

# Symmetry species conversion in CD<sub>3</sub> systems

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## Abstract

The symmetry species conversion rates of CD<sub>3</sub> 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<sub>2</sub> [6, 7], D<sub>2</sub> [8], CH<sub>4</sub> [9] and CH<sub>3</sub> [10, 11]. Except for H<sub>2</sub> and D<sub>2</sub> 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<sub>3</sub> 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<sub>3</sub> group is of a comparable strength as the dipolar interaction among the protons of a CH<sub>3</sub> group. The calculations will be performed using second-order perturbation theory with respect to the rotor phonon interaction Hamiltonian.

## 2. Symmetry conversion rates

In this section we calculate the symmetry conversion rates of rotational tunnelling CD<sub>3</sub> groups using the Hamiltonian:

$$H = H^R + H^P + H^I + H^Q. \quad (1)$$

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]:

$$H^R = -B\hat{C}_\phi^2 + V_3 \cos 3\phi \quad (2)$$

$(B \approx 324 \mu\text{eV for CD}_3),$

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

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

where the symbols have their usual meaning [14]. The total rotational wave functions form products of a spatial and a spin part. For CD<sub>3</sub> there is no one to one correspondence between the symmetry species  $\Gamma$  and the total nuclear spin  $I$  of the CD<sub>3</sub> 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  $C_Q = (e^2 q Q / h)$  and using the rotational axis of the CD<sub>3</sub> group as magnetic quantization axis, one finds for the quadrupolar Hamiltonian:

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

Here,  $I_{\pm}^{(i)} = I_x^{(i)} \pm i I_y^{(i)}$ ,  $(I_{\pm}^{(i)})^+ = I_{\mp}^{(i)}$ ,  $(I_z^{(i)})^+ = I_z^{(i)}$ ,  $\varepsilon = \exp(2\pi i/3)$  and h.c. means hermitian conjugate.  $\vartheta$  is the angle between the nonvanishing component of the axially symmetric electric field gradient eq and the rotational axis. For the tetrahedral angle  $\vartheta_T$ , 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 ( $\sim 1$  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<sub>3</sub> case, the quadrupolar Hamiltonian also has nonvanishing matrix elements between E<sup>a</sup>- and E<sup>b</sup>-states [10, 12].

As in Ref. [10] (to be denoted as  $I$  in the following) we calculate the transition rates  $R_{\Gamma \rightarrow \Gamma'}(\Gamma, \Gamma' \in (A, E^a, E^b))$  taking the time derivatives of the expectation value of projectors  $P_{\Gamma}$  into the  $\Gamma$ -symmetric part of the Hilbert space for a  $\Gamma'$  symmetric thermal equilibrium state  $\rho_{\Gamma'} := P_{\Gamma'} \exp(-\beta H) P_{\Gamma'} / \text{Tr}(P_{\Gamma'} \exp(\beta H) P_{\Gamma'})$  in second order regarding  $H^I$ . Contrary to the CH<sub>3</sub> problem we now have to deal not only with  $R_{A \leftrightarrow E}$  but also with the transition rates  $R_{E^a \leftrightarrow E^b}$ .

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  $C_{\Gamma} := \langle P_{\Gamma} \rangle$ :

$$\frac{d}{dt} C_{\Gamma} = \sum_{\Gamma' \neq \Gamma} \{ R_{\Gamma \rightarrow \Gamma'} C_{\Gamma'} - R_{\Gamma' \rightarrow \Gamma} C_{\Gamma} \}, \quad (6)$$

where

$$R_{\Gamma \rightarrow \Gamma'} := \frac{d}{dt} \langle P_{\Gamma}(t) \rangle_{\Gamma'}. \quad (7)$$

The rate equations (6) can be written in matrix form. This transition rate matrix has eigenvalues  $\lambda_1 = 0$ ,  $\lambda_2 = -(1 + 2z)R_{A \leftrightarrow E}$ , and  $\lambda_3 = -2R_{E^a \leftrightarrow E^b} - R_{A \leftrightarrow E}$ , where  $z := Z^E/Z^A$  with  $Z^{\Gamma} = \alpha_{\Gamma} \sum_m \exp(-\beta E_m^{\Gamma})$  (where  $\beta$  is the inverse temperature and  $E_m^{\Gamma}$  denotes the energy of the  $m$ th librational eigenstate of  $H^R$  with symmetry  $\Gamma$ ),  $\alpha_A = 11$ ,  $\alpha_E = 8$ . Furthermore, we have anticipated the fact that the rates  $R_{\Gamma \rightarrow \Gamma'}$  have to fulfill the detailed balance condition.  $\lambda_1$  corresponds to the stationary solution at thermal equilibrium,  $\lambda_2$  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<sup>a</sup> or E<sup>b</sup>. Thus, for  $A \leftrightarrow E$  conversion the rates  $R_{E^a \leftrightarrow E^b}$  are irrelevant. Therefore, we restrict ourselves to the calculation of  $R_{A \leftrightarrow E}$  and  $1/\tau_{\text{con}}$ .

