PHYSICAL REVIEW B **68**, 172201 (2003)

Neutron scattering studies of low-fraction H_2O in silica gel

Yan Wang and Shunle Dong*
Physics Department, Ocean University of Qingdao, Qingdao, China, 266071

(Received 11 September 2003; published 3 November 2003)

Inelastic neutron scattering spectra of silica gel with low concentrations of water, 3 and 10%, were measured at 5 K. The experimental spectrum for the lower fraction of water (3%) in silica gel shows dramatic changes compared to the spectra of other known ice phases in the energy transfer region of 2–140 meV. Its intermolecular librational band ranges from 47 to 102 meV shifted to lower energy by about 20 meV (or by a factor 1.43) compared to ice *Ih* (67–119 meV), and shows a similar librational band with liquid. A significant excess of low frequency vibration modes (<7 meV) over normal ice *Ih* and a very wide acoustic peak (4–15 meV) were observed. Experimental data indicate that little H_2O (3%) in silica gel exhibits a strong softening of hydrogen bonds compared to bulk normal ice and all other known ice phases.

DOI: 10.1103/PhysRevB.68.172201 PACS number(s): 61.12.−q, 63.20.Dj, 61.43.−j

Water in confined space has attracted considerable interest in recent years.[1–3] Understanding the modification from bulk liquid water behavior when water is introduced into pores of porous media or confined in the vicinity of metallic surfaces is important to technological problems such as oil recovery from natural reservoirs, mining, corrosion inhibition, enzymatic activity, the functions of membranes, and food conservation. Water in porous materials such as Vycor glass and silica gel has actively been under investigation because of their relevance in catalytic and separation processes.

The structural and dynamic properties of bulk water are now mostly well understood in some ranges of temperatures and pressures.[4,5] In the last decade many studies about the structure and dynamic properties of water behavior in confined geometry have been made using different techniques such as x-ray diffraction, neutron diffraction (ND),[6] and nuclear magnetic resonance,[7] in the deeply supercooled regime and in a situation where the effects due to the hydrogen bonding are dominant. In many common and relevant situations, water is not in its bulk form but is instead attached to some substrates or filling small cavities such as in porous media. Structural and dynamical properties of confined water may be affected by the presence of a surface that can be either hydrophilic or hydrophobic, by interaction forces at the interface, and by the geometrical confinement and/or volume of confinement, which can limit the extension of the hydrogen bond network in such a way as to reduce the density fluctuations of water. Strong structure perturbations at the surface are incongruent with the ordinary directional binding between water molecules in the bulk liquid. The resulting surface induced perturbative disruptions, therefore, modifies water's normal properties.

All the experimental studies of the dynamics of water molecules confined in different substrates agree in suggesting a slowing down of the translational single molecule motion[7] compared to the bulk liquid phase. However, the rotational diffusion of a single water molecule increases while its translational diffusion decreases, which is the basis of a ''fragmented cluster model'' that describes adsorbed water as a mixture of isolated monomers (H_3O^+) and small clusters ($H_5O_2^+$). Most neutron-diffraction studies are indeed interpreted in terms of more extensive hydrogen bonding than in bulk water, at least in the water layers closer to the interface and below room temperature.[8] A recent study of water confined in Vycor glass (with a average pore size of ~40 Å) was done in Ref. 6 using neutron diffraction. The authors reported that, although the limitations of the experimental technique did not allow them to draw definitive and quantitative conclusions, nevertheless it was apparent from their study that water confined in porous Vycor glass is still hydrogen bonded, but the bond network is strongly distorted even at room temperature. The inelastic neutron scattering (INS) of water in Vycor (with a pore size ~50 Å) with 52% hydration, measured at temperatures between −35 and 25 °C, has shown that the first (acoustical) peak in the translational part of the INS spectra was suppressed compared to that of bulk water.[9] The low-energy cutoff of the librational band for the spectrum at 25 °C was at slightly higher energy than in bulk water, and on cooling to −35 °C the shift was noticeably increased. The position of the low-energy cutoff of the librational band at −35 °C was close to that for ice *Ih*. Their results indicate that at rather high hydration ($>50\%$) the water behaves in many features similar to bulk water (at 25 °C) or normal ice *Ih* (at −35 °C). Other INS data on water in pores[10] also gave similar results.

