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Exploring the dynamics about the glass transition by muon spin relaxation and muon spin rotation

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Abstract

The capability of muon spin rotation and muon spin relaxation to explore dynamics in the vicinity of the glass transition is illustrated by results pertaining to three materials exhibiting two different glass-forming abilities. Measurements under transverse magnetic fields enable us to monitor the dynamics of muonium-labelled closed-shell molecules within the microsecond range. The results display the onset of stochastic molecular motions taking place upon crossing from below the glass-transition temperature. In turn, the molecular dynamics of radicals formed by addition of atomic muonium to unsaturated organic molecules can also be explored up to far shorter times by means of relaxation measurements under longitudinal fields. The technique is then shown to be capable of singling out stochastic reorientational motions from others, which usually are strongly coupled to them and usually dominate the material response when measured using higher-frequency probes such as neutron and light scattering.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

One of the most widely accepted views of the liquid \rightarrow glass transition portrays it as a pure dynamic phenomenon, that is a thermodynamic anomaly not related to any underlying phase transition [1]. Approaches of the kind usually referred to as kinetic theories of the mode-coupling family portray such a dynamic glass transition in terms of the onset of stochastic mass-transport and reorientational motions signalling liquid flow, that takes place beyond a characteristic temperature usually referred to as T_c , that is located a few tens of kelvins above the calorimetric glass-transition temperature T_g . The theory constitutes the only tool capable

of describing glassy phenomena in simple liquids [1], molecular liquids [4] and molecular crystals [5], at a predictive level.

Because of the huge viscosity characteristic of a deeply supercooled liquid (SCL), one expects the above referred motions to be strongly coupled to others of vibrational or molecular-deformation nature that persist even within the glass phase [2, 3]. The presence of such strongly coupled motions poses a number of difficulties to isolate by experimental means phenomena related to the glass transition from others pertaining to the material characteristics which may exhibit temperature dependences distinct from that followed by translational mass diffusion and may therefore hide any sign of criticality at T_c , as has now been recognized [4]. In fact, most of the techniques employed such as neutron and light scattering require sophisticated data treatments [6] to unveil hints of critical behaviour. This has led in some cases to disparate estimates for T_c [7, 8] which call into question the physical soundness of such a quantity since sometimes estimates for T_c are close to the lower limit of stability of the normal liquid, where particle movements usually reach the picosecond scale.

Here we report on results on the dynamics of two kinds of glassy materials having disparate glass-forming abilities as explored by implanted positive muons. This concerns relatively strong glasses such as 1-propanol (1 Pr) or glycerol (Glyc), and 2-methylpyridine (2MP), which is a prototypical weak glass-former, and both are studied from low temperatures up to their normal liquid ranges. A preliminary assessment of the capabilities of the muon spin rotation technique [9] to monitor the dynamics of some materials upon crossing the liquid \rightarrow glass and crystal \rightarrow liquid transitions has already been given. In what follows we show how the capabilities of the technique can be extended to study dynamic phenomena within the normal liquid range up to timescales of the order of some tens of nanoseconds, thus allowing the study of relatively fast processes such as those about the melting of the stable crystals into their normal liquids.

2. Experiment

The measurements were carried out using the EMU and MuSR spectrometers at ISIS [10]. The glass samples were prepared by a deep quench into liquid nitrogen, prior to insertion into a cryostat kept well below the respective glass-transition temperatures $T_g \approx 98$ K for 1 Pr, 185 K for Glyc and 133 K for 2 MP. Spectra of the glassy samples under transverse (TF) or longitudinal (LF) fields were then measured from 5 K up to temperatures corresponding to the normal liquid range, corresponding to melting temperatures of 148 K (1 Pr), 291 K (Glyc) and 206 K (2MP).

