

# Ultrafast Electron-Induced Desorption of Water from Nanometer Amorphous Solid Water Films

Ellen H. G. Backus,<sup>†</sup> Mihail L. Grecea,<sup>†</sup> Aart W. Kleyn,<sup>†,‡</sup> and Mischa Bonn<sup>\*,†,§</sup>

*Leiden Institute of Chemistry, Leiden University, P.O. Box 9502, 2300 RA Leiden, The Netherlands,*

*FOM Institute for Plasma Physics Rijnhuizen, 3430 BE Nieuwegein, The Netherlands, and FOM Institute for Atomic and Molecular Physics, 1098 SJ Amsterdam, The Netherlands*

*Received: February 13, 2007; In Final Form: April 4, 2007*

Laser-induced desorption of water molecules from nanometer amorphous solid water films supported on a single-crystal platinum substrate is reported. A femtosecond laser pulse creates hot substrate electrons, which are injected into the water layer, resulting in significant desorption at the water–vacuum interface. The dependence of the desorption yield on film thickness and results for isotopic spacer and capping layers reveal that the desorbing water originates from relatively deep down into the water layer, i.e., from several nanometers below the surface. This is proposed to be the result of cooperative electronic effects resulting from the high electron densities in the thin water film, which cause a transient destabilization of the water H-bonded network. Motion of excited water molecules through the layer is enabled by mixing within the layer on ultrafast timescales during the desorption process.

## Introduction

The mechanisms of energy and charge transport through water are of interest from both a fundamental and technological point of view. The fundamental interest arises from processes which are of importance for, e.g., biology, environmental sciences, and astrochemistry. For the latter, for example, ionizing radiation in the interstellar medium may trigger chemistry at the surface of ice particles. The radiation will be predominantly absorbed in the bulk of the material, whereas many of the important chemical processes occur on the particle surface. Transport of energy or electrons is therefore necessary in these processes. On the other hand, our understanding of electron-mediated processes in aqueous systems is important for technological applications as diverse as electrochemistry, radiation processing, and medical diagnosis and therapy. As such, there has been much effort trying to understand the fundamentals of electron-initiated processes in water and aqueous systems. An excellent recent review is provided by ref 1.

Ultrathin ice layers can be prepared by deposition of water vapor onto a metal support under ultrahigh vacuum (UHV). The interaction of such films with free electrons can be probed directly, with a low-energy electron beam (see, e.g., ref 2 and references therein), or indirectly, by driving conduction electrons from the support into the film with a laser.<sup>3–7</sup> These and other studies have provided detailed insights into the dynamics of excited states, water–substrate interactions, the role of water film morphology, and the solvation dynamics of energetic electrons. One important aspect that has not yet been studied in much detail is the mechanism of water transport through the supported ice layers, following electron-induced excitation of the molecules.

Here, we use the low-energy electron-induced desorption of amorphous solid water (ASW) supported on a single-crystal Pt-

(533) substrate to study transport of ‘hot’ water molecules. The scheme of the experiments is presented in Figure 1a. A femtosecond laser pulse drives conduction electrons from a Pt surface into a water layer, the thickness of which can be controlled to within a few angstroms. The electrons are injected in one side of the water layer, the Pt–water interface, while desorption occurs at the other side, the water–vacuum interface. By using unmixed layers of D<sub>2</sub>O on top of H<sub>2</sub>O or vice versa, we can trace the original position of the desorbing water molecules: remarkably, water does not desorb solely from the outermost part of the layer, but from inside as well. The water molecules desorb from many water bilayers below the water–vacuum interface, i.e., from a distance to the free surface in excess of 1 nm. This is the result of ultrafast destabilization of the water layer due to extreme nonequilibrium conditions: relatively large amounts of energy (in the form of low-energy electrons; roughly 1 for every 10 water molecules) are injected into the water layer on very short (femtosecond) timescales. This causes a significant disruption of the hydrogen-bonded network, resulting in mixing on ultrashort timescales of water molecules during the ultrafast desorption process.

