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Isotope effects on the dynamics of a supercooled van der Waals liquid

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Abstract. – Deuteron magnetic resonance was used to study three differently isotope-labeled species of the fragile glass-forming liquid ortho-terphenyl. The calorimetric glass transition of the isotope deuterated only at the central phenyl ring is significantly lower than that of the perdeuterated one. It is shown that while the ortho-terphenyl molecule is not as rigid as previously often assumed, its overall reorientation geometry is independent of deuteration. The characteristic jump angles are found to increase with temperature, thus resolving an apparent discrepancy previously noted when comparing typical jump sizes from NMR with other data.

In order/disorder phase transitions of crystalline solids isotope effects are known to play an important role [1]. But in studies of glass-forming liquids it is often tacitly assumed that such effects are negligible. This is surprising in view of the fact that isotope labeling is a much used tool in studies dealing with soft condensed matter when employing nuclear magnetic resonance (NMR) as well as other experimental techniques [2]. There are only a few reports where either anomalous [3] or else effectively missing [4] isotope effects have provided important insights into the dynamics of the amorphous state.

On the other hand, isotope shifts of melting points, T_m , particularly those emerging from proton *vs.* deuteron substitution are on the order of 0.5–5 K as documented for a large number of substances [1]. The calorimetric glass transition temperature, T_g , for many families of glass formers is related to T_m via the empirical relationship $T_m/T_g \approx 1.5$ [5]. This “rule” thus rationalizes the observation of corresponding T_g shifts detected in adiabatic calorimetry studies [6]. However, reports concerning the impact of deuteration on the dynamics of supercooled small molecule liquids do not seem to be available. We have observed significant isotope effects on differently deuterated samples of ortho-terphenyl (OTP). This substance has played a key role in previous theoretical and experimental investigations dealing with the vitrification of fragile van der Waals glass-forming liquids [7].

For our current ²H-NMR study we have not only used perdeuterated OTP (OTP-d₁₄) but also samples deuterated selectively at the central ring (C₁₈D₄H₁₀, OTP-d₄) and at the two outer rings (C₁₈D₁₀H₄, OTP-d₁₀). The synthesis, purification, and characterization of these

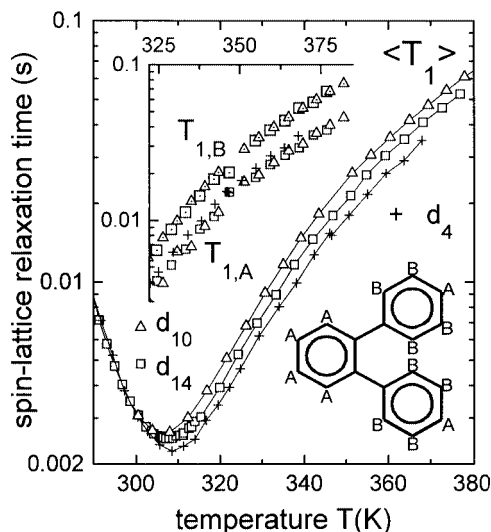


Fig. 1

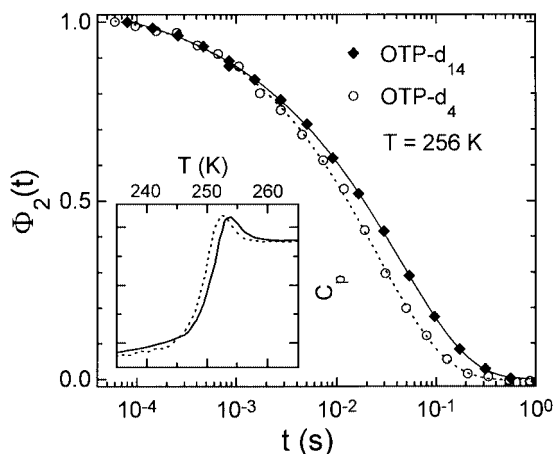


Fig. 2

Fig. 1 – Temperature dependence of the average spin-lattice relaxation times $\langle T_1 \rangle$ of three different isotopic OTP species. The lower inset shows a schematic representation of the OTP molecule with the C-D bonds involved in torsional motions of the outer rings labeled by the letter B. The upper inset shows the relaxation times $T_{1,A}$ and $T_{1,B}$ obtained from fits to the slightly non-exponential magnetization recovery using a bi-exponential function. The lines are drawn to guide the eye.

