Anomalous Ground State of the Electrons in Nanoconfined Water

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Water confined on the scale of 20 Å, is known to have different transport and thermodynamic properties from that of bulk water, and the proton momentum distribution has recently been shown to have qualitatively different properties from that exhibited in bulk water. The electronic ground state of nanoconfined water must be responsible for these anomalies but has so far not been investigated. We show here for the first time, using x-ray Compton scattering and a computational model, that the ground state configuration of the valence electrons in a particular nanoconfined water system, Nafion, is so different from that of bulk water that the weakly electrostatically interacting molecule model of water is clearly inapplicable. We argue that this is a generic property of nanoconfinement. The present results demonstrate that the electrons, and hence the protons as well, of nanoconfined water are in a distinctly different quantum state from that of bulk water. Biological cell function must make use of the properties of this state and cannot be expected to be described correctly by empirical models based on the weakly interacting molecules model.

Nanoconfined water is known to exhibit equilibrium and dynamical properties that are different from that of bulk water [1]. To the extent that the properties of nanoconfined water have been theoretically interpreted, it has been primarily on the basis of empirical potential models of water, which assume that water is made up of molecules weakly interacting (on the scale of the zero point bond energy $\sim.2$ eV) electrostatically with their neighbors [2,3]. In an earlier work, we have suggested that these models, even when polarization and flexibility are included, and calibrated against *ab initio* calculations, are inadequate to describe the proton momentum distribution in water confined in carbon nanotubes, xerogel, and Nafion [4]. Indeed, they are even quantitatively unable to explain the proton momentum distribution in bulk water at room temperature and atmospheric pressure [5]. We have suggested it is the electronic properties of the hydrogen bond network that are responsible for the differences; i.e., the electronic overlap between acceptor oxygens and donor protons in the hydrogen bond is sufficiently strong for nanoconfined water that the network as a whole can respond in ways which are not possible for a collection of molecules interacting weakly electrostatically. These changes in the spatial distribution of valence electrons in nanoconfined water will be reflected in the momentum distribution of the electrons, and, if the deviations of the ground state from that of bulk water are sufficiently large, should be observable utilizing x-ray Compton scattering.

We show, for the first time, that these changes in the electronic ground state of water upon confinement can indeed be observed, and are far too large to be explainable

within the weakly interacting molecule model. We present a reinterpretation of fluorescence [6] and pump probe experiments [7] by others to support the conclusion that the electronic state of nanoconfined water is qualitatively different from that of bulk water.

In this Letter, we restrict our discussion to water confined in Nafion. The results for water confined in carbon nanotubes will be presented separately. Nafion is a perfluorosulfonic acid ionomer widely used as the proton exchange membrane in commercial fuel cells. The samples used for the present measurements, Nafion 1120 and Dow 858 (a short side chain version of Nafion), were the same as those used in the neutron Compton scattering measurements [4]. The two samples have very different conductivities at the same water content, and were originally chosen to see if the conductivity difference was reflected in the proton momentum distributions, which it is. Here they provide a demonstration that the results we obtain are largely independent of the morphology of the samples. These are ionomers with hydrophobic poly-tetrafluoroethylene backbones and randomly pendant perfluoroether side chains terminating with sulfonic acids [8]. The ionomers when hydrated exhibit a nanophase separated morphology where the water and ions exist in domains which are only a few nanometers in diameter surrounded by ionomer backbones [9,10]. The sulfonic acid groups ($- SO_3H$) donate protons to the water, when there is sufficient water, making them very good proton conductors, and hence their use as the proton exchange membrane in commercial fuel cells. The samples prepared were cleaned in 20% nitric acid, and DI (deionized) water at 80 °C, then rinsed with room temperature