## Experimental Section

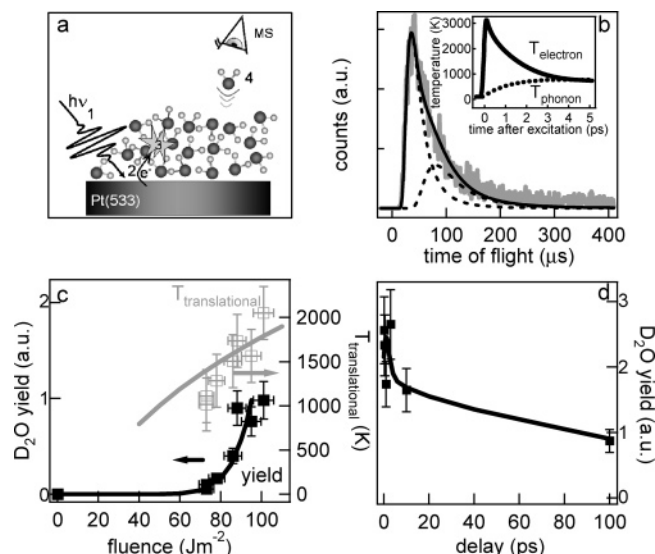
The experiments were performed in a UHV chamber in combination with an amplified Ti:Sa femtosecond laser system (~2.7 mJ, 130 fs, 1 kHz). Roughly 2 mJ of the 800 nm laser output was used to induce desorption of water. Water layers (H<sub>2</sub>O or D<sub>2</sub>O) were grown by an effusive molecular beam with the sample at 100 K resulting in compact, nonporous ASW films.<sup>8</sup> Desorbed water molecules were detected with a mass spectrometer after a 70 mm flight path along the surface normal. After amplification with a fast amplifier the molecules were counted with a multichannel scaler as a function of their flight time. No desorbed water clusters or photoproducts (such as H<sub>2</sub>) were detected in the mass range 2 to 50 amu. Similarly, no photoproducts were observed in thermal desorption experiments after irradiation. Direct excitation of water by the laser pulse is

\* Corresponding author. E-mail: m.bonn@amolf.nl.

<sup>†</sup> Leiden University.

<sup>‡</sup> FOM Institute for Plasma Physics Rijnhuizen.

<sup>§</sup> FOM Institute for Atomic and Molecular Physics.



**Figure 1.** (a) Schematic representation of the experimental approach: (1) The laser excites the electrons in the Pt(533) substrate, which (2) are injected into the thin ASW film, where (3) sufficient energy is released during the relaxation process so that (4) water desorbs which is detected with a mass spectrometer (MS) in TOF experiments. (b) TOF spectrum, for a 15 BL  $D_2O$  film. A two-component Maxwell–Boltzmann fit (black lines) reveals a translational temperature of  $\sim 2000$  K (components:  $\sim 2350$  K (80%) and  $\sim 450$  K (20%)). The inset shows the time evolution of the electron and phonon (lattice) temperature for a typical excitation fluence of  $\sim 90$  J  $m^{-2}$ . The electrons are heated to  $\sim 3000$  K, whereas the phonons remain relatively cold. (c) The first shot yield and the translational temperature as a function of the laser fluence for an ASW ( $D_2O$ ) film of 15 BL thick. The lines are obtained with a model described in the text. (d) Two pulse correlation spectrum for an ASW ( $D_2O$ ) film of 15 BL thick. The line is to guide the eye.

negligible as water does not significantly absorb light with a wavelength of 800 nm. Experiments were single pulse, enabled through the combination of a mechanical chopper and a shutter. The film thickness was obtained from temperature-programmed desorption experiments and expressed in bilayer (BL). Note that 1 BL corresponds to a layer of two water molecules.<sup>9</sup> In this paper we focus on desorption of layers thicker than a few bilayers. Water is known to wet the Pt(533) surface,<sup>9</sup> and accordingly, we find no evidence indicating that the structure of the water layer changes with layer thickness. TPD measurements of  $CHCl_3$  on the water-covered surface and the bare Pt surface indicate that the effective surface area of the ASW films is larger by  $\sim 10\%$  compared to the bare surface. This indicates that the ASW films are relatively flat.

## Results and Discussion

**Evidence for Electron-Induced Desorption.** The use of femtosecond laser pulses to induce desorption, rather than pulses of longer duration, has a unique advantage: femtosecond laser pulses initially excite only the electrons in the Pt substrate resulting in hot electrons. These electrons equilibrate with the phonons on a picosecond time scale. As the heat capacity of the electrons is very small, electronic temperatures can be reached that well exceed the equilibrium melting temperature of the bulk metal, while the lattice remains relatively cold. In the experiments presented here (typical fluence:  $\sim 90$  J  $m^{-2}$ ), the electrons are heated to  $\sim 3000$  K and the phonons to  $\sim 800$  K (see inset of Figure 1b). Under such conditions, electron-mediated desorption commonly occurs (see, e.g., ref 10). Indeed, Figure 1b demonstrates that this mechanism is operative for water on Pt as

