



ACADEMIC  
PRESS

Available online at [www.sciencedirect.com](http://www.sciencedirect.com)

SCIENCE @ DIRECT®

Journal of Magnetic Resonance 164 (2003) 60–64

JMR  
Journal of  
Magnetic Resonance

[www.elsevier.com/locate/jmr](http://www.elsevier.com/locate/jmr)

# NMR lineshape equations for hindered methyl group: a comparison of the semi-classical and quantum mechanical models

P. Bernatowicz and S. Szymański\*

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

Received 29 January 2003; revised 27 May 2003

## Abstract

The semiclassical and quantum mechanical NMR lineshape equations for a hindered methyl group are compared. In both the approaches, the stochastic dynamics can be interpreted in terms of a progressive symmetrization of the spin density matrix. However, the respective ways of achieving the same limiting symmetry can be remarkably different. From numerical lineshape simulations it is inferred that in the regime of intermediate exchange, where the conventional theory predicts occurrence of a single Lorentzian, the actual spectrum can have nontrivial features. This observation may open new perspectives in the search for non-classical effects in the stochastic behavior of methyl groups in liquid-phase NMR.

© 2003 Elsevier Science (USA). All rights reserved.

*Keywords:* NMR lineshape; Hindered rotation; Methyl group; Quantum rate process; Spin-echo

## 1. Introduction

Recent NMR lineshape studies on hindered methyl groups reveal that not only at cryogenic but at ambient temperatures as well the wave-like properties of such objects are experimentally detectable [1–3]. Certain features of the resonance signals observed cannot be reproduced when use is made of the semi-classical Alexander–Binsch (AB) lineshape theory [4,5]. The problem is not in the possible occurrence of coherent tunneling (for a recent review of this topics, see [6]) which can easily be taken into account in the AB approach [7–9], but in a classical treatment of the stochastic dynamics. Actually, the lineshape equation derived within the consistently quantum mechanical model of damped quantum rotor (DQR) [10] has proven perfectly adequate for the spectra of CD<sub>3</sub> [1] and CH<sub>3</sub> [2,3] groups, measured under diverse conditions. The results obtained for 9-methyltritycene derivatives in solution [2,3] are particularly interesting since they pose a challenge to the popular view that, at ambient temperatures, molecular rate processes are *par excellence*

classical. In the present paper, a comparison of the AB and DQR lineshape equations is made. It is shown that in both the classical and quantum pictures, the stochastic dynamics can be viewed as processes of a progressive symmetrization of the spin density matrix. The symmetry that emerges in the limit of motional narrowing is the same in both the pictures. However, in the regime of intermediate exchange the predicted signal shapes can be remarkably different, which may be of interest in experimental studies of the methyl group dynamics in liquids.

In the AB approach, the stochastic dynamics are pictured as a sequence of classical jumps of a hindered methyl group between its three equivalent, equilibrium orientations [9,11]; they are described by a single rate constant  $k = 1/(2\tau)$ , where  $\tau$  is the mean residence time in a given orientation. In the DQR model [10], these dynamics appear as quantum rate processes parameterized by two rate constants,  $k_t$  and  $k_K$ . They measure damping rates of two specific quantum coherences between the torsional sublevels  $A$ ,  $E_a$ , and  $E_b$  of the methyl rotor, where the labels denote the irreducible representations of the relevant permutation symmetry group isomorphic with  $C_3$ . Specifically,  $k_t$  involves the so-called tunneling coherence which engages the pairs

\*Corresponding author. Fax: +48-22-6326681.

E-mail address: [sszym@icho.edu.pl](mailto:sszym@icho.edu.pl) (S. Szymański).

$(A, E_a)$  (or  $(A, E_b)$ ), while  $k_K$  describes the so-called Kramers coherence comprising the pairs  $(E_a, E_b)$ . Both the coherences are temperature-dependent combinations of the corresponding coherences at the individual torsional levels. For methyl groups exhibiting resolved tunneling patterns in the inelastic neutron scattering spectra at cryogenic temperatures, the rate constants  $k_t$  and  $k_K$  can be identified with the widths of the inelastic and quasielastic scattering lines, respectively [12–14].

