Nonclassical dynamics of the methyl group in 1,1,1-triphenylethane. Evidence from powder ^1H NMR spectra

Agnieszka Osior, Przemysław Kalicki, Bohdan Kamieński, Sławomir Szymański, Piotr Bernatowicz, and Aleksander Shkurenko

Citation: *The Journal of Chemical Physics* **146**, 104504 (2017); doi: 10.1063/1.4978226

View online: <http://dx.doi.org/10.1063/1.4978226>

View Table of Contents: <http://aip.scitation.org/toc/jcp/146/10>

Published by the [American Institute of Physics](#)

Articles you may be interested in

Significance of symmetry in the nuclear spin Hamiltonian for efficient heteronuclear dipolar decoupling in solid-state NMR: A Floquet description of supercycled rCW schemes

The Journal of Chemical Physics **146**, 104202104202 (2017); 10.1063/1.4977738

Announcement: Top reviewers for *The Journal of Chemical Physics* 2016

The Journal of Chemical Physics **146**, 100201100201 (2017); 10.1063/1.4978399

^1H – ^2H cross-polarization NMR in fast spinning solids by adiabatic sweeps

The Journal of Chemical Physics **146**, 104201104201 (2017); 10.1063/1.4976980

Photoswitching of azobenzene-containing self-assembled monolayers as a tool for control over silicon surface electronic properties

The Journal of Chemical Physics **146**, 104703104703 (2017); 10.1063/1.4978225

**PHYSICS
TODAY**

**COMPLETELY
REDESIGNED!**

Physics Today Buyer's Guide
Search with a purpose.

Nonclassical dynamics of the methyl group in 1,1,1-triphenylethane. Evidence from powder ^1H NMR spectra

Agnieszka Osior,¹ Przemysław Kalicki,¹ Bohdan Kamieński,¹ Sławomir Szymański,^{1,a)} Piotr Bernatowicz,^{2,b)} and Aleksander Shkurenko^{2,c)}

¹*Institute of Organic Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warszawa, Poland*

²*Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warszawa, Poland*

(Received 30 January 2017; accepted 21 February 2017; published online 14 March 2017)

According to the damped quantum rotation (DQR) theory, hindered rotation of methyl groups, evidenced in nuclear magnetic resonance (NMR) line shapes, is a nonclassical process. It comprises a number of quantum-rate processes measured by two different quantum-rate constants. The classical jump model employing only one rate constant is reproduced if these quantum constants happen to be equal. The values of their ratio, or the nonclassicality coefficient, determined hitherto from NMR spectra of single crystals and solutions range from about 1.20 to 1.30 in the latter case to above 5.0 in the former, with the value of 1 corresponding to the jump model. Presently, first systematic investigations of the DQR effects in wide-line NMR spectra of a powder sample are reported. For 1,1,1-triphenylethane deuterated in the aromatic positions, the relevant line-shape effects were monitored in the range 99–121 K. The values of the nonclassicality coefficient dropping from 2.7 to 1.7 were evaluated in line shape fits to the experimental powder spectra from the range 99–108 K. At these temperatures, the fits with the conventional line-shape model are visibly inferior to the DQR fits. Using a theoretical model reported earlier, a semiquantitative interpretation of the DQR parameters evaluated from the spectra is given. It is shown that the DQR effects as such can be detected in wide-line NMR spectra of powdered samples, which are relatively facile to measure. However, a fully quantitative picture of these effects can only be obtained from the much more demanding experiments on single crystals. *Published by AIP Publishing.* [<http://dx.doi.org/10.1063/1.4978226>]

I. INTRODUCTION

At cryogenic temperatures, nuclear magnetic resonance (NMR) spectra of nuclear groupings making up molecular rotators like the methyl groups and ammonium cations -NH_3^+ can spectacularly exemplify some consequences of the symmetrization postulate of quantum mechanics. Because it correlates the spin and space coordinates of identical particles according to the Pauli principle, the tunneling splittings of the torsional levels of the rotator can appear in the spectra as some apparent couplings between the nuclear spins of the identical nuclei constituting it. For protons (and other spin- $1/2$ particles), these are the familiar Heisenberg couplings, i.e., scalar J-couplings, identical for each proton pair in the considered threefold rotator.¹ For particles of spin $I > 1/2$ (e.g., deuterons), these are generalized Heisenberg couplings because they are no longer separable into pairwise spin-spin interactions.^{2–4}

The Heisenberg couplings (and the generalized Heisenberg couplings) are independent of the orientation of the rotator in the external magnetic field of a NMR spectrometer. The

other interactions relevant to NMR, the dipole-dipole (DD), chemical shift anisotropy (CSA), and quadrupole (Q) interactions (in deuterated rotators) are all orientation-dependent. For protonated rotators investigated by solid-phase NMR at cryogenic temperatures, the Heisenberg couplings are readable directly from the spectra if the torsional barriers concerned are in the narrow range of 2.7–3.5 kcal mol^{−1}. For higher torsional barriers, the tunneling splittings are generally too small to cause readily noticeable modifications of the spectral multiplets resulting from the DD couplings. For lower barriers, the Heisenberg couplings greatly exceed the DD and CSA terms in the spin Hamiltonian and are only indirectly manifested in the spectra. Because the former have threefold symmetry, they render the symmetry-violating parts of the latter ineffective in consequence of which the observed spectral multiplet undergoes a considerable simplification.^{5,6}

With increasing temperature, the coherent tunneling will be progressively dominated by thermally activated incoherent dynamics which ultimately prevail. In the high temperature limit, the spectral pattern of a protonated rotator approaches essentially the same form as it would have at low temperatures if the Heisenberg couplings were large against the DD and CSA interactions. For low torsional barriers, below, say, 2.5 kcal mol^{−1}, such a simple form, compatible with the threefold symmetry, is maintained by the spectral pattern over the whole temperature range, with no detectable lineshape effects at the intermediate temperatures.^{5,6} For protonated rotators, the impact on the spectral line shapes of the incoherent processes

a)slawomir.szymanski@icho.edu.pl

b)pbernatowicz@ichf.edu.pl

c)Current address: Functional Materials Design, Discovery and Development Research Group (FMD3), Advanced Membranes and Porous Materials Center, Division of Physical Sciences and Engineering, King Abdullah University of Science and Technology (KAUST), Thuwal 23955-6900, Saudi Arabia.

can in practice be observed only for systems characterized by sufficiently high torsional barriers, above about $2.7 \text{ kcal mol}^{-1}$.

