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Theory of spinconversion in XH_3 -systems

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In a simple model of (mechanically and magnetically) isolated methyl groups with mutual *intramolecular* dipolar coupling between the nuclear magnetic moments of the three protons the conversion rate (i.e. for the symmetry changing transitions $E^{a,b} \leftrightarrow A$) is investigated. It turns out, that within the model of a fixed rotational axis only half of the E -symmetric rotor states can convert into A -symmetric ground states.

The usual coupling to the phonon bath of thermal lattice excitations is considered in lowest order perturbation theory, and used to describe the temperature dependence of shift and broadening of tunnelling- and librational lines by inelastic neutron scattering (INS). For the two possible types of this phonon coupling, *breathing* and *shaking*, a different temperature dependence of the conversion rate is obtained. The temperature dependence of the INS-spectra and of the conversion rate are predicted to be mutually interdependent.

Only in case of a non zero phonon coupling of breathing type a non vanishing conversion rate at zero temperature is found; this rate is estimated to be proportional to ω_t^3 .

1. Introduction

Since the discovery of the stability of the hydrogen ortho-species [1] over times, which are long compared to typical thermal relaxation processes determined by lattice anharmonicities, the phenomenon of nuclear spin changing transitions in systems with rotational degrees of freedom encouraged an increasing number of experimental [1–20] and theoretical [21–25] investigations. So far, it is generally accepted that this long time stability results from the invariance of all pure spatial operators (i.e. the potential operators depending on interatomic distances) with respect to rotational symmetry operations that correspond to permutations of the (identical)

protons. These even operators do not mediate symmetry changing transitions, in case of H_2 between adjacent rotational states of the dumbbell rotor (of alternating even and odd symmetry). Insofar, the physical situation in the XH_3 or XH_4 systems is analogous to the H_2 case; one important dissimilarity lies in the magnitude of the energy difference between the lowest states of unlike symmetry (tunnelling energy ω_t): in solid hydrogen this energy is about 170 K (even bigger than the Debye frequency), whereas in CH_3 systems, which are the main subject of this paper, the maximum value is 7.13 K, more typically is 10–100 mK (cf. Fig. 1). In the hydrogen case the relevant lattice temperatures are therefore always small compared to the lowest transition energy for a conversion process.

After a short review over some experiments in Sect. 2.1, the characteristics of operators inducing symmetry changing transitions will be discussed in Sect. 2.2. In Sect. 3 the model is formulated and the results for the conversion rate is calculated. As an example the effect of a Debye type density of phonon states will be investigated in Sect. 4.

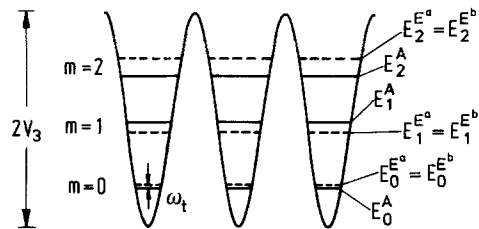


Fig. 1. Energy level scheme of a XH_3 rotor; typical values for ω_t are some μeV whereas the librational energy $E_1^E - E_0^E$ is typically 10 meV. The spatial parts of the wave function are of different symmetry ($\Gamma = A, E^a, E^b$). In order to achieve totally symmetric states with respect to even proton permutations (corresponding to a $2\pi/3$ rotation) a spin space wave function of appropriate symmetry has to be multiplied [25]

2. The state of the art

2.1. Experimental findings

In the following a short survey over experimental methods and important findings will be given:

In specific heat measurements [2–4] one observes the Schottky anomaly at different cooling rates. Inaba et al. even have been able to determine the dependence of the conversion rate $1/\tau_{\text{con}}$ on the temperature. Two important results for NH_4 -ions in a KBr matrix are:

1. for temperatures between 4–10 K the activation energy derived from an Arrhenius plot corresponds quite well to the librational energy, i.e. the difference between the lowest states of same symmetry
2. down to the lowest temperatures investigated (this part was done by INS), a finite conversion rate is found

In classical nuclear magnetic experiments the nuclear susceptibility is measured, which is proportional to $\langle \mathbf{I}^2 \rangle$ (\mathbf{I} denotes the total nuclear spin operator of one rotor) [5–7]. This quantity changes with varying relative populations of the rotational symmetry species (see below). In solid methane phase II the conversion rate was found to be inconsistent with a tunnel activated process.

A new NMR method uses the inversion in the occupation of the tunnelling system which could be realized by suitable coupling to the Zeeman system [9, 10]. This technique does not use the thermal depopulation of the tunnelling levels and is therefore the only method available to determine conversion rates at lattice temperatures well above ω_r . In copper acetate, a roughly librational activated rate was found at temperatures large compared to the tunnelling energy [11], deviations occur at lower temperatures.

The most direct and detailed observation of the relative populations of different tunnelling levels, especially in systems containing inequivalent rotors and/or rotors with more than two symmetry species (as in CH_4), is possible by inelastic neutron scattering (INS). In particular, $(\text{CH}_4)_x\text{Kr}_{1-x}$ -mixtures are investigated intensively at the ILL Grenoble [26, 12] by this technique. It has been demonstrated for the first time that pure *A*-symmetric methane had been created [13].

