

## Breathing Volume into Interfacial Water with Laser Light

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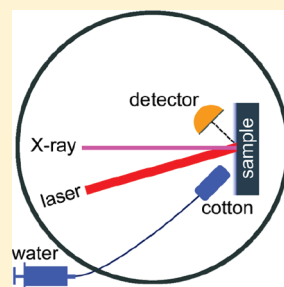
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**ABSTRACT:** The molecular structure of nanoscopic interfacial water layers is changed by irradiation with 670 nm laser light, a wavelength to which bulk water is practically transparent. Whereas the phenomenon was confirmed in several experimental studies, its intrinsic cause was not clear. We use X-ray spectroscopy to analyze nanoscopic interfacial water layers on nanocrystalline diamond films and demonstrate that the structural change is due to collective hydrogen bond excitation in the water layers. K-edge X-ray fluorescence yield reveals a change in  $\text{H}_2\text{O} \cdots \text{H}_2\text{O}$  orbital hybridization upon light exposure. The corresponding electronic picture is indicative of a density drop in the condensed-phase layer. The associated volume expansion is relevant to systems involving nanoconfined liquids and may inspire innovative design principles both in nanotechnology and nanomedicine. Potential applications range from anticancer strategies to the design principles of nano steam engines.



**SECTION:** Surfaces, Interfaces, Catalysis

The hypothesis that ordered interfacial water layers (IWL) play a fundamental role in biological systems has been put forward in a visionary paper by Szent-Györgyi.<sup>1</sup> Today, there is growing evidence for a distinct molecular organization of the water layering at material interfaces.<sup>2–4</sup> The ordering manifests itself in unusual properties such as a significant change in density,<sup>5–7</sup> an increased viscosity as compared to that of bulk water,<sup>8–10</sup> and a strongly reduced dielectric constant.<sup>11,12</sup> A most striking property of nanoscopic IWL is their interaction with visible light as it is unknown for normal bulk water or ice.<sup>13</sup> The effect was observed only recently, being indirectly evidenced by different experimental techniques as instant depletion of the IWL upon irradiation<sup>14–16</sup> but is still not well understood.

To investigate the effect of visible light irradiation on the nanoscopic IWL, we used soft X-ray absorption spectroscopy and measured the fluorescence yield X-ray absorption (XA) at the oxygen K-edge of water on nanocrystalline hydrogenated diamond under ambient conditions. The experiments were performed at the Berlin Synchrotron Radiation Facility (BESSY II) third generation light source beamline U41-PGM, using the Liquidrom ambient setup, which has been described before.<sup>17</sup> Due to the unique combination of chemical inertness with no release of chemical compounds and hydrophobicity, nanocrystalline hydrogenated diamond serves as a model platform for the systematic investigation of nanoscopic IWL. The molecular order of IWL on hydrogenated diamond and diamond-like carbon films is in the focus of current research efforts.<sup>18</sup> The nanocrystalline diamond film was deposited on silicon wafers using a hot filament chemical vapor deposition process, resulting in a layer of a thickness of  $\sim 1 \mu\text{m}$ , average grain size of 15 nm and roughness of 14 nm. In order to measure the X-ray absorption of

nanoscopic water layers under controlled conditions, a molecular covering of the diamond surface was prepared by nanospray deposition of ultrapure water (conductivity  $5.5 \mu\text{S m}^{-1}$ ), under an atmosphere of neat helium at ambient pressure (approximately 930 mbar). Immediately after the spray deposition, the water evaporates from the surface, until an equilibrium state with the content of the gas-phase water is reached, which defines the relative humidity within the chamber. The equilibrium state was controlled by purging the chamber with fresh helium, which allowed us to perform the measurements at arbitrarily chosen humidity conditions.

