28 September 2001

ELSEVIER

Chemical Physics Letters 346 (2001) 61–68

CHEMICAL PHYSICS LETTERS

www.elsevier.com/locate/cplett

A supercooled glycerol–water mixture: evidence for the large-scale heterogeneity?

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Received 16 January 2001; in final form 14 August 2001

Abstract

The results of an experiment on the time-resolved spectral dynamics of the eosin phosphorescence in a low-temperature glycerol–water mixture are explained supposing a cluster structure of the supercooled liquid and the glass. An estimation of the size and the restructurization dynamics time of the clusters at about 237 K are performed. A modification concerning the procedure for the calculation of the relaxation function of a time-resolved spectral shift obtained in a supercooled liquid, possessing a cluster structure, is suggested. A conclusion on the existence of a new amorphous phase is inferred from the change in the spectral dynamics of the eosin phosphorescence observed in the low-temperature mixture.

1. Introduction

Structure and dynamics of supercooled liquids and glasses is a subject of considerable theoretical and experimental efforts in studying amorphous phases. Non-exponentiality of relaxation processes in supercooled liquids and glasses arises, as recently recognized, from the heterogeneity of these systems [1,2]. But the question concerning the details of this heterogeneity remains still open. One point of view is that supercooled liquids and glasses consist of structurally correlated regions denoted by clusters [3–5], with the cluster size ranging from several to hundreds of nanometers [6,7]. Clusters are supposed to possess some local structure. Decreasing temperature induces a growth of the cluster size and the degree of molecular ordering within a cluster. This process is limited and is not able to bring the system to its lowest energy state. As a result, a supercooled liquid is a metastable system and a glass is a nonstable one.

This Letter deals with the effects observed in a study of the spectral dynamics of the eosin phosphorescence in a low-temperature glycerol–water mixture [8] that may provide some additional support for the cluster structure of supercooled liquids and glasses.

2. Experimental

Eosin Y (Serva) and glycerol (Sigma) were used as received. The decay of the eosin phosphorescence was studied in the 94% (w/w) glycerol–water mixture. The concentration of eosin in samples

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0009-2614/01/$ - see front matter
PII: S0009-2614(01)00951-4

was $1–2 \times 10^{-5}$ M. The measurements were performed in thin-walled silica ampoules 5 mm in diameter. The temperature of samples was controlled with an accuracy of 1 K by blowing a cell chamber with nitrogen vapors. The temperature was varied in the range of 140–260 K by means of a VRT-2 temperature regulator, attached to the liquid nitrogen supply. The temperature was measured with a thermocouple embedded in the sample. The sample was first frozen at a cooling rate of 6–8 K/min 30–40 K below the glass transition. Then the temperature was gradually increased at a rate 3–5 K/min. The sample was kept for 2–3 min at a fixed temperature to obtain a constant temperature and the phosphorescence decay was measured.

The phosphorescence decay was detected with a pulsed laser setup. The emission was excited by a pulsed Nd:YAG laser ($\lambda = 532$ nm, $\tau_{1/2} \leqslant 10$ ns, $E \cong 70$ mJ). The phosphorescence emitted in a direction perpendicular to the excitation beam was focused onto the entrance slit of a LOMO MDR-2 monochromator outfitted with a FEU-84 photomultiplier and then was collected with a Datalab-912 transient recorder. The setup time resolution was 15 μs, however, phosphorescence signals were considered beginning with the 50th microsecond for the reason of the elimination of the multiplier saturation because the strong emission at the shorter wavelengths dominated in the spectra at initial times. This emission could be due to the delayed fluorescence of eosin [9], the eosin fluorescence and the excitation light partially passed through the monochromator. The spectral reconstruction method [10] was used to obtain the time-resolved Stokes shift of the eosin phosphorescence spectrum [11]. Typically, 12–15 decays at 5–7 nm intervals were obtained at each temperature. The shape of the instantaneous phosphorescence spectrum was fitted to a polynomial or the log-normal distribution function [12].