## 2. Theory

The DQR lineshape equation, formulated in the way exposing its relationship to the AB equation, reads:

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

where  $\hat{H}_s$  is the standard NMR Hamiltonian of the three identical nuclei in an orientationally localized methyl group,  $\hat{P}$  is the (unitary) operator of cyclic permutation of the spin coordinates of these nuclei, and  $\hat{U}$  is a unitary selfinverse operator defined according to [10]:

$$\hat{U} = \frac{1}{3} [2(\hat{P} + \hat{P}^{-1}) - \hat{1}]. \quad (2)$$

In Eq. (1), the effect of coherent tunneling is described by the term dependent on  $\Delta$ , where  $\Delta$  is the oscillation frequency of the tunneling coherence (i.e., a temperature-dependent combination of the tunneling splittings  $\Delta_n = (E_A^{(n)} - E_{E_a,b}^{(n)})/\hbar$  at the individual torsional levels). For spin-1/2 nuclei, it can be expressed as an appropriate  $J$ -coupling Hamiltonian, with the coupling constant  $J_t = 2\Delta/3$  [8].

When  $k_t$  and  $k_K$  happen to be equal, the DQR equation becomes formally identical with the AB equation for the classical rate constant  $k = k_t/3$  ( $= k_K/3$ ). In the Liouville representation, where  $\hat{\rho}$  is treated as a column vector (superket)  $|\rho\rangle$ , the dissipative part of the AB equation can be expressed as

$$-3k \left[ \frac{1}{3} (2\hat{1} \times \hat{1}^* - \hat{P} \times \hat{P}^* - \hat{P}^{-1} \times \hat{P}^{-1*}) \right]. \quad (3)$$

The superoperator in square brackets can be recognized to be the sum of the group superprojectors  $\mathbf{Q}_\gamma$ , concerned with the irreducible representations  $\gamma = E_a$  and  $E_b$  ( $= E_a^*$ ) of  $C_3$ , where  $E_a(C_3^1) = \epsilon$  and  $E_a(C_3^2) = \epsilon^*$ , with  $\epsilon = \exp(2\pi i/3)$ . Because the sum of all three superprojectors  $\mathbf{Q}_\gamma$ ,  $\gamma = A, E_a, E_b$ , is the unit superoperator  $\mathbf{1} = \hat{1} \times \hat{1}^*$ , with an increasing magnitude of  $k$  the rate process described in the AB equation can be viewed as a progressive damping of the coherences that are

comprised by the symmetry partitions  $\mathbf{Q}_{E_a}|\rho\rangle$  and  $\mathbf{Q}_{E_b}|\rho\rangle$  of the spin density superket. In the sequel, such a damping process will be briefly referred to as damping of the symmetry partitions themselves. For large values of  $k$ , the observable properties of the spin system are determined by the totally symmetric projection,  $|\rho_A\rangle = \mathbf{Q}_A|\rho\rangle$ , only. In that regime, only the projection  $\mathbf{Q}_A \mathbf{L} \mathbf{Q}_A$  of the spin superHamiltonian  $\mathbf{L}$  is relevant. The corresponding motionally averaged Hamiltonian has the familiar form

$$\hat{H}_{av} = \frac{1}{3} (\hat{H}_s + \hat{P}\hat{H}_s\hat{P}^{-1} + \hat{P}^{-1}\hat{H}_s\hat{P}) + \frac{\hbar\Delta}{3} (\hat{P} + \hat{P}^{-1}) \quad (4)$$

and its effective nuclear permutation symmetry is isomorphic with  $C_3$ . Note in passing that the fundamental chirality of the methyl group in an external magnetic field, whose spectacular manifestation is the effect of rotational polarization [15], has never been observed in NMR lineshape experiments. Therefore, in the limit of rapid exchange the effective symmetry of the methyl group is normally assumed to be isomorphic with  $C_{3v}$ .

