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²H-NMR study of the glass transition in supercooled ortho-terphenyl

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The glass forming molecular liquid ortho-terphenyl has been investigated by ²H-NMR techniques providing spin-relaxation times (T_1, T_2) , and spin-alignment data which yield information on the time scale and geometry of ultra-slow molecular reorientation. The main results are as follows: The primary glass transition (α process) is characterized by rotational molecular jumps with a jump size distribution weighted in favor of large jump angles, and by a distribution of correlation times. In addition intramolecular flip-flop jumps of the lateral phenyl rings are found which do not take part in the α process. Apart from this (secondary) intramolecular dynamics no residual small angle reorientation persists below T_g on the time scale (10⁻⁴ to 10² s) of the spin-alignment experiment.

I. INTRODUCTION

The nature of the glass transition has been investigated in a wide variety of substances by many different experimental techniques.¹⁻⁴ The complex dynamical behavior in the vicinity of the glass transition temperature T_g has been described phenomenologically by distributions of relaxation times.⁵ In particular, the Kohlrausch-Williams-Watts (KWW) distribution^{6,7} has been discussed in many recent theoretical treatments (reviewed in Refs. 8 and 9) since it is the Fourier transform of a "stretched exponential" relaxation function [see Eq. (2)] which can be related to physical models of the glass transition. However, comparisons of these models with experiment meet with the problem that most relaxation experiments provide rather indirect information upon the molecular mechanisms involved. The advantage of NMR methods is their potential in probing the motion of well defined molecular vectors. In ²H-NMR of CH compounds, all primary information relates to the reorientation of C-²H bonds. Whereas, NMR relaxation was previously restricted to relatively rapid motions, the development of special two- and three (or four)-pulse techniques^{10,11} yields information upon the rate and the mechanism of molecular reorientation for slow and "ultraslow" motions at time scales in a range from about 10^{-5} to 10^2 s. Our previous ²H-NMR studies of the glass process in toluene¹² and polystyrene¹³ have already demonstrated the potential of the technique though only tentative conclusions were possible prior to more extensive measurements performed along with model calculations (see below).

In the present investigation, we have chosen *o*-terphenyl which is perhaps the best studied example of a nonpolar organic liquid in which the supercooled state is characterized by weak intermolecular forces, and the relaxation times show a particular large temperature dependence close above T_{g} . Thus, the viscosity η of o-terphenyl increases by 10 decades in the small temperature range between 275 K and T_{g} = 243 K (see Fig. 2).^{14,16} Further dynamical studies of oterphenyl include NMR relaxation,¹⁷ self-diffusion,¹⁷ dielectric relaxation,¹⁸ and dynamic light scattering.^{19,20} In liquid o-terphenyl, the two vicinal phenyl groups have their planes, on the average, perpendicular to that of the benzene ring and they perform large amplitude librations around their bonds to the ring. This internal motion persists below the glass transition, and will be discussed further below in Sec. III B. In Sec. III A, we discuss a range of temperatures $T \gtrsim 280$ K where motional narrowing of the ²H-NMR spectrum occurs, and the spin-relaxation time T_2 is given by the inverse half-width of the Lorentzian line shape. Here, the well known Bloembergen-Purcell-Pound (BPP) theory of the spin-lattice relaxation times T_1 and T_2 applies,²¹ and the results can be described by a mean rotational correlation time $\bar{\tau}_c$ to be compared with corresponding data from other relaxation experiments.¹⁴⁻²⁰ We then present in Sec. III B a first set of ²H spin-alignment¹⁰ results characterizing the viscous and glassy regimes at lower temperatures T < 280 K. In the temperature regime below $T_g = 243$ K, the theory of Cohen and Grest²² and recent numerical simulations^{23,24} predict the presence of "liquid clusters" where the molecules perform rapid large amplitude motions, whereas outside of these clusters the motion should be essentially frozen. Although NMR techniques yield no direct information upon spatial heterogeneity, the related motional heterogeneity should be observable by NMR. Since it will turn out that no traces of liquid clusters are seen in our experiments, we conclude that the glass transition cannot be described by an unmodified liquid solid percolation transition.²²

II. EXPERIMENTAL

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o-Terphenyl was deuterated by catalytic exchange in benzene- d_6 solution using AlCl₂C₂H₅ as catalyst.²⁵ The fully