In contrast to the spin-lattice relaxation studies, the NMR line shape effects evidencing the solid state dynamics of methyl groups and ammonium cations have never been a popular research subject. A consistent theory of the line shape effects caused by the coherent and incoherent dynamics was formulated only at the end of the past century.⁷ The earlier model explicitly addressing hindered methyl groups in solids was reported in 1976.⁸ It involves an adaptation of the Alexander-Binsch line shape formalism originally developed for molecular rearrangements in fluids.^{9,10} It is still generally believed to be adequate, because it usually affords an acceptable reproduction of the experimental spectra. However, it is an eclectic combination of two completely discordant pictures of the same object. That underlying the Heisenberg couplings implies both a delocalization of the rotator's space states over the three equivalent wells of the torsional potential and correlation of these states with spin states of appropriate symmetries. In the description of the incoherent dynamics, the rotator is treated as a classical object localized in one of the three equivalent minima of the potential and making thermally activated jumps between them. In this picture, the Pauli principle is disregarded, despite of the experimental evidences that the Heisenberg interactions can coexist with the incoherent processes over a considerable temperature range.

In the cited above, consistent theory of the line shape effects, to be further called damped quantum rotation (DQR) theory, the coherent tunneling effects also come as the (possibly generalized) Heisenberg couplings. However, in place of one rate constant describing the classical jumps, in the DQR approach, there appear two quantum-rate constants. They measure the environment-induced damping of some peculiar coherences between spin-space correlated states of the rotator. Now the jump model is obtained as a limiting case where these quantum rate constants become equal.

In solid state NMR, the DQR approach combined with rigorous iterative procedures of line shape fits was first employed^{11,12} to readdressing some earlier investigated cases^{6,13} where use of the eclectic model was made. The DQR model afforded a much better theoretical reproduction of the experimental spectra. Similar improvement of line shape fits was also achieved for several systems with methyl groups suffering extremely high torsional barriers, investigated in solutions at temperatures above 170 K.^{14–17} The cited studies on solids have revealed that the ratio of the quantum rate constants can fall far from the value of 1 corresponding to the jump model. For a moderately hindered protonated methyl group in a solid, this ratio exceeds 5.¹² For the strongly hindered groups investigated in solution, it can reach 1.30.¹⁷

In practice, most pronounced DQR effects can be sought in solids for protonated methyl groups suffering torsional barriers in the range $2.7\text{--}5 \text{ kcal mol}^{-1}$. As already mentioned, for barriers below $2.5\text{--}2.7 \text{ kcal mol}^{-1}$, the resonance patterns concerned are insensitive to the incoherent dynamics in the whole temperature range. A selectively deuterated isotopomer of the compound has to be used, in which only the methyl protons are left. For the spectra to be quantitatively

interpretable, it is important that the methyl groups in the unit cell be crystallographically equivalent. It is a challenge to find model compounds that fulfill all these criteria. The previous systematic solid state studies of the DQR effects in protonated methyl groups involved only NMR spectra of oriented single crystals of selectively deuterated materials.^{12,18}

The compound investigated presently, which is the deuterated in aromatic positions isotopomer, (**1**), of 1,1,1-triphenylethane, (**1a**), crystallizes in the monoclinic group $P2_1/n$, with all four methyl groups in the unit cell being crystallographically equivalent.¹⁹ The NMR line shape studies were carried out on the powder samples of **1**. Apart from the powder spectra, single-crystal spectra of **1** were also measured. Because only a small single crystal could be obtained, only its NMR spectra at low (and high) temperatures could be interpreted. The potentially most interesting dynamically broadened spectra at the intermediate temperatures were too strongly dominated by noise to be interpretable. The limited quantitative data obtained for the single crystal helped only to strengthen the inferences derived from the powder spectra but were not used in the interpretation of the latter. This policy was adopted to show that the readily obtainable wide-line powder spectra can provide enough information for the DQR effects to be unequivocally identified. The accuracy of the quantitative assessments of these effects is a separate question.

II. THEORY

The theory to be recapitulated below was presented in full in 1999 in the already cited paper.⁷ It is based on the ideas once introduced to explain inelastic neutron scattering experiments on the methyl groups.^{20–22} It was later generalized to n -fold rotators.^{23,24} A concise presentation of its version for threefold rotators was reported recently.²⁵

The eigenstates of a hindered methyl group, a prototypical threefold rotator, are delocalized over the three wells of the hindering potential. They are classified into three symmetry species, A , E_a , and E_b , of the rotator's feasible permutation group isomorphic with C_3 . The symmetrization postulate requires that they have to be combined with spin states of symmetries A , E_b , and E_a , respectively. The states of symmetries E_a and E_b occur in degenerate Kramers pairs. The peculiar dynamic properties of the considered atomic groupings derive ultimately from the structure of their energy levels below the torsional barrier. All these levels come in nearly degenerate triplets separated by torsional quanta. Each such triplet includes a degenerate Kramers pair and a state of symmetry A which is shifted in energy from the Kramers pairs by a tunneling quantum, the absolute magnitude of which grows with growing torsional energy and its sign alternates on passing on to the next torsional level. The considerations of the DQR approach involve the rotator embedded in a condensed environment perturbing its torsional potential and acting as a quantum mechanical thermal bath. Under such conditions, the quantum states of the rotator are entangled with those of the bath. An effective description of the former is given by a reduction of the density matrix of the whole system, the rotator, and the bath, over the degrees of freedom of the

latter.^{26,27} The reduced density matrix can be expanded into coherences between pairs of torsional levels, $|p\Gamma\rangle\langle p'\Gamma'|$, where $\Gamma, \Gamma' = A, E_a, E_b$, and $|p\Gamma\rangle$ is the p th torsional eigenstate of the isolated rotator, of symmetry Γ . The spin-dependent interactions of the atomic nuclei forming the rotator, despite being of central importance in NMR, have practically no impact on the dynamics of the spatial degrees of freedom which are of fundamental significance for the effects observed in NMR. The spin parts of these coherences need not be explicitly addressed if the spatial, i.e., angular, dynamics are concerned. The central observation of the DQR theory is derived from the properties of the superoperators governing the evolution of the reduced density matrix. Namely, the evolution proceeds on two incommensurate time scales. Of the possible quantum coherences entering the expansion of the reduced density matrix, nearly all decay fast, at rates compatible with the rates of vibrational relaxation and dephasing processes stimulated by the rotator-bath interactions. Only two types of coherences can live long enough to be detectable in NMR experiments through their spin parts, where the term “coherence” is now extended to any combination of the coherences mentioned above. For the sake of transparency, the latter will further be termed “primitive coherences.” In the low temperature limit, the long-lived coherences can be described as Boltzmann combinations of the primitive coherences between pairs of sublevels on the sequential torsional levels, $|p\Gamma\rangle\langle p'\Gamma'|$, where each such combination occurs multiple times in the expansion of the reduced density matrix, as being associated with different primitive coherences between spin states of appropriate symmetries. At higher temperatures, the combination coefficients are no longer exactly equal to Boltzmann factors, and the long-lived combinations can also include admixtures of other types of primitive coherences between the spatial states. The coefficients entering these peculiar combinations can be evaluated numerically.

