

Symmetry species exchange in rotational tunnelling systems

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Abstract

The rate for the exchange of symmetry species due to nuclear dipolar interaction between the protons of two rotational tunnelling systems is calculated taking the example of methyl groups. Its temperature dependence is related to the broadenings of the tunnelling lines and is caused by the same phonons that determine the temperature dependence of the rotational tunnelling. Equivalent rotors show rapid exchange at lowest temperatures which decreases with increasing temperature while a non-monotonic temperature dependence is predicted for inequivalent rotors.

1. Introduction

The extremely slow thermal equilibrations, characteristic for rotational tunnelling systems, have attracted interest already since the discovery of the long time stability of ortho-hydrogen. The corresponding transitions are often accompanied by simultaneous changes in the total nuclear spins [1–3] (‘spin conversion’) – however the more decisive quantity is the *symmetry state* of the rotor which changes during the transition as can be seen for deuterated rotors [4]. In the present contribution we concentrate on systems with small tunnelling splittings, like CH₄ [5], or CH₃ [6, 7], embodied in molecular crystals. In all theoretical approaches to describe the symmetry species conversion the dipolar interaction between the protons or the quadrupolar interaction of the deuterons with local electric field gradients [8, 9] mixes the states of different symmetries. Energy conservation for the relaxation is provided by coupling of the rotor

to phonons. Two reasons, the smallness of the magnetic energies and the lack of low frequency phonons, explain the observed conversion times exceeding the inverse of phonon or tunnelling frequencies often by more than 12 orders of magnitudes. Any mechanism speeding up the relaxation times will be very effective. In the presence of dilute but strong paramagnetic centres in the crystal [5, 7] the diffusion of symmetry species through the bulk of the sample via the dipolar interaction of the protons of neighbouring rotors can provide such a mechanism as we will show.

A quantitative theory of the “elementary” symmetry exchange process and its temperature dependence will be given for the frequent cases where rate equations are applicable and the number of rotors is large so that the overall dynamics is diffusive. Here we consider the example of methyl groups which are characterized by three possible symmetry states A, E^a and E^b. The most interesting type of transition is the exchange (A₁ E₂) → (E₁ A₂) of symmetry states between two adjacent rotors “1” and “2”. This process is similar to the flip-flop transition between dipolarly coupled spins.

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2. The transition rate

To describe the symmetry exchange rate between two methyl groups 1 and 2 two basic contributions to the Hamiltonian

$$H = H_{\text{RP}} + V \quad (1)$$

will be considered. The first part

$$H_{\text{RP}} = H_{\text{R}}^{(1)} + H_{\text{R}}^{(2)} + H_{\text{P}} + H_{\text{I}}^{(1)} + H_{\text{I}}^{(2)} \quad (2)$$

includes the large non-magnetic and therefore symmetry conserving parts usually taken to describe the temperature dependence of rotational tunnelling [10–14]. $H_{\text{R}}^{(\alpha)} = -B\hat{\partial}_{\varphi_x}^2 + V_3^{(\alpha)} \cos(3\varphi_x)$ denotes the rotational Hamiltonians of the isolated rotors ($\alpha = 1, 2$) that are coupled via $H_{\text{I}}^{(\alpha)}$ to the lattice vibrations represented by H_{P} . Explicit expressions for these operators can be found e.g. in Ref. [11].

The most important contribution to the magnetic interaction between the protons of one rotor with the protons of the other rotor is the part of the dipolar interaction being E-symmetric in either of the rotors [15], which we denote by V . They determine the transitions $(A_1E_2) \leftrightarrow (E_1A_2)$ that do not change the total amounts of symmetry species. Other terms either leave both rotor symmetries unchanged and renormalize slightly the energies of H_{RP} or contribute only to the conversion process. Implicitly we will also assume the presence of an energy reservoir consisting of all the nuclear spins of the sample to which the methyl rotors are dipolarly coupled. In the simplest approximation this reservoir can be characterized by the spin-spin relaxation rate T_2^{-1} .

The explicit expression for V in terms of the relative positions of the rotors and the two rotational angles can only be given as a series expansion [5, 16] in powers of $(r/R_{(1,2)}^{(0)})$, where r is the methyl radius and $R_{(1,2)}^{(0)}$ is the equilibrium distance of the two CH_3 groups, see Refs. [5, 8, 15].