deuterated o-terphenyl $-d_{14}$ was purified by recrystallization

from CH₃OH/H₂O mixtures and distillation. The sample

used in the NMR experiments was 99% deuterated and had

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a melting point of 329 K. The ²H-NMR experiments were performed with a Bruker SXP pulse spectrometer at 55.2 MHz. T_1 was measured by the inversion recovery technique in the motional narrowing regime ($T \ge 279$ K). At lower temperatures, the recovery of the solid echo amplitude after a saturation pulse sequence was measured. Some T_1 values at a Larmor frequency of 15 MHz were determined using the Freeman-Hill pulse sequence.²⁶ T_2 was determined at $T \ge 296$ K using the Carr-Purcell-Gill-Meiboom sequence, and below 296 K from the free induction decay (FID). The shortest T_2 values (below ~20 μ s) given in Fig. 1 refer to the long time tail of the FID which is not fully observable within the dead time of the receiver ($\sim 12 \,\mu s$). Because of the finite dead time no NMR signals could be detected in a range of 279-273 K. Solid echoes¹¹ were observable below 273 K. The relaxation time $T_{2,SE}$ was determined by measuring the decay of the solid echo amplitude as a function of the distance τ_1 , between the two 90° pulses of the solid echo sequence. Solid echo spectra were obtained by computing the Fourier transform of the echo shape starting from the echo maximum. The relaxation time T_{10} characterizing spin-lattice relaxation of quadrupolar ordering (spin-alignment) was determined from the decay of the alignment echo maximum as a function of the distance τ_2 between the second and third pulse of the Jeener-Broekaert pulse sequence.³⁸ T_{10} represents the long time limit of this decay. Further details of the spin-alignment experiments are given below in Sec. III B.

III. RESULTS AND DISCUSSION

A. Motional narrowing regime

In the motional narrowing regime, which refers in Fig. 1 to the range $T^{-1} \le 3.6 \times 10^{-3} \text{ K}^{-1}$, the spin-lattice relaxation time T_1 is given by the usual expression:

$$T_{1}^{-1} = \frac{3\pi^{2}}{10} \left(\frac{e^{2}Qq}{h}\right)^{2} [J(\omega_{0}) + 4J(2\omega_{0})]$$
(1)

for quadrupole relaxation of the spin I = 1 of ²H, and a corresponding expression²¹ holds for T_2 . In Eq. (1), ω_0 is the Larmor frequency, and $e^2 Qq/h = 182$ kHz is the ²H quadrupole constant of the $C^{-2}H$ bond of the *o*-terphenyl molecule determined from the solid glass line shape at 213 K. $J(\omega)$ is the Fourier transform of the rotational correlation function g(t) for the second Legendre polynomial of the angle θ between the $C^{-2}H$ bond and the static magnetic field. For a Debye process, $g(t) = \exp(-t/\tau_c)$, and $J(\omega_0)$ $\tau_c (1 + \omega_0^2 \tau_c^2)^{-1}$. For this process, Eq. (1) yields the value $T_1^{(\min)} = 2.5$ ms for the T_1 minimum at $\omega_0/2\pi = 55.2$ MHz. The experimental value (3.4 ± 0.2) ms determined from Fig. 1 is much larger. A similar discrepancy has been found in other viscous liquids, e.g., polymer melts,¹⁵ glycerol,¹⁶ methanol,¹⁷ and toluene.¹² One can discuss whether the e^2Qq/h value determined in the solid state at low temperature is the appropriate quantity to be placed in Eq. (1). However, the alternative of a reduced quadrupole coupling constant is not acceptable and leads to other inconsistencies of the interpretation.^{12,27–29} In a recent study of ¹H- and ²Hrelaxation in partially deuterated *i*-propanol Frech and Hertz³⁰ have found that the intramolecular coupling con-



FIG. 1. Spin-lattice relaxation times T_1 and spin-spin relaxation times T_2 as measured in deuterated supercooled o-terphenyl. ($\oplus:T_1$ at $\omega_0 = 2\pi \cdot 55$ MHz; $A:T_1$ at $2\pi \cdot 15$ MHz; $\Box:T_2$ in the liquid regime at $2\pi \cdot 55$ MHz; $\diamond:T_2$ in the viscous regime (solid echo) at $2\pi \cdot 55$ MHz).

stants, the apparent activation energies, and parameters in models of internal motion become highly unphysical if one insists that the time correlation functions for molecular reorientation and internal motions are single exponentials in the vicinity of the T_1 minimum. We favor the alternative of assuming nonexponential correlation functions and describing them by a "distribution of correlation times."⁵ In the motional narrowing regime, one cannot decide from T_1 and T_2 experiments whether the system is homogeneous in that all molecules reorient with the same nonexponential correlation function, or the system is heterogeneous, but allows for exchange of molecules (or spins) between the different spatial regions at a rate larger than the spin-relaxation rates T_1^{-1} and $T_2^{-1.31}$ NMR relaxation can be described in both cases by a distribution of correlation times which is formally related to exponential correlation functions which may or may not reflect "true" molecular processes. In the viscous and glassy regimes discussed below the situation is different since the NMR observables have a direct relation with the mechanism of molecular reorientation. We have analyzed our T_1 and T_2 data in the fluid regime of Fig. 1 by assuming a Kohlrausch-Williams-Watts (KWW) correlation function6,7

$$g(t) = \exp\left[-(t/\tau_K)^{\alpha}\right].$$
 (2)

