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Symmetry-species conversion in CD₃ systems

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Abstract. The rates for symmetry-species conversion of CD₃ groups are calculated using a model in which the interaction between the quadrupolar moment of the deuterons with electric-field gradient at the site of the nucleus causes symmetry-changing transitions. Just the same phonons are considered for energy conservation as are used to describe the temperature dependence of inelastic neutron scattering experiments. For the conversion rate, a similar temperature dependence is found as has already been obtained for CH₃. For temperatures around the tunnelling energy, a behaviour is predicted for CD₃ that is different from the behaviour in protonated systems according to all theories known to us.

In comparison with the corresponding protonated species embedded in the same surroundings, the conversion rate at elevated temperatures turns out to be larger by orders of magnitude. Only the low-temperature conversion rate is suppressed owing to the lack of resonance phonons at the usually smaller tunnelling frequency in CD₃.

The relative increase of the conversion rate with deuteration due to Raman processes is predicted to be independent of temperature but strongly dependent on the height of the orientational potential in the case of shallow potentials. If the tunnelling energy is smaller than 25 μ eV, the conversion rates increase by a constant factor of ~ 10 compared to the protonated species at a given temperature.

1. Introduction

The rotational dynamics of light molecules like hydrogen X₂ or methane CX₄ and molecular groups such as methyl groups CX₃ (X = H,D) has been studied extensively in the past [1,2]. Their main common feature is that rotation between two equilibrium orientations corresponds to a permutation of identical particles. Consequently, the rotational potential has to be invariant under these rotations, i.e. the Hamiltonian has to transform according to the totally symmetric irreducible representation of the corresponding rotational group. This allows the classification of all eigenstates of the Hamiltonian with respect to the irreducible representations Γ of the point group: for X₂, $\Gamma \in (g, u)$; for CX₃, $\Gamma \in (A, E^a, E^b)$; and for CX₄, $\Gamma \in (A, T, E)$.

For high potential barriers between the equilibrium orientations, the ground-state energies of the various Γ differ only by a small amount. This energy difference is called the tunnelling energy. Experimentally, tunnelling energies cover a range of many orders of magnitude, starting from nearly free rotation down to the lowest splittings of several kilohertz observed by sophisticated nuclear magnetic resonance (NMR) techniques.

The symmetry arguments for the spatial space part of the wavefunctions also hold in the presence of a coupling to other spatial degrees of freedom, in particular coupling to

phonons. As a consequence, the symmetry Γ also remains a good quantum number if dissipation is included.

So far, we did not consider the nuclear spin degree of freedom. The complete wavefunctions have to be totally symmetric (totally antisymmetric) for deuterons/bosons (protons/fermions) with respect to particle enumeration. It turns out that the total wavefunctions can be written as a product of a spatial part times a spin part, if either the number of identical particles is two (hydrogen) or only the even permutations are considered (these correspond just to the proper rotations of CX_3 or CX_4 molecules). Under this assumption, the spin wavefunctions can be classified with respect to irreducible representations of the point group of the rotations because this group is isomorphic to the group of (even) permutations. For protonated systems, it turns out that for H_2 , CH_3 and CH_4 there exists a one-to-one correspondence between the symmetry Γ and the total nuclear spin I . In particular, we have

$$\begin{array}{ccc}
 \text{H}_2 & \begin{array}{c} \Gamma \quad I \\ \hline \text{g} \quad 1 \quad (\text{ortho}) \\ \text{u} \quad 0 \quad (\text{meta}) \end{array} & \text{CH}_3 \quad \begin{array}{c} \Gamma \quad I \\ \hline \text{A} \quad 3/2 \\ \text{E} \quad 1/2 \end{array} & \text{CH}_4 \quad \begin{array}{c} \Gamma \quad I \\ \hline \text{A} \quad 2 \\ \text{T} \quad 1 \\ \text{E} \quad 0 \end{array}
 \end{array} \quad (1)$$

Therefore, the spin rotational states are frequently called spin species and a symmetry-changing process is connected intimately with a change in the total nuclear spin. The nomenclature 'nuclear spin conversion' is not misleading in protonated systems.

In the deuterated cases the quoted one-to-one correspondence between Γ and I does not exist. Instead, there are spin states of the same symmetry Γ but *different* nuclear spin I , namely

$$\begin{array}{ccc}
 \text{D}_2 & \begin{array}{c} \Gamma \quad I \\ \hline \text{g} \quad 0, 2 \quad (\text{ortho}) \\ \text{u} \quad 1 \quad (\text{meta}) \end{array} & \text{CD}_3 \quad \begin{array}{c} \Gamma \quad I \\ \hline \text{A} \quad 0, 1, 3 \\ \text{E} \quad 1, 2 \end{array} & \text{CD}_4 \quad \begin{array}{c} \Gamma \quad I \\ \hline \text{A} \quad 0, 2, 4 \\ \text{T} \quad 1, 1, 2, 3 \\ \text{E} \quad 0, 2 \end{array}
 \end{array} \quad (2)$$

The title of the present paper is chosen to signify that we are interested in transition rates between the symmetry species Γ , characterized by the potential energy, and not in the rate for a change of the total nuclear spin quantum number I (which does not necessarily include a change in the symmetry quantum number Γ [3, 4]).

Such symmetry-changing transitions necessarily require operators that contain the nuclear spin [5]. However, the energy of the system depends only very weakly on the nuclear spin (examples are the dipolar energy and the quadrupolar energy), which is one reason for the slowness of symmetry-changing transitions. Usually their rate is much smaller than *any* other relaxation rate in these systems.

There have been several theoretical approaches to this problem. In solid H_2 the conversion rates have been calculated assuming the dipolar interaction between two H_2 molecules to be responsible for the transitions [6–8]. Owing to the dependence of this interaction upon the intermolecular distance, energy conservation is guaranteed by direct coupling to the phonons. Nijman and Berlinsky [9] considered solid CH_4 . They found that the intramolecular dipolar interaction is more effective in causing $\text{T} \leftrightarrow \text{A}$ conversion than the intermolecular dipolar interaction owing to the smaller distance between protons of the same molecule compared to the distance between two distinct methane molecules. However, the intramolecular dipolar interaction does not couple to the lattice modes directly. Therefore, the authors proposed a 'hybrid' mechanism in which the intramolecular dipolar

Hamiltonian mixes states of different symmetry and the coupling to the lattice is achieved by the distance dependence of the intermolecular octupole–octupole coupling. Concerning the temperature dependence of the conversion rates, the H_2 case differs qualitatively from the methane case, because in H_2 the energy splitting between *ortho* and *para* hydrogen is larger than the Debye temperature. Thus two phonons are required to conserve energy. The calculation of Nijman and Berlinsky was restricted to the low-temperature regime, where they found a dependence of the conversion rates on the occupation number of phonons with energy resonant to the $T \leftrightarrow A$ splitting. The idea of the ‘hybrid’ mechanism was recently transferred to the problem of symmetry conversion in CH_3 [5, 10]. The same rotor phonon coupling is used as in theoretical approaches [11] to the temperature dependence of dissipative influences, visible, for example, in neutron scattering spectra. In [5] (referred to as I in the following) some parallels between both temperature dependences are drawn. The temperature dependence of the conversion rates was calculated in I for the model of an isolated CH_3 group, where only the intra-methyl dipolar interactions were considered. This interaction mixes the A and E states and the rotor phonon coupling guarantees the conservation of energy. Intermolecular contributions to the dipolar interaction have not been considered.

As one of the few investigations about deuterated rotors, the *ortho*–*para* conversion in solid D_2 has been studied [12]. Here the situation is more complicated than in H_2 , since deuterons possess a quadrupolar moment Q . The interaction of this moment with the electric-field gradient at the site of the nuclei, that originates from the charge distributions of neighbouring molecules, provides an additional conversion mechanism. The conversion rate due to this quadrupolar interaction was found to be of the same order of magnitude as the conversion rate due to dipolar interaction between the D_2 molecules.

