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Symmetry species conversion in CD_3 systems

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Abstract

The symmetry species conversion rates of CD_3 groups are calculated using a model in which the interaction between the quadrupolar moment of the deuterons with the electric field gradient at the site of the nucleus causes symmetry changing transitions. The results are compared with those for the corresponding protonated species embedded in the same surrounding.

1. Introduction

There has been increasing interest in the problem of spin conversion in rotational tunnelling systems in recent years. Besides several experimental investigations [1–5], theoretical treatments of the conversion rates have been presented for H_2 [6, 7], D_2 [8], CH_4 [9] and CH_3 [10, 11]. Except for H_2 and D_2 the proposed conversion mechanism is a "hybrid" mechanism in which the intramolecular dipolar interaction mixes states of different symmetry and the rotor phonon coupling induces energy-conserving transitions between these states.

Here, we consider CD_3 groups [12]. The mechanism considered by us is a "hybrid" mechanism in which the interaction between the quadrupolar moment of the deuterons with the electric field gradient at the site of the nuclei mixes states of different symmetry and the rotor phonon interaction provides energy conservation. These electric field gradients have their origin almost exclusively in the charge distribution of the chemical bond between the deuteron and the carbon atom. The strength of the quadrupolar interaction for a CD_3 group is of a comparable strength as the dipolar interaction among the protons of a CH_3 group. The calculations will be performed using second-order perturbation theory with respect to the rotor phonon interaction Hamiltonian.

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2. Symmetry conversion rates

In this section we calculate the symmetry conversion rates of rotational tunnelling CD_3 groups using the Hamiltonian:

$$\boldsymbol{H} = \boldsymbol{H}^R + \boldsymbol{H}^P + \boldsymbol{H}^I + \boldsymbol{H}^Q . \tag{1}$$

The first three terms on the right-hand side of Eq. (1) are usually considered in theoretical treatments of the temperature dependence of rotational tunnelling [13, 14]:

$$\boldsymbol{H}^R = -\boldsymbol{B}\partial_\varphi^2 + \boldsymbol{V}_3 \cos 3\varphi$$

$$(\boldsymbol{B} \approx 324\,\mu\mathrm{eV} \text{ for } CD_3), \tag{2}$$

$$H^P = \sum_k \omega_k (b_k^+ b_k + \tfrac{1}{2}), \tag{3}$$

$$H^I = \sum_k (g_k^c \cos 3\varphi + g_k^s \sin 3\varphi)\,(b_k + b_k^+), \tag{4}$$

where the symbols have their usual meaning [14]. The total rotational wave functions form products of a spatial and a spin part. 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 A-states with $I = 0, 1, 3$ and E-states with $I = 1, 2$ [15, 16]. Thus, the name "spin" conversion would be misleading in the present context.

Defining the so-called quadrupolar coupling constant $C_Q = (e^2qQ/h)$ and using the rotational axis of the CD_3 group as magnetic quantization axis, one finds for the quadrupolar Hamiltonian:

$$\begin{aligned} H^Q = \frac{\pi}{2} C_Q [\tfrac{1}{2}(3\cos^2\vartheta - 1)\{3(I_z^{(1)})^2 + 3(I_z^{(2)})^2 \\ + 3(I_z^{(3)})^2 - (I^{(1)})^2 - (I^{(2)})^2 - (I^{(3)})^2\} \\ - (\tfrac{3}{4}\sin 2\vartheta \exp(i\varphi)\{(I_z^{(1)} I_+^{(1)} + I_+^{(1)} I_z^{(1)}) \\ + \varepsilon(I_z^{(2)} I_+^{(2)} + I_+^{(2)} I_z^{(2)}) \\ + \varepsilon^*(I_z^{(3)} I_+^{(3)} + I_+^{(3)} I_z^{(3)})\} + \text{h.c.}) \\ + (\tfrac{3}{4}\sin^2\vartheta \exp(-2i\varphi)\{(I_+^{(1)})^2 + \varepsilon (I_+^{(2)})^2 \\ + \varepsilon^* (I_+^{(3)})^2\} + \text{h.c.})]. \end{aligned} \tag{5}$$

Here, $I_\pm^{(i)} = I_x^{(i)} \pm i I_y^{(i)}$, $(I_+^{(i)})^+ = I_-^{(i)}$, $(I_z^{(i)})^+ = I_z^{(i)}$, $\varepsilon = \exp(2\pi i/3)$ and h.c. means hermitian conjugate. ϑ is the angle between the nonvanishing component of the axially symmetric electric field gradient eq and the rotational axis. For the tetrahedral angle ϑ_T, one has $\cos\vartheta_T = \frac{1}{3}$. Q denotes the quadrupolar moment of the deuterons.