water, and finally loaded with water by equilibration with the saturated vapor of a 1 molal LiCl salt solution, beginning with a fully saturated sample, for two weeks [11]. The LiCl is used only to calibrate the water vapor pressure, and hence the absorption of the water by the Nafion films. The LiCl is left back in solution. The concentration of water relative to the number of sulfonic acid groups, λ, was 14, the same as was used in the neutron experiments. The samples were sealed in the x-ray sample cells while in contact with the vapor to avoid any loss of water in the atmosphere. The samples were carefully monitored, weighed before and after the measurements, and showed no significant weight change. A dry sample was prepared by leaving the sample in vacuum for five days at room temperature. A measurement of the dry sample was performed as background as shown in Fig. 1, before filling the samples with water. The signal from the dry Nafion was subtracted from that of the hydrated sample to obtain the signal for the confined water (Fig. 1). It is known from the

atomic CP [12] that the core electron contribution from water is almost zero for momentum higher than $q \sim 3$ a.u. (~ 112.3 keV in Fig. 1). The background signal subtraction for both water in Nafion and DI water was performed very carefully (Fig. 1) by scaling the amplitudes of the signal and background in such a way that resultant Compton profile of water in Nafion and DI water becomes zero at momenta higher than $q \sim 3$ a.u. i.e., since the tail of the distribution for both wet and dry samples is due entirely to the core electrons in the Nafion (and sample holder), matching the intensity there allows for the subtraction of the background from the dry sample at all momenta. We note that even if the nominally dry sample still contains some water (1–3 molecules per sulfonic acid group) this subtraction will remove their contribution, so we see only the signal from the free water that was added.

The experiments were performed at the BL08W, high energy inelastic scattering beam line at SPring-8, Japan. The measurements were performed at incident energy of 182 keV, at a scattering angle of 178.3° and the scattered photons were collected utilizing a ten-element Ge solid-state detector. The samples were confined in a 3 mm thick Al sample holder, with Kapton windows (~ 10 μm thick) used as the x-ray window and the sample was placed in a vacuum chamber to minimize the background due to scattering from air. All the measurements were performed at room temperature and as large statistics are necessary to observe the small changes between the confined and the bulk water, the data were constantly monitored by checking for consistency, i.e., for variation larger than the statistical accuracy, after every 12 minutes. To obtain good statistics, the total counts in each raw spectrum under the Compton peak was more than 1×10^9 counts. The measured spectra were then corrected for the necessary energy dependent corrections, absorption, detector efficiency, and multiple scattering, before converting to the momentum scale utilizing the relativistic cross-section correction. Furthermore, during our data processing, we also did careful evaluation of the effects of the multiple scattering contributions and changing thickness due to the swelling of the Nafion, on our results. For this we performed number of simulations [13] of double scattering contributions with different sample compositions (dry and wet) and different thickness from Nafion swelling. These simulations showed that the effect of different multiple scattering between dry and wet Nafion on the result is $\Delta J(q)/J(0) \sim 0.05$, which is ten times smaller than the experimental results. The effect of swelling ($\sim 5\%$ difference of thickness) is $\Delta J(q)/J(0) \sim 0.001$. In both cases, the difference profiles are smaller than the experimental results. Hence, we here can neglect the possibility of different multiple scattering effect and the sample swelling effect. The Compton profiles (CPs) were then binned at steps of 0.1 a.u. and the positive and the negative momentum sides were folded to increase the statistical accuracy (see Supplemental
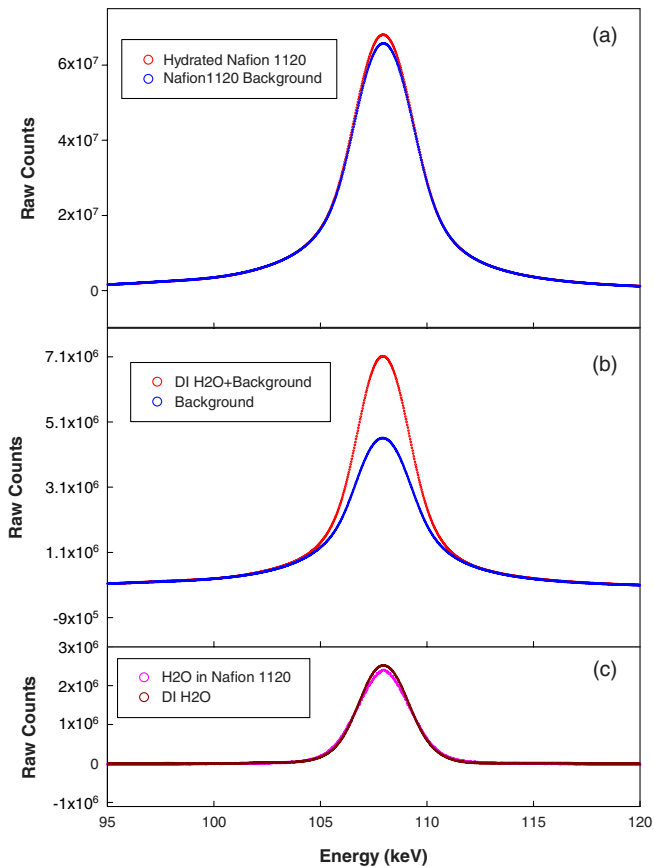

