

Vacuum ultraviolet surface photochemistry of water adsorbed on graphite

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We report a study of the vacuum ultraviolet (VUV) surface photochemistry of H₂O (D₂O) films on a graphite substrate at 80 K. Experiments utilized a He discharge lamp to generate VUV photons. For 21 eV excitation, H⁺ (D⁺) is the only ionic fragment observed in desorption. When 41-eV photons are used, H⁺ (D⁺) is again observed; however, photochemically produced H₃O⁺ (D₃O⁺) is also detected. The ratio of D⁺ to D₃O⁺ depends upon the water coverage. Furthermore, the D₃O⁺ signal is larger than D⁺, whereas the H₃O⁺ signal is smaller than H⁺ for irradiation of adsorbed D₂O and H₂O, respectively. At low coverages where the average coordination of water is also lower, D₃O⁺ production is enhanced compared with higher coverages. The formation of D₃O⁺ is attributed to the reaction of the photodissociation product D⁺ with adsorbed D₂O. We suggest that the opening of the D₃O⁺ product channel at 41 eV and its preponderance over D⁺ is related to the higher kinetic energy of, and consequently greater momentum transfer by, the D⁺ ions created through D₂O photodissociation at this photon energy. We also suggest that there is a propensity for a hydrogen bonded O-D to break preferentially over a free O-D bond after photoexcitation.

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I. INTRODUCTION

Diverse phenomena, ranging from the evolution of interstellar and protoplanetary clouds^{1,2} to semiconductor processing,^{3,4} are influenced by surface photochemistry. The chemistry induced by electronic excitation of water ices at energies corresponding to the vacuum ultraviolet (VUV) region is of particular interest in an astrochemical setting.^{5–15}

Noell *et al.*¹⁶ performed detailed studies of the yield and kinetic energy distribution of H⁺ desorbed from H₂O adsorbed on Ni(111) via electron-stimulated desorption (ESD). The threshold for H⁺ desorption lies at an incident energy of 20–21 eV. This is significantly above the gas-phase threshold for dissociative photoionization (DPI) of 18.76 eV, where a significant H⁺ yield is observed. The kinetic energy of H⁺ ions desorbed by electrons near threshold peaks at <1 eV, whereas electrons incident with energies above 25 eV lead to substantially hotter H⁺ ions with a kinetic energy distribution extending above 10 eV. In this study, as well as earlier ESD (Ref. 17) and photon-stimulated desorption (PSD) (Ref. 18) studies, Stulen and co-workers determined that H⁺ was the majority cationic species being desorbed. This is consistent with a number of other desorption induced by electronic transition (DIET) studies of adsorbed H₂O, both for ESD (Refs. 19–21) and PSD (Refs. 22 and 23).

Orlando and co-workers have carried out extensive studies of desorption and chemistry induced by 5–100 eV elec-

trons on water films adsorbed on Pt(111).^{13,24–35} They observed two thresholds for D⁺ desorption from adsorbed D₂O near 22–24 and ~40 eV. The time-of-flight (TOF) distribution is at least bimodal, indicating multiple desorption channels. The ground electronic configuration of the water molecule is $1a_1^2 2a_1^2 1b_2^2 3a_1^2 1b_1^2$. In water ice, the electronic states are localized so that the same notation can be used to describe the electronic states. Orlando and co-workers ascribe the relevant electronic excitations to $3a_1^{-1} 1b_1^{-1} 4a_1^1$ and/or $3a_1^{-2} 4a_1^1$, which lead to slow D⁺ ions, and $1b_1^{-2} 4a_1^1$, which leads to the desorption of fast D⁺ ions. In other words, two-hole, one-electron states are thought to be primarily responsible for excitations that lead to D⁺ desorption. The D⁺ yield from amorphous ice rises very rapidly up to ~2 monolayers (ML), then rises more slowly to a maximum near 5 ML, before falling to an asymptotic level above ~25 ML. The thickness dependence of the D⁺ signal from amorphous ice is very different from that observed in crystalline ice and is ascribed to the formation of clusters and their coalescence at higher coverage. For 100-eV electrons, D⁺ is the primary cation desorbed.

