

## Does the Standard Model of Low-Temperature Glass Dynamics Describe a Real Glass?

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We present the first experimental single-molecule (SM) spectroscopy study of the local dynamics in molecular glasses (frozen *toluene* and *deuterated toluene* weakly doped with a substituted *terrylene*) at  $T = 2\text{--}30$  K. Surprisingly, the dynamics does not follow the standard model of low-temperature glasses. An extra contribution to the dynamics was detected causing drifts and irreproducible jumps of the SM spectra. The isotope effects in the SM linewidth distribution and the density of states (boson peak) show that the fast dynamics at  $T = 2$  K is due to excitations of tunneling nature, whereas at  $T > 7$  K it is related to vibrations; H/D atoms are directly involved in both types of excitations.

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It has been well known for many years that amorphous solids differ fundamentally from crystals by their anomalous dynamics at low temperatures (below a few tens of  $K$ ). These anomalies are explained in the framework of a few simple phenomenological models [1–9]. The main idea behind these models is to replace the complicated multi-dimensional potential surface of a disordered solid by a set of elementary excitations which correspond to simple independent motions of groups of atoms or molecules: tunneling two-level systems (TLSs), thermally activated TLSs, and quasilocalized low-frequency vibrational modes (LFMs).

In the tunneling TLS model, the glass dynamics at temperatures below 1–2 K is determined by a system of TLSs, each of which corresponds to tunneling transitions of atoms between two localized isolated potential minima.

At temperatures from a few  $K$  to a few tens of  $K$ , amorphous materials also exhibit a set of universal properties, which are different from those of perfect crystals (e.g., the existence of the “boson peak”). These properties cannot be explained by the tunneling model; instead they can be described with the concept of LFMs [5,6]. These excitations correspond to vibrational modes which are localized due to the inhomogeneities intrinsic to disordered solids.

The soft-potential (SP) model allows one to describe the glass dynamics in a broad temperature range by comprising both of the above elementary modes [10–13].

In spite of the fact that these models were successfully used for explaining a number of experimental results, several fundamental questions have so far remained unanswered. Among others, the questions concerning the microscopic nature of the excitations and the scope of validity of the models are most important.

The dynamics of solids can be studied by different experimental techniques. Among these, only single-molecule spectroscopy (SMS) of impurity centers (e.g. [14,15]) has a principal advantage for the study of localized excitations. Namely, it completely eliminates the averaging over ensembles of elementary excitations and provides

information about dynamical processes in the local environment of one single chromophore molecule. For example, the parameters of single TLSs [16] and LFMs [17,18] in polymers could be determined from SMS experiments.

Numerous experiments have shown that the anomalous dynamics of amorphous solids is surprisingly universal and does not depend strongly on the structure and chemical composition of the material. It is understood that this similarity of the dynamical properties has fundamental physical reasons, the main point being the local disorder and heterogeneity of glassy media. As a result, all the disordered (amorphous) solids have been referred to as “glasses.” Nevertheless, the question as to which degree the dynamics and its microscopic details are really identical for all glasses and can be described in the framework of a unified theory is still open. The unique method to investigate this point is SMS. Yet, to the best of our knowledge, SMS experiments have not been performed in low-molecular weight glasses so far. In this Letter we present the first results of such a study.

We performed SMS measurements on two frozen liquids—protonated toluene ( $C_6H_5CH_3$ ) and perdeuterated toluene ( $C_6D_5CD_3$ ) weakly doped with tetra-*tert*-butylterrylene (TBT) molecules. Glassy phases were obtained by fast freezing of the liquid solutions.

The first question of the present study was the same as investigated by Orrit and co-workers in [19] for amorphous polymers: “Are the spectral trails of single molecules consistent with the standard TLS model of glasses at low temperatures?”

For this purpose we also used the technique of repeatedly recording the fluorescence excitation spectra of SMS in a selected spectral interval. This method yields the spectral histories or spectral trails of SMS, which show the integral redshifted fluorescence signal, encoded on a gray scale, in a two-dimensional (2D) representation [20] as a function of laser frequency (horizontal axis) and scan number or time (vertical axis). The experimental procedure was described in detail in [21].

We obtained the following intriguing result: Most of the spectral trails of SMs measured on a time scale of minutes to hours cannot be described in the framework of the standard tunneling model (see Fig. 1). The most frequently seen anomalies were spectral drifts and irreproducible jumps of SM spectra. This is in striking contrast to the results obtained in a number of SMS studies on amorphous polymers [14,16–22] (see Fig. 2). The spectral trails measured in polymer matrices at temperatures below a few tens of  $K$  usually show  $2^N$  spectral positions, corresponding to the interaction of the chromophore with  $N$  nearby and strongly coupling active TLSs. Smaller spectral shifts due to a “sea” of distant TLSs contribute to the observed linewidth. Interactions with very fast flipping TLSs and excitations of vibrational type (LFMs, phonons) are responsible for the true homogeneous broadening.

