

## Structural relaxations in amorphous water studied by hole-burning spectroscopy

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### Abstract

The annealing behavior of dye-doped amorphous water below its glass transition temperature was investigated by means of spectral hole-burning and IR spectroscopy. The dye molecules act, at low concentration, as optical probes of the water matrix. Measurements of the time-resolved spectral diffusion of spectral holes confirm that the narrowing of the quasi-homogeneous linewidth observed upon annealing is due to a reduction of the number density of two-level systems. Further information is gained from temperature cycling experiments. The results strongly indicate a transformation from a fragile to a strong glass by the formation of an H-bond network.

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### 1. Introduction

Water plays a fundamental role in nature and, thus, numerous studies of this unique material have been performed. Besides exhibiting many crystalline phases solid water was also found to exist in an amorphous state which is stable at low temperatures up to a weakly pronounced glass transition at about 135 K [1]. Due to the narrow temperature range between the glass transition temperature and the onset of crystallization, special attention was attributed to various temperature dependencies below the glass transition. For example, in this regime pronounced structural relaxations were observed by various techniques. Above all, the latter showed that, depending on the preparation techniques, amorphous water exists in different modifications. Two of them, namely hyperquenched glassy water (HW), prepared by fast quenching of  $\mu\text{m}$  size water droplets

[2–4], and the vapor-deposited solid (ASW) [5] are comparable with respect to their structure and calorimetric properties after the latter (ASW) is annealed in vacuo below the glass transition temperature [6].

The narrow spectral holes found in dye-doped amorphous water [4] stimulated rising interest to apply the powerful tool of spectral hole-burning [7] to this interesting material and a number of publications [8–11] came out which used this technique to characterize amorphous water.

In our experiments we investigated structural relaxations induced by sub- $T_g$  annealing of dye-doped matrices of vapor-condensed amorphous water (ASW) with the techniques of spectral hole-burning and IR spectroscopy. Detailed experiments on the time-resolved spectral diffusion enable us to confirm that the narrowing of the quasi-homogeneous linewidth which is observed upon annealing is in fact due to a reduction of the two-level systems (TLS)

number density as previously proposed by Small and coworkers [8,9] on the basis of measurements of the temperature dependence of spectral holes. We then focus on the properties of the potential hypersurface of ASW and its changes upon annealing below  $T_g$ . To this aim we report temperature cycling data of hole-burning spectra and connect them to Böhmer and Angell's classification of glass formers according to the shape of their potential hypersurfaces [12]. Upon annealing a transition from a fragile to a strong glass behavior is being proposed which can be understood by assuming the formation of a hydrogen-bonded network.

## 2. Experimental

In order to prepare dye-doped matrices of amorphous water we used a setup which has been described in Ref. [10]. Water (Aldrich, degassed in two freeze–thaw cycles) was evaporated and its gas flow controlled with a computer-operated nozzle leading into a furnace where it was doped with the dye-free base phthalocyanine ( $H_2Pc$ , Aldrich). The dye was previously purified by repeated sublimation under vacuum conditions. The gas mixture was condensed onto a cold sapphire substrate mounted on the cold finger of a continuous-flow cryostat (substrate temperature  $\approx 5$  K, see Ref. [13] for details). During a deposition time of typically one hour the nozzle was opened for about 100 pulses. Their length was less than 1 ms and was adjusted in a way that the temperature measured with a sensor (Lake Shore DT470) mounted on the cold finger did not exceed 6 K. By this procedure a film of approximately  $50 \mu\text{m}$  thickness was deposited as inferred from its mass which corresponds to a dye concentration of approximately  $10^{-4}$  mol/l. Annealing cycles were performed using a temperature controller (CryoVac TIC304-M) and were monitored with the temperature sensor. A single-mode dye laser (Coherent 599-21, linewidth 2 MHz) was used to perform the hole-burning experiments at the center of the  $Q_x$ -absorption band of  $H_2Pc$  ( $14436 \text{ cm}^{-1}$ ). The spectral holes were burned using intensities of some nW and irradiation times between 2 and 120 s corresponding to relative hole depths between 2.5 and 25%. They were detected in transmission with an intensity re-

duced by a factor of  $10^2$ – $10^3$ . All spectral holes shown in this contribution were burnt and scanned at a temperature of  $T = 4.2$  K. Infrared spectra of the films were recorded to verify the amorphous character of the films. For this purpose  $\text{CaF}_2$  windows were used and the cryostat was placed inside a Fourier transform IR spectrometer (Bruker IFS 55). This opened access to the spectral region between  $1600$  and  $8000 \text{ cm}^{-1}$ .