3. Results and discussion

The idea underlying the method used is that the spectral dynamics of the emission of a probe dissolved in a polar solvent is controlled by the ratio between relaxation times of the medium and the excited solute lifetime [13]. The normalized relaxation function of the time-resolved spectral shift, $C(t)$, is usually used to scale solvent relaxation [10]:

$$C(t) = \frac{\nu(t) - \nu(\infty)}{\nu(0) - \nu(\infty)}, \tag{1}$$

where $\nu(0)$, $\nu(t)$ and $\nu(\infty)$ are the positions of some point of an emission spectrum at $t = 0$, t and $t \to \infty$, respectively. Typically, $\nu(0)$ and $\nu(\infty)$ in Eq. (1) are the values of the peak frequency of a stationary emission spectrum in frozen and high-temperature media, respectively.

The temperature-dependent changes in the rates of relaxation processes in the medium were reflected in the behavior of the eosin phosphorescence both for the decay at a particular wavelength and for the shift of the entire emission band. The low-temperature glass, 140–180 K, was characterized by a small short-wavelength shift of the spectrum, Fig. 1. In this temperature range the decay at any particular wavelength was exponential, Fig. 2a , with the phosphorescence lifetime decreasing towards the long-wavelength edge of the spectrum. This spectral dynamics resulted from the inhomogeneous broadening of the spectrum, static on the experiment time scale, and the higher non-radiative deactivation rate of the excited solute states at the long-wavelength side of the phosphorescence band [8,14,15].

As temperature increased above the glass transition temperature, $T_g = 185–187$ K, the rate of relaxation of solvent molecules became comparable to that of the radiative deactivation of triplet eosin. This circumstance was monitored by the time-dependent long-wavelength Stokes shift of the phosphorescence spectrum, Fig. 1a. Fig. 2b demonstrates that the behavior of the decays in this temperature interval depended on a particular wavelength: upon movement to the longer wavelengths, the gradual transition from the fast initial decrease in the phosphorescence intensity at the shortest wavelengths to its enhancement at the initial interval of the longest wavelength decays was exhibited. The spectral shift and the relevant behavior of the decay curves were caused by two parallel processes: (i) the emission from the excited

