

## Extended X-Ray Absorption Fine Structure from Hydrogen Atoms in Water

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We report the first quantitative measurement of extended x-ray absorption fine structure (EXAFS) from hydrogen atoms. A single oscillation is observed from gaseous water consistent with the location of the covalently bonded hydrogen in H<sub>2</sub>O. The experimental phase and amplitude of the oscillation are in excellent agreement with curved wave multiple scattering calculations for isolated water molecules. With this determination of the O-H scattering phase shift we have quantified the covalent hydrogen bond distance ( $0.95 \pm 0.03$  Å) in liquid water, thus demonstrating that hydrogen EXAFS can become a valuable complement to existing structural methods in chemistry and biology.

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X-ray scattering is one of the principal tools used for modern structure determination in chemistry and biology. It is conventional wisdom that hydrogen atoms remain “invisible” to traditional x-ray and electron diffraction techniques. As a result, x-ray studies of many important chemical and biological systems yield only partial structure functions. For example, the atom pair correlation function for liquid water can be obtained only by the synthesis of x-ray and neutron diffraction measurements [1]. Clearly, techniques which directly probe H atoms in covalent and intermolecular hydrogen bonds could significantly enhance the scope of structure determination in aqueous solutions and biological systems. In this Letter, we report the first definitive measurements of the covalently bound hydrogen atom in water vapor by extended x-ray absorption fine structure (EXAFS).

EXAFS refers to small amplitude oscillations in the x-ray absorption coefficient that can extend hundreds of electron volts above a core-level absorption edge. These oscillations arise from final state interference effects of backscattered photoelectrons from neighboring atoms. In contrast, an isolated atom exhibits a smooth and essentially structureless absorption background corresponding to the photoionization process induced by a core-level excitation. The well-known utility of EXAFS as a structural probe arises from the ability to selectively excite individual atomic species, thereby allowing the local environment (e.g., solvent cage) around a selected absorbing atom to be directly characterized. Within the single scattering formalism, modulation in the absorption coefficient ( $\Delta\mu$ ) for *K*-edge spectra normalized to the isolated atomic background ( $\mu_0$ ) is

$$\chi(K) = \frac{\Delta\mu}{\mu_0} = - \sum_j \frac{S(k)N_j}{kr_j^2} |f_j(k, \pi)| \times \sin[2kr_j + \varphi_j(k)] e^{-2\sigma_j^2 k^2} e^{-2r/\lambda(k)},$$

where  $N_j$  is the number of nearest neighbors,  $k$  is the photoelectron wave vector,  $f_j$  is the scattering amplitude,

$S(k)$  is the amplitude reduction term due to many-body effects, and  $r_j$  is the radial distance from the absorbing atom.  $\lambda(k)$  is the electron mean free path which is nearly proportional to  $k$  allowing the exponential term to be approximated as  $e^{-2\gamma r/k}$ . Mean square fluctuations in  $r_j$  are accounted for in the exponential Debye-Waller factor by  $\sigma_j$ , and  $\varphi_j(k)$  accounts for the total phase of the curved wave scattering amplitude along the scattering trajectory. Contributions from all other scattering paths can be represented in a similar way. EXAFS oscillations arise from the scattering of relatively high energy ( $>30$  eV) photoelectrons, and as a result the cross section for scattering increases rapidly with the number of core-level electrons. Since hydrogen possesses a single core electron,  $\Delta\mu$  is expected to be a small fraction of the absorption background and is generally thought to be undetectable in state-of-the-art experiments. Some tentative evidence for hydrogen EXAFS has been reported by Yang and Kirz [2] in liquid water and Bouldin *et al.* [3] in GeH<sub>4</sub>, but their respective analyses were inconclusive. In addition, the presence of hydrogen has been inferred from its effect on multiple scattering contributions where the EXAFS signal is enhanced; such measurements are indirect and limited to collinear paths [4,5].