There are two kinds of the long-lived coherences, once dubbed “tunneling” and “Kramers” coherences.⁷ The leading component of a representative tunneling coherence is a combination of the primitive coherences between sublevels A and one of the Kramers sublevels, say E_a . Apart from this one, denoted by (A, E_a) , the term “tunneling coherence” involves its complex-conjugate counterpart (A, E_b) and the corresponding Hermitian adjoints, $(E_{a,b}, A)$. In absence of spin-dependent interactions, the tunneling coherences would evolve as damped oscillations with frequencies $\pm\Delta$ and damping-rate constant k_t . At low temperatures, Δ can be approximated by Boltzmann combination of the tunneling frequencies on the ground and first torsional levels. In this work, Δ is defined as the oscillation frequency of the coherences of symmetries $(A, E_{a,b})$ such that its limiting, low temperature values will be negative.

The leading components of the long lived Kramers coherences include the Kramers pairs, $(E_{a,b}, E_{b,a})$. They evolve with damping-rate constant k_K and zero oscillation frequency, which is a reminiscence of the perfect Kramers degeneracy. Unlike for Δ , for k_t and k_K , simple formulations are non-existent even in the low temperature limit, but at any temperature they can be calculated numerically using a parametrized model described earlier.^{7,24,25} For a given set of model parameters, it consistently delivers temperature-dependent values of Δ , k_t , and k_K .

The DQR approach finalizes in the equation of motion for the long-lived part of the reduced density matrix. It involves delocalized rotator and is described in the spin-space manifold spanned by the tunneling and Kramers coherences, of which each occurs multiple times, each time associated with a primitive spin coherence of appropriate symmetries as dictated by the Pauli principle. This manifold has the same dimension as the pure spin manifold. The equation of motion can be transcribed to the latter, by localizing the rotator using the uncorrelation/recorrelation technique described earlier, which does not imply any loss of accuracy.^{7,28} The final equation of motion for the spin density matrix of the localized rotator is⁷

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

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

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

and $\hat{H}$ is the standard spin Hamiltonian describing the Zeeman, CSA, and DD interactions (and, for deuterated rotators, the quadrupole interactions) for the rotator specifically oriented in the external magnetic field. The term multiplied with Δ describes (generalized) Heisenberg couplings between the nuclei in the rotator, arising from the coherent rotational tunneling. For spin-1/2 nuclei, these couplings appear as the familiar J -couplings¹

$$\frac{\Delta}{3}(\hat{C} + \hat{C}^{-1}) = \frac{2\Delta}{3}(\hat{\mathbf{I}}_1\hat{\mathbf{I}}_2 + \hat{\mathbf{I}}_2\hat{\mathbf{I}}_3 + \hat{\mathbf{I}}_1\hat{\mathbf{I}}_3). \quad (3)$$

It is seen from Eq. (1) that, indeed, for $k_t/k_K = 1$, the description of the incoherent dynamics reduces to that based on the jump model. An alternative formulation of the DQR terms entering Eq. (1) is as follows (see Ref. 23 and Erratum to it):

$$\begin{aligned} & -i[\frac{\Delta}{3}(\hat{C} + \hat{C}^{-1}), \hat{\rho}] - \frac{k_K}{3}(2\hat{\rho} - \hat{C}\hat{\rho}\hat{C}^{-1} - \hat{C}^{-1}\hat{\rho}\hat{C}) - \frac{k_t - k_K}{2}(\hat{\rho} - \hat{U}\hat{\rho}\hat{U}) \\ & = -(T_t\hat{G}_A\hat{\rho}\hat{G}_E + T_t^*\hat{G}_E\hat{\rho}\hat{G}_A) - k_K(\hat{G}_{E_a}\hat{\rho}\hat{G}_{E_b} + \hat{G}_{E_b}\hat{\rho}\hat{G}_{E_a}), \end{aligned} \quad (4)$$

where $T_t = i\Delta + k_t$, and $\hat{G}_A, \hat{G}_{E_a} = \hat{G}_{E_b}^*$, and $\hat{G}_E = \hat{G}_{E_a} + \hat{G}_{E_b}$ are group projectors of the feasible group C_3 , thus

$$\hat{G}_\Gamma = \frac{1}{3}(\hat{I} + \lambda\hat{C} + \lambda^*\hat{C}^{-1}), \quad (5)$$

with $\lambda = 1$ for $\Gamma = A$, and $\lambda = \exp i2\pi/3$ for $\Gamma = E_a$. The formulation in Eq. (4) allows one to immediately see that for $|\Delta| \ll k_t$, the evolution of $\hat{\rho}$ and, therefore, the spectral line-shape becomes virtually independent of Δ , regardless of

the magnitude of this parameter. Indeed, in this limit, in Eq. (4) one can put $T_i \approx T_i^* \approx k_i$.

III. EXPERIMENTAL AND COMPUTATIONAL PROCEDURES

The isotopic purity of 1,1,1-triphenylethane- d_{15} (**1**) is such as that of benzene- d_6 (99.98 at. %) used as one of the reagents in the synthesis of **1**. The synthesis and details of the NMR measurements on the powdered and single-crystal samples of **1** and of the single crystal orientation are described in the [supplementary material](#). Unlike the common practice employed also in Ref. 12, the initial points of the free induction decay (FID) signal, being lost due to instrumental limitations, were not reconstructed. Conditions of variable-temperature X-ray diffraction (XRD) measurements on a single crystal of **1** and of differential scanning calorimetry (DSC) measurements on **1** and **1a**, as well as details of quantum chemical calculations, are also given there. The latter involve evaluations of the torsional barrier for the methyl group and of the CSA tensors for the methyl group protons. They were carried out using the Gaussian 09 package.³¹ The calculated torsional energy data, and the CSA tensors, are given in the [supplementary material](#).

