A theoretical and experimental study on translational and internal energies of H$_2$O and OH from the 157 nm irradiation of amorphous solid water at 90 K

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The photodesorption of H$_2$O in its vibrational ground state, and of OH radicals in their ground and first excited vibrational states, following 157 nm photoexcitation of amorphous solid water has been studied using molecular dynamics simulations and detected experimentally by resonance-enhanced multiphoton ionization techniques. There is good agreement between the simulated and measured energy distributions. In addition, signals of H$^+$ and OH$^+$ were detected in the experiments. These are inferred to originate from vibrationally excited H$_2$O molecules that are ejected from the surface by two distinct mechanisms: a direct desorption mechanism and desorption induced by secondary recombination of photoproducts at the ice surface. This is the first reported experimental evidence of photodesorption of vibrationally excited H$_2$O molecules from water ice.

1. Introduction

A number of studies have been performed on the photochemistry of water ice, because of the interest in photodesorption and photodissociation in the fields of atmospheric chemistry and astrophysics. Water ice has been observed on bodies in the outer Solar system, e.g., satellites of Jupiter and Saturn, and Kuiper Belt objects as well as in interstellar and circumstellar regions of space. Observational evidence suggests that water ice in the Solar system is mostly crystalline with some smaller amounts of amorphous ice. The balance between the two types of ice is governed by amorphization through irradiation by ions and electrons from the Solar wind and by Solar ultraviolet (UV) photons, and thermal recrystallization, which means that warmer ices are more likely to be crystalline than colder ones given equal radiation intensity. A large part of gas phase water in interstellar and circumstellar space has been attributed to photodesorption of water molecules induced by absorption of UV photons at ice-covered grains. Interstellar and circumstellar ices are most likely predominantly amorphous, but some crystalline ice may exist, e.g., close to young stellar objects.

Photo-ejection of water molecules from ice surfaces has been investigated in the wavelength range from vacuum ultra-violet (VUV) to the visible region via one- and multi-photon absorption, and an energy threshold of ~9 eV identified. Since this value is compatible with the width of the ice band gap, it has been speculated that the observed photo-ejection results from formation of excitons in ice. Westley et al. investigated the desorption mechanism of H$_2$O from water ice films by 10.2 eV (Lyman-α) photons. The authors suggested that the accumulation and diffusion of photoproduced radicals in/on the ice was necessary for water desorption to occur. Öberg et al. reached a different conclusion, however. They used a VUV lamp emitting in the range 7.0–10.5 eV to irradiate ices at surface temperatures in the range 18–100 K and detected desorbing species such as H$_2$O, OH, H$_2$, and O$_2$ as well as determining the composition of the ice, and concluded that desorption of H$_2$O and OH from the ice occurs mainly via primary processes. Since the reaction mechanisms are inferred by identifying photodesorbed products and species formed in/on ice, they were not able to reveal the formation dynamics or finer details of the reactions. In our previous studies, we investigated photodissociation of water in/on amorphous solid water (ASW) at 90 K using pulsed 157 nm laser radiation, i.e., at a wavelength within the first absorption band of the ice, to reveal the translational and...
internal energy distributions of \( \text{OH}(v = 0, 1) \) and \( \text{H}_2\text{O}(v = 0) \).\textsuperscript{33-35} The photodesorption of \( \text{OH} \) and \( \text{H}_2\text{O} \) from the VUV photolysis of ASW was also studied by molecular dynamics (MD) calculations.\textsuperscript{36-38} These simulations predicted the existence of the previously unknown “kick-out” mechanism for water photodesorption, whereby an energetic \( \text{H} \) atom, formed by photodissociation of a molecule in the ice, “kicks” a neighboring molecule out of the surface, often assisted by a repulsive interaction induced by the excitation in the ice. The desorption mechanisms for \( \text{H}_2\text{O}(v = 0) \) discussed in our previous papers\textsuperscript{34,35} can be grouped into three types. These are distinguished on the basis that the desorbing molecule is: (A) the one that experiences the initial electronic excitation, (B) expelled as a result of electronic excitation of a neighboring molecule, or (C) formed by the recombination of photofragments arising from different photodissociated molecules. Types (A) and (B) are considered to be direct processes, whereas (C) involves secondary processes. Initially, type (A) and (C) mechanisms will involve high internal energies in the desorbing molecules (due to photoexcitation and recombination, respectively). Both might thus be expected to favor formation of vibrationally excited \( \text{H}_2\text{O} \) molecules, whereas the type (B) mechanism could well result in desorbed \( \text{H}_2\text{O}(v = 0) \) molecules.

The exact mechanism underpinning type (B) desorption is difficult to specify. Part of the excitation energy is somehow transferred from the surface into translational energy of a \( \text{H}_2\text{O} \) molecule. This could occur via an exciton-induced process, either through a repulsive electronic interaction, or by kinetic energy transfer from a vibrationally excited \( \text{H}_2\text{O} \) molecule formed by electronic relaxation to the ground state. The kick-out desorption mechanism is closely related to the exciton-induced process in as much that it also involves a change in the binding properties of the desorbing molecule but, additionally, requires a kick from an incident \( \text{H} \) atom to ensure desorption. In the electronic relaxation process, the vibrational excitation that promotes desorption comes from de-excitation of the excited state molecule, with the initial electronic energy transformed into nuclear kinetic energy. This can occur “directly”, before the molecule has dissociated, or “semi-directly”, through dissociation and prompt (geminate) recombination of the resulting photofragments. This semi-direct desorption mechanism was evident in the previous simulations by Andersson and van Dishoeck,\textsuperscript{35} albeit with a much lower probability than the other desorption mechanisms. In conclusion, therefore, there are several different detailed mechanisms that could lead to direct photodesorption of \( \text{H}_2\text{O}(v = 0) \) molecules.

