High-field spin-lattice relaxation of methyl groups: relation to neutron scattering

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Abstract. The modern theory of high-field spin–lattice relaxation is applied to methyl group rotation. It is shown that the same time correlation functions are observed in nuclear magnetic resonance (NMR) relaxation experiments and in inelastic neutron scattering (INS) experiments. A linear relationship is derived between the spectral function $S(\omega)$ observed in INS and the spin–lattice relaxation rate $T_1^{-1}(\omega)$ as a function of the Larmor frequency. The similarities between the two methods are pointed out. For CD_3, NMR experiments on systems with high tunnelling frequencies yield the width of the quasi-elastic $E^a \leftrightarrow E^b$ line of INS. For CH_3, the effect of intermolecular dipolar interactions on the spin–lattice relaxation time T_1 is calculated using a series expansion in r/R_i, where r is the radius of the methyl group and R_i is the distance of the considered proton i from the centre of the CH_3 group. It is shown that for systems with high tunnelling frequencies T_1 is mainly determined by intermolecular dipolar interactions, whereas these have a negligible effect on spin conversion. T_1 experiments on diluted CH_3-containing systems yield the width of the inelastic $A \leftrightarrow E$ line, also in the so-called 'quasi-classical' temperature regime.

1. Introduction

The rotational dynamics of light molecules like hydrogen or methane and molecular groups like methyl groups has been investigated in a variety of experimental and theoretical studies in the past [1–3]. A common feature of all these systems undergoing rotational tunnelling is that they consist of end-standing identical particles. Owing to the indistinguishability of identical particles, minima of the rotational potential have to be strictly equivalent. In the case of methyl groups, on which we will focus in the following, the rotational potential has to be invariant under permutations of the three end-standing protons (CH_3) or deuterons (CD_3). For our purpose it is sufficient to disregard odd permutations corresponding to the exchange of two particles. This means that we can restrict ourselves to 'right-handed' or 'left-handed' states of methyl groups [4], since the barriers for transitions between these states are outside the energy range considered here. Consequently, the Hamiltonian has the symmetry group C_3 (which is isomorphic to the permutation group A_3), and all eigenstates can be classified according to the irreducible representations Γ of C_3, i.e. $\Gamma \in \{A, E^a, E^b\}$. We shall call Γ the 'symmetry' or 'rotor symmetry' in the following.

The eigenstates of the Hamiltonian describing the rotational motion of the methyl groups will be denoted as $|\nu\Gamma\rangle$, where ν is a librational quantum number and Γ

the symmetry. States $|\nu E^a\rangle$ and $|\nu E^b\rangle$ are degenerate, the degeneracy being of Kramers type [5], and are different in energy from states $|\nu A\rangle$ by a separation Δ_ν $(:= E_\nu^E - E_\nu^A)$. The ground state of the spectrum of the rotational Hamiltonian is $|0A\rangle$ (cf figure 1). The splitting Δ_0 $(= E_0^E - E_0^A)$ typically ranges from 0.1 to 100 μeV for CH_3 whereas the lowest librational energy E_{lib}, i.e. the energy difference between states with $\nu = 1$ and $\nu = 0$, is of the order 5 to 15 meV. Furthermore, the signs of the splittings Δ_ν alternate with the librational quantum number ν (Δ_1 is negative), and for sufficiently high barriers of the rotational potential $|\Delta_1| \gg |\Delta_0|$ holds.
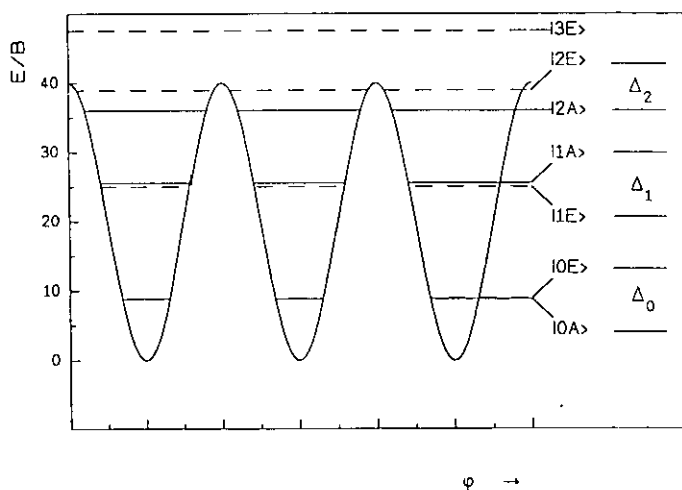

Figure 1. Energy levels of CH_3/CD_3 groups for a three-fold potential. The potential barrier V_3 is chosen to be $40B$ ($\Delta_0 = 2.54 \times 10^{-2}B$), where B is the rotational constant. The rotational states are labelled by a librational quantum number ν and a symmetry quantum number Γ, $|\nu\Gamma\rangle$. Also indicated are the splittings Δ_ν (see text).

The main difference between CH_3 and CD_3 experiencing the same rotational potential lies in the increase of the moment of inertia Θ by a factor of two when CH_3 is substituted by CD_3. Thus, in units of the rotational constant B ($B = \hbar^2/2\Theta$, $B(CH_3) \simeq 647$ μeV, $B(CD_3) \simeq 323.7$ μeV), CD_3 'sees' a potential of doubled height, which decreases the ground-state 'tunnelling' splitting Δ_0 by factors of 10–50 relative to CH_3 (Δ_0 is exponentially small in the potential barrier height).

The symmetry arguments given above also hold in the presence of coupling of the rotational motion of the methyl groups to other spatial degrees of freedom, e.g. in the presence of coupling to phonons. Physically, this means that phonons cannot induce transitions between states of different symmetry Γ but only between states of the same symmetry and different librational quantum numbers ν. Thus, the symmetry Γ is a constant of motion with respect to any pure spatial operator. This fact distinguishes rotational tunnelling systems qualitatively from other (e.g. translational) tunnelling systems where phonons or electrons are able to induce transitions between the tunnel split states. This means that in methyl-containing compounds quantum effects are observable up to temperatures $T \gg \Delta_0$ and the energy scale for which dissipation becomes important is given by the librational energy.

Interactions that are able to change the rotor symmetry Γ are the spin-dependent dipolar interaction among the particles, the interaction of the quadrupolar moment of the deuterons with the electric field gradients in the case of CD_3 or the spin-dependent interaction of the protons or deuterons with neutrons. The weak dipolar

and quadrupolar interactions are considered to be responsible for the equilibration of the symmetry species of rotational tunnelling systems (conversion) [6–9].

These spin-dependent interactions allow the observation of transitions between different rotational states and the influence of dissipation on these. Typical observations of inelastic neutron scattering (INS) experiments might be summarized in the following way [1–3]. At low temperatures ($T \ll E_{\text{lib}}$) usually three sharp lines are observed, two of which are located at energy transfers $\pm\Delta_0$. These correspond to A↔E transitions and allow the determination of Δ_0. The third line with zero average energy transfer originates from $E^a \leftrightarrow E^b$ transitions and from symmetry-conserving transitions $\Gamma \leftrightarrow \Gamma$. With increasing temperature, all lines broaden and the inelastic tunnelling (A ↔ E) lines shift towards zero energy transfer. (Also a positive shift at low temperatures has been observed [10].) Often, shift and broadenings in this temperature range ($T < E_{\text{lib}}$) follow an Arrhenius law with an apparent activation energy of the order of the librational energy E_{lib}. At elevated temperatures ($T \sim E_{\text{lib}}$) all three lines merge into a single broad quasi-elastic line; the activation energy of the broadening increases with temperature. Usually all lines are to an excellent approximation described by Lorentzians. In a few experiments the $E^a \leftrightarrow E^b$ line has been found to be narrower than the inelastic tunnelling lines at low temperatures [11, 12].

In most theoretical studies of the temperature dependence of rotational tunnelling [13–15] the coupling of the rotor to the phonons is treated in perturbation theory. The temperature dependence of the broadening is found to be librationally activated in second [14] and fourth [15] order. The increase of the activation energy might partly be understood from perturbation theory via phonon-induced transitions to the second librational states. However, the 'high-temperature' activation energy, which has often been found experimentally [16, 17] and is connected in some way to the potential barrier height, seems not to be explainable by a perturbational approach to the problem. The width of the $E^a \leftrightarrow E^b$ line has been found to be narrower than the widths of the inelastic (A ↔ E) tunnelling lines in a more careful second-order perturbational calculation [18], in qualitative agreement with the mentioned experiments.

Besides neutron scattering, nuclear magnetic resonance (NMR) experiments allow the measurement of line broadenings over a wide temperature range and also the determination of the splitting Δ_0 in some cases [19–21]. However, the relations between the two types of experiments seem not to be obvious.

It is the purpose of the present paper to show the connections between INS and high-field NMR relaxation experiments on methyl-containing compounds. Therefore, we briefly recall the main features of the theory of the temperature dependence of INS experiments in the next section. In section 3, we apply the standard theory of high-field nuclear spin relaxation [22, 23] to CH_3 and CD_3. It will be shown that INS and NMR relaxation experiments exhibit a number of similarities. The correspondence between quantities measured in INS or NMR relaxation is worked out for some examples of possible future experiments. Furthermore, the importance of intermolecular dipolar interactions in the case of CH_3 will be pointed out and their influence on the spin–lattice relaxation times is calculated approximately. Finally, we discuss our results in section 4.

2. The temperature-dependent scattering function

In this section we briefly recall the main results of the theory of inelastic neutron scattering on methyl groups. If we assume that the only scattering centres are methyl groups, we can write for the incoherent scattering function of a powder sample [15, 24]:

$$S(Q,\omega) = \sum_{n=0}^{\infty} f_n(Q) \frac{1}{2\pi} \int_{-\infty}^{\infty} dt \, e^{-i\omega t} \langle e^{in\phi(0)} e^{-in\phi(t)} \rangle \tag{1}$$

where we have collected all information concerning the scattering event in the structure factors $f_n(Q)$ (spin matrix, scattering length, etc). Furthermore, $f_n(Q)$ represents the nth term of a series expansion in $(Qr)^2$ [25], where Q is the modulus of the scattering vector Q and r is the radius of the methyl group ($r \simeq 1$ Å). Finally, ϕ is the methyl rotation angle and $\langle A \rangle$ denotes a thermal average, i.e. $\langle A \rangle = \text{Tr}[A \exp(-\beta H)] / \text{Tr} \exp(-\beta H)$, where β is the inverse temperature. Note that the term $n = 0$ yields a δ-function spectral line at zero energy transfer. This line has its origin in the fact that the motion of the methyl protons is restricted to a finite area. In principle, all other terms with $n \neq 0$ contribute to the scattering function.

The determination of $S(Q,\omega)$ has been the subject of many experimental and theoretical studies. In most of the proposed theories [14, 15, 18] the following Hamiltonian is investigated:

$$H = H_R + H_P + H_{RP} \tag{2a}$$

with

$$H_R = -B\partial_\phi^2 + V(\phi) \equiv \sum_{\nu,\Gamma} E_\nu^\Gamma X_{\nu\Gamma:\nu\Gamma} \tag{2b}$$

$$H_P = \sum_k \omega_k (b_k^+ b_k + 1/2) \tag{2c}$$

$$H_{RP} = \sum_k [g_k^c \cos(3\phi) + g_k^s \sin(3\phi)](b_k + b_k^+) \equiv \sum_{k,\Gamma} \sum_{\nu,\nu'} g_{k\nu\nu'}^\Gamma X_{\nu\Gamma:\nu'\Gamma}(b_k + b_k^+). \tag{2d}$$

Here, B is the rotational constant and usually only the lowest-order terms of the potential, $V(\phi) = V_3 \cos(3\phi)$, is retained in H_R. The coupling between the phonon bath and the rotor is assumed to be linear in the phonon coordinates b_k and cannot change the symmetry of the rotor. The operators $X_{\nu\Gamma:\nu'\Gamma'} \equiv |\nu\Gamma\rangle\langle\nu'\Gamma'|$ are the 'standard-basis' operators introduced by Hewson [14]. In terms of these operators the scattering function (1) reads

$$S(Q,\omega) = \sum_{n=0}^{\infty} f_n(Q) \sum_{\nu,\nu',\Gamma} \sum_{\mu,\mu',\Gamma'} \langle \nu\Gamma | e^{in\phi} | \nu'\Gamma' \rangle \langle \mu'\Gamma' | e^{-in\phi} | \mu\Gamma \rangle$$

$$\times \frac{1}{2\pi} \int_{-\infty}^{\infty} dt \, e^{-i\omega t} \langle X_{\nu\Gamma:\nu'\Gamma'}(0) X_{\mu'\Gamma':\mu\Gamma}(t) \rangle \tag{3}$$

where $X_{\mu'\Gamma':\mu\Gamma}(t) = e^{iHt} X_{\mu'\Gamma':\mu\Gamma} e^{-iHt}$. At low temperatures ($T \lesssim E_{\text{lib}}$), where mainly the librational ground state is occupied, the relevant time correlation functions

are of the type $\langle X_{0\Gamma:0\Gamma'}(0)X_{0\Gamma':0\Gamma}(t)\rangle$. Furthermore, the 'non-secular' terms with $\mu \neq \nu$ and $\mu' \neq \nu'$ turn out to be quite unimportant for $S(Q,\omega)$. The physical reason for this is that these terms describe the decay of correlations between distinct quantum coherences.

