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Quantum mechanical alternative to Arrhenius equation in the interpretation of proton spin-lattice relaxation data for the methyl groups in solids[†]

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Theory of nuclear spin-lattice relaxation in methyl groups in solids has been a recurring problem in nuclear magnetic resonance (NMR) spectroscopy. The current view is that, except for extreme cases of low torsional barriers where special quantum effects are at stake, the relaxation behaviour of the nuclear spins in methyl groups is controlled by thermally activated classical jumps of the methyl group between its three orientations. The temperature effects on the relaxation rates can be modelled by Arrhenius behaviour of the correlation time of the jump process. The entire variety of relaxation effects in protonated methyl groups has recently been given a consistently quantum mechanical explanation not invoking the jump model regardless of the temperature range. It exploits the damped quantum rotation (DQR) theory originally developed to describe NMR line shape effects for hindered methyl groups. In the DQR model, the incoherent dynamics of the methyl group include two quantum rate, i.e., coherence-damping processes. For proton relaxation only one of these processes is relevant. In this paper, temperature-dependent proton spin-lattice relaxation data for the methyl groups in polycrystalline methyltriphenyl silane and methyltriphenyl germanium, both deuterated in aromatic positions, are reported and interpreted in terms of the DQR model. A comparison with the conventional approach exploiting the phenomenological Arrhenius equation is made. The present observations provide further indications that incoherent motions of molecular moieties in condensed phase can retain quantum character over much broader temperature range than is commonly thought.

1 Introduction

Since the late 50s of the past century proton spin-lattice relaxation of the methyl group in solids has been recurrently addressed from different perspectives, becoming one of the most thoroughly approached theoretical problems in nuclear magnetic resonance (NMR) spectroscopy.^{1–12} For the instances of low torsional barriers where substantial quantum tunneling effects are at stake, several quantum mechanical treatments were reported.^{2,5,6,9,11,12} Nevertheless, in the interpretation of experimental relaxation

data, the quantum theories have invariantly been augmented with the familiar model of classical random jumps of the methyl rotator between its three equivalent orientations.^{9,13,14}

However, the jump model has recently proved insufficient for exact description of NMR line shape effects in variable-temperature spectra of even very strongly hindered methyl groups. On the other hand, the competing, consistently quantum mechanical theory of damped quantum rotation (DQR)^{15,16} was shown to be adequate not only in low-temperature solids^{17,18} but also in liquids above 170 K.^{19–22} In place of the single classical rate constant characterizing the jump process, the DQR model employs two rate parameters. These are the rate constants of certain coherence-damping processes in the system of spin-space correlated torsional/rotational (TR) states of the methyl group treated as a hindered quantum rotator. Both these rate processes are evidenced in the line shapes of hindered methyl groups. The prototypes of these processes were earlier recognized as the mechanisms of broadenings of the inelastic and quasielastic lines in incoherent neutron scattering (INS) spectra of tunnelling methyl groups.^{23–25} In the context of NMR spectroscopy,

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the above mentioned quantum rate constants can be used to quantify the degree of nonclassicality in the observed incoherent dynamics of methyl groups and similar threefold molecular rotators. Namely, if these constants happen to be equal, the DQR line shape equation assumes its familiar Alexander-Binsch form founded just on the jump model.^{26,27} The departures from unity of their ratio can therefore be used as the mentioned measure of nonclassicality. The highest values of this parameter reported so far exceed 5,¹⁸ which means that the problem of a breakdown of the jump model is by no means marginal. This finding prompted one of the present authors to readdress the considered relaxation problem in terms of the DQR model.¹² The obtained relaxation equation for the methyl group protons has proved formally identical with the Haupt equation.⁶ However, unlike in the work by Haupt and a related study by Diezemann,¹¹ both addressing extremely low temperatures, the rate parameter entering it remains well-defined over practically the whole temperature range of interest in the line shape and relaxation studies. This parameter is one of the two rate constants of the DQR model, and as such, when taken alone, has no direct connections to the rate constant of the jump process. A preliminary, yet unequivocal experimental confirmation of the validity of this recent approach has already been reported.¹²

In this work, proton spin-lattice relaxation rates were measured for two polycrystalline substances selectively deuterated in non-methyl positions, methyltriphenylsilane (MTPSi-d₁₅) and methyltriphenylgermanium (MTPGe-d₁₅). Each of them contains two crystallographically inequivalent methyl groups in the unit cell, suffering different hindering potential. The temperature behaviours of the relaxation rates have been interpreted in terms of both the conventional jump model employing the Arrhenius equation and the DQR model.

To give sufficient background for the considerations of this paper, a rather comprehensive outlook of the DQR theory seemed necessary because in its former presentations in the literature some topics of primary relevance to the present context were only briefly touched. A consistent recapitulation of its relevant aspects involving only threefold rotators will be given in the Theory section and the Appendix. The interpretation of our current experimental results and the relevant details of the applied, rather non-standard methodology will be reported under the heading Results and Discussion.

2 Theory

The system of interest in this work, i.e., the methyl group, isolated from its environment, can to a good accuracy be described by the Mathieu hamiltonian for a planar threefold rotator,

$$\hat{H}^\varphi = -\frac{\hbar}{2I} \frac{d^2}{d\varphi^2} + \frac{V}{2}(1 - \cos 3\varphi), \quad (1)$$

where φ is the torsional/rotational (TR) coordinate, I is the moment of inertia, and V is the amplitude of the torsional potential. Cyclic permutations of the rotator particles correspond to changes of φ by multiples of $\pm 2\pi/3$ and leave the hamiltonian unchanged. Because pairwise particle exchanges can be discarded

as unfeasible under the considered conditions, its feasible symmetry group²⁸ is isomorphic with C_3 , and its eigenstates transform according to the three irreducible representations, A , E_a , and $E_b = E_a^*$, of C_3 . The E eigenstates belonging to the complex conjugate representations come as degenerate Kramers pairs which, for the energy levels below the potential barrier (the torsional levels), are only slightly shifted in energy with respect to the A eigenstates. These shifts, i.e., the tunnelling splittings, grow in absolute magnitude with growing torsional energy, and their signs alternate. The peculiar arrangement of the torsional sublevels into nearly degenerate triplets, with considerable splittings between such sequential multiplets, is one of the distinctive features of threefold quantum rotators determining their dynamic properties in condensed environments. In what follows, the eigenenergies and eigenstates of the above hamiltonian will be denoted by $\hbar\omega_p^\Gamma$ and $|\rho^\Gamma\rangle$, respectively, where Γ stands for A , E_a , and E_b .

2.1 Overview of DQR model

Below, a brief recapitulation is given of the DQR theory in its version for threefold quantum rotators. Its full exposition can be found in Refs.^{15,16}, where the latter involves a general N -fold rotator.

The DQR theory addresses a "big system" composed of two parts: the quantum system of interest which, in its version of our present interest, is the hindered threefold rotator described above, and the macroscopic environment of the rotator acting as a quantum mechanical thermal bath influencing its dynamics. The rotator is placed in the external magnetic field of a NMR spectrometer. The impact on the TR states of such fields is negligible.

The bath comprises the lattice vibrations or phonons which can cause instantaneous perturbations of the torsional potential. It can be modelled by an infinite set of harmonic oscillators. The rotator-phonon interactions had been quantified by a number of authors approaching the INS and nuclear spin relaxation problems from a quantum mechanical perspective.^{6,23–25} The hamiltonian of the rotator-phonon couplings which must conform with the threefold symmetry of the rotator, has the form:

$$\hat{H}_{rp}^\varphi = \sum_k (Q_k \lambda_{Sk} \sin 3\varphi + Q_k \lambda_{Ck} \cos 3\varphi), \quad (2)$$

where Q_k are mass-weighted coordinates of the lattice oscillators and the scalars λ_{Ck} and λ_{Sk} describe couplings of these coordinates to the two modes, $\cos 3\varphi$ and $\sin 3\varphi$, of perturbations of the torsional potential. The individual terms in the rotator-phonon hamiltonian fluctuate in the interaction representation, and these fluctuations induce vibrational relaxation and dephasing processes in the rotator subsystem.

