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Ultrafast Alpha-Like Relaxation of a Fragile Glass-Forming Liquid Measured with 2D-IR Spectroscopy

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Ultrafast two-dimensional infrared (2D-IR) spectroscopy is used to study the picosecond dynamics of a vibrational probe molecule dissolved in a fragile glass former. The spectral dynamics are observed as the system is cooled to within a few degrees of the glass transition temperature (T_g). We observe non-exponential relaxation of the frequency-frequency correlation function, similar to what has been reported for other dynamical correlation functions. In addition, we see evidence for α -like relaxation, typically associated with long-time, cooperative molecular motion, on the ultrafast timescale. The data suggests that the spectral dynamics are sensitive to cooperative motion occurring on timescales that are necessarily longer than the observation time.

The complexity of dynamical phenomena in glass-forming liquids as they approach the glass transition temperature has attracted considerable experimental and theoretical interest [1-10]. Though there are few if any structural signatures, transport properties diverge rapidly as the transition temperature is approached [1-4, 6, 7]. The dynamical change is accompanied by a growth in dynamical heterogeneity characterized by a broad distribution of relaxation timescales [7-10]. The increase in dynamically distinct regimes results in a bifurcating of relaxation timescales, where fast β -relaxation results from local fluctuations and slower α -relaxation involves cooperative rearrangement of domains [11-13]. Fragile glasses are materials that display a greater configurational entropy than strong glasses, and, therefore, have an increased propensity for forming dynamically distinct regimes. Dynamical heterogeneity leads to the well characterized non-exponential relaxation of ensemble correlation functions, such as dipole-dipole correlation functions probed by fluorescence anisotropy measurements [8, 14, 15].

The two relaxation processes occurring in glasses can be distinguished by their behavior near T_g . The small scale motions typically associated with β -relaxation display a simple Arrhenius temperature dependence that is maintained through the glass transition temperature. In contrast, α -relaxation processes have a strong viscosity dependence and are sensitive to intermolecular couplings that do not generally influence β -type relaxation. In particular, when diffusive motion becomes a coordinated effort [2], for instance in crowded environments or in highly viscous liquids, the observed temperature dependence diverges from simple Arrhenius behavior. The partitioning into α and β processes reflects the heterogeneity in the ruggedness of the energy landscape, and since the fundamental dynamics is diffusive, it should be possible to sense the influence of both regimes using dynamical probes operating at any timescale.

The complexity of studying glassy dynamics lies in the spatially heterogeneous distribution of domains displaying unique dynamics and the cooperative motions involved in the reorganization of these domains. Ultrafast nonlinear spectroscopies and single-molecule spectroscopy methods have been used extensively to study glassy dynamics and have proven both indispensable and complementary, despite accessing different time scales [16-21]. There is no doubt that single-molecule techniques can expose heterogeneity directly, but ensemble experiments are also capable of capturing dynamic heterogeneity through non-exponential relaxation of dynamical correlation functions [8, 14]. At the single-molecule and ensemble level, fluorescence anisotropy measurements report orientational relaxation times where relaxation can occur on the microsecond timescale and longer [16, 17]. Optical Kerr effect experiments have also been able to reproduce many aspects of mode coupling theory of glassy dynamics by observing the ultrafast polarizability dynamics of fragile glass formers [22, 23].

The question remains as to whether it is possible to predict the long time dynamics of glasses based on picosecond measurements, which are substantially more compatible with detailed atomistic simulations. The coupling between short and long time dynamics in glass formers was suggested by Harrowell and coworkers, who used simulations of a two-dimensional glass forming alloy to demonstrate the connection between the Debye-Waller factor (β -like relaxation) and the long-time dynamic propensity (α -like relaxation) [24]. In this Letter, we show that it appears to be possible to sense α -type relaxation using ultrafast infrared spectroscopy on the picosecond timescale, indicating that the self-similarity of diffusive dynamics does indeed extend over tens of orders of magnitude in time.