## 3. Results

The most prominent absorption band accessible with our IR setup is the OH stretching band which is presented in Fig. 1. The matrix was doped with  $H_2Pc$  in the way described above but the concentration of the dye molecules was too low to cause its 'fingerprints' in the IR spectra. The high absorption of the OH stretching band necessitated to reduce the thickness of the sample to prevent a saturation of the spectrometer. Since a single pulse would not give a representative sample we used 13 pulses in this experiment to receive a matrix which is already slightly opaque. This shows up in the IR spectra as a pronounced asymmetry of the bands caused by the variation of the refractive index over the absorption band and is known as the Christiansen effect. In accordance with earlier publications [14,8] an increase in the band intensity and a shift of the band

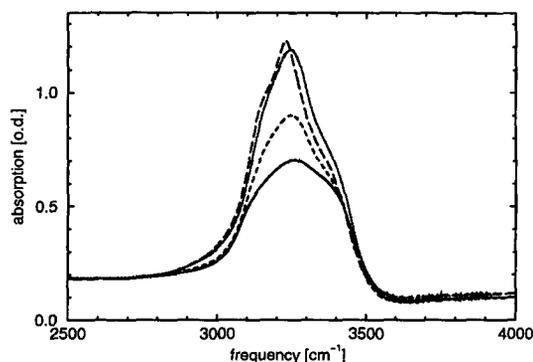


Fig. 1. Annealing behavior of the IR absorption spectra of the OH stretching band of ASW. The spectra were measured at an annealing temperature of 5 K (as deposited) (solid line), 71 K (dashed line) and 132 K (dotted line). The long dashed line corresponds to polycrystalline ice and was observed at 162 K.

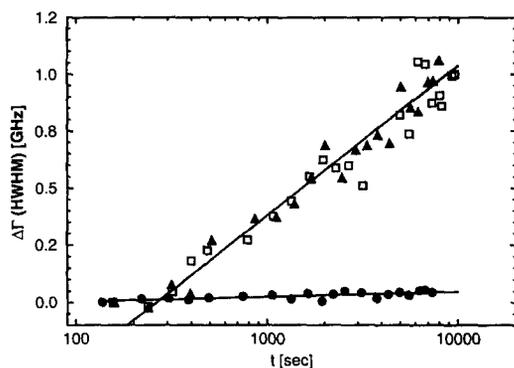


Fig. 2. Broadening of spectral holes burnt into a fresh matrix (4 (▲) and 13 (□) h after matrix preparation) and for the same matrix annealed for 15 min at 130 K (●).

maximum towards lower frequencies is observed upon annealing before the transition to polycrystalline ice narrows the spectrum and alters its shape. This development is protocolled in Fig. 1 for a matrix annealed (and measured) at temperatures of 5 (as deposited), 71, 132 and 162 K.

Fig. 2 shows, for a matrix of  $H_2Pc$ -doped ASW, the time evolution of the width of spectral holes scanned repeatedly at a constant temperature of  $T = 4.2$  K. In the formalism discussed below only the broadening of the holes is relevant. Therefore the initial widths were subtracted for better comparison. The time  $t$  between burning and scanning is plotted on a logarithmic scale. All three series of experiments were performed with the same sample. Datasets 1 and 2 were measured in the 'fresh' matrix (kept at 4.2 K, i.e. without annealing) after a respective waiting time of 4 and 13 h following the preparation of the sample. Dataset 3, in contrast, was measured at  $T = 4.2$  K after annealing the matrix for 15 min at a temperature of 130 K. All datasets show a logarithmic time dependence. While the two datasets measured in the fresh matrix exhibit the same pronounced broadening, the measured spectral diffusion effect is a factor of 29 smaller in the annealed matrix.