From the total neutron scattering cross section, using a neutron wavelength longer than the diameter of the rotor [21], it is also possible to determine the spin species population (particularly for not complicated tunnelling level schemes). As in the case of the nuclear susceptibility the total neutron scattering cross section depends on $\langle \mathbf{I}^2 \rangle$:

$$\sigma_{\text{tot}} = N \sigma_H \left\{ 1 + 2 \frac{1 - \cos x}{x^2} \left(\frac{\langle \mathbf{I}^2 \rangle}{\langle \mathbf{I}^2 \rangle_{\infty}} - 1 \right) \right\} \quad (1)$$

where N denotes the number of protons per rotor, σ_H the total incoherent scattering cross section of one proton, $x := 2k_i r$ contains the incident neutron momentum k_i on the scale of the proton-proton distance r . The expectation value $\langle \cdot \rangle$ depends on the relative populations of different symmetry species, the relaxation of this quan-

tity towards the expected value at the lattice temperature T is observed over the time; $\langle \cdot \rangle_{\infty}$ denotes the thermal expectation value at infinite temperature. For protonated methyl groups $\langle \mathbf{I}^2 \rangle$ varies between $\frac{15}{4}$ for pure *A* symmetric states to $\frac{9}{4}$ at equal populations of all symmetry species (high temperature limit). Only for $T \lesssim \omega_r$ and $1/k_i \lesssim r$ there is a measurable effect. Measurements are performed by the condensed matter research division of the PTB Braunschweig. The predicted dependencies of (1) on the incident neutron wave length [14] and on the temperature [15] have been verified. Moreover, experimental evidence was collected for numerous materials containing XH_3 and XH_4 . For those substances, that did convert at a time scale of hours to hundreds of hours, quite varying temperature dependencies of the conversion rates were found [16] (at temperatures around the tunnelling energy). In CH_4 , with 15% Kr, the temperature dependence of the conversion rate does not represent a tunnel activated process [12].

Only neutron scattering allows to determine absolute values for the spin temperature.

2.2. Transition operator

Many particle operators, that can induce transitions between states of different rotor symmetries, necessarily have to involve other degrees of freedom than only the spatial space, as e.g. the nuclear spin space.

Operators, that involve the nuclear spin space are:

- i) interaction of the nuclear magnetic moment with the magnetic field gradient due to a paramagnetic moment (of electronic or nuclear origin) in the neighbourhood
- ii) the electric quadrupolar interaction of the hydrogen nuclei with an electric field gradient caused by the electrons (this is considered to be the dominant conversion mechanism for deuterated rotors [17]). However, because protons have no quadrupole moment, we are left with the first type of operators, where the dipolar interaction can either be inter- or intra-molecular.

Experimentally it is found that the presence of strong paramagnetic centers like O_2 or Mn-ions always leads to rapid conversion [5, 16]. In that case, the phonon coordinates are involved directly via the distance dependence of the dipolar interaction between the paramagnetic moment and the proton magnetic moment. The corresponding theory resembles to the spin conversion theory in H_2 (where neighbouring ortho-molecules are treated as an effective $I = 1$ paramagnetic moment) [22]; the intermolecular dipolar mechanism in CH_4 is examined in [23]. Qualitatively the results of Sect. 3.3 for the temperature dependence of the conversion rate should also be valid for the intermolecular mechanism, in particular for $T \gtrsim \omega_r$.

In the context of the intermolecular magnetic interaction it is important to bear in mind the “symmetry restricted spin diffusion process” [24] (i.e. the exchange of symmetry quantum numbers of rotors via the secular part of the dipolar interaction – without involvement of phonons) that gives rise to an additional process in the conversion dynamics for the case of diluted conver-

sion centers. This process is investigated in [23, 18, 19]. In Ref. 13 the inefficiency of this diffusion for $\Delta I=2$ is clearly shown.

In absence of strong or very near lying paramagnetic centers, the magnetic interaction between the protons within the rotor has to be considered. It was established by Haupt [25] that in XH_3 molecules, the symmetry species A and $E^{a,b}$ are mixed by this dipolar interaction. Here essentially the same Hamiltonian is considered as in [25], however, the phonon contributions will be examined more thoroughly, because they play a central role in understanding the conversion process.

Nijman and Berlinsky [23] have shown that the dipolar interaction itself not necessarily has to involve the phonon coordinates directly (a fixed intramolecular distance between the protons assumed) in order to lead to a finite conversion rate. Nevertheless, the pronounced anharmonicity of the $1/r^3$ potential is now absent and consequently the importance of multiphonon contributions. In [23] the nuclear spin conversion rate for the low temperature phase of methane is calculated by taking into account a ‘‘hybrid mechanism’’ for the magnetic and the phonon part. Three important findings were:

1. the intramolecular dipolar mechanism dominates over the intermolecular one (though not by orders of magnitude; it turned out that the dipolar matrix elements are very similar, the dissimilarity is mainly due to different distances)
2. the phonon density of states plays an important role for the conversion rate and its temperature dependence
3. dilute paramagnetic impurities have only a limited radius of action for spin species conversion; for equilibration over the sample the symmetry restricted spin diffusion must be taken into account

For the temperature dependence of the conversion rate a $\bar{n}(\omega_i) \equiv (\exp(\omega_i/T) - 1)^{-1}$ law is found, using Fermi's Golden Rule for the transitions between the lowest tunnelling states.

