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## LETTER TO THE EDITOR

## The premelting of ice studied with photoelectron spectroscopy

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### Abstract

We address the century-old puzzle of the existence of a liquid-like layer at the ice surface near its melting point with new photoelectron spectroscopic tools using synchrotron radiation. Near-edge x-ray absorption shows that a liquid-like film exists at temperatures as low as  $-20^{\circ}\text{C}$ . Near  $0^{\circ}\text{C}$  this film is about  $20\text{ \AA}$  thick, i.e., six bilayers. With high-pressure x-ray photoelectron spectroscopy, we have further investigated the effect of surface contamination, which is ubiquitous in natural environments, on the state of the ice. Our results show that the premelting of ice can be strongly enhanced by the presence of hydrocarbon contamination.

At temperatures close to the melting point, ice forms a liquid-like layer at the surface. Premelting of the ice surface was first discussed by Faraday in 1840 [1], and is an important factor in the geology of polar ice caps, atmospheric chemistry, environmental science, and tribology [2]. Surprisingly, the literature on ice premelting is full of unresolved inconsistencies. For example, there is a spread of three orders of magnitude in the reported temperature-dependent thickness of the liquid film for different measurement techniques [3]. This is related to the fact that, except for in a recent grazing x-ray diffraction study [4], the measured properties are only indirectly related to the liquid or disordered nature of the ice surface. These properties include the refractive index (ellipsometry) and ionic conductivity. Another important factor is that surface contamination could not be monitored in previous studies; however, the presence of foreign species could have a profound effect on the structure of the ice surface [5].

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Since ice is in equilibrium with water vapour near its melting point at pressures in the torr range and in most cases is exposed to ambient air, a certain degree of contamination appears inevitable. Thus, in order to solve the century-old puzzle of ice premelting, both the degree of molecular order and surface contamination need to be determined under the same experimental conditions. Traditional electron spectroscopies are exquisitely sensitive to surface structure and composition but generally must operate in high vacuum, which is incompatible with the high vapour pressure of ice near its melting point.

To overcome these limitations, we have developed a new high-pressure electron spectrometer. Monochromatized soft x-ray photons from a synchrotron source pass through a thin silicon nitride window and strike the ice surface in an atmosphere of water vapour [6]. Emitted photoelectrons are transmitted through a 1 mm diameter aperture approximately 1 mm above the ice surface. This aperture is the entrance to a differentially pumped electrostatic lens system (the unique feature of our instrument), which refocuses the electrons into the object plane of a standard electron energy analyser situated downstream, in the high-vacuum region. With this instrument we have obtained for the first time x-ray photoemission spectra (XPS) and electron-yield near-edge x-ray absorption fine-structure (NEXAFS) spectra of ice and liquid water surfaces in equilibrium with water vapour at up to 4.6 Torr at 0 °C.

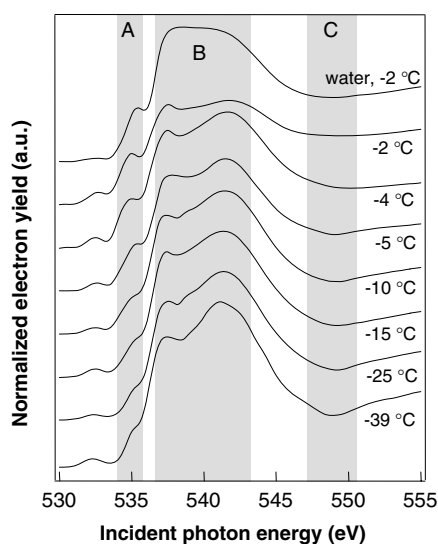
X-ray photoemission spectroscopy probes occupied electronic core levels and provides a quantitative measurement of the elemental composition of the ice surface [7]. Due to the short mean free path of electrons in a condensed phase, the XPS signal originates only from the top few nm of the sample. NEXAFS spectroscopy, on the other hand, probes unoccupied electronic states and is able to distinguish among liquid, vapour, and solid water, due to its sensitivity to the hydrogen bonds of the water molecules, as shown in a recent report [8].

Ice and water samples were condensed from vapour onto a cooled copper substrate. The samples were investigated in the temperature range of  $-40$  to  $0$  °C. The experiments were performed at the Advanced Light Source, Lawrence Berkeley National Laboratory [9]. The incident photon energy in the XPS measurements was set at 620 eV (energy resolution 0.5 eV). Auger-electron-yield NEXAFS experiments were performed near the O 1s region in the energy range of 530–620 eV (the photon energy resolution was set to 0.5 eV)<sup>6</sup>.