We wish to emphasize that in polymer matrices, spectral trails inconsistent with the standard model of low-temperature glasses were observed, too. For example, in our previous measurements on amorphous polyisobutylene (PIB) [21,22], the relative number of nonstandard spectral trails on the time scale of minutes to hours was around 10%. Also, the authors of [19] reported on the observation of spectral trails which were not in agreement with the standard TLS model; in their case the number of such trails was  $\sim 30\%$ . Moreover, early works reported about complicated (non-TLS) dynamics even in nonideal crystals [23]. A statistical analysis of the parameters of SM spectral shapes performed in [24], however, confirmed that the tunneling TLS model in general describes the SM spectra in amorphous PIB on the time scale of 2 min remarkably well.

In the low-molecular glasses toluene and toluene-d8 we found a very different situation (see Fig. 1). Virtually all the observed SM spectral trails ( $\sim 25$ ) showed anomalous dynamical phenomena on a slow time scale longer than a few minutes. Specifically, the behavior comprised slow drifts as well as irreproducible jumps of the SM spectra between several frequency positions. One can characterize this dynamics as being “similar to TLSs,” since the pres-

ence of slow jumps suggests that tunneling (or thermally activated) transitions between isolated potential minima take place. On the other hand, some of the dynamical features clearly require modifications of the TLS model. For example, the authors of Ref. [25] try to explain anomalies in spectral dynamics of polymers as observed in SMS experiments by taking the multilevel nature of some TLSs at  $T > 1$  K into account.

Qualitatively one can suggest at least a few reasons for the observed behavior. (i) “Weak” structural relaxations in the glassy matrix lead to the continuous spectral drifts. These relaxations could be related to lower energy barriers in the potential energy landscape of frozen toluene as compared to polymers. Note that the glass transition temperature of toluene ( $T_g = 117$  K) differs markedly from that of typical polymers (e.g.,  $T_g = 201$  K for PIB). This indicates indirectly that there must be a marked difference in the barrier heights of the energy landscapes of low-molecular glasses and polymers. (ii) Specific features of the potential energy landscape in frozen toluene. (iii) The dynamics of the impurity molecules themselves may have an influence on the observed glass dynamics, since the size of TBT significantly exceeds the size of the toluene molecule.

Moreover, it is possible that quickly frozen toluene, which is usually considered to be a glass, actually represents some more complicated type of solid state, consisting of nanostructures with short-range order and with a complicated disordered network of grain boundaries in between. This structure could be related to an energy surface which cannot simply be reduced to a number of noninteracting TLSs and LFMs. Such microscopic peculiarities of a glass most likely cannot be detected in macroscopic (i.e., ensemble) experiments, yet, the spectroscopy of single molecules is able to reveal them.

In order to characterize the low-temperature dynamics in a more quantitative way we measured the linewidth distributions of single TBT molecules in toluene and toluene-d8 at different temperatures (see Fig. 3). For details of the

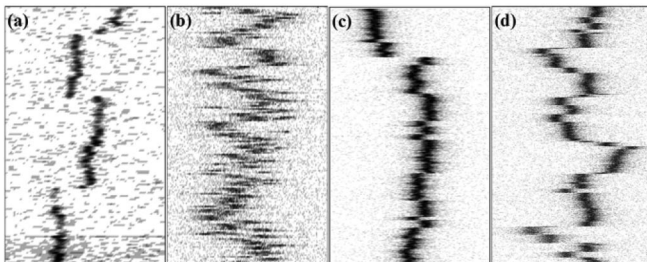


FIG. 1. Spectral trails measured for single TBT molecules in frozen toluene at  $T = 2$  K,  $t_m = 13, 5$  min, scan range 3 GHz (a) and  $T = 4.3$  K,  $t_m = 13, 5$  min, scan range 15 GHz (b), and in frozen toluene-d8 at  $T = 4.3$  K,  $t_m = 37$  min, scan range 9 GHz (c), and  $T = 7$  K,  $t_m = 83$  min, scan range 24 GHz (d). Types of spectral dynamics (drifts, irreproducible jumps) which are in disagreement with the standard model of glasses are clearly visible.