Fig. 2 – Normalized rotational correlation functions $\Phi_2(t)$ measured at 256 K. The lines represent Kohlrausch fits. The inset shows the DSC curves for OTP-d₄ (dashed line) and for OTP-d₁₄ (solid line).

species has been described elsewhere [2,8]. For OTP-d₁₀ only data for $T \geq 300$ K are reported below since the sample showed a tendency to crystallize at lower temperatures. For the ^2H -NMR experiments we used a home-built spectrometer operating at a Larmor frequency of $\omega_L = 2\pi \times 40.24$ MHz. The $\pi/2$ pulse length typically was set to $2.6 \mu\text{s}$. Within experimental uncertainty (about 3%) the solid echo deuteron spectra obtained near 250 K did not depend on the degree of deuteration. The longitudinal magnetization, $M(t)$, was found to relax exponentially for OTP-d₄. The corresponding spin-lattice relaxation times, T_1 , are given by the lowest curve in fig. 1. At high enough temperatures ($T > 325$ K) they are related with the time constant τ_C governing the rotational motion of the OTP molecules via $\tau_C^{-1} \propto T_1$ [9]. For OTP-d₁₀ and OTP-d₁₄ $M(t)$ showed slight deviations from exponential recovery that can be ascribed to the librational motions of the two outer rings of OTP [10]. This motion leads to an increased mobility at the ^2H sites labeled with the letter B in the lower inset of fig. 1. An excellent bi-exponential fit of $M(t)$ [11] yields the values $T_{1,A}$ and $T_{1,B}$ for the A and B deuterons, respectively, as shown in the upper inset of fig. 1. Our assumption that only the B deuterons are affected by the libration of the outer rings is confirmed by the perfect agreement of $T_{1,B}$ for OTP-d₁₀ and OTP-d₁₄ and by the fact that $T_{1,A}$ for both species coincides with T_1 of OTP-d₄. An important finding is that the average spin-lattice relaxation time $\langle T_1 \rangle$ (defined via $\int M(t)dt$) increases in the sequence $\langle T_1 \rangle_{d4} = T_1 < \langle T_1 \rangle_{d14} < \langle T_1 \rangle_{d10}$ (see fig. 1). This observation is readily explained by the different weight factors associated with the A and B deuterons [11] and by our finding that $T_{1,B} > T_{1,A}$. The latter can be described semi-

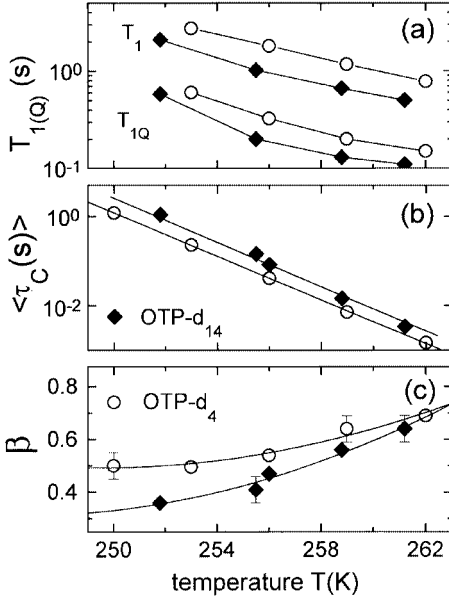


Fig. 3

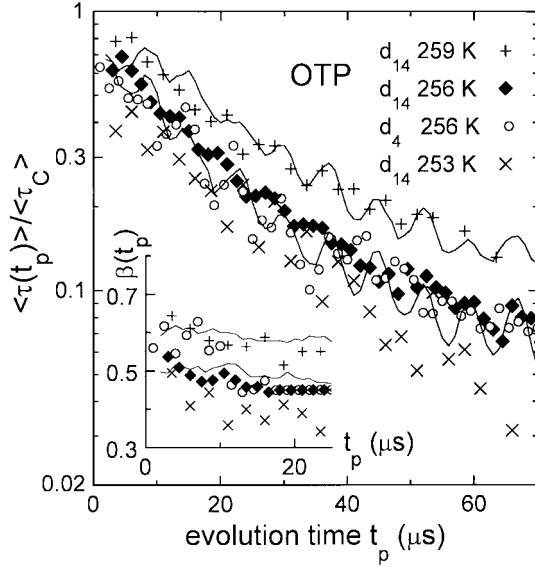


Fig. 4

Fig. 3 – Temperature dependence of (a) the longitudinal relaxation times T_1 and T_{1Q} , (b) the mean rotational correlation time $\langle \tau_C \rangle$, and (c) the stretching parameter β . For both isotopes one has $T_1/T_{1Q} = 5 \pm 1$. The correlation time of OTP-d₁₄ is about a factor of 2.2 slower as compared to OTP-d₄. The temperature shift deduced from $\langle \tau_C \rangle$ agrees nicely with results from DSC (cf. fig. 2). Typical error bars are shown in panel (c). For the data shown in panels (a) and (b) the statistical error bars are of the size of the symbols or smaller.