FIG. 1 (color online). Comparison of Compton profile of (a) Hydrated Nafion 1120 (red), and background from dry Nafion 1120 (blue); (b) deionized (DI) water with background (red) and background only (blue); (c) water in Nafion 1120, obtained from subtracting the CP of background from CP of hydrated Nafion 1120 (pink), de-ionized water, obtained from subtracting the CP of background from CP of DI water with background (dark red).

Material [14]). A sample, in the same sample holder containing bulk DI water was also measured under the same experimental conditions. The valence-electron CPs of the confined and bulk samples were obtained by subtracting the theoretical core electron profile contribution from the experimental profiles. The theoretical core-profile contribution was taken based on the free-atom Hartree-Fock simulations [12] where we have treated oxygen $(1s)^2$ as the core electrons, and finally as we are comparing the subtle shape changes of the CPs between the bulk and the confined water, the CP's were carefully again renormalized to 8 valence electrons, for proper comparison. The water profile was in good agreement with an earlier theoretical model [15] and is shown in the inset of Fig. 2.

The CP's for the two Nafion samples and bulk water are also shown in the inset of Fig. 2. The subtracted profile for the two samples has been compared with a calculation by Nygård *et al.* [16] of the difference between the CPs of H_2O and D_2O. This should be regarded as a phenomenological fit, as the amplitude of the difference profile has been adjusted to fit our data by a factor of nearly fifty. The D_2O was chosen for comparison as the shape of the difference profile was qualitatively similar to the profile in the nanoconfined water, and we expect the effects we are seeing to be due to differences in the zero point motion of the nanoconfined protons from that in bulk water. These calculations are based on the use of a dimer approximation, in which the molecules retain their identity as the distribution of angles and bond lengths for the hydrogen bond is varied. Within this approximation, which is based on the weakly interacting molecules picture, it is assumed that all the reordering of the electron distribution is due to changes in the configuration of the hydrogen bond between a
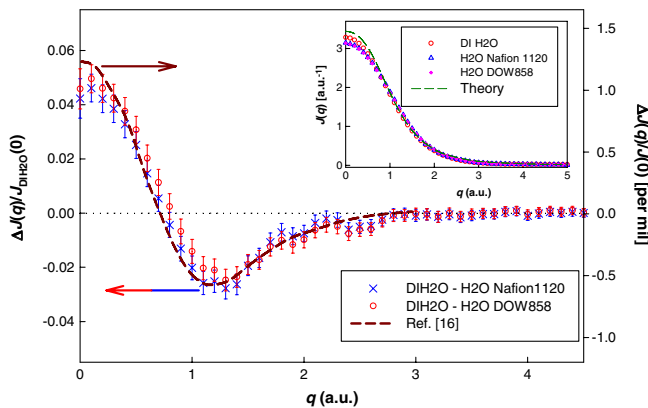
single donor and single acceptor water molecule. This approximation has been used to satisfactorily fit a series of CPs for bulk water between temperatures 5 °C and 90 °C [17].

