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Near-Infrared Spectra of Water Confined in Silica Hydrogels in the Temperature Interval 365–5 K

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We have used a sol–gel technique to obtain optically transparent hydrogels in which water is trapped within a tridimensional disordered silica matrix. A suitable aging of these hydrogels enables to have transparent noncracking samples down to cryogenic temperatures. We report the optical absorption spectra, in the near-infrared region, of water trapped in our silica hydrogels, measured in the temperature range 365–5 K, and we compare them with the same spectra of liquid water, measured in the temperature range 365–263 K. The data show that it is possible to have noncrystallizing water even at 5 K: indeed, the overtone bands at $\sim 1.41 \mu\text{m}$ and at $\sim 1.155 \mu\text{m}$ —typical of “weakly bonded” water molecules—are still detected at liquid helium temperature. Deconvolution of the $\sim 1.45 \mu\text{m}$ water band in terms of Gaussian components enables to have a van’t Hoff plot for the “weakly bonded” component which, contrary to liquid water, does not show any critical behavior at 228 K. The reported data open the possibility of investigating, even with optical techniques, the properties of confined water in an exceptionally wide temperature range.

I. Introduction

In recent years, water in confined geometry has been widely used to investigate the physical and chemical properties of this ubiquitous liquid. In particular, the dynamics of supercooled water confined within layered vermiculite clay has been investigated with dielectric relaxation spectroscopy¹ and the nonfreezing behavior of water confined between layers of multilamellar phospholipids has been evidenced with X-ray diffraction.² The structure and dynamics of water confined in commercial porous silica gels and glasses have also been investigated with differential scanning calorimetry³ and neutron scattering.^{4–6} Studies on water in restricted geometry are important, not only to understand the physical and chemical properties of water, but also for their biophysical implications, since water at protein surface has unique properties^{7,8} and has been shown to be relevant to protein stability and function.⁹

In this work we use a sol–gel technique to obtain optically transparent hydrogels in which water is trapped within a tridimensional vitreous silica matrix. This technique has been developed in the last 10 years to encapsulate proteins in vitreous silica gels.^{10–12} A mixture of liquid alkoxide (typically TMOS, tetramethyl orthosilicate, or TEOS, tetraethyl orthosilicate) and water, after sonication in the presence of acid, is mixed with a protein solution. The first hydrolysis step is followed by polycondensation which gives rise to a tridimensional SiO_2 matrix in whose pores (typical diameter $\sim 50 \text{ \AA}$) protein molecules are encapsulated. Our idea was that the sol–gel technique could be used to prepare water in confined geometry and that water in hydrogels might show unique physical–chemical properties. On the other hand, preparation of transparent samples could enable to use well-established optical

techniques, such as optical absorption spectroscopy in the near-infrared region (NIR), to study the properties of water.

Furthermore, the characterization of the state of water trapped in silica hydrogels is an essential prerequisite for the study of the conformational stability and dynamics of proteins encapsulated within these hydrogels, and of their interrelationships with the properties of the embedding matrix.

II. Materials and Methods

Sample Preparation. (A) “Wet” Silica Hydrogel. A solution containing 75% v/v TMOS (Merck, Darmstadt), 25% H_2O (Millipore purified, resistivity $\approx 18 \text{ M}\Omega \text{ cm}$) and $2 \times 10^{-3} \text{ M}$ HCl is sonicated for $\sim 20 \text{ min}$ and diluted with an equal quantity of water. After gentle mixing the resulting sol is poured into semimicro polystyrene cuvettes (Kartell, 1 cm path length). In these conditions, gelification of the sample occurs in about 1 h at room temperature. After 1 day the sample can be extracted from the cuvette: in such a way a $3.1 \times 1.0 \times 0.44 \text{ cm}^3$ slab of wet vitreous transparent material is obtained. We call this sample “wet” hydrogel.

(B) “Dry” Silica Hydrogel. If the silica hydrogel is left to age at room temperature, it progressively loses weight and reduces its volume until it reaches, after about 15 days, approximately one-seventh of its initial volume. The final dimensions of the slab are about $1.7 \times 0.5 \times 0.24 \text{ cm}^3$. No further relevant volume contraction is observed upon prolonged aging, although the structure of the matrix and the water content of the hydrogels keeps evolving, as shown by the NIR absorption spectrum (see Figures 3 and 4). The data reported in this paper refer mainly to a “dry” hydrogel that was left to age at room temperature for about 3 months. Data referring to “dry” hydrogels having about 20, 40, and 60 days of aging are also reported in Figures 3 and 4.

From the initial weight of TMOS and from the absorption at $\sim 1.45 \mu\text{m}$, we estimate that, in our three months aged dry