Two samples with different concentrations of water (3% and 10% by weight) in silica gel were prepared. The silica gel (grade 62, 60-200 mesh, 150 Å is made by the Aldrich Chemical Company of the United States. Its pore volume is 1.1 cm^3 g and its surface area is 315 m^2/g. The concentrations of 3% and 10% H_2O will roughly cover the pore surface by 0.32 and 1.08 layers, respectively. The silica gel was dried by exposure in a vacuum (10^{-2} torr) at 80 °C for 24 h before adding pure water (99.6% double-distilled H_2O). The samples were wrapped in aluminum foil and attached to a center stick. In order to reduce the Debye-Waller factor and to maximize the INS intensity, all samples were cooled below 15 K. The instrument used was the Time Focussed Xtal Analyzer (TFXA, which is now called TOSCA) spectrometers at the ISIS (Rutherford Appleton Laboratory, UK).[11] TFXA was an inverse geometry time-of-flight spectrometer. A ''white'' energy neutron beam is inelastically scattered by sample, analyzed by graphite crystals (placed at 135° to the direction of the incident neutrons) and beryllium filters, and

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neutrons with a final energy of ~4 meV are registered. In the whole energy range of interest (2–120 meV) the instrument provides very good energy resolution, about 1.5% ($\delta E/E$). The spectrum for dry silica gel and the empty can was also measured under the same conditions and subtracted from the spectra of hydrated silica gel to get the spectra representing the contribution resulting entirely from scattering on water molecules. The time of flight spectrum was converted to dynamic structure factor $S(Q,\omega)$ vs energy transfer $\hbar\omega$ by using the standard program at ISIS.

Before the comparison of bulk water (measured at 290 k) to pore ice (3% H_2O at 5 K) is carried out, the temperatures should be set at the same value by using the following calculations (temperature affecting dynamical factor through both the Debye-Waller factor and the population factor):

$$S_{T=5\,\mathrm{K}}=\frac{S_{T=290\,\mathrm{K}}(Q,\omega)e^{-2W(Q,T=5\,\mathrm{K})}\langle n(T=5\,\mathrm{K})+1\rangle}{e^{-2W(Q,T=290\,\mathrm{K})}\langle n(T=290\,\mathrm{K})+1\rangle}, \qquad (1)$$

where e^{-2W} is average Debye-Waller factor. It could be obtained by

$$e^{-2W(Q,T)}=\frac{\dfrac{f_\mathrm{O}\sigma_\mathrm{O}}{m_\mathrm{O}}e^{-2W_\mathrm{O}(Q,T)}+\dfrac{f_\mathrm{H}\sigma_\mathrm{H}}{m_\mathrm{H}}e^{-2W_\mathrm{H}(Q,T)}}{\dfrac{f_\mathrm{O}\sigma_\mathrm{O}}{m_\mathrm{O}}+\dfrac{f_\mathrm{H}\sigma_\mathrm{H}}{m_\mathrm{H}}}, \qquad (2)$$

where $\sigma_\mathrm{O}/\sigma_\mathrm{H}$ and $f_\mathrm{O}/f_\mathrm{H}$ are neutron scattering cross section and atomic fraction of element oxygen/hydrogen, respectively. From the definition of generalized phonon density of states[12]

$$G_i(\omega)=\frac{1}{3Nm_i}\sum_{j,q}|\mathbf{e}_i(\mathbf{q},j)|^2\delta[\omega-\omega_j(\mathbf{q})], \qquad (3)$$

the Debye-Waller factor in Eq. (2) could be derived as

$$W_i(Q,T)=\frac{\hbar Q^2}{4m_i}\int\frac{G_i(\omega)}{\omega}[2n+1]d\omega, \qquad (4)$$

where

$$n=\frac{1}{e^{\hbar\omega/kT}-1}. \qquad (5)$$

When $i=1$ or 2, formula (4) is for hydrogen or oxygen, respectively. From the geometry of TFXA/TOSCA there exists the relation between energy and momentum transfer given by