The effects of the bath on the interested dynamic behaviour monitored in NMR experiments can be presented as a side effect of the vibrational relaxation/dephasing processes stimulated by the perturbations described above.^{15,16} These vibrational effects are described by the equation of motion for the density matrix of the rotator embedded in the phonon bath, derived using a variant of the Nakajima-Zwanzig theory.^{29,30} A brief description of the essential properties of this crucial equation of motion is given in the

Appendix. Below, only a qualitative account of these properties is given.

The reduced over the bath density matrix, describing the perturbed rotator embedded in an external magnetic field of a NMR spectrometer, will be denoted by $\hat{\rho}^{\varphi s}$, where the superscripts indicate its dynamic dependence on the space coordinate φ and the spin coordinates correlated with the former according to the Pauli principle. It operates in the state space spanned by the TR eigenstates of the isolated rotator, of symmetries A , E_a , and E_b of C_3 , all of which are delocalized over all three minima of the torsional potential, and are correlated with spin states of symmetries A , E_b , and E_a , respectively. Taking these eigenstates to be the basis states, on any stage of its evolution the reduced density matrix can be expanded into the set of all possible coherences between pairs of the basis states, thus

$$\hat{\rho}^{\varphi s}(t) = \sum_{\Gamma'\Gamma''\alpha'\alpha''} C_{\Gamma'\Gamma''\alpha'\alpha''}^{\Gamma\Gamma'}(t) \hat{C}_{\Gamma'\Gamma''\alpha'\alpha''}^{\Gamma\Gamma'}, \quad (3)$$

where $C_{\Gamma'\Gamma''\alpha'\alpha''}^{\Gamma\Gamma'}(t)$ are complex numbers describing time-dependent amplitudes of the coherences

$$\hat{C}_{\Gamma'\Gamma''\alpha'\alpha''}^{\Gamma\Gamma'} = |p\alpha\Gamma\bar{\Gamma}'\rangle\langle p'\alpha'\Gamma'\bar{\Gamma}'| = (|p\Gamma\rangle\langle p'\Gamma'|)(|\alpha\bar{\Gamma}\rangle\langle\alpha'\bar{\Gamma}'|), \quad (4)$$

with $\bar{\Gamma}$ denoting the spin symmetry correlated with space symmetry Γ . According to the symmetry types of the space basis states, the coherences $\hat{C}_{\Gamma'\Gamma''\alpha'\alpha''}^{\Gamma\Gamma'}$ can in a natural way be classified into nine symmetry partitions: three homogeneous partitions (Γ, Γ) and six inhomogeneous ones, (Γ, Γ'), where $\Gamma \neq \Gamma'$. Each space coherence $|p\Gamma\rangle\langle p'\Gamma'|$ is associated with an appropriate number of spin coherences $|\bar{\Gamma}\alpha\rangle\langle\bar{\Gamma}'\alpha'|$. For instance, coherence $|pA\rangle\langle p'E_a|$ will occur in combinations with 8 spin coherences $|\alpha A\rangle\langle\alpha'E_b|$, because the eight methyl proton spin states classify into four states of symmetry A , two of symmetry E_a , and two of symmetry E_b .

The DQR model is based on the observation that the free evolution of $\hat{\rho}^{\varphi s}(t)$ proceeds on two totally different time scales. One is compatible with the rates of the vibrational relaxation and dephasing processes in the rotator system which typically occur in the 10^{-10} - 10^{-12} s range. The other is much longer and, contrary to the former, commensurate with the time scale of NMR experiments. The physical reasons for such a discrepancy between the time scales are recapitulated in the Appendix. In these considerations the spin-dependent interactions are immaterial and are neglected.¹⁵ They are included on a later stage of the reasoning.

In the above context, the spin parts of the basis vectors can be dropped with no loss of accuracy, what implies a reduction of the size of the density matrix. The purely space density matrix will be denoted by dropping superscript "s" at $\hat{\rho}^{\varphi s}(t)$. The evolution of $\hat{\rho}^{\varphi}(t)$ under action of interactions not engaging nuclear spins can be concisely described in the Liouville space spanned by the space coherences mentioned above,

$$d|\rho^{\varphi}\rangle\rangle/dt = (-i\mathbf{L}^{\varphi} + \mathbf{R}^{\varphi})|\rho^{\varphi}\rangle\rangle \quad (5)$$

where $|\rho^{\varphi}\rangle\rangle$ is a column vector composed of the matrix elements of $\hat{\rho}^{\varphi}$, and the square matrices $\mathbf{L}^{\varphi}$ and $\mathbf{R}^{\varphi}$ are Liouville representations of the Mathieu hamiltonian and the rotator-bath interac-

tions transformed into a vibrational relaxation/dephasing matrix, respectively.

As discussed in the Appendix, the evolution matrix $\mathbf{T}^{\varphi} = -i\mathbf{L}^{\varphi} + \mathbf{R}^{\varphi}$ in Eq. (5) consists of independent diagonal blocks describing the individual symmetry partitions. In each such submatrix, one of its eigenvalues is sharply distinct from the remaining eigenvalues. While the smallest of the latter are of absolute magnitude of typical vibrational relaxation/dephasing rates, the unique eigenvalue is either exactly zero or has absolute magnitude compatible with NMR time scale. The zero eigenvalues occur for the homogeneous partitions. A consideration of the above properties of $\mathbf{T}^{\varphi}$ and other relevant details of its structure discussed in the Appendix summarizes in the following conclusions involving evolution of $\hat{\rho}^{\varphi}(t)$ after any external stimulation driving the system out of its thermal equilibrium state.

(i) The coherences that live long enough to be relevant to NMR are not just the individual space coherences that could be expected to occur in isolated rotator but appropriate weighted combinations thereof, appearing as a side effect of the rapid vibrational relaxation/dephasing processes.

(ii) In each symmetry partition there is only one long-lived space coherence (understood as a combination of appropriate space coherences $|p\Gamma\rangle\langle p'\Gamma'|$ from the partition).

(iii) The long-lived, and in fact, infinitely long-lived space coherences in the homogeneous partitions (Γ, Γ) are Boltzmann combinations of the self-coherences $|p\Gamma\rangle\langle p\Gamma|$ representing level populations,

$$\hat{C}^{\Gamma\Gamma}(T) = \frac{1}{Z_{\Gamma}} \sum_p \exp(-\hbar\omega_p^{\Gamma}/k_B T) |p\Gamma\rangle\langle p\Gamma|, \quad (6)$$

where Z_{Γ} is the corresponding partition function

(iv) At low temperatures the long-lived space coherences in the inhomogeneous partitions (Γ, Γ') can be roughly described as Boltzmann combinations of the coherences $|p\Gamma\rangle\langle p\Gamma'|$ between the torsional sublevels on the sequential torsional levels,

$$\hat{C}^{\Gamma\Gamma'}(T) \approx \frac{1}{Z} \sum_p \exp(-\hbar\omega_p^{\Gamma\Gamma'}/k_B T) |p\Gamma\rangle\langle p\Gamma'|, \quad (7)$$

where $\omega_p = (\omega_p^{\Gamma} + \omega_p^{\Gamma'})/2$ and the partition function Z is defined accordingly. At higher temperatures, the weighting factors entering the above coherences can only be evaluated numerically by diagonalizing $\mathbf{T}^{\varphi}$

In absence of spin-dependent interactions, the free evolution of the long-lived coherences in the six inhomogeneous partitions are damped oscillations,

$$C^{\Gamma\Gamma'}(t) = C^{\Gamma\Gamma'}(0) \exp \theta^{\Gamma\Gamma'} t \quad (8)$$

where $C^{\Gamma\Gamma'}(t)$ is the complex amplitude of long-lived coherence $\hat{C}^{\Gamma\Gamma'}(T)$ contributing to $\hat{\rho}^{\varphi}(t)$. The complex quantities $\theta^{\Gamma\Gamma'}$ describing the oscillation frequencies and damping-rate constants of these peculiar coherences are the uniquely small eigenvalues of the individual partitions (Γ, Γ') of $\mathbf{T}^{\varphi}$. They obey the following

relationships:

$$\begin{aligned}\theta^{AE_{a,b}} &= \theta^{*E_{a,b}A} \equiv i\Delta - k_t \\ \theta^{E_aE_b} &= \theta^{E_bE_a} \equiv -k_K,\end{aligned}\quad (9)$$

The coherences in partitions $(A, E_{a,b})$ and $(E_{a,b}, A)$ were once dubbed "tunnelling coherences" because at any temperature their dominating components are "primitive" coherences between tunnelling-split torsional sublevels. By analogy, the coherences in partitions $(E_{a,b}, E_{b,a})$ were named "Kramers coherences". They evolve without oscillations what is a reminiscence of the perfect degeneracy of the Kramers pairs on the sequential torsional levels.