In this paper we consider CD_3 groups. Here, the electric-field gradient at the site of a given deuteron has its origin almost exclusively in the charge distribution of the chemical bond between the deuteron and the carbon atom. (Note that this intramolecular energy contribution is also present and of comparable magnitude in D_2 , but it is of even parity and therefore does not mix rotational states of different symmetry.) Intermolecular contributions to the electric-field gradient are usually negligibly small [13]. Additionally, the quadrupolar interaction is stronger than the dipolar interaction among the deuterons of a CD_3 group by a factor ~ 100 – 200 . Thus, all dipolar interactions can safely be neglected in a calculation of the symmetry-species conversion rates for CD_3 . The strength of the quadrupolar interaction for a CD_3 group is of a comparable strength to the dipolar interaction among the protons of a CH_3 group. The mechanism considered by us is a ‘hybrid’ mechanism in which the quadrupolar interaction mixes states of different symmetry and the rotor phonon interaction provides energy conservation. An important difference from the CH_3 problem considered in I is given by the fact that the quadrupolar interaction mixes not only A and E states but also E^a and E^b states. (For CH_3 , matrix elements of the dipolar Hamiltonian between E states vanish.) Thus, we have to deal with $E^a \leftrightarrow E^b$ conversion in addition to $A \leftrightarrow E$ conversion. However, the $A \leftrightarrow E$ conversion rate observed in experiments is not influenced by the $E^a \leftrightarrow E^b$ conversion. The calculations will be performed using second-order perturbation theory with respect to the rotor phonon interaction Hamiltonian.

The organization of the paper is as follows. In section 2 we introduce the model Hamiltonian. Section 3 is devoted to the calculation of the conversion rates, and the specific results obtained for a Debye phonon density of states are discussed in section 4. In section 5 we compare the general findings to those of paper I and discuss the similarities and differences to earlier theories.

2. The model

In this section we introduce the Hamiltonian that will be used later to calculate the symmetry conversion rates of rotational tunnelling CD_3 groups:

$$\mathbf{H} = \mathbf{H}^R + \mathbf{H}^P + \mathbf{H}^I + \mathbf{H}^Q. \quad (3)$$

The first three terms on the right-hand side of equation (3) do not involve nuclear spin operators and are usually considered in theoretical treatments of the temperature dependence of rotational tunnelling [11, 14]:

$$\mathbf{H}^R = -B\partial_\varphi^2 + V_3 \cos(3\varphi) = \sum_{m\Gamma\mu} E_m^\Gamma |m\Gamma\mu\rangle \langle m\Gamma\mu| \quad (4)$$

$$\mathbf{H}^P = \sum_k \omega_k (b_k^+ b_k + \frac{1}{2}) \quad (5)$$

$$\mathbf{H}^I = \sum_k [g_k^c \cos(3\varphi) + g_k^s \sin(3\varphi)] (b_k + b_k^+) = \sum_{kmm'} \sum_{\Gamma\mu} g_{kmm'}^\Gamma |m\Gamma\mu\rangle \langle m'\Gamma\mu| (b_k + b_k^+) \quad (6)$$

where B is the rotational constant ($B \simeq 324 \mu\text{eV}$ for CD_3) and b_k^+ and b_k are creation and annihilation operators for phonons enumerated by k with energy ω_k . The form of the interaction between the rotor and the phonons is diagonal in the symmetry Γ . It is usually considered to describe the temperature dependence of inelastic neutron scattering (INS) spectra. Both terms $\sim g_k^c$ and $\sim g_k^s$ refer to a breathing or a shaking type of coupling to the k th phonon mode, respectively. Both types of coupling cause an opposite shifting behaviour of the tunnelling line [14b]. The linear coupling in the phonon coordinates is experimentally well justified since it leads to the usually observed Arrhenius-type temperature dependence of the line broadenings in INS experiments.

The eigenstates of \mathbf{H}^R will be denoted by $|m\Gamma\rangle$, where $m \in \mathbb{N}_0$ ($\mathbb{N}_0 =$ non-negative integers) is the librational quantum number and Γ indicates the symmetry type ($\Gamma = \text{A, E}^a$ or E^b). As already explained in the introduction, we classify the eigenstates of \mathbf{H}^R with respect to the symmetry group C_3 , regarding even permutations only. The matrix of \mathbf{H}^Q is not altered by this simplification [4]. The eigenstates form products of a spatial $|m\Gamma\rangle$ and a spin $|\Gamma_c\mu\rangle$ part:

$$|m\Gamma\mu\rangle = |m\Gamma\rangle \times |\Gamma_c\mu\rangle \quad (7)$$

where $\mu (\equiv \mu_\Gamma)$ denotes all other quantum numbers (i.e. total spin I and its z component I_z) within a given symmetry species. Γ_c is the representation conjugate to Γ , i.e.

$$\Gamma_c = \begin{Bmatrix} \text{A} \\ \text{E}^b \\ \text{E}^a \end{Bmatrix} \quad \text{for} \quad \Gamma = \begin{Bmatrix} \text{A} \\ \text{E}^a \\ \text{E}^b \end{Bmatrix}.$$

For CD_3 , there is no one-to-one correspondence between the symmetry species Γ and the total nuclear spin I of the CD_3 group. Instead, there are eleven A states with $I = 0, 1, 3$ and eight E^a and E^b states with $I = 1, 2$, respectively. The spin states for CD_3 may be found in [4, 15].

Finally, we consider the quadrupolar Hamiltonian \mathbf{H}^Q in equation (3). For methyl deuterons it is well known [16] that the electric-field gradient (EFG) tensor is axially

symmetric to an excellent approximation. The principal axis of the EFG coincides with the C-D bond axis in most cases. The quadrupolar energy of a single deuteron in the presence of an EFG of strength eq along the z axis is given by

$$(e^2qQ/4\hbar)(3I_z^2 - I^2). \quad (8a)$$

H^Q is the sum of the quadrupolar interactions of the three deuterons:

$$H^Q = \sum_{i=1}^3 H_{(i)}^Q. \quad (8b)$$

Q is the quadrupolar moment of the deuteron, I_z and I represent spin operators acting on the spin states of the deuteron [13]. Defining the quadrupolar coupling constant

$$C_Q = e^2qQ/\hbar \quad (9)$$

and using now, contrary to (8a), the rotational axis of the CD_3 group as magnetic quantization axis, one finds

$$\begin{aligned} H^Q = & (\pi/2)C_Q \left[\frac{1}{2}(3\cos^2\vartheta - 1)[3(I_z^{(1)})^2 + 3(I_z^{(2)})^2 + 3(I_z^{(3)})^2 - (I^{(1)})^2 - (I^{(2)})^2 - (I^{(3)})^2] \right. \\ & - \frac{3}{4}\sin(2\vartheta)\exp(i\varphi)[(I_z^{(1)}I_+^{(1)} + I_+^{(1)}I_z^{(1)}) \\ & + \epsilon(I_z^{(2)}I_+^{(2)} + I_+^{(2)}I_z^{(2)}) + \epsilon^*(I_z^{(3)}I_+^{(3)} + I_+^{(3)}I_z^{(3)})] + \text{HC} \} \\ & \left. + \frac{3}{4}\sin^2\vartheta\exp(-2i\varphi)[(I_+^{(1)})^2 + \epsilon(I_+^{(2)})^2 + \epsilon^*(I_+^{(3)})^2] + \text{HC} \right]. \quad (10) \end{aligned}$$

Here, $I_{\pm}^{(i)} = I_x^{(i)} \pm iI_y^{(i)}$, $(I_+^{(i)})^+ = I_-^{(i)}$, $(I_-^{(i)})^+ = I_+^{(i)}$, $\epsilon = \exp(2\pi i/3)$ and HC means Hermitian conjugate; ϑ is the angle between the non-vanishing component of the EFG and the rotational axis. For the tetrahedral angle ϑ_T one has $\cos\vartheta_T = 1/3$. Deviations from this value of about 5% have been observed by ^2H NMR [17].