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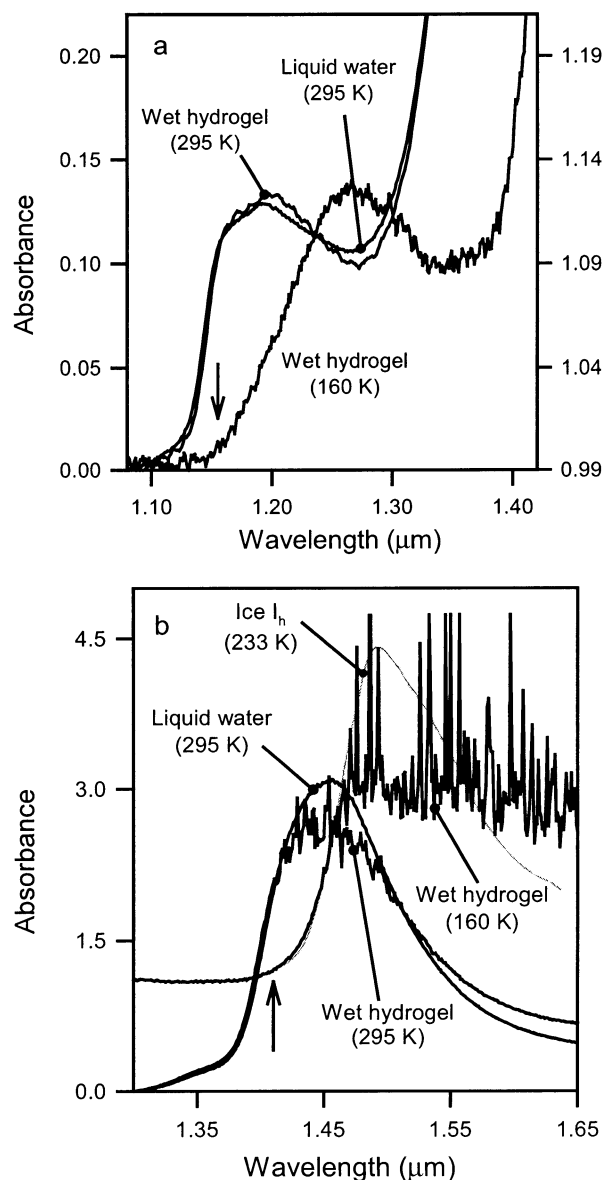


Figure 1. (a) Absorption spectra ($\sim 1.2 \mu\text{m}$ water overtone band) of the wet hydrogel at 295 K, of liquid water at 295 K suitably normalized (left ordinate scale) and of the wet hydrogel at 160 K (right ordinate scale). The arrow indicates the wavelength of $1.155 \mu\text{m}$, where “weakly bonded” water molecules absorb. (b) Same as part a, for the $\sim 1.45 \mu\text{m}$ water overtone band. Spectra at 295 K have been shifted to zero absorbance at $\lambda = 1.30 \mu\text{m}$. The spectrum of ice I_h at 233 K (taken from Figure 3 of ref 13) is also reported for comparison. The arrow indicates the wavelength of $1.41 \mu\text{m}$, where “weakly bonded” water molecules absorb. The noise in part b is due to instrument saturation.

sample, are present approximately 1.2 water molecules per SiO_2 unit, corresponding to an hydration level $h = 0.35$ (h is defined as the ratio $\text{g H}_2\text{O/g SiO}_2$). This is substantially higher than the hydration levels previously investigated with Vycor glasses.⁴ The hydration level was checked also by weighting the sample: an h value of 0.36 was found with this method.

Spectral Measurements. To perform optical measurements, the gel slabs were stuck on the suitable modified copper sample holder of an Oxford Instruments Optistat cryostat (Aldington, UK). Absorption spectra were measured in the wavelength interval $1.9\text{--}1.0 \mu\text{m}$ with a Jasco V-570 spectrophotometer (spectral resolution at $1.45 \mu\text{m}$ of about 10 cm^{-1}) and digitized at 1.0 nm intervals. The temperature was measured in the copper sample holder and was controlled within $\pm 0.5 \text{ K}$ with an Oxford Instruments ITC 503 temperature controller. The cooling rate

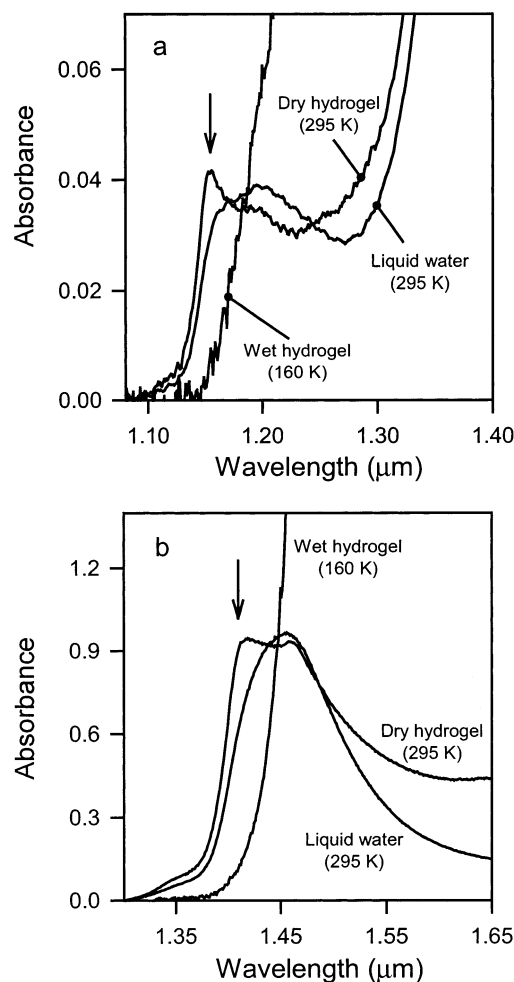


Figure 2. (a) Absorption spectra ($\sim 1.2 \mu\text{m}$ water overtone band) of the dry hydrogel and of liquid water at 295 K. (b) Same as part a, for the $\sim 1.45 \mu\text{m}$ water overtone band. The liquid water spectra have been normalized so as to have a band area equal to the hydrogel one. In both parts the spectrum of a cracked wet hydrogel at $T = 160 \text{ K}$ is reported for comparison. Arrows same as those in Figure 1.

was about 1 K/min ; at each temperature the sample was left to equilibrate for at least 15 min prior to the spectral measurement. Repeated scans at selected temperatures gave indistinguishable results, thus confirming the full thermal equilibration of the sample. Hysteresis upon temperature cycling was not observed.