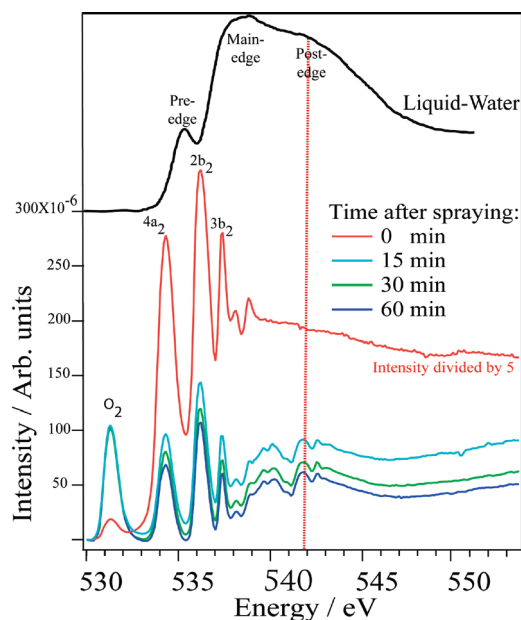
Figure 1 shows a series of XA fluorescence yield spectra monitoring the evaporation process directly after the spray injection, used to determine the establishment of stable humidity conditions. In order to get a readout of the evaporated water-gas, a continuous flow of pure helium gas (99.999%) is maintained in the chamber. As presented in the evaporation series, the XA spectra obtained under ambient pressure show strong contributions from the oxygen gas absorption peak (labeled  $\text{O}_2$  in Figure 1) and water vapor ( $4a_1$ ,  $2b_2$ , and  $3b_2$  molecular orbitals labeled in Figure 1). The sources of the oxygen gas are traces of oxygen remaining in the chamber after evacuation and purging with helium.

Additionally, we used a cotton roll as a local moisture buffer, which was brought close to the sample (approximately 3 mm) and loaded with water by spray injection. The slow evaporation rate of the moist cotton at ambient pressure facilitated the

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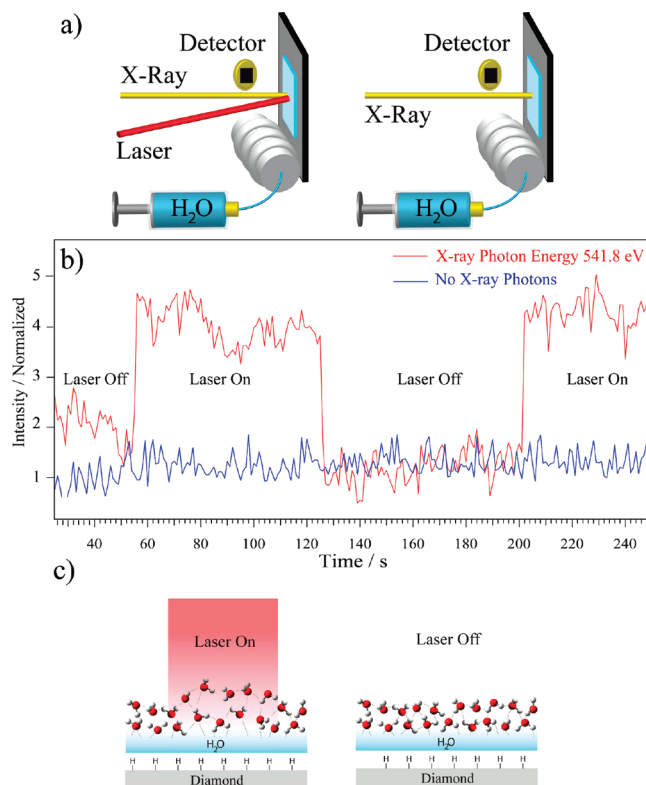
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**Figure 1.** Series of XA fluorescence yield spectra registered after spray deposition of water, showing the evolution of the system toward equilibrium with the relative humidity in the chamber (red to blue spectra). On the top, the XA fluorescence yield spectrum of pure water is presented (taken from ref 19), with the pre-edge at 535 eV, the main edge with maximum at approximately 537.5 eV, and the postedge at approximately 541.5 eV. All spectra of IWL comprise characteristic contributions from the gas-phase oxygen ( $O_2$ ) and the gas-phase water ( $4a_1$ ,  $2b_2$ ,  $3b_2$ ). In order to avoid interference with the gas-phase signal, the IWL are investigated specifically at the postedge energy of 541.8 eV (marked by the red line) of pure water.