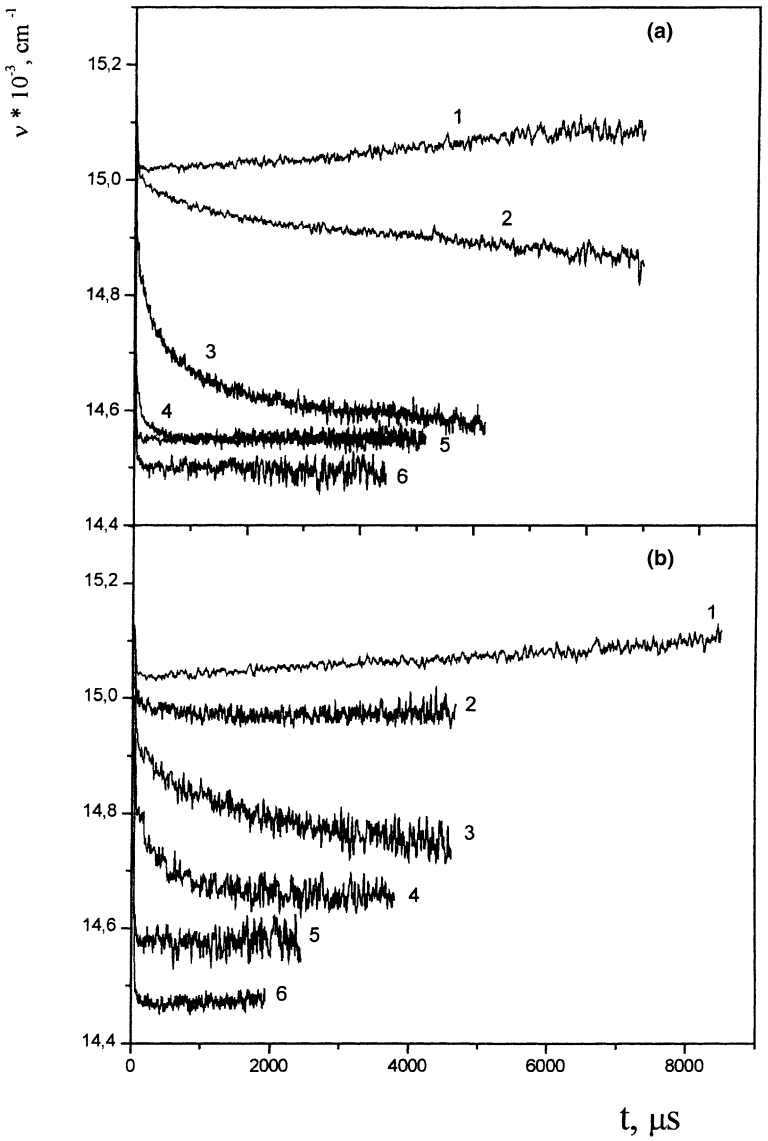

Fig. 1. Temporal evolution of the peak frequency position of the eosin phosphorescence spectrum in the 94% glycerol–water mixture for different regimes of freezing out. (a) 1 – 145, 173 K; 2 – 191 K; 3 – 203 K; 4 – 212 K; 5 – 219, 237, and 241 K; 6 – 224 K. (b) 1 – 149, 191, and 212 K; 2 – 219 K; 3 – 224 K; 4 – 233 K; 5 – 237, 241 K; 6 – 248 K.

solute state; (ii) lowering the electronic energy level of the excited solute state because of solvation dynamics [8,16]. Analysis of the integrated phosphorescence intensity showed some non-exponentiality in its decay at initial times at temperatures near T_g, Fig. 3. According to Agmon [17], this means that the inhomogeneous broadening of the spectrum could contribute to the spectral dynamics on the time scale of 100–200 μs depending on temperature. Subsequent intensity decays were exponential and were due to solvent relaxation.

Further increasing the temperature of the supercooled liquid resulted in accelerating relaxation of solvent molecules. At temperatures above 219 K

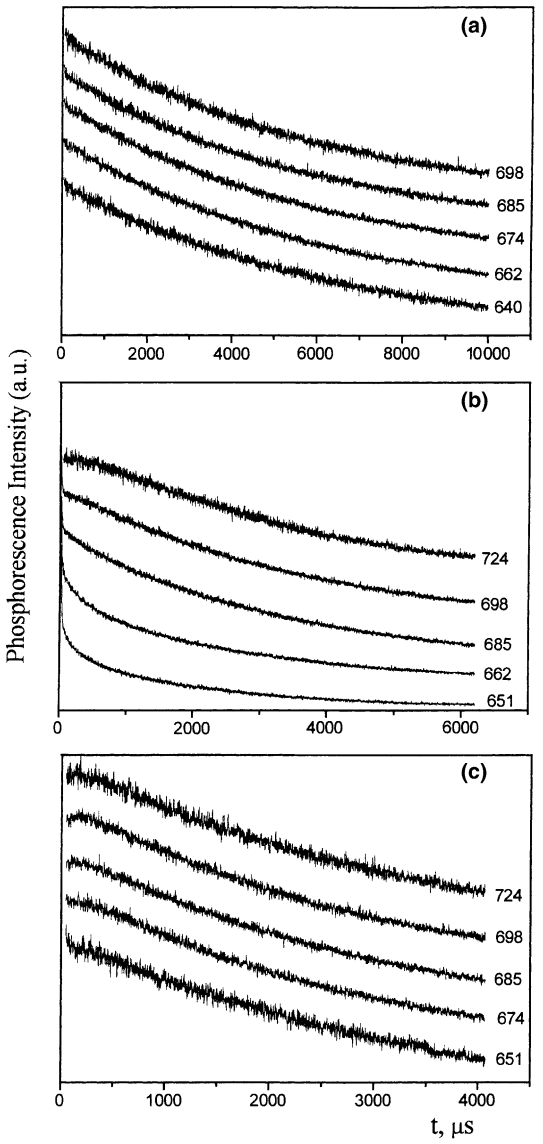

Fig. 2. Normalized eosin phosphorescence decays in the 94% glycerol–water mixture measured at different wavelengths for three temperatures: (a) 173 K; (b) 203 K; (c) 237 K. Numbers near the decays denote appropriate wavelengths.

