangle$ which remain eigenfunctions of I_z and I^2. New transition matrix elements are calculated by rotating the submatrix of T to T transitions to the new matrix

$$\mathcal{O}_N=R^T\mathcal{O}R\ . \tag{5.6}$$

In practice it is more appropriate to start from spin functions $|\eta\rangle$ which are constructed such that they are symmetrized (i.e., classified according to T_x, T_y, and T_z) and eigenfunctions of I_z without demanding that they should be eigenfunctions of I^2. For CH_4 these functions automatically are eigenfunctions of I^2, too. This is not the case for CD_4. There one obtains

$$\mathcal{O}=\begin{vmatrix} Aa & Zb_z & Yb_z\\ Zb_z & Aa & Xb_x\\ Yb_y & Xb_x & Aa \end{vmatrix}\ . \tag{5.7}$$

If transition matrix elements only are calculated for

TABLE VI. Elements of the diagonal matrices A, X, Y, and Z [Eq. (5.7)] for XD_4; $a=\frac{3}{2}$, $b=1$, $c=\frac{1}{2}$.

i	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
A_{ii}	$-a$	$-b$	$-b$	$-c$	$-c$	$-c$	$-c$	0	0	0	0	c	c	c	c	b	b	a
X_{ii}	c	0	b	$-c$	$-c$	a	$-c$	$-b$	$-b$	0	0	c	$-c$	$-c$	$-a$	0	$-b$	$-c$
Y_{ii}	c	0	b	a	$-c$	$-c$	$-c$	0	$-b$	$-b$	0	c	$-a$	$-c$	$-c$	0	$-b$	$-c$
Z_{ii}	c	0	b	$-c$	a	$-c$	$-c$	$-b$	0	$-b$	0	c	$-c$	$-a$	$-c$	0	$-b$	$-c$

TABLE VII. Intensity of T-T transitions for CH_4 (and CD_4) for reduced site symmetries: the left side refers to a threefold symmetry axis; T_1 denotes the nondegenerate level, T_2 and T_3 the degenerate ones; the right side refers to a twofold symmetry axis; T_1, T_2, and T_3 denote the states with energy eigenvalues $-\delta$, 0, and $+\delta$, respectively. A common factor $\sigma_{\text{inc}}/864$ has been extracted from both tables. The corresponding tables for CD_4 are obtained by multiplication with $\frac{14}{9}$. The intensities of A-T_i and E-T_i transitions remain unaffected by reduced symmetry.

$\Gamma \backslash \Gamma'$	T_1	T_2	T_3	T_1	T_2	T_3
T_1	$63+45j_0$	$9-9j_0$	$9-9j_0$	$54+54j_0$	$27-27j_0$	0
T_2	$9-9j_0$	$54+54j_0$	$18-18j_0$	$27-27j_0$	$27+81j_0$	$27-27j_0$
T_3	$9-9j_0$	$18-18j_0$	$54+54j$	0	$27-27j_0$	$54+54j_0$

the z component of the neutron scattering operator, all four matrices A, X, Y, and Z are diagonal matrices. Their elements are listed explicitly in Tables V (CH_4) and VI (CD_4). Obviously they only account for the scattering without spin flip of the neutrons. Intensities are calculated for the transformed matrix $\mathcal{O}_N$ by summing over the moduli squared of all transitions between states with energies E_{Ti} and E_{Tj}. In addition there is spin-flip scattering with twice the intensity of the non-spin-flip part.

Explicit results shall only be quoted for negligible 180° overlap matrix elements H_x, H_y, and H_z and the following symmetries: (a) for a threefold axis at the crystal site which yields the relation $h_1 \neq h_2 = h_3 = h_4$ for the 120° overlap matrix elements h_i, (b) for a twofold axis at a crystal site which yields $h_1 = h_2 \neq h_3 = h_4$. If there are more than two independent elements h_i, the matrix R also depends on the relative magnitude of the elements h_i. Table VII lists the results for powder samples and the two symmetries indicated above. Apart from a factor the $\vec{Q}$ dependence of the powder averaged intensities is the same for CH_4 and CD_4. In case of single crystals the intensities of the transitions can be calculated on the basis of Tables V and VI. In Ref. 30, where the transition matrix elements were explicitly calculated for trigonal symmetry (a), intensities are also listed for a single crystal with protonated molecules (note correction in Table VIII of Ref. 30). For a twofold symmetry axis, a symmetric splitting into states with

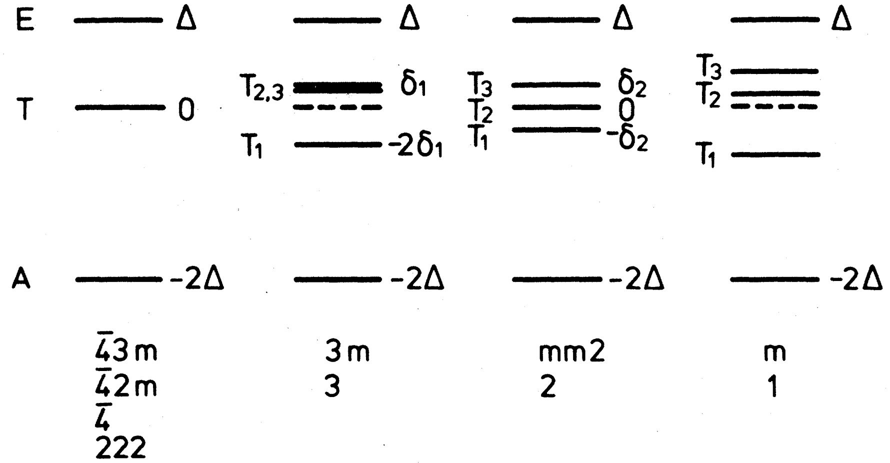

FIG. 4. Level scheme for the rotational ground state of a tetrahedral molecule at crystal sites with different symmetry (only the 120° overlap matrix elements h_i are included). The reduction of symmetry causes a splitting of the otherwise degenerate T states. $\Delta = 4h$ denotes the main splitting, while $\delta_1 = h_2 - H_1$ and $\delta_2 = 2(h_1 - h_3)$ refer to the T-state splitting for sites with three- and twofold symmetry axes, respectively. Transition from A to E states are forbidden, as well as the T_1-T_3 transition in presence of a twofold axis. Except for very low symmetries there is always a pair of transitions with an energy ratio 2:1.

$E_{T1}=\delta$, $E_{T2}=0$, $E_{T3}=-\delta$ results and there is no transition between the upper state (E_{T1}) and the lower state (E_{T3}).

We now may ask whether the site symmetry of a tetrahedron can unambiguously be determined on the basis of a neutron scattering experiment. No exhaustive discussion shall be attempted. Indicative for the absence of 180° overlap is a energy ratio 2:1 for transitions from the A state and the E state to an averaged T-state energy $[E_{\bar{T}}=\frac{1}{3}(E_{T1}+E_{T2}+E_{T3})]$. In this case we may distinguish between four groups of site symmetries (Fig. 4).

If there is no T-state splitting all h_i have the same magnitude. For only two levels remaining degenerate three h_i have identical values. No unambiguous conclusion on the basis of observed energies is possible for the other two groups of symmetries: a symmetric splitting (see above) is also possible for site symmetry 1. In this case the forbidden transition from T_1-T_3 is indicative of the higher symmetry. More generally this means that intensity information needs to be included into the considerations. The general case is described by seven independent parameters (three H_j, four h_i). From a neutron scattering experiment four independent pieces of information are contained in the energies of the tunneling transitions. In addition there are eight intensities which can be used if the elastic intensity is measured as well.

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