adjustment of the relative humidity, together with the flowing helium. In order to induce the light interaction effect, the sample was irradiated with 670 nm laser light. The XA fluorescence signal was detected using a GaAsP photodiode type Hamamatsu G1127 placed at a  $45^\circ$  angle at a distance of  $\sim 20$  mm from the sample. The photodiode was shielded against stray light from the laser by means of an aluminum foil of 500 nm thickness. A schematic of the experimental setup is shown in Figure 2a.

Figure 2b shows a time scan obtained at X-ray excitation energy of 541.8 eV with the laser (wavelength, 670 nm; power, 4.5 mW; spot diameter at sample surface, 1.2 mm; intensity,  $3.98 \text{ kWm}^{-2}$ ) switched on and off correspondingly. The selected irradiation parameters, standard in a variety of biological applications including wound healing<sup>20</sup> and skin rejuvenation,<sup>21</sup> allow us to establish a connection with previous studies.<sup>15,16</sup> A schematic drawing of the experimental setup is shown in Figure 2a. Note that in order to track the signal from the condensed-phase water adsorbate at the sample surface, without interfering with the peak signals obtained from the gas phase, the X-ray energy was selected to be higher than 540 eV. The postedge XA spectrum of bulk liquid water is located at this energy region (cf. the liquid water spectrum in Figure 1).<sup>19</sup> An instant increase in the XA fluorescence yield was detected upon laser irradiation and an equally sudden decrease to the previous intensity when the laser was switched off, as shown in Figure 2b (red line). A corresponding time scan without X-ray excitation, as presented in parallel in Figure 2b (blue line), shows no correlation with the laser irradiation, thus proving the efficiency of the diode shielding against stray light from the laser. The effect is still reproducible at



**Figure 2.** (a) Schematic drawings of the experimental setup, showing XA fluorescence yield measurements with and without simultaneous laser irradiation of the sample. The detector diode is shielded by aluminum foil against the laser light. A cotton roll close to the sample serves as local humidity buffer. (b) Time scan at 541.8 eV, showing the sudden increase of the fluorescence intensity upon laser irradiation (red line). A corresponding time scan obtained from the IWL without X-ray excitation shows no correlation with the laser irradiation, thus proving the efficiency of the detector shielding (blue line). (c) Corresponding idealized representation, illustrating the breathing-like volume expansion of the topmost water layers at the sample surface in response to the laser irradiation.

an energy range of 540–545 eV (the postedge of the liquid water XA spectrum). The induced increase of the postedge intensity of the oxygen K-edge absorption fluorescence can be related to an increase in the orbital hybridization of the H-bonding upon stretching the hydrogen bond between the water molecules.<sup>22</sup> This stretching correlates with a macroscopic volume expansion of the IWL upon excitation with laser light. The postedge absorption is also affected by the symmetry of the electronic orbital structure, thus allowing us to draw distinct conclusions on the structural properties of the system.<sup>19</sup> Notably, comparable spectra were obtained on substrates made of crystal clear polystyrene, a material that is virtually transparent to 670 nm light.