Figure 1 shows a set of NEXAFS spectra of water and ice obtained at different temperatures. The spectrum of ice and liquid water exhibits several differences. First there is a small peak at 532.5 eV, which is present in all spectra to different degrees. This peak is due to residual contamination and will be discussed in detail later<sup>7</sup>. Here we will concentrate on the temperature-induced changes. The pure water spectrum starts with the peak at 535 eV (region A). The intensity of this peak changes when going from ice to liquid water. It corresponds to a transition from the O 1s core level to empty states derived from the  $4a_1$  LUMO orbital of gas-phase water [10]. Because of the dipole selection rule, the intensity of this transition depends on the degree of s or p character of the state. In ice, where O is tetrahedrally coordinated, symmetry arguments indicate that the state is largely of s-type symmetry, and should therefore have a low excitation probability [11]. When this symmetry is broken, more p character is expected and consequently also an increase in excitation probability. Myneni *et al* [8] have shown that the largest contribution to this peak comes from water molecules with hydrogen atoms that do not form hydrogen bonds with other water molecules. As can be seen, the peak at 535 eV is indeed more prominent for liquid water (supercooled at  $-2$  °C) than for ice at  $-39$  °C. In the following we will refer to this peak as the ‘free-hydrogen peak’. Other differences occur in the energy range of 537–543 eV (region B), where ice shows a

<sup>6</sup> In our partial-electron-yield NEXAFS measurements, we have collected electrons with kinetic energies in the range between 412 and 437 eV.

<sup>7</sup> The contamination level in the curves of figure 1 roughly corresponds to 10% of a monolayer.



**Figure 1.** Auger-electron-yield NEXAFS spectra of ice and water as a function of temperature at the corresponding equilibrium vapour pressure. The spectra of ice at  $-39\text{ }^{\circ}\text{C}$  and liquid water differ in the strength of the peak at 535 eV (region A), the shape of the broad feature between 537 and 543 eV (region B), and in the dip in the intensity at about 549 eV (region C). The spectra at  $T > -15\text{ }^{\circ}\text{C}$  show a gradual change from ice to water. The small peak at 532.5 eV is due to hydrocarbon contamination.

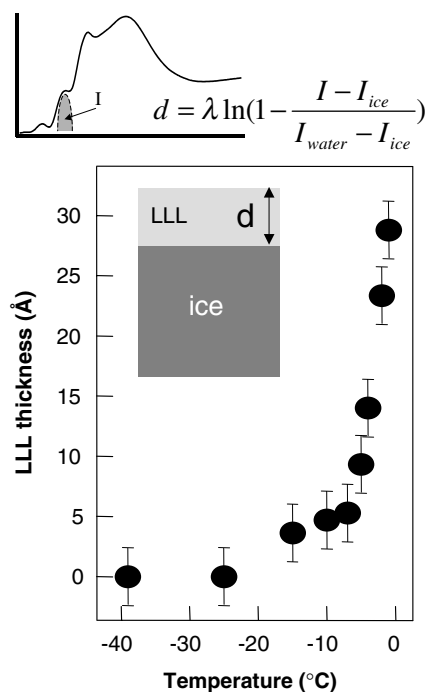
double-peak structure while liquid water exhibits just one broad peak. Also there is a dip in the intensity around 548 eV (region C), which is more pronounced in the case of ice than in the case of liquid water.

We have used the intensity of the free-hydrogen peak, A, to determine the thickness of the liquid-like layer as a function of temperature by assuming that the area under this peak corresponds to pure solid ice in the spectrum at<sup>8</sup>  $-39\text{ }^{\circ}\text{C}$  and to pure liquid in the spectrum of water. Using the known mean free path of the collected electrons (23 Å), we can obtain the thickness of the liquid-like layer<sup>9</sup>. The results are shown in figure 2. The thickness of the liquid-like layer is about 20 Å at  $-2\text{ }^{\circ}\text{C}$ , which is at the lower limit of literature values and comparable to the values found by Dosch *et al* [4] using x-ray diffraction ( $\sim 60\text{ }^{\circ}\text{Å}$  at the  $\{10\bar{1}0\}$  prism face), by Elbaum *et al* [3] using ellipsometry (up to 50 Å on the  $\{0001\}$  basal face), by Furukawa *et al* [13] using ellipsometry (20 Å on the basal plane, but 100 Å on the prism plane), and by molecular dynamics simulations (about 15 Å for both prism and basal plane) [14]. We also see that the thickness becomes negligible below  $-20\text{ }^{\circ}\text{C}$ .