Fig. 4 – Average time scale $\langle \tau(t_p) \rangle$ characterizing the two-time stimulated echo $F_2^{\text{COS}}(t)$ as a function of the evolution time t_p . At $T = 256$ K the results for OTP-d₄ and OTP-d₁₄ are identical within experimental error. The inset shows the exponents $\beta(t_p)$ for $t_p < 25 \mu$ s. The solid lines represent numerical simulations using bimodal distributions containing contributions at a small (2°) and a large (40 – 45°) jump angle. For 256 K (259 K) the fraction of the latter was 4% (8%).

quantitatively by models of increased internal motion [12]. The depths of the T_1 minima differ slightly for the various isotopic species. We ascribe this observation to minor differences in the effective widths of the correlation time distributions which are probed at the different deuteron sites.

The rotational correlation times of OTP increase to about 10 ns when lowering T down to ~ 300 K [10]. Upon further cooling to ~ 250 K the molecular correlation times increase dramatically reaching ~ 1 s. The time window ranging from 10^{-3} s to 1 s (upon which we focus in the following) is no longer directly accessible via T_1 experiments. Therefore, we have applied the stimulated echo technique which is particularly sensitive to excitations in the ultra-slow regime. Using the methods described elsewhere [13,14] we have recorded the sine and cosine parts, F_2^{SIN} and F_2^{COS} , of the two-time autocorrelation function $F_2(t_p, t) = \langle \exp[i\omega(0)t_p] \exp[-i\omega(t)t_p] \rangle$. This function characterizes the temporal evolution of ω , *i.e.* the orientation-dependent precession frequencies; t_p can be viewed to set a geometrical filter [14]. For $t_p \rightarrow 0$ the sine part yields $F_2^{\text{SIN}}(t_p \rightarrow 0, t) \propto \Phi_2(t) = \langle \omega(0)\omega(t) \rangle$, *i.e.*, the rotational correlation function [13]. However, the experimental F_2^{SIN} signal of supercooled liquids is

inevitably affected by the decay of the quadrupolar alignment, which takes place on a time scale T_{1Q} . A technique which permits a more reliable measurement of T_{1Q} [14] has been used to measure $\Phi_2(t)$ (fig. 2) and T_{1Q} (fig. 3a) for OTP-d₄ and OTP-d₁₄. The $\Phi_2(t)$ curves shown in fig. 2 can nicely be parameterized using the Kohlrausch function $\Phi_2(t) \propto \exp[-(t/\tau_C)^\beta]$ with the average correlation times $\langle\tau_C\rangle = \tau_C\beta^{-1}\Gamma(\beta^{-1})$ and the stretching parameters β given in figs. 3b and 3c, respectively. The $\langle\tau_C(T)\rangle$ curves for the two isotopes differ considerably but can be made to coincide (within experimental error) by a relative temperature shift of $\Delta T = 1.5 \pm 0.3$ K. This suggests that T_g of the perdeuterated compound is larger than that of OTP-d₄ by ΔT . In order to check this result we performed differential scanning calorimetry (DSC) experiments. As shown in the inset of fig. 2 we find virtually identical DSC traces except that T_g (onset temperature) is 1.3 ± 0.2 K larger for OTP-d₁₄ than it is for OTP-d₄ [15].

An interesting difference seen in fig. 2 is that $\Phi_2(t)$ of OTP-d₁₄ [16] is more stretched than that of OTP-d₄. The stretching parameter β of OTP-d₄ (see fig. 3c) is similar to that deduced from previous optical studies of protonated OTP [17]. In order to find out where this difference may come from it is instructive to discuss the longitudinal recovery times in the low temperature regime. First, we should note that the T_1 and T_{1Q} values shown in fig. 3a are *smaller* for OTP-d₁₄ than for OTP-d₄ indicating an increased mobility of the former in contrast to the isotope effect upon $\langle\tau_C\rangle$ (fig. 3b) discussed above. Thus, the fast librational motion identified at $T > 325$ K (fig. 1) must also be active at $T < 260$ K on the time scale of $1/\omega_L$ (≈ 4 ns) and it *overcompensates* the slow-down by the isotope effect detected via $\langle\tau_C\rangle$ in the ms...s regime. It is well known that ^2H spin-lattice relaxation close to T_g is caused by small amplitude motions related in a complex manner with β - and (high-frequency wing) α -relaxation, and further complicated by spin diffusion effects [18]. Thus, it is plausible that the axial librations of the two outer rings which only affect the B deuterons (see fig. 1) are responsible for the large decrease of T_1 in OTP-d₁₄ relative to OTP-d₄. These librations should also affect the short-time regime of the rotational correlation function $\Phi_2(t)$ shown in fig. 2 and cause the increased stretching in OTP-d₁₄ whereas the long time behavior governs the differences in $\langle\tau_C\rangle$.