III. Results and Discussion

Wet Hydrogel. Figure 1 shows NIR optical absorption spectra of wet hydrogel at $T = 295 \text{ K}$ and at $T = 160 \text{ K}$, both for the $1.2 \mu\text{m}$ (part a) and for the $1.45 \mu\text{m}$ (part b) water bands. The spectra of liquid water at 295 K and of ice I_h at 233 K (suitably normalized) are also reported for the sake of comparison. Data in Figure 1 show that the NIR spectrum of the hydrogel at 295 K is essentially indistinguishable from that of liquid water at the same temperature. This indicates that the NIR spectrum of the wet hydrogel monitors the water trapped within the silica matrix and that water-matrix interactions are not such to cause any relevant spectral alteration on the trapped water molecules.

Between 265 and 250 K the water in the wet sample crystallizes and the wet hydrogel cracks. This is clearly shown by the spectra at 160 K reported in Figure 1, which shows a baseline increase of about 1 absorbance unit due to the scattering, and the appearance of a spectrum typical of ice.¹³

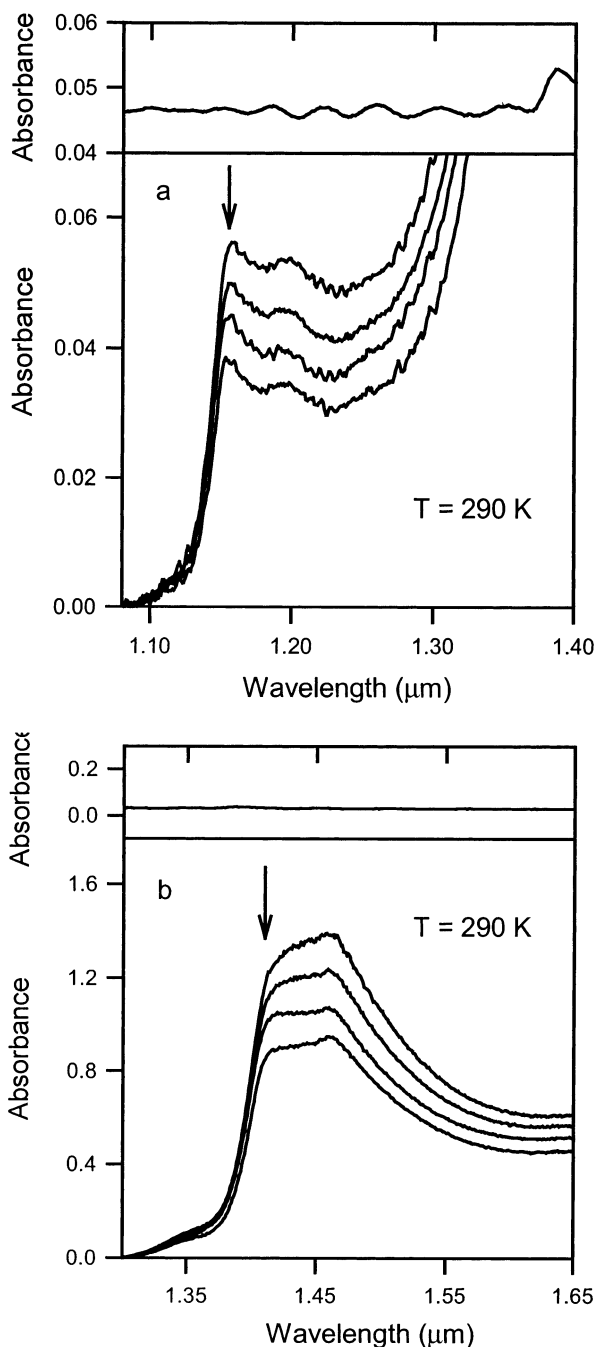


Figure 3. (a) Absorption spectra ($\sim 1.2 \mu\text{m}$ water overtone band) at $T = 290 \text{ K}$ of dry hydrogels having different aging times (20, 40, 60, and 90 days, from top to bottom). (b) Same as part a, for the $\sim 1.45 \mu\text{m}$ water overtone band. Arrows same as those in Figure 1. To have an idea of the effect of the background matrix, in the upper part of each part we report the absorption spectrum of a suprasil silica glass having 1000 ppm "water" content.