Thus, the relevant spectral functions are

$$S_{\nu,\nu'}^{\Gamma,\Gamma'}(\omega) := \frac{1}{2\pi} \int_{-\infty}^{\infty} dt\, e^{-i\omega t} \langle X_{\nu\Gamma:\nu'\Gamma'}(0)X_{\nu'\Gamma':\nu\Gamma}(t)\rangle. \tag{4}$$

In most of the theoretical treatments of the temperature dependence of rotational tunnelling, the spectral function $S_{0,0}^{\Gamma,\Gamma'}(\omega)$ is tackled in second-order perturbation theory with respect to H_{RP}. These calculations result in Lorentzian lines for $S_{0,0}^{\Gamma,\Gamma'}(\omega)$ with different widths. For the inelastic (A ↔ E) tunnelling lines a temperature-dependent renormalization of the transition frequency Δ_0, to be denoted as $\omega_t(T)$ in the following, is found. We shall not repeat the resulting expressions here, but only note the following. Hewson [14] and Häusler [15] found the broadenings of the inelastic (A ↔ E) tunnelling line and of the E^a ↔ E^b line to be almost the same (differences are mainly due to different values of $g_{k\nu\nu'}^A$ and $g_{k\nu\nu'}^E$). Würger [18] found a reduction of the width of the E^a ↔ E^b line, in qualitative agreement with experiment. The similar broadenings obtained by Hewson have their origin in the fact that the lifetime-broadening processes in the initial and the final state are treated independently and the resulting widths are added. This is allowed only for states with different energies. If the states have the same energy, the width of the corresponding line is reduced due to correlations between phonons resonating in the initial and the final state. This is the physical reason for the reduced linewidth of the E^a ↔ E^b line. However, Würger finds a zero width for 0Γ ↔ 0Γ lines, which means that here the mentioned mechanism would *exactly* cancel the linewidth. Perhaps this point needs further investigation.

Finally, we note that the spectral functions $S_{\nu,\nu'}^{\Gamma,\Gamma'}(\omega)$ might be written as

$$S_{\nu,\nu'}^{\Gamma,\Gamma'}(\omega) = \langle X_{\nu\Gamma:\nu\Gamma} \rangle L_{\nu,\nu'}^{\Gamma,\Gamma'}(\omega) \tag{5}$$

where $L_{\nu,\nu'}^{\Gamma,\Gamma'}(\omega)$ denotes a Lorentzian line (with real part $x/[x^2 + (y - \omega)^2]$) of width x centred at the renormalized transition frequency y, e.g. $\mathrm{Re}[S_{0,0}^{A,E}(\omega)] = \langle X_{0A:0A}\rangle\gamma/\{\gamma^2 + [\omega_t(T) - \omega]^2\}$, $\mathrm{Re}[S_{0,0}^{E,E}(\omega)] = \langle X_{0E:0E}\rangle\bar{\gamma}/(\bar{\gamma}^2 + \omega^2)$, where γ and $\bar{\gamma}$ denote the widths. If we approximate the thermal expectation value $\langle X_{\nu\Gamma:\nu\Gamma}\rangle$ by its value in the absence of any coupling, $H_{\mathrm{RP}} = 0$, we easily find

$$\langle X_{\nu\Gamma:\nu\Gamma}\rangle^{(0)} = \mathrm{Tr}\{\exp[-\beta(H_{\mathrm{R}} + H_{\mathrm{P}})]X_{\nu\Gamma:\nu\Gamma}\}/\mathrm{Tr}\{\exp[-\beta(H_{\mathrm{R}} + H_{\mathrm{P}})]\}$$
$$= \exp(-\beta E_\nu^\Gamma)/Z_{\mathrm{R}} \tag{6}$$

where $Z_{\mathrm{R}} := \sum_{\nu\Gamma} \exp(-\beta E_\nu^\Gamma)$. This clearly demonstrates that the low-temperature spectral function is determined mainly by $S_{0,0}^{\Gamma,\Gamma'}(\omega)$.

3. High-field spin–lattice relaxation of methyl groups

3.1. The equation of motion for the spin-density matrix

Before we turn to the specific problem of spin relaxation of methyl groups, we shall outline the general theory of high-field nuclear spin relaxation [22, 23] in a way

directly applicable to our situation. The Hamiltonian of a system of like spins in a static magnetic field reads

$$H = H_z + H_{IL} + H_L \tag{7}$$

where $H_z = -\gamma_1 B_0 I_z = -\omega_z I_z$ represents the Zeeman interaction of the spins with the static magnetic field B_0 aligned along the z axis, H_L is the Hamiltonian of the isolated lattice (all non-spin degrees of freedom of the sample) and H_{IL} stands for the spin–lattice interaction (dipolar or quadrupolar interaction). H_{IL} is decomposed into a static and a 'fluctuating' contribution, the former of which supplements the Zeeman Hamiltonian:

$$H = H_I + \Delta H_{IL} + H_L \qquad H_I = H_z + \langle H_{IL}\rangle_L \qquad \Delta H_{IL} = H_{IL} - \langle H_{IL}\rangle_L \tag{8}$$

where $\langle H_{IL}\rangle_L = \mathrm{Tr}(\rho_L H_{IL})$, and ρ_L is the lattice-density matrix. This decomposition ensures $\langle \Delta H_{IL}\rangle_L = 0$.

Using a standard projection operator technique [26, 27], the following non-Markovian equation of motion for the reduced density matrix $\sigma(t) := \mathrm{Tr}_L[W(t)]$, where $W(t)$ is the total density matrix, of the spin system is obtained:

$$\partial_t \sigma(t) = -\mathrm{i}[H_I, \sigma(t)] - \int_0^t \mathrm{d}\tau\, K(\tau)\sigma(t-\tau) \tag{9}$$

where $[A, B]$ denotes the commutator and $K(\tau)$ is the relaxation kernel to be specified later. The approximations made in the derivation of (9) have been exhaustively discussed in the literature, see e.g. [22, 23, 26, 27].

In the next step we expand the spin-density matrix into an orthonormal set of operators O_k:

$$\sigma(t) = \sum_{k=1}^{N} \langle O_k(t)\rangle_I O_k \tag{10a}$$

where

$$\langle O_k(t)\rangle_I = \mathrm{Tr}_I[O_k \sigma(t)]. \tag{10b}$$

For typical spin systems the operators O_k may be chosen as the irreducible tensor operators $T_{l,q}$, where l is the rank and q the order of the quantum coherences [23]. This yields the equation of motion for the expectation values $\langle O_k(t)\rangle_I$:

$$\partial_t \langle O_k(t)\rangle_I = -\sum_{n=1}^{N} \left(\mathrm{i}\mathrm{Tr}_I\{O_k[H_I, O_n]\} + \int_0^t \mathrm{d}\tau\, \mathrm{Tr}_I\{O_k[K(\tau)O_n]\} \right) \langle O_n(t-\tau)\rangle_I. \tag{9a}$$

We now make the following approximations.

(i) We restrict ourselves to high static magnetic fields, where ω_z is much larger than the energy shifts due to $\langle H_{IL}\rangle_L$. These are of the order of 50–200 kHz for protons and deuterons, whereas typical Larmor frequencies are of the order of MHz. Then the relaxation kernel $K(\tau)$ can be calculated in second order regarding ΔH_{IL}.

(ii) We assume the high-temperature approximation to be valid for the Zeeman spin energy ω_z, i.e. $\exp(-\beta\omega_z) \simeq 1 - \beta\omega_z$. This is allowed for $T \gtrsim 1$ mK. One implication of this high-temperature approximation is that we have to replace $\langle O_k(t)\rangle_{\mathrm{I}}$ by $\langle O_k(t)\rangle_{\mathrm{I}} - \langle O_k\rangle_{\mathrm{I}}^{\mathrm{eq}}$, where $\langle O_k\rangle_{\mathrm{I}}^{\mathrm{eq}}$ denotes the thermal equilibrium value of O_k.

(iii) We restrict our attention to the relaxation of operators corresponding to zero-quantum coherences (e.g. I_z). Then all operators O_k represent linear combinations of projectors onto the single spin states. A coupling of the time evolution of such operators to the time evolution of operators corresponding to multi-quantum coherences (e.g. I_x) will be neglected in the following. This is allowed exactly, if the initial spin-density matrix $\sigma(0)$ is diagonal (e.g. in an inversion recovery experiment). Even if this is not true, the neglect of couplings is allowed for times that are long compared to the decay time of the initial multi-quantum coherence. If e.g. $\sigma(0) \sim I_x$, this time is given by T_2, which is small compared to the timescale of the time evolution of longitudinal operators, e.g. I_z. Since in solids at low temperatures one has $T_1 \gg T_2$ ($T_1 \sim 1$ s, $T_2 \sim 100$ μs), this approximation provides no problem for our treatment.

With the definition

$$\langle \Delta_{\mathrm{eq}} O_k(t)\rangle_{\mathrm{I}} := \langle O_k(t)\rangle_{\mathrm{I}} - \langle O_k\rangle_{\mathrm{I}}^{\mathrm{eq}} \tag{11}$$

we have the following equation of motion for the expectation values of longitudinal operators O_k (e.g. I_z):

$$\partial_t\langle\Delta_{\mathrm{eq}}O_k(t)\rangle_{\mathrm{I}} = -\sum_{n=1}^{N}\int_0^t \mathrm{d}\tau\, K_{k,n}(\tau)\langle\Delta_{\mathrm{eq}}O_n(t-\tau)\rangle_{\mathrm{I}} \tag{12}$$

where the elements $K_{k,n}(\tau)$ of the relaxation kernel $\mathbf{K}(\tau)$ are given by

$$K_{k,n}(\tau) = -\sum_{\alpha,\beta}O_{k;\alpha}[P_{\alpha,\beta}(\tau)O_{n;\beta} - P_{\beta,\alpha}(\tau)O_{n;\alpha}]. \tag{13}$$

Here, $|\alpha\rangle$ and $|\beta\rangle$ are eigenstates of the spin Hamiltonian H_{I}, $H_{\mathrm{I}}|\alpha\rangle = E_\alpha|\alpha\rangle$, $O_{k;\alpha} = \langle\alpha|O_k|\alpha\rangle$ and the transition probabilities $P_{\alpha,\beta}(\tau)$ are given by

$$P_{\alpha,\beta}(\tau) = 2\,\mathrm{Re}[\langle\!\langle\beta|\Delta H_{\mathrm{IL}}(0)|\alpha\rangle\langle\alpha|\Delta H_{\mathrm{IL}}(\tau)|\beta\rangle\!\rangle_{\mathrm{L}}\exp(-\mathrm{i}\omega_{\beta\alpha}\tau)] \tag{14}$$

for any Hermitian ΔH_{IL} [28]. This transition probability is determined by the time correlation function $\langle\!\langle\beta|\Delta H_{\mathrm{IL}}(0)|\alpha\rangle\langle\alpha|\Delta H_{\mathrm{IL}}(\tau)|\beta\rangle\!\rangle_{\mathrm{L}}$, where time evolution is with respect to H_{L}, $\Delta H_{\mathrm{IL}}(\tau) = \exp(\mathrm{i}H_{\mathrm{L}}\tau)\Delta H_{\mathrm{IL}}\exp(-\mathrm{i}H_{\mathrm{L}}\tau)$, and the trivial time evolution due to H_{I} determines the oscillating function $\exp(-\mathrm{i}\omega_{\beta\alpha}\tau)$, where $\omega_{\beta\alpha} := E_\beta^{\mathrm{I}} - E_\alpha^{\mathrm{I}}$.

The equation of motion (12) is solved formally be means of Laplace transforms, if $\mathbf{K}(\tau)$ represents the matrix of the $K_{k,n}(\tau)$ and $\Delta_{\mathrm{eq}}O(t)$ denotes the 'vector' with elements $\langle\Delta_{\mathrm{eq}}O_k(t)\rangle_{\mathrm{I}}$, $k = 1, \ldots, N$:

$$\Delta_{\mathrm{eq}}O(s) = [s + K(s)]^{-1}\Delta_{\mathrm{eq}}O(0). \tag{15}$$

It is evident that the equation of motion (15) yields a multi-exponential law $\langle\Delta_{\mathrm{eq}}O_k(t)\rangle_{\mathrm{I}} = \sum_i a_i \exp(b_i t)\langle\Delta_{\mathrm{eq}}O_i(0)\rangle_{\mathrm{I}}$ for the time evolution of $\langle\Delta_{\mathrm{eq}}O_k(t)\rangle_{\mathrm{I}}$ only if $\mathbf{K}(s) = \mathbf{K}(0)$ independent of the Laplace parameter s. This condition is equivalent to setting the upper limit of the integral occurring in equation (12) to infinity. We shall not do this here, since some of the transition probabilities relevant for the relaxation of methyl groups show singularities for some frequencies, which have to be handled with care.

3.2. Application to methyl groups

It is our purpose to calculate the transition probabilities $P_{\alpha,\beta}(\tau)$ for the specific example of methyl groups. Here H_L is given explicitly by equation (2), but we need not make any assumption about the strength of the coupling between the methyl rotors and the phonons nor about its specific form. We shall only need the fact that the rotor–phonon coupling does not mix different symmetries in some of the calculations. Our main aim is to show that the transition probabilities $P_{\alpha,\beta}(\tau)$ are related very closely to the spectral functions $S_{\nu,\nu'}^{\Gamma,\Gamma'}(\omega)$ and to discuss these relations in detail.