Comparison with experiments showed that the measured translational and rotational energy distributions of desorbing \( \text{H}_2\text{O}(v = 0) \) closely matched the energies predicted by the MD simulations for the kick-out mechanism, lending credibility to this as a plausible mechanism for water photodesorption.\textsuperscript{34,35} Initially the MD simulations were run only for \( T = 10 \text{ K} \),\textsuperscript{36,37} but in the most recent study\textsuperscript{38} the focus was on the temperature dependence of photodesorption in the range \( T = 10-90 \text{ K} \). It was found that \( \text{H}_2\text{O} \) and \( \text{OH} \) photodesorption probabilities show a significant dependence on temperature, in qualitative agreement with experiments.\textsuperscript{32} The experimental photodesorption yields from \( \text{D}_2\text{O} \) and \( \text{H}_2\text{O} \) ice showed a more pronounced rise with increasing temperature than predicted by the MD simulations. The latter only included direct photodesorption caused by absorption of a single VUV photon in the ice and thus did not allow for secondary processes (which must involve multiple excitations). Thus it was suggested that the increased desorption induced yields at higher temperatures might be associated with secondary recombination of photoproduced \( \text{H} \) and \( \text{OH} \) radicals, which will have higher mobility at higher temperatures.

The present work describes further advanced experimental studies and additional classical MD calculations of the translational and rotational energies of \( \text{H}_2\text{O} \) and \( \text{OH} \) species desorbing from an ASW ice surface exposed to 157 nm laser radiation. A small part of the results have been presented before,\textsuperscript{34,35} but are repeated here to add context. The new MD results presented in this paper are translational energy distributions of the \( \text{H}_2\text{O} \) molecules photodesorbed by the kick-out mechanism and by the direct recombination mechanism, as well as energy distributions of desorbing \( \text{OH}(v = 0 \text{ and } 1) \). We also report a previously undetected photodesorption component evident through the experimental detection of \( \text{H}^+ \) and \( \text{OH}^+ \) signals, which we propose as a signature of highly vibrationally excited \( \text{H}_2\text{O} \) molecules. Comparison with our previous experimental results and the new detection of \( \text{H}^+ \) and \( \text{OH}^+ \) signals provide new insights into the prevailing reaction mechanisms and dynamics.

2. Molecular dynamics simulations

Details of the MD calculations of ice photochemistry have been described elsewhere.\textsuperscript{36-38} Here we mostly focus on what is different from the previous calculations. To obtain a realistic model of the experimental setup, we have created an amorphous ice surface by rapidly cooling a liquid water surface from 300 K to 90 K, in the manner described by Al-Halabi \textit{et al}.\textsuperscript{39,40} and Andersson \textit{et al}.\textsuperscript{46} Initially, a periodic slab of the equivalent of 8 crystalline bilayers was created with 480 molecules in each periodic cell. Out of these molecules, 120 were kept frozen at all times to simulate bulk ice. The remaining, fully mobile, 360 molecules were divided into 12 monolayers of 30 molecules each. The monolayers are defined as the equivalent of half a bilayer of crystalline ice.\textsuperscript{36}

All molecules are initially treated as rigid rotors and their interactions are treated with the TIP4P potential.\textsuperscript{41} One molecule is selected for photoexcitation and this molecule is then made completely flexible. The excitation model uses a Monte Carlo sampling over a Wigner distribution of the ground vibrational state of \( \text{H}_2\text{O} \)\textsuperscript{36} and the sampled geometries are projected from the electronic ground state to the first excited state potential energy surface (PES). The latter is based on the PES of the first excited state of gas phase \( \text{H}_2\text{O} \).\textsuperscript{42-44} Combined with modified partial charges on the excited molecule. The partial charges were set as atom-based charges of \(-0.2e\) for \( \text{O} \) and \( 0.1e \) for \( \text{H} \).\textsuperscript{36} This adjustment was made so as to obtain the best fit to the peak of the experimental UV absorption spectrum of ice previously reported by Kobayashi.\textsuperscript{45} The excitation energy was calculated as the energy difference between the sampled configuration in the
energies for OH and desorbing rigid H$_2$O, vibrational energies were monitored for all species, as well as the rotational degree of freedom of the desorbing species. The translational energies of H$_2$O were binned to the closest vibrational quantum state. Note that this analysis does not invoke explicit quantum mechanics, only a population distribution over vibrational quantum state. Given the potential used in the present MD calculations, we expect that most of the molecules excited at 157 nm are very close to the vacuum interface: of the configurations sampled with excitation energies 7.8–8.0 eV, about half (49%) are in the top monolayer, 36% in the second and 17% in the third monolayer. Since most photodesorption occurs when the excitation is in the top monolayers, 36–38 excitations in this energy range should lead to a high probability of photodesorption. Support for this view is provided by previous simulations showing that the H atom photodesorption probability per absorbed photon declines with increasing excitation energy—because lower energy excitations are concentrated in the top layers.