Ultrafast 2D-IR spectroscopy has been extensively used to study equilibrium solvation dynamics on ultrafast timescales [25, 26]. 2D-IR provides a direct means of extracting the frequency-frequency correlation function $C(t)$ of a vibrational transition, where $C(t) = \langle \delta\omega(t) \delta\omega(0) \rangle$ and $\delta\omega(t)$ is the time-dependent fluctuation of the transition frequency ω from its average [27]. The decay of $C(t)$ reveals the solvation dynamics near the probe as well as how these dynamics map to the probed transition. The experimentally observed decay of $C(t)$ is referred to as “spectral diffusion”. Using a vibrational probe avoids structural and dynamical perturbations introduced through electronic excitations, and thus allows more direct access to equilibrium dynamics. In earlier studies we demonstrated the correlation between spectral diffusion time scales and solvent viscosity within the Stokes-Einstein regime [26]. Here we present the observation of non-exponential relaxation of $C(t)$ in a fragile glass former, as well as the non-Arrhenius temperature dependence of $C(t)$ that is consistent with observations made of other dynamical properties, such as orientational relaxation, near the glass transition.

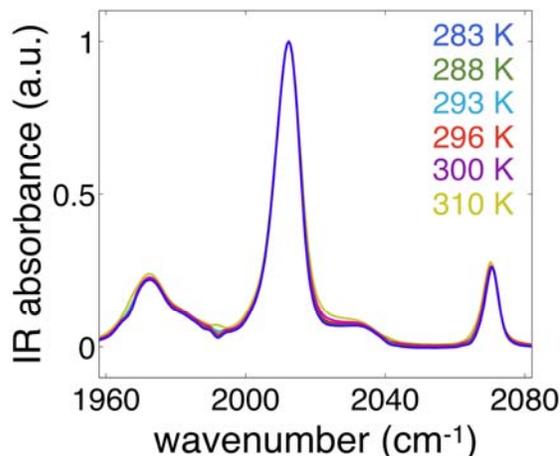


FIG 1. (color online) Linear FTIR spectra of DRDC in 1,2-hexanediol at six temperatures, ranging from 310 to 283 K. The glass transition temperature of 1,2-hexanediol is roughly 278 K. There is little to no change in the linear spectrum of DRDC as the glass transition is approached.

The spectral diffusion of a dilute vibrational probe dirhenium decacarbonyl ($\text{Re}_2(\text{CO})_{10}$, DRDC) in 1,2-hexanediol was observed as the system was cooled towards its glass transition (experimental details in Supplementary Material [28]). DRDC acts as a non-perturbative vibrational probe of the solvent dynamics of 1,2-hexanediol, a fragile glass-former with an accessible T_g at ~ 279 K. This system was studied at temperatures ranging from 320–283 K, a range that extends from well above the glass transition temperature to only a few degrees removed from the glass transition. The temperature-dependent viscosity of 1,2-hexanediol is known [29], so we report the spectral dynamics both in terms of temperature and viscosity. Because of the well known super-Arrhenius behavior of viscosity in fragile glasses, presenting the data as a function of viscosity obviates the need to correct for the non-Arrhenius viscosity behavior.

The temperature dependent Fourier transform IR (FTIR) spectra of DRDC in 1,2-hexanediol are shown in Figure 1. The negligible changes in the FTIR spectrum highlight the limitations of one-dimensional spectroscopy to discern changes in dynamics. That is, from the limited perspective provided by linear spectra, temperature appears to have no effect on the structure or dynamics of the vibrational probe. Previous transient grating and photon echo experiments on metal-carbonyl compounds dissolved in glasses have observed changes to the homogeneous and inhomogeneous dephasing of a metal carbonyl in glassy solvents. Namely, the absorption linewidths were observed to broaden while the homogeneous contribution was observed to decrease [19–21]. Near T_g both of these observables were seen to be hypersensitive to temperature. Here, the linear spectrum shows no observable change near T_g , suggesting that the total dephasing remains unchanged upon cooling. This difference could be due to the temperature ranges at which the experiments were conducted. In the experiments by Fayer and coworkers, the glass transition temperature was below 200 K, whereas 1,2-hexanediol forms glassy material near room temperature. For the present system, neither the homogeneous nor the inhomogeneous linewidths suggest any significant dynamical consequences associated with the glass transition.