$$\hbar^2Q^2=2m\{\hbar\omega+8-\sqrt{8(4+\hbar\omega)}\}. \qquad (6)$$

The spectra of crystalline ice phases (ice *Ih*, ice VI, and ice VIII) and amorphous ices [high density amorphous (hda) ice and low density amorphous (lda) ice] consist of well developed bands: the lower-energy band, 0–40 meV, associated with translational vibrations of water molecules, and the high energy one, in the region of 53–120 meV, due to their librations. There is a clear gap between these two bands. INS studies[5] of about all crystalline phases (<2.2 GPa) and amorphous forms of ice have shown the following common behaviors with increasing pressure (and density) of ice existence on *P-T* Phase diagram: (i) a shift to higher energy of the first (acoustical) peak of translational band (from 6.7 meV for lowest density ice *Ih* up to 15 meV for highest density ice VIII); and (ii) a shift to lower-energy cutoff of the librational band (from 67 meV for ice *Ih* down to 54 meV for ice VIII) as well as the whole librational band itself. It was determined from x-ray and ND measurements that for most ice phases the nearest neighbor water-water distances increase with increasing density.[13] Therefore, the softening of the transverse force constant between the nearest-neighbor water molecules could be due to longer and weaker hydrogen bonds. Alternatively, the origin of the librational band softening could be a deformation of the hydrogen bonds, as shown in ice II.[12]

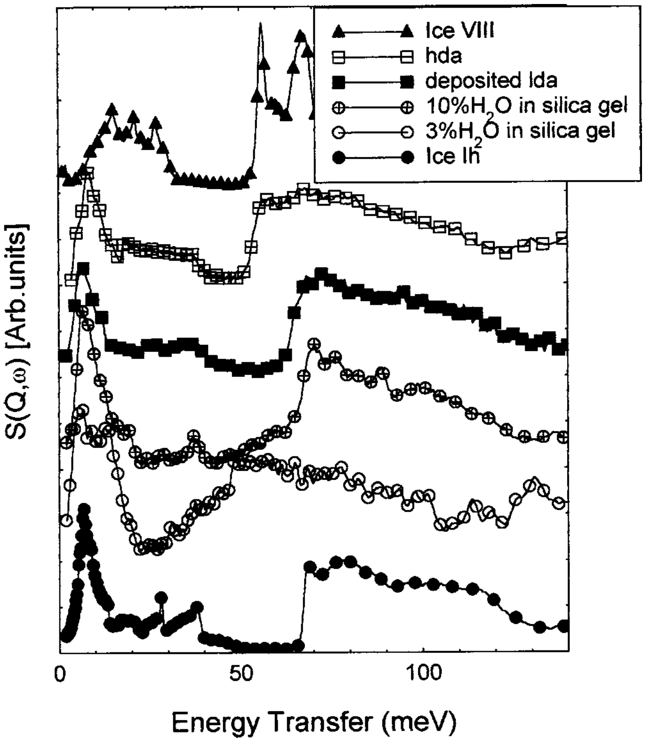

FIG. 1. INS spectrum comparison of 3% H_2O in silica gel with 10% H_2O in silica gel, ice *Ih*, lda ice, *hda* ice, and ice VIII in the energy transfer region of 2–140 meV.

Figure 1 shows the INS spectrum comparison of H_2O ice *Ih* with ice VIII, 10% H_2O, and 3% H_2O in silica gel, hda ice and lda ice measured at 5 K. The crystal feature peaks (28 and 37 meV) in translational high-energy region becomes slightly flattened for silica gel absorbing 10% water, and its low-energy cutoff of libration is not steep as normal ice *Ih*. Its acoustical peak shifts toward a low energy of about 1 meV compared to ice *Ih*. It dramatically goes to further for 3% H_2O in silica gel that shows its comparison to 10% H_2O in silica gel, in which the low-energy cutoff of libration moves toward a low energy of about 20 meV (or by a factor of 1.43) compared to ice *Ih*, and merges with a translational band. This indicates the softening of the corresponding transverse force constants by a factor 2. This is the highest shift