Recently, Lindsay and Patterson³² have analyzed the close similarity of the KWW and the Cole–Davidson (CD) distribution³³ of correlation times. The width parameter β and the long time limit (cutoff time ³³) τ_0 of the CD distribution are related with the corresponding parameters α and τ_K of the KWW distribution by

$$\alpha = 0.970 \beta + 0.144 \ (0.2 \le \beta \le 0.6),$$

$$\tau_K = \tau_0 (1.184 \quad \beta - 0.184). \tag{3}$$

The average correlation time $\overline{\tau}_c$ is almost the same for the CD and KWW distributions, and is given by

$$\bar{\tau}_c = \beta \tau_0. \tag{4}$$

Since no analytical expression can be given for the Fourier transform $J(\omega)$ of Eq. (2) we have analyzed the corresponding expression³⁴

$$J(\omega) = \omega^{-1} (1 + \omega^2 \tau_0^2)^{-\beta/2} \sin(\beta \tan^{-1} \omega \tau_0)$$
 (5)

for the CD distribution. A quantitative fit was obtained in the fluid regime for T_1 at 55.2 and 15 MHz and for T_2 as given in Fig. 1 by assuming $\beta = 0.50$. This is a relatively narrow distribution where 80% of the spins correspond to correlation times within one decade below the cutoff time τ_0 . Our previous fit of T_1 and T_2 measurements in deuterated toluene¹² showed a broader CD distribution with $\beta = 0.32$.

In Fig. 2, the Arrhenius plot of the average correlation time $\bar{\tau}_c$ of our CD fit is given. We find³⁵ that the temperature dependence of $\overline{\tau}_c$ is in quantitative agreement with that of corresponding relaxation times determined from ¹H-NMR,¹⁷ self-diffusion,¹⁷ dielectric relaxation,¹⁸ Brillouin scattering,²⁰ and shear viscosity.^{14,16} Since this agreement holds through the whole motional narrowing regime above and below the T_1 minimum (see Fig. 1) it lends strong sup-



FIG. 2. Average correlation times as obtained from T_1 and T_2 data assuming Cole–Davidson distributed isotropic reorientational processes (•: from T_1 data at $2\pi \cdot 55$ MHz; \blacktriangle : from T_1 data at $2\pi \cdot 15$ MHz; \Box : from T_2 data in the liquid regime). The dashed curve represents the behavior of the α process as given by viscosity and dielectric relaxation measurements. The deviation of T_1 from the expected curve closely above T_g is due to intramolecular flip-flops of the lateral phenyl rings (β process). At these temperatures, correlation times from spin-alignment experiments are also included which allow for separating the α process (\blacklozenge) and the β process (\diamondsuit) from each other.

port to our choice of the unsymmetrical CD distribution or KWW distribution. In the symmetrical Fuoss-Kirkwood or Cole-Cole distributions, one obtains

$$d\ln T_1/dT^{-1} = \pm \beta E_A/R,$$

where the plus sign holds in the limit $\omega_0 \tau_0 > > 1$ and the minus sign for $\omega_0 \tau_0 < < 1$, and $0 \le \beta \le 1$ is the width parameter of the distribution.³⁴ In the CD and KWW distributions, the same equation is valid at temperatures below the T_1 minimum ($\omega_0 \tau_0 > > 1$), however β (or α) is replaced by one for $\omega_0 \tau_0 < < 1$. In the log–Gauss distribution, β should be replaced by one in both limits $\omega_0 \tau_0 < < 1$ and $\omega_0 \tau_0 > > 1.^{34}$ Furthermore, $d \ln T_2 / d / T^{-1} = E_A / R$ for all distributions considered above in the limit $\omega_0 \tau_0 > > 1$, and $T_2 = T_1$ if $\omega_0 \tau_0 < < 1$. In conclusion, only the CD and KWW distributions provide a fit of the mean correlation time which has the correct temperature dependence in agreement with that from other relaxation experiments.

Fytas et al.¹⁹ have analyzed their results of photon correlation spectroscopy (in VH geometry) in o-terphenyl at temperatures between 271 and 257 K in terms of a KWW distribution, and they find a width parameter α decreasing from 0.60 at 271 K to 0.54 at 257 K. More recent data³⁶ show that α remains constant at temperatures below 257 K. We obtain $\alpha = 0.63$ if we place $\beta = 0.50$ into Eq. (3). This is in harmony with the photon correlation spectroscopy results since our measurements refer to higher temperatures. However, we have assumed that β remains constant in the temperature range between 279 and 440 K. This assumption is probably not justified at temperatures above ~ 320 K where $\omega_0 \tau_0 < < 1$, and T_1 becomes independent of the width parameter in the CD and KWW distributions (but not in the symmetric Cole-Cole and Fuoss-Kirkwood distributions). We should note that a recent analysis of dielectric relaxation has also provided a quantitative fit to the CD distribution with a width parameter that decreases on decreasing the temperature from the liquid to the viscous regimes.³⁷

B. Viscous and glassy regimes

At temperatures approaching T_g , the correlation times related with the glass process become very long, and eventually T_1 and T_2 are insensitive to the molecular motions to be studied. Moreover, it is likely that different physical processes (intramolecular vibrations, phonons,...) contribute and even dominate the relaxation rates.