well. This figure shows a time-of-flight (TOF) spectrum of water ( $D_2O$ ) desorbing from a 15 BL thick ASW film. A two-component Maxwell–Boltzmann fit reveals an average translational temperature of  $\sim 2000$  K, with 80% of the molecules in the fast channel with a temperature of  $\sim 2350$  K. Water molecules in the slower channel have a translational temperature of  $\sim 450$  K. As the translational temperature of the majority of the desorbing water exceeds the phonon temperature (and, indeed, the melting temperature of Pt), the desorption process is dominated by energy transfer processes involving the electrons, with a minor part of the desorption being phonon-mediated.

Additional information about the excitation mechanism can be obtained from the fluence dependence of the desorption yield (see, e.g., ref 11), as plotted in Figure 1c for a water ( $D_2O$ ) film with a thickness of 15 BL. The yield is obtained by integrating the corresponding TOF spectrum. The ratio of molecules in the fast and slow channel of the TOF was found to be independent of fluence and layer thickness, so that the integrated TOF spectrum provides a good measure of the electron-mediated yield. The spatial profile of the laser beam is explicitly taken into account by calculating the yield-weighted fluence in the manner described in refs 11 and 12. The desorption yield is strongly nonlinear in laser fluence, with a best-fit power law exponent of  $6_{-1}^{+2}$ .

From previous two-photon photoemission studies, it is apparent that one-electron injection into the water layer does not result in significant desorption from the water layer.<sup>5–7</sup> This indicates that the desorption of water observed here is caused by collective effects due to multiple electrons. Indeed, the electron density, based on estimates of the electron density from two-photon photoemission measurements<sup>13</sup> in the water layer immediately following excitation for the highest fluences used here, amounts to approximately  $\sim 1$  electron per 10 water molecules for a typical coverage of 10 BL. The physical picture that thus emerges is that the water layer is destabilized by electrons injected from the Pt substrate, after which additional electrons may readily induce desorption.<sup>14</sup> Indeed, a simple model that describes desorption as such a sequential process by electron injection from the Pt into the ice phase can account for both the fluence dependence and—to a lesser extent—the high translational temperatures. The absorbed laser radiation produces electron–hole pairs that thermalize rapidly to a Fermi–Dirac distribution, characterized by a temperature  $T_{elec}$ . Subsequent transfer of energy to the phonons due to electron–phonon interactions results in cooling of the hot electrons on  $\sim ps$  timescales. The time evolution of both electron and phonon temperatures can be described by the two-temperature model,<sup>15</sup> the result of which is shown in the inset of Figure 1b. To clarify how many electrons can be injected into the water phase, we consider the energetics of the system. The band gap of ice is approximately 8.2 eV.<sup>4</sup> The ice valence band typically lies 5–6 eV below the Pt Fermi level  $E_F$ ,<sup>4,16</sup> so that the ice conduction band lies some 2–3 eV above the Pt Fermi level. Given the time-dependent electron temperature exemplified in the inset in Figure 1b, it is easy to quantify the number of electrons exceeding the 2–3 eV threshold, which have a finite chance of being injected into the water phase. The electron energy distribution at a given electron temperature  $T_{elec}$  is given by the Fermi–Dirac distribution:

$$n(E; T_{elec}) = (\exp((E - E_F)/kT_{elec}) - 1)^{-1} \quad (1)$$

For one laser shot,  $T_{elec}$  depends on time in the manner exemplified in the inset of Figure 1b. Supposing that 2 eV

electrons are sufficiently energetic to be injected into the water layer, the desorption probability at time  $t$  is assumed to be proportional to the product of the instantaneous number of electrons above 2 eV at that time (triggering desorption) and the total number of electrons above 2 eV created with one laser shot up to that point in time (that have destabilized the water layer):

$$P_{\text{des}}(t) \propto n(t, E > 2 \text{ eV}) * \int_{t=0}^t n(\tau, E > 2 \text{ eV}) d\tau \quad (2)$$

with

$$n(t, E > 2 \text{ eV}) = \int_{E_F+2\text{eV}}^{\infty} dE n(E; T_{\text{elec}})$$

where  $n(E; T_{\text{elec}})$  defined as in eq 1 depends parametrically on time  $t$  through the electron temperature. The total desorption yield due to one laser shot is given by the time integral of  $P_{\text{des}}(t)$ .