The respective annealing behavior of the quasi-homogeneous linewidth (filled circles, FWHM), determined in the same sample, is displayed in Fig. 3. For this purpose new series of spectral holes were measured and their holewidths were extrapolated to

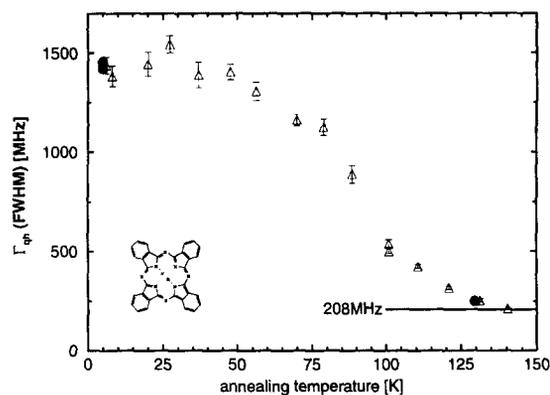


Fig. 3. Narrowing of the quasi-homogeneous linewidth  $\Gamma_{qh}$  as a function of the annealing temperature for the sample of Fig. 2 (●). Also shown is the annealing behavior measured for a second sample (△). The horizontal line corresponds to the calculated limit of the linewidth without any contribution of TLS. See text for details. The insert shows the structure of the dye molecule  $H_2Pc$  used for hole-burning.

zero burning fluence to exclude saturation effects of the photoprocess. The linewidth is the same for both series measured in the fresh matrix and narrows markedly upon annealing. The observed reduction of the linewidth agrees well with the previously published data of a different sample [10] of  $H_2Pc$ -doped ASW (also shown in Fig. 3, scaled to the linewidth of the fresh samples).

For both measurements reported so far the temperature was kept constant at  $T = 4.2$  K in the time

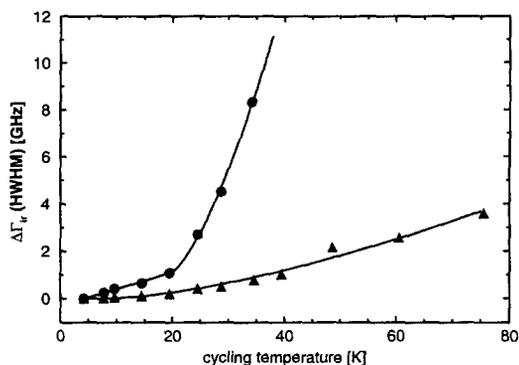


Fig. 4. Irreversible hole broadening  $\Delta\Gamma_{ir}$  versus cycling temperature  $T_c$  for a fresh matrix (●) and for the same matrix annealed at 130 K (▲). The fits to the model of Friedrich et al. are described in the text.

interval between burning and scanning of the spectral holes. Another kind of experiment is presented in Fig. 4. Again the spectral holes were burnt and scanned at  $T_0 = 4.2$  K; however, a temperature cycle to a temperature  $T_c > T_0$  was performed in between. This procedure results in an irreversible hole broadening which, for the fresh matrix follows an empirical  $T_c^3$  power law. The fit to an extended TLS model of Friedrich et al. [15] shows that thermally activated barrier crossing dominates in the fresh matrix above 20 K. The irreversible broadening is much less for the annealed sample and could therefore be observed up to a cycle temperature as high as 75 K. It shows a different temperature dependence ( $T_c^{1.8}$  if fitted empirically), the thermally activated regime dominating already at temperatures exceeding 9 K (see discussion below).

## 4. Discussion

### 4.1. IR spectroscopy

For the matrix annealed below its glass transition temperature the IR spectra shown in Fig. 1 compare well with spectra shown in earlier publications [14,2] for ASW. The OH stretching band is significantly broadened and shifted towards higher frequencies if compared to polycrystalline ice. The OH stretching band of a fresh matrix has its maximum at  $3290\text{ cm}^{-1}$  (measured in a sample avoiding the Christiansen effect). Due to the superposition with the refractive index the band maximum for the matrix shown in Fig. 1 is shifted to  $3260\text{ cm}^{-1}$  which corresponds to the value measured by Mayer [2] for a vapor diluted aerosol. We attribute the occurrence of the Christiansen effect to the formation of water clusters already in the gas phase [16]. We omitted a correction by coating with other gases (e.g. Ar [2]) due to the known difficulties of the devitrification caused by embedded gases [16]. From the deposition rate we can exclude high-density amorphous water and we may thus conclude that our experimental procedure forms low-density amorphous water (ASW). On annealing above the glass transition temperature the IR spectra transforms to the spectrum of polycrystalline ice  $I_c$ ,  $I_h$ . Changes of this transition

due to the embedded  $\text{H}_2\text{Pc}$  molecules could not be observed.