The quantum rate processes described in the DQR equation can also be interpreted in terms of a progressive symmetrization of the spin density superket and, accordingly, of the spin Hamiltonian. The stochastic terms in Eq. (1) can be rearranged in such a way that the contributions of the rate processes described by  $k_K$  and  $k_t$  are separated [1], namely,

$$\begin{aligned} & -\frac{k_K}{4} [\hat{\rho}(t) + \hat{U}\hat{\rho}(t)\hat{U} - \hat{V}\hat{\rho}(t)\hat{V} - \hat{V}^*\hat{\rho}(t)\hat{V}^*] \\ & - \frac{k_t}{2} [\hat{\rho}(t) - \hat{U}\hat{\rho}(t)\hat{U}]. \end{aligned} \quad (5)$$

where  $\hat{V}$  is a unitary selfinverse operator analogous to  $\hat{U}$ ,

$$\hat{V} = \frac{1}{3} [2(\epsilon^*\hat{P} + \epsilon\hat{P}^{-1}) - \hat{1}]. \quad (6)$$

Because the product of any two of the (selfinverse) operators  $\hat{U}$ ,  $\hat{V}$ , and  $\hat{V}^*$  gives the third, they form a group isomorphic with  $C_{2v}$ . (In [1], the operators  $\hat{U}$ ,  $\hat{V}$ , and  $\hat{V}^*$  were needlessly taken with the opposite sign, what was irrelevant for the formalism presented therein.) The irreps of  $C_{2v}$  are given in Table 1. It may seem a surprise that in the description of an object whose natural symmetry is threefold there appears a symmetry group of order 4. Actually, the unitary operators  $\hat{U}$ ,  $\hat{V}$ ,

Table 1  
Irreducible representations of the  $C_{2v}$  symmetry group

	$E(\hat{1})$	$C_2(\hat{U})$	$\sigma(\hat{V})$	$\sigma'(\hat{V}^*)$
$A_1$	1	1	1	1
$A_2$	1	1	-1	-1
$B_1$	1	-1	1	-1
$B_2$	1	-1	-1	1

and  $\hat{V}^*$  are in a straight way related to the group projectors  $\hat{Q}_A = \frac{1}{3}(\hat{1} + \hat{P} + \hat{P}^{-1})$ ,  $\hat{Q}_{E_a} = \frac{1}{3}(\hat{1} + \epsilon^* \hat{P} + \epsilon \hat{P}^{-1})$ , and  $\hat{Q}_{E_b} = \hat{Q}_{E_a}^*$ , of  $C_3$ :

$$\begin{aligned}\hat{U} &= 2\hat{Q}_A - \hat{1}, \\ \hat{V} &= 2\hat{Q}_{E_a} - \hat{1}, \\ \hat{V}^* &= 2\hat{Q}_{E_b} - \hat{1}.\end{aligned}\quad (7)$$

The relationships between the group projectors of  $C_3$  and those of  $C_{2v}$ ,  $\hat{S}_\gamma$ , where  $\gamma = A_1, A_2, B_1, B_2$ , are trivial, because  $\hat{Q}_A = \hat{S}_{A_2}$ ,  $\hat{Q}_{E_a} = \hat{S}_{B_1}$ , and  $\hat{Q}_{E_b} = \hat{S}_{B_2}$ , while  $\hat{S}_{A_1} = 0$ . In Liouville representation, this is no longer so. After some simple matrix algebra in which use is made of the definitions of  $\hat{U}$ ,  $\hat{V}$ , and  $\hat{V}^*$  in Eq. (7), one arrives at the following equalities for the corresponding group superprojectors:

$$\mathbf{S}_{A_1} = \mathbf{Q}_A \quad (8)$$

and

$$\mathbf{S}_{A_2} + \mathbf{S}_{B_1} + \mathbf{S}_{B_2} = \mathbf{Q}_{E_a} + \mathbf{Q}_{E_b}. \quad (9)$$