The kind of measurements reported here is closely analogous to those of T_1 (LF or spin-lattice relaxation) and T_2 (TF relaxation), familiar in conventional magnetic resonance. They are known collectively as μ SR (muon spin relaxation or rotation)—an acronym clearly contrived to resemble ESR (electron spin resonance). In fact, our μ SR studies combine analogies with both ESR and NMR (nuclear magnetic resonance), since the implanted positive muons can reach both electronically paramagnetic and diamagnetic states. These elementary particles mimic the chemical behaviour of protons, either picking up an electron to form muonium ($\text{Mu} = \mu^+e^-$)—the analogue of atomic hydrogen (we refer to this as the paramagnetic fraction)—or else thermalizing in diamagnetic states. In alcohols, ROH, this latter is undoubtedly the positive ion ROHMu^+ in the first instance, formed in the manner of direct protonation, but subsequent proton exchange can lead to effective substitution in the molecule, thus ROMu . The labelled molecule is neutral and diamagnetic, i.e. closed shell, and in its intra-molecular motion should closely mimic the host molecules. In contrast, addition of atomic muonium to an aromatic ring such as that of 2-methyl-pyridine (2MP) leads to the formation of a species with rather different electronic structure, namely a molecular radical,

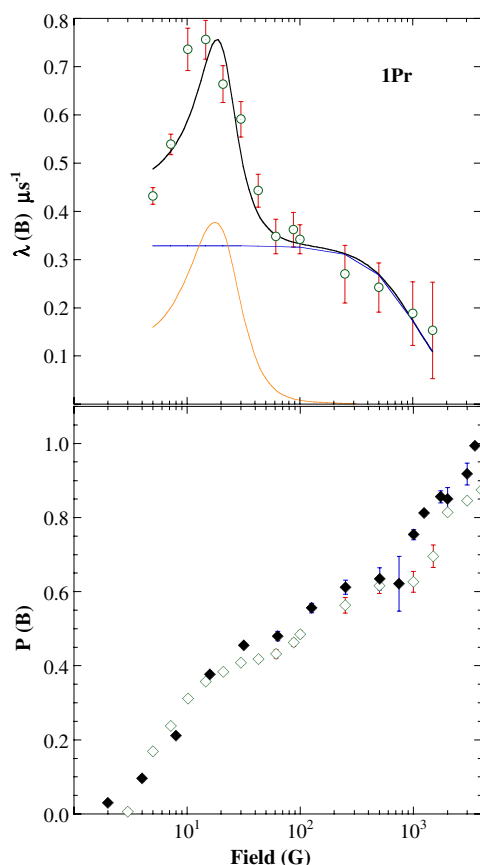


Figure 1. The upper frame shows the LF dependence of the relaxation rate for 1 Pr within the deeply supercooled liquid ($T = 100$ K). The solid line shows a fit in terms of equation (1), where the two components are depicted by dashed lines. The lower frame depicts the field dependence of the signal amplitude (polarization) for both 1 Pr (open symbols) and Glyc (solid symbols).

i.e. a paramagnetic or open-shell species. This occurs as a consequence of the chemical affinity of muonium (Mu) that is formed near the end of the muon thermalization track ($\text{Mu} \equiv \mu^+e^-$) towards unsaturated molecules and in the present case leads to the formation of an azacyclohexadienyl radical (referred to as Mu-MP in the following) [11].

The starting point of these studies concerns the characterization of the implanted muon site within the sample under study. The diamagnetic or closed-shell species, whether ionic or neutral, are easily detected by measuring the polarization under weak TF fields, where the muon spins precess at their Larmor frequency. On the other hand, the paramagnetic species, whether atomic muonium itself or the muonium-labelled radicals, are subject to hyperfine fields from nearby unpaired electrons. The signatures of such paramagnetic states are conveniently explored by measuring the LF polarization, its field dependence showing a characteristic decoupling of the hyperfine interaction.

Figure 1 shows how the relaxation amplitude varies with temperature and applied magnetic field for 1 Pr and Glyc. Such a field decouples the muon spin successively from the local fields generated by nearby proton nuclear moments (typically a few tens of Gauss) and then from the muonium electron (the hyperfine field in atomic muonium is 1600 G). The resultant two-step

increase in the relaxing signal amplitude is seen in the lower frame of figure 1. The muonium fraction, thus measured in fields at or above ≈ 100 G, may also depend on temperature, and such a variation also needs to be assessed. Our data on alcohols suggests that the ROHMu⁺ ion is a centre for muonium formation via capture of radiolytic electrons. The muonium yield is then a function of the ionic lifetime and the electron arrival time. The electron must arrive and be captured while the centre is still positively charged. That appears to be the case below 100 K in 1 Pr. For comparison, the corresponding temperature in H₂O ice is around 150 K, where the increase in diamagnetic fraction has been shown to correspond to its change from an ionic to a neutral species by means of ¹⁷O quadrupole resonance [12]. Above 200 K the proton-loss rate (i.e. the ROHMu⁺ to ROMu conversion rate) must be faster than the electron capture rate, suppressing that route to muonium formation and leaving only the prompt or epithermal yield.

