The Anisotropy of the Molecular Reorientational Motions in Liquid Methanol

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Dedicated to Professor W. Müller-Warmuth on the occasion of his 65th birthday

Nuclear magnetic resonance (NMR) relaxation time measurements on isotopically substituted samples yield a detailed understanding of the molecular reorientational dynamics in liquids. Reorientational correlation times obtained from such experiments are reported for two molecule-fixed vectors in pure liquid methanol. While the reorientational motions of single molecules are nearly isotropic at temperatures below 250 K, at 308 K the reorientational correlation time of the O–H vector becomes 2.3 times larger than that of the O–C vector. Molecular dynamics (MD) simulations give access to the complete correlation functions of the reorientational motions. Correlation times extracted from these functions fit well to the experiment in case of the O–C vector. At low temperatures, however, these times lie markedly above those obtained in the experiment for the O–H vector. Thus, the simulation yields reorientation times for the O–H vector that are, independent of the temperature, twice as large as those of the O–C vector.

Introduction

In the present communication we focus on the reorientational motions of single molecules in pure liquid methanol. We report results of new NMR relaxation time measurements on the reorientational motions of the intramolecular O–C vector. Combined with results obtained earlier [1] for the reorientational motions of the O–H vector, and with Molecular Dynamics (MD) simulations, a picture of the reorientational dynamics in the liquid emerges. In the limit of a solvent not too strongly perturbed by the solute, the reorientational motions investigated here are also relevant for the interpretation of time-resolved spectra typically obtained from pump-probe experiments [2].

Experiments and Simulations

NMR relaxation time measurements on isotopically substituted samples are a sensitive way to probe the reorientational dynamics of single molecules [3, 4]. Earlier studies of liquid methanol measuring deuteron relaxation rates depend on proper estimation of the deuterium quadrupole coupling constant for the evaluation of the reorientational correlation time [5–8]. The calculation of reorientational correlation times from ^{17}O relaxation rates [9] requires the knowledge of the ^{17}O quadrupole coupling constant and of the orientation of the field gradient at the ^{17}O nucleus. More reliable values for the reorientational correlation time τ_2 of the intramolecular O–H vector were extracted from the additional dipolar proton relaxation rate induced by ^{17}O in $CD_3{}^{17}OH$ [1]. For the evaluation of these measurements no assumptions about any quadrupole coupling constants have to be made, but the exact knowledge of the intramolecular O–H distance is critical.

In this paper the additional ^{13}C relaxation rate induced by dipole-dipole interactions with ^{17}O is used to calculate the reorientational correlation time of the intramolecular O–C vector. Up to now this value could only be estimated indirectly by measuring the part of the ^{13}C relaxation rate induced by dipolar interactions with the methyl group protons [10], by measuring the part of deuteron relaxation rate in the methyl group induced by quadrupolar interactions [6] or by measuring the proton relaxation rate induced by dipolar interactions with other protons in the methyl group [6]. Assuming fast methyl group rotation, one

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can calculate the reorientational correlation time of the O–C vector from these measurements.

The samples used previously [1] were also employed in the present measurements. They had been carefully degassed by several freeze-pump-thaw cycles. The ^{13}C-relaxation time T_1 was measured by the $180° - \tau - 90°$ pulse sequence at 75.47 MHz on a Bruker CXP spectrometer as a function of enrichment in ^{17}O and temperature. The temperature was controlled with an improved apparatus to ± 1 K.

The measured ^{13}C relaxation rates $(1/T_1)_\mathrm{C}$ for CD_3OH are given in Table 1 as functions of the mole fraction of ^{17}O and of temperature. Using the following expression for the measured total relaxation rate

$$\left(\frac{1}{T_1}\right)_\mathrm{C} = x\left(\frac{1}{T_1}\right)_\mathrm{C}^\mathrm{O} + \left(\frac{1}{T_1}\right)_\mathrm{C}^\mathrm{H,D} + \left(\frac{1}{T_1}\right)_\mathrm{SR},$$

where x is the mole fraction of ^{17}O, the additional rate due to this isotope (upper index O) is separated from the contributions due to all other mechanisms by a least squares fitting procedure. The second term on the right hand side of the above equation comprises the intra- and intermolecular dipolar interactions between the carbon and the hydroxyl proton and the three methyl deuterons. The last term is the relaxation rate due to spin-rotation. There was no need to separate this part since it is constant for all $CD_3{}^{17}OH$ species at one temperature, and we are only interested in the additional contribution due to the ^{17}O.