solvation was complete for times lesser than the setup time resolution and we observed only the relaxed spectra. The decays at these temperatures were exponential and had approximately equal decay times at different wavelengths at a fixed temperature. This suggests [18] that thermal fluctuations of solvent molecules become 3–4 order of

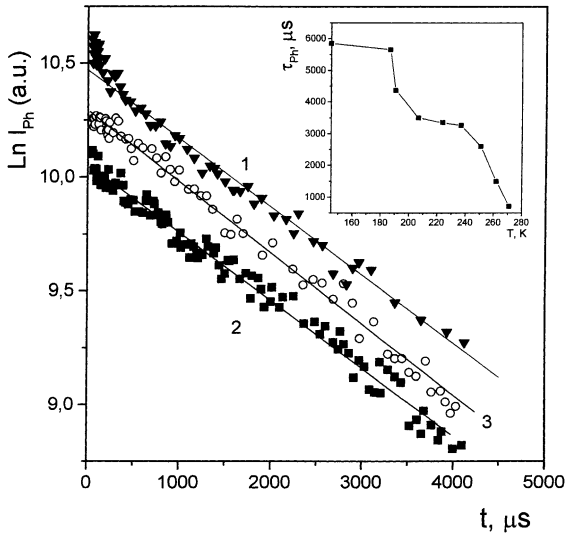

Fig. 3. Logarithm of the eosin integrated phosphorescence intensity in the 94% glycerol-water mixture at different temperatures: 1 – 203 K; 2 – 224 K; 3 – 237 K. (Inset) Temperature dependence of the eosin phosphorescence lifetime in the 94% glycerol–water mixture.

magnitude faster compared to the phosphorescence lifetime ($\sim 10^3$ μs) to create the thermal equilibrium distribution of solvent configurations around excited solutes prior to the emission.

An interesting feature of the high-temperature range was the phosphorescence enhancement at the initial parts of the decays at about 237 K, Fig. 2c. The enhancement took place at any particular wavelength, with the entire phosphorescence spectrum being relaxed. The decays were well fitted to a sum of two exponentials:

$$f(t) = A_1 \exp\left(-\frac{t}{\tau_1}\right) - A_2 \exp\left(-\frac{t}{\tau_2}\right). \qquad (2)$$

The longer time constant, τ_1, in this fit corresponded to the eosin phosphorescence lifetime (τ_{Ph}) and was approximately the same over the emission band. The shorter time constant, τ_2, characterized the enhancement process. Fig. 4 demonstrates the results of the fitting. The data on τ_2 at different wavelengths at 237 K are summarized in Table 1. It should be noted that the results of the fitting for the decays at the shortest and longest wavelengths are omitted because the magnitude of the phosphorescence signal in these

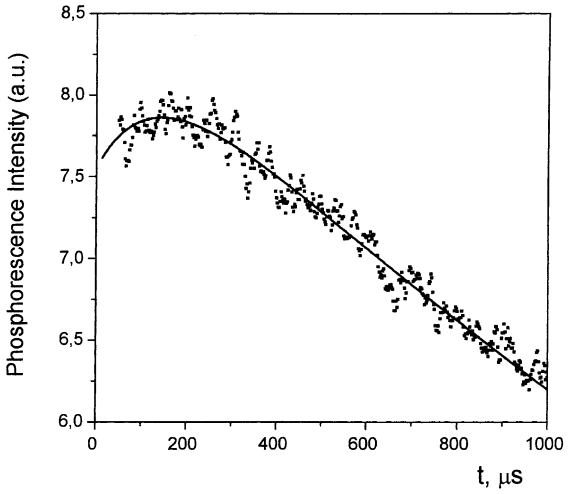

Fig. 4. The intensity enhancement at initial part of a phosphorescence decay in the 94% glycerol–water mixture at 237 K (dotted line) and the result of fitting the decay to a sum of two exponentials, Eq. (2), (solid line).