The spin–lattice interactions to be considered here are different for CH_3 and CD_3. In the case of CH_3, it is well known that the dipolar interaction among the protons is the only interaction that is of relevance. We shall first concentrate on the intra-methyl dipolar interactions, but also consider intermolecular contributions later and discuss their relevance for T_1. For CD_3, the main interaction is the interaction of the quadrupolar moment of the deuterons with the electric field gradients (EFG) at the site of the nuclei. These EFG originate from the electronic charge distribution of the chemical C–D bonds [29]. Furthermore, for CD_3 the EFG are axially symmetric to an excellent approximation [30]; there is only one non-vanishing component of the EFG. Of course, deuterons also are coupled via the dipolar interaction among the deuterons. However, the strength of this interaction is smaller by a factor of 100–200 than the strength of the quadrupolar interaction. Thus, we can neglect the influence of the dipolar interaction completely in the case of CD_3.

In order to treat both cases, the relaxation of CH_3 and of CD_3, in the same formalism, we write for the spin–lattice interaction Hamiltonians $H_{IL} \equiv H_{IL}^D$ for CH_3 and $H_{IL} \equiv H_{IL}^Q$ for CD_3 and denote the corresponding Hamiltonian by H_{IL}^λ, where $\lambda = D$ means dipolar interaction for CH_3 and $\lambda = Q$ means quadrupolar interaction for CD_3. The coupling Hamiltonians might be written as

$$H_{IL}^\lambda = \sum_{(k)} (H_{IL}^\lambda)^{(k)} \tag{16}$$

where the sum (k) means the sum over the three single-particle quadrupolar Hamiltonians of the deuterons in the case of CD_3, i.e. $k = 1, 2, 3$. In the case of the dipolar interaction ($\lambda = D$) among the protons of a CH_3 group, one has to take the sum over the three possible pairs of protons, i.e. $k = (1,2), (1,3), (2,3)$. In appendix 1 explicit expressions for the $(H_{IL}^\lambda)^{(k)}$ are given and H_{IL}^λ is written in symmetry-adapted form. It is shown that the form is

$$H_{IL}^\lambda = d_\lambda \sum_\Gamma \sum_{m=-2}^{2} (-1)^m R_{2,-m}^\Gamma(\Theta_\lambda; \Omega_0; \phi) T_{2,m}^{\Gamma_c}(\lambda) \tag{17}$$

where the summation over k in (16) is now replaced by a summation over Γ, cf (A1.5). Here d_λ, $R_{2,m}^\Gamma(\Theta_\lambda; \Omega_0; \phi)$ and $T_{2,m}^{\Gamma_c}(\lambda)$ denote the coupling strengths, 'space-part' operators and 'spin' operators, respectively. Γ denotes the irreducible representations of C_3 ('symmetry'); Γ_c is conjugate to Γ, i.e. $\Gamma_c = \{A, E^a, E^b\}$ for $\Gamma = \{A, E^b, E^a\}$. Θ_λ is the angle between the principal axis of the coupling tensor ($\lambda = D$: the internuclear vector; $\lambda = Q$: approximately the C–D bond axis) and the rotation axis of the methyl group and ϕ is the methyl rotation angle. $\Omega_0 \equiv (\beta_0; \alpha_0)$ defines

the orientation of the static magnetic field B_0 in a crystal-fixed frame, where the z axis is chosen as the methyl rotation axis. This orientation is assumed to be fixed throughout our discussion, since the methyl group is kept at its site. Thus, the operators $R_{2,m}^{\Gamma}(\Theta_\lambda; \Omega_0; \phi)$, given by

$$R_{2,m}^{A}(\Theta_\lambda; \Omega_0) = v_0(\Theta_\lambda) D_{0,m}^{(2)}(\Omega_0) \tag{18a}$$

$$R_{2,m}^{E^a}(\Theta_\lambda; \Omega_0; \phi) = -v_1(\Theta_\lambda) D_{1,m}^{(2)}(\Omega_0) e^{i\phi} + v_2(\Theta_\lambda) D_{-2,m}^{(2)}(\Omega_0) e^{-2i\phi} \tag{18b}$$

$$R_{2,m}^{E^b}(\Theta_\lambda; \Omega_0; \phi) = (-1)^m [R_{2,-m}^{E^a}(\Theta_\lambda; \Omega_0; \phi)]^* \tag{18c}$$

are time dependent *only* due to their dependence on ϕ. The fact that we keep Ω_0 fixed physically means that we exclude phonon modes that incline the rotor from our treatment. Otherwise we have $\Omega_0(\tau) = \exp(iH_P\tau)\Omega_0 \exp(-iH_P\tau) \neq \Omega_0(0)$, see equation (2). The functions $v_n(\Theta_\lambda)$ are given explicitly in appendix 1, (A1.6), and the $D_{n,m}^{(2)}(\Omega_0)$ denote Wigner rotation matrix elements. Note that for CH_3 $v_1(\Theta_D) = 0$ and thus operators $e^{i\phi}$ do not contribute, whereas for CD_3 all terms are non-vanishing, which has some interesting implications for the angular dependence of the spin–lattice relaxation time T_1 in this case [31].

In order to calculate the transition probabilities we have to specify the spin states of the methyl group. As already pointed out in the introduction, it is sufficient to disregard odd permutations from our treatment. This means that we can build simple product functions of rotational and spin states with the only requirement from the Pauli principle that the product functions are of A symmetry. Otherwise we have to construct antisymmetric states for CH_3 and totally symmetric states for CD_3. We shall denote the spin states for CH_3 and CD_3 as $|\Gamma m\rangle$ in the following, where $m \equiv m_\Gamma$ is the magnetic quantum number. The product states can then be written as

$$|\nu\Gamma m\rangle := |\nu\Gamma\rangle|\Gamma_c m\rangle \tag{19}$$

in both cases. The only difference between CH_3 and CD_3 is the accessible values of the magnetic quantum numbers m. We do not indicate this, to keep the formulation more transparent. Furthermore, the Pauli principle is manifested in (19), which implies that a strong statistical correlation between the spin and rotational states must be kept in mind in the general formalism of section 3.1. This is qualitatively different from other spin systems.

For the decomposition of the spin–lattice Hamiltonians (8) we have to calculate $\langle H_{IL}^\lambda\rangle_L$ and thus $\langle R_{2,m}^\Gamma(\Theta_\lambda; \Omega_0; \phi)\rangle_L$. Since $R_{2,m}^A$ is independent of the rotation angle ϕ, we have

$$\langle R_{2,m}^{A}(\Theta_\lambda; \Omega_0)\rangle_L = R_{2,m}^{A}(\Theta_\lambda; \Omega_0) \tag{20a}$$

and for the remaining terms the expectation values $\langle e^{in\phi}\rangle_L$ are needed. Since $e^{in\phi}$, $n \neq 3m$, is purely off-diagonal with respect to the symmetry Γ in the basis $\{|\nu\Gamma\rangle\}$ and

$$\langle X_{\nu\Gamma; \nu'\Gamma'}\rangle_L = \delta_{\Gamma,\Gamma'} \langle X_{\nu\Gamma; \nu'\Gamma}\rangle_L \tag{21}$$

holds because H_L is diagonal with respect to Γ, it is immediately evident that

$$\langle R_{2,m}^{E^a}(\Theta_\lambda; \Omega_0; \phi)\rangle_L = \langle R_{2,m}^{E^b}(\Theta_\lambda; \Omega_0; \phi)\rangle_L \equiv 0. \tag{20b}$$

Therefore, we have

$$\langle H_{IL}^\lambda \rangle_L = d_\lambda \sum_{m=-2}^{2} (-1)^m R_{2,-m}^A(\Theta_\lambda; \Omega_0) T_{2,m}^A(\lambda) \tag{22a}$$

and correspondingly

$$\Delta H_{IL}^\lambda = d_\lambda \sum_{\Gamma=E^a,E^b} \sum_{m=-2}^{2} (-1)^m R_{2,-m}^\Gamma(\Theta_\lambda; \Omega_0; \phi) T_{2,m}^{\Gamma_c}(\lambda). \tag{22b}$$

This decomposition immediately leads to the conclusion that only symmetry-changing transitions are relevant for the transition probabilities. This conclusion is independent of the perturbational calculation of the transition probabilities and is due only to the independence of the $R_{2,m}^A$ of the rotation angle ϕ. It explains Haupt's [32] finding that symmetry-conserving transitions do not contribute to T_1 in CH_3 systems in second order. It will be seen later that this does not hold rigorously if intermolecular dipolar interactions are taken into account additionally.

For the static Hamiltonian $\langle H_{IL}^\lambda \rangle_L$, which supplements the Zeeman Hamiltonian, it is sufficient to retain only the so-called secular part $\langle H_{IL}^{\lambda'} \rangle_L$, which commutes with H_z [23]:

$$\langle H_{IL}^{\lambda'} \rangle_L = d_\lambda R_{2,0}^A(\Theta_\lambda; \Omega_0) T_{2,0}^A(\lambda). \tag{23}$$

This operator does not mix spin states of different magnetic quantum number. Then, the spin states $|\Gamma m\rangle$ are the ones given e.g. in [32] for CH_3, where $\langle H_{IL}^{D'} \rangle_L$ does not mix spin states of different spin quantum number I. This does not hold for CD_3. Here the secular static part of the quadrupolar Hamiltonian mixes spin states of different spin quantum number I but the same magnetic quantum number m. Thus, I is not a good quantum number in the case of CD_3. The eigenstates of H_I are given as linear combinations of states with different I in appendix 2. Thus, we have for both cases, CH_3 and CD_3,

$$H_I |\Gamma m\rangle = E_{\Gamma m}^I |\Gamma m\rangle \tag{24}$$

where the deviations of $E_{\Gamma m}^I$ from $E_{\Gamma m}^z = -m\omega_z$ are small, of the order of $O(d_\lambda/\omega_z)$ ($\simeq 10^{-2}$). Consequently, we find for the transition probabilities (14):

$$P_{\Gamma' m';\Gamma m}^\lambda(\tau) = 2\,\mathrm{Re}\{\langle\langle \Gamma m|\Delta H_{IL}^\lambda(0)|\Gamma' m'\rangle\langle\Gamma' m'|\Delta H_{IL}^\lambda(\tau)|\Gamma m\rangle_L$$

$$\times \exp[-i(E_{\Gamma m}^I - E_{\Gamma' m'}^I)\tau]\} \tag{25}$$

and we are allowed to approximate $E_{\Gamma m}^I - E_{\Gamma' m'}^I$ by $(m'-m)\omega_z$. For the calculation of the time correlation functions occurring in (25), it is convenient to proceed similarly to section 2, i.e. to write

$$\Delta H_{IL}^\lambda(\tau) = \sum_{\nu\Gamma m} \sum_{\nu'\Gamma'm'} \langle\nu\Gamma m|\Delta H_{IL}^\lambda|\nu'\Gamma'm'\rangle X_{\nu\Gamma:\nu'\Gamma'}(\tau)|\Gamma_c m\rangle\langle\Gamma_c'm'|. \tag{26}$$

Thus, (25) becomes

$$P_{\Gamma_c' m';\Gamma_c m}^\lambda(\tau) = 2\,\mathrm{Re}\left(\sum_{\nu\nu'} \sum_{\mu\mu'} \langle\nu\Gamma m|\Delta H_{IL}^\lambda|\nu'\Gamma'm'\rangle\langle\mu'\Gamma'm'|\Delta H_{IL}^\lambda|\mu\Gamma m\rangle \right.$$

$$\left. \times \langle X_{\nu\Gamma:\nu'\Gamma'}(0) X_{\mu'\Gamma':\mu\Gamma}(\tau)\rangle_L \exp[-i(m'-m)\omega_z\tau]\right). \tag{27}$$

Again, the terms with $\nu \neq \mu$ and $\nu' \neq \mu'$ are of minor relevance. Introducing the spectral representation

$$\langle X_{\nu\Gamma;\nu'\Gamma'}(0)X_{\nu'\Gamma';\nu\Gamma}(\tau)\rangle_L = \int_{-\infty}^{\infty} d\omega\, e^{i\omega\tau} S_{\nu,\nu'}^{\Gamma,\Gamma'}(\omega) \tag{28}$$

we have for the Laplace transform of the transition probabilities

$$P_{\Gamma'_e m';\Gamma_e m}^{\lambda}(s) = \int_0^{\infty} d\tau\, e^{-s\tau} P_{\Gamma'_e m';\Gamma_e m}^{\lambda}(\tau)$$

$$= 2\,\mathrm{Re}\left(\sum_{\nu\nu'} |\langle \nu\Gamma m|\Delta H_{IL}^{\lambda}|\nu'\Gamma'm'\rangle|^2 \int_{-\infty}^{\infty} d\omega\, \frac{S_{\nu,\nu'}^{\Gamma,\Gamma'}(\omega)}{s - i[\omega - (m'-m)\omega_z]}\right). \tag{29}$$

Thus, the transition probabilities are determined by the Hilbert–Stieltjes transform [23] of the spectral function $S_{\nu,\nu'}^{\Gamma,\Gamma'}(\omega)$, which also determines the incoherent dynamical structure factor $S(Q,\omega)$ in INS experiments. This is also evident directly from equation (18), which shows that the relevant time correlation functions are of the type $\langle e^{in\phi(0)}e^{-im\phi(\tau)}\rangle_L, n, m = 1, 2$, which are similar to the lowest-order terms in the expansion (1). Therefore, INS and high-field NMR relaxation experiments are determined by exactly the same time correlation functions and we can write

$$P_{\Gamma'_e m';\Gamma_e m}^{\lambda}(s) \propto S(Q \ll r^{-1}, s + i(m'-m)\omega_z).$$

It is easily seen by considering the uncoupled case,

$$S_{\nu,\nu'}^{\Gamma,\Gamma'}(\omega) = \exp(-\beta E_{\nu}^{\Gamma})\delta(E_{\nu}^{\Gamma} - E_{\nu'}^{\Gamma'} - \omega)/Z_R$$

that the most dominant terms in (29) are those with $\nu = \nu'$. In the case of dissipation the δ-function has to be replaced by the appropriate Lorentzian, cf (5). However, $E_{\nu}^{\Gamma} - E_{\nu'}^{\Gamma'} \gg \omega_z$ for $\nu \neq \nu'$ in almost all situations of physical interest. Furthermore, the matrix elements of ΔH_{IL}^{λ} between states of different librational quantum numbers are smaller than those between states of the same librational quantum number for not too small potentials and states with energies well below the barrier height V_3.