The peculiar properties of methyl groups and similar molecular rotators, evidenced in NMR spectra and spin-lattice relaxation effects, are described by the three DQR quantities Δ , k_t , and k_K . At low temperatures, the oscillation frequency Δ of the tunnelling coherences is approximately given by Boltzmann combination of the tunnelling splittings on the two lowest torsional levels. Even in this temperature limit, no simple expressions could be proposed for the damping-rate constants k_t and k_K . At any temperature that might be of interest in NMR studies all of the three above DQR parameters can be modelled numerically using one set of parameters. In the once reported simple but physically well-justified approach¹⁵ to be also used presently, this set include only four items: the amplitude, V , of the torsional potential, two parameters measuring the strengths of the sine and cosine-type modes of perturbations of the torsional potential, and one parameter describing the harmonic bath.¹⁵ A detailed description of these parameters will be given later on.

If each of the long-lived coherences discussed above is augmented with spin coherences of appropriate symmetries, the obtained in this way spin-space Liouville manifold will have the same dimension as the purely spin manifold for the system of nuclei in the rotator. The complete equation of motion, including the spin-dependent interactions, given in Eq. (27) in the Appendix, can be represented in this spin-space manifold in the form adjusted for the purposes of NMR, i.e., with neglected short-lived coherences. The spin-dependent interactions now appear in the equation of motion as first order corrections, which level of approximation is more than adequate here.¹⁵ The obtained density matrix, $\hat{\rho}'$, will include only the coherences that are relevant to NMR. However, the equation of motion governing the evolution of $\hat{\rho}'$ will still involve delocalized rotator and as such it will be inconvenient in use. The troublesome dependence on the space variable of both $\hat{\rho}'$ and the entities governing its evolution is no longer dynamic and can be removed by integration over this variable. If this operation is applied in combined with the uncorrelation-recorrelation technique proposed earlier,^{15,31} the final equation of motion obtained in this way will involve the rotator localized in one of its three equivalent potential energy minima. In this equation, $\hat{\rho}'$ is transformed into purely spin density matrix $\hat{\rho}$ of the same dimensions, and the operators governing its evolution are transformed into their familiar counterparts involving localized rotator. The final equation of motion converted

to its spin state space form reads:

$$\begin{aligned}d\hat{\rho}/dt = & - i[\hat{H} + \frac{\Delta}{3}(\hat{C} + \hat{C}^{-1}), \hat{\rho}] \\ & - \frac{k_K}{3}(2\hat{\rho} - \hat{C}\hat{\rho}\hat{C}^{-1} - \hat{C}^{-1}\hat{\rho}\hat{C}) - \frac{k_t - k_K}{2}(\hat{\rho} - \hat{U}\hat{\rho}\hat{U}),\end{aligned}\quad (10)$$

where $\hat{C}$ is the operator effecting cyclic permutation of the spin variables of the three particles in the rotator, $\hat{U}$ is an unitary, self-inverse operator

$$\hat{U} = \frac{1}{3}[\hat{I} - 2(\hat{C} + \hat{C}^{-1})],\quad (11)$$

and $\hat{H}$ is the standard spin hamiltonian describing the Zeeman, chemicals shift anisotropy (CSA) and dipole-dipole (DD) interactions in the (localized) rotator specifically oriented in the external magnetic field. The term multiplied with Δ describes the apparent couplings (i.e, the Heisenberg couplings) between the nuclei in the rotator, arising from the coherent rotational tunnelling. For spin-1/2 nuclei these couplings appear as the familiar J -couplings.³²

The equation of motion in Eq. (10) establishes a unique platform for a precise quantification of the actual departure of the considered incoherent dynamics from the classical limit. For $k_t = k_K$ it becomes the familiar Alexander-Binsch equation based on the classical jump model. This is a remarkable property of the DQR formalism because in none of its stages has the concept of jumps been introduced. However, as is commented further on in the Discussion subsection, the jump model emerging from the formalism of the DQR theory is not identical with that introduced ad hoc in the conventional descriptions of the methyl group dynamics. Nevertheless, for practical purposes it is convenient to consider it as the classical limit of the DQR approach. The magnitude of deviation of the ratio k_t/k_K from the "classical" value 1 can thus serve as a precise measure of the degree of nonclassicality of the observed dynamics. As has already been mentioned, the values of this ratio exceeding 5 were determined from fits of the discussed equation to the experimental spectra of a hindered CH_3 group.¹⁸ With properly modified spin hamiltonian, Eq. (10) is also valid for methyl groups in molecules freely tumbling in fluids. For several systems containing extremely hindered methyl groups, investigated in solution, the experimentally determined values of k_t/k_K also noticeably deviate from 1.^{19–22}

2.2 Spin-lattice relaxation in the DQR approach

For k_t and k_K greatly exceeding the intra-group DD couplings, and with included nonsecular terms of the DD interactions, the equation of motion in Eq. (10) is a valid spin-lattice relaxation equation, if applied to the difference density matrix describing deviations of the system from the state of thermal equilibrium with the environment.¹² In its formulation aimed at the description of line shape effects it would be impractical in use for the spin relaxation, because of considerable redundancies occurring in it in the above limit. In the cited paper, its Liouville space version with an alternative formulation of the dissipative terms was Fourier-transformed to the frequency domain, where the redundancies could be eliminated by considering the structure of its ma-

trix representation at zero frequency. Upon return to the time domain, spin-lattice relaxation matrix was obtained. It involves protonated methyl group specifically oriented in the external magnetic field. The obtained relaxation matrix has the same form as that reported once by Haupt.⁶ However, in place of a quantum mechanical correlation time appearing in the latter, having imprecise meaning⁹ except for the case where only the lowest torsional level is populated, now there appears the quantum-rate constant k_t which remains consistently defined over the whole temperature range of interest in relaxation (and line shape) studies of methyl groups. The finding that for protonated methyl groups only the processes measured by k_t are relevant is in line with an earlier result by Diezemann¹¹ who addressed the same limiting instance as that investigated by Haupt. For polycrystalline materials, the initial relaxation rate constant calculated for the relaxation matrices obtained in the DQR approach is given by¹²

$$\frac{1}{T_1} = \frac{9d^2}{40} \sum_{m=2}^{-2} \frac{m^2 k_t}{k_t^2 + (\Delta - m\omega_0)^2}, \quad (12)$$

where $d = \mu_0 \gamma_H^2 \hbar / 4\pi r^3$ is the DD coupling constant between methyl group protons (separated by $r \approx 0.180$ nm). For $\Delta = 0$ and k_t replaced by the inverse correlation time τ^{-1} of the classical jumps, it is known as the Bloembergen-Purcell-Pound (BPP) expression.^{33,34}

For protonated methyl groups relaxing by the DD mechanism, addressed in the DQR approach, the Kramers quantum process could contribute to relaxation in the presence of non-negligible inter-molecular DD interactions.¹²

Details of a preliminary validity test of the considered spin-lattice relaxation theory, relevant for the findings reported in this work are given in the Discussion subsection.

3 Experimental and computational procedures

The syntheses of selectively deuterated in the aromatic positions methyltriphenylsilane (MTPSi-d₁₅) and methyltriphenylgermanium (MTPGe-d₁₅) are described in the Electronic Supplementary Information (ESI). To the best of the present authors' knowledge, MTPGe in its protonated and selectively deuterated forms was synthesized for the first time. Details of the X-ray diffraction and NMR measurements are given in the ESI.