The magnetic field dependence of the relaxation rates displays a two-component shape as shown in figure 1. A Lorentzian centred at zero field

$$\lambda(B) = 2(\Delta\gamma_\mu)^2\tau/(1 + \tau^2(\gamma_\mu H_{\text{ext}})^2) \quad (1)$$

with characteristic parameters given in terms of the static field distributions $\Delta \approx 300$ G and a characteristic time for muonium diffusion $\tau \approx 10^{-8}$ s arises from muonium motions. A narrow component centred at about 20 G is also seen for both materials. Its origin can be understood as arising from the presence of axially symmetric Mu [15] and the maximum would appear at fields corresponding to energy-level avoidances between the two lowest lying energy levels corresponding to a spin Hamiltonian that comprises in addition to dipolar terms a Fermi contact interaction.

TF μ SR measurements on the Mu-MP radical may show, using continuous muon sources, spin precession at frequencies corresponding to transitions between the magnetic states of the muonated radical. These take place between four energy levels defined by the spin Hamiltonian. Such transitions can be likened to ENDOR processes and will provide direct information on hyperfine coupling constants between Mu and the electron density. The spectrum of such an adduct is composed by a number of resonance peaks appearing due to the different binding positions of Mu to the aromatic ring. From previous work [11, 14] one expects to find several resonances which are classified according to magnetic selection rules. Flip-flop exchanges of polarization between the muon and a nuclear spin involve no net change of the magnetic quantum number ($\Delta M = 0$). These transitions will be responsible for the observed depolarization under fast isotropic motions such as happens in a liquid since these are driven by purely isotropic hyperfine couplings in the spin Hamiltonian. In contrast, $\Delta M = 1$ or muon-flip transitions are extremely sensitive to small anisotropies in the muon environment and vanish in isotropic, fast-motion conditions. This results from the coupling of Zeeman states through the anisotropic dipolar part of the muon hyperfine interaction and is thus dependent upon the relative orientation of the principal axis of the hyperfine tensor (i.e. a molecule-fixed frame) with respect to the applied field. Preliminary measurements carried out under weak TF fields are not intended to study in detail any of these resonances but will rather serve to quantify the fraction of muons ending up in diamagnetic states. Our data show a weak TF signal that show a very weak dependence of the precession signal on phase changes undergone by our sample.

Repolarization curves measured under LF fields up to 0.3 T fields for glass (5 and 60 K), crystalline (180 K) and liquid (206 K) samples are shown in figure 2.

Data for all the solid phases depict a sigmoid-shaped curve. Its shape could be reproduced by a slight generalization of a quadratic function in the applied field proposed to deal with the effects of axial anisotropy on nuclear interactions [16] such as

$$P(T, B) = \frac{a + f^2}{1 + f^2}; \quad a = c \frac{d + f_l^2}{1 + f_l^2}; \quad f = B/B_0; \quad f_l = B/B_1 \quad (2)$$

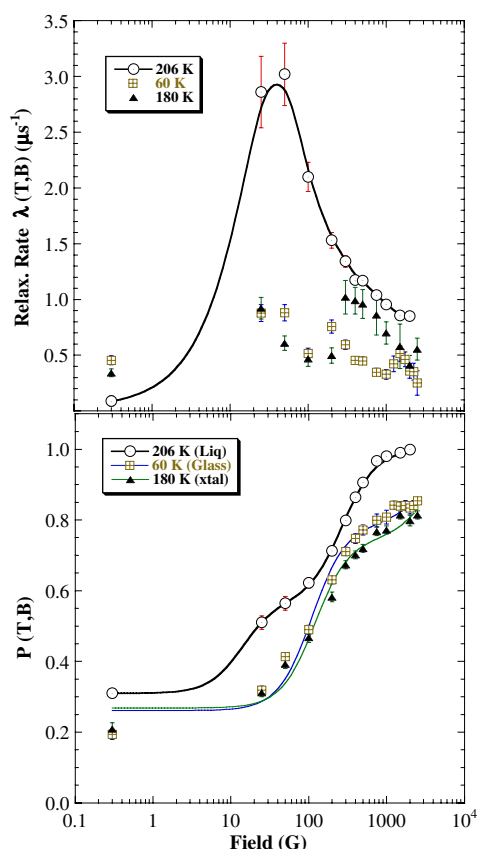


Figure 2. LF dependence of signal relaxation rates as measured for several condensed phases for 2 MP (see inset). The lower frame displays the LF dependence of the fractional amplitudes.