The spectral relaxation observed by 2D-IR spectroscopy presents a remarkably different picture. Figure 2A shows $C(t)$ at 296 K for the main vibrational mode located at 2012 cm^{-1} . The plot also shows several functional forms used to fit the data, including single and double ex-

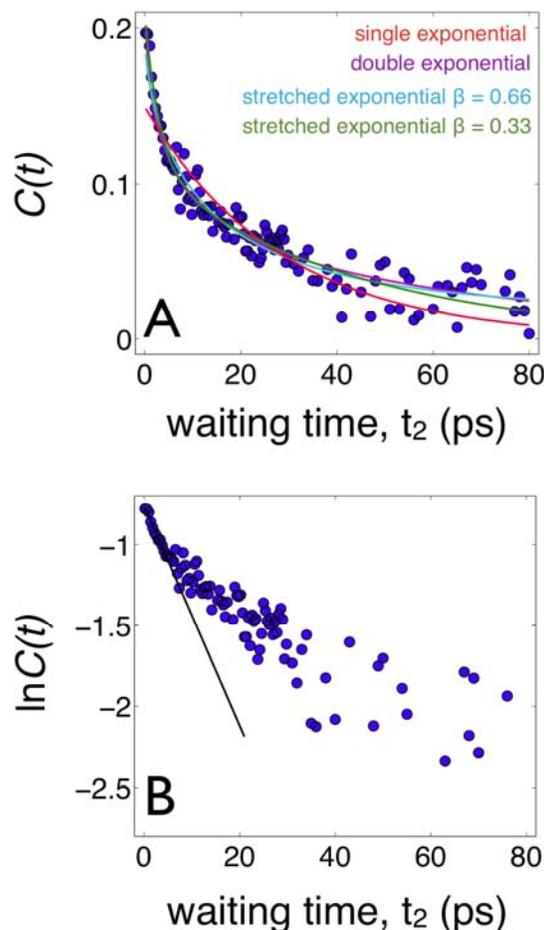


FIG 2. (color online) (A) Frequency-frequency correlation function of the main vibrational mode of DRDC in 1,2-hexanediol at 296 K. Several fits are shown, demonstrating that the data is best represented by a stretched exponential with a small β value of 0.33. (B) Log plot of the correlation function showing non-exponential relaxation. A linear fit is shown of the first 5 ps.

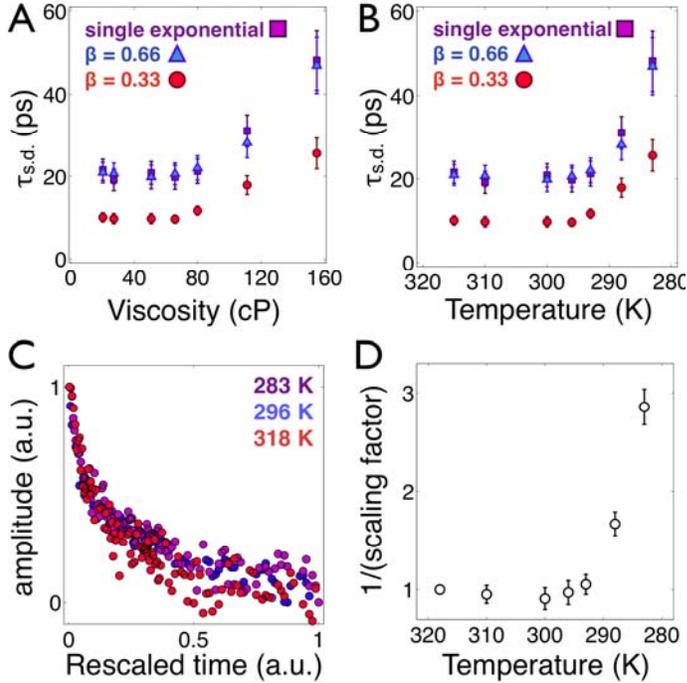


FIG 3. (color online) Spectral diffusion time constants plotted as a function of viscosity (A) and temperature (B) for three functional fitting forms, single exponential and stretched exponential. It is clear that the observed trend is independent of fitting procedures, despite the absolute time constants obtained from the fitting having a dependence on the fitting function. We also present a master curve approach where the correlation functions are collapsed onto a single curve (C). Three correlation functions are shown as an example and for figure clarity, but all decays can be collapsed onto a single curve. Plotting the inverse of the scaling factor versus temperature reproduces the trend (D).

ponentials, as well as two different stretched exponentials (where $C(t) = C(0)\exp[-(t/\tau_{sd})^\beta]$). For the 296 K data set, both double exponential and stretched exponential ($\beta \approx 0.33$) functions provided good fits to the data, but over the full data set for all temperatures only the $\beta = 0.33$ stretched exponential form fit the data consistently well. The non-exponential relaxation is verified by a plot of $\ln C(t)$ (Fig. 2B), clearly demonstrating that the observed relaxation is not a simple single exponential relaxation. It should also be noted that despite differences in the extracted absolute relaxation times using different functions, the observed temperature dependence described below was retained regardless of the fitting procedures (Fig. 3A-B.). For example, single exponential fits and stretched exponential fits with $\beta \approx 0.66$ show the same trend, but with spectral diffusion time constants that are roughly twice as large. By treating the glass transition as a random first order phase transition, the β value can be related to changes in the heat capacity of the system [30].