The additional relaxation rate due to the ^{17}O is related to the correlation time τ_2^OC by [11]

$$\left(\frac{1}{T_1}\right)_\mathrm{C}^\mathrm{O} = \frac{4}{3}\left(\frac{\mu_0}{4\pi}\right)^2 \gamma_{^{13}\mathrm{C}}^2 \gamma_{^{17}\mathrm{O}}^2 \hbar^2 S(S+1) r_\mathrm{CO}^{-6} \tau_2^\mathrm{OC},$$

where μ_0 is the permeability, γ are the magnetogyric ratios for ^{13}C and ^{17}O, and $S = 5/2$ is the nuclear spin of ^{17}O. The average intramolecular O–C distance in the liquid, r_OC, is needed for the evaluation of the correlation time τ_2 from the measured relaxation time T_1. Values of $r_\mathrm{OC} = 1.44$ Å are found in the liquid phase from neutron [12] and X-ray [13, 14] diffraction. These values are slightly larger than the ones reported for the gas phase, 1.42–1.43 Å [15–18]. The value 1.44 Å is used here.

Table 1. ^{13}C relaxation rates $(1/T_1)_\mathrm{C}$, in s^{-1}, as a function of the mole fraction x of $CD_3{}^{17}OH$ in $CD_3{}^{16}OH$ and of the temperature.

T/K	$x_{CD_3{}^{17}OH}$			
	0.000	0.060	0.117	0.268
233	0.0237	0.0249	0.0266	0.0303
243	0.0248	0.0268	0.0305	0.0373
253	0.0263	0.0303	0.0338	0.0438
263	0.0302	0.0340	0.0365	0.0490
273	0.0324	0.0380	0.0423	0.0575
283	0.0356	0.0430	0.0489	0.0687
288	0.0393	0.0497	0.0594	0.0858
308	0.0436	0.0552	0.0712	0.1030

Pure liquid methanol under various conditions [19–31], methanolic mixtures [32–36] as well as ionic solutions in methanol [37] and solutions of argon in methanol [38] have been studied earlier by MC and MD simulations. In most instances, the methanol molecule was represented by a "three-site" model. In this approximation the CH_3 group is treated as one force center (called here Me). This kind of model is also used in the present work. The intermolecular interaction potential consists of Coulomb-interactions between partial charges located on the three force centers and empirical terms. The model molecules are assumed to be flexible by including an intramolecular potential containing harmonic and anharmonic contributions up to fourth order in terms of intramolecular O–H and O–Me stretches and the Me–O–H bend. The total potential is assumed to be the sum of these inter- and intramolecular terms. Details and the potential constants are given in [22]. We note that a slightly modified set of parameters for the Me–Me and O–Me interactions was introduced later [33]. These models have been used previously in many instances [22, 23, 33–35].

The reorientational correlation functions and the corresponding correlation times presented here are obtained from NVE-MD simulations of 200 model molecules. The present simulations are performed at four different temperatures and corresponding densities taken from the literature: 208 K: 0.8768 g/cm^3 [39], 237 K: 0.8479 g/cm^3 [39], 294 K: 0.7869 g/cm^3 [40] and 325 K: 07627 g/cm^3 [40]. We note that the temperature-density pairs in the simulations do not match exactly those of the literature because of the difficulty to adjust the temperature in an NVE-ensemble to a given value. The simulations extend over 50 ps at the higher temperatures, and up to 1200 ps for the run at the lowest temperature. An Ewald procedure is used for the computation of the energies and forces resulting from the Coulomb interactions.