Typical values for C_Q are 0.1–0.132 neV [16], whereas the strength of the dipole–dipole interaction among the deuterons (γ_D^2/r^3 , γ_D = gyromagnetic ratio) is of the order of 1 peV. (Note that the gyromagnetic ratio of deuterons is a factor 6.5 smaller than that of protons.) The strength of the quadrupolar interaction compared to that of the dipole–dipole interaction allows us to neglect the latter completely in the following discussion.

In the basis (7) the quadrupolar Hamiltonian reads

$$H^Q = \sum_{m\Gamma\mu} \sum_{m'\Gamma'\mu'} Q_{mm'}^{\Gamma\mu\Gamma'\mu'} |m\Gamma\mu\rangle \langle m'\Gamma'\mu'|. \quad (11)$$

The $Q_{mm'}^{\Gamma\mu\Gamma'\mu'}$ are collected in table 1.

In contrast to the dipolar Hamiltonian in the CH_3 case, the quadrupolar Hamiltonian also has non-vanishing matrix elements between E^a and E^b states, $Q_{mm'}^{E^a\mu E^b\mu'}$ [4, 18]. In CD_3 , all three symmetry species are mixed by the quadrupolar interaction.

In the following we want to treat H^Q perturbationally. If we assume for $m \neq m'$

$$\Delta_m \ll |E_m^\Gamma - E_{m'}^{\Gamma'}| \quad (12)$$

with $\Delta_m := E_m^E - E_m^A$, it is sufficient to diagonalize the matrix of $H^R + H^Q$ within each librational multiplet. This assumption can safely be justified since the lowest tunnelling

Table 1. Matrix elements $Q_{mm'}^{\Gamma\mu\Gamma'\mu'}$ of the quadrupolar Hamiltonian (10) as they are defined in equation (11). All matrix elements are proportional to the quadrupolar energy C_Q (defined in (9)) and depend upon the angle Θ between the C-D bond and the rotational axis. The symmetry-changing matrix elements (parts (c) and (d)) furthermore depend upon the rotational wavefunction $|m\Gamma\rangle$ (cf equation (4)).

(a)	A_{33}	A_{32}	A_{31}	A_{30}	A_{3-1}	A_{3-2}	A_{3-3}	A_{11}	A_{10}	A_{1-1}	A_{00}
A_{33}	P										
A_{32}											
A_{31}			$-\frac{3}{5}P$					$\frac{4}{5}P$			
A_{30}				$-\frac{4}{5}P$					$\frac{\sqrt{24}}{5}P$		
A_{3-1}					$-\frac{3}{5}P$					$\frac{4}{5}P$	
A_{3-2}											
A_{3-3}							P				
A_{11}			$\frac{4}{5}P$					$\frac{3}{5}P$			
A_{10}				$\frac{\sqrt{24}}{5}P$					$-\frac{6}{5}P$		
A_{1-1}					$\frac{4}{5}P$					$\frac{3}{5}P$	
A_{00}											
(b)	E_{22}^a	E_{21}^a	E_{20}^a	E_{2-1}^a	E_{2-2}^a	E_{11}^a	E_{10}^a	E_{1-1}^a			
E_{22}^a						P					
E_{21}^a											
E_{20}^a											
E_{2-1}^a								$-P$			
E_{2-2}^a											
E_{11}^a		P									
E_{10}^a											
E_{1-1}^a				$-P$							
(c)	E_{22}^b	E_{21}^b	E_{20}^b	E_{2-1}^b	E_{2-2}^b	E_{11}^b	E_{10}^b	E_{1-1}^b			
E_{22}^b		$-\frac{\sqrt{3}}{2}C$				$\frac{1}{\sqrt{12}}C$					
E_{21}^b			$-\frac{1}{\sqrt{8}}C$				$-\frac{1}{\sqrt{24}}C$				
E_{20}^b	$-\frac{1}{\sqrt{2}}D$			$\frac{1}{\sqrt{8}}C$				$-\frac{1}{\sqrt{8}}C$			
E_{2-1}^b		$-\frac{\sqrt{3}}{2}D$			$\frac{\sqrt{3}}{2}C$	$-\frac{1}{\sqrt{12}}D$					
E_{2-2}^b			$-\frac{1}{\sqrt{2}}D$				$-\frac{1}{\sqrt{6}}D$				
E_{11}^b			$-\frac{1}{\sqrt{8}}C$				$\frac{\sqrt{3}}{\sqrt{8}}C$				
E_{10}^b	$\frac{1}{\sqrt{6}}D$			$-\frac{1}{\sqrt{24}}C$				$-\frac{\sqrt{3}}{\sqrt{8}}C$			
E_{1-1}^b		$\frac{1}{\sqrt{12}}D$			$\frac{1}{\sqrt{12}}C$	$\frac{\sqrt{3}}{2}D$					
(d)	E_{22}^c	E_{21}^c	E_{20}^c	E_{2-1}^c	E_{2-2}^c	E_{11}^c	E_{10}^c	E_{1-1}^c			
E_{22}^c			$-\frac{1}{\sqrt{2}}\bar{D}$				$\frac{1}{\sqrt{6}}\bar{D}$				
E_{21}^c	$-\frac{\sqrt{3}}{2}\bar{C}$			$-\frac{\sqrt{3}}{2}\bar{D}$				$\frac{1}{\sqrt{12}}\bar{D}$			
E_{20}^c		$-\frac{1}{\sqrt{8}}\bar{C}$			$-\frac{1}{\sqrt{2}}\bar{D}$	$-\frac{1}{\sqrt{8}}\bar{C}$					
E_{2-1}^c			$\frac{1}{\sqrt{8}}\bar{C}$				$-\frac{1}{\sqrt{24}}\bar{C}$				
E_{2-2}^c				$\frac{\sqrt{3}}{2}\bar{C}$				$\frac{1}{\sqrt{12}}\bar{C}$			
E_{11}^c	$\frac{1}{\sqrt{12}}\bar{C}$			$-\frac{1}{\sqrt{12}}\bar{D}$				$\frac{\sqrt{3}}{2}\bar{D}$			
E_{10}^c		$-\frac{1}{\sqrt{24}}\bar{C}$			$-\frac{1}{\sqrt{6}}\bar{D}$	$\frac{\sqrt{3}}{\sqrt{8}}\bar{C}$					
E_{1-1}^c			$-\frac{1}{\sqrt{8}}\bar{C}$				$-\frac{\sqrt{3}}{\sqrt{8}}\bar{C}$				

Table 1. (continued)

(d)	A ₃₃	A ₃₂	A ₃₁	A ₃₀	A ₃₋₁	A ₃₋₂	A ₃₋₃	A ₁₁	A ₁₀	A ₁₋₁	A ₀₀
E ₂₂ ^a	$\frac{1}{\sqrt{2}}A$			$-\frac{1}{\sqrt{10}}B$					$-\frac{1}{\sqrt{15}}B$		$\frac{1}{\sqrt{2}}B$
E ₂₁ ^a				$-\frac{\sqrt{3}}{\sqrt{10}}B$						$-\frac{1}{\sqrt{30}}B$	
E ₂₀ ^a			$-\frac{1}{\sqrt{5}}A$			$-\frac{1}{\sqrt{2}}B$		$\frac{1}{\sqrt{20}}A$			
E ₂₋₁ ^a			$-\frac{\sqrt{2}}{\sqrt{5}}A$				$-\frac{1}{\sqrt{2}}B$		$\frac{1}{\sqrt{60}}A$		$\frac{1}{\sqrt{2}}A$
E ₂₋₂ ^a				$-\frac{\sqrt{3}}{\sqrt{10}}A$						$-\frac{1}{\sqrt{30}}A$	
E ₁₁ ^a		$-\frac{1}{\sqrt{3}}A$		$\frac{1}{\sqrt{30}}B$						$-\frac{\sqrt{3}}{\sqrt{10}}B$	
E ₁₀ ^a			$-\frac{2}{\sqrt{15}}A$			$\frac{1}{\sqrt{6}}B$		$-\frac{\sqrt{3}}{\sqrt{20}}A$			
E ₁₋₁ ^a				$-\frac{1}{\sqrt{10}}A$			$\frac{1}{\sqrt{2}}B$		$\frac{\sqrt{3}}{\sqrt{20}}A$		