Iterative least-squares, multi-parameter fits to the single-crystal, and powder spectra were performed using computer programs written in-house, the essential elements of which were described earlier.^{12,29} The procedure of theoretical calculations of the DQR quantities from first principles was reported previously.^{7,24,25}

IV. RESULTS

As already mentioned, 1,1,1-triphenylethane **1a** crystallizes in the $P2_1/n$ space group with four crystallographically equivalent molecules in the unit cell which are pairwise magnetically equivalent.¹⁹ A magnetically non-equivalent pair is shown in Fig. 1. An NMR spectrum of a single crystal of **1** in a general orientation in the magnetic field would be a superposition of signals from two differently oriented, structurally equivalent methyl groups. Intermolecular distances between the methyl protons (the only protons in the investigated sample) are large, above 0.6 nm. For this reason, the resonance lines remain relatively narrow in the absence of broadenings by the incoherent methyl group dynamics. In a theoretical description of the powder spectra of **1**, it is sufficient to accumulate spectra of only one methyl group in its various, isotropically distributed orientations.

The powder spectra of **1** were measured from room temperature down to 35 K. Below about 92–93 K, the spectra become free from the dynamic line broadenings. Such spectra will further be referred to as “static” while those evidencing molecular rate processes in their line shapes as “dynamic,” following the nomenclature used in liquid-phase NMR.

A. Analysis of static spectra

The patterns of the static spectra show small, systematic changes with further decrease of temperature to 45 K, which are concerned with systematic changes of Δ with temperature. Below 45 K the spectral pattern no longer changes, due to

FIG. 1. View along axis a^* of two magnetically non-equivalent molecules in the unit cell of 1,1,1-triphenylethane **1a** ($P2_1/n$ space group).

the stabilization of Δ which reaches its limiting value equal to the tunneling splitting of the ground torsional level. Examples of spectra from the considered temperature range are shown in Fig. 2. As already mentioned, the initial points of the FID signal, which were being lost because of instrumental limitations, were not reconstructed. Accordingly, in the frequency spectra, the signals come with growing admixture of their dispersion components along with increasing offsets from the center. These admixtures have opposite signs on the opposite offsets. It is evident at a first glance that the values of Δ must be at most comparable to or smaller than the DD coupling otherwise the spectral envelopes would include small outer components appearing in strange phases.

FIG. 2. Experimental static ^1H powder spectra of **1** at selected temperatures (black) superposed with best fit theoretical spectra (red). The average values of spectral parameters extracted in the fits are: $d = 0.18040$ nm (DD coupling constant = -20.46 kHz), $w_L = 855$ Hz, $w_G = 1890$ Hz, $\tau_D = 3.8$ μs , $\sigma = 9.8$ ppm, $\xi = 134^\circ$, and $\eta = 0.02$ (y axis of the CSA tensor lying in the C–C_{methyl}–H plane). The values of Δ determined in the range 35–87 K are displayed in Fig. 3.

The static spectra were fitted with a theoretical line shape model based on the standard spin Hamiltonian for methyl group protons including the Zeeman, DD, CSA, and Heisenberg coupling terms. Examples of the fits are shown in Fig. 2. All the fits, including those not shown in Fig. 2, are virtually perfect, to the extent earlier unreported. The relevant technical details affording such a high quality of the fits need to be exposed in some detail because in the main part of this work subtle line shape effects will be considered. The physical origin of these should be beyond any question.

In the calculations of the spectra, the effect of delayed acquisition of the FID signal was modeled as follows. The theoretical state of the spin system at the beginning of acquisition of the FID signal was calculated from the theoretical state immediately after the radiofrequency (r.f.) pulse. A perfect performance of the pulse was assumed such that the considered state included only the set of single-quantum coherences of the same phase. That state was evolved under the action of the spin Hamiltonian mentioned above through an adjustable interval τ_D whose nominal value in the experiment settings was fixed at 4.5 μ s. It was assumed that the (absorption-dispersion, see below) signal shapes of all individual resonances in the static spectra are independent of the position of the signal on the frequency axis and of the orientation of the crystallite in the magnetic field. The spectrum is calculated in two steps. After the first step, it comes as a superposition of contributions from individual crystallites, taken with appropriate weights.³⁰ At this stage, the spectra of individual crystallites include Lorentzian signals with the half width at half height equal w_L , which have mixed absorption-dispersion phases, according to the calculated effects of the free evolution through interval τ_D . At this stage, the spectra in the frequency domain are calculated for equidistant frequency points separated by 1/4 of the frequency interval in the experimental spectrum. At the second step, the theoretical powder spectrum function is numerically convoluted with Gaussian function $\exp(\omega^2/2w_G^2)$, where the values of the final spectral envelope are calculated only at the experimental frequencies.

As a sensitive parameter of the calculated spectral functions, τ_D was adjusted in the fits to the static spectra. A number of further simplifying assumptions were adopted in the theoretical model of the static spectra. They are as follows: (i) The methyl groups in **1** have the standard tetrahedral geometry with adjustable distance d between the methyl protons. (ii) The CSA interactions of the individual methyl protons conform with an idealized threefold symmetry of the methyl group such that only one CSA tensor needs to be specified. It is characterized by anisotropy parameter σ , asymmetry η defined according to Haeberlen's convention,³² and angle ξ between the principal z axis and the threefold axis. In the fits to the static experimental spectra, the list of adjusted parameters included Δ (the tunneling frequency), d , w_L , w_G , τ_D , σ , ξ , and η and a number of purely experimental parameters such as the overall amplitude of the spectrum, baseline intercept and slope, and the reference frequency (the magnetic field shows a slight drift in time). The parameter values delivered at convergence are consistent and temperature-independent to within the respective standard errors obtained in the fits, except for

the values of Δ showing a significant, smooth dependence on temperature in the range 35–87 K. The average values of the temperature-independent parameters are given in the caption of Fig. 2.

The static spectra were measured and analyzed to evaluate the CSA, d , w_L , w_G , and τ_D spectral parameters. These were further used as fixed quantities in the fits to the dynamic spectra. The spectra have also provided data for a prediction of the temperature behavior of Δ over a wider temperature range. The determined temperature trend of Δ in the range 35–87 K is shown in Fig. 3, together with its hypothetical, linear extrapolation to higher temperatures. In the fits to the dynamic spectra, the values of Δ calculated from the linear relationship in Fig. 3 were also used as fixed parameters.

