PHYSICAL REVIEW B **79**, 132203 (2009)

# Angular anisotropy of resonant inelastic soft x-ray scattering from liquid water

Johan Forsberg,[1] Johan Gråsjö,[2] Barbara Brena,[1] Joseph Nordgren,[1] Laurent-C. Duda,[1] and Jan-Erik Rubensson[1]
[1]*Department of Physics and Materials Science, Uppsala University, Box 530, SE-751 21 Uppsala, Sweden*
[2]*Department of Pharmacy, Uppsala University, Box 580, SE-751 23 Uppsala, Sweden*

(Received 5 December 2008; published 13 April 2009)

Resonantly excited soft x-ray emission spectra of liquid water have been measured at two different angles relative to the polarization direction of the exciting radiation. The results demonstrate that the emission is much more isotropic than expected for the free water molecule but that the trends in the remaining anisotropy qualitatively agree. It is found that the two sharp oxygen peaks at high emission energy correspond to states of different symmetry.

DOI: 10.1103/PhysRevB.79.132203 PACS number(s): 61.20.−p, 78.70.En, 33.15.Fm, 79.90.+b

The water molecule is of paramount importance for many kinds of vital processes in fields ranging from biology to environmental science. An obstacle for reaching a deeper understanding of the role of water in these processes is that the electronic structure of the water molecule is influenced by its chemical environment. In soft x-ray spectroscopy, transitions involving quasiatomic core levels are used to gain information about local electronic structure, and in addition the short lifetime of the core hole states gives access to the femtosecond time scale, which is relevant for nuclear rearrangements. With these assets it is natural to suggest that soft x-ray spectroscopy may contribute to the efforts in developing a microscopic description of aqueous systems. In practice, there are substantial complications, and it is difficult to reach a consensus even regarding the interpretation of the spectra of pure liquid water, in soft x-ray absorption (SXA)[1–4] as well as in soft x-ray emission (SXE).[5–8] Other x-ray techniques have also been employed to probe the short-range structure of water.[9]

When excited with radiation of well-defined energy and polarization, SXE shows significant angular anisotropy also from systems without long-range order, such as gas-phase samples.[10] Angular anisotropy in the scattering process is expected whenever the local symmetry of the states involved in the transitions is defined, and via congruence requirements it can be used for assignments both of SXE and SXA spectra.[11] Although strong angular anisotropy is predicted for resonantly excited SXE spectra of the free water molecule,[12] it has been argued that any excitation-energy dependent anisotropy would vanish in the liquid due to rehybridization of the unoccupied orbitals.[6] Here we present resonantly excited SXE spectra of liquid water measured in two different directions relative to the polarization direction of the exciting radiation. Significant angular anisotropy is observed, albeit much less pronounced than expected for the free molecule. We briefly discuss the impact on the interpretations of recent high-resolution SXE spectra, and hope that these results will aid the efforts in making x-ray spectroscopy fulfill its potential to become a useful tool for studying aqueous systems.

The experiments were carried out at the I511–3[13] at MAX-lab. Water was introduced in a flow cell equipped with an ultrathin carbon membrane.[14] SXE spectra were measured in the polarization direction of the incident radiation (denoted "parallel" direction), and at an angle of 65° relative to this direction (denoted "perpendicular" direction), using a Gammadata Scienta XES-300 Rowland spectrometer,[15] equipped with a grating of 5 m radius and a groove density of 1200 lines per mm. The spectrometer was adjusted to reach a resolution comparable to the resolution in recent published SXE spectra of liquid water.[7,8]

The x-ray fluorescence spectra of liquid water excited on the prepeak in the SXA spectrum (534.7 eV) and on the main peak (537.5 eV) are shown in Fig. 1. The three valence orbitals of the water molecule give rise to three main features in the spectra: the $1b_2$ and $3a_1$ derived orbitals correspond to intensity at 520.5 and 523.5 eV, respectively, features which