Actually, bulk water shows an extremely weak absorption for visible wavelengths of light. The effect is attributed primarily to combinations of higher harmonics and fundamentals of stretching and bending modes.<sup>13</sup> However, these effects are too weak to provoke a significant structural phase transition of the molecular network. Therefore, we arrive at the conclusion that the transition is triggered by a different modality of interaction. Indeed, there is evidence that the dissipation of vibrational energy of water molecules at surfaces shows considerably increased time constants.<sup>23</sup> It was recently shown that the decrease of the

density of states of the low-frequency modes, as induced by an incomplete solvation of the first (surface-bound) interfacial water layer, can lead to a longer vibrational lifetime of interfacial O—H groups.<sup>24</sup> However, according to the experimental observation here, the light interaction does only affect the IWL on top of the first surface-bound monolayer and does not depend on a specific surface material. In fact, there is only one precondition for the activation of IWL by visible light, a substantial relative humidity, a key parameter for observing the effect. When the relative humidity (or laser intensity) is too low, the IWL, presumably thinning with decreasing relative humidity, is apparently too stable (surface bound) to be affected by the laser light.<sup>15</sup> Moreover, the activation is not due to a specific molecular ordering of the adsorbate water imprinted by the material surface. Furthermore, the activation was also observed for other adsorbate species, including alcohols, and for a wide range of light wavelengths ranging between 523 and 785 nm.<sup>14,16</sup> In all of the reported cases, evaporative heating, that is, heating of the substrate by the laser light, is excluded.<sup>14–16,25</sup>

Considering these findings, the observed light interaction may be interpreted in terms of the intermediate structure of the interfacial molecular layering, facilitating a collective excitation of the molecular network. This is neither possible in bulk water due to the higher degree of random motion and the fast dissipation of (vibrational) energy nor in the tightly bonded first adsorbate layer. It is appealing here to imagine the observed light interaction in the IWL in terms of a breathing-like expansion of the topmost molecular water sheets, as illustrated schematically in Figure 2c.

The appearance of collective electronic states in liquid water was explored both theoretically and experimentally.<sup>26–30</sup> Early considerations of Fano and Fröhlich<sup>31,32</sup> suggest the prevalence of quasi-stationary liquid states at solid surfaces. Interestingly, there is experimental evidence for spatial correlations of hydrogen bonds in supercooled water, indicating the appearance of collective bands in a liquid phase.<sup>30</sup> In IWL, the concept of collective excitation by visible light receives support from the observation that the strength of the light interaction depends strongly on the polarization of the incident laser radiation.<sup>16</sup> Polarization normal to the surface resulted in a stronger response, which indicates an enhanced molecular ordering along the same direction. In such terms, the observed structural change of the IWL may be assigned to an energy transfer of the O—H stretching mode excitation over many water molecules. This is mediated by dipole–dipole interactions, thus leading to longer collective persistence of excited states of the water molecules.

In accord with the picture of partially immobilized molecules by spatial restriction,<sup>2–4</sup> we propose that, generally, the restraint of the degrees of freedom of the water molecules, as imposed by the geometric boundary condition at a material surface, encourages the formation of an ordered network. As noted here, and in earlier studies with IWL,<sup>15,16</sup> the ordering effect is independent of the character of the specific substrate. Upon going away from the interfacial region, one can imagine that the structure of the water layers becomes less ordered as the system gradually merges into the bordering vapor or bulk liquid phase. We propose that this intermediate water phase will undergo electronic structural changes upon interaction with visible light. Accordingly, the properties of the substrate surface, such as polarity and surface charge, have a moderate influence on the strength of the light interaction, in agreement with experimental results.

In summary, we provide clear “electronic evidence” for a strong, direct light activation of IWL on a hydrogenated diamond surface under ambient conditions as it is not known for the bulk water phase. The observation is interpreted as a breathing-like volume expansion of the topmost sheets of water molecules. The effect can be traced back to a collective excitation of water molecules, which is, to a large extent, independent of a specific substrate. It is supposed to have practical relevance in systems with aqueous liquids under nanoscale confinement, in particular, in nanotechnology (design of nanofluidic devices based on nanotubes) and in nanomedicine, eventually explaining the facilitated uptake of anticancer drugs by tumor cells in response to their irradiation with pulsed laser light of 670 nm.<sup>33</sup> Reportedly, 25–30% of the water in (cardiac) cells is prevalent as IWL, approaching 100% in mitochondria.<sup>34</sup> The present study gives relevance to these data and accentuates the need for further research.

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