### 4.2. Hole-burning studies

The linewidth of probe molecules doped in disordered solids is caused to a large extent by various dephasing mechanisms, coupling to tunneling centers (TLS) being the most prominent at low temperatures. This allows the investigation of the TLS dynamics which can be observed over many orders of time starting from femtoseconds where it may be detected via photon echo experiments [17,18] up to the timescale of weeks using hole-burning spectroscopy [19,20]. In these experiments TLS dynamics lead to a line broadening  $\Delta\Gamma$  called spectral diffusion. For intermediate times accessible with our hole-burning experiments  $\Delta\Gamma$  can be modeled within the standard TLS model [21]:

$$\Delta\Gamma = \bar{P}c \ln(t/t_0) \quad (1)$$

The broadening is proportional to the TLS number density  $\bar{P}$ , the TLS–dye coupling constant  $c$ , and follows a logarithmic time dependence. Very recently deviations from the logarithmic time behavior were reported, however, solely in the long time regime [20]. Eq. (1) describes the TLS equilibrium dynamics and therefore only holds if the TLS ensemble is in thermal equilibrium. Especially for experimental procedures which involve rapid cooling, one has to be aware of a second process that may contribute to spectral diffusion. Analogous to heat release experiments [22] the relaxation of TLS into thermal equilibrium contributes to the spectral diffusion. The concomitant hole broadening also follows a logarithmic time dependence, yet, its amplitude decreases with time [19].

### 4.3. Time-resolved experiments and quasi-homogeneous linewidth

For a fresh sample of ASW Fig. 2 shows the time evolution of the spectral diffusion measured 4 and 13 h after the sample preparation. Both data sets show logarithmic time dependencies with the same amplitude. We may therefore conclude that (i) on the timescale of our experiment the standard TLS model is applicable and (ii) non-equilibrium contributions

to the hole broadening can be neglected. Therefore the results are independent of the time which has elapsed after the preparation of the sample. The time evolution of a spectral hole burnt into the annealed matrix shows a markedly smaller broadening. Assuming an unaltered coupling mechanism between the TLS and the dye molecules Eq. (1) allows us to determine the reduction of the TLS number density  $\bar{P}$  upon annealing. From the least-squares fits plotted in Fig. 2 the ratio of the TLS number densities in the fresh ( $\bar{P}_f$ ) and the annealed matrix ( $\bar{P}_a$ ) can be calculated as  $\bar{P}_f/\bar{P}_a = 29$ .

To connect these experiments with the measured ‘quasi-homogeneous’ linewidths we will discuss some salient features of the expected line broadening mechanisms. In a recent study Small and coworkers [9] showed that for a sulfonated phthalocyanine in HGW the quasi-homogeneous linewidth is ruled by the coupling to two pseudolocal modes (with frequencies of 50 and 180  $\text{cm}^{-1}$ ) above  $\approx 10$  K. They note that the lower frequency mode which dominates the dephasing to temperatures up to  $\approx 70$  K and the phonon-sideband hole have the same origin. Based on the equality of the phonon-sideband frequency ( $38 \pm 2 \text{ cm}^{-1}$  in HGW [8] versus  $36 \pm 1 \text{ cm}^{-1}$  in ASW [10]), it is reasonable to restrict ourselves to dephasing by pseudolocal modes and TLS in our system, too. We call the associated width quasi-homogeneous since it contains spectral diffusion contributions taking place on the timescale of our experiments. In analogy to ultrasonic measurements [23] and from the measurement of the temperature dependence of the quasi-homogeneous linewidth it was previously argued that the observed narrowing (Fig. 3) is due to a decrease in the TLS density  $\bar{P}$  [8].