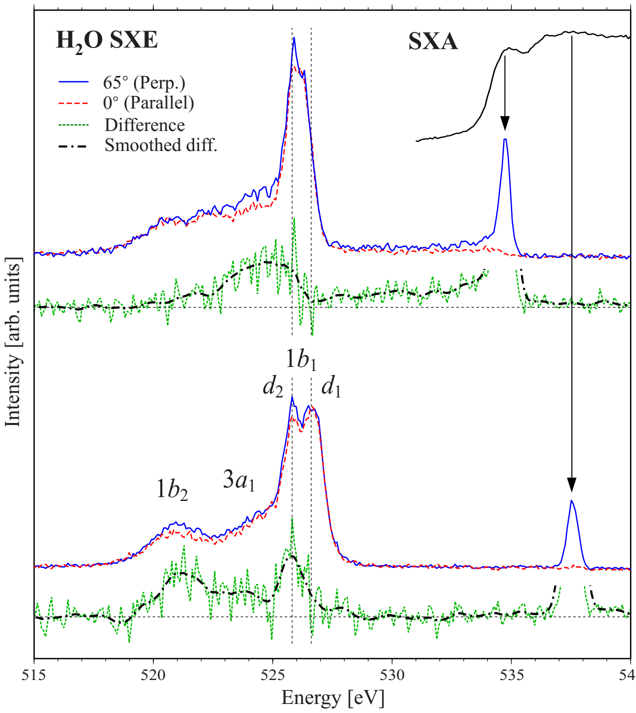

FIG. 1. (Color online) The excitation energies used for recording the SXE spectra are marked in the SXA spectrum (inset), which is measured in total fluorescence yield and is strongly saturated. SXE spectra excited at 534.7 (top) and at 537.5 eV (bottom) are measured in the parallel and perpendicular directions. Also shown are the differences between the spectra from the two directions, multiplied by 10, together with smoothed versions. These were normalized to minimize the difference while keeping it positive, disregarding noise.

©2009 The American Physical Society

are pronounced in the high-energy excited spectra and smeared out in the low-energy excited spectra. The "lone-pair" $1b_1$ derived orbital gives rise to two close peaks around 526 eV in the high-energy excited spectra. We denote the high-energy peak $d_1$ and low-energy $d_2$. Only $d_2$ seems to remain in the prepeak excited spectra. The phenomenology agrees with recently published spectra of liquid water.[7,8]

Here we turn the attention to the angular dependence. While practically absent in parallel geometry, the "elastic peak" (the energy of which coincides with the excitation energy) has much intensity in the perpendicular direction. At lower energies there are small but significant differences between the two directions. In the low-energy excited spectrum, rotation to perpendicular direction gives a relative enhancement of intensity in the region around $3a_1$. In the high-energy excited spectrum instead a relative enhancement of $1b_2$ is found, together with an increased $d_2/d_1$ intensity ratio.

Before discussing these results we briefly recall what is expected for the free molecule. Assuming that the incident radiation is perfectly plane polarized and that the spectrometer does not have any polarization sensitivity, the angular dependence can be derived from scattering theory:[12,16]

$$I(\theta) = I_0\left[1 + R\left(\frac{3}{2}\sin^2 \theta - 1\right)\right],$$

where $\theta$ is the angle between the polarization vector of the incident radiation and the direction of the emitted radiation, $I_0$ is proportional to the total intensity, and $R$ is the anisotropy parameter. In the two-step model $R$ has a simple form, and for the $C_{2v}$ point group it has been shown that $R=\frac{2}{5}$ if the emission comes from an orbital of the same symmetry as the initially excited orbital, and $R=-\frac{1}{5}$ if it comes from an orbital of different symmetry.[16] For the free water molecule we would thus expect that the emission intensity associated with orbitals of the *same* symmetry as the excited electron's orbital, $I_s(\theta)$, would be relatively attenuated in the parallel direction, and enhanced in the perpendicular, whereas the opposite would hold for intensity from orbitals of *different* symmetry, $I_d(\theta)$. In the present experimental geometries we get the following relevant intensities:

$$I_s(0) = 0.6I_0, \quad I_d(0) = 1.2I_0,$$

$$I_s(65) \approx 1.093I_0, \quad \text{and} \quad I_d(65) \approx 0.953I_0.$$

The anisotropy is observed as changes in the relative intensity of the emission features, and we express the predictions by the ratios:

$$A_s = \frac{I_s(65) - I_s(0)}{I_s(65) + I_s(0)} = 0.29,$$

$$A_d = \frac{I_d(65) - I_d(0)}{I_d(65) + I_d(0)} = -0.11.$$

Thus, the strongest anisotropy is expected to be due to the attenuation of intensity from states of the same symmetry as the excited electron in the parallel geometry. The angular anisotropy is reduced when symmetry mixing occurs, e.g., due to large nuclear rearrangements or large interaction with the surrounding. The strong attenuation of $I_s$ in the parallel case leads us to suggest that any anisotropy remaining in the liquid phase indicates emission from orbitals with predominantly the same symmetry as the initially excited electron. Therefore we have chosen to normalize the spectra in Fig. 1 so that rotation to perpendicular symmetry may enhance but not attenuate spectral intensity at any emission energy.