Due to excessive noise and spectral distortions arising from the large absorption, we will not try to analyze quantitatively spectra in Figure 1. We note however that the band at $1.39 \mu\text{m}$ —typical of Si—OH groups^{14,15}—is not detected, and that the crystallized sample does not exhibit any absorption at 1.155 and at $1.41 \mu\text{m}$ (see the arrows in Figure 1) where "weakly bonded" water molecules are reported to absorb.¹³

The crystallizing behavior of the wet sample is in agreement with the observation of an undistorted spectrum at 295 K ; it confirms that, in wet hydrogels, the geometrical constraints imposed by the silica matrix on the trapped water molecules

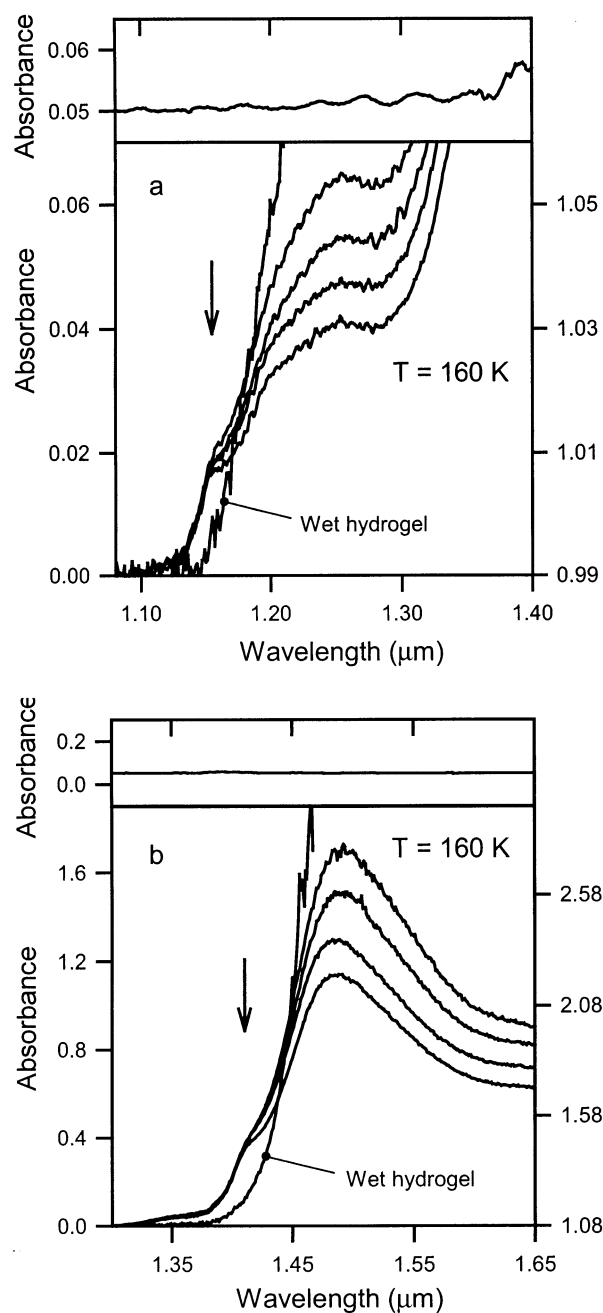


Figure 4. (a) Absorption spectra ($\sim 1.2 \mu\text{m}$ water overtone band) at $T = 160 \text{ K}$ of dry hydrogels having different aging times (20, 40, 60, and 90 days, from top to bottom). (b) Same as part a, for the $\sim 1.45 \mu\text{m}$ water overtone band. In both parts the spectrum of a cracked wet hydrogel at $T = 160 \text{ K}$ is reported for comparison. Arrows same as those in Figure 1. To have an idea of the effect of the background matrix, in the upper part of each part we report the absorption spectrum of a suprasil silica glass having 1000 ppm "water" content.

are not such to prevent ice formation and crystallization at low temperatures.

Dry Hydrogels. Figure 2 shows NIR optical absorption spectra of a dry hydrogel (three months aging) and of liquid water (suitably normalized) at 295 K , both for the $1.2 \mu\text{m}$ (part a) and for the $1.45 \mu\text{m}$ (part b) bands. We first note the lower intensity of the hydrogel spectrum as compared to that in Figure 1: this confirms that we are observing the water bands and that, in the aged dry hydrogel, a relevant amount of water has evaporated. Contrary to Figure 1, the NIR spectrum of the hydrogel is modified with respect to that of liquid water at the same temperature. Surprisingly, for both bands, the modification

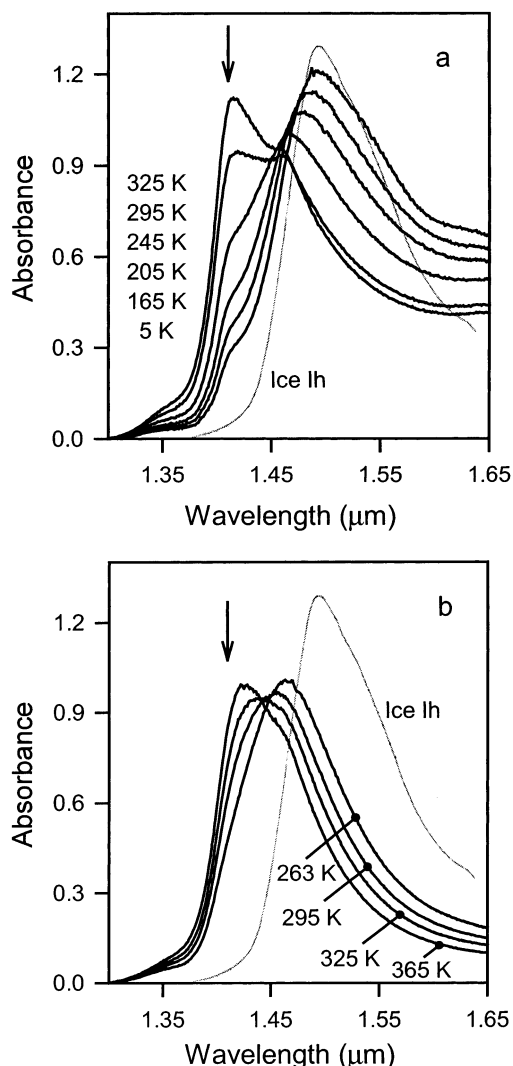


Figure 5. (a) Absorption spectra ($\sim 1.45 \mu\text{m}$ water overtone band) of the 3 months aged dry hydrogel, at selected temperatures, in the range 325–5 K. (b) Same as part a, for the liquid water in the temperature range 365–263 K. In both parts the spectrum of ice I_h at 233 K is reported for comparison. Arrows same as those in part b of Figure 1.