As already said in Sect. 2.1, most of the experimental results do not show this ω_i – activated temperature dependence of a resonant one phonon process; in particular at temperatures much larger than ω_i , an activation energy around the librational energy is found.

3. Conversion rate of individual methyl groups

3.1. The model

In this section, the results will be presented for the simplest Hamiltonian H , that allows spin conversion of a rotational tunnelling XH_3 -system.

$$H = H^{\text{rot}} + H^{\text{ph}} + H^{\text{DD}} + H^{\text{I}}$$

$$H^{\text{rot}} := -B \partial_\varphi^2 + V_3 \cos 3\varphi \equiv \sum_{m,\Gamma} E_m^\Gamma |m\Gamma\rangle \langle m\Gamma|$$

$$H^{\text{ph}} := \sum_k \omega_k b_k^+ b_k$$

$$H^{\text{DD}} := \sum_{\substack{m,m',\Gamma,\Gamma' \\ \Gamma \neq \Gamma'}} h_{mm'}^{\Gamma\Gamma'} |m\Gamma\rangle \langle m'\Gamma'| = H_{12}^{\text{dd}} + H_{23}^{\text{dd}} + H_{31}^{\text{dd}}$$

$$\begin{aligned} H^{\text{I}} &:= \sum_k (g_k^s \sin 3\varphi + g_k^c \cos 3\varphi) (b_k + b_k^+) \\ &\equiv \sum_{k,m,m',\Gamma} g_{kmm'}^\Gamma |m\Gamma\rangle \langle m'\Gamma| (b_k + b_k^+) \end{aligned} \quad (2)$$

B is the rotational constant ($\approx 650 \mu\text{eV}$), the $h_{mm'}^{\Gamma\Gamma'}$ are the matrix elements of the sum over three dipolar interactions H_{ij}^{dd} in the eigenbasis of H^{rot} (m denotes the librational quantum numbers) and will be discussed in Sect. 3.2. Note that H^{rot} and H^{DD} act only upon the rotor space and that H^{I} contains only one phonon processes.

$$\begin{aligned} H_{ij}^{\text{dd}} &= \frac{\gamma^2}{r^3} (I_i^z I_j^z (1 - 3 \cos^2 \theta) \\ &\quad - \frac{1}{4} (1 - 3 \cos^2 \theta) (I_i^+ I_j^- + I_i^- I_j^+) \\ &\quad - \frac{3}{2} \sin \theta \cos \theta e^{-i\phi} (I_i^z I_j^+ + I_i^+ I_j^z) - \text{h.c.} \\ &\quad - \frac{3}{4} \sin^2 \theta e^{-2i\phi} I_i^+ I_j^+ - \text{h.c.}) \end{aligned}$$

r being the mutual distance between two protons, γ the nuclear magnetic moment, θ and ϕ the polar angles of the distance vector between the i^{th} and the j^{th} proton and I_i the nuclear spin operator of the i^{th} proton. The Hamiltonian $H^{\text{rot}} + H^{\text{ph}} + H^{\text{I}}$, which has strictly C_3 symmetry and therefore does not mix different symmetry species, is usually considered to describe the temperature dependence of INS spectra [27]. The two parts of the rotor – phonon coupling H^{I} modulate amplitude (g_k^c : *breathing* coupling type) and phase (g_k^s : *shaking* coupling type), respectively of the single rotor potential.

The symmetry changing transition rates due to H^{DD} will not be calculated by using Fermi's Golden Rule for the $|0E\rangle \rightarrow |0A\rangle$ transition, but rather by determining the time evolution in the occupation probabilities of different rotor symmetries. The transition rates $R_{\Gamma \leftarrow \Gamma'}$ between different symmetry species are calculated as time derivatives of the expectation values of the projectors $P_\Gamma(t)$ into the Γ -symmetric Hilbert space for a Γ' -symmetric thermal equilibrium state $\rho_{\Gamma'} := P_{\Gamma'} e^{-\beta H} P_{\Gamma'} / \text{Tr}\{P_{\Gamma'} e^{-\beta H} P_{\Gamma'}\}$ (where β is the inverse *lattice* temperature) and for times long compared to all other time evolutions, including the inverse tunnelling frequency.

$$\begin{aligned} R_{\Gamma \leftarrow \Gamma'} &= \frac{d}{dt} \langle P_\Gamma(t) \rangle_{\Gamma'} \\ &\equiv \frac{d}{dt} \text{Tr}\{\rho_{\Gamma'} e^{iHt} (\sum_m |m\Gamma\rangle \langle m\Gamma|) e^{-iHt}\}. \end{aligned} \quad (3)$$

So $R_{\Gamma \leftarrow \Gamma'}$ describes the change of probability for the system to be Γ symmetric presupposing a Γ' symmetric thermal equilibrium state. This is done in second order time dependent perturbation theory with respect to H^{I} . It is important to consider the transition rate from the *whole* Γ' -symmetric Hilbert space into the *whole* Γ -symmetric Hilbert space, because on the time scale of the very slow symmetry changing transitions due to H^{DD} ,

all the symmetry conserving transitions between the librational levels through absorption or emission of a resonant phonon are fast, eventually even for temperatures around the tunnelling energy. Otherwise one easily overlooks important symmetry changing transitions across the librational energy. Second order perturbation theory is used despite the fact that in typical physical situations, H^I is not small [28].