We report experiments conducted on Beamline 9.3.2. at the Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, CA. The experiments were conducted in a typical gas cell configuration backfilled with  $\sim 20$  mtorr vapor introduced from a bulb of vacuum degassed Millipore filtered high purity water (18 MΩ). A 100 nm thick aluminum window separated the gas cell from the ultrahigh vacuum environment of the beamline. Appropriate blanks were conducted by backfilling the evacuated cell with argon to test for artifacts that could produce signals that would interfere with the water vapor measurements. Various pressures were introduced into the cell to check for saturation effects and the experiments were conducted in the regime determined to yield EXAFS signals that were strictly linear with

pressure. The synchrotron radiation was tuned using the 600 lines/mm spherical grating monochromator to the oxygen  $K$  edge ( $\sim 530$  eV). The collection geometry for positive ions consisted of two plates: the extraction plate was positively biased at +500 V, while the collection electrode was connected through a picoammeter to ground. Incident x-ray intensity ( $I_0$ ) was obtained from a gold grid located well upstream of the gas cell window. High resolution ( $R = 0.1$  eV) spectra of water vapor were recorded between 510–560 eV and were used to calibrate the absolute photon energy from previous studies [6]. Subsequently, lower resolution scans ( $R = \sim 1$  eV) were collected from 500 to 900 eV for the hydrogen EXAFS studies.

The raw absorption spectrum measured by total ion yield ( $I$ ) and normalized by the incoming photon intensity ( $I_0$ ) is displayed in Fig. 1. The observed x-ray absorption near edge structure (XANES) spectrum (Fig. 1, inset) is in close agreement with previous electron energy loss results for water vapor [6]. A smooth atomic background function,  $\mu_0$  (Fig. 1), represented by a cubic spline, is fit to the absorption spectrum to extract the EXAFS oscillation [7,8]. It should be noted that no smoothing functions or Fourier filtering have been applied to the data at any point in this analysis. The resulting EXAFS function [ $\chi(k)$ ] shown in Fig. 2 was converted from photon energy ( $E$ ) to photoelectron wave vector ( $k$ ) via the relation  $k = [2m(E - E_0)]^{1/2}/\hbar$  and parametrized with an ionization threshold of  $E_0 = 533$  eV. This choice of  $E_0$  is probably not optimal, and errors are correlated with distance shifts. The EXAFS oscillations are indeed weak ( $\sim 1\%$  of  $\mu_0$ ) but clearly observable. For direct comparison, the calculated EXAFS spectrum of  $\text{H}_2\text{O}_{(g)}$  is also shown in Fig. 2. Finally, the phase corrected fast Fourier transform of  $\chi(k)$  using a Kaiser window function from 1.8 to 8.0  $\text{\AA}^{-1}$  is shown in the inset of Fig. 2, confirming the existence of a single

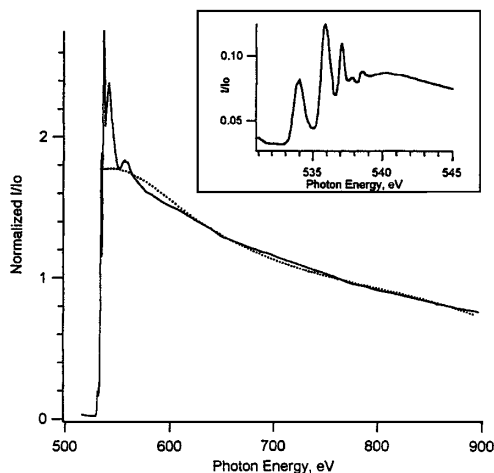


FIG. 1. Raw x-ray absorption spectra of 20 mtorr water vapor recorded at low resolution (1 eV) and (inset) high resolution (0.1 eV) showing the sharp XANES states arising from core-level transitions to valence/Rydberg orbitals.

scattering distance consistent with the covalently bound hydrogen in water vapor. Shown in Fig. 3 is the O-H phase shift function ( $\varphi^{\text{O-H}}$ ) derived using the known O-H distance (0.958  $\text{\AA}$ ) [9] in  $\text{H}_2\text{O}_{(g)}$  for both the experimentally measured and calculated  $\chi(k)$ . Similarly, the backscattering amplitude,  $f(k, \pi)$  was determined by parametrizing the Debye Waller factor ( $\sigma = 0.05$   $\text{\AA}$ ) for both the experimental and the calculated EXAFS function (Fig. 3).