consists of an increased absorption at 1.155 and $1.41 \mu\text{m}$ (where weakly bonded water molecules are reported to absorb), with concomitant reduction in the absorption at higher wavelengths (where strongly bonded water molecules are reported to absorb). Thus, the spectrum of the hydrogel at 295 K is similar to the spectrum of liquid water at higher temperature (see Figure 5b). The $1.45 \mu\text{m}$ band in the hydrogel is also characterized by an increased tail at high wavelengths that we attribute to contributions from lower frequency water bands.

The spectral alterations observed for the aged dry hydrogel cannot be attributed to the presence of Si–OH groups since these alterations are not seen in the wet hydrogel, where a greater number of Si–OH groups are expected, being our sol–gel protocol such to favor hydrolysis with respect to polycondensation.

The data reported in Figure 2 therefore indicate that, in the dry hydrogel, the constraints imposed by the silica matrix are such to alter the structural properties of the trapped water molecules, as monitored by their NIR absorption spectrum.

Effect of Aging. Figure 3 shows the NIR optical absorption spectra at 290 K of dry hydrogels having different aging times (20, 40, 60, and 90 days, from top to bottom) both for the $1.2 \mu\text{m}$ (Figure 3a) and for the $1.45 \mu\text{m}$ (Figure 3b) bands. To have an idea of the silica gel background, we report in the upper

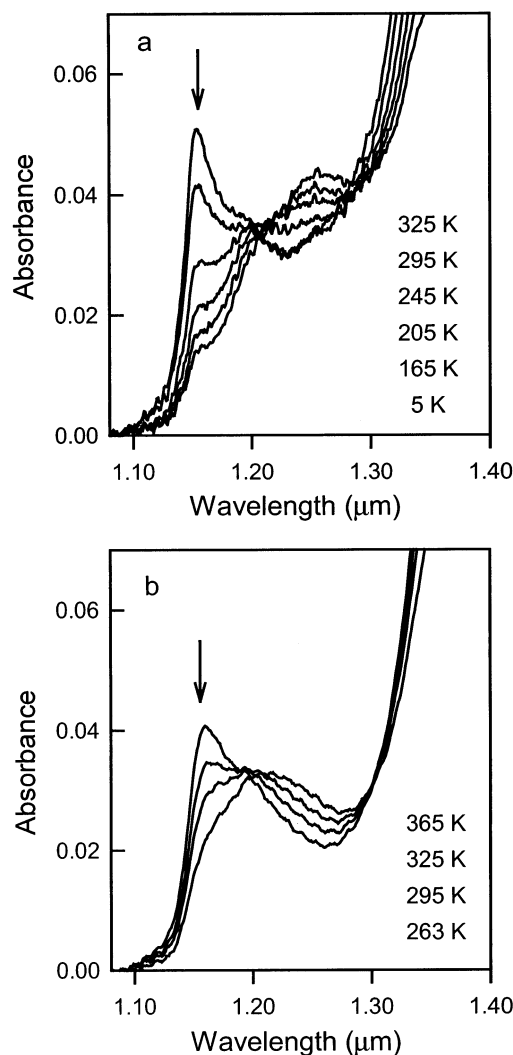


Figure 6. (a) Absorption spectra ($\sim 1.2 \mu\text{m}$ water overtone band) of the 3 months aged dry hydrogel, at selected temperatures, in the range 325–5 K. (b) same as part a, for liquid water in the temperature range 365–263 K. Arrows same as those in part a of Figure 1.

parts the NIR spectra of a suprasil silica glass having 1000 ppm “water” content.

Data in Figure 3 show that aging essentially causes loss of water. However, a spectral deformation also occurs, consisting mainly in increased absorption at 1.155 and at $1.41 \mu\text{m}$ (where “weakly” bonded water molecules absorb) with respect to the absorption at higher wavelengths. Data in Figure 3 also show that contributions from the silica matrix are likely to be negligible in the spectral regions investigated.

Since dry hydrogels remain homogeneous and transparent even at cryogenic temperatures (see next paragraph), it is possible to study the effect of aging also at lower temperatures. This is reported in Figure 4 at $T = 160 \text{ K}$, where we report also the spectra of the cracked wet hydrogel at the same temperature, for the sake of comparison. Data in Figure 4 fully confirm those in Figure 3; moreover, they also show that the bands at 1.155 and $1.41 \mu\text{m}$ are indeed totally absent in the spectra of the cracked wet hydrogel.

Effect of Temperature. Figure 5a shows the $1.45 \mu\text{m}$ absorption band of the three months aged dry hydrogel at various temperatures in the range 365–5 K; the same band of liquid water in the temperature interval 325–263 K is reported in Figure 5b. Figure 6 is the same as Figure 5, relative to the $1.2 \mu\text{m}$ absorption band.