Typical values for C_Q are 0.1–0.132 neV [15], which is much larger than the strength of the dipole–dipole interaction among the deuterons (~ 1 peV). Thus, we neglect the dipole–dipole interaction completely in the following discussion.

The matrix elements of H^Q can be found in Ref. [12]. In contrast to the dipolar Hamiltonian in the CH_3 case, the quadrupolar Hamiltonian also has nonvanishing matrix elements between E^a- and E^b-states [10, 12].

As in Ref. [10] (to be denoted as *I* in the following) we calculate the transition rates $R_{\Gamma \leftarrow \Gamma'}$($\Gamma, \Gamma' \in$(A, E^a, E^b)) 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 $\rho_{\Gamma'} := P_{\Gamma'} \exp(-\beta H) P_{\Gamma'} / \mathrm{Tr}(P_{\Gamma'} \exp(\beta H) P_{\Gamma'})$ in second order regarding H^I. 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 $C_\Gamma := \langle P_\Gamma \rangle$:

$$\frac{\mathrm{d}}{\mathrm{d}t} C_\Gamma = \sum_{\Gamma \neq \Gamma'} \{R_{\Gamma \leftarrow \Gamma'} C_{\Gamma'} - R_{\Gamma' \leftarrow \Gamma} C_\Gamma\}, \tag{6}$$

where

$$R_{\Gamma \leftarrow \Gamma'} := \frac{\mathrm{d}}{\mathrm{d}t} \langle P_\Gamma(t) \rangle_{\Gamma'}. \tag{7}$$

The rate equations (6) can be written in matrix form. This transition rate matrix has eigenvalues $\lambda_1 = 0$, $\lambda_2 = -(1 + 2z) R_{A \leftarrow E^a}$ and $\lambda_3 = -2R_{E^a \leftarrow E^b} - R_{A \leftarrow E^a}$, where $z := Z^E/Z^A$ with $Z^\Gamma = \alpha_\Gamma \sum \exp(-\beta E_m^\Gamma)$ (where β is the inverse temperature and E_m^Γ denotes the energy of the mth librational eigenstate of H^R with symmetry Γ), $\alpha_A = 11$, $\alpha_E = 8$. Furthermore, we have anticipated the fact that the rates $R_{\Gamma \leftarrow \Gamma'}$ have to fulfill the detailed balance condition. λ_1 corresponds to the stationary solution at thermal equilibrium, λ_2 is connected with A$\leftrightarrow$E conversion, $1/\tau_{con} = -\lambda_2$ and $\lambda_3 = -1/\tau_{E^a \leftrightarrow E^b}$ with $E^a \leftrightarrow E^b$ conversion.

$1/\tau_{con}$ 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 A$\leftrightarrow$E conversion the rates $R_{E^a \leftarrow E^b}$ are irrelevant. Therefore, we restrict ourselves to the calculation of $R_{A \leftarrow E^a}$ and $1/\tau_{con}$.

$R_{A \leftarrow E^a}$ is calculated in time-dependent perturbation theory in second order with respect to H^I and H^Q. For H^Q it is assumed that it mixes the symmetry species A and E slightly without changing the eigenvalues of H^R. In a calculation similar to

that performed in *I* (note that this procedure is not applicable for the calculation of $R_{E^a \leftrightarrow E^b}$, since E^a- and E^b-states are degenerate) we find