3.2. Matrix elements of H^{DD}

The traceless matrix of the intramolecular dipolar interaction H^{DD} in the basis of the eigenstates of H^{rot} has the following structure:

$$\begin{pmatrix} A_{3/2} & A_{1/2} & A_{-1/2} & A_{-3/2} & E_{1/2}^a & E_{-1/2}^a & E_{1/2}^b & E_{-1/2}^b \\ \frac{3}{4}a & 0 & 0 & 0 & 0 & 0 & 0 & h_{m'm}^{AE} \\ 0 & \frac{7}{4}a & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \frac{7}{4}a & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & \frac{3}{4}a & h_{m'm}^{AE} & 0 & 0 \\ 0 & 0 & 0 & h_{m'm}^{EA} & -\frac{5}{4}a & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -\frac{5}{4}a & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -\frac{5}{4}a & 0 \\ h_{m'm}^{EA} & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{5}{4}a \end{pmatrix} \begin{matrix} A_{3/2} \\ A_{1/2} \\ A_{-1/2} \\ A_{-3/2} \\ E_{1/2}^a \\ E_{-1/2}^a \\ E_{1/2}^b \\ E_{-1/2}^b \end{matrix} \quad (4)$$

where

$$a := \frac{\gamma^2}{r^3} \delta_{m,m'}, \quad h_{m'm}^{\Gamma\Gamma'} := -\frac{\gamma^2}{r^3} \sqrt{\frac{3}{4}} \langle m' \Gamma' | e^{-2i\varphi} + e^{2i\varphi} | m \Gamma \rangle$$

and $\frac{\gamma^2}{r^3} = 1.6 \cdot 10^6 \text{ s}^{-1}$, which is much smaller than typical tunnelling rates $\sim 10^9 \text{ s}^{-1}$. The matrix elements $h_{m'm}^{\Gamma\Gamma'}$ have the properties

- i) $|h_{m'm}^{\Gamma\Gamma'}| = |h_{m'm}^{\Gamma'\Gamma}|$
- ii) $h_{m'm}^{\Gamma\Gamma'} \frac{\gamma^2}{r^3} \in \mathbb{R}$, $h_{m'm}^{E^a A} = h_{m'm}^{E^b A}$
- iii) $H_{m'm}^{\Gamma\Gamma} = 0$, $h_{m'm}^{E^a E^b} = 0$
- iv) $h_{m'm}^{\Gamma\Gamma'} \xrightarrow{V_3/B \rightarrow \infty} \delta_{m,m'}$ apart from a positive constant.

The structure of the H^{DD} matrix (4) follows immediately from

$$H^{\text{DD}} = \frac{\gamma^2}{r^3} [(I_1^z I_2^z + I_1^+ (I_2^- + I_3^-)) + \text{cycl.}] - \frac{3}{4} \varepsilon^{-2i\varphi} (I_1^+ I_2^+ + \varepsilon I_2^+ I_3^+ + \varepsilon^* I_3^+ I_1^+) - \text{h.c.}]$$

where $\varepsilon := e^{i2\pi/3}$ and the direction of the magnetic quantization axis is chosen to be the rotational axis. Then the terms $\sim e^{i\phi}$ of H_{ij}^{dd} do not contribute. It is important to note that possible inclinations of the rotational axis against the z -axis due to certain phonon modes are now neglected. (4) is in accordance with [25], its structure remains the same when using correctly antisymmetrized states according to [29, 30] for the rotor (regarding also odd permutations of the protons).

As a consequence of (4) there is no mixing of z -components of the total spin without symmetry changing, there are no $E^a \leftrightarrow E^b$ symmetry – changing transitions and there is no way for $E_{-1/2}^a$ and $E_{1/2}^b$ states to convert into A -symmetric states. However, choosing a new coordinate system modifies the matrix (4), e.g. $z \rightarrow -z$, leads to an interchange of E^a and E^b ; important is, that only half of the E -symmetric states could decay into ground states via H^{DD} . Furthermore, there is no mutual mixing of the two pairs $(E_{1/2}^a, A_{-3/2})$ and $(E_{-1/2}^b, A_{3/2})$. Therefore, the conversion time will be determined directly by the transition rates $R_{\Gamma \leftarrow \Gamma'}$, it is not necessary to solve a more complicated rate equation.