$$P \equiv P_{mm'} := (\frac{1}{2}\pi C_Q)(3/2)(3 \cos^2 \vartheta - 1)\delta_{m,m'}$$

$$C \equiv C_{mm'} := (\frac{1}{2}\pi C_Q)(3\sqrt{3}/2) \sin(2\vartheta) \langle mE^a | e^{-i\varphi} | m'E^b \rangle \quad \bar{C} \equiv C^*$$

$$D \equiv D_{mm'} := (\frac{1}{2}\pi C_Q)(3\sqrt{3}/2) \sin^2 \vartheta \langle mE^a | e^{2i\varphi} | m'E^b \rangle \quad \bar{D} \equiv D^*$$

$$A \equiv A_{mm'} := (\frac{1}{2}\pi C_Q)(3\sqrt{3}/2) \sin(2\vartheta) \langle mE^a | e^{i\varphi} | m'A \rangle$$

$$B \equiv B_{mm'} := (\frac{1}{2}\pi C_Q)(3\sqrt{3}/2) \sin^2 \vartheta \langle mE^a | e^{-2i\varphi} | m'A \rangle$$

energies are smaller than all librational energies by a factor of usually $< 10^{-3}$. In deuterated systems this factor is even smaller. The unitary 27×27 dimensional matrix, which achieves the diagonalization

$$S_{(m)}(\mathbf{H}^R + \mathbf{H}^Q)_{(m)}(S_{(m)})^{-1} = (\text{Diagonal})_{(m)}$$

formally yields the eigenstates

$$|\Psi_m^{\Gamma\mu}\rangle = \sum_{\Gamma'\mu'} (S_m^{\Gamma'\mu'\Gamma\mu})^* |m\Gamma'\mu'\rangle. \quad (13)$$

In the following we concentrate on systems in which the tunnelling frequencies Δ_0 are large compared to the energy differences of \mathbf{H}^Q . This is valid for tunnelling frequencies $\Delta_0 \geq 10C_Q \approx 1$ neV. The elements $S_m^{E\mu A\mu'}$ of the unitary matrix are given in first order by

$$S_m^{E\mu A\mu'} \simeq Q_{mm}^{E\mu A\mu'} / \Delta_m \ll 1 \quad (14)$$

and they are proportional to C_Q , whereas the $S_m^{E^a\mu E^b\mu'}$ are of order unity since E^a and E^b states are degenerate. Equation (14) allows us to write

$$\sum_{\Gamma'' \in (E^a, E^b)} \sum_{\mu''} S_m^{\Gamma''\mu''\Gamma\mu} (S_m^{\Gamma'\mu'\Gamma''\mu''})^* = \delta_{\Gamma,\Gamma'} \delta_{\mu,\mu'} [1 + O(\eta^2)] - (1 - \delta_{\Gamma,\Gamma'} \delta_{\mu,\mu'}) O(\eta) \quad (15)$$

where $\eta \ll 1$, which has the value of a typical non-vanishing element $S_m^{E\mu A\mu'}$, will be taken into account only in lowest non-vanishing order (note that $\mu' \equiv \mu'_{\Gamma'}$, cf equation (7)).

3. Symmetry conversion rates

As in I we calculate the transition rates $R_{\Gamma \rightarrow \Gamma'}$ taking the time derivatives of the expectation value of projectors P_{Γ} into the Γ -symmetric part of the Hilbert space for a Γ' -symmetric thermal equilibrium state

$$\rho_{\Gamma'} := P_{\Gamma'} \exp(-\beta \mathbf{H}) P_{\Gamma'} / \text{Tr}[P_{\Gamma'} \exp(-\beta \mathbf{H}) P_{\Gamma'}]$$

in second order regarding \mathbf{H}^1 . Contrary to the CH_3 problem, we now have to deal not only with $R_{A \leftarrow E}$ but also with the transition rates $R_{E^a \leftarrow E^b}$.

For times long compared to all other relaxation times of our system we have to solve the following linear rate equations for the symmetry species concentration $C_\Gamma := \langle P_\Gamma \rangle$:

$$\frac{d}{dt} C_\Gamma = \sum_{\Gamma' \neq \Gamma} (R_{\Gamma \leftarrow \Gamma'} C_{\Gamma'} - R_{\Gamma' \leftarrow \Gamma} C_\Gamma) \quad (16)$$

where

$$R_{\Gamma \leftarrow \Gamma'} := \frac{d}{dt} \langle P_\Gamma(t) \rangle_{\Gamma'}. \quad (17)$$

The rate equations (16) can be written in matrix form:

$$\frac{d}{dt} \begin{pmatrix} C_A \\ C_{E^a} \\ C_{E^b} \end{pmatrix} = \begin{pmatrix} -2z R_{A \leftarrow E^a} & R_{A \leftarrow E^a} & R_{A \leftarrow E^a} \\ z R_{A \leftarrow E^a} & -R_{A \leftarrow E^a} - R_{E^a \leftarrow E^b} & R_{E^a \leftarrow E^b} \\ z R_{A \leftarrow E^a} & R_{E^a \leftarrow E^b} & -R_{A \leftarrow E^a} - R_{E^a \leftarrow E^b} \end{pmatrix} \begin{pmatrix} C_A \\ C_{E^a} \\ C_{E^b} \end{pmatrix} \quad (18)$$

where $z := Z^E/Z^A$ with

$$Z^\Gamma = \alpha_\Gamma \sum_m \exp(-\beta E_m^\Gamma) \quad \alpha_A = 11, \quad \alpha_E = 8.$$

We have anticipated the fact that the rates $R_{\Gamma \leftarrow \Gamma'}$ have to fulfil the detailed balance condition

$$R_{\Gamma \leftarrow \Gamma'} / R_{\Gamma' \leftarrow \Gamma} = Z^\Gamma / Z^{\Gamma'}. \quad (19)$$

The transition-rate matrix has eigenvalues $\lambda_1 = 0$, $\lambda_2 = -(1 + 2z)R_{A \leftarrow E^a}$ and $\lambda_3 = -2R_{E^a \leftarrow E^b} - R_{A \leftarrow E^a}$, the first of which corresponds to the stationary solution at thermal equilibrium. λ_2 is connected with $A \leftrightarrow E$ conversion, $1/\tau_{\text{con}} = -\lambda_2$ and $\lambda_3 = -1/\tau_{E^a \leftrightarrow E^b}$ with $E^a \leftrightarrow E^b$ conversion.

$1/\tau_{\text{con}}$ describes changes in $C_E := \frac{1}{2}(C_{E^a} + C_{E^b})$ due to $A \leftrightarrow E$ transitions, irrespective of E being E^a or E^b . Thus, for the description of experiments designed to obtain information about the $A \leftrightarrow E$ conversion time, the rates $R_{E^a \leftarrow E^b}$ are irrelevant. Therefore we restrict ourselves to the calculation of $R_{A \leftarrow E^a}$ and $1/\tau_{\text{con}}$.