The next important question is that of what the influence of surface contamination is on the premelting of ice. This question can be answered for the first time, thanks to the unique capability of our instrument for allowing acquisition of XPS before and after each NEXAFS spectrum. Contamination at the ice surface occurred as a result of the exposure to residual gases in the chamber and its extent depends on the exposure time. Contamination could be minimized by continuously refreshing the sample surface through condensation of more ice from the water vapour.

<sup>8</sup> The assumption is based on the fact that the spectrum is identical, within experimental error, to the one obtained at  $-100\text{ }^{\circ}\text{C}$ . There could still be a very small amount of liquid-like water at these temperatures. So the curve in figure 2 represents the amount (or thickness) above that.

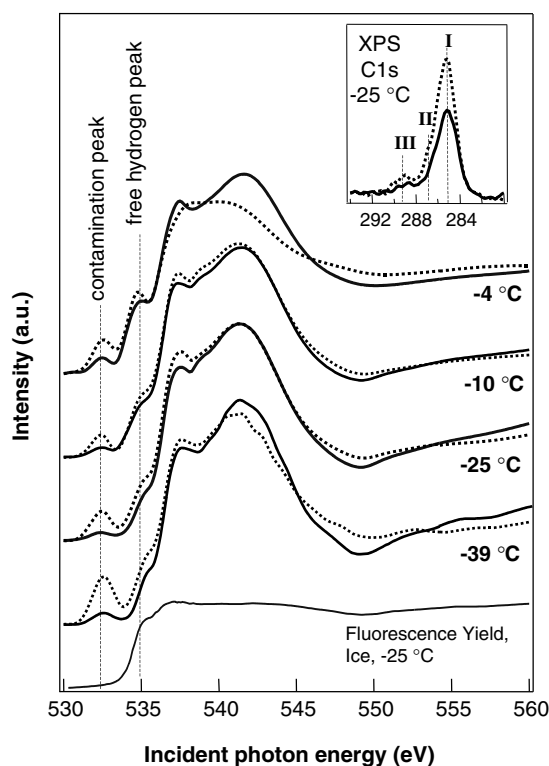
<sup>9</sup> The mean free path of photoelectrons from the O 1s core level is calculated using the relations for oxides in [12].



**Figure 2.** Thickness of the liquid-like layer as a function of temperature obtained by measuring the area of the free-hydrogen peak at 535 eV ( $I$  in the top inset). The peak area at  $-39^\circ\text{C}$  is assigned to pure ice, and the peak area in the water spectrum is assigned to the completely melted surface. The thickness of the liquid-like layer was calculated (see footnote 8), using the mean free path of the collected electrons (about 23 Å).

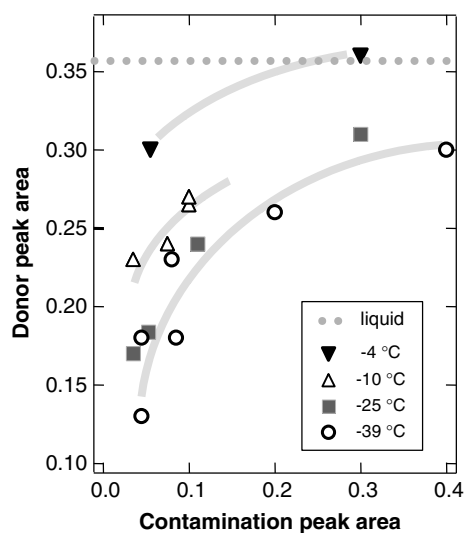
Figure 3 shows NEXAFS spectra of ice at  $-39$ ,  $-25$ ,  $-10$ , and  $-4^\circ\text{C}$  with two different levels of contamination. Only oxygen (the only component of water seen in XPS) and carbon (due to contaminants) were detected using XPS. The inset of the figure shows the carbon 1s region for the  $-25^\circ\text{C}$  data. The intensity of this C spectrum scales with the NEXAFS peak at 532.5 eV. The dotted curves represent the more contaminated samples and the solid ones represent the relatively clean samples. The shape and the multicomponent structure of the C XPS peak fit published spectra of organic acids [15]. The ratio of the peak areas in regions I ( $\text{CH}_n$  bonds), II ( $\text{C-O}$  bonds), and III ( $\text{C=O}$  bonds) indicates an average  $\text{C}_4$ -type carboxyl-containing hydrocarbon. Using the C-to-O XPS peak area ratio, we determined the degree of contamination to be approximately one monolayer in the most contaminated case. The NEXAFS peak at 532.5 eV also resembles the recently observed  $\pi^*$ -resonance in the NEXAFS spectrum of glycine, which is an organic acid as well [16]. Additional confirmation that the 532.5 eV peak is due to surface contamination is provided by fluorescence-yield measurements (bottom spectrum in figure 3), where the peak at 532.5 eV was never observed. Fluorescence yield is largely insensitive to the surface since the signal averages over a depth of 500 nm.