For MTPSi, quantum chemical calculations of torsional barriers for the methyl groups were carried out at the DFT/B3LYP/6-311G(2d,p) level of theory using the Gaussian 09 package.³⁵ The calculations were performed for clusters of 6 molecules, including the hosting molecule, whose fragments are most proximate to the methyl group of interest. In the calculations, crystallographic coordinates of all non-hydrogen atoms were assumed, and the hydrogen atoms' positions were optimized on the above mentioned level of theory. For each nonequivalent methyl group the profile of the torsional barrier was calculated for 10° increments of the torsional angle, keeping all the remaining atomic coordinates fixed at their crystallographic (or, for protons, optimized) positions. For both groups, the calculated torsional energy data fairly fit with the potential in Eq. (1). The fits are shown in Fig. S1 of

the ESI.

4 Results and discussion

4.1 Model compounds

Both MTPSi and MTPGe crystallize in the $P2_1/c$ space group, with 8 molecules in the unit cell, where the asymmetric unit comprises 2 molecules. The crystal structure of MTPSi is known.^{36,37} For MTPGe it was determined in this work. The asymmetric units of the unit cells of MTPSi and MTPGe are shown in Figs. 1a and 1b, respectively. In both cases the molecules in the asymmetric unit are interrelated by a non-crystallographic translation. The quantum chemical calculations for MTPSi revealed that the torsional barriers for the methyl groups in these molecules are considerably different, 862 cm⁻¹ for molecule A and 744 cm⁻¹ for molecule B. The torsional barriers evaluated from the relaxation data for MTPGe-d₁₅ are also different. In this compound labels A and B were assigned to the methyl groups with higher and lower torsional potential, respectively.

Fig. 1 Views along crystallographic axis a of the asymmetric units in the crystal structures of MTPSi (a) and MTPGe (b). For molecules A and B of MTPSi the calculated torsional potential amplitudes are 862 and 744 cm⁻¹, respectively.

MTPSi and MTPGe were chosen as model compounds because there had been facile routes to obtain them in the selectively deuterated forms where only the methyl group protons are left. One more reason rendering these substances suitable models for the present purposes was that in both of them the neighbourhoods of the methyl groups have approximate three-fold symmetries. For such structural arrangements it could be anticipated that the torsional potentials would be fairly approximated by simple cosine functions of the torsional angles. These predictions were confirmed by the above mentioned quantum chemical calculations for MTPSi. On this basis, the simple cosine potentials were assumed for all methyl groups in the investigated compounds, what facilitated the interpretation of relaxation data in terms of the DQR model.

Because for either compound the smallest intermolecular distances between the methyl protons are similar for groups A and B

and are rather large, with the smallest value of about 0.35 nm, intermolecular contributions to spin lattice relaxation of intergroup dipolar interactions could be neglected. These convenient properties of the crystal structures were also taken into account when use of the considered compounds as models was considered. The problem of model selection has been given so much attention because it is of a primary importance in the present studies designed to pursue subtle effects predicted by a novel relaxation theory.

4.2 Theoretical fits of experimental data

The interpretation of the spin-lattice relaxation data was made under the standard assumption that, in consequence of the rapid spin diffusion, the initial recovery rate is a weighted average of contributions from both methyl groups. Because these occur in equal amounts, the initial rate constant is given by:

$$\frac{1}{T_1} = \frac{1}{2} \left(\frac{1}{T_{1A}} + \frac{1}{T_{1B}} \right). \quad (13)$$

For both compounds, the observed magnetization recovery curves could be fitted with a bi-exponential model

$$M(t) = M - M_1 \exp(-k_1 t) - M_2 \exp(-k_2 t). \quad (14)$$

With decreasing temperature, the relative contribution of the faster recovering component was decreasing. At all temperatures, the two-component model afforded a perfect description of the whole recovery curve, including its most interesting initial fragment. The initial recovery rate constants were approximated by

$$\frac{1}{T_1} = \frac{M_1 k_1 + M_2 k_2}{M_1 + M_2}. \quad (15)$$

Fig. 2 Experimental spin lattice relaxation rate constants for MTPSi-d₁₅ (squares) with superposed theoretical best-fit curves obtained in the DQR (solid line) and BPP (dotted line) fits.

The temperature-dependent experimental relaxation data for MTPSi-d₁₅ and MTPGe-d₁₅ are displayed in Figs. 2 and 3, respectively. In the figures, the continuous solid curves represent best least squares fits of the quantum mechanical expression

$$\frac{1}{T_1} = \frac{9d^2}{80} \sum_{m=2}^{-2} \frac{m^2 k_{tA}}{k_{tA}^2 + (\Delta_A - m\omega_0)^2} + \frac{m^2 k_{tB}}{k_{tB}^2 + (\Delta_B - m\omega_0)^2}, \quad (16)$$

obtained by substituting for $1/T_{1A}$ and $1/T_{1B}$ in Eq. (13) the right hand sides of Eq. (12) with values of k_t and Δ specific for the individual methyl groups A and B; the DD coupling constant d was assumed the same for both groups. In the fits with Eq. (16) (to be further referred to as the DQR fits), the values of d and of the parameters defining the temperature dependences of $k_{tA,B}$ and $\Delta_{A,B}$ were adjusted. For each group the modelling of the temperature dependences of its specific DQR quantities involved two adjustable parameters, out of the four parameters employed in the theoretical model. Thus, five parameters were adjusted in these fits. In the next subsection it will be explained why such a reduction of the number of adjustable parameters is justified.

The dotted curves in Figs. 2 and 3 represent best least squares fits of the weighted sum of the standard BPP expressions,

$$\frac{1}{T_1} = \frac{9d^2}{40} \sum_{m=1,2} \frac{m^2 \tau_A}{1 + (m\tau_A \omega_0)^2} + \frac{m^2 \tau_B}{1 + (m\tau_B \omega_0)^2}, \quad (17)$$

with the assumed Arrhenius behaviour of the correlation times $\tau_{A,B}$,

$$\frac{1}{\tau_{A,B}} = \frac{1}{\tau_{A,B}^0} \exp(-E_{A,B}/k_B T). \quad (18)$$

Like in the DQR model, in this conventional model, to be further named the BPP model, five parameters were fitted: the Arrhenius parameters for groups A and B, and d , again assumed to be the same for both groups.

One of the principal results of this work is that the DQR fits are at least as good as the BPP fits. Some superiority of the quantum approach over the conventional one can be seen in Fig. 3 for the low-temperature data for MTPGe-d₁₅. At these temperatures, the experimental temperature trend, although somewhat obscured because of experimental errors, appears to be better reproduced by the DQR fit. Similar, but less pronounced effect occurs for the conventional and DQR fits shown in Fig. 2.

4.3 Details of the DQR fits

In these fits, the crucial step involves numerical evaluation of the smallest eigenvalue of partition (A, E_a) of the superoperator $\mathbf{T}^\varphi = -i\mathbf{L}^\varphi + \mathbf{R}^\varphi$ entering Eq. (5) whose matrix elements are given in Eq. (28) in the Appendix. Results of such calculations for the methyl group, obtained using a simplified formalism developed mainly for treatment of data obtained from line shape studies, were already reported.^{12,15,18,38} Presently the formalism has been extended to improve its performance in the high temperature range where the considered dynamics tend to the classical limit, with the ratio k_t/k_K approaching 1. To this end, apart from the low-frequency coherences between the nearly degenerate torsional states, mentioned explicitly in the Appendix, further TR co-

Fig. 3 Same as Figure 2, but for MTPGe-d₁₅.

herences, ones engaging different TR states, have been included in the relevant block of $\mathbf{T}^\varphi$. (They are optically inactive, yet their homogeneous counterparts would generally be detectable in the infrared/far infrared range.) For inert molecular rotators like the benzene ring, the inclusion of coherences between different TR states appears to be of a critical significance for the calculated rate constants to have physical sense.³⁹ For the methyl groups it has minor significance unless, such as in the present case, the dynamics near the classical limit are of interest. These peculiar features of the methyl group, as compared to rotators with large moment of inertia, are concerned with substantial differences between the corresponding frequency spectra. In the latter case the frequency gap separating the coherences between nearly degenerate torsional sublevels from those between different TR levels is relatively small as compared to the off-diagonal elements of $\mathbf{R}^\varphi$ between the diagonal elements describing the considered frequencies. For the methyl group, the difference is larger such that the corresponding off-diagonal elements of $\mathbf{R}^\varphi$ are roughly non-secular and can play less prominent role in shaping the considered dynamics.