However, there are NMR methods, generally termed "stimulated echo" methods, 38 which overcome these limitations. Although only rarely applied in the past, stimulated echos are well suited to study molecular dynamics with correlation times up to T_1 . In the present work, we apply the deuteron spin-alignment technique¹⁰ which traces ultraslow molecular dynamics, and also allows to identify the type of the molecular reorientation process.

Thus, a few points can be checked independently:---Do the molecules really reorient isotropically as is assumed in the interpretation of the T_1 and T_2 data?—Are there significant degrees of freedom which are not frozen out in the glass transition (secondary processes) and eventually persist below T_g ?

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1. The deuteron spin-alignment experiment

As indicated above, deuteron spin-alignment experiments¹⁰ can determine directly and independently the time scale and geometry of molecular reorientation processes slower than 10^{-4} s. Recently, it has been pointed out that spin alignment yields a single particle correlation function which is to a large extent analogous to the intermediate scattering function $I_s(\mathbf{Q},t)$ of incoherent quasielastic neutron scattering.³⁹ In an appropriate three pulse experiment

 $(90^{\circ})_{x} - \tau_{1} - (45^{\circ})_{y} - \tau_{2} - (45^{\circ})_{y},$

the rf pulse spacings τ_1 and τ_2 take over the roles of the momentum transfer Q and the time t, respectively.

In its simplest and most straightforward version, the spin-alignment echo amplitude $F(\tau_1,\tau_2) = F(\tau_1,\tau_2,t=\tau_1)$ at time $t = \tau_1$ after the third pulse is measured. $F(\tau_1,\tau_2)$ is given by the single particle correlation function

$$F(\tau_1, \tau_2) = \langle \sin[\tau_1 \omega_Q(0)] \sin[\tau_1 \omega_Q(\tau_2)] \rangle.$$
(6)

 $\omega_Q(0)$ and $\omega_Q(\tau_2)$ are the ²H quadrupolar frequencies at times $\tau = 0$ and $\tau = \tau_2$ depending explicitly on the C-²H bond direction via

$$\omega_{\mathcal{Q}}(\tau) = \frac{\delta_{\mathcal{Q}}}{2} \{ 3\cos^2[\theta(\tau)] - 1 \},\tag{7}$$

where $\delta_Q = \frac{3}{4} e^2 q Q / \hbar$; θ is the angle between C-²H bond and the applied magnetic field direction.

The significance of Eq. (6) is as follows: A "phase" $\tau_1 \cdot \omega_Q(0)$ of a C-²H bond is correlated with its phase $\tau_1 \cdot \omega_Q(\tau_2)$ at a later time. Thus, τ_2 represents a parameter tracing the *timescale* of the motion. On the other hand, variation of τ_1 allows to focus the correlation function onto different angular ranges of the molecular reorientation. Thereby, we can distinguish between different reorientation geometries in very much the same way as is done in a scattering experiment with a variation of Q. For details, see Ref. 39. In general, a two-dimensional set of data, $F(\tau_1, \tau_2)$, is measured. In the following, we will discuss the two types of cuts, namely, the τ_1 dependence of the long time tail ("static structure" at $\tau_2 \rightarrow \infty$) and the τ_2 dependence for fixed τ_1 values ("dynamic structure"), separately.

The experimental data are compared with model calculations. For doing so, the dynamic process is assumed to be a stationary Markov process defining a joint probability density $P_2(\Omega', \Omega''; \tau_2)$ that a given C-²H bond points towards a direction Ω' at some time 0 and towards a direction Ω'' at a later time τ_2 . P_2 is obtained by solving the master equation for the particular model process. The correlation function (Eq. 6) is then calculated numerically using the following representation:

$$F(\tau_1, \tau_2) = \int d\Omega' \int \Omega'' \sin[\tau_1 \omega_Q(\Omega')] \\ \times \sin[\tau_1 \omega_Q(\Omega'')] P_2(\Omega', \Omega''; \tau_2).$$
(8)

Here we do not go into details of the solution of Eq. $(8)^{40}$ but rather use the relevant results.

2. Spin-alignment final state (static structure)

First, we concentrate on the geometry of molecular reorientation in the viscous and glassy regimes and neglect for a moment the time scale. If we do so, it is sufficient to analyze the normalized final state spin-alignment echo height

$$F_{\infty}(\tau_1) = \frac{F(\tau_1, \tau_2 \to \infty)}{F(\tau_1, \tau_2 \to 0)}$$
(9)

as a function of the "reduced" geometry parameter $\delta_Q \cdot \tau_1$. As has been pointed out in Ref. 39, $F_{\infty}(\tau_1)$ contains information about the spatial structure scanned by all orientations of a given C-²H bond in the run of the dynamic process. In view of the close analogy to the "elastic incoherent structure factor" given by the long time limit of the single particle propagator as measured by incoherent neutron scattering, $F_{\infty}(\tau_1)$ can be looked upon as the *static structure* of the reorientation process. In Ref. 39, F_{∞} has been calculated for a number of selected types of reorientation. Further, some experimental case studies have been reported.