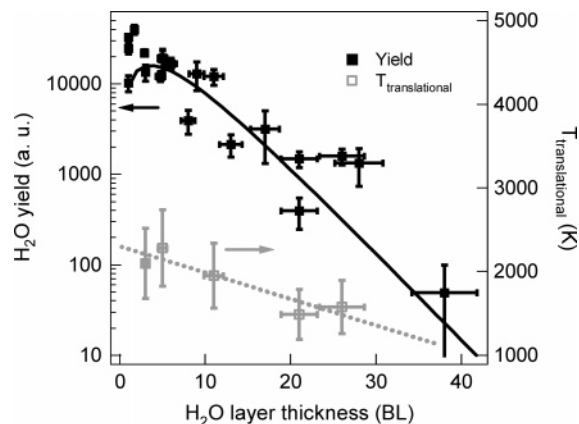
An estimate of the translational energy  $T_{\text{translational}}$  can be obtained from weighting the instantaneous electron temperature with the number of sufficiently energetic electrons and normalizing to the latter:

$$T_{\text{translational}} = \frac{\int_{t=0}^{\infty} dt P_{\text{des}}(t) T_{\text{elec}}(t)}{\int_{t=0}^{\infty} dt P_{\text{des}}(t)} \quad (3)$$

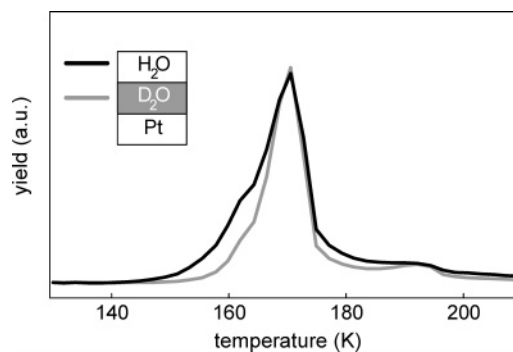
The result of this simple procedure—repeated for different fluences—is plotted as lines in Figure 1c. It captures the essential features of the data: the strongly nonlinear increase of the yield with fluence, and the concurrent more or less linear increase of the translational temperature. In the figure, the calculated translational temperature has been offset by  $-1200 \text{ K}$ . It is not surprising that the model overestimates the translational temperature, as no loss channels are included in this simple model (see below). Note, however, that the trend is reasonably well reproduced, although the slope is underestimated, which could indicate fluence dependent loss channels. We conclude that hot electrons injected from the Pt interface trigger the observed desorption events. Increasing the threshold for the required electron energy to 3 eV, rather than 2 eV, changes the results very little.

Thanks to the nonlinear fluence dependence a two-pulse correlation (2PC) measurement is possible. The pulse is split into two equal parts, which excite the same spot with a variable delay. In Figure 1d the desorption yield is plotted as a function of the delay between pulses. The limiting value at infinite long delay is simply twice the one-pulse yield, which is over an order of magnitude smaller than the yield at zero delay. The observed 2PC decays on a time scale of tens of picoseconds—surprisingly long for an electronic relaxation. This indicates that an additional, phonon-mediated desorption channel exists, as was observed in the TOF spectrum as well. The amount of phonon-mediated desorption ( $\sim 10\%$  of %) is also consistent with the TOF result. Indeed, one would expect that the thermal water layer destabilization is long-lived: the equilibrated electron and phonon temperatures at long times (10s–100s of ps) are well above the bulk melting temperature of water. It seems intuitive that desorption from such a preheated layer is relatively efficient.<sup>17</sup>

**Spatial Origin of the Desorbing Water.** Figure 2 reveals that both the desorption yield and the translational temperature decrease with increasing layer thickness. The fluence is chosen such that for an initial coverage of one bilayer, roughly 50% of the water desorbs in a single shot, as observed in depletion curves (the desorption yield as a function of the laser shot



**Figure 2.** First shot yield and translational temperature as a function of the layer thickness of an ASW ( $\text{H}_2\text{O}$ ) film at a fluence of  $\sim 90 \text{ J m}^{-2}$ . The first shot yield is obtained from recording the yield of 10 sequential laser shots at one place on the crystal (8 times averaged) and fitting an exponential decay to the data. The solid line through the data is the result of a model calculation described in the text. A dashed line serves to guide the eye.



