X-Ray Emission Spectroscopy of Hydrogen Bonding and Electronic Structure of Liquid Water

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We use x-ray emission spectroscopy to examine the influence of the intermolecular interaction on the local electronic structure of liquid water. By comparing x-ray emission spectra of the water molecule and liquid water, we find a strong involvement of the a_1-symmetry valence-orbital in the hydrogen bonding. The local electronic structure of water molecules, where one hydrogen bond is broken at the hydrogen site, is separately determined. Our results provide an illustration of the important potential of x-ray emission spectroscopy for elucidating basic features of liquids.

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Water is the most abundant substance on our planet, and it is the principal constituent of all living organisms. Chemical reactions taking place in liquid water are essential for many important processes in electrochemistry, environmental science, pharmaceutical science, and biology in general. Many models have been proposed to view the details of how liquid water is geometrically organized by hydrogen-bond network. Hydrogen bond is an attractive interaction in a link between hydrogen atom and one of the highly electronegative and nonmetallic elements which contains a lone pair of electrons. Although H bonds are much weaker than conventional chemical bonds, they have important consequences on the properties of water. Diffraction of x rays [1] and neutrons [2] provides strong evidence that tetrahedral hydrogen-bond order persists beyond the melting transition, but with substantial disorder present [3]. Important questions remain about the precise nature of the disorder and how it is spatially manifested.

Questions about intermolecular forces and hydrogen-bond rearrangements have been addressed by studying the structure and dynamics of small water clusters by far-infrared vibration-rotation tunneling spectroscopy [4–8]. A very important but hitherto less addressed question is that of the hydrogen-bond effect on the electronic structure. This effect is essential for understanding the physical and chemical properties of many chemical and biological systems. The reason for this neglect, however, is the limited experimental access to the electronic structure of liquids. Hence, even understanding the properties of pure liquid water remains a challenge. Several investigations concerning the electronic structure of water vapor and ice have been carried out, using photoelectron spectroscopy [9–11] and x-ray emission spectroscopy [12–15]. In all cases the spectral differences between water vapor and ice suggested that upon solidification the water molecule undergoes appreciable changes in its electronics structure. In a recent x-ray absorption spectroscopic study of liquid water the signature of specific hydrogen-bond breaking was identified in the spectra [16]. In spite of intense research activities it is still largely unknown how the electronic structure of the water molecule is affected by the hydrogen bonds in the liquid phase.

In this Letter we report resonant x-ray emission spectra of liquid water, monitoring the influence of the intermolecular interaction on the local electronic structure. By comparing x-ray emission spectra of H_2O molecule and liquid water, we observe a strong involvement of a_1-symmetry valence orbitals in the hydrogen bonding. The local electronic structure of water molecules, where one hydrogen bond is broken at the hydrogen site, is separately determined.

X-ray transitions, where a core-level vacancy is filled by a valence-orbital electron, give direct information about the chemical bonding. While such transitions have been analyzed using x-ray spectrometers since the late 1920s, the interest in the technique is presently booming due to the advent of third generation synchrotron radiation sources. The feasibility to selectively excite core hole states using photons of well-defined energy, momentum, and polarization has substantially enhanced the potential of x-ray spectroscopy. In addition to the inherent elemental selectivity of x-ray spectra, energy selective excitation allows separation of features that pertain to different atoms of a sample. Emission from chemically nonequivalent sites of the same atomic species can be separated [17,18]. Today the method is frequently applied in research fields ranging from atomic and molecular physics to materials research [19].

The application of spectroscopic methods to study the electronic structure of liquids has been hampered by the incompatibility of wet samples and high-vacuum conditions. Here we take advantage of the large photon attenuation length to perform the first x-ray emission study of liquid water. A thin window (1000 Å silicon nitride), separating the liquid from the surrounding vacuum, is penetrated both by the exciting synchrotron radiation and the secondary x-ray emission. The transmission of such thin silicon nitride window for x rays at the O *K* edge (525 eV) is up to 70%. The base pressure in the experimental chamber was maintained at 1×10^{-9} Torr during the measurements. The experiments were performed at beamline 7.0.1 at the Advanced Light Source (ALS), Lawrence Berkeley National Laboratory [20]. X-ray emission spectra of the H_2O molecule were recorded for reference, again using thin windows to separate the water vapor sample from the vacuum. The detailed description of the gas cell can be found in previous publications where the same experimental system was used in the study of small molecules [21,22]. We used a high resolution grating spectrometer [23], mounted parallel to the polarization vector of the incident photon beam. X-ray absorption spectra of liquid water were also measured in fluorescence yield mode with the same setup.