$$\frac{1}{\tau_{\text{con.}}} = 3^4 \left(\frac{\pi}{2}\right)^3 C_Q^2 \left(\frac{1}{Z^E} + \frac{2}{Z^A}\right) \sum_{m_0 m} \exp(-\beta E^E_{m_0}) \times \{n(|E^E_{m_0} - E^A_m|) + \Theta(E^E_{m_0} - E^A_m)\} \times \sum_k \left\{ \sin^2 2\vartheta \left| g^A_{kmm_0}\left(\frac{A_{m_0}}{A_{m_0}}\right) - g^E_{kmm_0}\left(\frac{A_m}{A_m}\right)\right|^2 + \sin^4 \vartheta \left| g^A_{kmm_0}\left(\frac{B_{m_0}}{A_{m_0}}\right) - g^E_{kmm_0}\left(\frac{B_m}{A_m}\right)\right|^2 \right\} \times \delta(|E^E_{m_0} - E^A_m| - \omega_k). \quad (8)$$

Here, $n(E) := (\exp(\beta E) - 1)^{-1}$ is the phonon occupation number,

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

and we have defined $A_m := \langle mE^a | e^{i\varphi} | mA \rangle$ and $B_m := \langle mE^a | e^{-2i\varphi} | mA \rangle$. 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 $E^E_{m_0} - E^A_m$. Therefore, at temperatures somewhat above the tunnelling energy A_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 prominent difference of Eq. (8) to the conversion rates obtained for protonated systems is the temperature dependence at low temperatures $T \approx A_0$. Then only the term $m = m_0 = 0$ contributes and the complete low-temperature dependence is proportional to the function

$$f(A_0) := \frac{(1 + \frac{16}{11}\exp(-\beta A_0))}{(1 - \exp(-\beta A_0))}, \quad (9)$$

which differs slightly from the usual $(1 + 2n(A_0))$ behaviour (n is the Bose function). The temperature dependence of the CD_3 conversion rate is enhanced as compared to CH_3 for $T > 0$. For $T = A_0$, this enhancement factor is ≈ 1.12.

As an explicit example, we specify the coupled phonon density of states. Similar to I we choose the Debye model for the phonons and fix the angle ϑ in (8) by the tetrahedral angle $\cos \vartheta_T = \frac{1}{3}$.

For low temperatures $T \lesssim A_0$ the conversion rate becomes

$$\frac{1}{\tau_{\text{con}}} = \frac{3\pi^3}{2} C_Q^2 \frac{V_3 g^2}{\omega_D^3} A_0 |M^A_{00} - M^E_{00}|^2 \times (|A_0|^2 + 2|B_0|^2) f(A_0). \quad (10)$$

Here, ω_D denotes the Debye frequency,

$$M^\Gamma_{mm'} := \langle m\Gamma | \begin{Bmatrix} \cos 3\varphi \\ \sin 3\varphi \end{Bmatrix} | m'\Gamma \rangle$$

$$\text{for} \begin{Bmatrix} \text{breathing: } \sim \cos 3\varphi \\ \text{shaking: } \sim \sin 3\varphi \end{Bmatrix}$$

type of coupling (cf. also Eqs. (2–4)) and $g := g^{s,c}_k / \sqrt{V_3 \omega_k}$ is a dimensionless factor for the coupling strength.

An important property of Eq. (10) is the $1/\tau_{\text{con}} \sim A_0^3$ proportionality, which is a consequence of $M^E_{00} - M^A_{00} \sim A_0$. This A_0^3 dependency is obtained already in all other theories on symmetry conversion rates in rotational tunnelling systems. M^Γ_{00} 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 $f(A_0)$, which is defined in Eq. (9). The deviation from the $(1 + 2n(A_0))$-law in the temperature dependence has its origin solely in the different multiplicity of the spin states of A- and E-symmetry in case of CD_3.

In the temperature range of librational activation (Orbach process) $(A_0 \ll T \ll E_{\text{lib}})$ the dominant contribution to the conversion rate reads

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

where we have ignored the Γ-dependence of M_{01}. The A_0^{-2} proportionality as a direct consequence of

Eq. (8) 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 [3] of a Raman-type rotor–phonon coupling, we give the result for the conversion rate due to those inelastic phonon scattering processes [11]. A rotor–phonon coupling quadratic in the phonon coordinates:

$$H_{\mathrm{Raman}}^I = \sum_{kk'} (\tilde{g}_{kk'}^{\mathrm{c}} \cos 3\varphi + \tilde{g}_{kk'}^{\mathrm{s}} \sin 3\varphi) \times (b_k + b_k^+)(b_{k'} + b_{k'}^+) \tag{12}$$

is assumed.