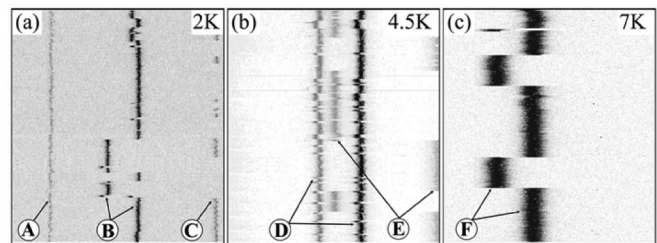


FIG. 2. Spectral trails of six different TBT molecules in polyisobutylene as measured at  $T = 2, 4.5,$  and  $7$  K (scan range 20 GHz). The slow spectral jumps are in agreement with the TLS model and represent a typical behavior in polymers. A: no strong coupling with TLSs in the near environment of the SM; B: strong interaction with two TLSs; D: strong interaction with two TLSs, one of which is much faster than the other; F: strong interaction with one TLS.

experimental setup see [26]. The analysis of isotope effects is a powerful tool for the investigation of the dynamics in solids [27–29]. In particular, it yields information about the characteristic masses of particles involved in different types of elementary excitations.

Figure 3(a) shows the distributions of the SM linewidths in the protonated and the perdeuterated matrix at  $T = 2$  K. The difference between the two distributions clearly indicates the presence of an isotope effect. Replacing the H atoms in toluene by D leads to a decrease of the optical linewidths of the chromophore molecules. This effect most clearly shows up as a shift of the maximum of the distribution from  $\sim 125$  MHz in toluene to  $\sim 94$  MHz in toluene-d8. At  $T = 7$  K, an isotope effect is also present, but in the opposite direction [see Fig. 3(b)]. Replacing the H atoms in toluene by D shifts the maximum of the linewidth distribution from  $\sim 3.3$  GHz (toluene) to  $\sim 4.6$  GHz (toluene-d8).

A simple analysis of the tunneling model shows that if the molecular tunneling motions involve hydrogen atoms, the characteristic rate of the transitions is expected to decrease upon deuteration. As a consequence, the spectral broadening caused by these motions should also decrease and the SM linewidth distribution is expected to shift to narrower widths. If the SM spectra are mainly broadened by interactions with LFMs of the matrix, the situation is different. The homogeneous linewidth caused by the dephasing due to a single vibrational mode with frequency  $\nu$  is approximately given by [27–30]

$$\Gamma(\nu) \propto \exp(-h\nu/kT), \quad (1)$$

where  $h$  and  $k$  are Planck's and Boltzmann's constants, respectively. Equation (1) is valid in the low-temperature limit  $kT \ll h\nu$ . Elementary considerations yield

$$\nu \sim \sqrt{k_{\text{eff}}/m_{\text{eff}}}, \quad (2)$$

where  $k_{\text{eff}}$  is the effective spring constant and  $m_{\text{eff}}$  the effective reduced mass of the atoms involved in the vibration. From Eqs. (1) and (2) one can see that an increasing mass  $m_{\text{eff}}$  leads to a broadening of the linewidth  $\Gamma$ . This is exactly the opposite effect as compared to the coupling to TLSs.

In our experimental data we can analyze these effects on the level of single molecules. The shift of the linewidth distribution to smaller values upon deuteration [Fig. 3(a)] clearly shows that at  $T = 2$  K the tunneling dynamics dominates the broadening of the SM spectra in toluene glass. Thus, in spite of the presence of the strong “non-TLS” dynamics, the excitations mainly determining the observed broadening of the SM spectra on the time scale of  $t_m = 2$  min have a tunneling origin. At  $T = 7$  K, matrix deuteration gives rise to broader SM spectra [Fig. 3(b)]. Hence, at this temperature the contribution of *vibrational excitations* predominates over the tunneling dynamics. Furthermore, it is evident that H/D atoms are involved in both the tunneling and the vibrational degrees of freedom.

To obtain more detailed information about the vibrational excitations in toluene glasses, we determined their energy spectrum (i.e., the density of the vibrational states) for both systems. This was accomplished with the following procedure which was described in [31]: For each impurity SM the temperature dependence of the spectral linewidth was measured. The  $T$  dependence was fitted with the exact version of Eq. (1) (which is valid for a broader temperature range), viz.  $\Gamma(T) = w \exp(-h\nu/kT) \times [1 - \exp(-h\nu/kT)]^2$ . This yields the effective vibration frequency  $\nu$  of the LFM(s) in the nearest environment of the selected single impurity molecule [18,32]. Such measurements were performed for a number of dopant molecules at different locations of the sample, giving a set of local values  $\nu$ . Their distribution  $P(\nu)$  can be considered as the density of vibrational states in the investigated system. It was found in [31] that this distribution is in close agreement with the boson peak as measured in the pure matrix material (without impurities) by inelastic neutron scattering.

Figure 4 shows the energy spectra of the LFMs as measured for  $\text{C}_6\text{H}_5\text{CH}_3$  and  $\text{C}_6\text{D}_5\text{CD}_3$  doped with TBT. Again the isotope effect is obvious: Matrix deuteration leads to a clear decrease of the LFM frequencies, visible as a shift of the maximum of the spectrum from  $\sim 15.5$   $\text{cm}^{-1}$  to  $\sim 12$   $\text{cm}^{-1}$ .