$R_{A \leftarrow E^a}$ is calculated in time-dependent perturbation theory in second order with respect to \mathbf{H}^1 and \mathbf{H}^Q . For \mathbf{H}^Q it is assumed that it mixes the symmetry species A and E slightly without changing the eigenvalues of \mathbf{H}_0 (cf I). (Note that this procedure is not applicable for the calculation of $R_{E^a \leftarrow E^b}$, since E^a and E^b states are degenerate.) Accordingly, we use as unperturbed Hamiltonian:

$$\mathbf{H}_0 = \sum_{m\Gamma\mu} E_m^\Gamma |\Psi_m^{\Gamma\mu}\rangle \langle \Psi_m^{\Gamma\mu}| + \mathbf{H}^P. \quad (20)$$

The rotor-phonon interaction reads in the basis (13):

$$\mathbf{H}^1 = \sum_{km\mu'} \sum_{\Gamma\mu} \sum_{\Gamma'\mu'} \sum_{\Gamma''\mu''} g_{km\mu'} S_m^{\Gamma\mu\Gamma'\mu'} (S_{m'}^{\Gamma'\mu\Gamma''\mu''})^* |\Psi_m^{\Gamma'\mu'}\rangle \langle \Psi_{m'}^{\Gamma''\mu''}| (b_k + b_k^\dagger). \quad (21)$$

In a calculation similar to that performed in I we find in $O(\eta^2)$ for the inelastic transition rate $R_{A \leftarrow E^2}$:

$$\begin{aligned}
 R_{A \leftarrow E^2} = & 2\pi \sum_{m_0 m} \frac{\exp(-\beta E_{m_0}^E)}{Z^E} [n(|E_{m_0}^E - E_m^A|) \\
 & + \Theta(E_{m_0}^E - E_m^A)] \sum_k \sum_{\mu\mu'} \left| g_{kmm_0}^A \frac{Q_{m_0 m_0}^{E^2 \mu' A \mu}}{\Delta_{m_0}} - g_{kmm_0}^E \frac{Q_{m m}^{E^2 \mu' A \mu}}{\Delta_m} \right|^2 \\
 & \times \delta(|E_{m_0}^E - E_m^A| - \omega_k) + O(\eta^3). \quad (22)
 \end{aligned}$$

Here, β is the inverse temperature, $n(E) := [\exp(\beta E) - 1]^{-1}$ the phonon occupation number and

$$\Theta(x) = \begin{cases} 1 & x > 0 \\ 0 & x < 0. \end{cases}$$

This rate depends on (i) the bare tunnelling energy Δ_0 , (ii) the librational energies, which for a pure $V_3 \cos(3\varphi)$ orientational potential are related to Δ_0 , (iii) the strength of the rotor-phonon coupling, (iv) the type of the rotor-phonon coupling (breathing or shaking) and (v) the temperature.

With the abbreviations

$$A_m := \langle m E^a | e^{i\varphi} | m A \rangle \quad (23a)$$

$$B_m := \langle m E^a | e^{-2i\varphi} | m A \rangle \quad (23b)$$

we eventually find for the $A \leftrightarrow E$ conversion rate:

$$\begin{aligned}
 \frac{1}{\tau_{\text{con}}} = & 3^4 \left(\frac{\pi}{2}\right)^3 C_Q^2 \left(\frac{1}{Z^E} + \frac{2}{Z^A}\right) \sum_{m_0 m} \exp(-\beta E_{m_0}^E) [n(|E_{m_0}^E - E_m^A|) \\
 & + \Theta(E_{m_0}^E - E_m^A)] \sum_k \left[\sin^2(2\vartheta) \left| g_{kmm_0}^A \left(\frac{A_{m_0}}{\Delta_{m_0}}\right) - g_{kmm_0}^E \left(\frac{A_m}{\Delta_m}\right) \right|^2 \right. \\
 & \left. + \sin^4 \vartheta \left| g_{kmm_0}^A \left(\frac{B_{m_0}}{\Delta_{m_0}}\right) - g_{kmm_0}^E \left(\frac{B_m}{\Delta_m}\right) \right|^2 \right] \delta(|E_{m_0}^E - E_m^A| - \omega_k). \quad (24)
 \end{aligned}$$

This conversion rate, in particular its temperature dependence, has much similarity to the one obtained for the CH_3 system. For a detailed discussion of its properties we refer to I. It depends on the phonon density of states at all possible energy differences between unperturbed rotor levels of different symmetry (cf equation (4)). Therefore, at temperatures somewhat above the tunnelling energy Δ_0 , a thermally activated behaviour is obtained for the temperature dependence, with an activation energy that corresponds to the librational energy $E_{\text{lib}} := E_1 - E_0$. The conversion rate at zero temperature is proportional to $|g_k^c|^2$, where g_k^c is the rotor-phonon coupling strength of breathing type only (equation (6)). Furthermore, this rate is proportional to Δ_0^3 , if the phonon density of states at low frequencies is $\sim \omega^2$ (cf section 4).

The prominent difference of (24) to the conversion rates obtained for protonated systems is the temperature dependence at low temperatures $T \simeq \Delta_0$ when the librational activation

contribution is not important. Then only the term $m = m_0 = 0$ contributes and the complete low-temperature dependence is proportional to the function

$$f(\Delta_0) := [1 + \frac{16}{11} \exp(-\beta \Delta_0)] / [1 - \exp(-\beta \Delta_0)]. \quad (25)$$

In figure 1 the ratio between the behaviour in CD_3 and the usual $[1 + 2n(\Delta_0)]$ behaviour (n is the Bose function) is shown in Arrhenius representation. This $[1 + 2n(\Delta_0)]$ factor determines the low-temperature conversion rate in all theories for protonated systems known to us. The temperature dependence of the CD_3 conversion rate is enhanced as compared to CH_3 for $T > 0$. For $T = \Delta_0$, this enhancement factor is $\simeq 1.12$.

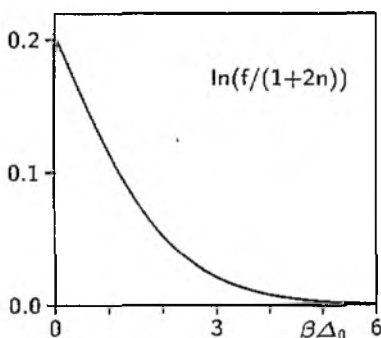


Figure 1. Ratio of the low-temperature conversion rate in CD_3 and the $[1 + 2n(\Delta_0)]$ factor in Arrhenius representation. This factor is obtained in all theories known to us describing the conversion in protonated systems. The temperature-dependent function $f(\Delta_0)$ is defined in (28) and $n(\Delta_0) := [\exp(\beta \Delta_0) - 1]^{-1}$ denotes the Bose function.

4. Debye phonons

As an explicit example, we specify the coupled phonon density of states. Introducing Debye phonons similar to I and assuming the rotor-phonon coupling to be proportional to the modulus of the phonon wavevector, leads to

$$\sum_k |g_{kmm'}^\Gamma|^2 \delta(\omega - \omega_k) = 3g^2 \left(\frac{\omega}{\omega_D} \right)^3 V_3 |M_{mm'}^\Gamma|^2 \Theta(\omega) \Theta(\omega_D - \omega). \quad (26)$$

Here ω_D denotes the Debye frequency,

$$M_{mm'}^\Gamma := \langle m\Gamma | \begin{Bmatrix} \cos(3\varphi) \\ \sin(3\varphi) \end{Bmatrix} | m'\Gamma \rangle \quad \text{for } \begin{Bmatrix} \text{breathing} \\ \text{shaking} \end{Bmatrix} \text{ type of coupling}$$

(cf also equations (4)–(6)) and $g := g_k^{s,c} / (V_3 \omega_k)^{1/2}$ is a dimensionless factor for the coupling strength; within this approximation the conversion rate becomes proportional to g^2 . Additionally, the angle ϑ for the polar angle between the CD bond with respect to the

rotational axis may be fixed by the tetrahedral angle $\cos \vartheta_T = 1/3$. Both assumptions lead to a conversion rate

$$\begin{aligned} \frac{1}{\tau_{\text{con}}} = & 3\pi^3 (2C_Q)^2 \frac{V_3 g^2}{\omega_D^3} \left(\frac{1}{Z^E} + \frac{2}{Z^A} \right) \sum_{m_0 m} \exp(-\beta E_{m_0}^E) |E_{m_0}^E - E_m^A|^3 [n(|E_{m_0}^E - E_m^A|) \\ & + \Theta(E_{m_0}^E - E_m^A) \Theta(\omega_D - |E_{m_0}^E - E_m^A|) \left[\left| M_{mm_0}^A \left(\frac{A_{m_0}}{\Delta_{m_0}} \right) - M_{mm_0}^E \left(\frac{A_m}{\Delta_m} \right) \right|^2 \right. \\ & \left. + 2 \left| M_{mm_0}^A \left(\frac{B_{m_0}}{\Delta_{m_0}} \right) - M_{mm_0}^E \left(\frac{B_m}{\Delta_m} \right) \right|^2 \right] \end{aligned} \quad (27)$$

which is very similar to the corresponding expression (9) of I.