Of an indirect significance for the interpretation of the results of the DQR fits are also calculations of k_K as the unique eigenvalue of partition (E_a, E_b) of $\mathbf{T}^\varphi$. Like for partition (A, E_a) , apart from the perfectly degenerate coherences between the Kramers sublevels, the coherences oscillating with nonzero TR frequencies were presently included in the diagonalized block of $\mathbf{T}^\varphi$. The calculated unique eigenvalue remains a purely real quantity because these oscillating coherences come in pairs differing only by signs of their oscillation frequencies.

The matrix elements of $\mathbf{T}^\varphi$ given in Eq. (28) in the Appendix are dependent on the matrix elements of the rotator-phonon hamiltonian in Eq. (2) between the eigenvectors of the Mathieu

hamiltonian in Eq. (1). Evaluations of the latter involve numerical calculations of integrals of the form $\langle p\Gamma | \cos 3\varphi | p'\Gamma \rangle$ and $\langle p\Gamma | \sin 3\varphi | p'\Gamma \rangle$. The relevant eigenvectors were calculated in the basis of exponential functions $\exp i3(j+m)\varphi$, with $m = 0, 1, 2$ depending on the symmetry type, using the standard variational approach. In the present case 81 basis functions were used, i.e., $j = -40, -39, \dots, 40$. The assumed moment of inertia was that of a perfectly tetrahedral methyl group, with the C-H bond lengths of 0.109 nm. The other quantities defining the matrix elements of $\mathbf{T}^\varphi$ are the spectral density functions $J^X(\omega)$, where X stands for C (cosine) and S (sine) modes of perturbations of the torsional potential.

To evaluate them in a reasonable way, in Ref.¹⁵ the discrete phonon frequencies were described by a continuum, with function $D(|\omega|)$ measuring density of bath oscillators of frequency ω . Accordingly, the discrete rotator-phonon couplings λ_k^X in Eq. (2) were replaced by continuous (scalar) functions $\lambda^X(\omega)$, where $\omega \approx \omega_k$. Additionally, independence of these couplings of the propagation directions of the individual lattice vibrations was assumed. Then, with no further approximations beyond that the lattice oscillators are perfectly harmonic, the considered spectral density functions could be obtained in the following closed form:^{15,40}

$$J^X(\omega) = \frac{\pi [\lambda^X(\omega)]^2 D(|\omega|)}{\hbar \omega [\exp(\hbar \omega / k_B T) - 1]}. \quad (19)$$

A suitable parametrization of $\lambda^X(\omega)$ poses a challenge because little is known about microscopic details of the effects they measure. Similar problem involves function $D(|\omega|)$ in molecular crystals of complicated structure. For the latter a modified Debye model was used. Namely, in place of the the rapid decay of the density of lattice oscillators above the Debye cut-off frequency ω_c , an exponential decay with ω_c measuring the decay rate was assumed,¹⁵ thus

$$D(|\omega|) = C \omega^2 \exp(-|\omega|/\omega_c). \quad (20)$$

In this way, by taking a value of ω_c falling above the true Debye frequency not only the genuine lattice vibrations but some intramolecular low-frequency oscillators can be taken into account as factors possibly influencing the considered torsional potential. Finally, to minimize the set of model parameters, independence of the rotator-phonon couplings $\lambda^X(\omega)$ of the phonon frequency was assumed. By renormalizing them with an account of the phonon densities,

$$f_X = \frac{\lambda^X}{2} \sqrt{\frac{N}{2\hbar\omega_c}}, \quad (21)$$

where N is the integral of $D(|\omega|)$ in the limits between $-\infty$ and ∞ , the spectral density functions dependent on only two parameters were obtained,¹⁵

$$J^X(\omega) = \frac{2\pi f_X^2 \omega \exp(-|\omega|/\omega_c)}{\omega_c^2 [\exp(\hbar \omega / k_B T) - 1]}. \quad (22)$$

(Unfortunately, in Eq. (39) in Ref.¹⁵ describing the renormalization, there have been overlooked typos; they do not proliferate to the final expression for the spectral density in Eq. (40) in the cited paper.) In Eq. (22), f_X measures the effective impact on the torsional potential of not only the lattice but some intramolec-

ular vibrations as well, and ω_c roughly defines the upper limit of available energy quanta exchanged between the rotator and its surrounding. The physical meaning of f_X as a measure of the rotator-phonon couplings becomes clear if one considers that, with temperature tending to 0, the value at time 0 of the quantum correlation function reproduced from the density function in Eq. (22) converges to f_X^2 .¹⁵

Trial calculations of the values of k_t and Δ with the above parametrization of the matrix elements of $\mathbf{T}^\varphi$ show that for the torsional potentials high enough to hold at least three torsional levels the calculated values remain virtually insensitive to the individual values of f_C , f_S , and ω_c if the following ratio of their squares is kept constant,

$$\frac{f_C^2 + f_S^2}{\omega_c^2} = \text{const.}, \quad (23)$$

while ω_c and the ratio f_C/f_S can be varied within rather broad limits of 350 - 700 cm^{-1} and 0.5 - 2, respectively. (The units of cm^{-1} used for quantities whose natural units are rad s^{-1} are practical in the present context.) The same involves the calculated values of k_K . With increasing temperature, the values of k_t and k_K show a limiting Arrhenius behaviour, with the ratio k_t/k_K invariably approaching from top the "classical" value 1. Simultaneously, the ratio Δ/k_t rapidly tends to 0. The latter behaviour can be interpreted as a sort of thermal quenching of the coherent tunneling even if the values of Δ itself remain large or show apparently divergent oscillations with increasing temperature.¹² It was noticed earlier that if Δ/k_t is close to 0, Δ can be dropped from the denominators in the spin-lattice relaxation rate expressions like that in Eq. (12), regardless of the relative magnitudes of Δ and ω_0 .¹² (If $|\Delta|$ is comparable with k_t yet small against the Larmor frequency, it can obviously be discarded.)

In view of the above correlations between the parameters defining the interested dynamics, the quantum fits presented in Figs. 2 and 3 were performed for fixed value of $\omega_c = 600 \text{ cm}^{-1}$ and for

$$f_C = f_S \equiv f, \quad (24)$$

with f optimized. The other optimized parameter was V , the amplitude of the torsional potential. In this way, the number of fitted parameters per one methyl group remains effectively the same as in the BPP fits. For altered proportions of f_C to f_S , and for assumed values of $\omega_c = 400$ and 700 cm^{-1} , the fits delivered values of V and of the ex post calculated ratio in Eq. (23) varying only within the limits of the corresponding standard errors also evaluated in the fits. The rms errors of the fits remained unchanged.

For the two investigated substances, the optimized values of the quantum and Arrhenius parameters, and of the DD coupling constant are collected in Table 1. All the values are given to the last significant digit.

4.4 Discussion

The values of d extracted in both sorts of the fits are mutually consistent. The HH distance reproduced from them is 0.187 - 0.188 nm, somewhat above the standard distance 0.180 nm. The

discrepancy can to a large extent be attributed to the vibrational corrections to the DD couplings, the ubiquity of which is well documented in reported relaxation studies. The obtained values of d indirectly confirm the absence in the investigated materials of other relaxation mechanisms than that by intra-group DD interactions.