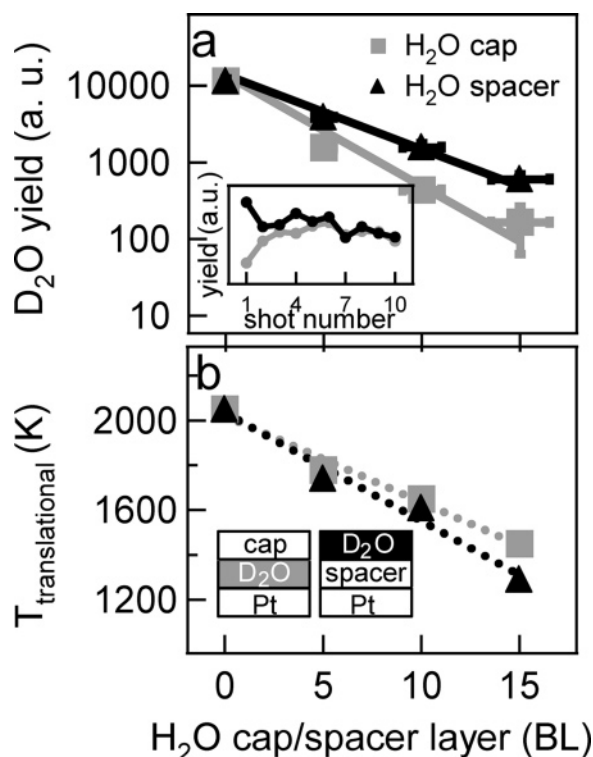
**Figure 3.** TPD spectra of a  $\text{D}_2\text{O}/\text{H}_2\text{O}$  layered system (10 + 10 BL,  $\text{H}_2\text{O}$  on top) that demonstrate that mixing of the two isotopic phases does not occur until desorption sets in. The isotope near the Pt surface,  $\text{D}_2\text{O}$ , desorbs delayed with respect to the top layer, which is also observed for the reverse case ( $\text{H}_2\text{O}$  below  $\text{D}_2\text{O}$ ). The effect becomes increasingly pronounced for thicker layers.

number on one place; data not shown). For thicker layers ( $> 5 \text{ BL}$ ) no significant depletion ( $< 10\%$ ) is observed within the first 10 laser shots. From Figure 2 it is apparent that the decay of the desorption yield with layer thickness is more or less exponential, with a  $\sim 6 \text{ BL}$  exponential length scale. This decay is appreciably slower than that expected from the previously determined 2.3 BL electron mean free path of electrons ejected from a Pt(111) surface with an excess energy of 0.4 eV with respect to the vacuum level.<sup>18</sup> This implies that either additional water transport or excitation transport occurs through the film, prior to desorption.

Transport through the water film is investigated in more detail by performing experiments on stratified  $\text{H}_2\text{O}/\text{D}_2\text{O}$  layers. We first dose a layer of  $\text{D}_2\text{O}$  and cover it with a layer of  $\text{H}_2\text{O}$  (referred to as an  $\text{H}_2\text{O}$  capping layer) or vice versa ( $\text{H}_2\text{O}$  spacer layer).<sup>19</sup> We detect  $\text{D}_2\text{O}$  at 20 amu, as the  $\text{H}_2\text{O}$  signal may be contaminated by OD fragments. It has been shown that the diffusivity of water molecules is exceedingly small at 100 K ( $D \ll 10^{-20} \text{ cm}^2 \text{ s}^{-1}$ ), so that mixing prior to the experiment cannot occur.<sup>20</sup> This is further corroborated by the TPD spectra shown in Figure 3, which demonstrate that the outer isotopomer desorbs first.

The laser-induced desorption yield is plotted in Figure 4a for layers with 5 BL of  $\text{D}_2\text{O}$  and a variable thickness in the  $\text{H}_2\text{O}$  spacer or capping layer. In both cases  $\text{D}_2\text{O}$  desorbs and

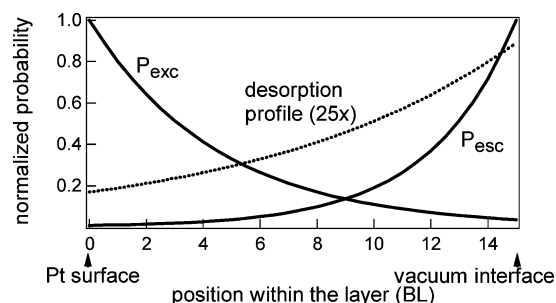




**Figure 4.** D<sub>2</sub>O first shot yield (a) and translational temperature (b) after laser-induced desorption from 5 BL D<sub>2</sub>O on Pt covered with (cap) or spaced by (spacer) H<sub>2</sub>O layers (see inset panel b for schematic pictures of the two conditions) of various thickness. The data points are averaged over typically six fresh spots on the sample. The solid line through the data in panel a is the result of a model calculation described in the text. Dashed lines in panel b serve to guide the eye. The inset in panel a shows the dependence of the yield for the cap and spacer layer as a function of the laser shot number for a 5 BL D<sub>2</sub>O layer on Pt capped with (gray) or spaced by (black) a 5 BL thick H<sub>2</sub>O layer.