To interpret the experimental results, calculations were carried out at the Hartree-Fock level with Sadlej [24] basis set using the DALTON program [25] on 32 nodes of the T3E computers at the National Supercomputer Center (NSC) in Linköping, Sweden. The Hartree-Fock approach has been successfully applied to calculate the x-ray emission spectra of molecules, fullerenes, and polymers [26–28]. More importantly, the orbital picture provided by the Hartree-Fock model can be directly used to interpret the experimental spectra. The theoretical x-ray emission spectra of the H_2O molecule and liquid water were generated by the group theory formulation developed by Luo *et al.* [29]. Spectra were calculated for liquid water structures containing 26 to 28 water molecules, generated by molecular dynamic simulations [30]. The long-range molecular interactions have been taken into account by embedding the clusters into a dielectric medium.

The water molecule has C_{2v} symmetry with the electronic configuration $1a_1^2 2a_1^2 1b_1^2 3a_1^2 1b_1^2$. The x-ray emission spectrum (Fig. 1) of the water molecule is dominated by transitions from the three occupied oxygen $2p$-derived orbitals, $1b_2$, $3a_1$, and $1b_1$, to the oxygen $1s$ orbital ($1a_1$). The $1b_2$ and $3a_1$ orbitals, which are oriented in the plane defined by the nuclei, are mainly responsible for the OH bonding, and they mix considerably with the hydrogen orbitals. The $1b_2$ orbital is antisymmetric with respect to the bonds, whereas the $3a_1$ orbital has its nodal plane perpendicular to both symmetry planes of the molecule (Fig. 1). The $1b_1$ orbital is the so-called "lone pair" orbital with the nodal plane coinciding with the plane defined by the nuclear positions. The intensity and the natural width of the peaks in the x-ray emission spectrum reflect the characters of the orbitals. The almost pure p character of the lone pair orbital implies large x-ray intensity for transitions to the $1s$ orbital. Transitions from the $1b_2$ and $3a_1$ orbitals give less intensity because they have less oxygen p character. In addition, vibrational excitations associated with their bonding character give rise to broader spectral lines compared to the $1b_1$ band. As we have shown earlier, the x-ray emission spectrum of the free molecule [15] can be accurately described [31], only when the vibrations are taken explicitly into account. Since the present analysis disregards vibrational effects there is a small discrepancy between theory and experiment regarding linewidths and energy positions. The nonresonantly excited x-ray emission spectrum of liquid water is similar to that of the free water molecule. The most evident change upon condensation is an apparent relative intensity loss in the region corresponding to the $3a_1$ orbital. This behavior is accounted for by theory. We note also that the general trend is the same when comparing x-ray emission spectra of water vapor and ice.

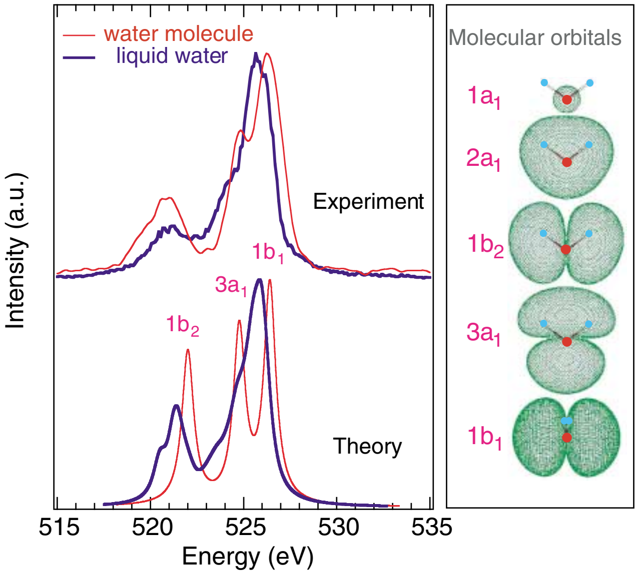

FIG. 1 (color online). X-ray emission spectra of the water molecules and liquid water, formed as electrons from the three outermost occupied molecular orbitals, schematically depicted in the right panel, fill a vacancy in the $1a_1$ core-level. The excitation-energy is 543 eV, well above the ionization limit but sufficiently low so that the emission from multiply excited states can be neglected.

The width of the $1b_1$ band in the gas-phase spectrum is dominated by the experimental broadening, since the natural width of this peak is less than 0.3 eV [15]. The width of the $1b_1$ band in liquid water (1.5 eV) is not limited by the experimental resolution, and hence, the predicted broadening upon condensation is confirmed by the observation. Below we present a detailed analysis of how the influence of hydrogen bonding on electronic structure is reflected in the x-ray emission spectrum.