Chakarov and Kasemo have investigated the photochemistry of the water-graphite system at low photon energies (<6 eV).^{36–38} Such low-energy photons are only able to induce desorption or dissociation in the presence of coadsorbed alkali-metal atoms. They have also shown that the water-graphite interaction is extremely weak. At low coverage, the adsorbed layer is composed of a mixture of two-dimensional (2D) and three-dimensional (3D) islands. Because of the weak interaction with the surface, adsorbed water clusters probably have structures close to those found in the gas phase,^{39,40} consistent with recent calculations by

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Cabrera Sanfeliix *et al.*⁴¹ Small gas-phase water clusters ($n \leq 7$) form 2D ring structures. Larger clusters form 3D cubic structures; however, numerous isomers have similar energies.

In this paper, we describe experiments in which we have irradiated water layers adsorbed on graphite at 80 K. The water coverage was varied from the submonolayer regime to ~ 7 ML. Photons of energy 21 and 41 eV were used. We find that the yields of ionic fragments in photon stimulated desorption depend on the isotopomer of water, the water coverage, and the incident photon energy. We propose a two-step model for the production of D_3O^+ , the majority species desorbed at 41 eV excitation, in which an ion-molecule reaction in the adsorbed layer follows dissociative photoionization of adsorbed D_2O . This appears to be the first system involving adsorbed D_2O in which the DIET yield of the D_3O^+ ion exceeds that of D^+ ion.

II. EXPERIMENT

All experiments were performed in an ultrahigh-vacuum chamber with a base pressure below 2×10^{-10} Torr. The substrate was highly oriented pyrolytic graphite (HOPG), grade ZYXB (Advanced Ceramics), which was cleaned by electron bombardment heating. The sample could be cooled with liquid nitrogen to ~ 80 K, the temperature at which both dosing and irradiation were performed. The temperature of the substrate was monitored either with a rhodium-iron resistance thermometer attached to the sample holder or with a K-type thermocouple clamped directly on the substrate.

Triple-distilled H_2O or D_2O (99.8% isotopically pure) was purified by multiple freeze-pump-thaw cycles before being dosed onto the substrate. Adsorption of water was performed by backfilling an antechamber with 2.0×10^{-8} Torr of the gas through a leak valve. After dosing, the gate valve between the antechamber and main chamber was opened and the substrate moved to the main chamber in front of a high-intensity VUV helium lamp (VSI model UVS 300). In this manner the main chamber was not exposed to water. The lamp delivered photons with 21.21 eV (He I) and 40.82 eV (He II), with intensities that depended on the helium pressure used. The angle of incidence was 50° with respect to the surface normal. The photon flux at the surface was $\sim 2 \times 10^{13} \text{ cm}^{-2} \text{ s}^{-1}$. The graphite substrate was $1.4 \times 0.75 \text{ cm}^2$, which was partially illuminated by a Gaussian beam profile with a 2σ diameter of 0.40 cm.

Desorbed positive ions were detected during irradiation with a pulse counting quadrupole mass spectrometer (QMS) placed normal to the surface. In all experiments, the sample was grounded through a picoammeter that allowed measurement of the sample current. Multiplexed mass spectra were recorded with a dwell time of 100 ms per amu. For D_2O , 100 scans of 50 masses were typically averaged into one spectrum, yielding a total acquisition time of 500 s.