The atomic background function used to extract the hydrogen EXAFS was fit to a line in order to examine any residual oscillations in  $\mu_0$ . The resulting frequencies are shown in Fig. 2. The slowly varying component ( $\chi(k)_{\text{AXAFS}}$ ) represents atomic scattering known as atomic XAFS (AXAFS) arising from distances shorter than the OH bond in water, as seen in the Fourier transform (Fig. 2, inset) [10,11]. It should be noted that while a linear fit to  $\mu_0$  can extract background oscillations it cannot adequately account for the curvature of this function, therefore exaggerating the amplitude of AXAFS. Also, included in Fig. 2 is the same analysis applied to the background function used to extract the calculated hydrogen EXAFS signal.

The calculated EXAFS spectra in Fig. 2 are obtained with the FEFF8 code [12], which is based on a novel real space Green's function method that includes simultaneous, self-consistent calculations of electronic structure (e.g., potentials, densities of states, charge transfer) as well as XANES. This code has already been extensively tested for EXAFS and XANES simulations, including hydrates [13]. There is a general difficulty in including hydrogen atoms within a muffin tin potential approximation. The problem

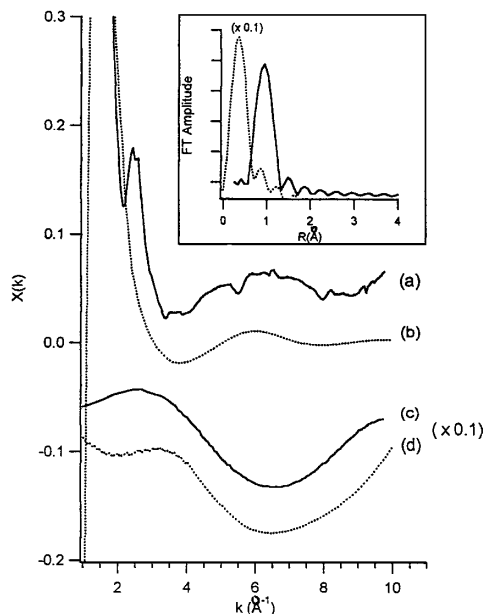


FIG. 2. EXAFS oscillations: (a)  $\chi(k)$ , experiment. (b)  $\chi(k)$ , FEFF8. Oscillations in the background function ( $\mu_0$ ) extracted with a least squares fit linear function: (c)  $\chi(k)_{\text{AXAFS}}$  experiment, and (d)  $\chi(k)_{\text{AXAFS}}$ , FEFF8. (Inset) Fast Fourier transform of experimental: (solid line)  $\chi(k)$  and (dashed line)  $\chi(k)_{\text{AXAFS}}$ .

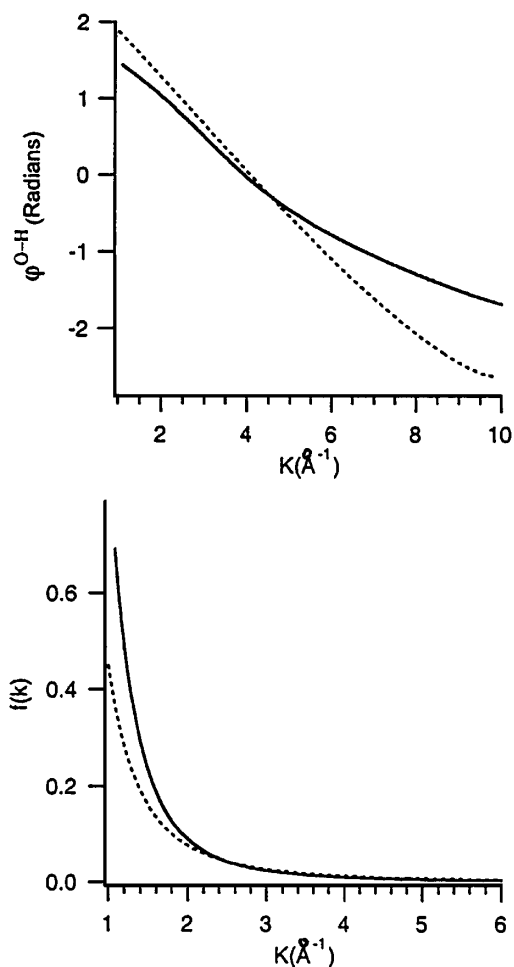


FIG. 3. (Top) O-H phase shift function,  $\varphi^{\text{O-H}}$ : (dashed line) experiment and (solid line) FEFF8. (Bottom) Amplitude functions (dashed line) experiment and (solid line) FEFF8.