A more complex dynamic process may consist of two independent types of reorientation on two different time scales, described by correlation times $\tau_c^{(1)}$ and $\tau_c^{(2)}$. In such a



FIG. 3. (a) Deuteron spin-alignment final state amplitudes [Eq. (9)] at $T = (263 \pm 0.5)$ K vs reduced geometry parameter $\delta_Q \cdot \tau_1$ ($\delta_Q = 2\pi \cdot 140$ kHz). The solid curve represents the calculated amplitude for isotropic reorientation. (b) Spin-alignment final state amplitude [Eq. (9)] obtained at $T = (250 \pm 0.5)$ K. The experiment describes an intramolecular flip-flop process of the two lateral out of plane rings. The curves are calculated for flip angles equally distributed around $\phi = 60^{\circ}$ within $\Delta \phi = 0^{\circ}$ (dashed curve) and $\Delta \phi = \pm 6^{\circ}$ (solid curve).

case it is possible to look at the faster process by "intermediate" state measurements with an appropriate setting of τ_2 , namely $\tau_c^{(1)} < \tau_2 < \tau_c^{(2)}$. The intermediate state then represents the final state relative to the fast process.

Figures 3(a) and 3(b) contain final state measurements in two characteristic dynamic domains. Whereas the physics of these final states will be discussed in the following, we postpone the way F_{∞} is extracted from the full set of data (see Sec. III B 3).

a. Viscous state: Figure 3(a) contains measured final states for o-terphenyl at $T = T_g + 20$ K where the α process dominates. As is expected from spin-lattice relaxation data, the α process in the viscous regime is well described by isotropic motion. This expectation is proved by our $F_{\infty}(\tau_1)$ result when compared with the numerical model calculation for isotropic reorientation (solid curve). Note the characteristic curve of this model and the remarkable agreement with the experimental data.

b. Glassy state: On further cooling the α process becomes slow enough (cf. Fig. 2) to allow for final state measurements of a second process [Fig. 3(b)]. This second process is not seen in Fig. 3(a) which only documents that by starting at some orientation at $\tau_2 = 0$ any orientation is attained in the limit $\tau_2 \rightarrow \infty$ with equal probability. At 250 K (7 K above T_g) the situation becomes more complex: The α process is in the rigid glass limit $[F_{\infty}(\tau_1) = 1]$ on the time scale⁴¹ of the spin-alignment experiment. Thus, the experimental results seen in Fig. 3(b) must originate from a different process which is called " β " process in the following. From our T_1 data a residual motional process is expected leading to a significant deviation of correlation times from the dashed line in Fig. 2 which represents the α process. These T_1 anomalies coincide with our final state results in the glassy state [Fig. 3(b)]. The data can be understood by flop jump of the two lateral out of plane phenyl rings. Thus, the o-terphenyl molecules jump stochastically forth and back between two isomeric molecular states:



Note that only 8 out of 14 C-²H bonds take part in this motion. From the limiting value F_{∞} ($\tau_1 \rightarrow 0$) an estimate of the mean jump angle ϕ of the lateral phenyl rings can be read. In Fig. 3(b), the upper curve was calculated for $\phi = 60^{\circ}$. The decrease of the experimental F_{∞} values for large τ_1 can be accounted for by assuming a spread of $\Delta \phi = \pm 6^{\circ}$ around the mean jump angle of 60° which corresponds to fluctuations of $\pm 3^{\circ}$ around both orientations.

The possible errors of ϕ and $\Delta \phi$ are estimated to be around \pm 20%. The reason for this large uncertainty is

discussed below. The intramolecular β process does not take part in the glass process and persists even below T_g .

3. Spin-alignment decay curves (dynamic structure)

Further information in addition to what is contained in $F_{\infty}(\tau_1)$ can be obtained from analyzing the τ_2 dependence of $F(\tau_1,\tau_2)$. Such decay curves contain two types of information:

(i) For small τ_1 values Eqs. (6) and (7) become

$$\mathbf{F}(\tau_1 \to 0, \tau_2) = (\tau_1 \delta_Q)^2 \langle P_2[\cos \theta(0)] \\ \cdot P_2[\cos \theta(\tau_2)] \rangle$$
(10)

yielding the autocorrelation function of the pure Legendre polynomial $P_2(\cos \Theta)$ [not to be confused with the probability density P_2 of Eq. (8)] independent of the type of motion.