Suitable choice of the projector (for the technical details we refer to the forthcoming publication [15]) generates equations of motion for $\mathbf{C}_{\Gamma_1\Gamma_2}(t) := \text{Tr}\{\rho(0)\mathbf{P}_{\Gamma_1\Gamma_2}(t)\}$ within the Mori projector formalism [17, 18]. Here $\rho(0)$ is the initial *non-equilibrium* density operator of the whole system, including the environment, and $\mathbf{P}_{\Gamma_1\Gamma_2}$ projects on the subspace of rotor-plus-environment wave functions where the first

and the second rotor are in the symmetry states Γ_1 and Γ_2 , respectively. The time evolution of $\mathbf{P}_{\Gamma_1\Gamma_2}(t)$ is determined through Eq. (1) in the Heisenberg picture. One of the Γ_1 and Γ_2 should equal A while the other should be either E^a or E^b . For small V the equations become generalized Master equations, linear in $\mathbf{C}_{\Gamma_1\Gamma_2}$. The Markov approximation can be applied if the times of interest are large compared to the decay time of the relaxation kernels, the latter being determined by the dissipative influence of the phonons. Correct up to second order in V we obtain

$$\begin{aligned} \partial_t \mathbf{C}_{(\Gamma_1\Gamma_2)}(t) = & \sum_{(\Gamma'_1\Gamma'_2) \neq (\Gamma_1\Gamma_2)} \left(R_{(\Gamma_1\Gamma_2) \leftarrow (\Gamma'_1\Gamma'_2)} \mathbf{C}_{(\Gamma'_1\Gamma'_2)}(t) \right. \\ & \left. - R_{(\Gamma'_1\Gamma'_2) \leftarrow (\Gamma_1\Gamma_2)} \mathbf{C}_{(\Gamma_1\Gamma_2)}(t) \right) \end{aligned} \quad (3)$$

with the transition rates

$$\begin{aligned} R_{(\Gamma_1\Gamma_2) \leftarrow (\Gamma'_1\Gamma'_2)} := & \lim_{\varepsilon \rightarrow 0} \int_0^\infty d\tau e^{-\varepsilon\tau} \left\langle \mathbf{P}_{(\Gamma'_1\Gamma'_2)} \right. \\ & \left. [V, [V(\tau)\mathbf{P}_{(\Gamma_1\Gamma_2)}]] \right\rangle \end{aligned} \quad (4)$$

given as a zero-frequency limit; time dependent operators refer to the Heisenberg picture.

The rate equations (3) are four coupled differential equations for the composite symmetry species concentrations $\mathbf{C}_{A_1E_2^{ab}}$ and $\mathbf{C}_{E_1^{ab}A_2}$. Transforming to sums and differences of E -states, $\mathbf{C}_{A_1E_2} := (\mathbf{C}_{A_1E_2^a} + \mathbf{C}_{A_1E_2^b})/2$ and $\mathbf{C}_{A_1\delta E_2} := (\mathbf{C}_{A_1E_2^a} - \mathbf{C}_{A_1E_2^b})$ and similarly for rotor (2) being A-symmetric, decouples the sets $(\mathbf{C}_{A_1E_2}, \mathbf{C}_{E_1A_2})$ and $(\mathbf{C}_{A_1\delta E_2}, \mathbf{C}_{\delta E_1A_2})$, the latter being irrelevant for us in the following. Finally, transforming the former set to $\mathbf{C}_{\text{total}} := (\mathbf{C}_{A_1E_2} + \mathbf{C}_{E_1A_2})$ and $\mathbf{C}_{\text{ex}} := \mathbf{C}_{A_1E_2} - \mathcal{Z}\mathbf{C}_{E_1A_2}$ with $\mathcal{Z} = \mathcal{Z}_{A_1E_2}/\mathcal{Z}_{E_1A_2}$, $\mathcal{Z}_{\Gamma_1\Gamma_2} = \text{Tr}\{\mathbf{P}_{\Gamma_1\Gamma_2}e^{-\beta H_{\text{RP}}}\}$ yields $\partial_t \mathbf{C}_{\text{total}}(t) = 0$ due to the required conservation of the total concentration of different symmetries and $\partial_t \mathbf{C}_{\text{ex}}(t) = -R_{\text{ex}} \mathbf{C}_{\text{ex}}(t)$ for the “exchange” concentration with

$$R_{\text{ex}} := (1 + \mathcal{Z}) \left\{ R_{(E_1^a A_2) \leftarrow (A_1 E_2^a)} + R_{(E_1^b A_2) \leftarrow (A_1 E_2^b)} \right\}. \quad (5)$$