where B_0 stands for the value of the contact-interaction field and B_1 characterizes the repolarization at low fields. Setting $c = 1/2$, $d = 1/3$ the equation given above gives equation (3) of [16], that describes a muon embedded within a polycrystalline sample where the hyperfine coupling between the muon and the unpaired electron has an axial symmetry and can thus be described in terms of an isotropic coupling plus a traceless dipolar part. The obtained values for the glass and crystal are (in frequency units $\gamma_e B$ with $\gamma_e = 2.8025 \text{ MHz G}^{-1}$) $B_1 = 308 \pm 5 \text{ MHz}$ and $339 \pm 6 \text{ MHz}$ respectively, while those for the B_0 could not be determined accurately due to lack of high field data. Here $c = 0.75$ and $d = 1/3$. In contrast, data for the liquid are well fitted by $B_0 = 759 \pm 25 \text{ MHz}$, $B_1 = 29 \pm 5 \text{ MHz}$, $c = 1/2$, and $d = 1/2$. The estimated values for the largest fields give estimates of the strength of hyperfine coupling while that for the smaller value may yield an indication of the anisotropy.

Since all the data are well accounted for by a single exponential plus a field-independent background, we ascribe the observed relaxation to spin-lattice relaxation taking place at a rate $\lambda(T, B)$. Therefore, here we disregard any chemical transformation to a final diamagnetic state, which, if it occurs, has to follow rather fast kinetics.

2.1. Muon spin rotation

The TF μ SR measurements on the two alcohols display only the diamagnetic fraction, i.e. either ROHMu^+ or ROMu (according to temperature, as we see below). The inclusion of a small

HMu fraction, formed by an abstraction reaction of atomic muonium, is not excluded either. The TF signals are thus analogous to free induction decays in proton NMR and correspond to precession of the muon spin at or near its Larmor frequency. (The much higher precession signals corresponding to atomic muonium are invisible at a pulsed muon source such as ISIS, at the magnetic fields used.) The LF signal, on the other hand, subsumes both paramagnetic and diamagnetic fractions: one expects to find exponential spin–lattice relaxation of the muonium fraction towards a baseline set by the diamagnetic fraction. One must bear in mind that thermal-equilibrium polarization is negligible compared with the initial muon polarization on implantation (which is close to 100%) but that mechanisms of longitudinal relaxation on the microsecond timescale of these measurements (set by the muon lifetime, $\tau_\mu = 2.2 \mu\text{s}$) exist only for the paramagnetic fraction [13].

Measurements performed in TF are sensitive to static or ‘frozen-in’ spatial variations of the local magnetic field, since these induce a dephasing of the muon spin precession. At low temperatures, strong damping of the cosine precession signals results from the vector sum of internal plus applied fields, so that individual muons precess at slightly different Larmor frequencies. Some explicit examples of the relaxation spectra for this material are shown in our previous communication [9].

The spectra yield relaxation or damping rates that are the simple inverse of the T_2 relaxation times: $\lambda_{\text{TF}}(T) = T_2^{-1}(T)$. These relaxation rates are expected to decrease with increasing temperature due to the onset of molecular motions: this is analogous to motional narrowing in NMR, though there can also be a reduction in the static linewidth on going from the ionic to the substituted species ($\text{ROHMu}^+ \rightarrow \text{ROHMu}$). In contrast, the corresponding amplitude of the precession signal is expected to increase as muonium formation is suppressed, so that the diamagnetic muon fraction increases. The results are shown in figure 3, where one sees a mild decrease in relaxation rate accompanied by a small increase in signal amplitudes up to the calorimetric glass-transition temperatures. There are no clear features at T_g but strong drops in the relaxation rates, accompanied by marked increases in signal amplitude, are clearly seen at higher temperatures. Finally, a clear change of régime is attained for temperatures some 1.3 times T_g , where the relaxation rates follow a smooth, approximately linear, dependence on increasing temperature. No data were taken at higher temperatures since more rapid motions (faster than 10^{-8} s) go beyond the dynamic range of our instrument.