To validate the Δ values extracted from powder spectra, the corresponding data determined from static spectra of an oriented single crystal of **1** are also shown in Fig. 3. The fits to the single crystal spectra are displayed in Fig. 4. Details about the orientation of the crystal are given in the caption of Fig. 4 and in the [supplementary material](#). At variance with the treatment of powder spectra, fixed CSA parameters obtained in quantum chemical calculations using the Gaussian 09 package,³¹ described in the [supplementary material](#), were used in these fits, because the bulk susceptibility effects in the investigated, non-spherical crystal prevented the determination of the CSA tensors from the rotation pattern. The values of Δ extracted from both kinds of low temperature spectra are somewhat different. However, the differences do not exceed the “natural” line widths and bulk susceptibility effects which are differently evidenced in the single crystal and powder spectra. Actually, the values of Δ extracted from 7 spectra of the single crystal, measured at 68.5 K for different orientations thereof, show some scatter, such that the average value of $\Delta/2\pi = -6.9$ kHz comes with the standard error of 1.2 kHz. The observed differences between the powder and single-crystal data are commensurate with the latter quantity.

FIG. 3. Temperature trends of the values of Δ obtained from the static powder (black squares) and single-crystal (red triangles) ^1H spectra of **1**. Straight line: linear approximation of the trend of Δ evaluated from the powder spectra in the range 58–87 K.

FIG. 4. Experimental static ^1H spectra of a single crystal of **1** (black) superposed with best fit theoretical spectra (red). Each spectrum is a superposition of signals of two magnetically non-equivalent methyl groups in the unit cell. The crystal is oriented in such a way that the threefold axis of one of these groups is perpendicular to the direction of the static magnetic field. (See [supplementary material](#) for further details about the orientation and the experimental rotation pattern confirming the orientation.)

B. Analysis of dynamic spectra

Around 93–94 K there is the onset of incoherent processes influencing the proton spectra of **1**. The dynamic powder spectra of **1** were measured in the range 99–121 K in the intervals of 2° – 3° . Two series of fits to these spectra were performed. For the sake of brevity, the fits from these series will further be referred to as CFs (conventional fits) and QFs (quantum or DQR fits). The CFs were performed using the conventional “classical” model where the nonclassicality coefficient $c = k_t/k_K$ is assumed equal to 1 in which instance the DQR line shape equation in Eq. (1) becomes the standard Alexander-Binsch equation with parameter k_K ($=k_t$) now interpreted as the classical rate constant k of random jumps of the methyl group rotator between its three equilibrium orientations. The QFs were performed using the full, quantum version of the cited equation. In the QFs, apart from k_K , the coefficient c was also adjusted.

In all series of the fits, the CSA, d , w_L , w_G , and τ_D spectral parameters were given fixed values, evaluated in fits to the static spectra (see caption of Fig. 2). The evolution during the initial period of length τ_D was calculated using Eq. (1) with the parameter values entering it having been appropriately updated at the sequential iterative steps. In both series, the tunneling frequencies at the individual temperatures were fixed at the values calculated from the linear extrapolation of the (approximately linear) experimental trend evaluated from static spectra in the range 58–87 K, as shown in Fig. 3. Use of the fixed values of Δ appeared to be the only reasonable policy, considering that even in the static spectra with relatively narrow resonance lines, the Heisenberg couplings are only indirectly readable from the experimental patterns.

In spite of fixing numerous line shape parameters, obtaining unbiased estimates of the DQR quantities k_K and c from the

iterative line-shape fits could hardly be expected for the whole temperature range. The experience from the previous investigations of the DQR effects in single-crystal spectra¹⁸ is that if the nonclassicality coefficient c does not depart much from its limiting, “classical” value 1, faithful estimates of these parameters can be obtained only in the slow exchange limit. With increasing exchange rates, statistical correlations between the discussed estimates grow stronger and stronger, to the extent that the fitting procedures become eventually divergent. For powder spectra, the situation cannot be better in this respect. The fit results to be presented in this subsection involve temperature range where the convergence problems did not occur. However, above a threshold temperature of 108–110 K, the physical significance of the observed temperature trend of c can be questioned as having been severely affected by either the statistical correlation or other effects of an unknown origin. These effects are considered in Sec. V. In the graphical data presentations in this section, the fit results whose physical significance can be disputable are distinguished.

Examples of the QFs are shown in Fig. 5. Like those not shown in the figure, they are of an excellent quality. Above 113–114 K, the quality of the CFs is similar to that of the QFs. However, as shown in Fig. 6, at lower temperatures, the quality of the former is noticeably worse. In this range, the ratios of the respective rms errors can exceed 2 in favor of the QFs. As pointed out in Sec. V using simple statistical arguments, the sole fact that in the QFs one more parameter is adjusted could not explain such an improvement of the fits. The superiority of the DQR to the conventional model, although not very spectacular in the investigated case, has a solid physical basis.

The values of c obtained in the QFs are shown in Fig. 7. In the whole temperature range, they substantially differ from 1. However, contrary to expectations based on general grounds and theoretical calculations,^{7,25,33,34} the decreasing with temperature trend of the values of c shows an unexpected reversal above 110–112 K. In Fig. 7, the increasing part of the trend is displayed with open symbols. Such a behavior might indicate a phase transition in **1** around 110–112 K. However, neither the DSC nor variable temperature, single-crystal XRD measurements could support

FIG. 5. Experimental dynamic ^1H powder spectra of **1** at selected temperatures (black) superposed with best fit theoretical spectra calculated according to the DQR model (red).

FIG. 6. A comparison of the conventional (blue) and quantum (red) fits to the experimental dynamic ^1H powder spectra of **1** (black) at the displayed temperatures. At 104.5, 107.1, and 108.6 K, the ratios of the rms errors in the conventional and DQR fits are 1.96, 2.15, and 2.10, respectively.

this supposition. As pointed out in Sec. V, this behavior of c is most likely non-physical while that observed at lower temperatures can be corroborated by theoretical arguments.

Over the range 99–121 K, the values of k_K obtained in the QFs do not show a consistent growth with increasing temperature. However, the product $ck_K \equiv k_t$ does show such a growth, being in a reasonable agreement with the Arrhenius law. The Arrhenius plots of these values and those of $k = k_K \equiv k_t$ obtained in the conventional fits are displayed in Fig. 8.

In the low-temperature range, the experimental values of k_t deviate somewhat up from the ideal Arrhenius trend and those of k deviate stronger and in the opposite direction. The latter effect is understandable, considering the form of the line-shape equation in Eq. (1). It suggests that the conventional fits

FIG. 7. Values of $c = k_t/k_K$ obtained in the DQR fits. The increasing part of the temperature trend is distinguished because of its probably non-physical character (see text).