III. RESULTS

The mass spectra measured during VUV irradiation of adsorbed D_2O layers depend on the photon energy. For He I radiation ($h\nu = 21.21 \text{ eV}$), only D^+ is observed to desorb. For He II radiation ($h\nu = 40.82 \text{ eV}$), not only D^+ , but also

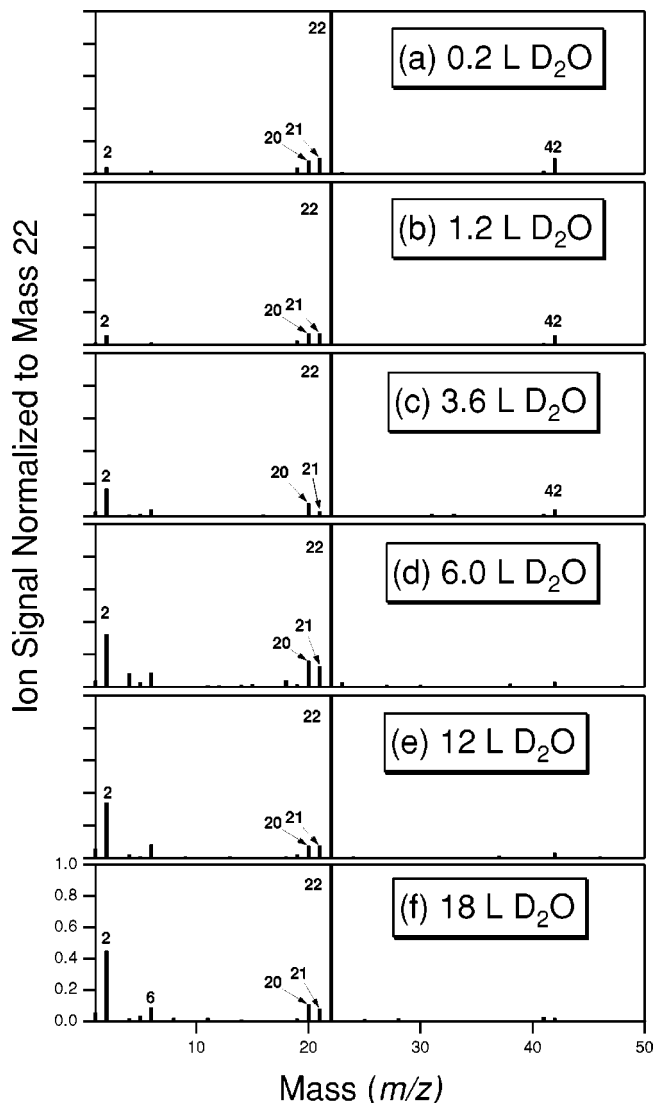


FIG. 1. Mass spectra recorded from D_2O physisorbed on graphite at $T_s = 80$ K during irradiation with He II light ($h\nu = 40.82 \text{ eV}$) as a function of D_2O exposure given in langmuirs ($1 \text{ L} = 10^{-6} \text{ Torr s}$). The corresponding coverages range from ~ 0.08 to ~ 7.5 ML. The ion yields are normalized to the D_3O^+ signal.

D_3O^+ is found to desorb (Fig. 1). The total ion yield is significantly higher at 41 eV than at 21 eV. At the higher energy, several other masses that are possibly observed: 6 (D_3^+), 20 (D_2O^+ , DH_2O^+), 21 (HD_2O^+), and 42 ($D_5O_2^+$). Partial exchange of H atoms for D atoms in the gas handling system or on the chamber walls is unavoidable and, thus, explains the appearance of mixed isotope signals. Note, however, that these signals are near the noise limit of our QMS detector. The noise limit is ~ 0.028 in the units of Fig. 1 and was calculated by determining the standard deviation in the signals for all masses not suspected of containing a legitimate signal. The mean of these signals was subtracted off to account for the electronic background. Whereas mass 6 appears only at high coverage, the mass 42 peak was only observed at low coverage. The weakness of the mass-20 peak may seem surprising and indicates that the desorption probability of the molecular ion of water (D_2O^+) is very low after photoionization. There may be some contribution to the