$R_{A \leftrightarrow E}$  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

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

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  $A_m := \langle m E^a | e^{i\varphi} | m A \rangle$  and  $B_m := \langle m E^a | e^{-2i\varphi} | m A \rangle$ . This conversion rate, in particular its temperature dependence has much similarity to the one obtained for the  $\text{CH}_3$  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  $E_{m_0}^E - E_m^A$ . Therefore, at temperatures somewhat above the tunnelling energy  $\Delta_0$ , 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  $T \approx \Delta_0$ . Then only the term  $m = m_0 = 0$  contributes and the complete low-temperature dependence is proportional to the function

$$f(\Delta_0) := \frac{(1 + \frac{16}{11} \exp(-\beta \Delta_0))}{(1 - \exp(-\beta \Delta_0))}, \quad (9)$$

which differs slightly from the usual  $(1 + 2n(\Delta_0))$  behaviour ( $n$  is the Bose function). The temperature dependence of the  $\text{CD}_3$  conversion rate is enhanced

as compared to  $\text{CH}_3$  for  $T > 0$ . For  $T = \Delta_0$ , this enhancement factor is  $\approx 1.12$ .

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  $\vartheta$  in (8) by the tetrahedral angle  $\cos \vartheta_T = \frac{1}{3}$ .

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

$$\begin{aligned} \frac{1}{\tau_{\text{con}}} = & \frac{3\pi^3}{2} C_Q^2 \frac{V_3 g^2}{\omega_D^3} \Delta_0 |M_{00}^A - M_{00}^E|^2 \\ & \times (|A_0|^2 + 2|B_0|^2) f(\Delta_0). \end{aligned} \quad (10)$$

Here,  $\omega_D$  denotes the Debye frequency,

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

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

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

An important property of Eq. (10) is the  $1/\tau_{\text{con}} \sim \Delta_0^3$  proportionality, which is a consequence of  $M_{00}^E - M_{00}^A \sim \Delta_0$ . This  $\Delta_0^3$  dependency is obtained already in all other theories on symmetry conversion rates in rotational tunnelling systems.  $M_{00}^{\Gamma}$  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 Eq. (9). 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 case of  $\text{CD}_3$ .

In the temperature range of librational activation (Orbach process) ( $\Delta_0 \ll T \ll E_{\text{lib}}$ ) the dominant contribution to the conversion rate reads

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

where we have ignored the  $\Gamma$ -dependence of  $M_{01}$ . The  $\Delta_0^{-2}$  proportionality as a direct consequence of

Eq. (8) is of general validity, whereas the  $E_{\text{lib}}^3$  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:

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

is assumed.

If we neglect the energy difference  $\Delta_0$  between the two phonons involved, a calculation similar to the one performed before yields a conversion rate due to this process:

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

where  $\tilde{g} := \tilde{g}_{kk'}^c / (V_3 \omega_k \omega_{k'})^{1/2}$ . This rate is proportional to  $T^7$  for  $\beta\Delta_0 \ll 1$ . The corresponding rate for  $\text{CH}_3$  derived by Würger [11] reads in our notation:

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

For  $\Delta_0 < 25 \mu\text{eV}$  the conversion rate is insensitive on  $\Delta_0$  because  $M_{00}^A - M_{00}^E$  and  $\Delta_0$  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  $\Delta_0$  approaches  $B_{\text{CH}_3}$ :  $B_0 \rightarrow 0$ , 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 $\text{CH}_3$

In this section, we compare the conversion rates for  $\text{CD}_3$  to those for  $\text{CH}_3$ . We disregard differences in the coupling strengths  $g, \tilde{g}$  and in the Debye

frequencies  $\omega_D$ . The latter is expected to decrease slightly when  $\text{CH}_3$  is substituted by  $\text{CD}_3$ . 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  $B_{\text{CD}_3} = \frac{1}{2} B_{\text{CH}_3}$ . 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  $\alpha := (\tau_{\text{con}}^{-1})_{\text{CD}_3} / (\tau_{\text{con}}^{-1})_{\text{CH}_3}$ , 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.

The ratios  $\alpha$  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  $\alpha_{\text{Raman}}$  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  $V_3 \lesssim 18 B_{\text{CH}_3}$  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  $V_3$ ,  $\alpha_{\text{Raman}}$  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 Eq. (13).