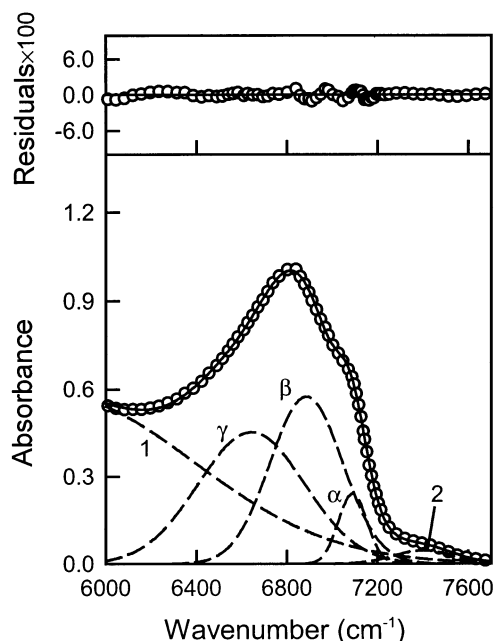


Figure 7. Deconvolution of the absorption spectrum of the 3 months aged dry hydrogel at $T = 245$ K in terms of Gaussian components (eq 1 in the text). Circles are the experimental points (not all the measured points are reported, for the sake of figure readability), dashed lines are the Gaussian components, the continuous line is the overall fitted spectral profile, and the residuals are reported on the upper part on an expanded scale. Components marked 1 and 2 are used as extrapolations: to reduce the number of fitting parameters their peak position and width are kept constant in the fittings of spectra at various temperatures. At difference, the peak positions and the widths of components α , β , and γ are left free to vary. Fittings of analogous quality are obtained at all temperatures.

A few facts are evident already from inspection of the raw spectra in Figures 5 and 6:

- as shown in Figures 5a and 6a, the dry hydrogel remains homogeneous and transparent down to 5 K; indeed, no baseline increase due to scattering is observed, even at 400 nm;
- as the temperature is lowered, the spectra monotonically move toward an “ice-like” spectrum, with however one relevant difference: in fact, the absorption bands at ~ 1.155 and $1.41 \mu\text{m}$, which are characteristic of “weakly bonded” water molecules and are totally absent in the 160 K spectrum of the cracked wet hydrogel (see Figures 1, 2, and 4), are detected at all temperatures, even at 5 K.

To analyze more quantitatively the spectral temperature dependence we performed fittings of the $\sim 1.45 \mu\text{m}$ band in terms of Gaussian components. The following expression was used:

$$A(\nu) = \sum_{j=1}^N M_j \nu \frac{1}{\sigma_j \sqrt{2\pi}} \exp\left[-\frac{(\nu - \nu_j)^2}{2\sigma_j^2}\right] \quad (1)$$

where M_j , ν_j , and σ_j are the area, peak frequency, and width of the j th component. A typical fit is shown in Figure 7, together with the residuals, on an expanded scale. It must be stressed that the deconvolution procedure shown in Figure 7 owes much to the early works by Luck and Ditter,¹⁶ by Choppin and Violante,¹⁷ and by the group of Prof. M. B. Palma-Vittorelli in Palermo.^{18,19}

As can be seen, five components are needed to fit the spectrum. Component labeled 2 in Figure 7 at $1.346 \mu\text{m}$ has been tentatively assigned^{20,21} to a rotational mode of water, while component 1 takes into account the high-frequency wing of the

TABLE 1: Values of Peak Frequency (ν_α) and Width (σ_α) of Component α .

sample		ν_α (cm ⁻¹)	σ_α (cm ⁻¹)
dry hydrogel	$T = 325$ K	7087 ± 2	66 ± 2
	$T = 295$ K	7088 ± 2	66 ± 2
	$T = 165$ K	7085 ± 3	60 ± 3
	$T = 5$ K	7075 ± 4	59 ± 4
liquid water	$T = 325$ K	7065 ± 2	80 ± 2
	$T = 295$ K	7066 ± 3	80 ± 3
	$T = 263$ K	7076 ± 4	70 ± 4

band: in the present analysis both components are considered as extrapolations and their peak frequency and width are maintained constant in the fittings. The three components which, following the notation of Andaloro et al. 1977¹⁸ and Andaloro et al. 1981,¹⁹ are labeled α , β , and γ in Figure 7, take into account the $1.45 \mu\text{m}$ band. This band arises from the combination of symmetric and antisymmetric OH stretching modes (first overtone) of water molecules with different extent of hydrogen bonding. Gaussians β and γ may be considered as heuristic: they do not represent well defined molecular classes, but rather they account for spectral contributions likely originating from a continuum of strongly bonded water molecules, as discussed in ref 13. At difference, Gaussian α at about $1.41 \mu\text{m}$ ($\sim 7100 \text{ cm}^{-1}$) likely reflects a more defined “weakly hydrogen bonded” molecular class or a “broken bond” class. The above attribution of component α is strongly supported by the fact that, as shown in Table 1:

- very similar values of peak frequency ν_α and width σ_α are observed for liquid water and for the aged dry hydrogel;
- for both samples ν_α and σ_α remain almost constant in the whole temperature range investigated.

Our spectral assignment is consistent with previous investigations by Angell and Rodgers¹³ who analyzed the NIR overtone spectra of H_2O and HOD , by Hare and Sorensen^{22,23} who studied the Raman spectra of bulk water and dilute HOD in the OH stretch region, and by Segtnan et al.²⁴ who analyzed the $1.45 \mu\text{m}$ band of liquid water using two-dimensional correlation spectroscopy and principal component analysis.