FIG. 8. Arrhenius plot of the values of k (open black squares) and k_t (red full squares) obtained in the conventional and DQR fits. The Arrhenius parameters k_{t0} and E_{aQ} evaluated from the values of k_t (red best-fit line) are $(1.05 \pm 0.25) \times 10^{13} \text{ s}^{-1}$ and $4.11 \pm 0.05 \text{ kcal mol}^{-1}$, respectively, and those of k_0 and E_{aC} evaluated from the values of k (black best-fit line) are $(2.10 \pm 0.51) \times 10^{13} \text{ s}^{-1}$ and $4.25 \pm 0.06 \text{ kcal mol}^{-1}$, respectively.

should deliver values of k falling somewhere between the quantum rate constants if, as it does take place herein, c considerably exceeds 1.

V. DISCUSSION

A. Comments to inferences from static spectra

At low temperatures, where the static spectra extend over a considerable frequency range, the optimized values of τ_D , about $3.8 \mu\text{s}$, are about one dwell time ($1 \mu\text{s}$) smaller than the nominal value $4.5 \mu\text{s}$. The motionally narrowed, quasi-static spectra near room temperature are twice narrower. For the latter, the fits exactly reproduce the nominal value $4.5 \mu\text{s}$. The deviations from the nominal value are evidently inversely correlated with the overall width of the spectral pattern. In the approach aimed at a possibly exact reproduction of the experimental spectra, the adjustable τ_D parameter compensates for non-ideal performance of the applied radiofrequency pulses.

The parameters w_L and w_G were introduced to model the “natural” shape of the resonance signals in the absence of the exchange effects. These parameters describe mainly the envelopes of the unresolved patterns due to intra- and intermolecular DD interactions not included in the spin Hamiltonian. They also act as effective measures of the bulk magnetic susceptibility effects on the Larmor frequencies of the methyl protons. These effects vary with varying size, shape, and orientation of the crystallites.

The values characterizing the CSA tensor, extracted in the fits, fall not far from the values calculated theoretically for the XRD geometry of **1a**, given in the [supplementary material](#), although the latter deviate somewhat from the idealized threefold symmetry of the methyl group, assumed in the fits to the powder spectra. The most pronounced difference involves the asymmetry parameters which in the calculated CSA tensors substantially depart from zero and are different for different methyl protons. In a motionless powdered sample, the orientation-dependent resonance frequencies are controlled not only by the “true” CSA tensors but also by the bulk susceptibility effects as well. Therefore, in the considered fits, the proton CSA tensors had to be treated as effective quantities.

The correctness of the adopted way of theoretical modeling of the powder patterns is confirmed by the perfect quality of the fits obtained for the static spectra. It is noteworthy that the evaluated proton-proton distance of 0.1804 nm is in a very good agreement with the standard value of 0.1790 nm for a perfectly tetrahedral methyl group with C–H bonds of 0.109 nm.

B. Differences between the conventional and DQR fits

A considerable worsening of the fit quality on coming from the DQR to the conventional line-shape model, although visually not spectacular, is a clear indication of the usefulness of powder spectra in the pursuing of the DQR effects. The counterargument that in fits to experimental data an increased number of fitted parameters will generally lead to improved fits is meaningless in the present case if a quantitative measure of the improvement is taken into account. In the Fisher-Snedecor approach to the evaluation of theoretical models of experimental data, the model is characterized by the number of degrees of freedom for error. For both types of the discussed fits, these numbers, i.e., the differences between the numbers of spectral points and fitted parameters, are nearly the same even if the experimental points on the signal wings are not counted. The more than twice reduction of the rms error (i.e., more than fourfold reduction of the variance), with practically no decrease of the number of the degrees of freedom, should remove any doubts involving both the validity of the DQR model and the applicability of powder spectra to the considered purpose.

C. Interpretation of the obtained DQR parameters

The strange course of the nonclassicality coefficient c above about 110 K is most probably non-physical. Among the possible reasons of such a behavior, a failure of the linear extrapolation of the Δ values to these temperatures may be suspected. On the other hand, the values of k_t evaluated in the QFs, shown in Fig. 8, appear to be close to the true values over the whole temperature range.

To assess the adopted assumption about a linear dependence of Δ on temperature, the temperature behavior of k_t was simulated theoretically using the already cited DQR model.^{7,23,25} Formerly it afforded a perfect theoretical reproduction of the DQR effects evaluated from spectra of a single crystal¹² and of the spin-lattice relaxation data reinterpreted in the spirit of the DQR approach.^{25,34} Before going into details

of these calculations, a brief description of the relevant model parameters will be given.

For the assumed input values of its free parameters, the model delivers temperature trends of Δ , k_t , and k_K , calculated in a consistent way in the requested temperature range. For the methyl groups attached to a sp^3 -hybridized atom where, moreover, there are at least three torsional levels below the top of the torsional barrier, the model employs only three free parameters. These include the following: (i) the amplitude, V , of the cosine-shaped potential, $V(1 - \cos 3\varphi)/2$, where φ is the torsional coordinate; (ii) the rotator-bath coupling constant f measuring the strengths of the perturbation of the torsional potential by the bath oscillations; and (iii) the generalized Debye frequency ω_c determining the maximum frequency of the bath (harmonic) oscillators. In the previous applications of the model, a relatively high value of ω_c , of 600 cm^{-1} if expressed in wave numbers, was being usually used. In this way, the lattice oscillations could be augmented by some purely intramolecular vibrations potentially affecting the torsional potential. The parameter f actually describes perturbations of two different sorts, the sine- and cosine-shaped ones, of the, in general different, respective strengths f_s and f_c .^{7,20–22} However, for strongly and moderately hindered groups, the calculated values of Δ , k_t , and k_K are in practice dependent only on the ratio $(f_s^2 + f_c^2)/\omega_c^2$ if the values of these individual quantities are varied in reasonable limits.²⁵ Therefore, the use of the somewhat arbitrary value of ω_c is legitimate in the calculations for the system of the present interest. The moment of inertia of the methyl group is not treated as a free parameter. Like in the previous calculations, its value corresponding to the tetrahedral methyl group, with the C–H bonds of 0.109 nm, is used.