The rates obey the detailed balance condition $R_{(A_1E_2) \leftarrow (E_1A_2)}/R_{(E_1A_2) \leftarrow (A_1E_2)} = \mathcal{Z}$. Similar to the

theory of conversion [5, 9] we assume that the modulation of the distance between the rotors in V by phonons is less effective than the coupling described by H_1 (consequences of the former at lowest temperatures will be discussed in Ref. [15]). This makes the thermal lifetime broadening of the magnetic states, described by Eq. (4), very similar to the broadenings of the tunnelling lines as they are directly observed in inelastic neutron scattering (INS) [11]. The results given in the next section are obtained by again applying projector techniques and considering the perturbation H_1 in second order. Furthermore, librational excitations due to V are neglected which is valid if the single particle potentials are not too low $V_3^{(x)} \gtrsim 8B$.

3. Discussion

The exchange rates R_{ex} for equal or different methyl groups $V_3^{(1)} = V_3^{(2)}$ or $V_3^{(1)} \neq V_3^{(2)}$ differ considerably in their temperature dependence. In the first case the transitions do not require an energy change while in the second case an energy reservoir must account for the difference $\Delta^{(1,2)} := \Delta^{(1)} - \Delta^{(2)}$ in tunnelling the energies. The nuclear spin system and the phonons cause level broadenings $w^{(1,2)} = w_s + w_1(T) + w_2(T)$, $V = w_s + w(T)$, where $w_x(T)$ is the broadening of the inelastic tunnelling line of one rotor and $w_s \sim 10^{-11}$ eV is typical for the dipolar reservoir. The (constant) dipolar energy of the rotors, $E_D = \frac{3}{2} \frac{\gamma_p^2}{r^3}$, $\simeq 6 \times 10^{-10}$ eV $\simeq 10^6$ s $^{-1}$, provides (the inverse of) the time scale on which the spin correlation function decays in the case of equal rotors.

Let us consider first the case $V_3^{(1)} = V_3^{(2)}$. At very low temperatures $w = 0$ and the exchange rate saturates at

$$R_{\text{ex}} \simeq 147 \left(\frac{\gamma_p^2}{r^3} \right)^2 \left(\frac{r}{R_{(1,2)}^{(0)}} \right)^{10} |A_0|^4 \frac{2w_s^2 + E_D^2}{w_s^2 + E_D^2} / V w_s$$

$$\simeq 2.3 \times 10^9 \left(\frac{r}{R_{(1,2)}^{(0)}} \right)^{10} |A_0|^4 \text{s}^{-1} \quad (6)$$

The last estimate holds for $w_s \simeq E_D$ and γ_p denotes the proton gyromagnetic ratio. $A_0(\alpha)$ is the matrix

¹ In the present work we ignore the possible influence of an orientational coupling between the methyl groups [19].

element of the operator $e^{i\phi_z}$ between lowest rotor states of different symmetries which depends only weakly on $V_3^{(x)} > 8B$.

At higher temperatures, where $w(T)$ is much larger than both, w_s and E_D , the exchange rate can be approximated by

$$R_{\text{ex}} \simeq 147 \left(\frac{\gamma_p^2}{r^3} \right)^2 \left(\frac{r}{R_{(1,2)}^{(0)}} \right)^{10} |A_0|^4 / w(T) \quad (7)$$

The Arrhenius-like increase of $w(T)$ with an activation energy given as the first librational excitation, leads to the corresponding decrease of R_{ex} . The cross-over to the low temperature saturation (6) depends delicately on the ratio of the breathing and shaking types of the rotor-phonon coupling and is difficult to estimate. In view of the presence of other possible sources for line broadenings (strong dissipation at $T = 0$ [12] or orientational coupling between large numbers of rotors[20]), Eq.(6) provides an upper bound for the exchange rate at $T = 0$. Eq.(7) is of the same form as the expression estimated by Nijman and Berlinsky [5] for the exchange rate between methane molecules (from our point of view, the R^{-8} dependence of their rate is due to a typographical error, it rather should read R^{-10} also in the context of methane).