At low temperatures, where the librational ground state is predominantly occupied thermally, the transition probabilities are given by the $\nu = \nu' = 0$ terms of (29). If we assume the form (5) for $S_{0,0}^{\Gamma,\Gamma'}(\omega)$, we explicitly have in this case

$$P_{E^a m';Am}^{\lambda}(s) = 2|\langle 0Am|\Delta H_{IL}^{\lambda}|0E^b m'\rangle|^2 \langle X_{0A:0A}\rangle_L$$

$$\times (\gamma + s)/\{(\gamma + s)^2 + [\omega_t(T) - (m'-m)\omega_z]^2\} \tag{30a}$$

$$P_{E^a m';E^b m}^{\lambda}(s) = 2|\langle 0E^a m|\Delta H_{IL}^{\lambda}|0E^b m'\rangle|^2 \langle X_{0E:0E}\rangle_L$$

$$\times (\tilde{\gamma} + s)/\{(\tilde{\gamma} + s)^2 + [(m'-m)\omega_z]^2\}. \tag{30b}$$

Here γ and $\tilde{\gamma}$ denote the broadenings and $\omega_t(T)$ is the temperature-dependent renormalized ground-state splitting Δ_0. The transition probabilities $P_{E^a m';E^b m}^{\lambda}(s)$ are zero in the case of CH$_3$. It is easy to see from (30) that $P_{\Gamma'_e m';\Gamma_e m}^{\lambda}(s)$ can be replaced by $P_{\Gamma'_e m';\Gamma_e m}^{\lambda}(0)$ if $\gamma, \tilde{\gamma} \gg s$. This is the condition to set the upper limit

of the integral in the equation of motion, equation (9), to infinity. However, this is not allowed if γ and $\bar{\gamma}$ are of the order of the inverse measuring time s. It is shown explicitly in appendix 3 that even in this case the substitution of $P^\lambda_{\Gamma'_\epsilon m';\Gamma_\epsilon m}(s)$ by $P^\lambda_{\Gamma'_\epsilon m';\Gamma_\epsilon m}(0)$ induces an error that is formally of the order $O((d_\lambda/\omega_z)^4)$. This is negligible in second order. Furthermore, the same substitution is shown to be allowed also in the area of resonances $\omega_i(T) = (m' - m)\omega_z$. These results are in accord with the more general ones of [23, 33].

Even though we will concentrate ourselves on the discussion of the relations between the spin–lattice relaxation time T_1 and $S(Q, \omega)$, which means we choose only the specific operator $O_{k_0} = I_z$, the following remark concerning the operators O_k seems to be appropriate. There are different ways to choose these operators. One way is to start with an expansion of the spin-density matrix into irreducible tensor operators $T_{l,m}$, where $l = 0, 1, \ldots, 2I$. Then $l = 0, 1, 2, 3$ for a dipolar coupled three-spin-1/2 system ($T_{1,0}$: Zeeman energy; $T_{2,0}$: dipolar energy; $T_{3,0}$: octopolar energy, three-spin order [34]). For deuterons, there are only the Zeeman energy $T_{1,0}$ and the quadrupolar energy $T_{2,0}$. In the next step the number of relevant operators can be reduced for some physical situations; e.g. for protons often the spin temperature concept is valid, which implies $\langle T_{3,0}\rangle_I = 0$. The most important operators are always such operators that are constants of motion with respect to $H_1 + H_L$ and change in time only due to ΔH_{IL}. Such operators are also called quasi-constants of motion [35]. In the case of methyl groups the symmetry species concentrations are additional quasi-constants of the motion as compared to other typical spin systems. These might be represented by operators of the form $O_\Gamma = [\mathrm{Tr}_I(O_\Gamma^2)]^{-1/2}\sum_m |\Gamma m\rangle\langle\Gamma m|$, to be compared to e.g. $I_z = [\mathrm{Tr}_I(I_z^2)]^{-1/2}\sum_{\Gamma m} m|\Gamma m\rangle\langle\Gamma m|$. For CH$_3$, the choice of the operators O_k has been discussed for a variety of physical situations [36]. Whatever the specific choice of the O_k might be, it turns out that the relaxation of the Zeeman energy is coupled to the relaxation of other quasi-constants of motion at low temperatures, i.e. $K_{z,k} \neq 0$, $k \neq z$. However, it is always possible to extract the autorelaxation rate of the Zeeman energy, $K_{z,z} \equiv T_1^{-1}$, from inversion recovery or similar spin–lattice relaxation experiments [37].

Noting that $\langle\Gamma m|I_z|\Gamma m\rangle = m\omega_z$, one finds the Hebel–Slichter equation [38]:

$$T_1(\lambda)^{-1} = \tfrac{1}{2}\sum_{\Gamma m}\sum_{\Gamma' m'} W^\lambda_{\Gamma'_\epsilon m';\Gamma_\epsilon m}(m' - m)^2\omega_z^2 \Big/ \sum_{\Gamma m}(E^z_{\Gamma m})^2 \tag{31}$$

where we have defined

$$W^\lambda_{\Gamma'_\epsilon m';\Gamma_\epsilon m} := \lim_{s\to 0} P^\lambda_{\Gamma'_\epsilon m';\Gamma_\epsilon m}(s) \tag{32}$$

and the $P^\lambda_{\Gamma'_\epsilon m';\Gamma_\epsilon m}(s)$ are given by (29). Thus $T_1(\lambda)$ is a measure of $S(Q \ll r^{-1}, \omega)$ at some multiples of the Larmor precession frequency ω_z and the information from both quantities is directly comparable. What has been called 'correlation time' in much of the NMR literature is identical to the line broadening. Introducing the imaginary part of the Hilbert transform

$$\bar{S}^{\Gamma,\Gamma'}_{\nu,\nu'}(n\omega_z) := \pi\,\mathrm{Re}\left(i\int_{-\infty}^{\infty} d\omega\, \frac{S^{\Gamma,\Gamma'}_{\nu,\nu'}(\omega)}{\omega - n\omega_z}\right) \tag{33a}$$

we find for the transition probabilities

$$W^\lambda_{\Gamma'_c m';\Gamma_c m} = 2\sum_{\nu,\nu'}|\langle\nu\Gamma m|\Delta H^\lambda_{\text{IL}}|\nu'\Gamma'm'\rangle|^2 S^{\Gamma,\Gamma'}_{\nu,\nu'}((m'-m)\omega_z). \quad (33b)$$

This relates the relevant spectral function (4) of neutron scattering with the transition probabilities causing spin–lattice relaxation, one of the main results of this paper.

The squared matrix elements of the interaction Hamiltonian $\Delta H^\lambda_{\text{IL}}$ are given by

$$|\langle\nu\Gamma m|\Delta H^\lambda_{\text{IL}}|\nu'\Gamma'm'\rangle|^2$$
$$= d^2_\lambda|\langle\nu\Gamma|R^{\Gamma''}_{2,m'-m}(\Theta_\lambda;\Omega_0;\phi)|\nu'\Gamma'\rangle|^2|\langle\Gamma_c m|T^{\Gamma''_c}_{2,m-m'}(\lambda)|\Gamma'_c m'\rangle|^2$$
$$(34)$$

where Γ'' is determined by the pair (Γ,Γ').

T_1 experiments are frequently performed on powder samples. In this case it is often allowed to perform an average over T^{-1}_1 rather than over the law governing the time evolution of the magnetization, e.g. $\exp(-t/T_1)$ [31], where averaging is with respect to the orientations of the methyl groups in the sample (i.e. integration over the unit sphere Ω_0). Utilizing the orthogonality of the Wigner rotation matrices [39] one easily finds

$$\langle D^{(2)*}_{m_1,m_2}(\Omega_0)D^{(2)}_{m'_1,m'_2}(\Omega_0)\rangle_{\text{powder}} = \tfrac{1}{5}\delta_{m_1,m'_1}\delta_{m_2,m'_2} \quad (35a)$$

where

$$\langle f(\Omega_0)\rangle_{\text{powder}} := (\tfrac{1}{4}\pi)\int_0^{2\pi}\mathrm{d}\alpha_0\int_0^\pi\sin\beta_0\,\mathrm{d}\beta_0\,f(\Omega_0).$$

This immediately yields

$$\langle|\langle\nu\Gamma|R^{E^a}_{2,n}(\Theta_\lambda;\Omega_0;\phi)|\nu'\Gamma'\rangle|^2\rangle_{\text{powder}}$$
$$= \tfrac{1}{5}[v_1(\Theta_\lambda)^2|\langle\nu\Gamma|e^{i\phi}|\nu'\Gamma'\rangle|^2 + v_2(\Theta_\lambda)^2|\langle\nu\Gamma|e^{-2i\phi}|\nu'\Gamma'\rangle|^2] \quad (35b)$$

which is independent of n (recall that in the case of CH_3 $v_1(\Theta_\lambda)\equiv 0$, cf appendix 1). The transition probabilities (33) can be used to calculate the relaxation matrix occurring in equation (15).

We now turn to the specific cases of CH_3 and CD_3 relaxation. The matrix elements needed in the following have been given earlier in several publications. The matrix elements of the dipolar Hamiltonian can be found in [32] and the ones of the quadrupolar Hamiltonian in the case of CD_3 are given in [31].

3.3. Quadrupolar relaxation of CD_3 groups

For the calculation of $T_1(Q) \equiv T_1(CD_3)$ we use the spin matrix elements given in [31]. Note that for the calculation of T_1 it is irrelevant which basis for the spin states is chosen, since T_1 reflects the relaxation of the Zeeman energy $\langle I_z\rangle_1$. This does not hold if we wanted to calculate, for example, the autorelaxation rate of the quadrupolar energy, T^{-1}_{1Q}. The spin matrix elements are to be combined with the corresponding elements of the type $\langle\nu\Gamma|R^{\Gamma''}_{2,m}(\Theta_Q;\Omega_0;\phi)|\nu'\Gamma'\rangle$. When the squared matrix elements

of $\Delta H_{\rm IL}^{\rm Q}$ are inserted into equation (33) for the transition probabilities, we eventually find

$$T_1(CD_3)^{-1} = T_1(CD_3; A \leftrightarrow E)^{-1} + T_1(CD_3; E \leftrightarrow A)^{-1} + T_1(CD_3; E \leftrightarrow E)^{-1} \quad (36)$$

where

$$T_1(CD_3; A \leftrightarrow E)^{-1} = \tfrac{1}{18} d_Q^2 \sum_{\nu\nu'} \sum_{m=-2}^{2} [|\langle \nu E^a | R_{2,m}^{E^a}(\Theta_Q; \Omega_0; \phi) | \nu' A\rangle|^2$$
$$+ |\langle \nu E^a | R_{2,-m}^{E^a}(\Theta_Q; \Omega_0; \phi) | \nu' A\rangle|^2] m^2 \bar{S}_{\nu,\nu'}^{E,A}(m\omega_z) \quad (37a)$$

$$T_1(CD_3; E \leftrightarrow E)^{-1} = \tfrac{1}{18} d_Q^2 \sum_{\nu\nu'} \sum_{m=-2}^{2} [|\langle \nu E^b | R_{2,m}^{E^a}(\Theta_Q; \Omega_0; \phi) | \nu' E^a\rangle|^2$$
$$+ |\langle \nu E^b | R_{2,-m}^{E^a}(\Theta_Q; \Omega_0; \phi) | \nu' E^a\rangle|^2] m^2 \bar{S}_{\nu,\nu'}^{E,E}(m\omega_z) \quad (37b)$$

and $T_1(CD_3; E \leftrightarrow A)^{-1}$ is obtained from $T_1(CD_3; A \leftrightarrow E)^{-1}$ if $\bar{S}_{\nu,\nu'}^{E,A}(m\omega_z)$ is replaced by $\bar{S}_{\nu,\nu'}^{A,E}(m\omega_z)$ in (37a). To obtain (37) in this form we made use of equation (18c) and the fact that the E states are complex conjugate to each other.