From Fig. 2, the maximum amplitude of $[\Delta J(0)/J(0)]$, the fractional change in the Compton profile at zero momentum ($q = 0$), for confined water is 0.05. By way of contrast, the maximum difference in $[\Delta J(0)/J(0)]$ between water at 5 °C and 90 °C is only 0.003 [17]. Taken as a measure of the electronic disorder of the hydrogen bond network, the disordering of the hydrogen bond network due to the confinement is 17 times that produced by the thermal disordering in going from just above freezing to just below boiling. It is 46 times the difference between the CPs of H_2O and D_2O at comparable temperatures.

The distribution of valence electrons determines the potential (Born-Oppenheimer) seen by the protons. The electron picture can now be related to the proton picture. The proton momentum distribution for the two Nafion samples compared to that of water is shown in Ref. [4] and the Supplemental Material [14]. The oscillations are indicative of the proton being coherently distributed in a double well with a separation of the wells on the order of 0.3 Å, as determined by the position of the minimum [18]. The kinetic energy has gone up because each of these wells is more tightly binding the proton than the covalent bond of the isolated water molecule. The kinetic energy is 245 and 268 meV for the Nafion and Dow samples respectively, compared to 148 meV for bulk water at room temperature. The change in kinetic energy in going from 5 °C to 90 °C for bulk water, including the changes in the kinetic energy of the translational and rotational modes of the free molecule, is only ~3 meV [3]. The change in kinetic energy of the protons measures the degree of localization of the proton provided by the potential due to the electronic system. Thus we expect much larger changes in the CP from nanoconfining water than we do in heating it, as observed.

The direction of the change for the electron CP is also consistent with the tighter binding of the proton, which we would expect to require a greater localization of the valence electrons in the vicinity of the proton, and hence a broader electron CP, as observed. Based on the calculations of Ref. [17], to achieve the large changes observed in the CP in the Nafion samples by disordering individual hydrogen bonds would require unphysical hydrogen bond lengths, and would put us far outside the weakly interacting molecules picture.

It is conceivable that the changes we are seeing here are the result of changes in the electron distribution in the ionomer due to the morphological changes that occur as the water swells the dry Nafion. This is unlikely, since the carbon-fluorine bonds that describe the ionomer (Teflon) are unlikely to be affected significantly by the physical displacements of the ionomer or by interaction with the

FIG. 2 (color online).   The difference CP of Nafion 1120 and Dow 858 subtracted from the CP of bulk water. The red dashed line (Ref. [16]) is a fit to the difference (H_2O-D_2O) between H_2O and D_2O, rescaled to fit our data; a rescaling by a factor of 46 is needed. The inset shows the experimental CP for DI water, confined water in two types of Nafion (Nafion 1120 and DOW 858) and a previous reported (Ref. [15]) theoretical CP (green dashed line) of isolated water molecule.

water molecules. Furthermore, the two different samples have distinct morphologies, due to the difference in the length of the side chains containing the sulfonic acid groups, but nevertheless, yield very similar subtracted *CP*s (between the confined water in these materials and bulk water), Fig. 2, that are nearly within the error bars of each other.

It might also be thought that the presence of the extra protons, donated by the sulfonic acid groups (and responsible for the conductivity of Nafion) is changing the electron distribution in its vicinity sufficiently to make up the large difference in the subtracted electron *CP*. Beyond the fact that there is only 1 proton in 28 which is free, we have the evidence of experiments and calculations on LiCl, which is known to strongly disorder the hydrogen bond network, that the changes of $[\Delta J(0)/J(0)]$ from bulk water at similar concentrations of Li, are of the order of 0.005 [19]. The lack of a dramatic effect from free protons in the electron Compton scattering is mirrored in the neutron Compton scattering from weak acids (HCl), where only small deviations of the momentum distribution from that of bulk water are seen at proton concentrations equivalent to that of the Lithium in the experiment above [20] or the free protons in the Nafion materials of this experiment.