Now, the dissipative term in Eq. (5) multiplied by  $k_K$  can be recognized to be the group superprojector  $\mathbf{S}_{A_2}$  of  $C_{2v}$ ,

$$\begin{aligned}-k_K \left[ \frac{1}{4}(\hat{1} \times \hat{1}^* + \hat{U} \times \hat{U}^* - \hat{V} \times \hat{V}^* - \hat{V}^* \times \hat{V}) \right] \\ = -k_K \mathbf{S}_{A_2}.\end{aligned}\quad (10)$$

Similarly, the term multiplied by  $k_t$  in Eq. (5) is a sum of the group superprojectors  $\mathbf{S}_\gamma$  concerned with the irreps  $\gamma = B_1$  and  $B_2$  of  $C_{2v}$ . The quantum rate processes described in the DQR equation can thus be viewed as damping processes of the symmetry partitions  $\mathbf{S}_\gamma |\rho\rangle$ , where  $\gamma = A_2, B_1$ , and  $B_2$ . Because for  $\gamma = A_1, A_2, B_1, B_2$  the superprojectors  $\mathbf{S}_\gamma$  sum up to  $\mathbf{1}$ , only the partition  $|\rho_{A_1}\rangle = \mathbf{S}_{A_1} |\rho\rangle$  will survive for fast damping. From Eq. (8) it therefore follows that for both the AB and DQR equations, the motionally averaged symmetries of the spin density matrix are exactly the same. Accordingly, the motionally averaged spin Hamiltonian is exactly the same as that arrived at in the limit of fast classical exchange (Eq. (4)). Also, the part of  $|\rho\rangle$  that ultimately undergoes damping,  $|\rho_d\rangle$ , is the same in both the approaches. However, on passing from the classical to the quantum picture of the stochastic dynamics, the uniform damping process of  $|\rho_d\rangle$ , with the classical rate constant  $3k$ , undergoes splitting into two such processes. Now, the part  $|\rho_{A_2}\rangle$  of  $|\rho_d\rangle$  is damped with the rate constant  $k_K$  while the remaining part,  $|\rho_{B_1}\rangle + |\rho_{B_2}\rangle$ , is damped with the rate constant  $k_t$ . It is important to realize that such a diversification of the damping rates can be maintained also in the regime of motional narrowing. In what follows, a possible significance of the latter observation for liquid-phase NMR studies on strongly hindered methyl groups is considered.

### 3. Discussion

For the already mentioned 9-methyltritycene derivatives [2,3], separate signals of the anisochronous methyl protons could still be observed at temperatures as high as 220 K. In that slow exchange region, the nonclassical character of the rate processes could easily be detected in the spectra. The degree of nonclassicality in the stochastic dynamics of methyl groups can be defined as the ratio  $c = k_t/k_K$  (although, in view of what was said above, it may be disputable whether for  $c$  approaching 1 the dynamics do become classical). For two of the triptycene derivatives investigated, the values of  $c$ , determined in the slow exchange region, are about 1.20 [2,3]. For most compounds containing methyl groups, the potential energy barriers involved are much lower than in these triptycene derivatives so that the regime of slow and moderate exchange might be inaccessible experimentally. However, the possibility of accessing the regime of intermediate exchange may be quite realistic. From the perspectives of the AB theory, the spectrum of the methyl protons would lack any non-trivial features in that regime: as long as the magnitude of the classical rate constant  $k/(2\pi)$  remains fairly greater (say, by more than a factor of 3) than the span of the relevant Larmor frequencies, the spectrum would appear as a superposition of Lorentzian signals centered at the average frequency and having the same width. In the case where the methyl protons form an  $A_2B$  spin system, to which the following discussion will be confined, the full-width-at-half-height of such signals is approximately equal to  $8\pi\delta^2/(27k)$ , where  $\delta$  is the Larmor frequency difference between the sites A and B, which is assumed to be much larger than the spin coupling constant,  $J$  (the possible contribution to the latter of the coherent tunneling may be of the order of a hertz [3]). In order to see whether the nonclassical effects in the stochastic dynamics can still be detected in the regime of intermediate exchange, numerical simulations using the DQR equation were performed for the values of the ‘‘classicality factor’’  $c$  from the range 0.6–1.75. At a first sight, the calculated spectra do resemble single Lorentzians whose apparent widths are nearly the same as the width of the ‘‘classical’’ spectrum calculated for the value of  $k = (2k_t + k_K)/9$ . However, a consideration of the pertinent, second-order perturbation expansion of the spectral matrix reveals that the individual overlapping Lorentzians, which contribute to the averaged spectrum, would in general have unequal widths. For values of  $c$  substantially departing from 1, these widths can be considerably different. However, a unambiguous experimental identification of such differences may be difficult. In our studies in the slow exchange limit [2,3], the spectra obtained from the FID signal collected after the Carr–Purcell echo sequence  $(\pi/2)_x - \tau - (\pi)_x - \tau$  [16,17] afforded a better visualization of the inadequacy of