In contrast, for a rotor-phonon coupling linear in the phonon coordinates (cf. Eq. (4)), the ratio  $\alpha$  strongly depends on temperature.

For the direct 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

$$\alpha \sim \left( \frac{\Delta_0(\text{CD}_3)}{\Delta_0(\text{CH}_3)} \right)^3 \quad (14)$$

owing to the small density of low-energy phonons. Since  $\Delta_0(\text{CD}_3) \ll \Delta_0(\text{CH}_3)$ , the direct process is strongly suppressed with deuteration as a direct consequence of the  $\Delta_0^3$  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

$$\alpha \sim \left( \frac{\Delta_0(\text{CH}_3)}{\Delta_0(\text{CD}_3)} \right)^2, \quad (15)$$

which is much larger than 1. Because the librational energy  $E_{\text{lib}}(\text{CD}_3)$  is smaller than  $E_{\text{lib}}(\text{CH}_3)$ , one additionally has to be aware of the Arrhenius factors  $\exp(-\beta[E_{\text{lib}}(\text{CD}_3) - E_{\text{lib}}(\text{CH}_3)])$ . According to Eq. (15)  $\text{CD}_3$  systems are expected to convert much faster than the corresponding  $\text{CH}_3$  systems in the temperature range, where both systems convert via the Orbach process.

The temperature dependence for the ratio  $\alpha$  ( $H'$  according to Eq. (4)) is shown in Fig. 1. At temperatures below the tunnelling energy of the deuterated compound,  $\Delta_0(\text{CD}_3)$ ,  $\alpha$  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  $f(\Delta_0(\text{CD}_3))$  (cf. Eq. (9)) starts to increase. The resulting increase in  $\alpha$  is only compensated, when the temperature comes close to  $\Delta_0(\text{CH}_3)$ ; then also  $(\tau_{\text{con}}^{-1})_{\text{CH}_3}$  increases proportional to  $(1 + 2n(\Delta_0(\text{CH}_3)))$ . The subsequent raise in  $\alpha(T)$  around  $T \approx 2\Delta_0(\text{CH}_3)$  takes place because the deuterated compound starts to convert via the librationaly 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  $T > 4\Delta_0(\text{CH}_3)$ , leading to the maximum at  $T/\Delta_0(\text{CH}_3) \approx 4$ . In the high-temperature limit  $\Delta_0(\text{CH}_3) \ll T \ll E_{\text{lib}}(\text{CH}_3)$ ,  $\alpha$  is determined by the factor (15).

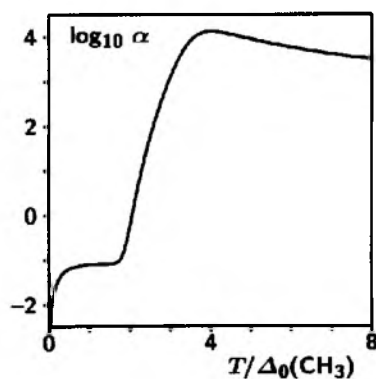


Fig. 1. Logarithm of the ratio  $\alpha := (\tau_{\text{con}}^{-1})_{\text{CD}_3} / (\tau_{\text{con}}^{-1})_{\text{CH}_3}$  versus temperature (in units of the tunnelling energy  $\Delta_0(\text{CH}_3)$ ) for the Debye phonon model and for breathing and shaking coupling types of equal strengths. The parameters chosen are  $V_3 = 10B_{\text{CH}_3}$  and  $\omega_D = 18B_{\text{CH}_3}$ , and the quadrupolar and dipolar energies are assumed to be equal:  $C_Q = \gamma^2/r^3$ .

Also the dependence of  $\alpha$  on the barrier height  $2V_3$  is determined by the factors (14) and (15). Thus, for a direct process (low temperatures),  $\alpha$  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 1.

The temperature dependence of  $\tau_{\text{con}}$  in  $\text{CD}_3$  is found to be quite similar to that of the corresponding stronger hindered  $\text{CH}_3$  system, except for low temperatures  $T \leq \Delta_0$ , 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  $\text{CD}_3$  with the corresponding  $\text{CH}_3$  containing system, we have plotted the ratios  $\alpha := (\tau_{\text{con}}^{-1})_{\text{CD}_3} / (\tau_{\text{con}}^{-1})_{\text{CH}_3}$  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,  $\alpha$  may raise by several orders of magnitude. This gives rise to a peculiar temperature dependence of the ratio  $\alpha$  in case of a linear phonon coupling.

For the Raman process  $\alpha_{\text{Raman}}$  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  $\alpha_{\text{Raman}} \approx 10$  is obtained.

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