Table 1
Phosphorescence intensity enhancement times, τ_2, at different wavelengths in the 94% glycerol–water mixture at 237 K

λ (nm)	τ_2 (μs)
662	168
668	159
674	176
679	161
685	176
692	166
698	151
704	169
710	153
717	155

regions of the spectrum was not sufficient to reliably fit the curves. As seen from Table 1, there is an approximate equality of the enhancement times for the decays at different wavelengths. The average time evaluated from Table 1 is 165 ± 15 μs. As mentioned above, relaxation of solvent molecules occurs on the time scale of microseconds or less at temperatures above 219 K. This is 2–3 orders of magnitude faster than the enhancement time and, therefore, solvation dynamics cannot be a reason for the much slower enhancement process.

We also observed deviations from common patterns of the temperature dependences of the integrated phosphorescence intensity and the phosphorescence lifetime. As the glass transition occurred, when temperature getting higher, the intensity started to decrease, Fig. 3. The minimum of the intensity was observed at about 224 K. Further increasing the temperature was accompanied by rising in the intensity. The reduction in the intensity at 191–224 K is most probably caused by solvent relaxation [15,19], since the appearance of the Stokes shift coincides with the sharp decreasing in τ_{Ph}, Fig. 3. However, the subsequent enhancement of the intensity at higher temperatures cannot be explained by the quenching of the phosphorescence due to solvation dynamics.

The temperature dependence of τ_{Ph} was not gradual in the low-temperature glycerol–water mixture, Fig. 3. At least two processes are mainly responsible for the magnitude of τ_{Ph}: (i) quenching by molecular oxygen; (ii) the non-radiative deactivation of excited solutes due to solvent orientation relaxation [15,19]. These processes occur on the different length scales. The former is controlled by translational diffusion of oxygen over substantial distances, whereas the latter occurs in the nearest solvent shells. The difference in length scales of two quenching processes should be reflected in the different temperature dependences of their efficiencies. Decreasing the temperature should first reduce the efficiency of the quenching by oxygen and then that of the quenching by solvent reorientation dynamics. The observed temperature dependence of τ_{Ph} cannot be explained on the basis of these two processes only. The onset of the abrupt decreasing in τ_{Ph} near 191 K coincides with the appearance of the long-wavelength Stokes shift and is most likely due to orientation relaxation of solvent. Another onset of the fast decreasing in τ_{Ph} occurs at about 240 K and arises most probably from the quenching by oxygen. In the range of 212–240 K there is an approximate permanency of τ_{Ph}. It is unlikely that oxygen diffusion, controlled by the solution viscosity, slowed down drastically at temperatures below 240 K, which is much higher than T_g.

Since spectral relaxation in the studied system was strongly non-exponential, we used the Cole–

Davidson (CD) distribution function [20] to describe the temporal evolution of $C(t)$. However, the function $C(t)$ calculated with $v(0)$ and $v(\infty)$ taken from a stationary phosphorescence spectrum in frozen and high-temperature media, respectively, did not provide us with reasonable values of the CD parameters. This resulted from the fact that the relaxation function did not tend to approach $C(\infty) = 0$ in the long-time limit at temperatures close to T_g. Analogous picture was observed in other low-temperature systems where $C(t)$ calculated on the basis of high-temperature $v(\infty)$ values did not approach the $C(t) = 0$ limit. In the experiment on solvation dynamics of the supercooled MTHF confined to mesopores of sol–gel glasses [6] this problem was resolved by an introduction to Eq. (1) a constant term that changed depending on a pore diameter and a temperature. At a fixed temperature, the less the pore diameter was, the larger the constant term became. The appearance of the constant term in Eq. (1) was explained by the geometric confinement effect, caused by pore walls, blocking the relaxation development.