Figure 8 reports a van't Hoff plot of the integrated intensities ratio $M_\alpha/(M_\alpha + M_\beta + M_\gamma)$ for the dry hydrogel and for liquid water. The total intensity of the $1.45 \mu\text{m}$ band is also reported in the upper part: the fact that the total band intensity is almost temperature independent gives further support to the validity of our analysis. Figure 8 shows that the behavior of water in the dry gel is profoundly different from that in the liquid state. Indeed, in agreement with previous reports,^{18,19} the data for liquid water indicate that the fraction of “weakly bonded” water molecules tends to zero as the temperature is lowered deep into the supercooled region and are consistent with a critical divergence at $T = 228$ K.^{25,26} On the contrary, data for the dry hydrogel show no evidence of a divergence at 228 K and indicate that a fraction ($\sim 5\%$) of weakly bonded water molecules is present even at 5 K. Moreover, at temperatures lower than 130 K, the equilibrium between components is frozen, suggesting that the sample has reached a “glassy state”. We tentatively attribute the presence of a “weakly bonded” component even at 5 K to the fact that, in the aged dry hydrogel, the geometric constraints, imposed by the silica matrix to the trapped water molecules, are not compatible with the presence of an extended hydrogen bonded ice-like network. This also rationalizes the fact that water does not crystallize and our sample does not crack. This interpretation is consistent with the so-called “fragmented cluster model” of adsorbed water.²⁷ This model, proposed on the basis of NMR and infrared data,

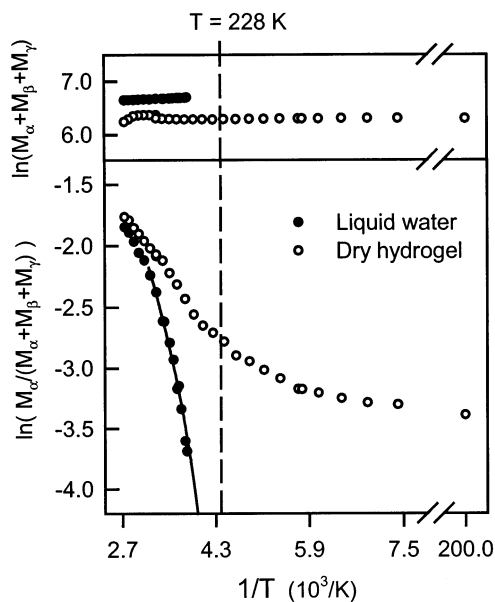


Figure 8. van't Hoff plots of the intensity ratio $M_\alpha/(M_\alpha + M_\beta + M_\gamma)$ for the 3 months aged dry hydrogel (open symbols) and for liquid water (closed symbols). The continuous line is a fitting of the data points relative to liquid water in the temperature range 315–263 K in terms of a power law^{25,26} (exponent 1.5) diverging at $T = 228$ K. The logarithm of the total spectra intensity ($M_\alpha + M_\beta + M_\gamma$) as a function of the inverse temperature is also shown in the upper part.

describes confined water as a mixture of isolated monomers and small clusters preventing the necessary cooperative aggregation needed for the formation of an ice-like structure.

Further insights can be obtained by comparing our results with data reported by Doster and co-workers on the behavior of water in hydrated myoglobin films using calorimetry⁸ and infrared spectroscopy.^{8,36} In analogy with our results, these authors find that, below an hydration $h \sim 0.39$ (g H₂O/g protein) water associated with protein does not freeze; instead of “nonfreezable” water, they use “solid amorphous water” or “amorphous ice” to describe this state. Investigation of the O–D stretching bands in partially deuterated samples, showed a red shift of the band, indicating stronger protein–water hydrogen bonds. At difference, our dry hydrogels spectra show an increased absorption at smaller wavelengths (i.e. higher frequencies) with respect to wet hydrogels or bulk water. This fact suggests that, at difference with protein powders, the topological constraints imposed by the matrix on the confined water molecules, more than direct water–silica hydrogen bonds, are responsible for the non crystallizing behavior of water in our dry hydrogels.

IV. Conclusions

Independent of the detailed interpretation given to the above spectral components, our data show that it is possible to obtain water confined in a silica gel matrix down to cryogenic temperature. Indeed, our samples remain transparent and homogeneous even at 5 K and the optical absorption spectra in the NIR overtone region remain distinctly different from those of ice I_h in that they show a residual absorption at 1.155 and at 1.41 μ m, characteristic of “weakly bonded” water molecules.

Further experiments and the use of different experimental techniques, for example, dielectric spectroscopy, calorimetry, and X-ray scattering, is needed in order to reach a more quantitative characterization of the structural and dynamic properties of water confined in our aged “dry” silica hydrogels. We stress, however, that the exceptionally wide temperature

range interval accessible with our samples opens the possibility to test the predictions, based on computer simulations^{28,29} and theories,³⁰ on the behavior of water in confined geometry. We stress also that, at difference with other techniques of water confinement in vitreous silica matrixes^{4,6} our approach enables to have optically transparent samples of relatively high hydration levels and therefore to use optical techniques, for example, Raman spectroscopy,^{31–35} to investigate the physical properties of confined water.