the yield decreases with increasing spacer or capping layer thickness. Clearly, significant amounts of D<sub>2</sub>O can penetrate the H<sub>2</sub>O layer, as D<sub>2</sub>O is also detected when a capping layer of H<sub>2</sub>O is present, even for capping layers of 15 BL. This demonstrates that the relatively slow decay of the yield with increasing thickness (Figure 2) is predominantly due to water transport through the layer, rather than excitation or electron transport. Note that only the first shot yield is measured, because after the first shot we observe that the layers are locally intermixed due to transient laser heating. This is illustrated in the inset of Figure 4a where the yield is plotted as a function of the laser shot number. After the fifth shot the yields for the capping and spacer layers are equal, indicating that the layers are then locally completely mixed.

A simple phenomenological model can be used to trace the spatial origin of desorbing water molecules from within the layer, independent of the precise desorption mechanism. Electrons from the Pt are injected in the water layer and excite the water layer. Electron-excited water molecules can subsequently traverse the remaining water layer across to the vacuum, allowing the molecule to desorb. The desorption yield is determined by the product of the probability that a certain water molecule is excited by an electron from the Pt and its subsequent escape probability through the water layer. We postulate that the excitation probability  $P_{\text{exc}}$  depends exponentially on the distance from the Pt surface and is determined by the electron mean free path, while the molecular escape probability  $P_{\text{esc}}$  depends exponentially on the distance from the excitation



**Figure 5.** Summary of the model parameters resulting from fits to the data presented in Figures 2 and 3 exemplified for a 15 BL thick water film: The electron injection length is determined by parameter  $P_{\text{exc}}$ , which decays on  $\sim 4.5$  BL length scales; the water escape probability  $P_{\text{esc}}$ , determined by the traverse length of a water molecule through ASW decays from the water–vacuum interface on a 3 BL length scale. The resulting desorption profile (dotted line), the product of the excitation and escape probability, reveals that desorption occurs from a large part of the layer.

location to the free surface. We assume a step function for the H<sub>2</sub>O/D<sub>2</sub>O concentration.

Using this model we can extract the electron mean free path length and the traverse length of a water molecule from our data. The best fit using this model is depicted in Figures 2 and 4a. We take into account a 10% higher yield for the desorption of H<sub>2</sub>O (Figure 2) compared to D<sub>2</sub>O (Figure 4a) as observed in independent experiments. From simultaneously fitting both the experimental yield vs layer thickness and the desorption data for various thicknesses of capping and spacer layer, we obtain an electron mean free path, which determines the spatial variation of  $P_{\text{exc}}$ , of 4.5 BL and a water traverse length, which determines the spatial variation of  $P_{\text{esc}}$ , of 3 BL. The inferred electron mean free path is somewhat larger than the value of 2.3 BL reported in literature,<sup>18</sup> indicating that either the electron mean free path is slightly higher for the laser-excited hot electrons, which exhibit a distribution of energies, or secondary processes such as electron–electron interactions enhance this excitation length. Moreover, preliminary molecular dynamics simulations indicate that the excitation can be transferred from one water molecule to a nearest neighbor, which could also be concluded from the decrease of the translational temperature as a function of the thickness of the spacer layer (see Figure 4b). The decrease in translational temperature with capping layer thickness (see also Figure 4b) illustrates the loss of kinetic energy when water molecules have to cross the remaining water molecules.

The result of this simple procedure is summarized in Figure 5, which shows the spatial decay of the excitation probability from the Pt interface into the water film and the escape probability from the film into the vacuum. The resulting desorption profile, the product of the excitation and escape probability, reveals that even for relatively thick films, desorption occurs from a large part of the film and is not localized to the Pt–water or water–vacuum interface. This results from the competition between the initial excitation that is mainly localized to the Pt interface, while the water escape is most probable at the vacuum interface.