4. Results

4.1 UV absorption of water ice

Given the potential used in the present MD calculations, we predict that most of the molecules excited at 157 nm are very close to the vacuum interface: of the configurations sampled with excitation energies 7.8–8.0 eV, about half (49%) are in the top monolayer, 34% in the second and 17% in the third monolayer. Since most photodesorption occurs when the excitation is in the top monolayers, 36–38 excitations in this energy range should lead to a high probability of photodesorption. Support for this view is provided by previous simulations showing that the H atom photodesorption probability per absorbed photon declines with increasing excitation energy—because lower energy excitations are concentrated in the top layers.

4.2 Photodesorption of H$_2$O molecules

4.2.1 Molecular dynamics. The MD calculations show two distinct mechanisms of H$_2$O photodesorption. One is the direct recombination mechanism, where the photodesorption...
products H and OH recombine instantly and subsequently desorb. The other is where a neighboring H$_2$O molecule is “kicked out” by momentum transfer from an energetic H atom produced from photodissociation. The efficiency of this momentum transfer is in many cases boosted by interactions between the photoexcited H$_2$O and a photoproduced proximate OH species. This leads to a repulsive potential for the neighboring ground-state H$_2$O which, as a result, gains translational energy. The subsequent momentum kick from the H atom supplies sufficient energy for the molecule to desorb. Since all H$_2$O molecules (except the one that is photoexcited) are kept internally rigid in the simulations, there is of course no possibility of energy transfer from the H atom to the intramolecular degrees of freedom of the kicked-out H$_2$O molecule. This means that all kicked-out molecules in these simulations are considered to remain in their vibrational ground state throughout the trajectory.

The simulated H$_2$O photodesorption probability was found to be $8 \times 10^{-3}$ per absorbed UV photon. Of these, ~25% were kicked out and the rest were recombined. The mean translational energy ($E_{\text{trans}}$) of the kicked-out molecules was 0.25 ± 0.03 eV, which would correspond to a translational temperature, $T_{\text{trans}} = 1450 \pm 150$ K, calculated by using $E_{\text{trans}} = 2k_BT_{\text{trans}}$. The mean rotational energy ($E_{\text{rot}}$) was 0.039 ± 0.006 eV, corresponding to $T_{\text{rot}} = 300 \pm 50$ K ($E_{\text{rot}} = 3/2k_BT_{\text{rot}}$). These results compare favorably with the previously reported experimental energy distributions for desorbing H$_2$O($v=0$), as can be seen from Table 1. The simulated translational energies are at the low end, but still within the experimental error bars, while the mean rotational energies show perfect agreement. The simulated translational energy distribution is quite close to the thermal distribution at 1450 K (Fig. 1), within the error bars, suggesting that this desorption process follows the behavior predicted by Zimmermann and Ho for particles desorbing on a repulsive potential. *A priori*, it was not clear that the simulated energies would agree with a M–B energy distribution, so this finding serves to reinforce the agreement with experiments.

The predicted energy distributions of H$_2$O molecules formed by recombination and subsequent desorption are very different. The predicted translational energy distribution is a little hotter, with $E_{\text{trans}} = 0.34$ eV, which equates to $T_{\text{trans}} \sim 2000$ K. The average rovibrational energy, however, is very much hotter—close to the H + OH dissociation limit (i.e., 5.3 eV above the minimum on the H$_2$O PES). Even the least excited H$_2$O molecules formed by this mechanism are predicted to have an internal energy of ~1.8 eV (relative to the vibrational ground state). This mechanism is thus predicted to yield H$_2$O molecules with very high levels of internal excitation (henceforth denoted as H$_2$O($v^*$)), and no

### Table 1  Translational and rotational temperatures of photodesorbed (λ = 157 nm) H$_2$O($v=0$) molecules from amorphous solid water at 90 K

<table>
<thead>
<tr>
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<th>$T_{\text{trans}}$ (K)</th>
<th>$T_{\text{rot}}$ (K)</th>
</tr>
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<tbody>
<tr>
<td>Experimental</td>
<td>1800 ± 500</td>
<td>300 ± 100</td>
</tr>
<tr>
<td>MD calculations</td>
<td>1450 ± 150</td>
<td>300 ± 50</td>
</tr>
</tbody>
</table>

*Ref. 34 and 35. *b Determined for a time of flight of 2.5 μs.
predisassociation, depending on the vibrational state. The reported 2 + 1 REMPI spectra are thus dominated by transitions involving C state levels with low $J'$ and $K'_z \sim 0$. The X and C states of H$_2$O, and the ground state of H$_2$O$^+$, all have similar equilibrium geometries (and vibrational frequencies). On Franck–Condon grounds, therefore, we can expect that the H$_2$O(C–X) transition would be dominated by diagonal (i.e. $\Delta v = 0$) excitations, and that H$_2$O(v*) molecules would give REMPI signals in the same spectral region as the C(000)–X(000) origin band. All of the prominent features in this region of the 2 + 1 REMPI spectrum recorded in the present study by monitoring the parent ion are attributable to H$_2$O(v = 0) molecules, but some weak H$^+$ and OH$^+$ signals were observed, with a different spectral signature to that of the H$_2$O(v = 0) molecules. This is not particularly surprising—reflecting (i) the relative efficiency of the kick-out mechanism for forming H$_2$O(v = 0) molecules and (ii) the (relative) stability of the resonance enhancing C(000) level with respect to predisassociation.\textsuperscript{53,54} The observation of fragment ions, with a different spectral signature to that of the H$_2$O(v = 0) molecules, could be due to REMPI of H$_2$O(v*) molecules rather than direct ionization of neutral H or OH fragments.