3.3. Calculation of the transition rate

In the following, the pair of symmetry labels (Γ, Γ') stands for $(E_{1/2}^a, A_{-3/2})$ or $(E_{-1/2}^b, A_{3/2})$ with nonvanishing mutual transition rates; the z -component will be omitted for notational clearness. It is convenient to use

$$H_0 = \sum_{m,\Gamma} E_m^\Gamma |\psi_m^\Gamma\rangle \langle \psi_m^\Gamma| + \sum_k \omega_k b_k^+ b_k \quad (5)$$

with

$$|\psi_m^\Gamma\rangle := |m \Gamma\rangle + \sum_{\substack{\Gamma' \neq \Gamma \\ m'}} \frac{h_{m'm}^{\Gamma\Gamma'}}{E_m^\Gamma - E_{m'}^{\Gamma'}} |m' \Gamma'\rangle \quad (5a)$$

as unperturbed Hamiltonian. The $|\psi_m^\Gamma\rangle$ form a complete orthonormalbasis of the rotor – space in first order of $h_{m'm}^{\Gamma\Gamma'}$, though they transform no longer Γ -symmetric with respect to the symmetry group C_3 . The modifications of the eigenvalues of the rotational part due to H^{DD} (proportional to a in (4)) are neglected because the matrix elements $h_{m'm}^{\Gamma\Gamma'}$ are very small compared to all energy differences of H^{rot} . Furthermore the $m' \neq m$ summands in (5a) may be neglected, as the low lying tunnelling energies $E_m^E - E_m^A$ are much smaller than the librational energies $E_m^E - E_{m'}^{\Gamma'}$ if $V_3 \gg B$. Then (5a) reads

$$|\psi_m^\Gamma\rangle := |m \Gamma\rangle + \eta_m |m \Gamma'\rangle, \quad \eta_m := \frac{h_{m'm}^{\Gamma\Gamma'}}{E_m^\Gamma - E_{m'}^{\Gamma'}} \quad (6)$$

Note, that Γ and Γ' belong to different A and $E^{a,b}$ symmetry species (cf. Sect. 3.2) and that $\eta_m \ll 1$. In the basis (6) the perturbation H^I becomes:

$$H^I = \sum_{k,m,m',\Gamma} g_{kmm'}^I [|\psi_m^\Gamma\rangle \langle \psi_{m'}^{\Gamma'}| - \eta_m |\psi_m^\Gamma\rangle \langle \psi_{m'}^{\Gamma'}| - \eta_{m'} |\psi_m^\Gamma\rangle \langle \psi_{m'}^{\Gamma'}| + \eta_m \eta_{m'} |\psi_m^{\Gamma'}\rangle \langle \psi_{m'}^{\Gamma'}|] (b_k + b_k^+)$$

Γ' here is determined by Γ ; H^I contains now the symmetry mixing matrix elements η_m .

The time evolution operator, written in second order with respect to H^I :

$$e^{-iHt} = e^{-iH_0 t} \left[\mathbf{1} - i \int_0^t dt' e^{iH_0 t'} H^I e^{-iH_0 t'} \right]$$

$$-\int_0^t dt' \int_0^{t'} dt'' e^{iH_0 t'} H^I e^{-iH_0(t'-t'')} H^I e^{-iH_0 t''} + O((H^I)^3) \Big] \quad (7)$$

is used to calculate $\langle |\psi_m^{\Gamma'}\rangle \langle \psi_m^{\Gamma'}(t) \rangle_{\Gamma'}$, according to (3). It turns out, that in the thermal equilibrium state $\rho_{\Gamma'}$ of (3) up to second order in H^I , $e^{-\beta H}$ could be replaced by $e^{-\beta H_0}$ and that for transitions with $\Gamma' \neq \Gamma$ only the square of the term $\sim i$ in (7) contributes. For $\langle |\psi_m^{\Gamma'}\rangle \langle \psi_m^{\Gamma'}(t) \rangle_{\Gamma'}$, the results is:

$$\frac{1}{Z^{\Gamma'}} \sum_{k,m'} e^{-\beta E_{m'}^{\Gamma'}} (g_{km'm}^{\Gamma'} \eta_{m'} - g_{kmm'}^{\Gamma'} \eta_m) (-g_{kmm'}^{\Gamma'} \eta_m + g_{km'm}^{\Gamma'} \eta_{m'}) \cdot \int_0^t dt' \int_0^{t'} dt'' e^{i(E_{m'}^{\Gamma'} - E_m^{\Gamma})(t'-t'')} [\bar{n}_k e^{i\omega_k(t'-t'')} + (\bar{n}_k + 1) e^{-i\omega_k(t'-t'')}]$$

with $Z^{\Gamma'} := \sum_m e^{-\beta E_m^{\Gamma'}}$, $\bar{n}_k := (e^{\beta \omega_k} - 1)^{-1}$; note that $g_{kmm'}^{\Gamma'}$ $= (g_{km'm}^{\Gamma'})^*$.
Using

$$\int_0^t dt' \int_0^{t'} dt'' e^{i\lambda(t'-t'')} = 2 \frac{1 - \cos \lambda t}{\lambda^2} \xrightarrow{\lambda t \rightarrow \infty} 2\pi t \delta(\lambda)$$

the rates (3) finally become:

$$R_{\Gamma \leftarrow \Gamma'} = \frac{2\pi}{Z^{\Gamma'}} \sum_{k,m,m'} e^{-\beta E_{m'}^{\Gamma'}} |g_{kmm'}^{\Gamma'} \eta_{m'} - g_{km'm}^{\Gamma'} \eta_m|^2 \cdot [\bar{n}_k \delta(E_{m'}^{\Gamma'} - E_m^{\Gamma} + \omega_k) + (\bar{n}_k + 1) \delta(E_{m'}^{\Gamma'} - E_m^{\Gamma} - \omega_k)]. \quad (8)$$

These rates depend on the coupled phonon density of states at all possible inelastic transition energies of the unperturbed rotor Hamiltonian H^{rot} ; they obey the requirement to establish global thermal equilibrium in the long time limit (detailed balance):

$$\frac{R_{E \leftarrow A}}{R_{A \leftarrow E}} = \frac{Z^E}{Z^A}.$$

This is used to test numerical calculations. The conversion rate is given by $1/\tau_{\text{con}} = R_{A \leftarrow E} + R_{E \leftarrow A}$.