In Fig. 1 the exchange rate R_{ex} for equal methyl groups is shown versus temperature, assuming Debye phonons [6, 9]. The full curve shows the rate calculated from Eqs.(4) and (5). The approximative expressions (6) and (7) are shown dashed. The competition between the diffusion mechanism and the on-site conversion can be seen from the ratio $\tau_{\text{ex}}/\tau_{\text{con}}$ between the exchange and the conversion times, Fig. 1, the latter has been discussed in detail in Refs. [6, 7, 9]. At low temperatures the symmetry exchange is, in the example shown, by about 15 orders of magnitudes more efficient than the conversion. The fastest converting rotors in the sample will determine the macroscopic thermal relaxation. With increasing temperature the development of τ_{ex} and τ_{con} is just the opposite. Above a cross-over temperature, where $\tau_{\text{ex}} = \tau_{\text{con}}$, the on-site conversion is *faster* than the exchange. This temperature depends sensitively on the details of the rotor-phonon coupling and on the distance between the rotors ($\propto (R_{(1,2)}^{(0)})^{10}$).

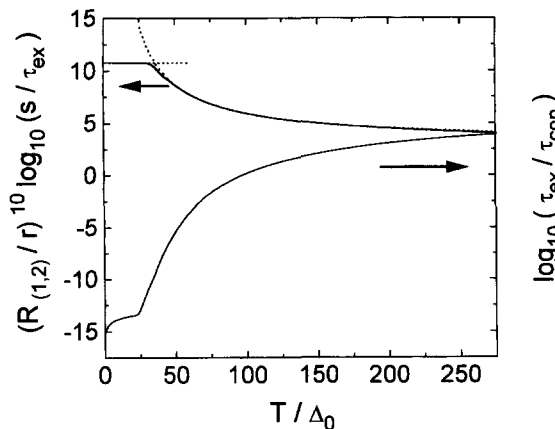


Fig. 1. Upper curve: $(R_{(1,2)}^{(0)}/r)^{10} \log(s/\tau_{ex})$, lower curve: $\log(\tau_{ex}/\tau_{con})$ for $R_{(1,2)}^{(0)} = 5r$ versus temperature in units of the tunnelling energy Δ corresponding to $V_3^{(1)} = V_3^{(2)} = 20B$. Debye phonons have been assumed with $\omega_D = 18B$, $g_k^c = g_k^s$ and $g := g_k^{c/s}/\sqrt{V_3^{(\alpha)}\omega_k} = 0.1$. At temperatures $T \gtrsim 95\Delta$ the conversion becomes more rapid than the exchange.

If $V_3^{(1)} < V_3^{(2)}$, so that the difference between the (through \mathbf{H}_I renormalized) tunnelling energies $\tilde{\Delta}^{(1,2)}$ is larger than E_D , the exchange rate

$$R_{ex} = 147 \left(\frac{\gamma_p^2}{r^3} \right)^2 \left(\frac{r}{R_{(1,2)}^{(0)}} \right)^{10} \times |A_0(1)|^2 |A_0(2)|^2 e^{-\beta(E_0^A(1) + E_0^E(2))} \times (Z_{A_1E_2}^{-1} + Z_{E_1A_2}^{-1}) \frac{w^{(1,2)}}{(w^{(1,2)})^2 + (\tilde{\Delta}^{(1,2)})^2} \quad (8)$$

differs considerably from Eqs. (6) and (7). $E_0^\Gamma(\alpha)$ are the eigenenergies of the α 's rotor and $Z_{\Gamma_1\Gamma_2} = Z_{\Gamma_1} Z_{\Gamma_2}$, $Z_\Gamma = \sum_m e^{-\beta E_m^\Gamma}$. A central ingredient is the combined broadening $w^{(1,2)}$ which for most applications can be taken as the sum of the line broadenings of the two rotors [15].