(ii) For finite τ_1 values the decay curves contain details on the path (dynamic structure) of a given C–²H bond towards its final state. For discrete models, the decay function is multiexponential with a τ_1 dependent distribution of time constants given by the eigenvalues of the exchange matrix.⁴⁰ Except for simple few-site models, the decay functions can only be calculated numerically via Eq. (8).

From a large set of data^{35,42} we present here only a small subset of decay curves as measured for several temperatures in the viscous and glassy regimes (Figs. 4–7). At each temperature, curves are shown for small and large values of the geometry parameter τ_1 . [For $\tau_1 = 3 \mu s$ the correlation function can reasonably well be approximated by Eq. (10). For $\tau_1 > 20 \mu s$ the dynamic structure becomes extremely sensitive to the details of the jump model.]

By inspection of Figs. 4 and 5 we can draw a first essential conclusion: The decay process cannot be described by only one mechanism. At least two independent reorientation processes are present. This is demonstrated best by the twostep decay in the doubly logarithmic representation of the experimental curves of Fig. 5. Both processes have different



FIG. 4. Spin-alignment decay curves at $T = (263 \pm 0.5)$ K for two different values of the geometry parameter $\tau_1 = 3 \mu s$ (upper curve), $\tau_1 = 40 \mu s$ (lower curve). The data are fitted using two different reorientation models: (a) rotational (random) jumps + intramolecular flip-flop process (—); (b) rotational diffusion + intramolecular flip-flop process (—). Comparison of both models show that the true mechanism is close to (a). The $\tau_1 = 3\mu s$ curve yields correlation times $\tau_c^{(\alpha)} = 1.5$ ms and $\tau_c^{(\beta)} = 0.15$ ms.



FIG. 5. Spin-alignment decay curves at $T = (258 \pm 0.5)$ K for the same geometry parameters as in Fig. 4, namely $\tau_1 = 3 \mu s$ (upper curve), $\tau_1 = 40 \mu s$ (lower curve). The data are fitted with reorientation models as in Fig. 4 yielding correlation times $\tau_c^{(\alpha)} = 45$ ms, $\tau_c^{(\beta)} = 0.39$ ms.

activation energies thus allowing to trace their temperature dependences. It turns out that at T > 265 K the isotropic reorientation becomes the leading process. At 263 K (Fig. 4) both processes have only slightly different correlation times. As the temperature is lowered, the isotropic reorienta-



FIG. 6. Spin-alignment decay curves at $T = (246 \pm 1)$ K for several values of the geometry parameter τ_1 . (\oplus : $\tau_1 = 5 \mu$ s; O: $\tau_1 = 10 \mu$ s; \triangle : $\tau_1 = 60 \mu$ s; \times : $\tau_1 = 100 \mu$ s). Extrapolation of the solid lines (spin-lattice relaxation) back towards $\tau_2 \rightarrow 0$ leads to a static structure (final state) dominated by the intramolecular flip-flop process, see Fig. 3(b).



FIG. 7. Spin-alignment decay curves at $T = (263 \pm 1)$ K for the following values of the geometry parameter $\tau_1: \tau_1 = 4 \,\mu_S$ (\Box), $6 \,\mu_S$ (0), $8 \,\mu_S$ (Δ), 10 μ_S (+), 13 μ_S (\times), 14 μ_S (\diamond). The whole set of data is simultaneously fitted to (a) rotational (random) jumps; (b) rotational diffusion. The fits are *not* forced to reproduce the data in the small τ_1 limit, thus yielding an unphysically slow decay of the model (b) curves at small τ_1 .

tion (α process) slows down significantly. At 258 K (Fig. 5) the second processs (β process) can already be separated. As T decreases further, the α process is frozen out completely thus leaving the pure β process. The possibility of separating the α process and β process by temperature variation allows us to analyze both mechanisms separately. First, we identify the β process by looking at spin-alignment decay curves in the glassy regime (Fig. 6).

a. Glassy regime. For several temperatures from about T_g + 10 K down to far below T_g sets of decay curves have been measured. A typical set of curves, taken 3 K above T_g , is shown in Fig. 6. The common feature of all these spin-alignment data is the initial decrease down to the τ_1 dependent "plateau" value F_{∞} (τ_1) as plotted in Fig. 3(b). As indicated by the solid straight line in Fig. 6, F_{∞} is obtained by extrapolating the long time tail due to spin-lattice relaxation (more precisely: T_{1Q} for the quadrupolar order¹⁰) back to $\tau_2 \rightarrow 0$. We further note the τ_1 independence of the time constant of the initial decay. A τ_1 independenct dynamic structure is obtained if the exchange matrix has only one nonzero eigenvalue which is the case for the intramolecular two-site jump as discussed above.

From the temperature dependence of the spin-alignment decay curves the activation energy of this process turns out to be of the order of 100 kJ mol⁻¹ (\pm 40%). The identification and isolation of this β process is not easy. Actual values for F_{∞} (τ_1) [Fig. 3(b)] could only be obtained in the fairly narrow temperature window 255 K > T > 246 K because of two reasons:

(i) At T > 255 K the α process becomes fast enough to interfere.