To explore this possibility further, we focused attention on spectral regions appropriate for $\Delta v_2 = -1$ and $\Delta v_1 = -1$ transitions, i.e. around the expected position for C(000)–X(010), and C(000)–X(100) transitions. The latter region also covers the expected region for $\Delta v_2 = -2$ transitions as the $v_1 = 1$ and $v_2 = 2$ levels of H$_2$O are close in energy. Structured excitation spectra for forming both H$^+$ and OH$^+$ ions were observed in both regions, but the corresponding spectrum for forming ions with $m/z = 18$ (H$_2$O$^+$) was weak and devoid of structure. Simulations of transitions involving C(000) in this region can easily be produced as the constants for both upper and lower states are readily available. Fig. 3 shows a simulation of the $\Delta v_2 = -1$ region calculated using PGOPHER\textsuperscript{55} together with spectroscopic parameters taken from the literature as described in ref. 50 assuming a Boltzmann distribution over rotational states with $T_{\text{rot}} = 350$ K. It is clear from the figure that, while the density of features is not unreasonable, there is no clear match with the calculated 2 + 1 REMPI spectrum of the H$_2$O C(000)–X(010) transition. Similar simulations of the 000–100 and 000–020 bands also gave no direct match with experiment. It is not possible to simulate transitions from excited vibrational states (e.g. 0(n – 1)–0n0 or (m – 1)00–m00) as the relevant C state constants and predissociation rates are not known. We would expect such transitions to be broadly similar, but with fewer sharp lines as levels with higher $J'$ or $K'_z$ are more likely to predisassociate giving a broad background to the spectrum.

The evident disagreement between the measured H$^+$ and OH$^+$ yield spectra and the H$_2$O C(000)–X(010) 2 + 1 REMPI spectrum is consistent with the results of the MD simulations, which predict that the H$_2$O(v*) molecules formed by the recombination/desorption mechanism have internal energies > 1.8 eV and, on average, \(~5.3 eV (cf. the \sim 0.2 eV vibrational energy associated with the v$_2$ = 1 level). Such molecules would be expected to follow the excitation scheme:

$$\text{H}_2\text{O}(v^*) + 2\hbar\nu \rightarrow \text{H}_2\text{O}(C,v^*)$$

(1)

Many of the H$_2$O(C,v*) molecules will predisassociate to neutral H atoms and OH radicals at this stage but, in the presence of the intense REMPI laser radiation, some will absorb another photon and ionise, i.e.

$$\text{H}_2\text{O}(C,v^*) + \hbar\nu \rightarrow \text{H}_2\text{O}^+(X,v^*)$$

(2)

Given the similar equilibrium geometries of the C state and the ion, we assume that the parent vibrational excitation is broadly conserved upon ionisation. The bond dissociation energies, $D_0(\text{H–OH}^+)$ and $D_0(\text{H}^–\text{OH})$ are 5.500 eV and 6.082 eV, respectively,\textsuperscript{56} so absorption of one further REMPI laser photon would suffice to yield the observed H$^+$ and OH$^+$ fragment ions, for all but the lowest few vibrational levels of H$_2$O$^+$ i.e.

$$\text{H}_2\text{O}^+(X,v^*) + \hbar\nu \rightarrow \text{H}^+ + \text{OH}$$

(3)

Any parent ions formed \textit{via} steps (1) and (2) would be expected to show the spectral signature of the initial C–X excitations, but the parent ion yield is small—presumably because the further one photon step (3) has high probability at the prevailing laser intensities. We can therefore understand the observed H$^+$ and OH$^+$ fragment ion signals as originating from photodissociation of H$_2$O$^+$ ions in a wide range of vibrational states, with no clear match with the spectral of simulations as only a few peaks from a few vibronic bands involving H$_2$O(v*) molecules give sharp peaks.

Fig. 4 shows typical TOF spectra of H$^+$ and OH$^+$, which are very similar to each other. The obvious temporal and spectral similarities of the H$^+$ and OH$^+$ signals support the view that both originate from a common species (photodesorbed H$_2$O(v*) molecules). Given this assumption, the H$^+$ and OH$^+$ TOF spectra in Fig. 4 are characterized by $T_{\text{trans}} = 10,000 \pm 2000$ K ($\langle E_{\text{trans}} \rangle = 1.73 \pm 0.34$ eV) and 1800 \pm 300 K ($\langle E_{\text{trans}} \rangle = 0.31 \pm 0.05$ eV) for the fast and slow components, respectively.
The time evolution curves of H⁺ and OH⁺ signals from the H₂O(ν*) molecules excited in the region of the C–X Δν₂ = −1 transition were measured as a function of 157 nm irradiation time for the TOF components at t = 0.5 and 3.0 μs, as shown in Fig. 5. The H⁺ and OH⁺ signals at t = 3.0 μs appeared promptly and thereafter remained constant, while those at t = 0.5 μs gradually increased but reached a limiting value after several thousand laser shots.