Near the melting point, the contamination layer significantly enhances the premelting of ice. The two NEXAFS spectra at  $-4^\circ\text{C}$  show substantial differences, with the spectrum corresponding to higher hydrocarbon coverage clearly resembling the liquid water spectrum. Much smaller changes are seen in the  $-39$ ,  $-25$ , and  $-10^\circ\text{C}$  spectra, but these also are in the direction of enhanced premelting in the presence of contamination.



**Figure 3.** The influence of hydrocarbon contamination on the premelting of the ice surface at  $-4$ ,  $-10$ ,  $-25$ , and at  $-39$  °C. The hydrocarbon coverage was measured using XPS. The inset displays XPS in the C region for two surfaces showing different degrees of contamination at  $-25$  °C. According to previous chemical shift measurements, XPS peak I corresponds to C–C and  $\text{CH}_n$  bonds, peak II to C–O bonds, and peak III to C=O bonds. The peak I:II:III intensity ratios point to carboxyl-group-containing hydrocarbons that are present at the ice surface. The main panel shows NEXAFS spectra of ice surfaces with different degrees of contamination. At both temperatures, the NEXAFS spectra of the more contaminated surface (dotted lines) show a correspondingly stronger peak at 532.5 eV. At  $-4$  °C, the more contaminated ice surface gives a spectrum that closely resembles the spectrum of liquid water shown in figure 1. The contamination at  $-10$ ,  $-25$ , and  $-39$  °C has only a minor effect on the structure of the ice surface, as can be seen from the spectra. A NEXAFS spectrum obtained using fluorescence photons is shown at the bottom. Since these photons originate from deep inside the ice ( $\sim 500$  nm), the spectrum reflects bulk properties and is insensitive to the surface. As a result, no contamination peak is observed. The saturation of the fluorescence-yield spectrum is caused by the effect of self-absorption [18].

To quantify the influence of surface contamination on the premelting, we have plotted in figure 4 the area under the ‘free-hydrogen peak’ at 535 eV (as a measure for the degree of premelting) versus the area of the contamination peak at 532.5 eV. Although there is some scatter in the data, the trends are clear: there is both a temperature effect (along a vertical line for a given degree of contamination) and a contamination effect. At any given temperature, the water peak area depends on the degree of surface contamination. It is known from sum frequency generation (SFG) experiments that the presence of hydrocarbon layers can affect the structure of the water near the surface. Saturated alkanes do not seem to alter the structure of the free OH bonds at the water or ice surface [17], but alcohols and organic acids do [18, 19]. Although SFG is sensitive to the interface monolayer while oxygen Auger-yield



**Figure 4.** Premelting of the ice surface as a function of temperature and hydrocarbon contamination. The area of the free-hydrogen peak at 535 eV relative to the integrated NEXAFS spectrum (which measures the amount of liquid) is plotted versus the contamination peak area (532.5 eV, also relative to the integrated NEXAFS spectrum). Premelting thus depends strongly on both temperature and hydrocarbon coverage. The horizontal dotted line indicates the area of the free-hydrogen peak for the liquid water.

NEXAFS spectroscopy probes approximately six layers, this is in agreement with our present observations, since the XPS results clearly indicate the presence of single and double C–O bonds (in addition to  $\text{CH}_n$  bonds) in the contaminant molecules.

In conclusion, by using surface-sensitive electron spectroscopies in a novel apparatus, we have shown that the premelting of ice, as determined by NEXAFS spectroscopy, occurs in the temperature range of  $-20$  to  $0$  °C. This is the first spectroscopic observation providing evidence for the disordering of the ice surface near its melting point. In addition, we have shown the important role of surface contamination in enhancing the extent of premelting. This finding is significant because organic contaminants are likely to be present on any ice surface exposed to ambient conditions. The results call for a more detailed study of the role of different types of contaminant that might also affect the premelting of ice, including, for example,  $\text{CO}_2$ , which could play an important role in the chemistry of ice in the Earth's atmosphere.

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