General considerations show that the frequencies of LFMs depend on the characteristic masses of the particles involved in the vibrations. In [33] it was demonstrated that the maxima of the phonon sidebands (i.e., the boson peak),

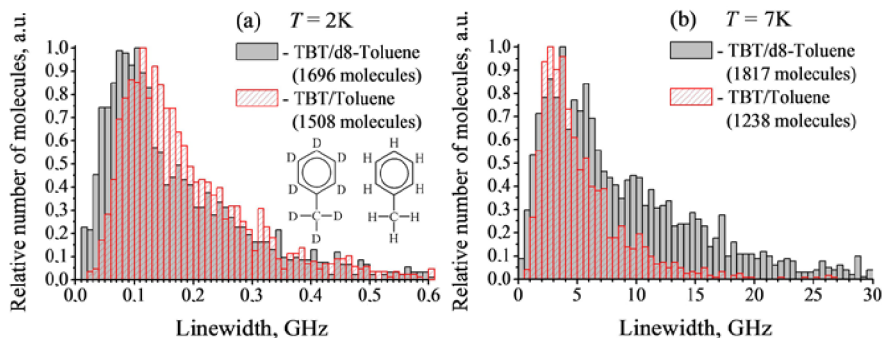


FIG. 3 (color online). Distributions of the SM linewidths of TBT as measured in toluene— $\text{C}_6\text{H}_5\text{CH}_3$  (hatched histograms) and perdeuterated toluene— $\text{C}_6\text{D}_5\text{CD}_3$  (gray histograms) at  $T = 2$  K (a) and  $T = 7$  K (b). The distributions have been normalized to their maxima.

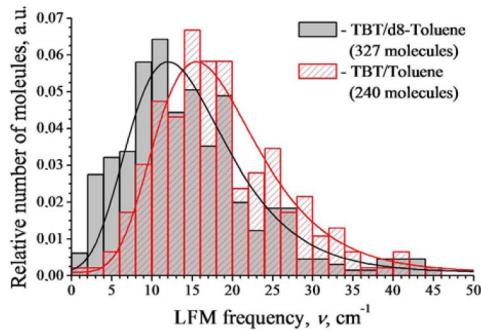


FIG. 4 (color online). Frequency spectra of the localized low-frequency vibrational excitations as measured for protonated toluene— $C_6H_5CH_3$  (dashed histograms) and perdeuterated toluene— $C_6D_5CD_3$  (gray histograms) doped with TBT. The distributions have been normalized to their areas. The smooth lines are guides for the eye.

as measured by hole-burning spectroscopy in a number of rigid molecular glasses, depend on the mass of the matrix molecule as  $\nu \sim m^{-1/2}$ . The author concluded that LFMs correspond to intermolecular vibrations between the whole matrix molecules. In [27,28] a different result was found: only a part of the matrix molecule is mainly involved in the LFMs.

Our present measurements yield  $\nu_{tol}/\nu_{tol-d8} \cong 1.29$  using the maxima of the frequency spectra. For the whole toluene molecule,  $(m_{C_7H_8}/m_{C_7D_8})^{-1/2} = 1.04$ ; for the  $CH_3$  group the corresponding value is  $(m_{CH_3}/m_{CD_3})^{-1/2} \cong 1.1$ . If the LFMs consist of librations of the  $CH_3$  group, their frequencies scale as the inverse square root of the moments of inertia, an upper bound of which can be estimated as  $(m_H/m_D)^{-1/2} \cong 1.41$ . The experimental value of 1.29 indicates that in toluene glass the methyl group is probably involved in the LFMs and that its motion is mainly of librational character. At least we can conclude that H/D atoms are certainly involved in the LFMs.

Our SMS studies have shown the unexpected result that the dynamics in a “real” (i.e., low-molecular) glass does not follow the standard TLS model. The dynamical behavior of SM lines is not only influenced by tunneling (TLS) and vibrational (LFM) degrees of freedom but, in addition, also by more complicated relaxations which lead to slow (minutes-hours) spectral drifts and irreproducible jumps. In spite of the presence of “non-TLS” dynamics on this slow time scale, the elementary excitations determining the SM spectral linewidths as measured at  $T = 2$  K in scans of 2 min duration have a *tunneling nature*, as the isotope effect proves. From our data we cannot decide whether these excitations are noninteracting TLSs or some kind of more complicated multilevel tunneling systems. At  $T = 7-30$  K, the comparison of the densities of states confirms the *vibrational nature* of the excitations dominating the fast dynamics. H/D atoms are directly involved in both the tunneling transitions and the vibrations.

The present study demonstrates that the term “glass” should be used with care. The similarity of macroscopic dynamical properties of disordered solids does not imply that the dynamics of these systems are the same also on the microscopic level.

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