The relaxation rates shown in figure 3 show a strong drop in relaxation rate that becomes far more marked at temperatures significantly above T_g . Such phenomena are ascribed to the onset of stochastic motions, which leads to a ‘motionally narrowed’ régime, much in the same way as in conventional NMR. Well above T_g both curves display a remarkable change of régime, where the temperature dependence of the relaxation rate is now far milder. To model such curves, recourse is made to the prediction made by mode-coupling theories (MCTs) [1, 4] of the glass transition concerning the Lamb–Mössbauer factor. On the grounds of such an analogy we describe our data using a term $\propto \sqrt{|T - T_c|/T_c}$, where T_c stands for a critical temperature. In other words, the temperature dependence of the relaxation rate provides clear evidence of criticality appearing about a temperature T_c and the data from the deep-glass phase up to the normal liquid can be accounted for by

$$\lambda(T) = \begin{cases} A\lambda_{\text{glass}}(T)\sqrt{T_{\text{red}}/} \\ + \zeta(T_{\text{red}}); & T \leq T_c \\ \zeta(T_{\text{red}}); & T > T_c \end{cases} \quad (3)$$

with

$$T_{\text{red}} = |T - T_c|/T_c, \quad \zeta(T_{\text{red}}) = \alpha_0 + \beta_0 T_{\text{red}}. \quad (4)$$

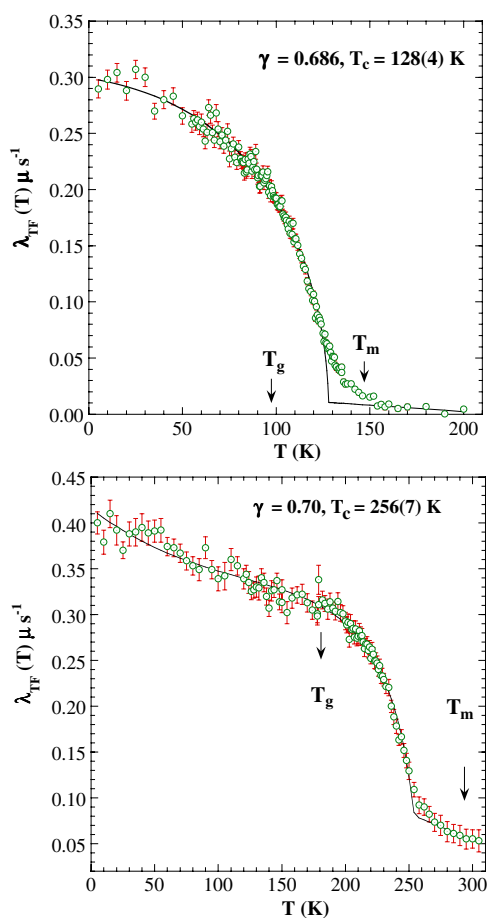


Figure 3. The upper frame shows the temperature dependence of the relaxation rate for 1 Pr under a TF of 20 G within its glass, deeply supercooled and normal liquid ranges. The solid line shows the approximation described in the text. The inset shows the estimate for the critical temperature and γ factor (see text). The lower frame depicts data for glycerol.

The high temperature data are in both cases modelled by a mild, linear temperature dependence with coefficient values easily calculated from the measured data once the value for T_c is set. Fitting the relaxation rates and leaving T_c and r as adjustable parameters yields values of $T_c = 128(4)$ K for 1 Pr and $256(7)$ for Glyc.

2.2. Muon spin relaxation

Here we show how changes in molecular dynamics translate into a distinctive behaviour of the longitudinal relaxation rates for our weak glass-former. Because of the strong hyperfine field in the radical, one expects the relaxation rate $\lambda(T, B)$ and the associated amplitude to be strongly dependent upon the applied field. The data corresponding to an LF of $B = 500$ G are shown in figure 4. Measurements heating the glass from low temperature again display a strong drop, much like that seen for the two alcohols in figure 3. Data for higher temperatures could not be measured due to the onset of crystallization. The decay with temperature of the LF relaxation rate is here stronger than that observed for the alcohols, a phenomenon that is understood on