The good quality of the presently reported DQR fits provides first unequivocal confirmation of the validity of this model for a variety of methyl groups experiencing diverse torsional potentials. The only previous test involving raw experimental data had been performed yet before the theoretical model was published,³⁸ and concerned an extremely hindered methyl group. In such context its confrontation with the standard BPP model lacked sufficient grounds. The already mentioned direct demonstration of its correctness was based on processed relaxation data taken from the literature.¹² Namely, temperature trend of the rate parameter extracted from proton relaxation data for a methyl group, believed to be the inverse correlation time of the jump process, with assumed Arrhenius dependence on temperature,⁴¹ was compared with the trends of the DQR parameters k_t and k_K determined in Ref. 18 from variable-temperature spectra of the same material, measured at lower temperatures. The relaxation and line shape investigations involved a single crystal of selectively deuterated methylmalonic acid in a fixed orientation in the external magnetic field.⁴¹ The Arrhenius trend obtained from the relaxation data have proved to exactly continue the temperature trend of k_t extracted in the DQR line shape fits using Eq. (10). A confusion with the trend of k_K also determined in the line shape fits was unlikely because in the low temperature range the ratio k_t/k_K exceeded 5 (see Fig. 2 in Ref. 12). These observations not only confirm the DQR model of spin-lattice relaxation but its full consistency with the DQR line shape theory as well. Moreover, the temperature trends of k_t , k_K , and Δ determined from the spectra could be reproduced theoretically using the already mentioned simplified version of the DQR formalism, limited to the coherences between torsional sublevels.¹⁸ Hence, results of similar calculations using the improved version of the formalism, to be discussed below, appear trustworthy.

In Fig. 4 plots of the values of k_t determined in the DQR fits for groups A in MTPSi-d₁₅ and B in MTPGe-d₁₅ are shown. Of the four types of methyl groups investigated presently, the former suffers the highest torsional potential, 920 cm^{-1} , and the latter the lowest, 483 cm^{-1} . For group B in MTPGe-d₁₅, Arrhenius plot of the values of $1/\tau$ obtained in the BPP fit is also shown. The differences between the compared curves are most notable in the region of low temperatures, where also the corresponding theoretical curves describing the relaxation rates in Fig. 3 differ substantially, and where the DQR curve goes closer to the experimental points. For group A in MTPSi-d₁₅, the temperature trend of k_t shown in Fig. 4 closely follows the Arrhenius law and coincides with the trend of $1/\tau$ obtained in the BPP fit. Thus, the DQR model is fully capable of reproducing the Arrhenius trends and also deviations from it, which can occur for methyl groups experiencing low torsional barriers. Both sorts of temperature behaviour of k_t , the nearly perfect Arrhenius trend and one showing significant deviations from such trend, could be consistently mod-

TABLE 1. Results of the BPP and DQR fits to the spin-lattice relaxation data for MTPSi-d₁₅ and MTPGe-d₁₅.^a

Cmpd.	Group	d_{BPP}	$1/\tau^0$	E	d_{DQR}	f	V	V_{calc}	$\bar{E}^b$
		kHz	$10^{12}s^{-1}$	$kJ\ mol^{-1}$	kHz	cm^{-1}	cm^{-1}	cm^{-1}	$kJ\ mol^{-1}$
Si	A		4	9.25		200	920	862	9.8
	B	-18.4	0.8	6.11	-18.1	90	720	744	7.6
Ge	A		2	6.23		140	663	-	6.9
	B	-18.1	1	3.93	-18.1	100	483	-	4.9

^aThe DQR fits were performed for the fixed value $600\ cm^{-1}$ of the cut-off frequency ω_c of the bath oscillators; ^b $\bar{E}$ is the difference between the experimental amplitude, V , of the torsional potential $V(1 - \cos 3\phi)/2$ and the calculated zero-point energy in this potential, expressed in $kJ\ mol^{-1}$.

Fig. 4 Temperature dependences of the values of k_t for methyl groups A in MTPSi-d₁₅ and B in MTPGe-d₁₅ (solid and dashed lines, respectively), reproduced from results of the corresponding DQR fits. Dotted line: the values of $1/\tau$ for group B in MTPGe-d₁₅, reproduced from results of the BPP fit.

elled with the same number of adjustable parameters, i.e. two, in each case. To obtain any departures from linearity for $1/\tau$ one would have to augment the Arrhenius equation with another empirical term. Therefore, the superiority of the DQR model in the interpretation of relaxation data for the methyl groups appears unquestionable.

Nevertheless, if cases with extremely low torsional barriers are excluded, a superficial inspection of the BPP and DQR fits in Fig. 2 may lead to the conclusion that the complicated DQR approach is essentially needless in the interpretation of the spin-lattice relaxation for such methyl groups. However, if the question is posed what sort of knowledge about the system can be delivered by the conventional approach, the answer is not obvious. In such approach, the obtained preexponential Arrhenius factors are hard to

Fig. 5 Correlation between Arrhenius preexponential factors in column 4 of Table 1 and the corresponding DQR quantities $(f/\omega_c)^2$ measuring relative strengths of impact of the environment on the dynamics of the methyl groups A and B in MTPSi-d₁₅ and MTPGe-d₁₅.

be interpreted. In the DQR model, the parameter f evaluated in the fits, even if not interpretable as such, gives some insight into relative susceptibilities of the investigated methyl groups to the perturbations by the environment. Because, as shown in Fig. 5, the obtained values of $(f/\omega_c)^2$ are in a nearly perfect linear correlation with the Arrhenius prefactors $1/\tau^0$, the present results allow one to interpret the latter accordingly, i.e., as measures of the impact of environment on the considered dynamics of methyl groups. This observation is one of the main results of this work.

On the other hand, the relationship between the evaluated Arrhenius activation energy and the genuine potential barrier (the assessment of which is one of the main targets of such relaxation studies), is still not obvious. The commonly adopted belief, consistent with the concept of jumps over potential barrier, is that the activation energy equals the energy gap between the zero-point-

energy (ZPE) and top of the barrier. However, it appears untenable in view of the data for group B in MTPSi-d₁₅. The Arrhenius activation energy obtained in the BPP fit, shown in column 5 of Table 1, substantially differs from the value given in column 10, calculated by subtracting the (calculated value of the) ZPE from the torsional barrier evaluated in the DQR fit. The former is by some 20 percent lower than the latter. By and large, the activation energies delivered by the BPP fits for all four methyl groups come consistently lower than those calculated from the potential amplitudes evaluated in the DQR fits. Note that for MTPSi-d₁₅ the latter values are in a fair agreement with those calculated using a quantum chemistry method. However, given the necessary simplifications made in the latter calculations, the experimental values appear to be closer to reality. (Because of the presence of heavy Ge atoms in the corresponding molecular clusters, for MTPGe theoretical evaluations of the torsional potentials were not undertaken.)

In view of the above discussion, further comments on the jump model are in order, because its validity in the interpretation of relaxation data for the methyl groups is generally considered unquestionable, at least for the groups experiencing torsional barriers above 400 - 500 cm⁻¹. As was mentioned in the comment to Eq. (10), in the DQR approach, the jump process emerges from the quantum dynamics if $k_t \approx k_K$. In this perspective, it has to be viewed as a composite construct because even in the above instance the corresponding quantum rate (i.e., coherence-damping) processes evolve separately. In the DQR relaxation theory for protonated methyl groups, only one of the two constitutive parts of the jump process understood in the above way stimulates the spin-relaxation effects. The other part, measured by rate constant k_K , is inactive (although for the DQR relaxation theory to be valid, not only k_t alone but k_K as well should be much greater than $2\pi d^{12}$). In the conventional interpretation of the relaxation data it is believed that the correlation time τ entering the relaxation expressions characterizes just the jump process understood as one of classical jumps over the barrier. (In practical applications of the Haupt approach to weakly hindered methyl groups, the jump process is invoked in the interpretation of relaxation rates at high temperatures^{9,13,14}). This is, however, hardly justified even if the relevant dynamics of the methyl group are in the "classical" regime of $k_t/k_K \approx 1$. Even if the Arrhenius equation is used in the interpretation of the relaxation data, the extracted values of $1/\tau$ will approximately be equal to k_t . Unlike for the classical jump process, the apparent activation energies for k_t are only loosely related to the barrier height. The magnitude of this rate constant is predominantly controlled by the tunnelling splittings at the individual torsional levels the methyl rotator randomly samples in the course of time. In the DQR approach, damping of the tunneling coherences associated with k_t has much in common with the mechanism of residual line broadenings in fast exchange limits of multisite exchange processes investigated in NMR spectroscopy.¹⁵ In both cases, the lifetime of the emerging, dynamically averaged coherence is limited by the effects of frequent jumps of the quantum system between its instantaneous states characterized by different oscillation frequencies - Larmor frequencies in the individual exchanged sites or dif-

ferent tunnelling frequencies at different torsional levels. For this reason, the evaluated Arrhenius activation energies will generally fall below the gap between the potential maximum and ZPE, as has actually taken place for all four methyl groups investigated presently.