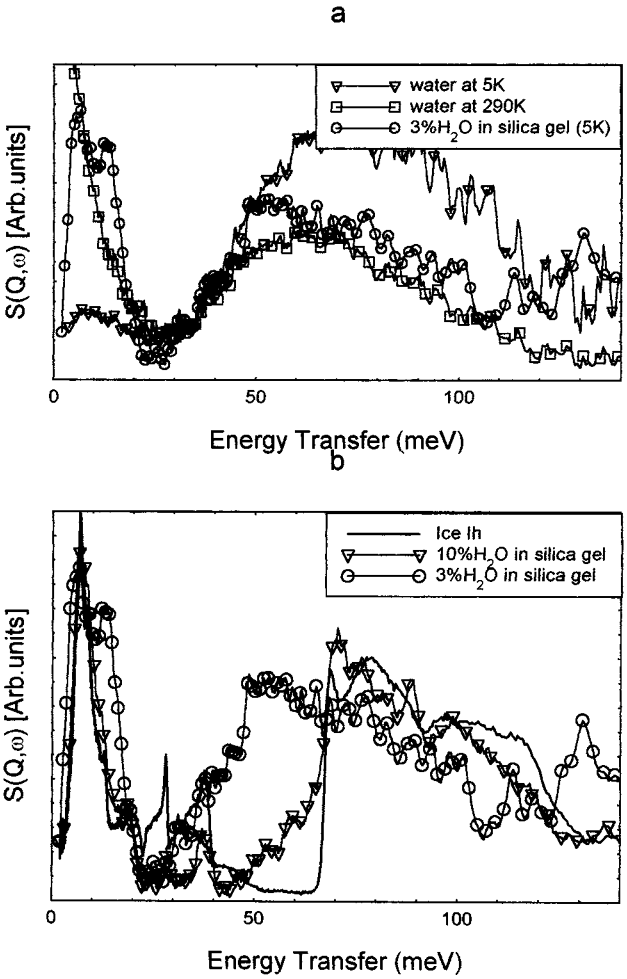

FIG. 2. (a) INS spectrum comparison of 3% H_2O in silica gel with bulk water [measured at 290 K and set at 5 K by using formulas (1)–(5); see the text]. (b). INS spectrum comparison of 3% H_2O in silica gel with 10% H_2O in silica gel and ice *Ih*.

compared to all other ice phases. This could be understood by assuming that the water molecules in monomer layers have a lot of broken and deformed hydrogen bonds, compared to bulk ices. This is in agreement with the structural results on water in Vycor glass.[6] At higher concentrations of water in silica gel its excess above 3% behaves as normal ice *Ih*.

INS spectra of 3%H_2O (measured at 5 K) in silica gel and pure water (measured at 290 K) are shown in Fig. 2(a). Their dynamical properties should be compared in this figure so the measurements should be set at the same temperature. Temperature affects the dynamical factor $S(Q,\omega)$ through both population factor and the Debye-Waller factor. Using formulas (1)–(5) the INS spectrum of water (at 5 K) was obtained, and is also shown in this figure for comparison. The INS spectrum of water has a small translational band (ranging from 0 to 25 meV, low intensity) and a gentle slope in librational low-energy cutoff that merges with the translation. This implies that water has much fewer translation vibration modes and no definite three-body bending force constant, as expected because it has no transverse force constants. This figure shows a strong similarity in the librational bands for both 3% water in silica gel and pure water (the same low-energy cutoff and similar band shape).

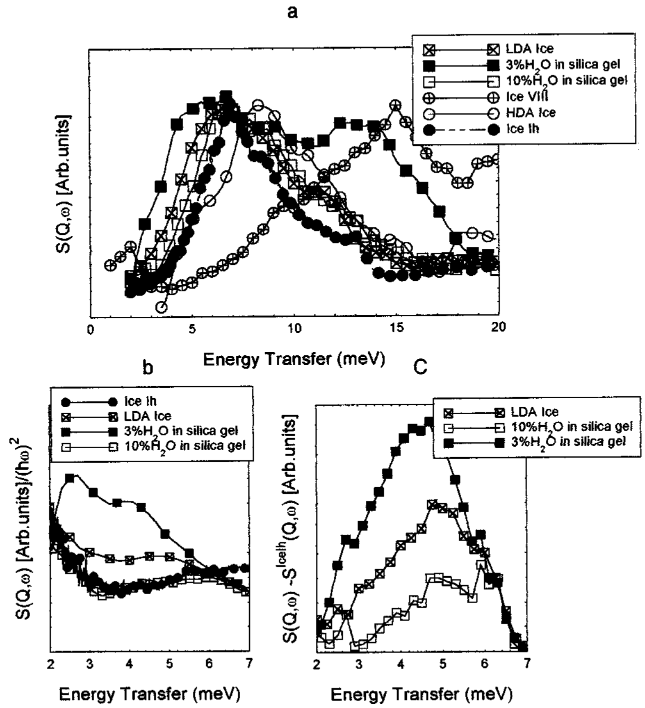

FIG. 3. (a) Acoustical peak comparison of these spectra shown in Fig. 1. (b). Four INS spectra (dynamical factor) were divided by neutron transfer energy square. (c) These spectra were subtracted by the ice *Ih* spectrum.