Our calculations show that the major influence of the hydrogen bonding on the local electronic structure is due to the first coordination shell. The energy levels are split (Fig. 2) as the three orbitals interact with the orbitals of the surrounding molecules. First we note the behavior of the $1b_2$ peak in the 520–521 eV region. An underlying two-peak structure is formed with the first hydrogen bond (Fig. 2(b)), but with two bonds some stabilization seems to occur so that only one of the three states gets appreciable x-ray intensity (Fig. 2(c)). This is repeated when

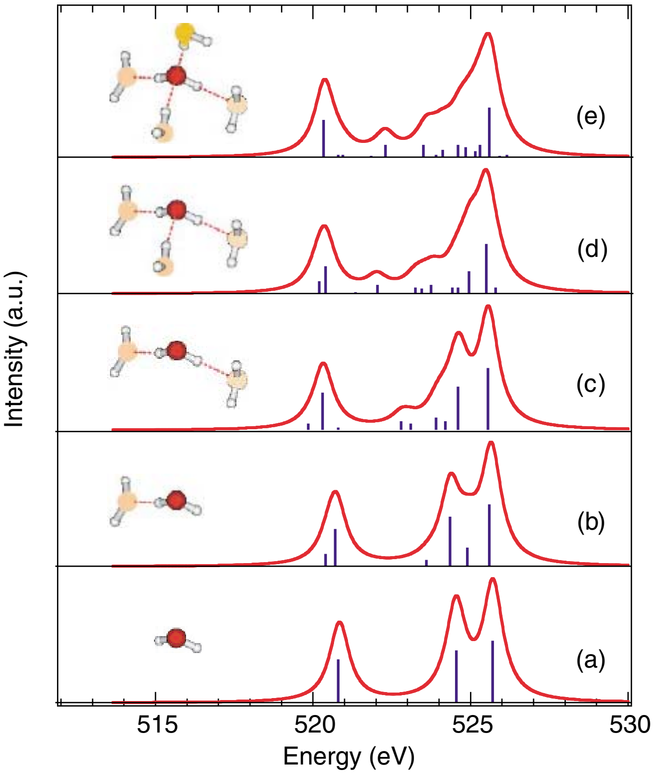

FIG. 2 (color online). The influence on the local electronic structure due to hydrogen bonds formed by surrounding water molecules, is monitored by calculated x-ray emission spectra. Note the single water molecule influenced by its neighbors (see spectrum *a*) and the strong mixing of the $3a_1$ states upon the formation of hydrogen bonds.

additional hydrogen bonds are introduced (Fig. 2(d)), so that the local character of the state is again restored with four hydrogen bonds (Fig. 2(e)). The discussion for the $1b_1$ peak, between 525 and 526 eV, is analogous.

The situation is completely different for the $3a_1$ state, the character of which is entirely changed due to the influence of the hydrogen bonding. From electrostatic considerations it is obvious that both donor and acceptor hydrogen bonds tend to increase the local dipole moment of the molecule. As the $3a_1$ orbital has the nodal plane perpendicular to the direction of the electric dipole moment of the water molecule, it is likely to show the largest polarizability in this direction. Electron density is transferred from the lobe enclosing the hydrogen nuclei towards the oxygen lobe. Here the orbital mixes substantially with the orbitals of the neighboring molecules and its original character is lost. From this analysis it is apparent that valence states of a_1 symmetry are most involved in the hydrogen bonding. We believe that the large increase in dipole moment upon condensation of water molecules [32] can be primarily attributed to polarization and hybridization of the $3a_1$ orbital.

Pauling stated that the electron sharing between water molecules results in the covalency in the hydrogen bond [33]. Isaacs *et al.* [34] observed periodic intensity variations in their Compton scattering measurement, which they claimed as a direct evidence for the substantial covalent nature of the hydrogen bond. Such an explanation was challenged by theoretical calculations of Ghanty *et al.* [35]. Their calculations for the water dimer reproduced the oscillation in the intensity of the scattered x-ray beam seen by Isaacs *et al.* but indicated no covalent bonding between the two molecules. The changes of the $3a_1$ orbitals revealed by the x-ray emission spectra provide direct experimental evidence that there is electron sharing between water molecules, which would nicely confirm the classical prediction of Pauling (similar changes of the $3a_1$ orbital have previously been observed in photoemission [9–11] and x-ray emission [12–14] spectra of gas-phase water and ice). However, it was claimed in the paper of Ghanty *et al.* that coordinate-covalent bonding (also called donor-acceptor or Lewis acid-base bonding) should be defined as the sharing of an electron pair of one molecule via an empty orbital of the other. Under this definition, the covalent bond between two water molecules would primarily affect the outmost orbital ($1b_1$). Covalency in this sense is not supported by our experimental results.