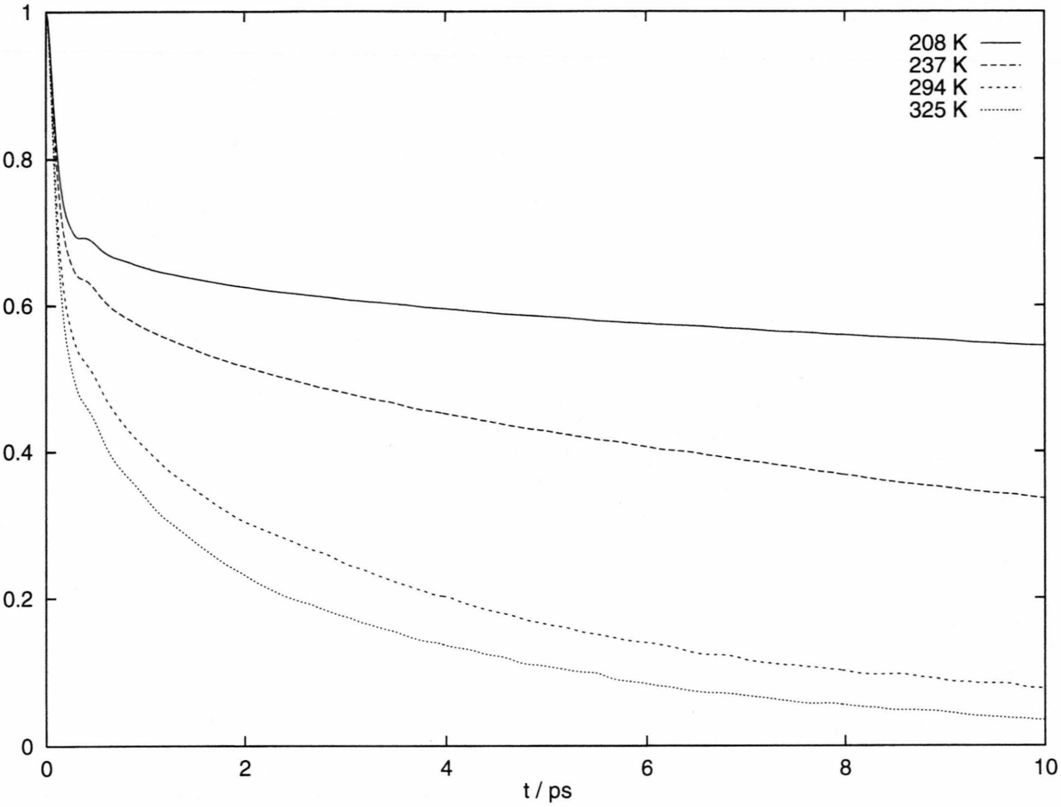

Fig. 1. Correlation functions $C_2(t)^{\mathrm{OC}}$ for the unit vector in direction of the O–C bond of methanol at four temperatures from simulation.

Results and Discussion

The correlation functions

$$C_2^{\mathrm{OX}}(t) = \frac{1}{NM} \sum_i^N \sum_j^M \langle P_2(e_{\mathrm{OX}}^i(t_j) \cdot e_{\mathrm{OX}}^i(t_j + t)) \rangle ,$$

where $e_{\mathrm{OX}}^i(t_j)$ is the unit vector along the O–C(O–Me) or O–H bond of the i-th molecule at time j and P_2 is the second Legendre polynomial

$$P_2(e_1 \cdot e_2) = \tfrac{3}{2}\cos^2(\angle\, e_1 e_2) - \tfrac{1}{2} ,$$

are computed from the simulation. N and M are the number of molecules and the number of time origins t_j. The correlation functions $C_2^{\mathrm{OC}}(t)$ are shown in Fig. 1 for the four temperatures studied in the simulations. The non-exponential behaviour of all these functions is quite obvious. Therefore we calculate the correlation times τ_2 in the following way:

$$\tau_2 = \int_0^\infty C_2(t)\,\mathrm{d}t = \int_0^{t_1} C_2(t)\,\mathrm{d}t + \int_{t_1}^\infty \hat{C}_2(t)\,\mathrm{d}t .$$

The integral from 0 to t_1 is computed numerically from the simulated correlation functions with different time resolutions. The function $\hat{C}_2(t)$ is an exponential function fitted to the long-time part of $C_2(t)$. Compromises have to be made between the length of the time interval taken for the fit, the non-exponential behavior at short times and the growing influence of statistical noise at longer times. The second integral introduces the largest error into the result, which can be estimated by using functions $\hat{C}_2(t)$ obtained by fits to different time intervals. The time t_1 ranges from 10 ps at 325 K to 100 ps at 208 K. The interval for the fit of $\hat{C}_2(t)$ ranges from [5 ps ... 10 ps] at 325 K to [50 ps ... 100 ps] at 208 K. Results for τ_2 for the O–H and O–C vectors from the simulation are compared in Table 2 with experimental ones from this work and from Ludwig et al. [1].