The temperature dependence of $T_1(CD_3)$ has been discussed in [31] and we will not repeat this here. Instead, we restrict ourselves to low temperatures ($\nu = \nu' = 0$ in (37)) and to systems for which the tunnelling frequency $\omega_t(T)$ is much larger than the Larmor precession frequency ω_z. In this situation only $T_1(CD_3; E \leftrightarrow E)$ contributes to the spin–lattice relaxation and $T_1(CD_3)$ is a direct measure of the linewidth of the quasi-elastic $E^a \leftrightarrow E^b$ line in INS experiments. If T_1 experiments are performed using different Larmor frequencies, the lineshape can be analysed in addition to the linewidth, which is not easy in INS owing to elastic intensity in the energy range of interest.

To illustrate this point, let us assume that we are allowed to perform the powder average $\langle T_1(CD_3)^{-1}\rangle_{\rm powder}$. Using (35b) we then have

$$\langle T_1(CD_3; A \leftrightarrow E)^{-1}\rangle_{\rm powder} = C_{AE} \sum_{m=-2}^{2} m^2 \bar{S}_{0,0}^{E,A}(m\omega_z) \quad (38a)$$

$$\langle T_1(CD_3; E \leftrightarrow E)^{-1}\rangle_{\rm powder} = C_{EE} \sum_{m=-2}^{2} m^2 \bar{S}_{0,0}^{E,E}(m\omega_z) \quad (38b)$$

where (cf appendix 1 and equation (18))

$$C_{\Gamma\Gamma'} := \tfrac{1}{45} d_Q^2 [v_1(\Theta_Q)|\langle 0\Gamma|e^{i\phi}|0\Gamma'\rangle|^2 + v_2(\Theta_Q)|\langle 0\Gamma|e^{-2i\phi}|0\Gamma'\rangle|^2]. \quad (38c)$$

For $\omega_t(T) \gg \omega_z$ it is clear that $\bar{S}_{0,0}^{E,A}(m\omega_z) \simeq 0$ and that $\langle T_1(CD_3)^{-1}\rangle_{\rm powder}$ is determined by the spectral functions $\bar{S}_{0,0}^{E,E}(m\omega_z)$. Thus, a T_1 experiment can be viewed as a fixed window measurement in INS [1]. If we furthermore assume that $\bar{S}_{0,0}^{E,E}(m\omega_z)$ is given by the Lorentzian $\langle X_{0E:0E}\rangle_L \bar{\gamma}/(\bar{\gamma}^2 + m^2\omega_z^2)$, cf (5) and (33), we have on the low-temperature side of the T_1 minimum

$$\langle T_1(CD_3)^{-1}\rangle_{\rm powder} = C\bar{\gamma}/\omega_z^2 \quad (39)$$

since here $\tilde{\gamma} \ll \omega_z$. The constant C is given by $C = 4C_{EE}\langle X_{0E:0E}\rangle_L$. Equation (39) allows one to analyse the shape of $\tilde{S}_{0,0}^{E,E}(\omega)$ if the Larmor frequency ω_z is varied in the experiment. The absolute values of $\tilde{\gamma}$ and its temperature dependence can be compared to those obtained from INS data. Thus, a combination of deuteron spin–lattice relaxation experiments and INS experiments performed at different Q values might yield more detailed information about the $E^a \leftrightarrow E^b$ line and the $\Gamma \leftrightarrow \Gamma$ lines than either experimental method alone.

3.4. Dipolar relaxation of CH_3 groups

In the case of CH_3 the dipolar Hamiltonian has only matrix elements between A and E states. Matrix elements between E^a and E^b states are forbidden by spin selection rules, since E states have spin $I = 1/2$ and the dipolar Hamiltonian only contains spin operators of second rank. An arbitrary spin matrix element can be written as $\langle E^b m | T_{2,m-m'}^{E^a}(D) | E^a m' \rangle = C(1/2, 2, 1/2; m', m - m')\langle E^b \| T_2^{E^a}(D) \| E^a \rangle$ where $C(1/2, 2, 1/2; m', m - m')$ is a Clebsch–Gordan coefficient in nomenclature of Rose [39] and $\langle E^b \| T_2^{E^a}(D) \| E^a \rangle$ denotes a reduced matrix element. All these matrix elements vanish identically, since $C(1/2, 2, 1/2; m, n) \equiv 0$. Consequently, it is evident immediately that the spin–lattice relaxation of an isolated CH_3 group is determined *only* by $A \leftrightarrow E$ transitions, as is well known [32]. Thus, we have from (33) and (31)

$$T_1(CH_3)^{-1} = T_1(CH_3; A \leftrightarrow E)^{-1} + T_1(CH_3; E \leftrightarrow A)^{-1} \qquad (40)$$

with

$$T_1(CH_3; A \leftrightarrow E)^{-1} = \tfrac{1}{24}d_D^2 \sum_{\nu\nu'} \sum_{m=-2}^{2} [|\langle \nu E^a | R_{2,m}^{E^a}(\Theta_D; \Omega_0; \phi)|\nu' A\rangle|^2$$

$$+ |\langle \nu E^a | R_{2,-m}^{E^a}(\Theta_D; \Omega_0; \phi)|\nu' A\rangle|^2]m^2 \tilde{S}_{\nu,\nu'}^{E,A}(m\omega_z) \qquad (41)$$

and $T_1(CH_3; E \leftrightarrow A)^{-1}$ is obtained from (39) in the same way as in the CD_3 case.

Thus, the spin–lattice relaxation rate of an isolated CH_3 group is a direct measure of the width of the inelastic $(A \leftrightarrow E)$ tunnelling lines. This means that a temperature- and frequency-dependent study of T_1 of isolated CH_3 groups will yield information about the broadening of the $A \leftrightarrow E$ lines even in the temperature range where the inelastic lines merge into the quasi-elastic lines in an INS experiment, i.e. in the so-called 'quasi-classical' regime. To be more specific, let us consider $\langle T_1(CH_3)^{-1}\rangle_{powder}$ in the same way as in the CD_3 case, which is easily obtained from (40) and (41) using (35b). Thus, we find

$$\langle T_1(CH_3)^{-1}\rangle_{powder} \propto \sum_{m} m^2 \tilde{S}_{0,0}^{E,A}(m\omega_z)$$

which intrinsically relates T_1 to $S(Q \ll r^{-1}, \omega)$. Here we have at low temperatures and for Lorentzian-shaped inelastic $A \leftrightarrow E$ tunnelling lines

$$\langle T_1(CH_3)^{-1}\rangle_{powder} \propto \sum_{m} m^2\gamma/(\gamma^2 + [\omega_t(T) - m\omega_z]^2)$$

which also can allow an analysis of the lineshape in some cases, namely for not too large tunnelling frequencies. In the 'quasi-classical' regime, $\omega_t(T)$ has decayed

to zero and $\langle T_1(CH_3)^{-1}\rangle_{\text{powder}}$ yields the width of the A $\leftrightarrow$ E line. In an INS experiment it is not easy to obtain this information, since there the quasi-elastic peak is a superposition of A $\leftrightarrow$ E, $E^a \leftrightarrow E^b$ and elastic scattering, including symmetry-conserving scattering. On the high-temperature side of the T_1 minimum, $\gamma \gg \omega_z$ holds and $\langle T_1(CH_3)^{-1}\rangle_{\text{powder}}$ is directly proportional to γ^{-1}. Consequently, T_1 experiments on isolated CH_3 groups in combination with INS experiments would be of particular interest to get more detailed information about $S(Q \ll r^{-1}, \omega)$ also at elevated temperatures. (More specific formulae will be given later in connection with the calculation of the intermolecular contributions to T_1.)

Additionally, the same A $\leftrightarrow$ E transitions, which determine the spin–lattice relaxation rate (40), are also responsible for the symmetry conversion rate (spin conversion rate) τ_{con}^{-1} [8], even though T_1 represents the relaxation of the Zeeman spin energy and τ_{con}^{-1} is the relaxation rate of the symmetry species concentration. In fact, both quantities are expected to be of comparable magnitude at low temperatures ($T \ll E_{\text{lib}}$) for systems with large Δ_0 [32]. This, however, is not found experimentally [40]. There is widespread belief that the intermolecular dipolar interactions between the methyl protons and surrounding protons are responsible for the much smaller values of T_1. Usually, the intermolecular contribution to T_1 is handled in a phenomenological way as was done e.g. by Haupt [32]. The only more systematic treatments of intramolecular dipolar interactions known to the author have been given by Clough [41] and Zweers and Brom [42]. Clough treated the problem of spin–lattice relaxation using time-dependent perturbation theory. Even though he did not give explicit expressions for the dependence of the intermolecular contributions to T_1 upon the proton–proton distances and the relative orientations, he showed that $E^a \leftrightarrow E^b$ transitions, which are much more effective than A $\leftrightarrow$ E transitions for large tunnelling frequencies, additionally contribute to T_1.

In order to render the discussion concerning the influence of intermolecular contributions to spin–lattice relaxation of CH_3 groups more quantitative, we now turn to calculation of the spin–lattice relaxation rates due to dipolar interactions between the methyl protons and surrounding protons. For this purpose we write the dipolar Hamiltonian for a proton i and the protons of the CH_3 group similarly to appendix 1 as

$$H_{\text{IL}}^{\text{D}}(i) = -\gamma_I^2 \sum_{\Gamma} \sum_{m=-2}^{2} (-1)^m \bar{R}_{2,-m}^{\Gamma}(i;\phi) T_{2,m}^{\Gamma_c}(i) \tag{42a}$$

where (cf (A1.4), [22, 29])

$$\bar{R}_{2,m}^{\Gamma}(i;\phi) = \sqrt{\left(\frac{8\pi}{5}\right)} \sum_{n=-2}^{2} D_{n,m}^{(2)}(\Omega_0)$$
$$\times \left(Y_{2,n}(\omega_{i1})/(R_{i1})^3 + \mathcal{E}^{-\kappa} Y_{2,n}(\omega_{i2})/(R_{i2})^3 + \mathcal{E}^{\kappa} Y_{2,n}(\omega_{i3})/(R_{i3})^3\right) \tag{42b}$$

and

$$T_{2,0}^{\Gamma}(i) = \sqrt{(2/3)}[I_z^{(i)} I_z^{\Gamma} - \tfrac{1}{4}(I_+^{(i)} I_-^{\Gamma} + I_-^{(i)} I_+^{\Gamma})]$$
$$T_{2,\pm1}^{\Gamma}(i) = \mp(I_z^{(i)} I_\pm^{\Gamma} + I_\pm^{(i)} I_z^{\Gamma}) \qquad T_{2,\pm2}^{\Gamma}(i) = \tfrac{1}{2} I_\pm^{(i)} I_\pm^{\Gamma}. \tag{42c}$$

Here $I_n^{(i)}$ acts on the spin states of the proton i and $I_n^\Gamma = (1/\sqrt{3})(I_n^{(1)} + \mathcal{E}^{-\kappa} I_n^{(2)} + \mathcal{E}^\kappa I_n^{(3)})$, $\mathcal{E} = \exp(i2\pi/3)$, $\kappa \equiv 0, 1, -1$ for $\Gamma \equiv A, E^a, E^b$, respectively, acts on the spin states of the methyl group. In (42b) ω_{iu} and R_{iu} denote the orientation of proton i relative to methyl proton u and their distance apart. The form of (42) is in accord with the one given by Clough [41]. To proceed, we perform a series expansion of the distance dependence of the operators $R_{2,m}^\Gamma(i;\phi)$ in powers of (r/R_i), where R_i is the distance of proton i from the centre of the group. This expansion is achieved by using the gradient formula of Rose [39] in the form given by Nijman and Berlinsky [7]:

$$(\boldsymbol{r}_u \cdot \boldsymbol{\nabla}) \frac{Y_{L,n}(\omega_{iu})}{(R_{iu})^{L+1}} = -(2L+1)\sqrt{\left(\frac{L+1}{2L+3}\right)}$$

$$\times \sum_m C(1,L,L+1;m,n)(r_u^m)^* \frac{Y_{L+1,n+m}(\omega_{iu})}{(R_{iu})^{L+2}} \tag{43}$$

where r_u^m is the mth spherical component of $\boldsymbol{r}_u$; in our case $r_u^0 = 0$, $r_u^{\pm 1} = \mp(1/\sqrt{2})r\exp(\pm i\phi_u)$, $\phi_1 := \phi$, $\phi_2 := \phi + 2\pi/3$, $\phi_3 := \phi - 2\pi/3$ in the rigid rotor approximation. The derivative has to be taken at $\omega_i \equiv (\Theta_i, \Phi_i)$ and R_i, where ω_i denotes the orientation of the proton with respect to the centre of the CH_3 group in a crystal-fixed frame. In the following we keep the protons i fixed at their equilibrium coordinates (ω_i, R_i). This means that we neglect the dependence of (ω_i, R_i) on the phonons and thus on time. This is a reasonable assumption for protons located on the same molecule to which the methyl group is attached. Otherwise there is no physical justification for this approximation, since it is the neighbours of a methyl group that are also responsible for the rotational dynamics. However, a careful treatment of this point is beyond the scope of the present paper. With the definition