It is known that a network with four hydrogen bonds connects the majority of the water molecules in the liquid phase. Such a network can often be terminated by local structures with three or even two hydrogen bonds. The recently published x-ray absorption spectrum of liquid water [16] suggests that the four hydrogen-bonding networks mainly contribute to a single broad feature, while a shoulder located at 534.7 eV suggests the presence of the broken hydrogen bonds. Indeed, recent theoretical simulations assign this pre-edge structure to a particular three-hydrogen bond structure with one missing hydrogen bond at the hydrogen site [16].

This assignment is fully confirmed by x-ray emission spectra, selectively excited on this particular pre-edge shoulder (Fig. 3). We use the same notations as Myneni *et al.* [16] for the local hydrogen-bond structures of the water molecules: a symmetric species with four H bonds (denoted as SYM) and other two structures defined as asymmetry in the length of the two H bonds *accepted* by the water molecule (A-ASYM) or asymmetry of the two H bonds *donated* by the water molecule (D-ASYM). Different local structures provide different nonresonant spectra because of their different valence band structures. The nonresonant spectrum should be a summation of the ones from all different structures. However, since the SYM is the dominating structure in the liquid water, its nonresonant spectrum is close to the experimental one. Compared to the nonresonant spectrum we observe a substantial narrowing of the $1b_1$ peak, and a further attenuation of the $3a_1$-associated structure. This is in excellent agreement with the predictions for the D-ASYM. Note that the alternative molecular arrangements

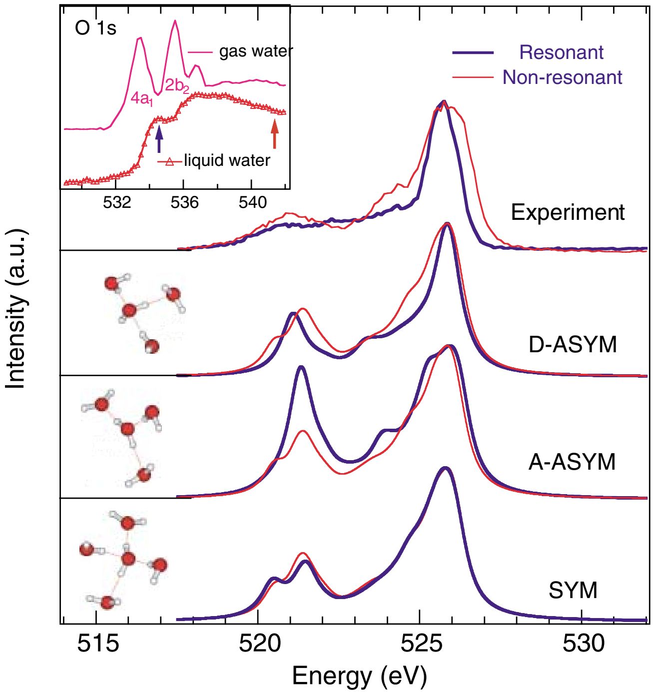

FIG. 3 (color online). The sharp structures in the x-ray absorption spectrum of the water molecule (inset) are smeared out in the liquid water due to the diffuse nature of the corresponding molecular orbitals. A prepeak is resolved at 534.7 eV in the spectrum of liquid water. The arrows indicate the photon energies used for resonantly and nonresonantly excited x-ray emission spectra. The resonantly excited spectrum is in good agreement with the prediction for the three-bonded D-ASYM configuration.

lead to predictions, which do not even qualitatively account for the observations: Contrary to the observations the A-ASYM structure would induce a large relative increase in $1b_2$ intensity, and a broadening of the $1b_1$ peak. If the prepeak were not associated with broken bonds, there would be no significant excitation-energy dependence at all.

We conclude that x-ray emission spectra reveal the influence of hydrogen bonding on the local electronic structure of liquid water. We found a strong involvement of a_1-symmetry valence orbitals in the hydrogen bonding. Nonresonantly excited spectra mainly reflect the electronic structure of molecules with four hydrogen bonds. Resonantly excited spectra show the electronic structure of configurations where one hydrogen bond has been broken at a hydrogen site. Our results provide an informative illustration of the important potential of x-ray emission spectroscopy for elucidating basic features of liquids.

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