Fig. 6 Temperature dependences of the ratios Δ/k_t for methyl groups A in MTPSi-d₁₅ and B in MTPGe-d₁₅ (increasing trends, solid and dashed lines, respectively), plotted against right Y axis, and of the corresponding ratios k_t/k_K plotted against left Y axis.

If k_t and k_K are substantially different, the very notion of jumps of the methyl rotator completely loses grounds in the spin-lattice relaxation (and line shape) studies. Even for the most strongly hindered of the methyl groups investigated presently, the dynamics underlying the observed relaxation behaviour are noticeably far from the classical limit at low temperatures, below, say, 120 K. This can be seen in Fig. 6, where the calculated ratios k_t/k_K for this group and group B in MTPGe-d₁₅ (the least hindered group) are plotted. For the former, this ratio drops from about 2 at 80 K, to about 1.5 at 120 K, and only above 150 - 170 K the "quantum" jump process starts to emerge from the quantum rate processes. The dynamics of the least hindered group remain strongly non-classical in the broad temperature range 55 - 120 K, with k_t/k_K dropping from a value above 7 at 55 K to about 2 at 120 K. Thus, even at relatively high temperatures the considered stochastic dynamics still retain their evidently quantum character. The popular view that at elevated temperatures molecular rate processes in condensed phases are necessarily classical needs to be revised.

In Fig. 6, there are also shown plots of the values of Δ/k_t against temperature, calculated for the two "extreme" methyl groups. These plots depict the processes of quenching of the coherent tunnelling under impact of the environment. For both groups, these temperature trends stabilize at values slightly different from 0, what may reflect some imperfections of the theoretical model.

Nevertheless, in both cases the coherent tunnelling becomes practically overdamped above 200 K and its impact on the denominators of the relaxation expressions like that in Eq. (12) (the so called Haupt denominators) would be negligible, regardless of the magnitude of the applied magnetic field determining the Larmor frequency. For the least hindered group, below 100 K $|\Delta|$ is comparable to or even strongly exceeds k_i . In this range, the values of $|\Delta|/2\pi$ are at least of the order of the applied Larmor frequency, 500 MHz. The divergence of the low-temperature trends of the theoretical relaxation rate constants, shown in Fig. 3, is caused by both the already discussed deviation of k_i from the Arrhenius law and the nonnegligible contribution of $|\Delta|$ to the Haupt denominators at the considered temperatures.

Unfortunately, unlike in the case of methylmalonic acid commented on in the foregoing, for the presently investigated substances the appropriate reference data from line shape studies could not be obtained. As is well known,⁴¹ in the instances of low torsional barriers even if the incoherent dynamics can be frozen at low temperatures, large coherent tunnelling effects appearing at such temperatures affect the spectral patterns in almost the same way as rapid incoherent processes do at elevated temperatures.

5 Conclusions

The results of this work show that the conventional interpretation of the spin lattice relaxation data for the methyl groups, based on the jump model combined with the Arrhenius law, may be deceptive despite the fact that a fair reproduction of the experimental relaxation data can be achieved. The proposed alternative model, fully consistent with the DQR line shape theory, affords at least as good description of the experimental data as the conventional model. As compared with the latter, the DQR approach can give a more reliable assessment of the torsional barriers for methyl groups placed in environments of approximate threefold symmetries. It can also deliver some estimates of the rotator-phonon interactions. Its most notable advantages as compared to the conventional approach involve an insight into the true nature of the underlying dynamics of the methyl groups. One of the most important inferences from the present studies is that the thermally activated incoherent processes stimulating the spin-lattice relaxation can retain quantum character over much wider temperature range than is generally thought. Accordingly, the hitherto unquestioned status of the jump model has been challenged. This does not mean that the use of the Arrhenius equation in the spin-lattice relaxation studies on methyl groups also lacks grounds. However, the Arrhenius parameters evaluated in such studies need to be interpreted in terms of the DQR model along the lines sketched in this work.

The proposed quantification of the tendency of the relevant dynamics to the classical limit, although involving an object of a limited interest, falls in line with the still open fundamental debate about the quantum to classical transition in the dynamic behaviour of microscopic objects. The relative indifference to the

destructive impact by the condensed environment of the quantum effects in the investigated systems is probably related to the fact that these effects are controlled by the symmetrization postulate. The current approach to the problem of the classical limit in quantum mechanics is the decoherence theory.⁴² Unfortunately, the systems which, like the methyl groups, include identical particles, are not in the focus in this theory, if the possible role of the symmetrization postulate is concerned. Therefore, a deepened discussion of the observations reported in this paper must be postponed.

6 Appendix

In a formal presentation of the DQR theory, a systematic use of the Liouville representation of quantum mechanics is indispensable. The Liouville space describing the evolution of the superket $|\rho^{\Phi s}\rangle\rangle$ representing $\hat{\rho}^{\Phi s}$ is spanned by coherences defined in Eq. (4) which form a complete orthonormal set of basis superkets,

$$\hat{C}_{pp'\alpha\alpha'}^{\Gamma\Gamma'} \equiv |pp'\alpha\alpha'\Gamma\Gamma'\rangle\rangle = |pp'\Gamma\Gamma'\rangle\rangle |\alpha\alpha'\bar{\Gamma}\bar{\Gamma}'\rangle\rangle, \quad (25)$$

where $|\alpha\alpha'\bar{\Gamma}\bar{\Gamma}'\rangle\rangle \equiv |\alpha\bar{\Gamma}\rangle\langle\alpha'\bar{\Gamma}'|$. The scalar product of two superkets, $|A\rangle\rangle$ and $|B\rangle\rangle$, $\langle\langle A|B\rangle\rangle$, representing the respective operators $\hat{A}$ and $\hat{B}$, is given by

$$\langle\langle A|B\rangle\rangle = \text{Tr}\hat{A}^\dagger\hat{B}, \quad (26)$$

where the superbra $\langle\langle A|$ equals $|A\rangle\rangle^\dagger$. Hence the coherence amplitudes $C_{pp'\alpha\alpha'}^{\Gamma\Gamma'}(t)$ entering Eq. (3) are the scalar products $\langle\langle pp'\alpha\alpha'\Gamma\Gamma'|\rho^{\Phi s}(t)\rangle\rangle$.

In the Liouville space, the considered equation of motion, involving also the short-lived coherences irrelevant to NMR, reads:

$$d|\rho^{\Phi s}\rangle\rangle/dt = [-i(\mathbf{L}^\Phi + \mathbf{L}^{\Phi s}) + \mathbf{R}^\Phi]|\rho^{\Phi s}\rangle\rangle, \quad (27)$$

where $\mathbf{L}^\Phi$ is the Mathieu superhamiltonian generated by the hamiltonian in Eq. 1, $\mathbf{R}^\Phi$ describes the vibrational relaxation/dephasing processes in the rotator subsystem, and $\mathbf{L}^{\Phi s}$ is the superhamiltonian of spin-dependent interactions of the rotator particles, including DD, quadrupole (for spin $>1/2$ nuclei) and Zeeman interactions with an account of the CSA effects. Because Eq. 27 conforms with the requirements of the symmetrization postulate, it involves delocalized TR states. The superhamiltonian $\mathbf{L}^{\Phi s}$ is small against the remaining terms in the right hand side of Eq. (27). In particular, it is small in comparison with the vibrational relaxation/dephasing rate constants entering $\mathbf{R}^\Phi$. Hence the spin-dependent interactions and, accordingly, the spin parts of the basis coherences, can be neglected as irrelevant for the identification of the time scale relevant to NMR. They will be included at a later stage of the reasoning as first-order corrections understood in the sense of time-independent perturbation calculus. The resulting equation of motion is given in Eq. (5). In the basis not including spin coherences, the matrix elements of the superoperator $\mathbf{T}^\Phi = -i\mathbf{L}^\Phi + \mathbf{R}^\Phi$ are given by