The temperature-dependent stretched-exponential spectral diffusion time constants display a marked slowdown near the glass transition, despite showing almost no changes at temperatures far from the transition. To better align this work with our previous studies of a nearly identical vibrational probe in a series of linear alcohols, we consider the spectral diffusion as a function of viscosity [26]. Away from T_g , the spectral diffusion shows no viscosity dependence, with a stretched-exponential decay time constant of ~ 9 -10 ps over a viscosity range of 20-80 cP ($\Delta\eta = 60$ cp). It is not unexpected for a dynamic quantity to become uncoupled from viscosity at such high values, an effect which has been observed previously in orientational relaxation [31]. Approaching the glass transition, however, the spectral diffusion recovers its viscosity dependence and nearly triples over a viscosity range of 80-140 cP ($\Delta\eta = 60$ cp).

To avoid any bias introduced by adopting specific fitting functions, we also employ an analysis that operates directly on the measured data [22, 23]. The correlation functions can be collapsed onto a master curve by rescaling the amplitude and time axis of the data (Fig. 3C), that is $C(t) \rightarrow \alpha C(t \times \tau_{scale})$. The coincidence of the FFCFs suggests that the decays arise from a similar underlying mechanism over the temperature range studied. The dynamical differences in the cor-

relation functions are contained in the scaling factor (τ_{scale}) needed to collapse the time axis onto the master curve. Figure 3D shows a plot of τ_{scale}^{-1} versus temperature, where, again, the pronounced retardation of dynamics is observed. We conclude that the observed slowdown in the spectral dynamics approaching the glass transition temperature is independent of specific fitting functional forms.

To distinguish the observed dynamical changes as being characterized as either α - or β -relaxation, we represent the data in an Arrhenius plot (Fig. 4). Within an Arrhenius law framework, the relaxation times would follow a simple relationship with temperature:

$$1/\tau_{sd} = A \exp(-E_a/RT) \quad (1)$$

where τ_{sd} is the spectral diffusion time constant. It is clear that the spectral diffusion of this system does not follow simple Arrhenius behavior. The phenomenon of non-Arrhenius behavior of glasses is well established and has been observed for other dynamical or bulk properties, such as orientational relaxation [6], self diffusion and viscosity [1,3]. Typically, a Vogel-Fulcher (VF) type equation is applied to temperature dependent glassy dynamics [1-3].

$$1/\tau_{sd} = B \exp(-E_a/R(T-T_0)) \quad (2)$$

Here, T_0 is a singularity temperature where dynamical and thermodynamical properties diverge. Figure 4 shows a VF fit (solid line), giving a $1/RT_0$ value of $1.86 \text{ (kcal/mol)}^{-1}$, or 277 K. The robustness of this fit, even for the small temperature range, suggests that the deviation from Arrhenius behavior is significant. Typically, these fits are best used when considering a substantially larger range of temperatures or viscosities; however, here we find that a reasonable fit is obtained even for the limited range of temperatures used. Though we lack a general microscopic theory linking transport properties and ultrafast spectral dynamics, studies have shown that spectral diffusion is primarily sensitive to short range diffusion and density fluctuations within the first and second solvation shells [25, 26]. In particular, we have shown that spectral diffusion depends on the bulk viscosity, suggesting that the spectral diffusion is sensitive to more than simply the rapid ballistic motion within the first solvation shell [26]. The decay of $C(t)$ is thus driven by small scale, stochastic molecular motion. Here, we report the first observation of super-Arrhenius behavior of the ultrafast dynamics observed in a fragile glass former near T_g . The observation of ultrafast α -like relaxation using vibrational chromophores can be rationalized by comparing the typical domain size involved in α relaxation to the typical solvation size of the vibrational chromophore. Domain sizes near T_g involved in relaxation are of the order of 4-8 molecules [32], which is similar in size to what would be expected for the number of 1,2-hexanediol molecules in the solvation shell of a molecule of DRDC. Larger organic dyes com-