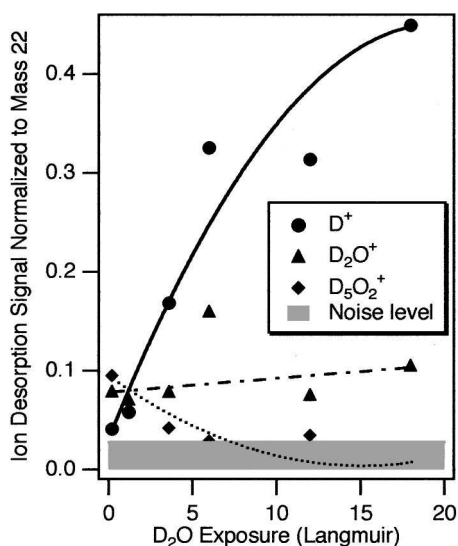


FIG. 2. Desorption yields of D^+ , D_2O^+ , and $D_5O_2^+$ as a function of D_2O exposure. The ion yields are normalized to the D_3O^+ signal. The noise level is given to indicate the level at which an ion signal is no longer significant.

mass-20 peak from the exchange product DH_2O^+ . H_2O layers, for which there is no interference from adventitious isotopic substitution, similarly exhibit an H_2O^+ peak that is $<10\%$ of the H_3O^+ peak when irradiated with 41-eV photons. Therefore, the dissociation and/or neutralization of water excited with either 21- or 41-eV photons is much more likely than desorption of D_2O^+ . The absence of several other peaks from D_2O -graphite, including 18 (OD^+), 32 (O_2^+), 34 (DO_2^+), and 36 ($D_2O_2^+$), is also significant. Such fragments would be expected if substantial quantities of photodissociation products were to accumulate on the surface, as has been observed for much higher integrated photon exposures.⁸⁻¹⁰ This finding supports the conclusion that we are looking at photodesorption products created directly from the adsorbed water film rather than from the buildup of photodissociation products. Another feature of the mass spectral data is that the D_3O^+ signal is always greater than the D^+ signal at 41 eV.

The coverage dependence of the ion desorption signals for D_2O -graphite is displayed in Fig. 2. The size of the D^+ signal relative to the D_3O^+ signal increases as the coverage increases. Nonetheless, it never exceeds 0.45. The D_2O^+ signal is roughly constant at ~ 0.08 , whereas the $D_5O_2^+$ signal drops rapidly from 0.09 at low coverage to below the noise level at high coverage. Note that the signal levels in Figs. 1 and 2 are normalized to the D_3O^+ intensity. When the absolute signal level is considered, the dramatic increase in the $D^+ : D_3O^+$ ratio is primarily due to a decrease in the magnitude of the D_3O^+ signal. The D^+ signal increases at low exposure, but levels off at high exposure.

If H_2O is adsorbed on graphite instead of D_2O , most of the trends in the data remain the same. For $h\nu = 21.21$ eV, only H^+ is desorbed. For $h\nu = 40.82$ eV, H^+ and H_3O^+ are desorbed. However, there is one major difference compared with D_2O : the H^+ signal is larger than the H_3O^+ signal at 41 eV excitation. This is significant because we expect the electronic excitations to be independent of the isotopomer. No signal is found at either mass 16 or 17, indicating the ab-

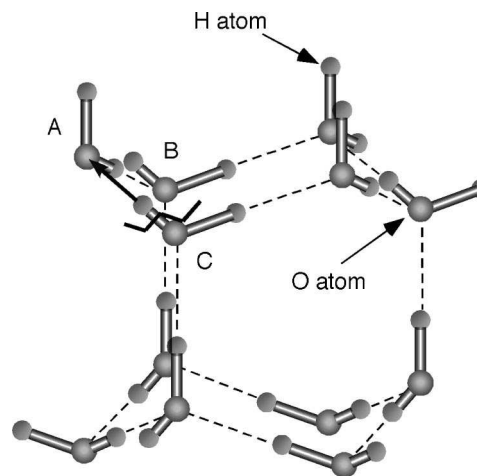


FIG. 3. Schematic drawing of the bulk structure of ice is shown to illustrate the momentum transfer model. Molecule A is initially hydrogen bonded to molecules B and C. After the O-D bond of molecule C dissociates, the D^+ ion collides with molecule A, which leads to the formation and desorption of D_3O^+ .

sence of O^+ and OH^+ desorption within our level of detection sensitivity.