For low temperatures $T \lesssim \Delta_0$ the conversion rate (27) becomes

$$1/\tau_{\text{con}} = (3\pi^3/2) C_Q^2 (V_3 g^2 / \omega_D^3) \Delta_0 |M_{00}^A - M_{00}^E|^2 (|A_0|^2 + 2|B_0|^2) f(\Delta_0). \quad (28)$$

An important property of (28) is the $1/\tau_{\text{con}} \sim \Delta_0^3$ proportionality, which is a consequence of $M_{00}^E - M_{00}^A \sim \Delta_0$. This Δ_0^3 dependence is obtained already in all other theories on symmetry conversion rates in rotational tunnelling systems. M_{00}^E vanishes for shaking-type contributions to the rotor-phonon coupling, so that the conversion rate at low temperatures is a measure for the coupling strength of breathing type. The whole temperature dependence is determined by the function $f(\Delta_0)$, which is defined in (25). The mechanism of this direct process is the absorption or emission of a phonon with energy Δ_0 , and the deviation from the $[1 + 2n(\Delta_0)]$ law in the temperature dependence has its origin solely in the different multiplicity of the spin states of A and E symmetry in the case of CD_3 .

As already stated in the previous section, the crossover from this direct process to a librally activated or Orbach-type process occurs at temperatures somewhat above the tunnelling energy Δ_0 , depending on the relative weights of shaking and breathing contributions to the rotor-phonon coupling (cf I). The dominant contribution to the conversion rate in this temperature range ($\Delta_0 \ll T \ll E_{\text{lib}}$) reads

$$\frac{1}{\tau_{\text{con}}} = 3(1 + \frac{16}{11}) \pi^3 C_Q^2 V_3 g^2 \left(\frac{E_{\text{lib}}}{\omega_D} \right)^3 \frac{1}{\Delta_0^2} |M_{01}|^2 (|A_0|^2 + 2|B_0|^2) \exp(-\beta E_{\text{lib}}) \quad (29)$$

where we have ignored the Γ dependence of M_{01} . The Δ_0^{-2} proportionality as a direct consequence of (24) is of general validity, whereas the E_{lib}^3 proportionality originates from the Debye assumption for the phonon density of states.

To allow comparison with recent experimental evidence [19] of a Raman-type rotor-phonon coupling, we give the result for the conversion rate due to those inelastic phonon scattering processes [10]. (Here, a phonon with energy ω is absorbed and another one with energy $\Delta_0 + \omega$ is emitted, or vice versa.) A rotor-phonon coupling quadratic in the phonon coordinates:

$$\begin{aligned} H_{\text{Raman}}^I = & \sum_{kk'} [\tilde{g}_{kk'}^c \cos(3\varphi) + \tilde{g}_{kk'}^s \sin(3\varphi)] (b_k + b_k^+) (b_{k'} + b_{k'}^+) \\ = & \sum_{kk'} \sum_{mm'} \sum_{\Gamma\mu} \tilde{g}_{kk'mm'}^{\Gamma} |m\Gamma\mu\rangle \langle m'\Gamma\mu| (b_k + b_k^+) (b_{k'} + b_{k'}^+) \end{aligned} \quad (30)$$

is assumed.

If we neglect the energy difference Δ_0 between the two phonons involved, a calculation similar to section 3 yields a conversion rate due to this process:

$$\left(\frac{1}{\tau_{\text{con}}}\right)_{\text{R}} = \frac{96\pi^9}{7} \left(1 + \frac{16}{11}e^{-\beta\Delta_0}\right) C_Q^2 \frac{V_3 \tilde{g}^2}{\omega_D^6} \frac{|M_{00}^A - M_{00}^E|^2}{\Delta_0^2} (|A_0|^2 + 2|B_0|^2) T^7 \quad (31)$$

where $\tilde{g} := \tilde{g}_{kk'}/(V_3\omega_k\omega_{k'})^{1/2}$. This rate depends only on breathing-type phonon coupling and is proportional to T^7 for $\beta\Delta_0 \ll 1$. The corresponding rate for CH_3 derived by Würger [10] reads in our notation:

$$(1/\tau_{\text{con}})_{\text{R};\text{CH}_3} = (2\pi)^7 (81/56) (\gamma^2/r^3)^2 (V_3 \tilde{g}^2/\omega_D^6) (|M_{00}^A - M_{00}^E|^2/\Delta_0^2) |B_0|^2 T^7.$$

Note that at temperatures $T \simeq \Delta_0$ the factor $\exp(-\beta\Delta_0)$ in (31), which is omitted in [10], adds a T^6 low-temperature contribution. For $\Delta_0 < 25 \mu\text{eV}$ the conversion rate is insensitive to Δ_0 because $M_{00}^A - M_{00}^E$ and Δ_0 both show the same exponential dependence on the barrier height $2V_3$ as can be seen from figure 2. On the other hand, the matrix elements A_0 and B_0 start to behave qualitatively differently as Δ_0 approaches B_{CH_3} : $B_0 \rightarrow 0$, whereas A_0 remains non-vanishing in this limit. This causes a drastic increase of the Raman-type conversion rate with deuteration in relatively weakly hindered systems. The recent experimental observation can be interpreted along these lines [19b].

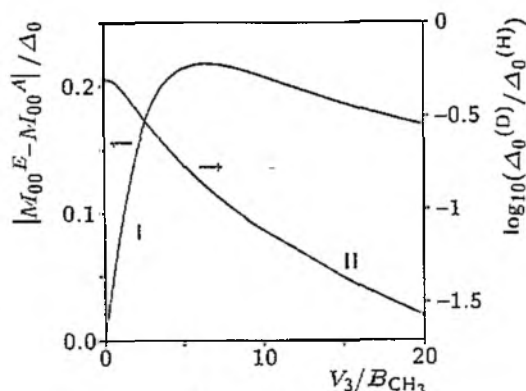


Figure 2. Curve I: $|M_{00}^E - M_{00}^A|/\Delta_0$ versus V_3/B for a threefold Mathieu Hamiltonian \mathbf{H}^R (cf (4)). $M_{mm'}^\Gamma := \langle m\Gamma | \cos(3\varphi) | m'\Gamma \rangle$, where $|m\Gamma\rangle$ are the eigenstates of \mathbf{H}^R to symmetry $\Gamma = A, E^a, E^b$. Curve II: $\log_{10}[\Delta_0(\text{CD}_3)/\Delta_0(\text{CH}_3)]$ versus V_3/B_{CH_3} .

It should be pointed out that in the case of CH_3 there exists another possibility of a Raman process via direct coupling of the dipolar interaction to the lattice modes. In CD_3 , the only possible origin for a Raman process stems from quadratic coupling of the rotor to the phonons.

5. Comparison with CH_3

In this section, we compare the conversion rates for CD_3 to those for CH_3 . We disregard differences in the coupling strengths g, \tilde{g} and in the Debye frequencies ω_D . The latter is

5.2. Orbach process

Here, just the opposite behaviour is found: the dominant factor in this case is

$$\alpha \sim \left(\frac{\Delta_0(\text{CH}_3)}{\Delta_0(\text{CD}_3)} \right)^2 \quad (35)$$

which is much larger than 1. Furthermore, neither the small factor $|M_{00}^A - M_{00}^B|^2$ nor the factor Δ_0^3 due to the coupled density of low-energy phonons occurs (cf (29)). Because the librational energy $E_{\text{lib}}(\text{CD}_3)$ is smaller than $E_{\text{lib}}(\text{CH}_3)$, one has to be aware of the Arrhenius factors

$$\frac{\exp[-\beta E_{\text{lib}}(\text{CD}_3)]}{\exp[-\beta E_{\text{lib}}(\text{CH}_3)]} \quad (36)$$

in addition to the prefactors discussed already. This is the reason for the maximum occurring in figure 3(a) around $T/\Delta_0 \simeq 4$. According to (35) CD_3 systems are expected to convert much faster than the corresponding CH_3 systems in the temperature range where both systems convert via the Orbach process.