arises since the O-H bond length (typically about  $1.0 \text{ \AA}$ ) is very short. Thus the oxygen atom is squeezed, and it becomes difficult to find a sufficiently large muffin tin radius for oxygen. As a result the usual muffin tin potential construction is a bad approximation to the molecular potential. In contrast to other methods [5] the approach used in FEFF8 to circumvent this problem is based on the assumption of phase transferability for the hydrogen atoms. That is, it is assumed that the partial wave phase shifts are insensitive to the O-H distance. Such an assumption is usually a reliable approximation for EXAFS analysis, but is not expected to be generally valid in XANES. However, the phase transferability assumption is better justified for hydrogen atoms, since they are weak scatterers even in XANES. Thus for the self-consistent field procedure, we first artificially increase the O-H distance to about  $1.5 \text{ \AA}$  and then calculate partial wave phase shifts and the Fermi energy for this shifted geometry. These phase shifts and Fermi energy are then used in the final calculations of XANES and densities of states, in which the original geometry is restored. This procedure has been tested before for Pu [12] and Cu hydrates [13].

Since AXAFS can also contribute to the absorption fine structure, we have used FEFF8 to calculate both EXAFS

and AXAFS for  $\text{H}_2\text{O}$  as well as  $\text{GeH}_4$ . The amplitude of two signals is roughly comparable in magnitude. However, the calculation of AXAFS for these molecules is not as reliable as EXAFS for several reasons. First, the AXAFS frequency is affected by a shift of hydrogen positions described above. For systems without hydrogens the frequency of AXAFS is usually reasonably well reproduced, but the amplitude is often too large due to the use of muffin tin approximation. In the case of our calculations for water, however, the agreement is quite good, as illustrated in Fig. 2. Experimentally the AXAFS can be removed by the background subtraction procedure, since it has a lower oscillation frequency than EXAFS (i.e., it comes from intra-atomic scattering at about  $\frac{1}{2}$  the near neighbor distance). Since the two mechanisms (AXAFS and EXAFS) have similar amplitude but different frequencies, a comparison with theoretical calculations is essential to ensure that the EXAFS oscillations are extracted properly. The close agreement between the simulated and experimental hydrogen EXAFS in Fig. 2 confirms that in this work the AXAFS is properly included into the background absorption.

To date the only published study of liquid water was reported by Yang and Kirz [2] in which the oxygen  $K$ -edge EXAFS was measured in a liquid cell configuration. The O-O pair correlation function was determined with the phase functions calculated by Teo and Lee [14] and confirmed experimentally by Rosenberg *et al.* [15]. In addition to O-O scattering, they found some indirect evidence for a hydrogen contribution ( $\sim 1 \text{ \AA}$ ) to their gross EXAFS signal measured for both the liquid and the vapor. However, a definitive assignment could not be made due to inadequate signal to noise ratio.

To illustrate the utility of our measured and calculated phase shift and amplitude function for the analysis of hydrogen EXAFS in complex systems, we have reanalyzed the liquid water EXAFS spectrum measured by Yang and Kirz [2]. Outlined in Fig. 4 is the procedure used to quantify the O-H distance in their measurement of liquid water. The raw absorption spectrum is refit with a cubic spline extending  $\sim 500 \text{ eV}$  above a selected ionization threshold of  $E_0 = 533 \text{ eV}$  (Fig. 4). The raw EXAFS signal is plotted in Fig. 4 in addition to the two Fourier filtered components that make up the raw signal, extracted by inverse Fourier transform of the individual shells with Gaussian window functions. The high frequency oscillation has been previously analyzed by Yang and Kirz and assigned to the O-O nearest neighbor distance in the liquid. Using the experimental and FEFF8  $\varphi^{\text{O-H}}$  and  $f(k, \pi)$  determined in this work, a least squares single scattering EXAFS fit of the slowly varying oscillation was conducted using a standard software package. A description of the analysis algorithms as well as the error analysis used in this package can be found in Ref. [16]. The results of these respective fits are reported in Table I. A  $R_{\text{O-H}}$  distance of  $0.95 \pm 0.03 \text{ \AA}$  was obtained using the experimentally