4.3 Photodesorption of OH

The calculated probability for photodesorption of OH is 1.6% per absorbed UV photon. Almost all of the desorbing OH originates in the top two monolayers, 72% from the top monolayer, 27% from the second, and only 0.2% from the third monolayer. 73 ± 3% of the photodesorbed OH radicals are predicted to be formed in their vibrational ground state, with ≈17% in ν = 1, 6% in ν = 2, and the remaining 4% in higher levels (ν ≤ 6). This gives a N(ν = 1)/N(ν = 0) population ratio of 0.24 ± 0.04 (Table 2), which compares well with the experimentally obtained value (0.30 ± 0.05). The predicted N(ν = 2)/N(ν = 0) population ratio is just 0.08 ± 0.02. No OH(ν = 2) desorption products have been observed experimentally; whether this indicates a real discrepancy between experiment and simulation, or simply reflects signal to noise considerations in the former, is unclear.

For OH(ν = 0), the simulated ⟨E₉trans⟩ is 0.29 ± 0.01 eV, which corresponds to T₉trans = 1700 ± 100 K (Table 2). The translational energy distribution is quite close to a M–B distribution (see Fig. 6), but somewhat hotter than the experimentally measured distribution (T₀trans = 1300 ± 200 K). The simulated rotational temperature is 480 ± 50 K, which is in good agreement with the experimental value 400 ± 100 K.33 As shown in Table 2 and Fig. 7, the simulated translational temperature of the OH(ν = 1) products (1350 ± 150 K) accords well with the corresponding experimental value (1300 ± 200 K), but the calculated rotational temperature is somewhat higher (520 ± 120 K, cf. the experimental value of 300 ± 100 K).

5. Discussion

The energy distributions found experimentally and predicted by the MD simulations are generally in good agreement. This is quite remarkable, given that the only adjustable parameter in the set-up of the simulations was the distribution of partial charges in the photoexcited H₂O molecule36—which was chosen to make the maxima of the calculated and experimental UV absorption spectra coincide. All other potentials were kept as initially derived by ab initio calculations or, as in the case of the TIP4P potential, based on empirical data for liquid water. The dynamical approximations, rigid H₂O molecules and the use of classical dynamics, also seem to be reasonable in light of the results presented here. We recognize, however, that for other observable properties it will likely be necessary to perform more advanced simulations.

5.1 H₂O photodesorption

The present experiments successfully monitor H₂O(ν = 0) molecules via H₂O⁺ detection, and the signals from H⁺ and OH⁺ additionally suggest the presence of H₂O molecules with significant vibrational excitation. As discussed in the Introduction, and as shown by the MD simulations, vibrationally
excited H₂O molecules can arise via more than one desorption mechanism. Both type (A) and type (C) mechanisms are expected to favor formation of vibrationally excited H₂O molecules, as a result of desorption induced by photoexcitation and photofragment recombination, respectively.

For the mechanism of type (A), our MD calculations provide internal energy distributions of desorbing H₂O molecules produced by the near-instantaneous geminate recombination of H and OH fragments formed by the photodissociation of a single H₂O molecule. These molecules are found to carry a large amount of vibrational excitation, with average internal energies equal to the dissociation energy of H₂O. We find no evidence for H₂O(ν = 0) molecules arising from this desorption mechanism. The simulated internal energy of desorbing recombined H₂O molecules most likely represents an upper limit to what would be observed in experiments. In the MD simulations, the recombined molecules are allowed to exchange energy with translational and rotational (librational) modes of the surrounding molecules, but not to the internal vibrational modes, as the other molecules are restricted to be internally rigid (see preliminary H–H₂O collision study reported below). The MD calculations also predict translational energy distributions that do not quite follow a single M–B distribution.

An alternative form of photoinduced desorption is the recombination of H and OH produced from photodissociation of different molecules in the ice (a secondary, type (C) process). Recombination of OH and OH could also yield H₂O molecules. The energy distributions of these desorbing molecules would probably differ somewhat from those produced directly upon photodissociation, since the fragments involved in the secondary recombination would have lost much of their initial translational energies, and would thus need to release more of the recombination energy in order to desorb than in the case of direct desorption, where the fragments still carry most of the initial translation energy. Therefore, one might expect cooler rovibrational energy distributions from this secondary process than from the direct recombination.

Whether these two different populations of desorbing recombined molecules would be discernible in experimental measurements is not clear. However, we might anticipate differences in the time evolution of desorbing molecules arising as a result of geminate and secondary recombination. Under the present experimental conditions geminate (type (A)) recombination would be fairly constant with time, while secondary (type (C)) recombination would increase with time as increasing amounts of reactive radicals are formed and accumulated in the ice. Recalling the time evolution of the signals in Fig. 5, it seems likely that the translationally hot component of the signal we associate with desorbing H₂O(v*)

### Table 2

Translational and rotational temperatures of OH (ν = 0.1) products from the 157 nm photoexcitation of ASW and their relative yields, and a comparison with the available gas phase quantities.