From inspection in Fig. 1 it is obvious that the observed variations are much less pronounced than anticipated for the free molecule. However, several trends expected for the free molecule are qualitatively retained in the liquid. The lower excitation energy corresponds to the prepeak in the SXA spectrum. Despite of disagreements regarding the influence on the hydrogen bond network, there seems to be a consensus that the pre-edge peak originates from transitions from the core level into local $4a_1$-derived states of the free water molecule.[1–4] In this case one would thus predict a relative attenuation of the emission from the $3a_1$ state (around 523–524 eV) in parallel geometry and a relative enhancement in perpendicular. This trend is indeed observed. The angular dependence in the elastic peak (534.7 eV) may to a large extent be determined by reflection in the carbon membrane, with *s*-type reflection being more efficient than *p*-type reflection. The long low-energy tail of the elastic peak, however, cannot be attributed to reflection. It must be assigned to recombination back to the electronic ground state with accompanying vibrational excitations. Following this two-step model further, the low-energy tail corresponds to emission from the $4a_1$ orbital, and one would expect a similar angular behavior as in the $3a_1$ region. This prediction is also confirmed by the observations.

The angular dependence in this case may be somewhat surprising, not only because of the rehybridization of the unoccupied states, but also because of the nuclear dynamics. For free water molecules the $1s^{-1} \rightarrow 4a_1$ excitation leads to ultrafast dissociation[17] prior to the emission, the necessity to address the nuclear dynamics when interpreting SXE spectra in liquid water has been emphasized,[6] and it has been proposed that the prepeak excited spectrum is primarily due to emission from $OH^-$,[7] subsequent to dissociation, rather than from intact $H_2O$ molecules. The long low-energy tail of the elastic peak, and the smearing out of the $1b_2$ and $3a_1$ features are indeed indications of substantial nuclear rearrangement. In spite of the strong coupling to the environment, the local-orbital geometry is still reflected in the angular dependence of the SXE spectra.

For the higher excitation energy it is likely that the $2b_2$ orbital of the free molecule largely contributes to the state formation. Assuming $b_2$ symmetry for the excited electron we would expect that $1b_2$ intensity is relatively attenuated in the parallel direction. This is confirmed by the observations, showing that indeed dominating $b_2$ character can be assigned to the states excited at 537.5 eV.

Intriguingly, the $d_1$ and the $d_2$ peaks show different angular dependence, indicating that they have different symmetry character. The trend in the angular dependence of the $d_2$ peak is the same as expected for $b_2$ symmetry, whereas the states responsible for the $d_1$ peak have more of the free molecule $b_1$

symmetry. This is consistent with the SXE interpretation of Tokushima *et al.*[8] who assign the $d_2$ peak to strongly hydrogen bonded molecules in a tetrahedral-like arrangement, and the $d_1$ peak to states where one or more hydrogen bonds are broken. It is plausible that the local molecular symmetry is less distorted with less hydrogen bonds so that the $1b_1$ character is retained for the states corresponding to the $d_1$ peak, whereas other symmetries mix to give more contribution of $b_2$ symmetry to the states responsible for the $d_2$ peak. The observation is also consistent with the SXE interpretation of Fuchs *et al.*,[7] who assign the $d_2$ feature to emission after complete dissociation, and the $d_1$ feature to intact water molecules which are rather independent of details in the hydrogen bond network. Also here, it is the $d_1$ peak that is expected to be closer to what is expected for the $1b_1$ peak of the free water molecule.

In conclusion, we have shown that the anisotropy of resonantly excited SXE spectra of liquid water is much less pronounced than expected for the free water molecule but that it qualitatively follows the predicted trends. The results also indicate that the two sharp peaks in liquid water, associated with the oxygen lone-pair orbital, correspond to states of different symmetries. We hope that these results will aid the efforts to provide an unambiguous assignment of the SXE spectra of liquid water.