$$d_D^i := -\gamma_I^2 R_i^{-3} \tag{44}$$

the Hamiltonian for the intermolecular dipolar interaction can be written as

$$H_{IL}^D(i) = d_D^i \sum_\Gamma \sum_{m=-2}^{2} (-1)^m R_{2,-m}^\Gamma(i;\phi) T_{2,m}^{\Gamma}(i) \tag{45}$$

where the operators $R_{2,m}^\Gamma(i;\phi)$ represent series expansions in powers of (r/R_i) of the form $R_{2,m}^\Gamma(i;\phi) = \sum_k R_{2,m}^\Gamma(i;\phi)^{(k)}$, where $R_{2,m}^\Gamma(i;\phi)^{(k)}$ is of order $O((r/R_i)^k)$. The expressions for the terms $R_{2,m}^\Gamma(i;\phi)^{(k)}$ up to $k = 3$ are given explicitly in appendix 4. Here we only note the following fact. The operators $R_{2,m}^{E^a}(i;\phi)^{(k)}$ are of the type $e^{i\phi}, e^{-2i\phi}$. In contrast to intra-methyl interactions, in $O((r/R_i)^3)$ one finds that $R_{2,m}^A(i;\phi)^{(3)}$ is a function $f(e^{3i\phi})$, which is an operator acting on the rotational states. Thus, in this order also correlation functions of the type $\langle e^{3i\phi(0)} e^{-3i\phi(t)} \rangle_L$ contribute to the transition probabilities and thus to spin–lattice relaxation. These types of time correlation functions are similar to higher-order terms in the expansion (1) of $S(Q,\omega)$ and consequently the correspondence between T_1^{-1} and $S(Q \ll r^{-1}, \omega)$ is violated if these terms are considered additionally. Furthermore, it is evident that the static part of $H_{IL}^D(i)$, $\langle H_{IL}^D(i) \rangle_L$, now contains terms $\langle e^{3i\phi} \rangle_L$, which are diagonal in the basis $\{|\nu\Gamma\rangle\}$. Thus, $\langle H_{IL}^D(i) \rangle_L$ is temperature

dependent in this case, which could be studied by recording the high-field NMR spectra of systems containing methyl groups closely surrounded by other protons as a function of temperature. However, it is not our present purpose to quantify this effect. Instead, we turn to the calculation of the intermolecular contribution to T_1 due to (45) in $O((r/R_i)^4)$, where symmetry-conserving transitions do not contribute. The calculation is very similar to the one performed before; only the spin states are to be modified. With the definition

$$|\Gamma M\rangle := |\Gamma m\rangle|m_i\rangle \tag{46}$$

where $|\Gamma m\rangle$ are the spin states of the CH_3 group and $|m_i\rangle$ those of the proton i, $M := m + m_i$, we have for the transition probabilities in close relation to (33):

$$W^D_{\Gamma_c'M';\Gamma_c M}(i) = 2\sum_{\nu,\nu'} |\langle\nu\Gamma M|\Delta H^D_{IL}(i)|\nu'\Gamma'M'\rangle|^2 \tilde{S}^{\Gamma,\Gamma'}_{\nu,\nu'}((M'-M)\omega_z). \tag{47}$$

Here only E-symmetric operators contribute to $\Delta H^D_{IL}(i)$ in $O((r/R_i)^2)$, cf (22) and (A4.4), and the states $|\nu\Gamma M\rangle$ are given by $|\nu\Gamma\rangle|\Gamma_c M\rangle$. Following Clough [41], we write for the spin–lattice relaxation rate

$$T_1(CH_3; \text{total})^{-1} = T_1(CH_3)^{-1} + \sum_i T_1(CH_3; i)^{-1} \tag{48}$$

where $T_1(CH_3)^{-1}$ is given by (40) and (41) and $T_1(CH_3; i)^{-1}$ is given by a Hebel–Slichter formula analogous to (31) but with the transition probabilities (47). Without giving the explicit evaluation of the spin matrix elements here, we quote that the results can be written as

$$T_1(CH_3; i)^{-1} = T_1(CH_3; i; A \leftrightarrow E)^{-1} + T_1(CH_3; i; E \leftrightarrow A)^{-1} + T_1(CH_3; i; E \leftrightarrow E)^{-1} \tag{49}$$

where

$$T_1(CH_3; i; A \leftrightarrow E)^{-1} = \tfrac{1}{42}(d^i_D)^2 \sum_{\nu\nu'} \sum_{m=-2}^{2} [|\langle\nu E^a|R^{E^a}_{2,m}(i;\phi)|\nu'A\rangle|^2$$
$$+ |\langle\nu E^a|R^{E^a}_{2,-m}(i;\phi)|\nu'A\rangle|^2]m^2 \tilde{S}^{E,A}_{\nu,\nu'}(m\omega_z) \tag{50a}$$

$$T_1(CH_3; i; E \leftrightarrow E)^{-1} = \tfrac{1}{42}(d^i_D)^2 \sum_{\nu\nu'} \sum_{m=-2}^{2} [|\langle\nu E^b|R^{E^a}_{2,m}(i;\phi)|\nu'E^a\rangle|^2$$
$$+ |\langle\nu E^b|R^{E^a}_{2,-m}(i;\phi)|\nu'E^a\rangle|^2]m^2 \tilde{S}^{E,E}_{\nu,\nu'}(m\omega_z) \tag{50b}$$

and $T_1(CH_3; i; E \leftrightarrow A)^{-1}$ is obtained from $T_1(CH_3; i; A \leftrightarrow E)^{-1}$ in the same manner as before.

   Thus, the intermolecular dipolar interactions modify the $A \leftrightarrow E$ relaxation rates and they lead to $E^a \leftrightarrow E^b$ relaxation rates. Using our formulae these contributions can be calculated in any desired order of r/R_i. It is evident immediately from (40), (48) and (49) that for systems with large tunnelling frequencies T_1 is mainly determined by

intermolecular dipolar interactions, as $T_1(\mathrm{CH_3}; \mathrm{A} \leftrightarrow \mathrm{E})^{-1}$ and $T_1(\mathrm{CH_3}; i; \mathrm{A} \leftrightarrow \mathrm{E})^{-1}$ are negligibly small in such situations.

In many proton spin–lattice relaxation experiments it is allowed to perform a powder average of $T_1^{-1}, \langle T_1^{-1} \rangle_{\text{powder}}$. Up to $O((r/R_i)^4)$ one finds from (35a) and (A4.4)

$$\langle T_1(\mathrm{CH_3}; i; \mathrm{A} \leftrightarrow \mathrm{E})^{-1} \rangle_{\text{powder}}$$

$$= (d_{\mathrm{D}}^i)^2 (r/R_i)^2 \sum_{\nu\nu'} A_{\nu\nu'}(\omega_i; r/R_i) \sum_{m=-2}^{2} m^2 \tilde{S}_{\nu,\nu'}^{\mathrm{E,A}}(m\omega_z) \tag{51a}$$

$$\langle T_1(\mathrm{CH_3}; i; \mathrm{E} \leftrightarrow \mathrm{E})^{-1} \rangle_{\text{powder}}$$

$$= (d_{\mathrm{D}}^i)^2 (r/R_i)^2 \sum_{\nu\nu'} B_{\nu\nu'}(\omega_i; r/R_i) \sum_{m=-2}^{2} m^2 \tilde{S}_{\nu,\nu'}^{\mathrm{E,E}}(m\omega_z) \tag{51b}$$

with

$$A_{\nu\nu'}(\omega_i; r/R_i) = \frac{24\pi}{175} \sum_{n=-2}^{2} |X_1^{\mathrm{E}}(n) Y_{3,n-1}(\omega_i) \langle \nu \mathrm{E^a}|e^{i\phi}|\nu'\mathrm{A}\rangle$$

$$+ (r/R_i) X_2^{\mathrm{E}}(n) Y_{4,n+2}(\omega_i) \langle \nu \mathrm{E^a}|e^{-2i\phi}|\nu'\mathrm{A}\rangle|^2 \tag{52a}$$

where $Y_{l,m}(\omega)$ are spherical harmonics and the $X_k^{\mathrm{E}}(n)$ are the expansion coefficients given in (A4.5). For $B_{\nu\nu'}(\omega_i; r/R_i)$ one has the same expression but with the rotor matrix elements $\langle \nu \mathrm{E^a}|e^{i\phi}|\nu'\mathrm{A}\rangle$ and $\langle \nu \mathrm{E^a}|e^{-2i\phi}|\nu'\mathrm{A}\rangle$ replaced by $\langle \nu \mathrm{E^b}|e^{i\phi}|\nu'\mathrm{E^a}\rangle$ and $\langle \nu \mathrm{E^b}|e^{-2i\phi}|\nu'\mathrm{E^a}\rangle$, respectively. If the rotor matrix elements are chosen to be real, one eventually finds a surprisingly simple expression:

$$A_{\nu\nu'}(\omega_i; r/R_i) = \tfrac{9}{70}[2(2 - \cos^2\Theta_i)\langle \nu \mathrm{E^a}|e^{i\phi}|\nu'\mathrm{A}\rangle^2$$

$$+ 5(r/R_i)\sin^3\Theta_i \cos(3\Phi_i)\langle \nu \mathrm{E^a}|e^{i\phi}|\nu'\mathrm{A}\rangle\langle \nu \mathrm{E^a}|e^{-2i\phi}|\nu'\mathrm{A}\rangle$$

$$+ \tfrac{1}{32}(r/R_i)^2(90\cos^4\Theta_i - 420\cos^2\Theta_i + 346)\langle \nu \mathrm{E^a}|e^{-2i\phi}|\nu'\mathrm{A}\rangle^2] \tag{52b}$$

and a similar one for $B_{\nu\nu'}(\omega_i; r/R_i)$.

Proton spin–lattice relaxation experiments are frequently analysed using the formula [17, 19–21]

$$\langle T_1^{-1} \rangle_{\text{powder}} \simeq C_1 \sum_{m=-2}^{2} \frac{m^2\tau}{1 + [\omega_t(T) + m\omega_z]^2\tau^2} + C_2 \sum_{m=1}^{2} \frac{m^2\tau}{1 + (m\omega_z)^2\tau^2} \tag{53}$$

where C_1, C_2, τ and $\omega_t(T)$ are usually fitted parameters and C_1 is of the order of $5C_2$ to $1000C_2$. Using (33b) and (5) with $\langle X_{0\Gamma;0\Gamma} \rangle_{\mathrm{L}} \simeq 1/3$ (high potential barriers) in addition to the expressions derived above, we find

$$C_1 \simeq \tfrac{3}{40} d_{\mathrm{D}}^2 \langle 0\mathrm{E^a}|e^{-2i\phi}|0\mathrm{A}\rangle^2 + \tfrac{2}{3}\sum_i (d_{\mathrm{D}}^i)^2 (r/R_i)^2 A_{00}(\omega_i; r/R_i) \tag{54a}$$

$$C_2 \simeq \tfrac{2}{3}\sum_i (d_{\mathrm{D}}^i)^2 (r/R_i)^2 B_{00}(\omega_i; r/R_i) \tag{54b}$$

if $\gamma \equiv \bar{\gamma} \equiv \tau^{-1}$ and $\nu = \nu' = 0$ are chosen.

The connection to the case of an isolated CH_3 group is made by simply setting $(r/R_i) = 0$ in the above expressions. Then only the first term of C_1 survives and $C_2 = 0$.

To give an illustrative example, we consider the following experiment performed by Müller-Warmuth *et al* [16]. These authors studied the spin–lattice relaxation of toluene and toluene-d_5 (only the methyl group protonated) diluted in perdeuterated toluene-d_8 and found an increasing spin–lattice relaxation time with increasing dilution, demonstrating the importance of intermolecular dipolar interactions. If we use as a simple model a CH_3 group surrounded by a sphere of protons, we have $[\frac{3}{7}\langle 0E^a|e^{i\phi}|0A\rangle^2 + \frac{9}{10}(r/R)^2\langle 0E^a|e^{-2i\phi}|0A\rangle^2]p$ for A_{00} instead of the sum over the different protons in (54), where R is the radius of the sphere and p denotes the number of protons. We only consider toluene-d_5 diluted in toluene-d_8. Since there are eight molecules per unit cell in α-toluene [43], we use $p = 24$ in this case and multiply A_{00} by 0.1 and 0.25 in the cases of 10% and 25% toluene-d_5, respectively. Estimating the rotor matrix elements in a harmonic oscillator approximation [44] yields $\langle 0E^a|e^{i\phi}|0A\rangle \simeq \langle 0E^b|e^{i\phi}|0E^a\rangle \simeq 0.97$ and $\langle 0E^a|e^{-2i\phi}|0A\rangle \simeq \langle 0E^b|e^{-2i\phi}|0E^a\rangle \simeq 0.87$. Using these values and $(r/R) = 0.51$ we have for 10% toluene-d_5 in toluene-d_8 $C_2/C_1 = 7\times 10^{-3}$ and for 25% toluene-d_5 $C_2/C_1 = 1.6\times 10^{-2}$, to be compared to the experimentally found ratios $C_2(\exp)/C_1(\exp)$ which equal 6.6×10^{-3} and 1.6×10^{-2}, respectively. Thus, even this quite unrealistic model for the intermolecular dipolar interactions yields reliable results. If we evaluate the spin–lattice relaxation times at $T = 12$ K with the parameters given by the authors, we find for pure toluene $T_1(12\ \text{K}) = 2.3$ s to be compared to the value $T_1^{\text{intra}}(12\ \text{K}) \simeq 30$ h for $C_2 = 0$. This latter value is easily seen to be of the order of magnitude of typical spin conversion times [8]. Additionally, we note that our simplified model yields an intermolecular contribution to the constant C_1 of less than 3%, which also is in accord with the experimental finding that $C_1(\exp)$ remains unaltered for all systems studied by the authors. This fact shows that the modification of the relaxation efficiency of A $\leftrightarrow$ E transitions due to intermolecular dipolar interactions is rather small. We expect that the same holds for intermolecular contributions to the spin conversion rate, which we consider as an indication of the validity of the model used in [8], namely to consider only intra-methyl dipolar interactions.