We used the following procedure for the calculation of $C(t)$. The temperature-dependent value of $v(\infty)$ was first determined by fitting a curve of a time-dependent peak frequency position of the spectrum to a sum of three exponentials. Then the obtained $v(\infty, T)$ was substituted to Eq. (1). It should be noted that our attempts to determine the probable peak frequency position of the relaxed spectrum were complicated by a strong non-exponential behavior of the Stokes shift and were characterized by some range of $v(\infty, T)$ values. Nevertheless, using $v(\infty, T)$ improved significantly the fitting of $C(t)$, Fig. 5, and provided the reasonable CD parameters, Table 2.

The observed phenomena may consistently be explained on the basis of a cluster structure of the low-temperature glycerol–water mixture. We suppose that the mixture consists of regions of the large heterogeneity with linear size about 10^3 nm at temperatures around T_g. Heating the system leads to decreasing the cluster size and intensification of solvation processes within a cluster. When the cluster size becomes comparable to the phosphorescence wavelengths, i.e., on the scale of

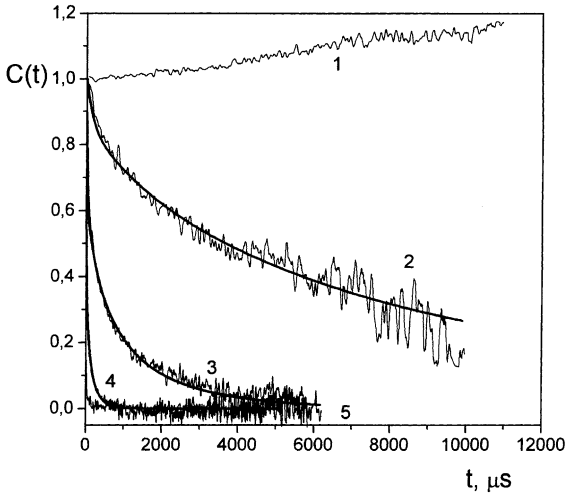

Fig. 5. Experimental relaxation function of the time-dependent Stokes shift of the eosin phosphorescence in the 94% glycerol–water mixture and the results of its fitting to the CD distribution function (solid line): 1 – 145, 173 K; 2 – 191 K; 3 – 203 K; 4 – 212 K; 5 – 219–250 K.

Table 2
Temperature dependence of parameters of the CD distribution function for orientation relaxation dynamics of solvent molecules in the 94% glycerol–water mixture

Parameters of the CD distribution function	Temperature (K)		
	191	203	212
β_{CD}	0.5	0.28	0.2
τ_{CD} (μs)	1.6×10^4	2.5×10^3	300
$\langle\tau_S\rangle$ (μs)[a]	8.0×10^3	653	60

[a] Average time of solvation dynamics: $\langle\tau_S\rangle = \int C(t)dt$.

10^2 nm, in addition to the quenching of the phosphorescence due to solvation dynamics, the reduction in the intensity due to Rayleigh scattering of the phosphorescence develops. The higher the temperature becomes, the lesser the cluster size is and the lesser Rayleigh scattering is. As a result, beginning with some temperature, most likely 224 K, we observe an increase in the integrated phosphorescence intensity with temperature.

It is probably that at temperatures about 237 K interactions responsible for the cluster formation are weak enough that excitation of eosin molecules, situated within a cluster, to the triplet state and subsequent solvation dynamics of surrounding solvent molecules could induce the cluster de-

composition process. The decomposition should be accompanied by the reduction in the Rayleigh scattering of the phosphorescence and its enhancement at initial parts of the decays should be observed, Fig. 2c. On the basis τ_2 values we estimate the times of cluster restructurization dynamics as being equal 165 ± 15 μs at 237 K.