Figure 2(b) shows the INS spectrum comparison of silica gel containing 3% H_2O with 10% H_2O and ice *Ih*. The peaks in translational optic (~20–40 meV) region imply ices as crystal (two peaks for ice *Ih* at 28 and 37 meV, no peak for amorphous ices, see Fig. 1). These peaks do not completely disappear but become much flatter for a silica gel containing 10% water. In particular, these peaks are merged into the libration band in the spectrum of silica gel with 3% water, and they could hardly be distinguished. However, its acoustical peak is much wider than other ice samples, which is probably due to high frequency vibration modes joining in.

Figure 3(a) is the acoustical peak comparison of the spectra shown in Fig. 1. Figure 1 shows that this peak is pushed to 8.5 meV for hda ice and to 15 meV for ice VIII from 7 meV for ice *Ih*. It has been demonstrated that this peak shift is due to strengthened intermolecular interactions in high-pressure phase ices.[14] Figure 3(b) shows four INS spectra divided by the neutron transfer energy square in the region from 2 to 7 meV. The INS spectra of crystal ices in the acoustical region could be fitted by a Debye expression $G(\omega)=A\omega^2$, where A is a constant that depends on elastic coefficients of ices.[15] Therefore, in this figure there should be no peaks in this region for crystalline ices and the height of the spectra inversely proportions to elastic coefficient (the interactions between cells). The spectrum of silica gel containing 3% water clearly shows two peaks (2.6 and 4 meV), while a peak located at 4.8 meV can been seen in the local-density approximation ice spectrum, and no peak appears in silica gel with 10% water spectrum. These peaks (with an excess of low-frequency vibration modes over the normal ice *Ih* spectrum) relate to transverse acoustic vibrations due to broken hydrogen bonds in these loose stacking amorphous ices or on surfaces/interfaces.[16] Figure 3(c) shows these amorphous ice spectra subtracted by the ice *Ih* spectrum. In lower water concentrations the peak is located at 4.5 meV. As water concentration increases to 10% the peak shifts to 5.8 meV and its intensity significantly decreases. The peak from lda ice lies between them at 5 meV. This peak moving to high energy means that more hydrogen bonds are built (cluster growing bigger).

In conclusion, a small amount of H_2O remaining in silica gel shows a series of abnormal properties compared to bulk ice. First, it stacks loosely and displays very weak bending interactions (even at 5 K it gives a librational band similar to that of liquid). Second, a significant excess of low frequency vibration modes over normal ice *Ih* was observed which is related to transverse acoustic vibrations due to broken or distorted hydrogen bonds. Third, a very wide acoustic peak was observed because of high frequency vibration mode dropping.

We acknowledge the RAL (ISIS, UK) for providing the neutron research facilities, and would also like to thank Dr. A.I. Kolesnikov for his guidance and support through the duration of the experiments. This work was supported by the National Natural Foundation of China (Grant No. 10274034) and by the Scientific Research Foundation for the Returned Overseas Chinese Scholars, State Education Ministry (SRF for ROCS, SEM).

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*Author to whom correspondence should be addressed.

[1] J. S. Clegg and W. Drost-Hansen, in *Phylogenetic and Biochemical Perspectives*, edited by P. W. Hochachka and T. P. Mommsen (Elsevier, New York, 1991), pp. 1–23.

[2] G. Litvan, J. Colloid Interface Sci. **38**, 75 (1972).

[3] D. C. Steytler, J. C. Dore, and C. J. Wright, J. Phys. Chem. **87**, 2458 (1983).