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References and Notes

- (1) Bergman, R.; Swenson, J. *Nature* **2000**, 403, 283.
- (2) Utoh, S. *J. Chem. Phys.* **2001**, 115, 601.
- (3) Ishikiriya, K.; Todoki, M. *Thermochim. Acta* **1995**, 256, 213.
- (4) Bruni, F.; Ricci, M. A.; Soper, A. K. *J. Chem. Phys.* **1998**, 109, 1478.
- (5) Soper, A. K.; Bruni, F.; Ricci, M. A. *J. Chem. Phys.* **1998**, 109, 1486.
- (6) Venturini, F.; Gallo, P.; Ricci, M. A.; Bizzarri, A. R.; Cannistraro, S. *J. Chem. Phys.* **2001**, 114, 10010.
- (7) Sartor, G.; Hallbrucker, A.; Mayer, E. *Biophys. J.* **1995**, 69, 2679.
- (8) Doster, W.; Bachleitner, A.; Dunau, R.; Hiebl, M.; Luscher, E. *Biophys. J.* **1986**, 50, 213.
- (9) Rupley, J. A.; Careri, G. *Adv. Protein Chem.* **1991**, 41, 37.
- (10) Ellerby, L. M.; Nishida, C. R.; Nishida, F.; Yamanaka, S. A.; Dunn, B.; Valentine, J. S.; Zink, J. I. *Science* **1992**, 255, 1113.
- (11) Shibayama, N.; Saigo, S. *J. Mol. Biol.* **1995**, 251, 203.
- (12) Samuni, U.; Navati, M. S.; Juszczak, L. J.; Dantsker, D.; Yang, M.; Friedman, J. M. *J. Phys. Chem. B* **2000**, 104, 10802.
- (13) Angell, C. A.; Rodgers, V. J. *Chem. Phys.* **1984**, 80, 6245.
- (14) Nishikawa, H. In *Silicon-Based Materials and Devices*; Nalwa, H. S., Ed.; Academic Press: San Diego, 2001; Vol. 2, pp 93–122.
- (15) Shelby, J. E.; Vitko, J., Jr.; Benner, R. E. *J. Am. Ceram. Soc.* **1982**, 65, C59.
- (16) Luck, W. A. P.; Ditter, W. *J. Phys. Chem.* **1970**, 74, 3687.
- (17) Choppin, G. R.; Violante, M. R. *J. Chem. Phys.* **1972**, 56, 5890.
- (18) Andalaro, G.; Chirico, P.; Guzzio, G.; Leone, M.; Palma-Vittorelli, M. B. *J. Chem. Phys.* **1977**, 66, 335.
- (19) Andalaro, G.; Leone, M.; Palma-Vittorelli, M. B. *Nuovo Cimento D* **1983**, 5, 1239.
- (20) Iwamoto, M.; Uosumi, J.; Nishinari, K. In *Proceedings of the International Near Infrared Spectroscopy/Near Infrared Technology Conference*; Hello, J., Kaffka, K. J., Goncsy, J. L., Eds.; Akademiai Kiado: Budapest, Hungary, 1986; pp 3–12.
- (21) Maeda, H.; Ozaki, Y.; Tanaka, M.; Hayashi, N.; Kojima, T. *J. Near Infrared Spectrosc.* **1995**, 3, 191.
- (22) Hare, D. E.; Sorensen, C. M. *J. Chem. Phys.* **1990**, 93, 25.
- (23) Hare, D. E.; Sorensen, C. M. *J. Chem. Phys.* **1990**, 93, 6954.
- (24) Segtnan, V. H.; Šašić, Š.; Isaksson, T.; Ozaki, Y. *Anal. Chem.* **2001**, 73, 3153.
- (25) Speedy, R. J.; Angell, C. A. *J. Chem. Phys.* **1976**, 65, 851.
- (26) Angell, C. A. *Annu. Rev. Phys. Chem.* **1983**, 34, 593.
- (27) Belfort, G.; Sinai, N. In *Water in Polymer*; Rowland, S. P., Ed.; ACS Symposium Series 127, American Chemical Society: Washington, DC, 1980; p 323.
- (28) Gallo, P.; Rovere, M.; Spohr, E. *Phys. Rev. Lett.* **2000**, 85, 4317.
- (29) Starr, F. W.; Harrington, S.; Sciortino, F.; Stanley, H. E. *Phys. Rev. Lett.* **1999**, 82, 3629.
- (30) Götze, W.; Sjögren, L. *Rep. Prog. Phys.* **1992**, 55, 241.
- (31) Sokolov, A. P.; Hurst, J.; Quitmann, D. *Phys. Rev. B* **1995**, 51, 12865.
- (32) Majolino, D.; Mallamace, F.; Migliardo, P.; Aliotta, F.; Micali, N.; Vasi, C. *Phys. Rev. E* **1993**, 47, 2669.
- (33) Rousset, J. L.; Duvall, E.; Boukenter, A. *J. Chem. Phys.* **1990**, 92, 2150.
- (34) Mizoguchi, K.; Hori, Y.; Tominaga, Y. *J. Chem. Phys.* **1992**, 97, 1961.
- (35) Mazzacurati, V.; Nucara, A.; Ricci, M. A.; Ruocco, G.; Signorelli, G. *J. Chem. Phys.* **1990**, 93, 7767.
- (36) Demmel, F.; Doster, W.; Petry, W.; Schulte, A. *Eur. Biophys. J.* **1997**, 26, 327.