The existence of clusters could also be the reason for the flat temperature dependence of τ_{Ph} at 212–240 K, Fig. 3. At these temperatures solvation dynamics is complete and no longer contributes to decreasing the phosphorescence lifetime. On the other hand, the existence of large structured clusters could prevent from free diffusion of oxygen within a cluster. Therefore, the observed weak temperature dependence of the phosphorescence lifetime at 212–240 K may originate from the absence of free oxygen diffusion due to molecular ordering within a cluster.

We suppose that the long-wavelength Stokes shift observed is due to orientation relaxation of solvent molecules closest to an excited solute and does not involve the whole cluster. This picture is consistent with an intra-cluster rearrangement model for the α-relaxation in supercooled liquids proposed by Oguni [21] in which distinction is made between the whole cluster and the rearranging unit of molecules within the cluster. The dynamics of the latter is responsible for the α-relaxation process in supercooled liquids. Our conclusion is based on the fact that the intensity enhancement induced by the cluster decomposition at 237 K occurs at the times of about 150–180 μs, whereas solvation dynamics takes place on the time scale of microseconds or less. This model explains reasonably the gradual blue shift of the relaxed spectrum when temperature is lowered. Decreasing the temperature of the solution is accompanied by an increasing in the degree of molecular ordering within the cluster and, as a consequence, should reduce a number of solvent molecules responding to the solute charge redistribution under excitation. The fewer number of rearranging solvent molecules means that the electronic level of the excited solute state will be less lowered because of solvation. Hence, the peak frequency of the relaxed spectrum should shift to the shorter wavelengths. On the other hand, decreasing the temperature will lead to an increasing in orientation relaxation times of solvent molecules. Therefore, we should observe shifting the relaxed emission spectrum towards the shorter wavelengths and, simultaneously, slowing down the spectral relaxation. This model is in a good agreement with conclusions made by Streck et al. [6]. Physically the pore diameter effect corresponds, in our case, to an increasing in the degree of molecular ordering among the solvent molecules within a cluster as temperature is lowered.

There is a possibility that the spectral dynamics discussed above may originate from the existence of liquid-like and glass-like regions in the supercooled liquid. Such a situation could also result in an intermediate peak frequency position of the relaxed spectrum. However, in this case we should observe broadening of the phosphorescence band with time. Analysis of the widths of the emission spectra showed their independence on the time.

We also observed the change in the spectral dynamics of the phosphorescence when the sample was kept at the temperature 191 K, just above T_g, no less than for 30 min, Fig. 1b. In this case increasing the temperature of the sample did not result in the long-wavelength spectral shift at 191–212 K, where it was detected under conditions described in the experimental section. Instead of the long-wavelength Stokes shift, the spectrum exhibited a small blue shift coinciding with that in the glassy matrix. The long-wavelength Stokes shift appeared when the temperature exceeded 212 K. It is probably that keeping the sample at 191 K for 30 min produced the transition from the supercooled liquid to another amorphous phase. As it is possible to conclude from the spectral dynamics, Fig. 1b, structural and dynamic properties of this phase should resemble those of the glass. Probably this phase is more stable and rigid than the supercooled liquid. Similar effect was observed by Cohen et al. [7] in supercooled triphenyl phosphite where keeping a sample at a fixed temperature from some temperature range resulted in appearing a new amorphous phase denoted as a glacial phase. This phase was more stable and denser than the supercooled liquid. The glacial phase in triphenyl phosphite is considered as a

defect-ordered crystal [7] or a plastic crystal [22]. This may mean that formation of the glacial phase is accompanied by the development of molecular ordering within clusters constituting the supercooled liquid. Such a picture is consistent with the above assumption about the cluster structure of the low-temperature glycerol–water mixture.

Acknowledgements

This work was supported by the Russian Foundation for Basic Research (Grants No. 00-04-48376 and 98-03-33187a).

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