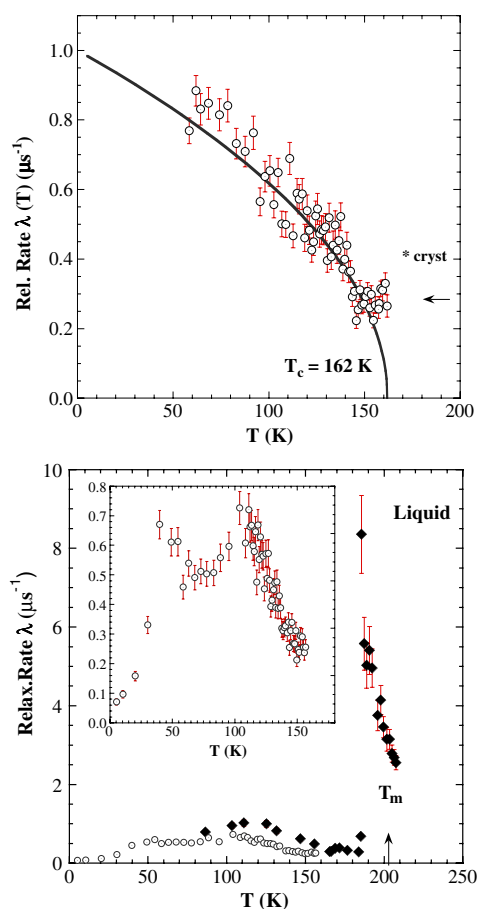


Figure 4. The upper frame shows the temperature dependence of the relaxation rate for 2 MP under an LF of 500 G within its glass and deeply supercooled liquid. The solid line shows the approximation in terms of a square-root singularity (see text). The lower frame depicts the temperature dependence of the relaxation rate under an LF field of 100 G corresponding to cooling of the normal liquid into crystal (lozenges) and heating a glass from low temperatures (open symbols). The inset depicts a blow-up of the glass data.

the basis of previous knowledge of the effects of motional narrowing effects on the $\Delta M = 0$ and $\Delta M = 1$ transitions that contribute to the relaxation. As a matter of fact, previous studies on cyclohexadienyl radicals [11, 14] show that $\Delta M = 1$ transition will not cause relaxation if motions are faster than some 50 ns.

The curve drawn through the data in figure 4 again represents the square-root singularity given by equation (3) and has been calculated for a value of $T_c = 162$ K that coincides with that corresponding to an extrapolation of the scaling law amplitudes obtained from analysis of the susceptibility measured by light-scattering and dielectric spectroscopies [8].

Data measured on cooling the normal liquid measured under $B = 100$ G are also shown in figure 4. There one sees that $\lambda(T)$ shows a strongly divergent behaviour as one approaches the freezing temperature that is here located about 190 K. The shape of the relaxation rate as one cools the liquid thus samples the critical dynamics associated with the liquid \rightarrow crystal transition. Our data show no dynamic anomaly about 180 K as postulated in [8] but rather shows that any estimate of T_c for this material cannot lie far beyond 162 K.

Figure 4 also compares the relaxation rates as measured under $B = 100$ G for both crystal and glass. The latter shows some remarkable temperature dependence below 40 K, which, in the light of high-resolution neutron spectroscopy data [17], cannot be ascribed to the onset of stochastic molecular motions. In fact, from previous experiments we know that motions at least within the nanosecond timescale are frozen within this range of temperatures. The strong rise in $\lambda(T)$ within these low temperatures is suggestive of the presence of migrating spin excitations reminiscent of those found in conducting polymers [18].

3. Conclusion

Data shown here illustrate how muon spectroscopy can be profitably employed for the study of single-particle dynamics in highly viscous liquids within mesoscopic timescales. Because of the time windows inherent to muon spectroscopy, motions faster than 10^{-8} s are too fast to be observable under weak TF fields and the same applies to those faster than a few tens of nanoseconds for radicals under LF fields. This means that motions with frequencies well beyond the MHz range are effectively excluded from the measured response under TF, thus making it unnecessary to subtract the spectrum corresponding to fast dynamics, as customarily done in light-scattering and dielectric relaxation studies.

Measurements of the Mu-MP radical exemplify the capability of the technique to explore relatively fast dynamics up to temperatures characteristic of the normal liquid range. The information extracted from such experiments has allowed us to reassess the physical soundness of the critical temperature in this material, an issue that has been under discussion in recent times.

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