We conclude that the quantum ground state of the electron-proton system when the hydrogen bond network is disordered by nanoconfinement is qualitatively different from the ground state of a weakly interacting collection of molecules. The network appears to be responding to the disorder due to nanoconfinement, not as collection of nearly uncorrelated molecules but as a correlated system over distances on the order of 20 Å.

Support for this point of view comes from excited state proton transfer measurements of a fluorescent molecule (8-hydroxypyrene-2,3,6 trisulfonate) used as a probe for the proton dynamics [6,7]. The molecule tends to stay in the middle of the water filled regions in the Nafion. The electronic state is excited by a laser pulse, which leads to the proton in the OH group of the molecule being ionized. The recombination time depends on the transport processes affecting the now free proton. Assuming a diffusion process for that transport leads to a $t^{-1.5}$ dependence of the rate of recombination for long recombination times. This is what has been observed in bulk water, while in Nafion the observed rate is $t^{-0.8}$. Evidently, the transport of the proton is not a diffusion process. It would be a diffusion process for long times as long as the "jumps" of the proton from one location to another are determined by the local conditions in the vicinity of the proton as it moves from one equivalent position to another, and there is no memory of where the proton came from on the next jump. One or both of these conditions must be violated in the transport of protons in Nafion. Any process in which there is a jump time to move from one position to another uncorrelated position will lead to a diffusion process at long times. To

change the exponent requires some collective response of the hydrogen bond electron-proton network to the motion of the proton. That this response is a property of confined water and not some peculiarity of Nafion is demonstrated by the fact that the same behavior is seen in reverse micelles of comparable size to the pores of Nafion [21].

Further support for our observation of dramatic changes in the electronic state of confined water is found in the observation in small reverse micelles of a fast (20 ps) nonradiative decay of the excited state of 8-hydroxypyrene-2,3,6 trisulfonate, without any ionization of the proton [7]. This has been attributed to the interaction with the ionomer, but we interpret this as due to transfer of the excitation to the excited states of the confined water electronic state, a possibility not available for the electronic state of bulk water.

We conjecture that correlated motion of the protons, together with the possibility of the electrons responding as a network, (thus not limited to charge fluctuations on a single molecule to lower the energy of the system), are responsible for the large deviations of the quantum ground state of the protons and electrons from that of bulk water. Some support for this is contained in the observation that correlated motion of the protons in KH_2PO_4 is necessary to produce the double well potentials and momentum distributions observed there [22]. This material has a polarizable core phosphate group hydrogen bonded to two protons that satisfy ice rules identical to those in water. Confinement presumably frustrates the usual tetragonal hydrogen bonded configuration of distinct molecules, allowing a different ground state to be present.

To summarize, the changes in the configuration of the valence electrons in water nano-confined in Nafion, as observed by the *CP*, are far too large to be interpreted within a model in which these changes are due to local variations in individual hydrogen bonds that have been disordered by the confinement. They are consistent with, and responsible for, the large changes in the proton ground state previously observed in the proton momentum distribution. The present results clearly demonstrate that the electron-proton system ground state is qualitatively different in nanoconfined water from that of bulk water. The state appears to be responding to the disorder of nanoconfinement not as a collection of molecules, but as a network with a coherence length of about 20 Å. As the fluorescence experiments already make clear, the transport of protons in Nafion is dramatically different from that in bulk water. That the coherence plays a role in this is suggested by the fact that the Dow material, with a visibly larger (See Supplemental Material [14]) percentage of the protons distributed coherently in double wells, has nearly 50% higher conductivity than the Nafion material [7]. In as much as 20 Å is the characteristic distance between elements of biological cells, the energetics of the interactions between these elements, and hence some of the properties

of water that make life possible, are determined by this state, not the molecular state. It has already been demonstrated that changes in the zero-point motion of the protons can produce binding of water molecules to dry DNA [23], and that the protons in a partial layer of water on the surface of lysozyme has a delocalized momentum distribution similar to those described here [24,25]. Simulations based on empirical potential models of water cannot be expected to give these properties correctly.

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