3.4. Discussion of the transition rates (8)

The properties of the $|\dots|^2$ for $V_3 \gg B$ (numerical values will be given in Sect. 4 for the special case of Debye phonons) lead to the following temperature dependence of $R_{\Gamma \leftarrow \Gamma'}$:

1. $T=0 \Rightarrow$
 - i) R is only non vanishing for finite phonon coupling of breathing type at $\omega_k = \omega_t$
 - ii) This conversion rate is proportional to ω_t^3 (cf. Sect. 4)
2. $T \ll \omega_t \Rightarrow$

$$\begin{cases} 1 + 2\bar{n}(\omega_t) & \text{behaviour for breathing type} \\ \bar{n}(E_1 - E_0) & \text{behaviour for shaking type} \end{cases}$$

3. $T \gtrsim \omega_t \Rightarrow$ sharp increase of the activation energy for breathing type

For the breathing type the crossover temperature from a tunnelling to a librationaly activated behaviour occurs somewhere above $T \gtrsim \omega_t$, depending on the coupled density of phonon states determined by the g_k^E at the libration energy and on the relative magnitudes of tunnelling and librational frequencies determined by V_3/B . Additional shaking type contributions may increase the librational activation. It is worth noting that the perturbational approach breaks down for high temperatures $T \gg E_1 - E_0$, as the matrixelements of H^I are increasing with increasing \bar{n}_k .

These properties are in agreement with a variety of experimental observations:

- CuAc shows a librationaly activated conversion rate in the temperature regime $15 \text{ K} \leq T \leq 30 \text{ K}$ ($\omega_t \approx 3 \text{ mK}$, $\omega_{\text{lib}} \approx 206 \text{ K}$) [11]
- 4-Methyl Pyridine has a finite conversion rate at temperatures $\sim 2 \text{ K}$ ($\omega_t \approx 6 \text{ K}$) [3, 16], no pronounced shift of the tunnelling line is reported [31] and one may find arguments for a finite phonon coupling of breathing type [32]
- NH₄Ac and NaAc do not convert at low temperatures and they both show a pronounced shift towards smaller energy transfers [33], which is an indication for a dominant shaking type of phonon coupling [34, 28]

Furthermore XH₄ systems follow qualitatively these trends:

- the conversion rate of the orientationally ordered rotors in solid CH₄ phase II shows an increasing activation energy towards higher temperatures [8], in contradiction to the behaviour expected from a tunnel resonant one phonon process [23]
- NH₄ClO₄ [16] and NH₄ in KBr [4] show a prominent change of the activation energy for temperatures greater than ω_t (in the second case, however, the tunnelling frequency is not small, but nevertheless the level distances between rotor states of the same symmetry are larger than ω_t).

In CH₃I, which is known to have a dominant phonon coupling of breathing type at low frequencies [34], a finite conversion rate at $T=0$ would be predicted.

The observation that CH₄, containing a few percent Kr substitutes, converts much more rapidly than pure methane [20, 35, 12] might be understood qualitatively: due to the ω_t^3 law for the low temperature conversion rate (this law I would expect to be true also in XH₄ systems, as it results from the low frequency density of phonon states and the rotation-phonon coupling potential $\sim |k|$) those rotors with many Kr neighbours and consequently high tunnelling frequencies could be regarded as conversion centers; equilibrium of the symmetry species concentration is established by symmetry restricted spin diffusion. Despite slightly different tunnelling frequencies at different sites, this diffusion could take place without phonons owing to broadened tunnelling states by the orientational coupling in this system.

4. Debye phonons

In order to give an illustrative example, I use a Debye density of phonon states and coupling constants $g_{kmm'}^r \propto \sqrt{\omega_k}$. This corresponds to the assumption, that the variance of the difference between the displacements of rotor and some neighbouring atom is proportional to the modulus of the wave vector and that the dispersion is linear. It is a reasonable assumption for low frequency acoustic phonons, however, in the vicinity of the libration this choice of phonon spectrum and coupling strength is certainly quite unrealistic due to large contributions of libronic states.