**Mechanism of Photodesorption.** Our data clearly show that water originating from several nanometers below the surface can desorb upon laser excitation with femtosecond pulses. These observations cannot be explained by the recently reported defect-mediated mechanism that accounts for photoejection of water molecules with nanosecond laser pulses.<sup>21</sup> The key observation there was that the surface water coverage is not significantly

depleted due to irradiation, and desorption is a minority process. In our experiments, depletion is readily achieved by the photoinjected electrons, especially at low coverage, ruling out a defect-mediated mechanism. Moreover, for thicker layers we observe a constant desorption yield as a function of laser shot number (see inset Figure 4a). If the mechanism was defect mediated, the signal should decrease as the amount of defects should be limited, which is indeed observed in ref 21. Although strictly speaking we cannot exclude a small contribution from defect-mediated desorption, we find no indications in our data.

For water layers on Cu(111) and Ru(001), ultrafast solvation of electrons in the water layer has been observed after laser excitation at relatively low excitation density,<sup>4,7</sup> prior to back-donation into the metal. This process does not result in significant desorption. Desorption requires higher electron excitation densities, which may also explain the observation that water originates from relatively deep down into the water layer: the injection of an electron in the water layer and the subsequent hydration process cause substantial rearrangement of the hydrogen-bonded network at high electron densities. Additional incident electron experiences a perturbed system, which will facilitate the desorption process; the loosened hydrogen-bonded structure facilitates the traverse of kinetically hot electrons through the water layer.

The inset in Figure 4a clearly demonstrates that the D<sub>2</sub>O and H<sub>2</sub>O layers mix upon excitation. This mixing can occur before, during, or after excitation. First we consider two simple limits in which mixing and desorption are temporally separated: in the first limit, mixing occurs *before* the onset of desorption. This is at odds with our observation that, for the 5 + 5 BL H<sub>2</sub>O/D<sub>2</sub>O system, the D<sub>2</sub>O desorption yield is 2.5 times higher when D<sub>2</sub>O is on top (Figure 4a), compared to the situation when H<sub>2</sub>O is on top. In the second limit, mixing occurs *after* the desorption process is complete. This is an equally improbable scenario, as it is highly unlikely that any D<sub>2</sub>O would be able to traverse 15 BL of H<sub>2</sub>O without any significant loss of translational energy. Mixing and desorption are thus concluded to occur simultaneously on ultrafast timescales. This is in agreement with a rough estimate of the diffusion length. At the transient temperature during the excitation process (>500 K, for only a few picoseconds) the diffusion constant for water amounts to  $\sim 10^{-4}$  cm<sup>2</sup> s<sup>-1</sup>,<sup>20</sup> resulting in a diffusion length of a couple of Å in a few picoseconds. Mixing prior to desorption (both triggered by the same laser shot) can in principle explain the data, except for one anomalous observation: the temperature for desorbing D<sub>2</sub>O molecules capped by an H<sub>2</sub>O layer (i.e., that have to penetrate the H<sub>2</sub>O layer) is significantly and reproducibly higher than for D<sub>2</sub>O with an H<sub>2</sub>O spacer layer; water originating close to the Pt substrate was consistently found to display higher translational temperatures (see, e.g., Figure 4b). One would expect that a simple sequence of mixing and desorption would result in a homogeneous translational temperature distribution and is thus at odds with the observation that water originating from different locations within the layer clearly exhibits different translational temperatures. If desorption from the outermost layers precedes the desorption of water molecules from deeper down into the layer, one might actually expect those water molecules originating from deeper down to be translationally cooler, as the electronic temperature transient is very short-lived:  $\sim 1$  ps after excitation. Molecules desorbing from deeper down would require time to reach the surface and would therefore be expected to be colder. The observation of relatively high translational temperatures for water desorbing from close to the Pt surface indicate that transport of water from the Pt–

water interface to the water–vacuum interface does not occur in a purely diffusive, equilibrated manner.

## Conclusion

Femtosecond laser-induced desorption of molecular water from metal-supported ASW layers reveals that electron-excited water molecules can traverse a layer of several water molecules thick in order to desorb from the water layer. This is concluded from isotopically labeled water layers and the relatively weak thickness dependence of the desorption probability. Mixing on ultrafast timescales within the isotopically stratified layer is responsible for this observation, although the translational temperatures and their distribution indicate that this is not a (quasi-)equilibrium process.

**Acknowledgment.** This work is part of the research program of the “Stichting voor Fundamenteel Onderzoek der Materie (FOM)”, which is financially supported by the “Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO)”. The authors are grateful to O. Berg and H. Bakker for their useful comments on the manuscript, and S. Andersson for preliminary MD calculations. E.H.G.B. and M.L.G. contributed equally to this work.