A number of uncertainties is involved in the evaluation of τ_2 both from the NMR experiment and from the simulations. The evaluation of the experiments thus involves, besides the experimental uncertainties,

Table 2. Reorientation correlation times τ_2, in ps, for the O–H and O–C vectors from MD simulations and from NMR experiments.

T/K	O–H (NMR)[a]	O–H (MD)	O–C (NMR)	O–C (MD)
208	34.6	185	50.7[b]	90
233	15.7	–	16.4	–
237	14.9[b]	32.2	15.5[b]	14.2
243	11.9	–	12.7	–
253	10.9	–	9.0	–
263	8.3	–	6.8	–
273	7.1	–	5.2	–
283	6.0	–	4.8	–
288	5.6	–	3.5	–
294	5.0[b]	5.2	3.0[b]	2.7
308	4.2	–	1.8	–
325	3.3[b]	3.3	1.6[b]	1.7

[a] Recalculated from [1] using an O–H distance of 98 pm [41] instead of 99 pm.

[b] Values taken from an Arrhenius fit to the experimental data.

the knowledge of the coupling constant which contains the average intramolecular O–C or O–H distance. Uncertainties in the values from the simulations may originate in insufficient lengths of the runs, leading to statistical errors in the correlation functions, or in insufficient energy conservation (in the NVE ensemble) in long runs. Of course, the potential model used may also be not adequate.

This being said, the agreement between the results from the present simulations and from the experiments (Table 2) is very satisfactory around room temperatures, both for the correlation times of the O–H and of the O–C vectors. This agreement between simulation and experiment deteriorates for the O–H correlation times below 237 K, where the simulations yield much longer correlation times than the NMR-experiment. The O–C value at 208 K in Table 2 extrapolated from the experimental values has to be considered quite uncertain due to deviations from Arrhenius behavior. Using an "extended" Arrhenius equation by adding a term of a/T^2 to the right side of the equation below, we obtain a value for τ_2^{OC} of 25.0 ps for this temperature.

A surprising result of the present experiments is the fact that the molecular reorientation seems to become more isotropic with decreasing temperatures. For the ratio $\tau_{\mathrm{OH}}/\tau_{\mathrm{CO}}$ one has for instance a value of 1.8 at 325 K, 1.4 at 273 K and of 1.0 at 233 K. In the simulations, this ratio remains constant at about 2 for all temperatures.

The reorientation of the O–H vector has been studied earlier in several instances. The reorientation of the O–C vector, however, has not been measured directly. All NMR measurements of molecular reorientation are based on one of two effects: The intramolecular dipolar interaction of two nuclei and the interaction of a nucleus with a quadrupole moment with the local electric field gradient. The latter method requires the knowledge of the quadrupole coupling constant in the respective system and is in fact used in most cases to determine this quantity. Theoretically calculated values of quadrupole coupling constants are only now becoming available [42, 43], so that a discussion of reorientational correlation times based on NMR quadrupole relaxation measurements at present still has to be considered questionable. There are also some measurements of relaxation rates resulting from intramolecular dipole-dipole interactions. For the protons in the methyl group an intramolecular $(1/T_1)$ of 4.7 s^{-1} at 298 K is reported by Zeidler [6]. Applying a version for equal spins of the formula above

$$\frac{1}{2}\left(\frac{1}{T_1}\right)_{\mathrm{H}}^{\mathrm{H}} = 2\left(\frac{\mu_0}{4\pi}\right)^2 \gamma_{\mathrm{H}}^4 \hbar^2 S(S+1)\, r_{\mathrm{HH}}^{-6}\, \tau_2^{\mathrm{HH}},$$