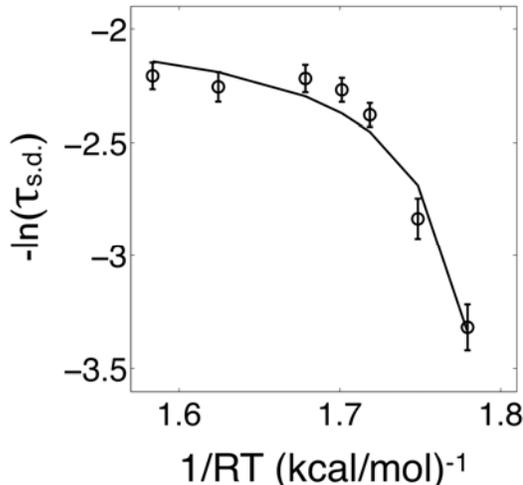


FIG 4. Arrhenius plot of the spectral diffusion time constants fit with a stretched exponential ($\beta = 0.33$), showing strong deviations from Arrhenius behavior near the glass transition. This behavior is consistent with α -like relaxation, which is typically considered a process that occurs on significantly longer timescales. Here, signatures of this relaxation process are observed on the ultrafast timescale. The solid line is a VF law fit (Eq. 2) to the data, showing that the non-Arrhenius behavior is well described by an expression typically applied to α -like relaxation.

monly used to study glassy dynamics would have solvation shells that average over several domains and could mask signatures of cooperative rearrangements on the sensed dynamics.

The decoupling between spectral diffusion and viscosity away from the glass transition temperature deserves additional note. There have been three distinct regimes of spectral diffusion observed that depend strongly on the bulk viscosity. Previously, we have observed a monotonic dependence of spectral diffusion on bulk viscosity using a $\text{Mn}_2(\text{CO})_{10}$ probe in linear alcohols with viscosities ranging from 1-4 cP, with the onset of decoupling at the highest viscosity of that range [26]. This breakdown of a hydrodynamic (i.e. Stokes-Einstein) description has also been observed in rotational diffusion at elevated viscosities, for example [31]. The low viscosity (20-80 cP) range of the present study is within the decoupled regime, but there is clearly a second crossover regime near the glass transition where the observed spectral diffusion becomes hypersensitive to the bulk viscosity. The onset of decoupling at high viscosities (but still far removed from T_g) likely is the result of local β -relaxation decoupling from bulk-solvent fluctuations, an effect that should indeed persist at all temperatures even absent a glass transition. The second crossover regime observed here near T_g , however, signals the emergence of significant cooperative motion in the liquid.

The universal observation of non-Arrhenius temperature-dependent relaxation on a wide range of timescales warrants further discussion. Experiments measuring translational and orientational diffusion have long been known to capture α -relaxation. Both of these diffusive processes occur with large motion along an effective coordinate of the free energy landscape. The timescale of this motion, however, is relative to the experiment being performed, and due to the fractal-like topology of the energetic landscape, transitions among free energy basins can only be characterized by relative timescales and relative motion along the effective coordinate. For instance, measurements probing glassy dynamics that are sensitive to diffusive motion, such as anisotropy (μs -s) [16, 17], solvation dynamics (ps-s) [33] or spectral diffusion (fs-ps), will display the same relaxation phenomena but will manifest these dynamics on timescales that correspond to the measurement details. The self-similarity of the energy landscape allows processes typically associated with slower dynamics to be observed on the ultrafast timescale corresponding to their fundamental molecular origins. This connection between hierarchies is often viewed from the perspective of dynamical slaving, and we present a brief discussion of our results within this picture in the supplementary materials [28].

In this Letter we have described the direct observation of dynamical heterogeneity on the ultrafast timescale, as well as the observation of picosecond α -like relaxation in a fragile glass forming liquid. Our results show that many of the characteristic phenomena of glassy dynamics—super-Arrhenius and nonexponential relaxation—emerge on the fastest of timescales. Through the use of 2D-IR spectroscopy we are able to demonstrate that the FFCF is sensitive to collective molecular motion, a characteristic of fragile glasses near T_g , even when these dynamics are invisible in the linear absorption lineshape. The use of relatively weakly interacting probe molecules that are small compared to the general dimensions of a dynamical domain allow for collective rearrangements to be observed without averaging over the dynamical heterogeneity. Furthermore, the observation of α relaxation on timescales that cover several orders of magnitude, including the picosecond timescales seen here, is a striking manifestation of the self-similar, or hierarchical, nature of the free energy landscape. Exploring the ultrafast dynamics of glass formers can aid in eventually understanding the dynamics occurring in other complex or crowded environments found in proteins or inside cells.

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