$$\begin{aligned} \ll pp'\Gamma\Gamma'|\mathbf{T}^\Phi|qq'\Gamma\Gamma' \gg = & - \delta_{pq}\delta_{p'q'}i\omega_{pq'}^{\Gamma\Gamma'} \\ & + [X_{qp p'q'}^{\Gamma\Gamma'} + X_{q'p'pq}^{\Gamma\Gamma'} - \sum_i (\delta_{p'q'}X_{q'ip}^{\Gamma\Gamma'} + \delta_{pq}X_{q'ip'}^{\Gamma\Gamma'})], \end{aligned} \quad (28)$$

where the elements of $\mathbf{L}^\Phi$, $\omega_{pq'}^{\Gamma\Gamma'} = \omega_p^\Gamma - \omega_{q'}^{\Gamma'}$, occur only on the diagonal and

$$\begin{aligned} X_{uvv'u'}^{\Gamma\Gamma'} = & \langle u|\Gamma| \cos 3\phi |v\rangle \langle v'|\Gamma'| \cos 3\phi |u'\rangle J^C(\omega_{vu}^{\Gamma\Gamma'}) \\ & + \langle u|\Gamma| \sin 3\phi |v\rangle \langle v'|\Gamma'| \sin 3\phi |u'\rangle J^S(\omega_{vu}^{\Gamma\Gamma'}), \end{aligned} \quad (29)$$

with $J^{C,S}(\omega)$ denoting spectral density functions which characterize the cos (C) and sin (S) modes of perturbations of the torsional potential, described in Eq. (2). These are quantum-mechanical spectral densities dependent on the lattice temperature, T , and obeying the Boltzmann-weighting relationship,

$$J^{C,S}(\omega) = \exp(-\hbar\omega/kT)J^{C,S}(-\omega). \quad (30)$$

Following the assumption made in related contexts,^{23,24} cross-correlations of the sine and cosine terms have been neglected. The elements $\ll pp'\Gamma\Gamma'|\mathbf{T}^\Phi|qq'\Gamma''\Gamma''' \gg$, where either $\Gamma \neq \Gamma''$ or $\Gamma' \neq \Gamma'''$ are identically zero. This is because the matrix elements of the rotator-phonon hamiltonian, of the form $\langle p|\Gamma|C,S|p'\Gamma'' \rangle$ and $\langle p|\Gamma'|C,S|p'\Gamma''' \rangle$, where C and S stand for $\cos 3\phi$ and $\sin 3\phi$, respectively, which would occur in such matrix elements of $\mathbf{T}^\Phi$, are identically zero. This is a consequence of conservation of the threefold symmetry even under action of the environment. Accordingly, $\mathbf{T}^\Phi$ in Eq. (5) is decomposed into nine independent blocks concerned with the individual symmetry partitions, $\mathbf{T}^\Phi(|\Gamma, \Gamma'|)$, such that the corresponding partitions of the density superket $|\rho^\Phi \gg$ evolve independently.

The only matrix elements that can couple the symmetry partitions of $\mathbf{T}^\Phi$ (in the Liouville space with restored spin degrees of freedom) come from these terms in the spin-dependent superhamiltonian $\mathbf{L}^\Phi$ s which violate the threefold symmetry of the spin-independent interactions (although $\mathbf{L}^\Phi$ s is symmetric under simultaneous cyclic permutations of the space and spin coordinates). All these elements are of the order of magnitude of the CSA and the dipole-dipole, and/or quadrupole interactions in the protonated or deuterated methyl groups. The C_3 -symmetric part of the Zeeman interaction, which exceeds the remaining spin-dependent interactions by few orders of magnitude, does not contribute to the coupling elements. The temporary neglect of this relatively large term is justified also by the fact that it commutes with the remaining superoperators in Eq. (27).

The possibility for certain coherences to survive the destructive action of the environment stems from peculiar features of the spectra of the individual partitions of $\mathbf{T}^\Phi$. The spectra are defined as the eigenproblems of the relevant (complex-valued, non-Hermitian) matrices:

$$\mathbf{T}^\Phi(|\Gamma, \Gamma'|)\lambda|\Gamma\Gamma' \gg = \theta_{\lambda|\Gamma\Gamma'}|\Gamma\Gamma' \gg, \quad (31)$$

where λ enumerates the eigenvalues and the associated eigensupervectors $|\lambda\Gamma\Gamma' \gg$ which are linear combinations of the basis coherences $|pp'\Gamma\Gamma' \gg$.

For each partition, precisely one of the eigenvalues is sharply distinct from the remaining eigenvalues if the respective absolute magnitudes are compared. The dominating terms in the "homogeneous" partitions (Γ, Γ') of $\mathbf{T}^\Phi$ are matrices of master equations for the level populations. Their off-diagonal elements are of the form $\ll pp\Gamma\Gamma'|\mathbf{T}^\Phi|qq\Gamma\Gamma' \gg$ and the diagonal elements are sums of the off-diagonal elements in the corresponding columns, taken with "-" sign. Accordingly, for each such partition the unique eigenvalue equals exactly zero, and its associated eigen-coherence is the Boltzmann combination of the self-coherences $|pp\Gamma\Gamma' \gg$ whose operator counterpart is given in Eq. (6). The remaining eigenvalues have absolute magnitudes at least of the order of vibrational relaxation and/or dephasing rates.

As can be seen in Eq. (28), the relevant sets of matrix elements in the "inhomogeneous" partitions $\mathbf{T}^\Phi(|\Gamma, \Gamma'|)$, ($\Gamma \neq \Gamma'$) are arranged in similar patterns as their counterparts in the master equations in the homogeneous partitions, and involve elements of the form $\ll pp\Gamma\Gamma'|\mathbf{T}^\Phi|qq\Gamma\Gamma' \gg$ which have similar magnitudes as their homogeneous counterparts $\ll pp\Gamma\Gamma'|\mathbf{T}^\Phi|qq\Gamma\Gamma' \gg$ and $\ll pp\Gamma'\Gamma'|\mathbf{T}^\Phi|qq\Gamma'\Gamma' \gg$. Now the self-coherences describing level occupancies are replaced by the basis coherences between degenerate or nearly degenerate sublevels of different symmetries at the sequential torsional levels. In an isolated rotator, such coherences would evolve with zero or very low frequencies, as compared to the torsional/rotational frequencies. In general, the spectra of the inhomogeneous partitions have similar structure as those of the homogeneous partitions. In the inhomogeneous analogs of the master equations the sums of the off-diagonal elements in individual columns only approximately match the corresponding diagonal elements. Moreover, in the partitions ($A, E_{a,b}$) and ($E_{a,b}, A$) the diagonal elements contain the generally small imaginary terms which are the tunnelling splittings at the individual torsional levels. Now, instead of the zero eigenvalue there appears one unique eigenvalue with relatively small absolute magnitude while the remaining eigenvalues are similarly large as their counterparts in the homogeneous partitions. The notice of the similarities between environment-induced dynamics of the level populations and those of the low- or zero-frequency coherences between the torsional sublevels was one of the main incentives to develop the DQR approach.

In the main text, the discussed above peculiar eigenvalues and their associated eigen-coherences (i.e., the tunnelling and Kramers coherences), are denoted by $\theta_{\Gamma\Gamma'}$ and $|\Gamma\Gamma' \gg$, respectively, i.e., by dropping in Eq. (31) label λ . The eigenvalues obey the relationships in Eq. (9).

If the long- and short-lived coherences determined above are augmented back with appropriate spin coherences, an equivalent basis set in the discussed Liouville space will be obtained (it may prove necessary to orthogonalize the sets of short-lived coherences in the individual partitions, before augmenting them with the spin parts). The complete equation of motion in Eq. (27) (i.e., with included spin-dependent terms), represented in this new basis set, will in a natural way decompose into two practically independent equations of motion. The matrix elements still connecting them can come only from the spin-dependent interactions, excluding the C_3 -symmetric part of the Zeeman interaction. These elements can safely be neglected because they are small in comparison with the difference in the time scales on which the corresponding coherences evolve. For NMR, of relevance is only the equation involving the long-lived coherences. Further processing of this equation to obtain it in a working form is described in the main text.

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