IV. DISCUSSION

As D^+ and D_3O^+ are the predominant desorption products, we concentrate our discussion on these two ions. We need to explain how D_3O^+ is formed, why it is only formed for excitation at $h\nu = 40.82$ eV excitation, and account for the dependence of the relative proton and hydronium desorption yields on coverage and isotopomer.

Let us consider the ice structure outlined in Fig. 3, in which a crystallite based on the bulk structure of water is depicted. The water-graphite interaction is very weak and water is thought to form a mixture of 2D and 3D clusters on the surface.³⁶ The binding energy of water is dominated by hydrogen bonding between water molecules.⁴¹ As the coverage increases, the thermal desorption peak shifts to higher energy.^{36,37} This can be understood by recognizing that, as the coverage increases and 3D clusters become predominant (eventually giving way to the bulk ice structure), the average coordination number of water will increase towards its bulk value of ~ 4 . Small 2D water clusters such as those known in the gas phase have a coordination number of just 2. Surface water molecules in the perfect bulk structure have a coordination number of 3 and some expose free OD bonds that point along the surface normal.⁴² Since our films are grown at 80 K, they will be amorphous. This means that at any coverage there will be some number of defect sites with coordination numbers less than 3. Nonetheless, we expect that, as the coverage increases, there will be an increase in the mean coordination number.

In Fig. 3 the consequences of excitation (either direct or substrate mediated) (Refs. 43-45) of the molecule labeled C are demonstrated. In the gas phase, excitation at both 21 and 41 eV leads to dissociative photoionization, which results in D^+ production. Molecule A is initially hydrogen bonded to molecules B and C. When C photodissociates, the D^+ ion

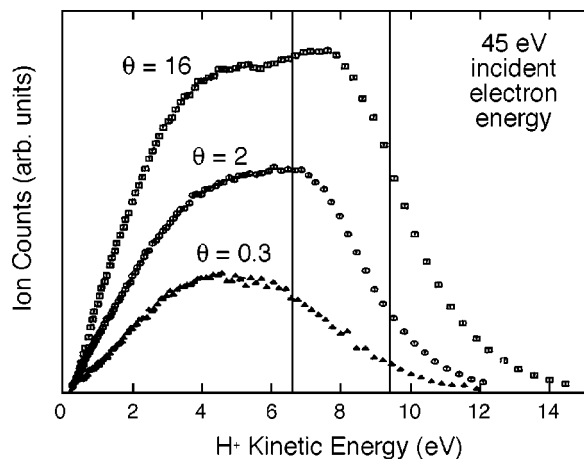


FIG. 4. Kinetic energy distribution of H^+ ions measured by Noell *et al.* (Ref. 16) for electron-stimulated desorption (incident energy of 45 eV) from H_2O films on Ni(111) of various coverages. The vertical lines indicate upper limits to the threshold D^+ kinetic energy required to desorb D_3O^+ via collision with a D_2O molecule initially having either one or two hydrogen bonds at the surface.

will move along the axis of its hydrogen bond with A. We can think of this as a type of surface aligned photochemistry.⁴⁶ Photon- or electron-driven dissociation at surfaces leading to neutral-neutral^{24–26,47–51} and ion-molecule^{52–54} reactions has been observed in several other systems.