<table>
<thead>
<tr>
<th></th>
<th>OH(ν = 0) Ttrans (K)a</th>
<th>OH(ν = 0) Trot (K)</th>
<th>OH(ν = 1) Ttrans (K)a</th>
<th>OH(ν = 1) Trot (K)</th>
<th>Population ratio N(ν = 1)/N(ν = 0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ASW</td>
<td>7500 ± 1000 (5%)</td>
<td>400 ± 1000</td>
<td>7500 ± 1000 (10%)</td>
<td>300 ± 1000</td>
<td>0.30 ± 0.05</td>
</tr>
<tr>
<td></td>
<td>1300 ± 200 (95%)</td>
<td></td>
<td>1300 ± 200 (90%)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MD calculations</td>
<td>1700 ± 100</td>
<td>480 ± 50</td>
<td>1350 ± 150</td>
<td>520 ± 120</td>
<td>0.24 ± 0.04</td>
</tr>
<tr>
<td>H₂O (gas phase)c</td>
<td>1200</td>
<td>600</td>
<td>—</td>
<td>450</td>
<td>1.06–1.14</td>
</tr>
</tbody>
</table>

a Numbers in the parentheses are the contribution of each TOF component. b Determined for a time of flight of 1.5 μs. c Ref. 62. d Ref. 64.
molecules is due to secondary recombination and that the
cooler component is due to direct recombination. It would be
helpful to have data from MD simulations to resolve the
mechanisms involved in secondary recombination, but the
present MD simulations cannot predict the outcome of
secondary processes. The recombination-induced desorption
that is found in the simulations is due to the recombination of
fragments originating from the same H2O molecule (i.e.
geminate recombination). A different set of simulations would
need to be run, in which, for example, translationally cool H
and OH recombine at the surface and possibly desorb by
transforming internal energy to translational energy.

The action spectra for forming H+ and OH+ ions following
two photon excitation in the region of the C–X Δv2 = −1 and
Δv1 = −1 transitions were similar, consistent with the pro-
posed excitation Scheme (1)–(3). The TOF spectra of these H+ and OH+ fragment ions both consist of two components with
H2O(v=0) translational temperatures of 10,000 K (⟨Etrans⟩ = 1.73 eV) and 1800 K (⟨Etrans⟩ = 0.31 eV), respectively. To
explore the origin of the H+ and OH+ signals further, the H+
and OH+ signals formed when exciting in the region of the C–X Δv2 = −1 transitions at t = 0.5 µs (probing the Ttrans = 10,000 K component) and at 3.0 µs (for the Ttrans = 1800 K component) were measured as a function of 157 nm irradiation
time, as shown in Fig. 5. The Ttrans = 1800 K products appeared promptly, while those with Ttrans = 10,000 K gradually
increased over time. The TOF spectrum of desorbing H2O(v=0) molecules is also dominated by a Ttrans = 1800 K component which, again, appears promptly. Thus we need to
consider if the corresponding component of the H+ and OH+
signals in Fig. 5 could be due to the kick-out of vibrationally
ercited H2O, since it is quite probable that energy is also
transferred to vibrational modes of the kicked-out molecule.
This possibility is “switched off” in our MD simulations due
to the imposed rigidity of the molecules in the ice; thus we
cannot rule out vibrational excitations on the basis of our
simulations. Nonetheless, we only expect relatively modest
levels of vibrational excitation in products arising via the
kick-out mechanism (see below) and, on that basis, we would
have expected rather better agreement between the measured
and simulated spectra originating from H2O(v=1), as
discussed in section 4.2. Following the discussion in the
previous paragraph and the relatively small differences in the
predicted translational energy distributions of desorbing H2O
resulting from the direct recombination and kick-out mechan-
isms (Fig. 1 and 2), it is also possible that prompt recombina-
tion is responsible for the Ttrans = 1800 K component—either
alone, or in combination with the kick-out mechanism.
As for the Ttrans = 10,000 K component, it could be formed
via secondary recombination processes involving photo-
fragments in/on the ice. We cannot decisively rule out any
other mechanism in these cases.

The present experimental results support the view that
157 nm irradiation of ASW leads to desorption of H2O
molecules in excited vibrational levels. The H2O photo-
desorption results of Öberg et al. were interpreted by assuming
a dominant role for direct photofragment recombination and
subsequent desorption, though these workers could not
exclude some contribution from the “kick-out” mechanism.32

Their results further suggested an increased importance of
desorption induced by secondary recombination of photo-
fragments with increasing surface temperature. It is quite
likely therefore that we have here been able to show evidence
of all three of these photodesorption mechanisms: kick-out,
direct recombination, and secondary recombination.