These calculations were aimed at a possibly fair reproduction of the temperature behavior of both k_t in the whole range 99–121 K and c at temperatures below about 110 K at which the latter quantity behaves qualitatively correctly. To this end, the values of two model parameters, V and f , were varied in a trial-and-error manner until, for $V = 1574 \text{ cm}^{-1}$ and $f (= f_s = f_c) = 190 \text{ cm}^{-1}$, an acceptable reproduction of these trends was obtained. In Fig. 9, the experimental values of Fig. 8 are superposed with the theoretical trend of k_t . The latter is almost perfectly linear in the Arrhenius coordinates, which is one more justification of this empirical law. The (rather small) discrepancies of the calculated trend with the actual Arrhenius curve fitted to the experimental points in Fig. 8 are commented below. In view of the inherent limitations of accuracy of quantum chemical computations for large molecules, the evaluated torsional barrier of 1574 cm^{-1} is in an acceptable agreement with that of 1685 cm^{-1} calculated with the Gaussian 09 package (see Fig. S2 in the [supplementary material](#)). The calculated trend of $c = k_t/k_K$ will be commented later on.

The discussed calculations of the DQR parameters delivered also the temperature dependence of Δ in the range 99–121 K. In a separate run, the calculations of Δ for the above values of V and f were extended to low temperatures at which the considered model gives zero values for both of the rate constants. The calculated temperature trend of Δ is compared in Fig. 10 with the experimental data from the single-crystal and powder spectra.

FIG. 9. The rate constants from Fig. 8 compared with the theoretical values of k_t calculated for $V = 1574 \text{ cm}^{-1}$ and $f = 190 \text{ cm}^{-1}$ (dotted line).

The obtained reproduction of the temperature behavior of k_t , although relatively fair, is not as good as that reported previously for a single crystal.¹² There may be two sources of the discrepancies. First, the values of k_t as well as other relevant parameters extracted from powder spectra may be less accurate as compared with the single-crystal data. Second, the adopted value of the moment of inertia may be somewhat different from the actual value due to the possible deviations of the geometry of the methyl group in **1** from its standard

shape. Nevertheless, in the range 70–90 K, the experimental Δ values obtained from the powder spectra are fairly reproduced theoretically (the single-crystal data are even perfectly matched). The discrepancies below 60 K are understandable because at such low temperatures, the actual torsional barrier may be somewhat higher due to a shrinkage of the crystals of **1** with decreasing temperature. As far as the linear extrapolation of the experimental trend is concerned, up to about 110 K the theoretical values of Δ do not deviate from it by more than 1.0–1.5 kHz, but with further increase of temperature they take a radically different course.

Even if both V and f are changed up or down by a few cm^{-1} , the calculated curve of $\Delta(T)$ remains almost unchanged in the range 65–110 K. This may mean that the theoretical values of Δ are realistic at least in this range.

The reversal around 110 K of the initially decreasing temperature trend of the values of c (see Fig. 7) was already commented upon as probably an artifact. In view of the model calculations discussed above, it may in part result from an increasing with temperature bias of the estimate of c by a widening gap between the values of Δ assumed in the fits and the true values of this parameter. The true temperature behavior of Δ above 110 K may be better represented by the theoretical values shown in Fig. 10, rather than the linearly extrapolated values. In Fig. 11 the discussed temperature behavior of c is compared with the theoretical predictions calculated for $V = 1574 \text{ cm}^{-1}$ and $f = 190 \text{ cm}^{-1}$. Simultaneously, the assumed linear trend of Δ is compared with the theoretical trend. It is seen from this data that, indeed, the counterintuitive change of the course of c roughly coincides with the onset of a rapid divergence of these two trends. If the QFs are repeated, but with the linearly extrapolated Δ values replaced by the theoretical values, the decreasing trend of c is continued up to about 115 K, as shown in Fig. 11 using red symbols. The persistent, strange behavior of c above 115–116 K may have yet another cause, as will be commented later on.

FIG. 10. Same as Fig. 3, but with added dotted line describing the theoretical behavior of Δ calculated for $V = 1574 \text{ cm}^{-1}$ and $f = 190 \text{ cm}^{-1}$.

FIG. 11. Left y axis: the values of c from Fig. 7 (black solid and open squares) compared with the theoretical values of c (solid line) calculated for $V = 1574 \text{ cm}^{-1}$ and $f = 190 \text{ cm}^{-1}$ and the values of c obtained in fits with assumed theoretical values of Δ (red solid and open squares). The values evidently lacking physical sense are displayed with open symbols. Right y axis: the values of Δ linearly extrapolated from the low temperature data and the theoretical values calculated for $V = 1574 \text{ cm}^{-1}$ and $f = 190 \text{ cm}^{-1}$ (dashed and dotted lines, respectively).

In the decreasing part of the trend augmented with these new fit results, the values of c , initially reaching 2.7, consistently drop to about 1.5. The corresponding theoretical curve calculated for $V = 1574 \text{ cm}^{-1}$ and $f = 190 \text{ cm}^{-1}$ also subsides in the entire range 99–121 K but much gentler than do the experimental values below 115 K. Although the obtained correspondence between the theoretical and experimental values is only semiquantitative, the conclusion that in the slow exchange region the values of c substantially depart from the “classical” value 1 has solid grounds. It is remarkable that it was reached on the basis of data extracted solely from powder spectra.

The extension up to 115 K of the decreasing trend of the experimental values of c by the use of the theoretical values of Δ may indicate that the latter values are realistic. At a first glance, their temperature behavior may appear non-physical, because with increasing temperature the coherent tunneling should give way to classical processes. However, for such a quantum-to-classical transition to occur, Δ as such need not tend to zero. As was argued previously,³⁴ for the temperature-driven quenching of the coherent tunneling to take place, it is sufficient that the ratio of $|\Delta|/k_t$ be tending to zero. This is because in the DQR formalism, these two quantities always occur jointly as the complex-valued quantities $T_i = -k_t \pm i\Delta$ describing evolution of the long-lived tunneling coherences (see comment to Eq. (4)). In the case considered presently, the theoretical values of the above ratio do show such a temperature behavior. Above 113 K, this ratio drops to 0.1 (but only above 300 K it falls below 0.05).

Above 115 K, the considered powder patterns are being gradually deprived of their information content involving the DQR effects. Consequently, they become insensitive to the values of c , and, with decreasing ratio $|\Delta|/k_t$, to the Δ values as well. Even with fixed Δ , the QFs with both c and k_K subject to adjustments become overparametrized. The separate values of these parameters delivered at convergence can then completely lose physical sense, as can be seen in Figs. 7 and 11 for the fit results for c at these temperatures. However, their

product $k_t = ck_K$ still behaves robustly such that its values do not change much even when the fixed values of Δ are considerably changed. For this reason, just the temperature behavior of k_t was taken as a primary benchmark in the discussed model calculations of the DQR parameters.