Our time-dependent measurements presented in Fig. 2 provide an independent experiment to analyze the contribution of spectral diffusion to the quasi-homogeneous linewidth. The linewidth can be expressed as a sum of two terms:

$$\Gamma_{\text{qh}}(T_a) = \Gamma_0 + \bar{P}(T_a)\hat{c}. \quad (2)$$

$\Gamma_0$  contains the lifetime-related linewidth as well as the width which is due to a coupling to pseudolocal modes and possible dye–dye interactions, whereas the second term in Eq. (2),  $\bar{P}(T_a)\hat{c}$  is due to spectral

diffusion processes [19]. We assume  $\Gamma_0$  to be independent of the annealing temperature  $T_a$ . Thus, the only parameter needed to calculate the contribution of TLS to the quasi-homogeneous linewidth is the ratio of the TLS densities  $\bar{P}(T_{\text{deposition}})/\bar{P}(T_a) = \bar{P}_f/\bar{P}_a$ . Our time-dependent measurements determined this ratio to be  $\bar{P}_f/\bar{P}_a = 29$ . This means that after annealing to 130 K, 97% of the TLS contribution to the linewidth are lost. Using Eq. (2) we are now able to calculate the homogeneous linewidth  $\Gamma_0$  without any contributions of spectral diffusion processes as  $\Gamma_0 = 208$  MHz. This value is shown in Fig. 3 as a horizontal line. Its value also corresponds well to the narrowest linewidths measured in other samples. We may thus conclude that the reduction of the TLS density is indeed the cause of the observed narrowing of the quasi-homogeneous linewidth upon annealing.

#### 4.4. Temperature cycling experiments

Further insight into the processes which occur in these cryogenic matrices upon annealing is gained by the investigation of the temperature dependence of spectral diffusion processes. To this extent the temperature cycling of hole-burning spectra is most suitable since this kind of experiment is exclusively sensitive to spectral diffusion whereas ordinary hole-burning experiments performed at elevated temperatures are also sensitive to other dephasing processes (phonon scattering, coupling to pseudolocal modes). For temperature cycling experiments a spectral hole is burned at a temperature  $T_0$  and the matrix is subsequently cycled to higher temperatures  $T_c$ . After cooling back down to  $T_0$  the holewidth is measured again. Fig. 4 shows the irreversible line broadening of spectral holes for both the fresh and the annealed matrix. The broadening is caused by TLS which are frozen in a defined state at the temperature  $T_0$  and thus do not contribute to the quasi-homogeneous linewidth but become ‘mobile’ at the cycle temperature. Upon lowering the temperature again their dynamics slow down again and leave these TLS in another state.

The fresh matrices of ASW show a strong increase in the irreversible hole broadening which follows an empirically  $T_c^3$  dependence over the mea-

sured temperature range. This simple power law, which reflects, by no means, a microscopic description of the problem, is mentioned here just to emphasize that the high power which is found for fresh matrices of ASW is characteristic for soft glasses as was demonstrated by Friedrich and coworkers [15] in alcohol glasses. They showed that the observed hole broadening can be understood on the basis of an extended TLS model considering barrier crossing by both tunneling and thermal activation. In the low-temperature limit the hole broadening is dominated by tunneling processes following a linear temperature dependence. With rising cycle temperature a relatively sharp crossover to a regime dominated by thermally activated processes is obtained which follows a  $T_c^{3/2}$  power law<sup>1</sup>. Consistent with ultrasonic experiments [23] we have to assume a Raman process which is dominated by thermal activated processes for cycle temperatures above 20 K to fit the broadening in the fresh matrix. In contrast, the broadening in the annealed matrix is much less pronounced and shows an almost pure thermally activated behavior ( $T_c^{1.8}$  versus  $T_c^{3/2}$ ). Tunneling processes only play a role for temperatures below 9 K.

#### 4.5. Conclusions

What can be learned about ASW from these experiments? The irreversible broadening of spectral holes due to temperature cycles is related to the shape of the potential hypersurface [24] since it is connected to the probability that the system falls back to the same potential minimum when the temperature is lowered again. In the idealized case of a perfect crystal the system would always find back to the 'only' potential minimum and no irreversible broadening would be observable at all. Due to the numerous potential minima found in disordered solids the system will fall back into a potential minimum different from the initial one which had been marked

previously by the hole burning process and, thus, an irreversible broadening will be observed.