In order to check whether the fast processes have a significant impact on the overall reorientational geometry of OTP we have recorded two-time stimulated echoes $F_2^{\text{COS}}(t_p, t)$ for a range of evolution times t_p and mixing times $100 \mu\text{s} < t < 3$ s (not shown) [19]. It has been demonstrated previously that this type of experiment when applied to supercooled liquids and polymers [14, 16, 20, 21] is well suited to map out the characteristic features of the distribution of molecular jump angles. Results are shown in fig. 4 [22] where we plotted the normalized decay time $\langle\tau(t_p)\rangle/\langle\tau_C\rangle$ and the exponent $\beta(t_p)$ from Kohlrausch fits, $F_2^{\text{COS}}(t_p, t) \propto \exp[-(t/\tau(t_p))^{\beta(t_p)}]$, as a function of t_p [23]. Although the data for OTP-d₄ are more noisy than for OTP-d₁₄ (because OTP-d₄ contains less deuterons) it is apparent from the results obtained at 256 K that, within experimental accuracy, the distribution of jump angles at constant temperature is essentially unaffected by the isotope substitution. This implies that the filter function, $F_2(t_p = 25 \mu\text{s}, t)$, used in previous reduced 4D-NMR experiments, and the conclusions concerning dynamic heterogeneity [13] are robust with respect to deuteration effects.

The T -dependence of the $\langle\tau(t_p)\rangle/\langle\tau_C\rangle$ pattern shown in fig. 4 clearly demonstrates that the mean rotational jump angles, φ , of the OTP molecules increase with increasing temperature. A rough estimate of φ and its T -dependence can be obtained from $V = \tau_2/\tau_C = \frac{3}{2}\sin^2\varphi$, where τ_2 is the decay time of F_2 in the limit of long t_p [14, 20, 24]. From V read off in fig. 4 near $t_p = 60 \mu\text{s}$ (where the specified limit may still not be entirely reached) we find that φ thus estimated increases from about 10° to about 19° when increasing T from 253 K to 259 K. For the data recorded at 256 K and 259 K [25] we have performed a quantitative evaluation of the

entire $\langle\tau(t_p)\rangle/\langle\tau_C\rangle$ pattern employing a random walk algorithm [20]. The solid lines in fig. 4 represent simulations using a bimodal jump size distribution [26]. From the good agreement between experiments and simulations we conclude that molecular reorientation occurs mainly via a small fraction of relatively large angular jumps. However, between each of these rare jumps the molecule performs numerous small angular steps ($< 3^\circ$). In this respect OTP shows a qualitatively similar behavior [27] as other monomer [14, 20] or polymer [21] glass formers. The fraction of large angle jumps found for OTP is intermediate between those in glycerol and toluene [14, 20].

Our finding of temperature-dependent characteristic jump angles confirms a recent suggestion made on the basis of a comparison of results from dielectric spectroscopy with those from impulsive thermal scattering on another fragile liquid [28]. The experimental evidence for an increase of jump angles with temperature thus resolves the apparent disagreement between results from NMR [14, 16, 20, 21] and techniques probing the dynamics at short time scales (electron-spin resonance [29], neutron scattering [30], or molecular dynamics simulations [31]). While the low-frequency (and consequently low T) stimulated echo experiments find evidence for relatively small characteristic jump angles, from high-frequency (or large T) techniques large jump angles are reported.

To summarize we have shown that the isotope shift of T_g seen in several differently deuterated ortho-terphenyl isomers does not alter the reorientational geometry of this glass former in the low-frequency regime. Predominantly at high frequencies, librational excitations of the outer phenyl rings were unambiguously shown to contribute to the motional spectrum of OTP. This implies that the OTP molecule is not as rigid as previously often assumed. The experimental finding of a significant increase of the mean jump angle with temperature resolves an apparent discrepancy that has been noted when comparing stimulated echo NMR with other data.

* * *

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