VI. CONCLUSIONS

It is shown that, in the pursuing of the DQR effects for a hindered methyl group, wide-line powder ^1H NMR spectra can be used. Such spectra are much easier to obtain than the single crystal spectra. As compared with single-crystal spectra, the accuracy with which the relevant parameters can be extracted from powder spectra in iterative line-shape fits is limited. Despite this, a substantial departure of the hindered dynamics of the methyl group from the classical limit could be stated unequivocally in this paper for 1,1,1-triphenylethane selectively deuterated in all aromatic positions. Measured by the ratio of the two quantum-rate constants appearing in the DQR approach, the degree of nonclassicality of the interesting dynamics in the investigated material can exceed 2.0 in the slow exchange limit, with the value of 1 corresponding to the classical picture. A semiquantitative reproduction of the observed temperature dependences of all three DQR quantities, the two quantum-rate constants and the effective tunneling frequency, was obtained using a theoretical model reported formerly. One of the highlights of this paper is that this result was achieved by adjusting only two free parameters of the model.

The present contribution points to a new, facile way of studies of the still insufficiently recognized DQR effects in methyl groups and similar atomic arrangements in molecular crystals.

SUPPLEMENTARY MATERIAL

See [supplementary material](#) for details of the synthesis of **1**, XRD, DSC, and NMR measurements on **1**, including the NMR single-crystal experiments, as well as theoretical

calculations of the torsional barrier and proton CSA tensors in this compound.

ACKNOWLEDGMENTS

P.B., A.O., and S.S. acknowledge partial financial support of this work by the National Center of Science (NCN Grant No. 2012/05/B/ST4/00103).

- ¹F. Apaydin and S. Clough, *J. Phys. C: Solid State Phys.* **1**, 932 (1968).
- ²T. Bernhard and U. Haeberlen, *Chem. Phys. Lett.* **186**, 307 (1991).
- ³A. Detken, P. Focke, H. Zimmermann, U. Haeberlen, Z. Olejniczak, and Z. T. Lalowicz, *Z. Naturforsch., A: Phys. Sci.* **50**, 95 (1995).
- ⁴E. M. Hiller and R. A. Harris, *J. Chem. Phys.* **98**, 2077 (1993).
- ⁵A. Detken, H. Zimmermann, and U. Haeberlen, *Mol. Phys.* **96**, 927 (1999).
- ⁶P. Gutsche, M. Rinsdorf, H. Zimmermann, H. Schmitt, and U. Haeberlen, *Solid State Nucl. Magn. Reson.* **25**, 227 (2004).
- ⁷S. Szymański, *J. Chem. Phys.* **111**, 288 (1999).
- ⁸S. Clough, *NMR. Basic Principles and Progress* (Springer-Verlag, 1976), Vol. 13, pp. 113.
- ⁹S. Alexander, *J. Chem. Phys.* **37**, 974 (1962).
- ¹⁰D. A. Kleier and G. Binsch, *J. Magn. Reson.* **3**, 146 (1970).
- ¹¹S. Szymański, Z. Olejniczak, A. Detken, and U. Haeberlen, *J. Magn. Reson.* **148**, 277 (2001).
- ¹²P. Gutsche, H. Schmitt, U. Haeberlen, T. Ratajczyk, and S. Szymański, *ChemPhysChem* **7**, 886 (2006).
- ¹³S. Szymański, Z. Olejniczak, and U. Haeberlen, *Physica B* **226**, 161 (1996).
- ¹⁴P. Bernatowicz and S. Szymański, *Phys. Rev. Lett.* **89**, 023004 (2002).
- ¹⁵I. Czerski, P. Bernatowicz, J. Jazwinski, and S. Szymański, *J. Chem. Phys.* **118**, 7157 (2003).
- ¹⁶P. Bernatowicz, I. Czerski, J. Jazwinski, and S. Szymański, *J. Magn. Reson.* **169**, 284 (2004).
- ¹⁷I. Czerski and S. Szymański, *Pol. J. Chem.* **80**, 1233 (2006).
- ¹⁸P. Bernatowicz, T. Ratajczyk, A. Shkurenko, B. Kamieński, and S. Szymański, *J. Phys. Chem. C* **119**, 3725 (2015).
- ¹⁹R. Destro, T. Pilati, and M. Simonetta, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **36**, 2495 (1980).
- ²⁰A. Hewson, *J. Phys. C: Solid State Phys.* **15**, 3841 (1982); **15**, 3855 (1982).
- ²¹A. Würger, *Z. Phys. B: Condens. Matter* **76**, 65 (1989).
- ²²A. Würger, *J. Phys. B: Condens. Matter* **1**, 6901 (1989).
- ²³T. Ratajczyk and S. Szymański, *J. Chem. Phys.* **123**, 204509 (2005); Erratum **137**, 029902 (2012).
- ²⁴T. Ratajczyk and S. Szymański, *J. Chem. Phys.* **127**, 184504 (2007).
- ²⁵P. Bernatowicz, A. Shkurenko, A. Osior, B. Kamieński, and S. Szymański, *Phys. Chem. Chem. Phys.* **17**, 28866 (2015).
- ²⁶S. Nakajima, *Prog. Theor. Phys.* **20**, 948 (1958).
- ²⁷R. Zwanzig, *J. Chem. Phys.* **33**, 1338 (1960); *Physica* **30**, 1109 (1964).
- ²⁸S. Szymański, *J. Chem. Phys.* **104**, 8216 (1996); Erratum **106**, 3430 (1997).
- ²⁹P. Bernatowicz, T. Ratajczyk, P. Kalicki, and S. Szymański, *Solid State Nucl. Magn. Reson.* **59-60**, 34 (2014).
- ³⁰T. Iwaniec, R. Kopiecki, and S. Szymański, *Solid State Nucl. Magn. Reson.* **68-69**, 25 (2015).
- ³¹M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, GAUSSIAN 09, Revision A.1, Gaussian, Inc., CT Wallingford, 2009.
- ³²U. Haeberlen, *Advances in Magnetic Resonance*, Suppl. 1 (Academic Press, New York, 1976).
- ³³N. Pislewski, J. Tritt-Goc, M. Bielejewski, A. Rachocki, T. Ratajczyk, and S. Szymański, *Solid State Nucl. Magn. Reson.* **35**, 194 (2009).
- ³⁴S. Szymański, *J. Chem. Phys.* **137**, 034513 (2012).