(ii) For T < 246 K the spin-lattice relaxation becomes nonexponential. It is about this temperature where the system becomes "glassy" on the NMR time scale $(\tau_c^{(\alpha)} > > T_1)$. Because of the nonexponential spin-lattice relaxation it is no longer possible to apply a simple procedure to extract F_{∞} . Qualitatively, however, we find from comparing spin-lattice relaxation curves and spin-alignment decay curves that the β process persists below T_g at least down to about 200 K.

from the spin-alignment data for Figs. 4-6 are in harmony with those from T_1 data in the low temperature regime of Figs. 1 and 2. It is apparent that below ≈ 270 K, T_1 is no longer determined by the α process. Instead, the "correlation times" determined by naively analyzing T_1 through Eq. (1) with a Cole-Davidson distribution ($\beta = 0.5$) are some decades below those of the α process (dashed line in Fig. 2), and agree with those determined for the β process from spinalignment data.

A detailed and quantitative discussion of the low temperature behavior ($T < T_g$) of the spin alignment and spin-latttice relaxation has to be postponed. The fact that T_1 is shorter by some orders of magnitude in the glass as compared with the corresponding crystalline substance is well known,⁴³ and has been related to the low temperature anomalies in a manner⁴⁴ very similar to the independent development of the Anderson model.

The shapes of the spin-alignment decay curves below T_g are similar to those shown in Fig. 6. In particular, apart from the intramolecular β process, no further τ_1 dependence of the decay curves occur. We can conclude that no residual diffusive (small angle) dynamics persists in the glass state on the time scale $(10^{-4} \text{ s} \cdots 10^2 \text{ s})$ of the spin-alignment experiment.

b. Viscous regime. After having identified the internal molecular motion (β process), we can come back to the discussion of the spin-alignment curves in the viscous regime. The analysis is now simplified by assuming that one of the two processes (i.e., the fast process in our *T*-domain) is identified with the β process as described above. Thus, the only fit parameter due of this process is a correlation time. All other properties [static structure $F_{\infty}(\tau_1)$] are well determined. In this sense the β process is taken to be "known" for the following discussion of the slow isotropic α process. Being interested in the reorientation mechanism (jump angle distribution) we consider the following two extreme opposite cases:

Random jumps: A given $C^{-2}H$ vector is allowed to jump to any other orientation with equal probability. It turns out⁴⁰ that the "reduced" spin-alignment decay curve becomes

$$\Delta_{\tau_1}(\tau_2) = F_{\tau_2}(\tau_1) - F_{\infty}(\tau_1) = \exp\left(-\frac{\tau_2}{\tau_c}\right), \quad (11)$$

where $F_{\tau_2}(\tau_1)$ corresponds to the definition of Eq. (9) for finite τ_2 , and τ_c is the average time between jumps, $\Delta_{\tau_1}(\tau_2)$ is strictly monoexponential for all values of τ_1 .

Rotational diffusion: A given $C^{-2}H$ vector is allowed to perform a step by step random walk on the unit sphere with infinitesimal step lengths. Large angle jumps are forbidden. In this case no analytical solution has been obtained yet. The numerical calculations⁴⁰ result in highly nonexponential decay curves.

All other "realistic physical" jump models are intermediate between the two cases defined above. Let us compare these two extreme models. For the data fitting itself we adopt the following point of view: Since we do not know the true jump model we do not fit the whole set of curves simultaneously. A better way of comparing the two models is to fit only one reference decay curve, namely the one for the shortest τ_1 value which should be identical for both models in the short τ_1 limit. For a given jump model the large τ_1 decay curves are then determined uniquely and can be compared with the experimental data.

This procedure is applied for the spin-alignment decay curves plotted in Figs. 4 and 5. The absolute amplitude of the curve with $\tau_1 = 40 \,\mu s$ is lowered because of the finite τ_2 . We see that the true reorientation path is neither described by a random jump nor by a rotational diffusion model. The truth is in between, but significantly closer to the random jump model. The significant deviations of the random jump curves in both figures may be due to a slight misassignment of the T_2 value which was not used as a fit parameter but obtained from independently measured relaxation data (Fig. 1). The qualitative results are also not affected by the inclusion of a distribution of correlation times or a stretched exponential decay. A stretched exponential decay only flattens the decay curves, but leads to no qualitative change of the dynamic structure. The β process is assumed as an exact ($\Delta \Phi = 0$) jump with angle $\Phi = 70^{\circ}$ [cf. $\Phi = 60^{\circ}$ (Fig. 3) as obtained from final state] yielding a slightly better fit to the decay curves shown here.

The discrepancy to $\Phi = 60^{\circ}$ illustrates the relatively large uncertainty in determining the correct jump angle in the presence of a coupled motion.