If the two extremes of a pure breathing and a pure shaking type of phonon coupling are investigated, the coupled density of states then may be written:

$$\sum_k |g_{kmm'}^r|^2 \delta(\omega - \omega_k) = 3g^2 \frac{\omega^3}{\omega_D^3} V_3 |M_{mm'}^r|^2 \Theta(\omega) \Theta(\omega_D - \omega)$$

with

$$\Theta(\omega) := \begin{cases} 0 & \text{if } \omega < 0 \\ 1 & \text{if } \omega > 0 \end{cases}$$

which is proportional to ω^3 . With $M_{mm'}^r := \langle m\Gamma | \begin{cases} \cos 3\varphi \\ \sin 3\varphi \end{cases} | m'\Gamma \rangle$ for $\begin{cases} \text{breathing} \\ \text{shaking} \end{cases}$ type and $g := g_k^{r,s} / \sqrt{V_3 \omega_k}$ a dimensionless prefactor controlling the overall strength of the phonon coupling, the rate will be simply proportional to g^2 . The rates $R_{\Gamma \leftarrow \Gamma'}$ become:

$$R_{\Gamma \leftarrow \Gamma'} = \frac{6\pi g^2}{\omega_D^3} V_3 \sum_{m,m'} A_{mm'} |\omega_{m'm}|^3 [\bar{n}(|\omega_{m'm}|) + \Theta(\omega_{m'm})] \frac{e^{-\beta E_{m'}}}{Z^{\Gamma'}} \Theta(\omega_D - |\omega_{m'm}|) \quad (9)$$

with

$$\omega_{m'm} := E_{m'}^{\Gamma'} - E_m^{\Gamma}, \quad \bar{n}(x) := (e^{\beta x} - 1)^{-1}, \\ A_{mm'} := |M_{mm'}^{\Gamma} \eta_{m'} - M_{mm'}^{\Gamma'} \eta_m|^2. \text{ Examples for the matrices } A_{mm'}$$

Table 1. Matrix elements $A_{mm'}/(r^3)^2$ (in units of B^{-2}) as defined in the text for pure breathing (Table 1a) or pure shaking type (Table 1b) of phonon coupling respectively and for $V_3 = 20B$. A_{00} is only nonvanishing in case of the breathing type. The magnitude of the elements decreases rapidly as $m, m' > 5$; the # entries denote very small elements

$m \setminus m'$	0	1	2	3	4	5
a) 0	0.037822	0.715976	153.0085	25.31636	5.046925	1.133939
1	0.000762	0.012606	0.079831	0.384394	0.054455	0.016518
2	165.3536	0.000040	0.000026	0.000061	0.000342	0.000018
3	0.000003	0.406948	0.000012	0.000007	0.000003	0.000068
4	30.250711	0.000001	0.000424	0.000001	#	#
5	#	0.007492	#	0.000073	#	#
b) 0	0	635.3859	17.40019	48.08953	4.932299	1.137103
1	673.6756	0	0.615832	0.197239	0.054403	0.016430
2	0.000009	0.514170	0	0.000291	0.000217	0.000016
3	35.45186	0.000020	0.000472	0	0.000002	0.000049
4	#	0.350531	0.000008	#	0	0.000002
5	0.410041	#	0.000008	0.000001	0.000010	0

Note, that for breathing type coupling $M_{00}^E - M_{00}^A \sim \omega_i$ for large V_3 (this was already used to show the ω_i^3 -dependence of the low temperature conversion rate in Sect. 3.4) and that there is a nonvanishing ω_{10} -activated contribution, because $M_{01}^E \neq 0$.

For two choices of the Debye energy the conversion rates are plotted in Figs. 2 and 3. The following qualitative trends are found:

- The high temperature behaviour is dominated by the shaking contribution with its librational activation.
- At low temperatures the breathing contribution dominates by many orders of magnitude; the temperature

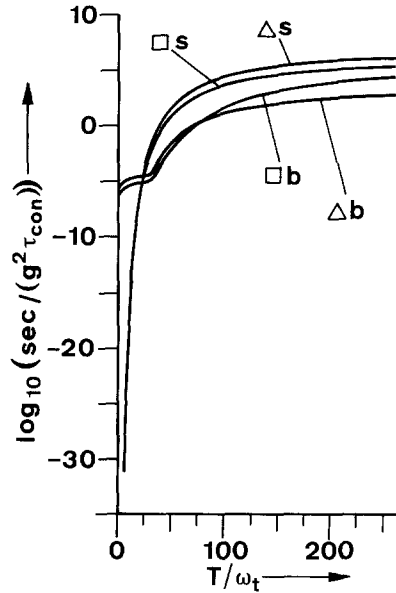


Fig. 2. Conversion rate $\frac{1}{\tau_{\text{con}} g^2}$ (in units of s^{-1}) versus T/ω_t for a Debye model. Two cases for the Debye frequency ω_D are shown: Δ denotes the case where $\omega_D = 18B$, which is between ω_{10} and ω_{20} , the \square -lines refer to $\omega_D = 30B$, which is larger than ω_{20} ; b means “breathing” and s “shaking” coupling type. In the low temperature regime pure shaking type leads to conversion rates, which are smaller than for breathing type by many orders of magnitude