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

$$\left(\frac{1}{\tau_{\mathrm{con}}}\right)_R = \frac{96\pi^9}{7}(1+\tfrac{16}{11}\mathrm{e}^{-\beta\Delta_0})\, C_Q^2 \frac{V_3 \tilde{g}^2 |M_{00}^{\mathrm{A}} - M_{00}^{\mathrm{E}}|^2}{\omega_{\mathrm{D}}^6 \Delta_0^2} \times (|A_0|^2 + 2|B_0|^2) T^7 \tag{13}$$

where $\tilde{g} := \tilde{g}_{kk'}^{\mathrm{c}}/(V_3 \omega_k \omega_{k'})^{1/2}$. This rate is proportional to T^7 for $\beta\Delta_0 \ll 1$. The corresponding rate for CH_3 derived by Würger [11] reads in our notation:

$$(1/\tau_{\mathrm{con}})_{R,\mathrm{CH_3}} = (2\pi)^7 (81/56)(\gamma^2/r^3)^2 (V_3 \tilde{g}^2/\omega_{\mathrm{D}}^6) \times (|M_{00}^{\mathrm{A}} - M_{00}^{\mathrm{E}}|^2/\Delta_0^2)|B_0|^2 T^7.$$

For $\Delta_0 < 25$ μeV the conversion rate is insensitive on Δ_0 because $M_{00}^{\mathrm{A}} - M_{00}^{\mathrm{E}}$ and Δ_0 both show the same exponential dependence on the barrier height $2V_3$. On the other hand, the matrix elements A_0 and B_0 start to behave different qualitatively as Δ_0 approaches $B_{\mathrm{CH_3}}$: $B_0 \to 0$, whereas A_0 remains nonvanishing 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 [3].

3. Comparison to 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 expected to decrease slightly when CH_3 is substituted by CD_3. Furthermore, we neglect any isotope effect on the hindering potential $V_3 \cos 3\varphi$ (cf. Ref. [16]). The important modification is a reduction of the (quantum) energy unit $B_{\mathrm{CD_3}} = \frac{1}{2} B_{\mathrm{CH_3}}$. This influences the rotational wave functions and the eigenvalues of H^R (cf. (2)).

One common prefactor in all expressions for the relative change in the conversion rates $\alpha := (\tau_{\mathrm{con}}^{-1})_{\mathrm{CD_3}}/(\tau_{\mathrm{con}}^{-1})_{\mathrm{CH_3}}$ 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.

The ratios α depend on both, the temperature and the rotational potential barrier height $2V_3$.

In case of a quadratic rotor–phonon coupling (12), Raman-type conversion takes place. The corresponding α_{Raman} ratios vary slightly with temperature for $T \lesssim \Delta_0$ due to the $\exp(-\beta\Delta_0)$ dependence, but become constant at higher temperatures. For $V_3 \lesssim 18 B_{\mathrm{CH_3}}$ 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 $V_3 \to 0$. 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 Eq. (13).

In contrast, for a rotor–phonon coupling linear in the phonon coordinates (cf. Eq. (4)), the ratio α strongly depends on temperature.

For the direct process process (cf. Eq. (10) and Eq. (9) of I, with $m = m' = 0$), which is relevant at low temperatures, the most important factor is given by

$$\alpha \sim \left(\frac{\Delta_0(\mathrm{CD_3})}{\Delta_0(\mathrm{CH_3})}\right)^3 \tag{14}$$

owing to the small density of low-energy phonons. Since $\Delta_0(\mathrm{CD_3}) \ll \Delta_0(\mathrm{CH_3})$, the direct process is strongly suppressed with deuteration as a direct consequence of the Δ_0^3 proportionality of the conversion rates.