the AB model than the standard spectra (following a common mispractice, in [2] the former were called Hahn-echo spectra). In the present context, use of such CP-echo spectra may also be advantageous: unlike for a true Lorentzian signal, for a superposition of Lorentzians with different widths the overall signal shape would be dependent on  $\tau$ . In order to get some insight in how exactly the shape of a broadened signal could be monitored, we performed experimental tests on a signal with a true Lorentzian shape. This was the methyl proton signal in 2-(dimethylamino)-4-cyanopyridine, DMACP. In DMACP, the symmetric doublet of the two anisochronous *N*-methyl groups undergoes coalescence at about 240 K, due to accelerated reorientation of the dimethylamino group around the partially double C2–N bond, and on further temperature increase it quickly becomes a pure Lorentzian. For the above-model system (3 mg DMACP dissolved in 0.8 ml CD<sub>2</sub>Cl<sub>2</sub>), the echo spectra for a series of  $\tau$  values were measured on our Bruker Avance DRX 500 NMR spectrometer in a single run, with cyclic repetition of the CP sequences for the individual  $\tau$ s. At 252 K, the full-widths-at-half-height of the (exchange-averaged) methyl proton signals, about 16.5 Hz, were constant to within 0.2 Hz for the range of  $\tau$  of 100  $\mu$ s (the “zero” echo time) to 40 ms, over which the signal amplitude drops by a factor of 50. Upon appropriate renormalization of the amplitudes, all of the echo spectra were fully superposable onto one another. At 263 K, where the FWHH is about 9.9 Hz and the range of  $\tau$  was 100  $\mu$ s to 80 ms, the reproducibility of the signal shape was even better (here, on passing from  $\tau = 100 \mu$ s to  $\tau = 80$  ms, the amplitude decreases 150 times). For the signals that comprise overlapping Lorentzians of different widths, one would observe a different behavior: a narrowing of the overall signal with increased echo time, due to gradually decreasing contribution of the broader components.

In Fig. 1, for theoretical echo spectra of a methyl group, calculated using the DQR equation, nonclassical effects in the stochastic behavior are illustrated in terms of a decrease with increased echo time of the apparent FWHH of the echo spectrum. In view of the test results described above, it is seen that in the instances where  $c$  falls outside the range 0.8–1.25, nonclassical character of the stochastic methyl dynamics can in principle be detected in the CP-echo spectra, although only at a qualitative level and with essentially no possibility to distinguish between the eventualities of  $c < 1$  and  $c > 1$ . Nevertheless, the above inferences may open new perspectives in the studies of non-classical behavior of methyl groups in liquids, since the class of methyl-bearing compounds for which the regime of intermediate exchange can be accessed may be quite broad.