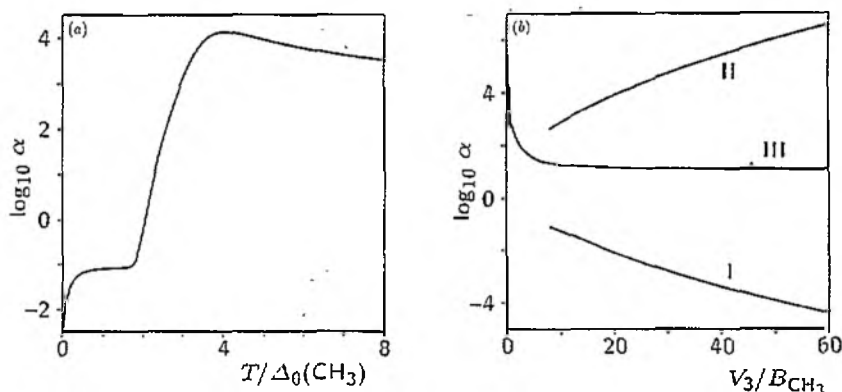


Figure 3. Logarithm of the ratio $\alpha := (\tau_{\text{con}}^{-1})_{\text{CD}_3} / (\tau_{\text{con}}^{-1})_{\text{CH}_3}$ for the Debye phonon model (26) and for breathing and shaking coupling types of equal strengths. Here, quadrupolar and dipolar energies are assumed to be equal: $C_Q = \gamma^2/r^3$. (a) Plot of α versus temperature in units of the tunnelling energy $\Delta_0(\text{CH}_3)$ of the protonated methyl group. The parameters chosen are $V_3 = 10B_{\text{CH}_3}$ and $\omega_D = 18B_{\text{CH}_3}$. (b) Plot of α versus V_3/B_{CH_3} for $\omega_D = 35B_{\text{CH}_3}$: (I) direct process, $T = 0.5$ K; (II) Orbach process, $T = 25$ K; (III) Raman process. Curves I and II are calculated according to (22), which is not valid for $V_3 \lesssim 8B_{\text{CH}_3}$.

Thus, for a rotor-phonon coupling linear in the phonon coordinates (cf (6)), the ratio α strongly depends on temperature. This is shown in figure 3(a). At temperatures below the tunnelling energy of the deuterated compound, $\Delta_0(\text{CD}_3)$, α saturates at a certain low-temperature value (for the parameters chosen in figure 3(a), this value is $\alpha \simeq 3 \times 10^{-3}$). At slightly elevated temperatures the factor $f(\Delta_0(\text{CD}_3))$ (cf (25)) starts to increase. The resulting increase in α is only compensated when the temperature comes close to $\Delta_0(\text{CH}_3)$; then also $(\tau_{\text{con}}^{-1})_{\text{CH}_3}$ increases proportionally to $[1 + 2n(\Delta_0(\text{CH}_3))]$, where n is the Bose factor. The subsequent rise in $\alpha(T)$ around $T \simeq 2\Delta_0(\text{CH}_3)$ takes place because the deuterated compound starts to convert via the librally activated (Orbach-type) process, before the protonated compound ($E_{\text{lib}}(\text{CD}_3) < E_{\text{lib}}(\text{CH}_3)$) also begins to convert via this mechanism at $T > 4\Delta_0(\text{CH}_3)$. In the high-temperature limit $\Delta_0(\text{CH}_3) \ll T \ll E_{\text{lib}}(\text{CH}_3)$, α is determined by the factor (35), which is generally large compared to 1 (cf curve II in figure 2).

expected to decrease slightly when CH_3 is substituted by CD_3 . Furthermore, we neglect any isotope effect on the hindering potential $V_3 \cos(3\varphi)$. The important modification is a reduction of the (quantum) energy unit $B_{\text{CD}_3} = \frac{1}{2}B_{\text{CH}_3}$. This influences the rotational wavefunctions and the eigenvalues of \mathbf{H}^R (cf (4)).

One common prefactor in all expressions for the relative change in the conversion rates $\alpha := (\tau_{\text{con}}^{-1})_{\text{CD}_3} / (\tau_{\text{con}}^{-1})_{\text{CH}_3}$ with deuteration is the square of the ratio of the quadrupolar and the dipolar energy $[C_Q / (\gamma^2 / r^3)]^2$, which varies between 1 and 2, depending on the system considered.

We discuss the influence of direct, Orbach and Raman processes on the relative modification of the conversion rate α , assuming unchanged surroundings of the rotor. This in particular means that V_3 and the coupled phonon density of states are supposed not to alter with deuteration. The three processes differ considerably not only in their temperature dependences but also in the dependence on the magnitude of the hindering potential. For direct and Orbach-type processes our rates (22) are not valid for nearly free rotors. On the other hand, if $V_3 \gtrsim 8B_{\text{CH}_3}$ the rotor matrix elements A_m and B_m for the lowest relevant values of the librational quantum number m are of the order of 1, independent of deuteration.

5.1. Direct process

For this process (cf (28) and equation (9) of I, with $m = m' = 0$), which is relevant at low temperatures, two factors depending weakly on V_3 appear in α :

$$(|A_0(\text{CD}_3)|^2 + 2|B_0(\text{CD}_3)|^2) / |B_0(\text{CH}_3)|^2 \quad (32a)$$

being roughly equal to 3 for not too small V_3 , and

$$\frac{|M_{00}^A(\text{CD}_3) - M_{00}^E(\text{CD}_3)|^2}{\Delta_0(\text{CD}_3)^2} \bigg/ \frac{|M_{00}^A(\text{CH}_3) - M_{00}^E(\text{CH}_3)|^2}{\Delta_0(\text{CH}_3)^2} \quad (32b)$$

which can be deduced from figure 2. Already more important is the factor

$$\frac{f(\Delta_0(\text{CD}_3))}{1 + 2n(\Delta_0(\text{CH}_3))} \quad (33)$$

which for temperatures larger than $\Delta_0(\text{CD}_3)$ but still smaller than $\Delta_0(\text{CH}_3)$ is strongly in favour of $(\tau_{\text{con}}^{-1})_{\text{CD}_3}$. The most important factor in the conversion rate due to the direct process is, however, given by

$$\alpha \sim \left(\frac{\Delta_0(\text{CD}_3)}{\Delta_0(\text{CH}_3)} \right)^3 \quad (34)$$

owing to the small density of low-energy phonons. This factor can easily surmount all the aforementioned factors by orders of magnitude (cf curve II in figure 2). Therefore, the direct process is strongly suppressed with deuteration as a direct consequence of the Δ_0^3 proportionality of the conversion rates in this temperature regime.

5.3. Raman process

In the case of quadratic rotor-phonon coupling (30), Raman-type conversion takes place. The corresponding α_{Raman} ratios vary slightly with temperature for $T \lesssim \Delta_0$ owing to the $\exp(-\beta\Delta_0)$ dependence, but become constant at higher temperatures.

We now turn to a discussion of the dependences of α and α_{Raman} on the height of the orientational potential V_3 . These dependences are visualized in figure 3(b). The curves I and II belong to linear phonon coupling and to temperatures $T = 0.5$ K (dominated by the direct process) and $T = 25$ K (Orbach process), respectively. The decrease of I and the increase of II are both direct consequences of (34) and (35), i.e. of the Δ_0 dependence of the individual conversion rates. The increase of α with temperature (via linear phonon coupling) becomes more pronounced, the smaller the tunnelling energy.

Curve III refers to the Raman process. For $V_3 \gtrsim 18B_{\text{CH}_3}$ the conversion due to this process is increased by a factor of about 10 upon deuteration, approximately independent of V_3 (and of the temperature). For lower values of V_3 , α_{Raman} increases drastically as $V_3 \rightarrow 0$. The reason for this peculiar isotope effect in nearly free rotating systems, which convert via a Raman process, has already been discussed in connection with equation (31): $(\tau_{\text{con}}^{-1})_{\text{CH}_3}$ depends only on the rotor matrix element B_0 , which vanishes as $V_3 \rightarrow 0$, whereas $(\tau_{\text{con}}^{-1})_{\text{CD}_3}$ additionally depends on A_0 , which remains finite in this limit. Furthermore, it should be noted that the Raman conversion rate is very sensitive to even slight changes in the Debye energy due to the ω_D^{-6} proportionality (cf (31)).