[4] P. V. Hobbs, *Ice Physics* (Clarendon, Oxford, 1974); C. A. Angell, in *Water: A Comprehensive Treatise*, edited by F. Franks (Plenum, New York, 1981), Vol. 7, Chap. 1; S. H. Chen and J. Teixeira, Adv. Chem. Phys. **64**, 1 (1985); M. C. Bellissent-Funal and J. Teixeira, J. Mol. Struct. **250**, 213 (1991).

[5] A. I. Kolesnikov, J. C. Li, D. K. Ross, O. I. Barkalov, V. V. Sinitsyn, and E. G. Ponyatovsky, Phys. Lett. A **168**, 308 (1992); A. I. Kolesnikov, J. C. Li, S. F. Parker, R. S. Eccleston, and C. K. Loong, Phys. Rev. B **59**, 3569 (1999); A. I. Kolesnikov, J. C. Li, S. Dong, I. E. Bailey, R. S. Eccleston, W. Hahn, and S. F. Parker, Phys. Rev. Lett. **79**, 1869 (1997).

[6] F. Bruni, M. A. Ricci, and A. K. Soper, J. Chem. Phys. **109**, 1478 (1998); A. K. Soper, F. Bruni, and M. A. Ricci, *ibid.* **109**, 1486 (1998); S. H. Chen and M. C. Bellissent-Funel, in *Hydrogen Bond Networks*, Vol. 435 of *NATO Advanced Study Institute, Series C: Mathematical and Physical Sciences*, edited by M. C. Bellissent-Funel and J. C. Dore (Kluwer, Dordrecht, 1994), p. 307.

[7] C. F. Polnazek, D. A. Hanggi, P. W. Carr, and R. G. Bryant, Anal. Chim. Acta **194**, 311 (1987); C. F. Polnazek and R. G. Bryant, J. Am. Chem. Soc. **106**, 428 (1984); J. Chem. Phys. **81**, 4038 (1984).

[8] J. C. Dore, D. C. Steytler, and C. J. Wright, J. Mol. Phys. **48**, 1031 (1983); D. C. Steytler, J. C. Dore, and C. J. Wright, J. Phys. Chem. **87**, 2458 (1983); M. C. Bellissent-Funel, J. Lal, and L. Bosio, J. Chem. Phys. **98**, 4246 (1993).

[9] M. C. Bellissent-Funel, S. H. Chen, and J. M. Zanotti, Phys. Rev. E **51**, 4558 (1995).

[10] E. F. Sheka, V. Khavryutchenko, I. Natkaniec, V. Ogenko, I. Markichev, A. Muzychka, and P. Nechitailov, Physica B **174**, 182 (1991); E. F. Sheka, I. Natkaniec, V. D. Khavryutchenko, P. B. Nechitailov, A. Yu. Musychka, V. M. Ogenko, I. V. Markichev, J. Brankowski, and J. Krawczyk, J. Electron Spectrosc. Relat. Phenom. **54/55**, 855 (1990).

[11] S. F. Parker, K. E. Horton and J. Tomkinson, *The TFXA User's Guide*, Rutherford Appleton Laboratory, Technical Report No. RAL-TR-95-036, 1995.

[12] S. L. Dong, Y. Wang, A. I. Kolesnikov, and J. C. Li, J. Chem. Phys. **109**, 235 (1998); K. Skold and D. L. Price, in *Neutron Scattering* (Academic, London, 1986), Part A, Vol. 23, p. 1.

[13] B. Kamb, W. C. Hamilton, S. J. LaPlace, and A. Prakash, J. Chem. Phys. **55**, 1934 (1971); W. F. Kuhs, J. L. Finney, C. Vettier, and D. V. Bliss *ibid.* **81**, 3612 (1984).

[14] S. Dong, A. I. Kolesnikov, and J. C. Li, J. Phys. Chem. B **101**, 6087 (1997).

[15] J. C. Li, J. Chem. Phys. **105**, 6733 (1996).

[16] M. T. Dove, M. J. Harris, A. C. Hannon, J. M. Parker, I. P. Swainson, and M. Gambhir, Phys. Rev. Lett. **78**, 1070 (1997); J. Horbach, W. Kob, and K. Binder, Eur. Phys. J. B **19**, 531 (2001); A. Paciaroni, A. R. Bizzarri, and S. Cannistraro, Phys. Rev. E **60**, R2476 (1999).