One interesting observation regarding molecules desorbing
via the kick-out mechanism is that their translational energies
are much higher than the rotational energies. The likely
explanation for this is that the H atom is released along the
hydrogen bond connecting it to the neighboring H2O mole-
cule. It thereby hits the O atom and not one of the H atoms.
The latter encounters might be expected to lead to reaction, or
high rotational excitation. If the H atom hits the H2O close
to its center of mass, however, most of the energy will be
transferred into translation (rather than rotation).
Impacting on the O atom in H2O will create an intermediate H2O
configuration that would be expected to re-dissociate into
H and H2O, rather than H2 + OH. Yabushita et al. have
observed desorbing H2 molecules following UV photoexcita-
tion of ASW, however, which were attributed to reaction of H
atoms with H2O molecules. Because the H2O molecules in our
MD simulations are restricted to be rigid, it is not possible at
present to study this reaction. For future simulation studies
it would be interesting to allow the molecules to be fully
flexible and to study the relative importance of the kick-out
mechanism versus reaction in H–H2O collisions. It is also not
clear whether the OH radical formed in the H + H2O reaction
will desorb and if, in that case, it would contribute significantly
to the observed OH energy distributions and desorption
probabilities (see below).

In order to evaluate the limitations of the use of the rigid
H2O model a preliminary study has been performed on H
atom–H2O collisions in the gas phase.59,60 We have carried out
quasi-classical trajectory calculations of the isolated H–H2O
system at different initial H atom kinetic energies (Ei(H) =
1–3 eV) where the H2O molecules are treated as fully flexible.
In total 1000 trajectories have been run. At Ei(H) = 1.5 eV
(representative of H atoms released in the ice photodissocia-
tion simulations) the resulting vibrational excitation of the
target H2O is on average 0.11 eV. Considering that the lowest
vibrational excitation energy possible out of the ground state
in a full quantum mechanical treatment of the system is
0.20 eV, this suggests that a large fraction of the H2O
molecules kicked out by H atoms from the ice would indeed
not be vibrationally excited—as suggested by the present
experiments and MD simulations. The use of the rigid H2O
actually allows us to describe the kick-out of vibrationally cold
(v = 0) molecules more realistically by restricting the flow of
energy into vibrational modes. Quantum mechanically, no
energy whatsoever would be transferred to vibrational modes
in this process, but in the classical treatment of flexible
molecules any small amount of vibrational energy would be
allowed. We thereby approximately take into account the
strongly quantized nature of the H2O vibrations by disallowing
vibrational excitations in the kick-out of vibrationally cold
molecules, but allowing excitation into the more “classical”
rotational and translational degrees of freedom. The obvious
limitation of the rigid model has so far been that no estimate of
the probability of vibrational excitation during kick-out has been possible. We hope to provide better estimates of these excitation probabilities in future studies.

5.2 OH photodesorption

The translational energies of the desorbing OH($v = 0$) and OH($v = 1$) products from fresh ASW are best fitted with a temperature $T_{\text{trans}} = 1300 \pm 200$ K. This temperature ($E_{\text{trans}} = 0.22 \pm 0.03$ eV) accords well with the $1500$ K value reported in the gas phase photodissociation of water at 157 nm by Mikulecky et al., and with the present MD calculations that predict $T_{\text{trans}} = 1700 \pm 100$ K for OH($v = 0$) and $1350 \pm 150$ K for OH($v = 1$). The small (5–10%) contribution of fast ($T_{\text{trans}} = 7500$ K) OH products (Table 2) is likely to be due to a secondary photoprocess involving H$_2$O$_2$ products on ASW, since the ASW surface used in the present experiments was not completely fresh even with intermolecular deposition of fresh water. Since OH photoproducts are readily trapped in the ice matrix, H$_2$O$_2$ was produced on the water ice surface and could be subsequently photodissociated. H$_2$O$_2$ formed via reaction (4) could be subsequently photodissociated to generate OH as a secondary photoproduct,

\[
\text{H}_2\text{O}_2 \rightarrow \text{OH} + \text{H}_2\text{O}_2. \tag{4}
\]

H$_2$O$_2$ formed via reaction (4) could be subsequently photodissociated to generate OH as a secondary photoproduct, which suggests that, on average, 26 kJ mol$^{-1}$ is partitioned into OH translation, 12 kJ mol$^{-1}$ into vibration and 6 kJ mol$^{-1}$ into rotation.

The MD calculations predict that the photodesorbed OH would be found in vibrational states up to $v = 6$. OH levels with $v \geq 2$ are predicted to constitute just 10% of the total population, however, with $v = 2$ accounting for some 6% and decreasing percentages in levels with higher $v$ quantum number. Experimentally, we found no evidence for any OH products in levels with $v > 1$. It could be that the populations in such levels are below the present experimental detection limit, or that their relative populations are over-predicted in the MD simulations. Additionally, the assignment and binning of classical trajectories into product vibrational quantum states is also admittedly not well defined, since a continuum of vibrational energies is found in the simulations. However, the good agreement between the experimental and calculated $N(v = 1)/N(v = 0)$ population ratios seems to suggest that the current approach is reasonable.