## References and Notes

- (1) Garrett, B. C.; Dixon, D. A.; Camaioni, D. M.; Chipman, D. M.; Johnson, M. A.; Jonah, C. D.; Kimmel, G. A.; Miller, J. H.; Rescigno, T. N.; Rossky, P. J.; Xantheas, S. S.; Colson, S. D.; Laufer, A. H.; Ray, D.; Barbara, P. F.; Bartels, D. M.; Becker, K. H.; Bowen, H.; Bradforth, S. E.; Carmichael, I.; Coe, J. V.; Corrales, L. R.; Cowin, J. P.; Dupuis, M.; Eiseenthal, K. B.; Franz, J. A.; Gutowski, M. S.; Jordan, K. D.; Kay, B. D.; LaVerne, J. A.; Lyman, S. V.; Madey, T. E.; McCurdy, C. W.; Meisel, D.; Mukamel, S.; Nilsson, A. R.; Orlando, T. M.; Petrik, N. G.; Pimblott, S. M.; Rustad, J. R.; Schenter, G. K.; Singer, S. J.; Tokmakoff, A.; Wang, L. S.; Wittig, C.; Zwier, T. S. *Chem. Rev.* **2005**, *105*, 355.
- (2) Petrik, N. G.; Kimmel, G. A. *J. Phys. Chem. B* **2005**, *109*, 15835.
- (3) Chakarov, D.; Kasemo, B. *Phys. Rev. Lett.* **1998**, *81*, 5181.
- (4) Gahl, C.; Bovensiepen, U.; Frischkorn, C.; Wolf, M. *Phys. Rev. Lett.* **2002**, *89*, 107402.
- (5) Bovensiepen, U.; Gahl, C.; Wolf, M. *J. Phys. Chem. B* **2003**, *107*, 8706.
- (6) Bovensiepen, U. *Prog. Surf. Sci.* **2005**, *78*, 87.
- (7) Bovensiepen, U.; Gahl, C.; Stähler, J.; Wolf, M. *Surf. Sci.* **2005**, *584*, 90.
- (8) Stevenson, K. P.; Kimmel, G. A.; Dohnálek, Z.; Smith, R. S.; Kay, B. D. *Science* **1999**, *283*, 1505.
- (9) Grecea, M. L.; Backus, E. H. G.; Riedmüller, B.; Eichler, A.; Kleyn, A. W.; Bonn, M. *J. Phys. Chem. B* **2004**, *108*, 12575.
- (10) Denzler, D. N.; Frischkorn, C.; Hess, C.; Wolf, M.; Ertl, G. *Phys. Rev. Lett.* **2003**, *91*, 226102.
- (11) Funk, S.; Bonn, M.; Denzler, D. N.; Hess, C.; Wolf, M.; Ertl, G. *J. Chem. Phys.* **2000**, *112*, 9888.
- (12) Struck, L. M.; Richter, L. J.; Buntin, S. A.; Cavanagh, R. R.; Stephenson, J. C. *Phys. Rev. Lett.* **1996**, *77*, 4576.
- (13) Wolf, M. Private communication, 2006.
- (14) For high electronic excitation of metal substrate–adsorbate systems, desorption is generally associated with a DIMET (desorption induced by multiple electronic transitions) picture of repeated electron attachment to a short-lived adsorbate electronic state. Such a picture is not expected to be applicable here, given the system properties. The multielectron effect here is presumably caused by the relatively high density of electrons injected into the water layer.
- (15) Anisimov, S. I.; Kapeliovich, B. L.; Perel'man, T. L. *Sov. Phys. JETP* **1974**, *39*, 375.
- (16) Henderson, M. A. *Surf. Sci. Rep.* **2002**, *46*, 5.
- (17) Note that a similar fluence dependence and 2PC have previously been observed for femtosecond laser-induced water desorption from Ag nanoparticles (ref 22). On these grounds, phonon-mediated desorption was concluded in that study, in which TOF measurements were not reported. Our results show that these results may also be explained by an electron-mediated, many-electron process.
- (18) Jo, S. K.; White, J. M. *J. Chem. Phys.* **1991**, *94*, 5761.
- (19) We carefully checked that the H<sub>2</sub>O does not contain traces of D<sub>2</sub>O.
- (20) Smith, R. S.; Kay, B. D. *Nature* **1999**, *398*, 788.
- (21) Bergeld, J.; Chakarov, D. *J. Chem. Phys.* **2006**, *125*, 141103.
- (22) Kwiet, S.; Starr, D. E.; Grujic, A.; Wolf, M.; Hotzel, A. *Appl. Phys. B* **2005**, *80*, 115.