one obtains a reorientational correlation time τ_2 of 0.9 ps. If we assume fast rotation of the methyl group around the O–C axis, all O–H vectors are "smeared" nearly immediately onto the surface of a cone. For the corresponding correlation function this results in a rapid decay from the value 1 to a value of $(\frac{3}{2}\cos^2\theta - \frac{1}{2})^2$, where θ is the angle between the molecular vector under consideration and the axis of the fast rotation. With $\theta = 90°$ a factor of 0.25 results, yielding a reorientational correlation time of the O–C vector of 3.6 ps. For ^{13}C, an additional relaxation rate caused by dipolar interactions with the methyl group protons of 0.027 s^{-1} at 308 K is reported by Lyerla et al. [10]. Applying the formula for unequal spins and considering the fact that the ^{13}C nucleus interacts with three protons, a reorientational correlation time of 0.41 ps for the O–H vectors can be calculated. Assuming the tetrahedral angle for the O–C–H angles, the correlation time for the O–C vector should be longer by a factor of 9, so that a reorientational correlation time for the O–C vector of 3.7 ps follows. These values are generally larger than those obtained in our own experiments. A possible explanation might be that the assumption of fast methyl group rotation is not correct.

Simulations are also known in the literature; most of them were carried out using a rigid three site methanol model. Matsumoto et al. [27] report values of 2.6 ps at 300 K and 48 ps at 200 K for the O–H vector. Their "z axis" is defined as the axis with the lowest moment of inertia and therefore can be used as an approximation for the O–C vector. The values τ_2^{OC} reported for this vector are 1.5 ps at 300 K and 22 ps at 200 K. Haughney et al. [25] report values of τ_2^{OH} for the O–H vector using four different potential models. At about 268 K their values scatter from 3.6 ps to 10.6 ps depending on the model used. Sindzingre et al. [31] report τ_2 for the O–H vector and the O–C vector. At 250 K they find values of 4.7 ps for the O–H vector and 2.7 ps for the O–C vector.

The temperature dependence of the τ_2 data can be described in most cases by an Arrhenius behavior:

$$\ln \tau_2 = \ln A + \frac{E_\mathrm{a}}{RT}\,.$$

The activation energy E_a found from NMR studies is 11.0 kJ/mol for the O–H vector [1] and 16.7 kJ/mol for the O–C vector (this work). From the simulations we find a value of 18.9 kJ/mol both for the O–H vector and for the O–C vector. Matsumoto et al. [27] obtain a value of 14.5 kJ/mol for the O–H vector and of 13.4 kJ/mol for the O–C vector. The simulations of Haughney et al. [25] yield values for the O–H vector ranging from 7.8 to 15.5 kJ/mol depending on the model used. From the work of Sindzingre et al. [31] we use only the data points in the temperature range from 210 K to 300 K for the fit, as we doubt that correlation times of more than 1 ns can be calculated with reasonable accuracy from simulation runs shorter than 2 ns, and because of the possibility of approaching the liquid-glass transition. The resulting values are 16.5 kJ/mol for both the O–H vector and O–C vector. In summary, the simulations yield more or less equal activation energies for the reorientation of both vectors, while the experiment shows a clear difference.

Summary and Conclusions

The reorientational dynamics of single methanol molecules is studied by NMR relaxation time measurements and by molecular dynamics computer simulations. The reorientational process is characterized by correlation times τ_2 for the intramolecular O–H and O–C vectors. The experiment yields times that are almost equal for both vectors at temperatures below 250 K, whereas at higher temperatures the reorientation of the O–H vector becomes slower than that of the O–C vector by a factor of about two. The simulations also show that the reorientation of the O–C vector is faster than that of the O–H vector. But here the factor of about two is nearly independent of temperature. The anisotropic reorientation of the methanol molecule is not unexpected, as the reorientation of the O–H vector is influenced by the hydrogen bond [44]. Surprising, however, is the fact that the experimental results suggest a more isotropic reorientation at lower temperatures. The question arises whether at lower temperatures a second, quantum mechanical, mechanism with a smaller temperature dependence becomes increasingly important for the reorientation of the O–H vector. Such a mechanism would be beyond the scope of our classical MD simulations.

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