It is interesting to note the difference between the gas phase and solid phase photodynamics for H$_2$O at 157 nm. Hwang et al., and Yang et al. showed that OH($v = 1$) is more populated than OH($v = 0$) in the gas phase photodissociation, but that the OH($v \geq 2$) population is below the detection threshold. This vibrational state distribution is very different from the condensed phase results presented in this paper. Reasons for this can be traced to differences in the excited state potentials, dissipation of energy, and/or the dynamics of the photodissociation process. The two first cases have already been discussed in some depth by Anderson et al., In short, there is evidence that the surrounding water molecules affect the electronically excited state of H$_2$O, by lowering the intramolecular part of the excitation energy. The product energy distributions resulting from photoexcitation to such a modified PES would be expected to differ from those formed if the excited molecule was unperturbed by its neighbors. The translational energy distribution of the desorbing H atoms seems to be influenced by this effect, possibly combined with the dissipation of excess energy. This dissipation of energy will most likely proceed through energy transfer to vibrational modes of water molecules in the ice and/or through reaction of energetic H atoms with H$_2$O.

\[
\text{H} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{OH}. \tag{6}
\]

The good agreement between the classical MD calculations and the experimental results could be fortuitous, but there may be a more fundamental explanation for this accord. In general, full quantum dynamics calculations are required in order to obtain reliable product quantum state distributions—as reported for the photodissociation of gas-phase H$_2$O molecules by van Harrevelt and van Hemert. In the case of multidimensional systems like a liquid or a solid, however, the most important quantum effects are often "static", e.g., the inclusion of zero-point energy, rather than dynamic interference effects. The reason for this is the rapid loss of coherence that is common in condensed phases. In a low-dimensional quantum system, like a single H$_2$O molecule, interference effects will be prominent and are likely to have a
significant influence on the product energy distribution. Poulsen and co-workers have demonstrated that it is possible to obtain good agreement with experimental data for different dynamic properties of a range of fluids, including water, by initializing classical dynamics using quantum mechanical initial distributions, the so-called “classical Wigner” approach. This approach is also the basis of the MD calculations presented here, albeit in a somewhat less sophisticated fashion than that used by Poulsen et al. We assume that it is sufficient to use a quantum initial distribution only for the intramolecular degrees of freedom of the photoexcited molecule, while the rest of the ice is initiated classically.

6. Summary

We report energy distributions for \( \text{H}_2\text{O}(v=0) \) molecules and \( \text{OH}(v=0,1) \) radicals desorbed following 157 nm photodissociation of amorphous solid water at 90 K. The translational and rotational energy distributions of photodesorbed \( \text{H}_2\text{O}(v=0) \) molecules measured by REMPI agree well with results from MD simulations on the kick-out mechanism, i.e., desorption induced by momentum transfer from an energetic \( \text{H} \) atom formed from photodesorption of another \( \text{H}_2\text{O} \) molecule in the ice. The MD simulations also predict another distinct \( \text{H}_2\text{O} \) desorption mechanism, wherein the \( \text{H} \) and \( \text{OH} \) fragments formed after excitation and dissociation of a \( \text{H}_2\text{O} \) molecule recombine and subsequently desorb. Whereas the kick-out mechanism mainly leads to desorption of vibrationally cold molecules, this direct recombination mechanism yields highly vibrationally excited molecules. Results from measurements and simulations of the translational and rotational energy distributions of desorbed \( \text{OH}(v=0) \) and \( \text{OH}(v=1) \) fragments were also in good agreement, as are the relative populations of \( \text{OH}(v=1) \) and \( \text{OH}(v=0) \). Both the \( \text{H}_2\text{O} \) molecules and the \( \text{OH} \) radicals are formed translationally hot, but with significantly cooler rotational distributions.

Measured \( \text{H}^- \) and \( \text{OH}^+ \) signals were deduced to originate from desorbing vibrationally excited water molecules. If this is the case, this forms the first experimental evidence of photodesorption of vibrationally excited \( \text{H}_2\text{O} \) from water ice. Two distinct populations were detected, one that appeared promptly and another that grew in relative importance with increasing irradiation time. The former was found to have the same translational temperature as \( \text{H}_2\text{O}(v=0) \), \( T_{\text{trans}} = 1800 \) K, as well as having a similar translational energy distribution to desorption resulting from the direct desorption mechanism predicted by the MD simulations. It, too, was considered to arise by the kick-out of vibrationally excited \( \text{H}_2\text{O} \) molecules, or by prompt geminate recombination of \( \text{H} \) and \( \text{OH} \) photoproducts followed by desorption, or a combination of both mechanisms. The latter population had a much hotter translational temperature, \( T_{\text{trans}} = 10000 \) K. The time evolution of this component suggests that it probably arises from the secondary recombination of photoproducts at the surface (since the concentration of photoproduced radicals will increase with irradiation time). In these experiments we might therefore have observed \( \text{H}_2\text{O} \) photodesorption resulting from three distinct mechanisms: kick-out, direct recombination, and secondary recombination.

We hope to extend our comparison between experiments and simulations in future studies. In the MD simulations we aim to make all \( \text{H}_2\text{O} \) molecules fully flexible to allow for the study of energy transfer into and out of vibrational degrees of freedom as well as the reaction of \( \text{H} \) and \( \text{H}_2\text{O} \). It would also be very interesting to simulate recombination of thermalized photofragments, \( \text{H} \) and \( \text{OH} \), to predict the behavior of the longer-time secondary processes following photodissociation. One application would be to estimate the probability of recombination-induced desorption discussed in this paper and the resulting distribution of excess recombination energy. Performing the experiment on solid \( \text{D}_2\text{O} \) could also be illuminating, as the spectroscopy for probing excited vibrational states of \( \text{D}_2\text{O} \) is more promising than for \( \text{H}_2\text{O} \) because of the lower dissociation rates in the C state of \( \text{D}_2\text{O} \).

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