6. Discussion

Let us start by discussing the approximations made in the calculation of the symmetry conversion rates.

Our approximation to restrict the diagonalization of $\mathbf{H}^R + \mathbf{H}^Q$ to a definite librational quantum number m is allowed if $\Delta_m \ll |E_m^r - E_{m'}^r|$ for $m \neq m'$ (equation (12)). This restriction should be justified for most physical systems—recall that CD_3 groups are always more hindered than CH_3 groups in the same surroundings—if the temperatures considered are small compared with the barrier height $2V_3$.

The most serious approximation is the perturbational approach with respect to the rotor-phonon coupling \mathbf{H}^I . Second-order perturbation theory is frequently used to describe the temperature dependence of rotational tunnelling despite the fact that the coupling strength is unknown.

Next, we neglected the energy shifts due to \mathbf{H}^Q in equation (20), which are of the order of C_Q . For $V_3 \gtrsim 100B_{\text{CD}_3}$, corresponding to 375 K, this approximation is no longer valid. We expect that sophisticated NMR methods—as applied to CH_3 [20]—are able to measure τ_{con} for such small tunnelling frequencies. However, for the temperature dependence of the transition rates $R_{A \leftrightarrow B}$ (equation (22)) the modification of the eigenenergies is irrelevant. An eventually altered low-temperature behaviour will hardly be observable for temperatures of the order of Δ_0 , i.e. $T \sim 11.6 \mu\text{K}$. At all higher temperatures mainly librational energy differences are of importance.

We did not take into account the dipolar interaction among the deuterons of the CD_3 group, since this is about 200 times weaker than the quadrupolar interaction. As an aside we want to point out that the long-ranging dipolar energies in CH_3 systems are expected to be important also between different methyl groups. If they are taken into account in CH_3 -containing systems, a qualitative modification occurs because then (in contrast to the pure intramolecular dipolar interaction) also $E^a \leftrightarrow E^b$ transitions are allowed. The argument

to neglect this intermolecular dipolar interaction was the larger distance of the CH_3 group from surrounding protons compared to the distance between the methyl protons. On the other hand, the significance of the intermolecular dipolar interaction clearly shows up in T_1 experiments [21]. For conversion only $A \leftrightarrow E$ transitions are relevant, which remain of the same order of magnitude also if the intermolecular dipolar interactions are taken into account. We are presently undertaking a study of this mechanism for CH_3 .

In the calculation of the conversion rates (22) and (24), we utilized equations (14) and (15). Owing to the limitations in the observable tunnelling energy $\Delta_0 \geq 0.1 \mu\text{eV}$, neutron scattering experiments should be explainable by our equation (24). In the following we restrict our discussion to physical situations in which $\eta \ll 1$.

The temperature dependence of τ_{con} in CD_3 is found to be quite similar to that of the corresponding more strongly hindered CH_3 system. In particular, for temperatures $E_{\text{lib}} \geq T \geq \Delta_0$ the behaviour is librally activated (cf (29)) as in I and the low-temperature conversion rate (28) is proportional to the rotor-phonon coupling strength of breathing type. As in I, a fast conversion at lowest temperatures should be accompanied by the tendency for a positive shifting of the inelastic tunnelling line with temperature and accordingly a pronounced negative shifting of the inelastic tunnelling line should be connected with very slow low-temperature conversion rates.

For low temperatures $T \leq \Delta_0$ a slightly different law for the temperature dependence is obtained than in *all* other rotational tunnelling systems (H_2 [6–8], CH_3 [5, 10] and CH_4 [9]) considered so far.

To our knowledge there exists only one experiment, performed by Buchman *et al* [22], that has measured conversion times of deuterated methane. They measured τ_{con} of CD_4 as a function of temperature for $35 \text{ mK} \leq T \leq 400 \text{ mK}$ by NMR susceptibility measurement. The authors emphasize that their data do not contradict a $[1 + 2n(\Delta_0)]$ law as predicted by Nijman and Berlinsky [9] for CH_4 . However, the error bars in [22] are too large to allow one to distinguish between a $[1 + 2n(\Delta_0)]$ low-temperature behaviour and a slightly modified law that follows from the different spin multiplicity in CD_4 in an analogous manner, as we found for CD_3 .

In the comparison of conversion rates of CD_3 with the corresponding CH_3 -containing system, we have made the following assumptions: first, the hindering potential was supposed to remain unchanged with isotopic substitution. In some cases this is known to be wrong [15]. However, it has been shown within a molecular-field approximation that a change of V_3 should occur only if $V_3 \lesssim 5B_{\text{CH}_3}$ [15]. Secondly, the coupled phonon density of states was assumed not to change with deuteration. If the rotors themselves contribute significantly to the phonon density of states (via their librational excitations), deuteration should be accompanied by a reduction of the phonon frequencies. In experiments like those described in [19] and [26], where the methyl rotors are diluted in a surrounding matrix, this source for change in the phonon coupling is expected to be negligible. Thirdly, we assumed that both the coupling mechanism—linear or quadratic in the phonon coordinates—and the coupling type—breathing or shaking—do not change with deuteration.

Using these assumptions, the ratios $\alpha := (\tau_{\text{con}}^{-1})_{\text{CD}_3} / (\tau_{\text{con}}^{-1})_{\text{CH}_3}$ are plotted in figures 3(a) and (b) versus temperature and barrier height, respectively. For a linear phonon coupling a reduction of the conversion rate is predicted for low temperatures (direct process), which is a consequence of the Δ_0^3 proportionality of the conversion rates (cf (28) and (34)). However, at elevated temperatures, when the Orbach process starts to become significant, α may rise by several orders of magnitude; recall the Δ_0^{-2} proportionality of the conversion rates in this temperature regime (cf (29) and (35)). The maximum in α as a function of temperature is connected with the smaller librational energy in CD_3 compared to CH_3 (cf

(36)). Specifically, for the Raman process α_{Raman} is (nearly) independent of temperature but this ratio strongly increases as V_3 becomes smaller than $\sim 18B_{\text{CH}_3}$, corresponding to tunnelling energies $\Delta_0(\text{CH}_3)$ larger than $25 \mu\text{eV}$. For stronger hindered rotors a constant value $\alpha_{\text{Raman}} \simeq 10$ is obtained. The vanishing of $(\tau_{\text{con}}^{-1})_{\text{CH}_3}$ when $V_3 \rightarrow 0$ is prevented in realistic situations by the intermolecular dipolar interaction between the methyl protons and protons located in the neighbourhood of the CH_3 group.

A large and nearly temperature-independent increase of the conversion rates with deuteration has been observed by optical hole burning experiments on dilute dimethyl-s-tetrazine molecules in an n-octane matrix [19b]. The experimentally obtained factor $\alpha_{\text{exp}} \simeq 60$ can be explained by supposing a low orientational barrier of $V_3 = 2.55B_{\text{CH}_3}$. This value also explains nicely the observed change in the side hole splitting with deuteration [19b].

Further experiments on systems containing CD_3 groups are desirable. It should be possible to observe the modified low-temperature behaviour in (i) neutron transmission experiments [23] (the enhancement factor $(\langle I^2 \rangle_T / \langle I^2 \rangle_{T=\infty} - 1)$ for the temperature-dependent part of the total scattering cross section for CD_3 equals 15/11 instead of 5/3 as in the case of CH_3), (ii) INS experiments [24], (iii) specific-heat experiments [25] and eventually (iv) optical hole burning experiments [19, 26]. The experimental data already obtained by the latter method can be explained by our theory. One system of recommendation would be γ -picoline, which even deuterated shows a tunnelling energy of $\Delta_0 \simeq 100 \mu\text{eV}$ [27].

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