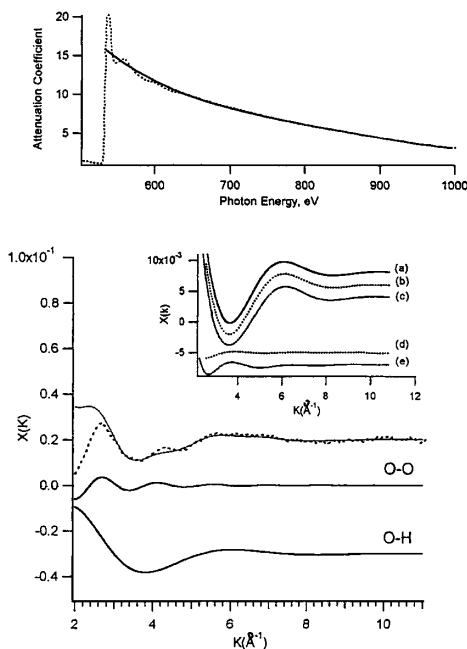


FIG. 4. Reanalysis of liquid water EXAFS measured by Yang and Kirz [2]. (Top) Raw absorption spectrum (dashed line) fit with a cubic spline background (solid line). (Bottom) Raw EXAFS oscillations (dashed line) with the sum of two different shells (solid line) corresponding to the O-O and O-H distances obtained by standard Fourier filtering. (Inset) Calculated single scattering EXAFS signal parametrized by phase and amplitude functions determined from (b) experiment and (c) FEFF8, fit to the slowly varying filtered experimental oscillation (a). Residual from fits: (d) experiment and (e) FEFF8.

determined phase shift and amplitude. This value is in reasonable agreement with previously reported values for liquid water (0.97 Å). A slightly shorter bond length was obtained with the FEFF8 phase and amplitude functions originating from differences in the derived  $\varphi^{\text{O-H}}$  function, probably due in part to the approximate choice of  $E_0 = 533$  eV. It is also interesting to note that both fits yielded rather large values for  $\sigma$  that may indicate a broadened distribution of covalent O-H bonds lengths in the liquid, influenced by the presence of intermolecular hydrogen bonds between neighboring molecules. These combined results clearly demonstrate that with a single EXAFS measurement both the O-O and O-H correlations can now be measured simultaneously in aqueous environments.

Hydrogen EXAFS signals have been tentatively observed in two previous cases, viz., the Yang and Kirz study of liquid water [2] and a study of gaseous  $\text{GeH}_4$  by Bouldin *et al.* [3]. These observations were suggestive, but in each case a conclusive analysis could not be presented due to a lack of simulations to provide knowledge of the phase and amplitude of the EXAFS oscillations from hydrogen atoms and from the relative contribution of the AXAFS to the measured signal. We have illustrated the general utility of H EXAFS as a new structural

TABLE I. Derived parameters and errors from single scattering EXAFS fit of the O-H oscillation in liquid water, using experimental and calculated (FEFF8) phase shift and backscattering amplitude functions.

Parameter	Experimental fit	FEFF8 fit
$S(k)$	0.94 ( $\pm 0.17$ )	0.82 ( $\pm 0.05$ )
$N$	1.95 (0.05)	1.80 (0.11)
$\sigma$ (Å)	0.13 (0.03)	0.11 (0.05)
$\gamma$ (Å <sup>-2</sup> )	1.78 (0.20)	1.38 (0.15)
$R$ (Å)	0.95 (0.03)	0.91 (0.05)
$\Delta E_0$	-3.33 (1.03)	-10.0 (1.2)
Fit rms (Å <sup>-1</sup> )	0.11	0.12

tool in the elucidation of hydrogen bonds in complex condensed phase samples. Advances in synchrotron x-ray spectroscopy coupled existing computational techniques imply that observations of hydrogen EXAFS are likely to become routine. The phase shift function reported here can be used to extract quantitative O-H bond distances, thus becoming a useful complement to existing structural methods in chemistry, biology, and materials science.

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