At higher temperatures, where conversion takes place via an Orbach process, just the opposite behaviour is found: The dominant factor in this case is

$$\alpha \sim \left(\frac{\Delta_0(\mathrm{CH_3})}{\Delta_0(\mathrm{CD_3})}\right)^2, \tag{15}$$

which is much larger than 1. Because the librational energy $E_{lib}(CD_3)$ is smaller than $E_{lib}(CH_3)$, one additionally has to be aware of the Arrhenius factors $\exp(-\beta[E_{lib}(CD_3) - E_{lib}(CH_3)])$. According to Eq. (15) 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.

The temperature dependence for the ratio α (H^I according to Eq. (4)) is shown in Fig. 1. At temperatures below the tunnelling energy of the deuterated compound, $\Delta_0(CD_3)$, α saturates at a certain low temperature value (for the parameters chosen in Fig. 1, this value is $\alpha \approx 3 \times 10^{-3}$). At slightly elevated temperatures the factor $f(\Delta_0(CD_3))$ (cf. Eq. (9)) starts to increase. The resulting increase in α is only compensated, when the temperature comes close to $\Delta_0(CH_3)$; then also $(\tau_{con}^{-1})_{CH_3}$ increases proportional to $(1 + 2n(\Delta_0(CH_3)))$. The subsequent raise in $\alpha(T)$ around $T \approx 2\Delta_0(CH_3)$ takes place because the deuterated compound starts to convert via the librationally activated (Orbach-type) process, before the protonated compound ($E_{lib}(CD_3) < E_{lib}(CH_3)$) also begins to convert via this mechanism at $T > 4\Delta_0(CH_3)$, leading to the maximum at $T/\Delta_0(CH_3) \approx 4$. In the high-temperature limit $\Delta_0(CH_3) \ll T \ll E_{lib}(CH_3)$, α is determined by the factor (15).

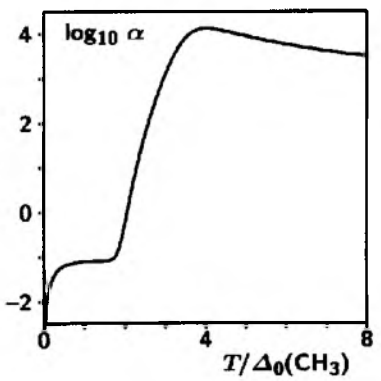

Fig. 1. Logarithm of the ratio $\alpha := (\tau_{con}^{-1})_{CD_3}/(\tau_{con}^{-1})_{CH_3}$ versus temperature (in units of the tunnelling energy $\Delta_0(CH_3)$) for the Debye phonon model and for breathing and shaking coupling types of equal strengths. The parameters chosen are $V_3 = 10B_{CH_3}$ and $\omega_D = 18B_{CH_3}$ and the quadrupolar and dipolar energies are assumed to be equal: $C_Q = \gamma^2/r^3$.

Also the dependence of α on the barrier height $2V_3$ is determined by the factors (14) and (15). Thus, for a direct process (low temperatures), α dramatically increases with increasing V_3, whereas the opposite behaviour is found for an Orbach process (high temperatures).

4. Conclusions

For a detailed discussion of the approximations made in the calculation of the symmetry conversion rates we refer to Refs. [12] and I.

The temperature dependence of τ_{con} in CD_3 is found to be quite similar to that of the corresponding stronger hindered CH_3 system, except for low temperatures $T \leqslant \Delta_0$, where a slightly different law for the temperature dependence is obtained than in *all* other rotational tunnelling systems considered so far.

For a comparison of conversion rates of CD_3 with the corresponding CH_3 containing system, we have plotted the ratios $\alpha := (\tau_{con}^{-1})_{CD_3}/(\tau_{con}^{-1})_{CH_3}$ under the aforementioned assumptions versus temperature for a linear phonon coupling. A strong reduction of the conversion rate is predicted for low temperatures (direct process). However, at elevated temperatures, when the Orbach process starts to become significant, α may raise by several orders of magnitude. This gives rise to a peculiar temperature dependence of the ratio α in case of a linear phonon coupling.

For the Raman process α_{Raman} is (nearly) independent of temperature but this ratio strongly increases as V_3 becomes smaller than $\sim 18B_{CH_3}$, corresponding to tunnelling energies $\Delta_0(CH_3)$ larger than 25 μeV. For stronger hindered rotors a constant value $\alpha_{Raman} \approx 10$ is obtained.

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