The simple procedure of monitoring differences between the CP-echo spectra measured for different echo times could be used in the instances where the exchange

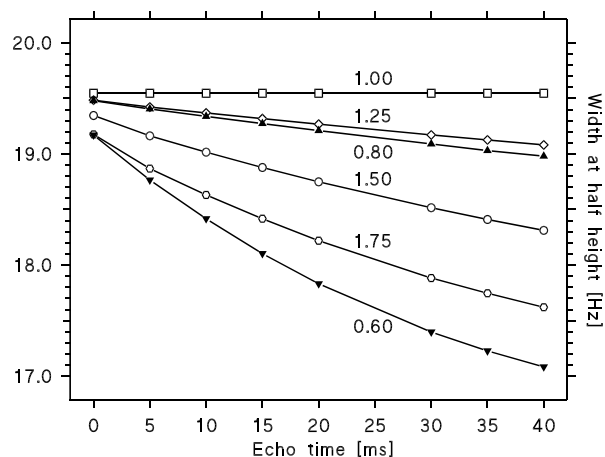


Fig. 1. Dependences on the echo time of the full-widths-at-half-heights of theoretical Carr–Purcell echo spectra of methyl protons forming an A<sub>2</sub>B system. The calculations were performed, using the DQR line-shape equation, for the Larmor frequency difference  $\delta = 500$  Hz, and for the displayed values of  $c = k_1/k_K$ , where the values of  $k_1$  and  $k_K$  were chosen such that the value of  $(2k_1 + k_K)/9$  be equal to  $2\pi \times 2000 \text{ s}^{-1}$  ( $= k$ , see text); with such a choice, the calculated spectra are in the regime of intermediate exchange. The instrumental and  $T_2$ -relaxation line broadening  $1/(\pi T_2^*) = 0.5$  Hz was assumed.

broadening is much greater than both the relaxation and field-inhomogeneity broadenings. Its drawback (involving also the standard spin-echo methods of  $T_2$  measurements for strongly broadened signals [17]) is the requirement that the spectral region near the exchange-averaged signal be free of even traces of narrow impurity signals; a strong increase of such signals for long echo times may bias a proper location of the baseline under the signal of interest. Suitably purified samples of selected methyltritycene derivatives, which we expect to obtain soon, will be used in such studies in the near future.

## References

- [1] S. Szymański, Z. Olejniczak, A. Detken, U. Haeberlen, J. Magn. Reson. 148 (2001) 277.
- [2] P. Bernatowicz, S. Szymański, Phys. Rev. Lett. 89 (2002) 023004.
- [3] I. Czerski, P. Bernatowicz, J. Jaźwiński, S. Szymański, J. Chem. Phys. 118 (2003) 7157.
- [4] S. Alexander, J. Chem. Phys. 37 (1962) 967.
- [5] D.A. Kleier, G. Binsch, J. Magn. Reson. 3 (1970) 146.
- [6] A.J. Horsewill, Prog. Nucl. Magn. Reson. Spectrosc. 35 (1999) 359.
- [7] W. Heisenberg, Z. Phys. 38 (1926) 411; Z. Phys. 39 (1926) 499; Z. Phys. 41 (1927) 239.
- [8] F. Apaydin, S. Clough, J. Phys. C, Ser. 2 1 (1968) 932.
- [9] S. Clough, in: NMR Basic Principles and Progress, vol. 13, Springer, Berlin, 1976, p. 113.
- [10] S. Szymański, J. Chem. Phys. 111 (1999) 288.
- [11] M. Nakamura, M. Oki, H. Nakanishi, O. Yamamoto, Bull. Chem. Soc. Jpn. 47 (1974) 2415.
- [12] A.C. Hewson, J. Phys. C. Solid State Phys. 15 (1982) 3855.

[13] A. Würger, J. Phys. Condens. Matter 1 (1989) 6901.

[14] A. Würger, A. Hüller, Z. Phys. B: Condens. Matter 78 (1990) 479.

[15] S. Emdin, R.A. Wind, S. Clough, Phys. Rev. Lett. 33 (1974) 769.

[16] H.Y. Carr, E.M. Purcell, Phys. Rev. 94 (1954) 630.

[17] R. Freeman, Spin Choreography. Basic Steps in High Resolution NMR, Oxford University Press, Oxford, 1998 (chapter 4).