4. Discussion

We have applied the modern theory of high-field nuclear spin–lattice relaxation to the specific problem of rotating methyl groups in solids. This way we showed that symmetry-conserving transitions do not contribute to spin relaxation of single methyl groups in accord with Haupt's [32] finding. The static spin Hamiltonian in our treatment corresponds to the so-called 'time-averaged' spin–lattice Hamiltonian in semiclassical spin relaxation theory.

Our formulation of the problem is chosen in such a way as to show that the transition probabilities relevant for spin relaxation are determined by exactly the same spectral functions as is the incoherent dynamical structure factor $S(Q \ll r^{-1}, \omega)$. Since this is true for all elements of the relaxation kernel (13), not only the relaxation rate of the Zeeman energy, T_1^{-1}, but also all other spin relaxation rates (e.g. the relaxation of the quadrupolar energy in the CD_3 case, T_{1Q}^{-1}) are related intrinsically

to $S(Q \ll r^{-1}, \omega)$. In all cases the spin relaxation rates are linear functions of the spectral functions $S_{\nu,\nu'}^{\Gamma,\Gamma'}(\omega)$ at some definite multiples of the Larmor frequency ω_z. Owing to the different spins of CH_3 and CD_3, the spin–lattice relaxation time is a measure of different transition lines in an INS experiment.

In the case of CD_3 it would be interesting to perform INS and NMR experiments on systems with large tunnelling frequencies in order to obtain detailed information about the shape and the width of the $E^a \leftrightarrow E^b$ line and also about the lines that do not involve symmetry-changing transitions. In addition to the already quoted possibility of an analysis of the lineshape, a comparison of the linewidths $\bar{\gamma}_{NMR}$ and $\bar{\gamma}_{INS}$ can be used for testing Würger's [18] result that symmetry-conserving transitions do not lead to a line broadening. If this holds, $\bar{\gamma}_{NMR}$ should equal $\bar{\gamma}_{INS}$. In the case of a finite broadening of the $0\Gamma \leftrightarrow 0\Gamma$ lines, the quasi-elastic widths extracted from deuteron T_1 experiments are expected to be smaller than those obtained from INS experiments at higher momentum transfer ($Q \gtrsim r$), since symmetry-conserving transitions do *not* contribute to deuteron T_1 at all.

Deuteron T_1 experiments can also be helpful in a more detailed analysis of the isotope effect in systems of coupled methyl groups, such as $(CH_3)_2SnCl_2$ [45] or lithium acetate [46]. In the case of coupled pairs of methyl groups, the spectral function contains a transition line at very low frequency due to a splitting of the E^aE^a and E^aE^b states in these systems [47], which is not easily resolved by means of INS. A study of the frequency dependence of deuteron T_1 at low temperatures can provide this information if the mentioned splitting does not exceed the range of accessible Larmor frequencies.

The reason for the direct comparability of deuteron NMR and INS experiments lies in the fact that the dominant interaction in the case of deuterons is the quadrupolar interaction. This is a single-particle interaction from an NMR point of view and thus allows the observations of single methyl rotors as in incoherent neutron scattering. This also means that deuteron T_1 experiments are able to distinguish inequivalent methyl groups in a crystal, as has recently been demonstrated for α-crystalline toluene [48].

In CH_3, the situation is quite different. The dipolar interaction is a many-particle interaction. Thus, dilute systems are to be considered in order to render NMR experiments directly comparable to INS experiments. In this case, T_1 is a measure of the shape and the width of the $A \leftrightarrow E$ lines in the whole temperature range of experimental interest. Therefore, a combination of INS and NMR experiments on diluted CH_3 systems would yield information about the structure factor $S(Q \ll r^{-1}, \omega)$ also in the temperature range where the lines in an INS experiment have merged into a single quasi-elastic feature. Once the width of the $A \leftrightarrow E$ lines is obtained from proton NMR, this can be used as input for the determination of the $E^a \leftrightarrow E^b$ linewidth from INS experiments as proposed by Würger [49]. Such an analysis of data has not been done until now to the author's knowledge and would be desirable for a deeper understanding of the broadening mechanisms in the 'high'-temperature range.

Furthermore, the importance of dipolar interactions between methyl protons and surrounding protons has been pointed out and we gave explicit expressions for these contributions to T_1 in $O((r/R_i)^4)$. These might be helpful for more quantitative interpretations of proton NMR T_1 data than has been possible up to now. Using our equations (51) and (52), the intermolecular dipolar interactions can be determined

up to fourth order in (r/R_i), if the proton–proton distances of the compound under study are known. The validity of the truncation of the series expansion used in our calculation could be checked by careful measurements of the temperature dependence of high-field NMR spectra, since temperature effects on these are expected in $O((r/R_i)^6)$. From (53) and (54) it is evident that the intermolecular contribution to A $\leftrightarrow$ E transitions is generally small. Thus, for systems with large tunnelling frequencies the spin–lattice relaxation time is mainly determined by intermolecular dipolar interactions, whereas the spin conversion time is a measure of the intra-methyl dipolar interactions.

When pure CH_3 systems are considered, the relation between T_1 and $S(Q \ll r^{-1}, \omega)$ is violated. From our treatment of the intermolecular dipolar interactions, one could conclude that in this case the situation for systems with large tunnelling frequencies would be comparable to the CD_3 case, the difference being mainly in the different ranges of Q values. Note, however, that we did not allow for a direct coupling of the intermolecular dipolar interactions to the phonons. Here, a combination of INS and NMR experiments might be able to test the validity of this approximation.

In conclusion, we have shown that specific combinations of INS and high-field NMR relaxation experiments can yield more detailed information about the motional spectrum of methyl groups than either experimental method alone. Such experiments could resolve some of the problems of each of the methods and allow more direct comparison to theoretical approaches to the problem than has been possible up to now.

Appendix 1. The spin–lattice coupling Hamiltonians $H_{\mathrm{IL}}^{\lambda}$

In the principal-axis-fixed frame 'P', the quadrupolar interaction of a deuteron $u = 1, 2, 3$ with an axially symmetric electric field gradient (EFG) can be written as

$$[H_{\mathrm{IL}}^Q(\mathrm{P})]^{(u)} = d_Q[3(I_z^{(u)})^2 - (I^{(u)})^2] \tag{A1.1}$$

where

$$d_Q = e^2 q Q/4.$$

Here, eq denotes the non-vanishing component of the EFG [29, 30] and Q the quadrupolar moment of the deuteron.

The dipolar interaction between two protons u and v reads as

$$[H_{\mathrm{IL}}^D(\mathrm{P})]^{(uv)} = d_D[2I_z^{(u)}I_z^{(v)} - \tfrac{1}{2}(I_+^{(u)}I_-^{(v)} + I_-^{(u)}I_+^{(v)})] \tag{A1.2}$$

$$d_D = -\gamma_I^2 r_{(uv)}^{-3}$$

where γ_I is the gyromagnetic ratio and $r_{(uv)}$ the separation of the protons and represents the z axis of the principal-axis-fixed frame. The operators $I_n^{(u)}$ are spin operators acting on the spin states of particle u.

In an arbitrary frame of reference the Hamiltonians (A1.1) and (A1.2) read in irreducible tensor operator notation [29]

$$(H_{\rm IL}^\lambda)^{(k)} = d_\lambda \sum_{m=-2}^{2} (-1)^m R_{2,-m}^{(k)}(\Omega_\lambda^{(k)}) T_{2,m}^{(k)}(\lambda) \tag{A1.3}$$

where $\lambda = {\rm D}$ means dipolar interaction between two protons and $\lambda = {\rm Q}$ means quadrupolar interaction in the case of deuterons. In the first case k stands for the pairs of protons considered (e.g. the pair u and v) and in the latter k stands for the deuteron under study. Transforming the $R_{2,m}^{(k)}(\Omega_\lambda^{(k)})$ successively into a crystal-fixed frame 'C', where the z axis coincides with the methyl rotation axis, and then into the laboratory-fixed frame 'L', where the z axis is determined by the direction of the external magnetic field, yields:

$$R_{2,m}^{(k)}(\Omega_\lambda^{(k)}) = \sqrt{6} \sum_{n=-2}^{2} D_{0,n}^{(2)}(\Omega_\lambda^{(k)}[{\rm PC}]) D_{n,m}^{(2)}(\Omega_0) \tag{A1.4}$$

where $\Omega_\lambda^{(k)}[{\rm PC}] \equiv (0, \Theta_\lambda, \pi - \Phi_\lambda^{(k)})$ defines the orientation of the 'P' system in the 'C' system and $\Omega_0 \equiv (\alpha_0, \beta_0, 0)$ defines the orientation of the 'L' system in the 'C' system. Note that Θ_λ is independent of the particles considered, since the methyl rotation axis is the z axis of the 'C' system. For CD_3, $\Theta_{\rm Q}$ is given approximately by the tetrahedral angle $\Theta_{\rm T}$ ($\cos \Theta_{\rm T} = 1/3$); and for CH_3, $\Theta_{\rm D} = \pi/2$. In the rigid rotor approximation [1, 15] we can write for the azimuthal angles $\Phi_\lambda^{(k)}$: $\Phi_\lambda^{(I)} = \phi$, $\Phi_\lambda^{(II)} = \phi + 2\pi/3$, $\Phi_\lambda^{(III)} = \phi - 2\pi/3$, where $\phi = \frac{1}{3}(\phi_1 + \phi_2 + \phi_3)$ and for $\lambda = {\rm Q}$ $({\rm I, II, III}) \equiv (1, 2, 3)$ (deuterons) and for $\lambda = {\rm D}$ $({\rm I, II, III}) \equiv ((1,2),(2,3),(3,1))$ (pairs of protons).

Symmetry adaptation of the Hamiltonian is achieved by defining (cf (17))

$$R_{2,m}^\Gamma(\Theta_\lambda; \Omega_0; \phi) := R_{2,m}^{(I)}(\Omega_\lambda^{(I)}) + \mathcal{E}^{-\kappa} R_{2,m}^{(II)}(\Omega_\lambda^{(II)}) + \mathcal{E}^\kappa R_{2,m}^{(III)}(\Omega_\lambda^{(III)}). \tag{A1.5}$$

Here, $\kappa \equiv 0, 1, -1$ for $\Gamma \equiv {\rm A}, {\rm E}^{\rm a}, {\rm E}^{\rm b}$. This way the $R_{2,m}^\Gamma(\Theta_\lambda; \Omega_0; \phi)$ given in (18) are obtained, where

$$v_0(\Theta_\lambda) = (3/\sqrt{2})(3\cos\Theta_\lambda - 1)$$
$$v_1(\Theta_\lambda) = (3\sqrt{3}/2)\sin(2\Theta_\lambda) \qquad v_2(\Theta_\lambda) = (3\sqrt{3}/2)\sin^2\Theta_\lambda. \tag{A1.6}$$

For CH_3, one has $(\Theta_{\rm D} = \pi/2)$: $v_0(\pi/2) = -(3/\sqrt{2}), v_1(\pi/2) = 0, v_2(\pi/2) = 3\sqrt{3}/2$. If we approximate $\Theta_{\rm Q}$ by $\Theta_{\rm T}$, we have for CD_3: $v_0(\Theta_{\rm T}) = -\sqrt{2}, v_1(\Theta_{\rm T}) = \sqrt{(8/3)}, v_2(\Theta_{\rm T}) = 4/\sqrt{3}$. Note that in the case of CH_3 operators of the type $e^{i\phi}$ do not contribute, since $v_1(\pi/2) = 0$. The symmetry-adapted spin operators are of similar type as given in (A1.5). Explicit expressions for these operators may be found in [29, 32, 38].