In Fig. 2 Eq. (8) is plotted versus temperature for $V_3^{(1)} = 15B$ and $V_3^{(2)} = 15.5, 16, 16.5, 17B$. The low temperature limit is determined by the ratio $w_s/(\tilde{\Delta}^{(1,2)})^2$. This suppression (compared to Eq.(6)) is due to the lack of low energy phonons that have to

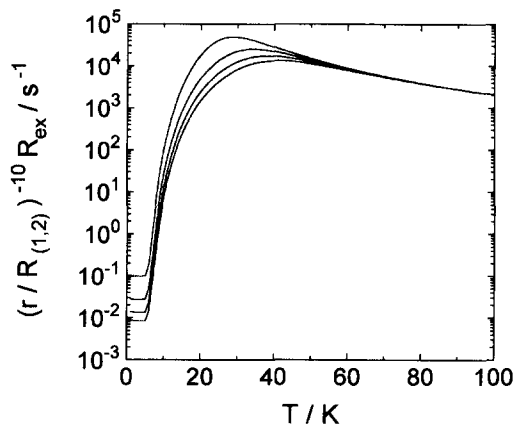


Fig. 2. $(R_{(1,2)}^{(0)}/r)^{10} R_{ex}/s$ versus temperature according to Eq. (8) for $V_3^{(1)} = 15B$ and $V_3^{(2)} = 15.5, 16, 16.5, 17B$, from top to bottom. The remaining parameters are the same as in Fig. 1.

account for the difference between the tunnelling energies of the rotors. The exchange rate first increases Arrhenius-like with an ‘‘activation’’ energy being roughly given as the mean of the librational energies of the two rotors. The maximum is determined by $w^{(1,2)} = \tilde{\Delta}^{(1,2)}$, and a further increase of the temperature reduces R_{ex} , again Arrhenius-like, similar to the case of equal rotors. The decrease of the maximum value for R_{ex} and its shifting towards higher temperatures with increasing difference between the rotors is clearly seen.

4. Conclusions

Results for the symmetry species exchange rate R_{ex} for $(A_1, E_2) \leftrightarrow (E_1, A_2)$ transitions between two adjacent methyl rotors are presented. This is the ‘‘elementary process’’ for the macroscopic thermalization by diffusion of symmetries through a sample that contains dilute paramagnetic centres which provide rapid conversion of rotors in their near vicinity. Its temperature dependence is traced back to the broadening behaviour of the tunnelling line as it is observed in INS. This relationship has been derived by using a projection operator technique. Taking Fermi’s golden rule would not have allowed to control this derivation.

The dipolar broadening w_S due to the energy reservoir of nuclear spins (characterized by the relaxation time T_2) determines R_{ex} at zero temperature. This fixes the upper bound for R_{ex} in the cases of equal methyl groups $V_3^{(1)} = V_3^{(2)}$. At elevated temperatures R_{ex} decreases Arrhenius-like with an “activation” energy given as the mean of the two librations. Simultaneously the conversion rate increases and overtakes the exchange rate above a certain temperature. Rotors with different $V_3^{(1)} \neq V_3^{(2)}$, so that $\Delta^{(1,2)} > w_S$, should show R_{ex} of the order of $w_S/(\Delta^{(1,2)})^2$ at zero temperature and a non-monotonic temperature dependence.

In a forthcoming publication [15] we include Raman type phonon processes, and the cases of low orientational potentials $V_3^{(1)}, V_3^{(2)} \lesssim 8B$. In the latter cases modulations of the distance between the rotors by phonons can yield a contribution $\propto (2n(|\Delta^{(1,2)}|) + 1)$ to R_{ex} at low temperatures, $n(x) = (e^{\beta x} - 1)^{-1}$ being the Bose function.

The dipolar magnetic interaction assumed here as the origin for the symmetry exchange transitions would be reduced in chemically equivalent deuterated samples by $\sim 10^{-3}$ due to the smaller dipole moment of deuterons. The conversion of not very weakly hindered deuterated rotors is, on the other hand, predicted to be not considerably different from the protonated isotopes [9]. The experimental observation of the symmetry species “diffusion front” by means of the neutron transmission method [21] through protonated and deuterated samples, enriched with oxygen on one side, would be extremely interesting [22]. A determination of R_{ex} should also be feasible by means of specially designed nuclear magnetic resonance experiments [23].

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