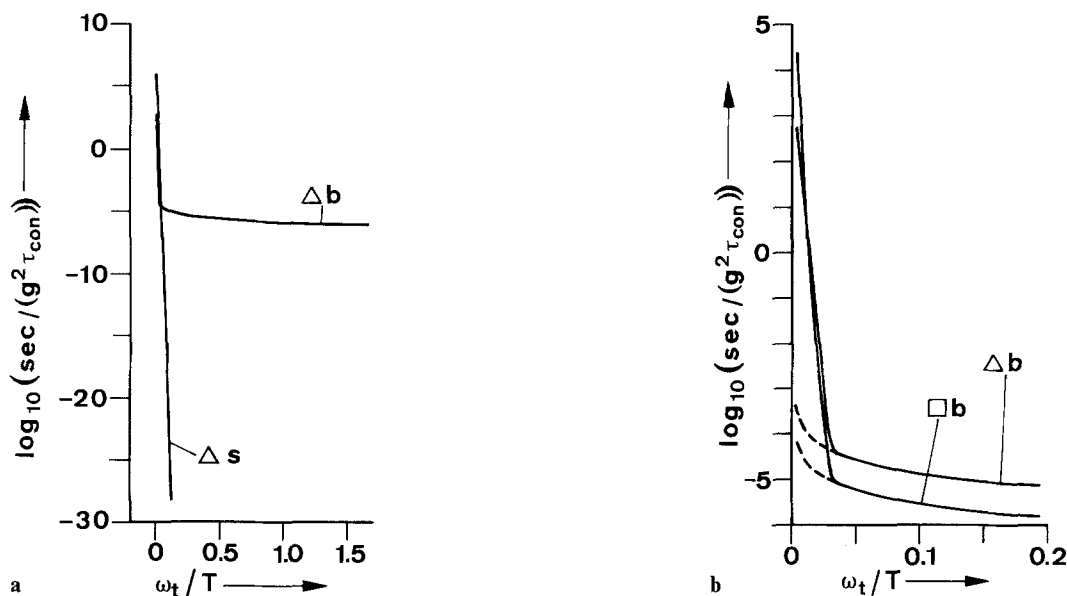


Fig. 3. Same as Fig. 2 but now in Arrhenius representation: ω_t/T as abscissa. The temperature range, where the activation energy changes in case of breathing coupling type, depends on V_3 (and on the relative weight of low and high frequency phonons, which is fixed in a debye model). In Fig. 3a breathing and shaking type

of coupling are compared for $\omega_D = 18B$, in Fig. 3b a section is shown for the breathing type and $\omega_D = 18B$ and $\omega_D = 30B$. The dashed lines correspond to a pure resonant one phonon process $\sim 1 + 2\bar{n}(\omega_t)$

dependence gives a $1 + 2\bar{n}(\omega_t)$ - behaviour; in this limit the result [23] is recovered.

- The increase in activation energy for breathing type coupling occurs here at $T \approx 20\omega_t$, which is higher than in the existing experimental observations [8, 16, 4]. This is taken as a strong hint for the relative importance of librational and/or shaking phonons.

- The influence of the second librational level is weak, even for a pure breathing type coupling.

For the considered tunnelling energy of 0.19 K (corresponding to $V_3 = 20B$) the resulting absolute values of the low temperature conversion time is about $20 \frac{\text{days}}{g^2}$ for pure coupling of breathing type. It is important to remark that the smallness of the conversion rate at low temperatures is not only determined by the smallness of the dipolar interaction $\frac{\gamma^2}{r^3}/B$ but even more crucially by the smallness of ω_t^3/ω_D^3 .

5. Conclusion

The considered model (2) of mechanically and magnetically isolated XH_3 -groups with fixed direction of the rotational axis allows no complete conversion into the A -symmetric ground state. This is a consequence of the restricted spatial degrees of freedom considered for the protons and has no analogy in XH_4 rotors. Complete conversion of methyl rotors (without paramagnetic centers) either requires the magnetic coupling between different rotors or coupling to phonons, that incline the rotor. In order to determine the significance of the sec-

ond mechanism, more detailed information on the rotor phonon coupling would be valuable.

The symmetry changing transition rates including all librational initial and final states has been calculated in presence of a weakly coupled phonon bath in order to resolve its temperature dependence. The often observed increase of the activation energy for $T \gtrsim \omega_t$ and the librally activated behaviour at temperatures not very small compared to the librational energy becomes understandable. So to speak, it is favourable for the system to do the conversion process across the librational transition (gaining the much larger density of coupled phonon states) provided the Boltzmann factor is not too small; in particular for a phonon coupling of shaking type, this is the only way for the rotor to come into global thermal equilibrium. The absolute values for the low temperature conversion rates due to the phonon coupling of breathing type, which result from model (2) are about $20 \frac{\text{days}}{g^2}$, depending on the low frequency acoustic phonon density and coupling strength.

The temperature dependencies of the conversion rate and of the shift of the tunnelling line are predicted to be mutually related, because they both depend on the coupled phonons. However, one has to bear in mind that the shift (even in lowest order perturbation theory [27]) is given by an integral over the coupled density of phonon states whereas the conversion rate depends only on its value at certain frequencies, which may be quite far separated from each other e.g. for high V_3 . But assuming a not too wild behaviour of both functions g_k^s and g_k^c (cf. (2)), I would formulate the rough statement: rotational tunnelling substances showing a pronounced shift of the tunnelling line towards smaller energy

transfers with increasing temperature are expected to convert very slowly at low temperatures and librational-ly activated at elevated temperatures whereas substances showing weak or even positive shifts should convert at lowest temperatures. Also the available experimental evidence seems to support this interrelation.

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Note added in proof

In the meantime a new optical method came to the knowledge of the author, developed at the University of Grenoble by C. Borczykowski, A. Oppenländer, H.P. Trommsdorff and J. Vial, which allows the determination of conversion times. For certain systems, where this method is applicable, the high temperature behaviour can be investigated, even in systems with large tunnelling frequencies.

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