The fresh sample has a high TLS density which contributes significantly to the quasi-homogeneous linewidth and leads to strong spectral diffusion phenomena. This behavior corresponds to a high number of potential minima and maxima which may be reached by tunneling at helium temperatures. The potential maxima are narrow and the tunneling masses are small since tunneling ( $\propto \exp(-\sqrt{md^2V/\hbar^2})$ ) dominates thermally activated barrier crossing ( $\propto \exp(-V/kT)$ ) up to cycle temperatures of about 20 K. It is the high number of potential minima and maxima which makes it improbable for the system to reach the same potential minimum again upon lowering the temperature and thus accounts for the experimentally observed strong irreversible broadening of spectral holes in temperature cycles. To recapitulate the findings for the fresh matrix, the potential hypersurface possesses a high number of minima separated by narrow barriers. This observation corresponds explicitly to the description of the potential hypersurface given by Böhmer and Angell [12] for a fragile glass. Although the original definition of materials termed fragile glasses was based on the viscosity behavior in the upper limit to the glass transition temperature the connection with the shape of the potential hypersurface outlined in Ref. [12] allows us to propose such a classification. The underlying reason is that we refer to static properties of the glass potential which do not change upon cooling below the glass transition temperature. We thus conclude that the preparation of vapor-condensed amorphous water produces a solid with the properties which are considered typical for a fragile glass.

The weak irreversible broadening observed in the annealed matrix immediately shows that the number of potential minima and maxima has decreased dramatically. Therefore the system falls back with a higher probability into the same potential minima after thermal cycling resulting in the observed weak irreversible broadening of spectral holes. The number of potential maxima which may be connected by tunneling processes at helium temperatures has also decreased which follows from the small contribution of TLS to the quasi-homogeneous linewidth. Tunnel-

<sup>1</sup> A single power law is not able to model the crossover between the two barrier crossing mechanisms, however, over the measured temperature range a single power law can also describe the data reasonably well.

ing through barriers which are formed by the annealing process dominates only below 9 K, which means that the latter have become broader and the tunneling masses have become larger. Thus, upon annealing the high density of potential minima found in fresh matrices is reduced leaving behind a smoothed potential hypersurface where only deep and broad barriers survive. These are the characteristic properties of strong glasses following Böhmer and Angell's classification [12]. Our observations are in accordance with a stabilisation of soft modes and a reduced number of double-well potentials in strong glasses as found by Heuer and Silbey [25] in numerical simulations. We may thus conclude that vapor-condensed ASW annealed in vacuo at temperatures slightly below the glass transition temperature produces a solid with the properties of a strong glass. In summary, our hole-burning experiments document the transition from a fragile to a strong glass with both structures occurring in the amorphous phase of ASW.

In the following we would like to discuss microscopic processes which may be responsible for the measured transition from a fragile to a strong glass. Strong glass-like behavior is commonly observed in matrices with well developed networks [25] where the fluctuations of the involved coordination numbers are small in comparison to fragile van der Waals glasses [26].

Simulations of water clusters designed to model vapor-condensed amorphous water revealed irregular and non-compact clusters with a broad distribution of H-bonds and weakly bound water molecules sticking out of the cluster surface [27]. It is known that clusters are already formed in the gas phase. Condensing the material on a cryoplate produces a network of voids whose structure is related to the gas phase clusters [16]. This formation process is interpreted as the origin of the huge inner surface of the initially formed microporous matrices [28]. Annealing causes a great deal of irreversible processes which we would like to interpret as the formation of a hydrogen-bonded network. For a hydrogen bond both the bond distance and the bond angle are of extreme importance.

In comparison to cubic ice amorphous water has an enlarged O–O distance. As may be observed by infrared spectroscopy of the OH stretching band [14],

annealing reduces the O–O distance and, thus, strengthens the H-bonding. The observed reduction of the O–O distance levels off above 80 K and reveals a second process, the optimization of the bond angle which can be investigated by infrared spectroscopy of the librational band up to the glass transition temperature.

In the same temperature range ( $T \approx 100$  K) the cluster simulations show a transition to a more compact structure where loosely bound molecules smoothen the surface forming H-bonds [27]. In bulk material this process may be observed by measuring the contribution of dangling bonds to the dielectric relaxation at about 100 K which vanishes upon annealing [29,30]. The transition found in our experiments also occurs in the same temperature range and has its maximum effect at about 90 K if derived from the slope of the narrowing of the quasi-homogeneous linewidth.

All these findings firmly suggest that there do exist two different kinds of ASW as proposed by gas adsorption measurements (transforming at  $T \approx 85$  K) [31], DSC [32], and by previous hole-burning studies [8]. Condensing the matrix from the vapor produces a fragile glass. Upon heating in vacuo to about 90 K the ASW samples transform into a strong glass by forming a hydrogen-bonded network, thus approaching a structural state which is known from hyperquenched glassy water (HGW) [33].

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