Appendix 2. Eigenstates of H_1 for CD_3

In the high-field approximation H_1 can be written as

$$H_1 = -\omega_z I_z + v_0(\Theta_Q) D^{(2)}_{0,0}(\Omega_0) T^A_{2,0}(Q) \tag{A2.1}$$

which is a pure spin operator. Diagonalization of the matrix (A2.1) yields the following eigenstates $|\Gamma,$ quadrupolar energy, $m\rangle$ starting from the eigenstates of I^2, $|\Gamma, I, m\rangle$, given in [31]:

$$|A, -q, \pm 3\rangle = |A, 3, \pm 3\rangle \qquad |A, 0, \pm 2\rangle = |A, 3, \pm 2\rangle$$
$$|A, -q, \pm 1\rangle = (1/\sqrt{5})(2|A, 1, \pm 1\rangle + |A, 3, \pm 1\rangle)$$
$$|A, q, \pm 1\rangle = (1/\sqrt{5})(|A, 1, \pm 1\rangle - 2|A, 3, \pm 1\rangle) \tag{A2.2}$$
$$|A, 2q, 0\rangle = (1/\sqrt{5})(\sqrt{2}|A, 3, 0\rangle - \sqrt{3}|A, 1, 0\rangle)$$
$$|A, 0_{(1)}, 0\rangle = (1/\sqrt{5})(\sqrt{3}|A, 3, 0\rangle + \sqrt{2}|A, 1, 0\rangle) \qquad |A, 0_{(2)}, 0\rangle = |A, 0, 0\rangle$$

and

$$|E^a, 0, \pm 2\rangle = |E^a, 2, \pm 2\rangle$$
$$|E^a, q, \pm 1\rangle = (1/\sqrt{2})(|E^a, 1, \pm 1\rangle \mp |E^a, 2, \pm 1\rangle)$$
$$|E^a, -q, \pm 1\rangle = (1/\sqrt{2})(E^a, 1, \pm 1\rangle \pm |E^a, 2, \pm 1\rangle) \tag{A2.3}$$
$$|E^a, 0_{(1)}, 0\rangle = |E^a, 1, 0\rangle$$
$$|E^a, 0_{(2)}, 0\rangle = |E^a, 2, 0\rangle$$

$$|E^b, \text{ quadrupolar energy, } m\rangle = (|E^a, \text{ quadrupolar energy, } m\rangle)^*.$$

Here we have used the abbreviation:

$$q := (1/\sqrt{2}) v_0(\Theta_Q) D^{(2)}_{0,0}(\Omega_0). \tag{A2.4}$$

Insertion of the tetrahedral angle yields $q = \frac{1}{2}(1 - 3\cos^2 \beta_0)$.

In the text, we have omitted the label q for the quadrupolar energy and have written $|\Gamma, m\rangle \equiv \Gamma,$ quadrupolar energy, $m\rangle$.

Appendix 3. The Markovian limit of the relaxation kernel

From equations (29) and (13) one has the following expression for the relaxation kernel occurring in the equation of motion (15) in symmetrized form:

$$K^\lambda_{k,n}(s) = \frac{1}{2} \sum_{\Gamma m} \sum_{\Gamma' m'} P^\lambda_{\Gamma'_\epsilon m'; \Gamma_\epsilon m}(s)(O^\lambda_{k,\Gamma_\epsilon m} - O^\lambda_{k,\Gamma'_\epsilon m'})(O^\lambda_{n,\Gamma_\epsilon m} - O^\lambda_{n,\Gamma'_\epsilon m'}). \tag{A3.1}$$

Diagonalization of the matrix $K(s)$ yields the eigenmatrix $\Lambda(s)$ and eigenoperators $\tilde{O}_k$, which are linear combinations of the originally chosen operators O_k. Omitting

the superscript λ in the following, we have for the elements of $\Lambda(s)$, using (30):

$$\Lambda_k(s) = \sum_{\Gamma m} \sum_{\Gamma' m} |\langle 0\Gamma m|\Delta H^\lambda_{\text{IL}}|0\Gamma' m'\rangle|^2 X_{\Gamma,\Gamma'}(\bar{O}^\lambda_{k,\Gamma_e m} - \bar{O}^\lambda_{k,\Gamma_e m'})^2$$

$$\times (\bar{\gamma} + s)/\{(\bar{\gamma} + s)^2 + [\bar{\omega} - (m' - m)\omega_z]^2\}$$

$$= : \sum_{n=-2}^{2} A_{k;n} \frac{(\bar{\gamma} + s)}{(\bar{\gamma} + s)^2 + (\bar{\omega} - n\omega_z)^2}. \tag{A3.2}$$

Here, $\bar{\gamma}$ is one of the broadenings γ or $\bar{\gamma}$, and $\bar{\omega}$ is either $\omega_t(T)$ or zero, cf equation (30). $X_{\Gamma,\Gamma'}$ reflects the detailed balance of the spectral functions and in the high-temperature approximation for Δ_0 it is given by $X_{\Gamma,\Gamma'} = \langle X_{0\Gamma:0\Gamma}\rangle_L$. We have restricted ourselves to low temperatures in (A3.2) since at higher temperatures $\bar{\gamma} \gg s$ is easily fulfilled in NMR experiments. Then the dependence of $\Lambda_k(s)$ on the 'inverse measuring time' s [23] can trivially be neglected. Thus we concentrate on situations where $\bar{\gamma}$ is of the order of or smaller than s. The only restriction we have to make is to choose s such that $\omega_z \gg |s|$ is fulfilled. Since $\omega_z \simeq 10^{-8}$ s, this situation is met in almost all spin–lattice relaxation experiments. Thus, we are allowed to replace $(\bar{\gamma} + s)/\{(\bar{\gamma} + s)^2 + [\bar{\omega} - (m' - m)\omega_z]^2\}$ by $(\bar{\gamma} + s)/[\bar{\omega} - (m' - m)\omega_z]^2$ in (A3.2) everywhere except for resonances $\bar{\omega} = \omega_z, 2\omega_z$. These will be considered explicitly later. The above replacement allows us to write

$$\Lambda_k(s) = \Delta_k(s) + \Delta_k(0) \tag{A3.3a}$$

$$\Delta_k(s) = \sum_{n=-2}^{2} A_{k;n} \frac{s}{(\bar{\omega} - n\omega_z)^2} \tag{A3.3b}$$

$$\Delta_k(0) = \sum_{n=-2}^{2} A_{k;n} \frac{\bar{\gamma}}{(\bar{\omega} - n\omega_z)^2}. \tag{A3.3c}$$

$\Delta_k(s)$ is of the order $O([d_\lambda/(\bar{\omega} - n\omega_z)]^2) \ll 1$. The equation of motion (15) then reads:

$$\langle \Delta_{\text{eq}} \bar{O}^\lambda_k(s)\rangle_I = [s + \Delta_k(s) + \Delta_k(0)]^{-1}\langle \Delta_{\text{eq}} \bar{O}^\lambda_k(0)\rangle_I \simeq [s + \Delta_k(0)]^{-1}\langle \Delta_{\text{eq}} \bar{O}^\lambda_k(0)\rangle_I \tag{A3.4}$$

yielding an exponential law for the time evolution of the operators $\Delta_{\text{eq}} \bar{O}^\lambda_k(t)$, $\langle \Delta_{\text{eq}} \bar{O}^\lambda_k(t)\rangle_I = c_k \exp[\Delta_k(0)t]$ in second order with respect to d_λ.

Next, we consider a resonance $\omega_t(T) = n_0\omega_z$, $n_0 = \pm1, \pm2$. Since this is of relevance only for A $\leftrightarrow$ E transitions, we have to use the broadenings γ. We decompose $\Lambda_k(s)$ in the following way:

$$\Lambda_k(s) = B_{k;n_0}(\gamma + s) + A_{k;n_0}(\gamma + s)^{-1} \tag{A3.5a}$$

where

$$B_{k;n_0} := \sum_{\substack{n=-2 \\ n\neq n_0}}^{2} A_{k;n}[\omega_t(T) + n\omega_z]^{-2} \tag{A3.5b}$$

and we have

$$\Delta_k(0) = B_{k;n_0}\gamma + A_{k;n_0}\gamma^{-1} \tag{A3.5c}$$

in this case. Here $B_{k;n_0}$ is of the order $O((d_\lambda/\omega_z)^2) \ll 1$. Neglecting this small term in the equation of motion, we have in second order with respect to d_λ:

$$\langle\Delta_{eq}\bar{O}_k^\lambda(s)\rangle_1 = [s + \Delta_k(0)\gamma/(\gamma + s)]^{-1}\langle\Delta_{eq}\bar{O}_k^\lambda(0)\rangle_1$$
$$\simeq [s + \Delta_k(0)]^{-1}\langle\Delta_{eq}\bar{O}_k^\lambda(0)\rangle_1 \tag{A3.6}$$

for times that are sufficiently long to determine $\Delta_k(0)$.

Consequently, the limit $s \to 0$ performed in the text in the calculation of the transition probabilities does not provide a problem in the high-field approximation.

Appendix 4. The intermolecular dipolar interaction

Inserting equation (42) for $H_{IL}^D(i)$ into the series expansion ($R_{iu} = R_i - r_u$):

$$\frac{Y_{2,n}(\omega_{iu})}{(R_{iu})^3} = \sum_{k=0}^{\infty} \frac{(-1)^k}{k!}\left((r_u \cdot \nabla)^k \frac{Y_{2,n}(\omega_{iu})}{(R_{iu})^3}\right)_{(0)} \tag{A4.1}$$

where the subscript '(0)' means that the derivative has to be taken at the coordinates (ω_i, R_i), yields, using the gradient formula (43) and the definition (44) for the coupling strength

$$R_{2,m}^A(i;\phi)^{(0)} = 3\sqrt{\left(\frac{8\pi}{5}\right)}\sum_{n=-2}^{2} D_{n,m}^{(2)}(\Omega_0)Y_{2,n}(\omega_i) \tag{A4.2a}$$

$$R_{2,m}^A(i;\phi)^{(1)} = 0 \tag{A4.2b}$$

$$R_{2,m}^A(i;\phi)^{(2)} = 3\sqrt{\left(\frac{8\pi}{5}\right)}\left(\frac{r}{R_i}\right)^2\sum_{n=-2}^{2} D_{n,m}^{(2)}(\Omega_0)X_2^A(n)Y_{4,n}(\omega_i) \tag{A.4.2c}$$

$$R_{2,m}^A(i;\phi)^{(3)} = 3\sqrt{\left(\frac{8\pi}{5}\right)}\left(\frac{r}{R_i}\right)^3\sum_{n=-2}^{2} D_{n,m}^{(2)}(\Omega_0)$$
$$\times [X_3^A(n)Y_{5,n-3}(\omega_i)e^{3i\phi} + X_{-3}^A(n)Y_{5,n+3}(\omega_i)e^{-3i\phi}] \tag{A4.2d}$$

where we have used the abbreviations:

$$X_2^A(n) := -\frac{5}{2}\sqrt{\frac{7}{3}}[C(1,2,3;1,n)C(1,3,4;-1,n+1)$$
$$+ C(1,2,3;-1,n)C(1,3,4;1,n-1)] \tag{A4.3a}$$

$$X_{\pm3}^A(n) := \pm\frac{15}{2}\sqrt{\frac{35}{66}}[C(1,2,3;\mp1,n)C(1,3,4;\mp1,n\mp1)C(1,4,5;\mp1,n\mp2)]. \tag{A4.3b}$$

The E-symmetric operators are given by

$$R_{2,m}^{E^a}(i;\phi)^{(0)} = 0 \tag{A4.4a}$$

$$R_{2,m}^{E^a}(i;\phi)^{(1)} = 3\sqrt{\left(\frac{8\pi}{5}\right)}\left(\frac{r}{R_i}\right)\sum_{n=-2}^{2} D_{n,m}^{(2)}(\Omega_0)X_1^E(n)Y_{3,n-1}(\omega_i)e^{i\phi} \tag{A4.4b}$$

$$R_{2,m}^{E^a}(i;\phi)^{(2)} = 3\sqrt{\left(\frac{8\pi}{5}\right)}\left(\frac{r}{R_i}\right)^2\sum_{n=-2}^{2} D_{n,m}^{(2)}(\Omega_0)X_2^E(n)Y_{4,n+2}(\omega_i)e^{-2i\phi} \tag{A4.4c}$$

$$R_{2,m}^{E^a}(i;\phi)^{(3)} = 3\sqrt{\left(\frac{8\pi}{5}\right)}\left(\frac{r}{R_i}\right)^3\sum_{n=-2}^{2} D_{n,m}^{(2)}(\Omega_0)X_3^E(n)Y_{5,n-1}(\omega_i)e^{i\phi} \tag{A4.4d}$$

with

$$X_1^E(n) := 5\sqrt{\tfrac{3}{14}}C(1,2,3;-1,n) \tag{A4.5a}$$

$$X_2^E(n) := \tfrac{5}{2}\sqrt{\tfrac{7}{3}}C(1,2,3;1,n)C(1,3,4;1,n+1) \tag{A4.5b}$$

$$X_3^E(n) := -\tfrac{15}{2}\sqrt{\tfrac{35}{66}}[C(1,2,3;1,n)C(1,3,4;-1,n+1)C(1,4,5;-1,n)$$
$$+ C(1,2,3;-1,n)C(1,3,4;1,n-1)C(1,4,5;-1,n)$$
$$+ C(1,2,3;-1,n)C(1,3,4;-1,n-1)C(1,4,5;1,n-2)] \tag{A4.5c}$$

$$R_{2,m}^{E^b}(i;\phi)^{(k)} = (-1)^m[R_{2,-m}^{E^a}(i;\phi)^{(k)}]^*. \tag{A4.6}$$

Note added in proof. In the meantime a theoretical work on the NMR spectra and spin–lattice relaxation rates of CD_3 groups has been published by Heuer [50]. He showed that for small momentum transfer and high rotational potentials, strong relations exist between the relaxation rates and the finite temperature spectra of CD_3 groups and the incoherent scattering function. His results concerning the spin–lattice relaxation rates coincide with the small momentum transfer and high rotational potential limit of our expressions given in section 3.3.

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