The work is supported by the Swedish Science Research Council (VR).

---

[1] P. Wernet, D. Nordlund, U. Bergmann, M. Cavalleri, M. Odelius, H. Ogasawara, L. Å. Näslund, T. K. Hirsch, L. Ojamäe, P. Glatzel, L. Pettersson, and A. Nilsson, Science **304**, 995 (2004).

[2] J. Smith, C. Cappa, B. Messer, W. Drisdell, R. Cohen, and R. Saykally, J. Phys. Chem. B **110**, 20038 (2006).

[3] L. Näslund, J. Lüning, Y. Ufuktepe, H. Ogasawara, P. Wernet, U. Bergmann, L. Pettersson, and A. Nilsson, J. Phys. Chem. B **109**, 13835 (2005).

[4] R. L. C. Wang, H. J. Kreuzer, and M. Grunze, Phys. Chem. Chem. Phys. **8**, 4744 (2006).

[5] J. H. Guo, Y. Luo, A. Augustsson, J. E. Rubensson, C. Såthe, H. Ågren, H. Siegbahn, and J. Nordgren, Phys. Rev. Lett. **89**, 137402 (2002).

[6] M. Odelius, H. Ogasawara, D. Nordlund, O. Fuchs, L. Weinhardt, F. Maier, E. Umbach, C. Heske, Y. Zubavichus, M. Grunze, J. D. Denlinger, L. G. M. Pettersson, and A. Nilsson, Phys. Rev. Lett. **94**, 227401 (2005).

[7] O. Fuchs, M. Zharnikov, L. Weinhardt, M. Blum, M. Weigand, Y. Zubavichus, M. Bar, F. Maier, J. D. Denlinger, C. Heske, M. Grunze, and E. Umbach, Phys. Rev. Lett. **100**, 027801 (2008).

[8] T. Tokushima, Y. Harada, O. Takahashi, Y. Senba, H. Ohashi, L. Pettersson, A. Nilsson, and S. Shin, Chem. Phys. Lett. **460**, 387 (2008).

[9] See Patrick H.-L. Sit, C. Bellin, B. Barbiellini, D. Testemale, J. L. Hazemann, T. Buslaps, N. Marzari, and A. Shukla, Phys. Rev. B **76**, 245413 (2007), and references therein.

[10] D. W. Lindle, P. L. Cowan, T. Jach, R. E. LaVilla, R. D. Deslattes, and R. C. C. Perera, Phys. Rev. A **43**, 2353 (1991).

[11] K. Gunnelin, P. Glans, P. Skytt, J. H. Guo, J. Nordgren, and H. Ågren, Phys. Rev. A **57**, 864 (1998).

[12] S. Kashtanov, A. Augustsson, Y. Luo, J. H. Guo, C. Såthe, J. E. Rubensson, H. Siegbahn, J. Nordgren, and H. Ågren, Phys. Rev. B **69**, 024201 (2004).

[13] R. Denecke, P. Väterlein, M. Bässler, N. Wassdahl, S. Butorin, A. Nilsson, J.-E. Rubensson, J. Nordgren, N. Mårtensson, and R. Nyholm, J. Electron Spectrosc. Relat. Phenom. **101-103**, 971 (1999).

[14] J. Forsberg, L. Duda, A. Olsson, T. Schmitt, J. Andersson, J. Nordgren, J. Hedberg, C. Leygraf, T. Aastrup, D. Wallinder, and J.-H. Guo, Rev. Sci. Instrum. **78**, 083110 (2007).

[15] J. Nordgren, G. Bray, S. Cramm, R. Nyholm, J.-E. Rubensson, and N. Wassdahl, Rev. Sci. Instrum. **60**, 1690 (1989).

[16] Y. Luo, H. Ågren, and F. Gelmukhanov, Phys. Rev. A **53**, 1340 (1996).

[17] I. Hjelte, M. N. Piancastelli, R. F. Fink, O. Björneholm, M. Bässler, R. Feifel, A. Giertz, H. Wang, K. Wiesner, C. Miron, S. L. Sorensen, and S. Svensson, Chem. Phys. Lett. **334**, 151 (2001).