From Figs. 4 and 5 we see that the temperature region where the α process can be studied is quite small. Below 258 K the slowing down of the process leads to correlation times τ_c larger than the spin-lattice relaxation times. If we extract τ_c values from the spin-alignment decay curves at $\tau_1 = 3 \, \mu s$ we do not need to specify the reorientational model. For the two temperatures used in Figs. 4 and 5 the correlation times are determined from the fits and are also included in Fig. 2. There is another illustrative way of comparing the two extreme reorientation models, namely a common fit of either model to a whole set of decay curves. This is represented in Figs. 7(a) and 7(b). For the purpose of comparison of the two isotropic models the β process has been disregarded. Furthermore, the fit is not forced to reproduce the small τ_1 limit of Eq. (11) with identical T_1 for both models, but rather optimizes for minimum χ^2 , the sum of quadratic deviations, separately for each model. From inspection of Figs. 7(a) and 7(b), we clearly see that the random jump model is a much better approximation than the rotational diffusion model. Let us again draw the attention to the strong τ_1 dependence of the initial slopes for a diffusive type of reorientation. Experimentally, such a strong τ_1 dependence of the dynamic structure is not observed in *o*-terphenyl, neither above or below T_g . This contrasts to network types of glasses (polymers, *H*-bridge networks) where preliminary results show a strong τ_1 dependence especially below T_g . Further, the smearing out of the experimental curves (Figs. 4 and 5) indicates the presence of a distribution of correlation times which has not been included in our analysis so far.

Finally, let us discuss the possibility of "liquid clusters"²² for a model where full molecular reorientation occurs below T_{g} . Even a few percent of molecules undergoing liquid-like reorientational motions with correlation times below about 1 μ s would be clearly observable as a motionally narrowed peak in the center of the ²H NMR spectrum. This can definitely be excluded from our experimental results. On the other hand, there are clear indications of motional heterogeneity below T_{α} in addition to the β process which has been identified with intramolecular rotational jumps of the out of plane phenyl groups relative to the cental ring. As we have mentioned above, the spin-lattice relaxation becomes nonexponential at $T \leq T_{\alpha}$, and is dominated by rapid processes other than the α and β processes; see the (average) T_1 value at the lowest temperature in Fig. 1. Though the nature of the sub- T_g motions is not yet clarified,⁴³ we can be sure that only small amplitude motions are involved. Recent neutron scattering experiments⁴⁵ have revealed small amplitude motions with correlation times in the ps regime where a correlation time distribution can possibly extend to much longer times and affect spin-lattice relaxation. These aspects and possible relations with a true β process¹⁸ and the low temperature anomalies of glasses⁹ need further investigation. However, we see no way of associating these small amplitude motions with any kind of liquid clusters.²² On the other hand, our results are in harmony with recent mode coupling theories where fast small amplitude motions are assumed to persist below T_g in supercoooled liquids.⁴⁶

IV. CONCLUSIONS

By combining deuteron T_1 , T_2 , and spin-alignment studies we show that the structural relaxation process (α process) of the glass forming liquid ortho-terphenyl involves isotropic reorientation of the molecules with a fairly narrow distribution of correlation times. A good fit is obtained using a Cole-Davidson distribution with $\beta = 0.5$. The reorientation mechanism lies between the two extreme cases, random jumps and rotational diffusion. A realistic jump angle distribution cannot be assigned yet. In addition to the rotational jumps of the entire molecule we observe intramolecular conformational changes by simultaneous jumps of the lateral out of plane phenyl rings relative to the central ring. This intramolecular β process is not affected by the glass transition.

At temperatures below T_{σ} we detect no further diffusive processes on the time scale $(10^{-4} \text{ to } 10^2 \text{ s})$ of the spin-alignment technique. This is in contrast to our findings in other glass forming systems. In deuterated glycerol and in chain deuterated polystyrene, we observe small angle diffusive motion with a broad distribution of correlation times at temperatures far below T_g . Thus, ²H NMR provides a tool for studying differences in the molecular dynamics of different types of amorphous material. It should be noted that the nonexponential spin-lattice relaxation and the anomalously short T_1 values in glasses (compared with crystalline solids) indicate further very rapid small amplitude motions. These may bridge the gap to the time window of 10^{-12} to 10^{-9} s accessible to quasielastic incoherent neutron scattering experiments where our preliminary results (anomalous Debye-Waller-factor, quasielastic spectra) yield evidence of small amplitude motions in o-terphenyl and trinaphthylbenzene⁴⁵ glasses which persist below T_{g} . On the other hand, no fast local motions are seen in glycerol glass by quasielastic neutron scattering. We hope that future NMR and neutron scattering studies will contribute considerably in clarifying the molecular origin of low temperature anomalies in glasses. Finally, we note that our experiments have given no indication of liquid clusters as predicted by an unmodified model of a liquid-solid transition,²² but they are in harmony with the predictions of mode coupling theories where fast small amplitude motions are calculated to exist below T_g .⁴⁶

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