If D_3O^+ were formed in this way, we must also explain how it desorbs. Within the example given in Fig. 3, the nascent D_3O^+ has to break its hydrogen bond to B as well as overcome any image charge attraction to the surface. Estimating the hydrogen bond strength as 0.25 eV and the image charge attraction as 0.6 eV (Ref. 52), we can calculate what the minimum initial kinetic energy of the D^+ ion must be if it is to transfer sufficient momentum to the D_3O^+ to engender desorption. The threshold D^+ kinetic energies when zero, one, two, three, or four hydrogen bonds are broken are 6.6, 9.4, 12.1, 14.9, and 17.6 eV, respectively. Consequentially, desorbed D_3O^+ is most likely to be formed from D_2O that is adsorbed in low coordination sites. Since one of the hydrogen bonds initially involves an atom that is incorporated into the product (i.e., D_3O^+), the number of hydrogen bonds that needs to be broken is one less than the original number of hydrogen bonds.

The H^+ kinetic energy distributions measured by Noell *et al.*¹⁶ in ESD from H_2O films at an incident energy of 45 eV are reproduced in Fig. 4. We see a highly energetic distribution extending beyond 10 eV. At 21 eV incident energy, the desorbed H^+ has a distribution that is substantially less energetic, peaking below 1 eV. If we assume that the same excited states are involved in ESD and PSD, the kinetic energy distributions measured by Noell *et al.* should be similar to those that pertain to our experiment. This gives us an immediate explanation as to why no D_3O^+ is produced at 21 eV excitation. The liberated D^+ simply does not have sufficient energy to form and then dislodge D_3O^+ from the surface (even in the absence of hydrogen bonding). As shown by the lines in Fig. 3, a substantial fraction of the D^+ liber-

ated by 41 eV excitation does have sufficient energy to form and dislodge D_3O^+ from low coordination sites. However, since the mean coordination number increases with increasing coverage, we expect that the relative D_3O^+ yield should drop with increasing coverage. This is again consistent with the measured data. Our momentum transfer model of D_3O^+ production is supported further by the H^+ to H_3O^+ signal ratio. Since H^+ is lighter than D^+ , it must have significantly more initial kinetic energy to impart enough momentum to form and dislodge H_3O^+ from the surface. This is borne out in the data since the H^+ signal is found to be much higher than the H_3O^+ signal at 41 eV.

The gas-phase reaction of a hydrogen ion with a water molecule to produce hydronium is exothermic by 7.3 eV.⁵⁵ Undoubtedly, some of this energy is used for desorption. This leads to a lower kinetic-energy threshold for the desorption of hydronium than that calculated above. However, the lack of significant hydronium desorption at 21 eV excitation and the dependence of the relative ion yields on isotopomer indicate that funneling of reaction exothermicity into the desorption channel is not a major pathway of energy dissipation and cannot on its own account for the ion desorption signal. The channeling of reaction exothermicity into desorption depends sensitively on the potential energy hypersurface.⁵⁶ Whereas significant energy transfer into product CO_2 occurs for CO oxidation,^{57–59} more relevant to the present case is H_2 oxidation to form H_2O , for which the possible involvement of hydrogen-bonded clusters has also been discussed.^{60,61} For the latter reaction, virtually the entire exothermicity is dissipated into the substrate on Pd (Ref. 62) and Pt (Ref. 63) surfaces.

It is startling, nonetheless, that the D_3O^+ signal exceeds the D^+ signal at 41 eV. The $D^+ : D_3O^+$ ratio changes from roughly 1:25 at low coverage to 1:2 at high coverage. As Fig. 3 shows, a significant fraction of the surface O-D bonds are directed along the normal at high coverages. This is consistent with ESD ion angular distribution (ESDIAD) measurements on ice multilayers.¹⁹ In small water clusters there is a 1:1 ratio of free to hydrogen-bonded O-D bonds. This ratio decreases with increasing cluster size and approaches 1:6 for the water molecules in the surface bilayer of a bulk ice crystal. All DPI events involving a free O-D bond lead to D^+ desorption as long as the D^+ is not recaptured by the surface; however, they cannot lead to the formation of D_3O^+ . Some fraction of the DPI events involving hydrogen-bonded O-D bonds engender D_3O^+ desorption—the majority do not because the the initial D^+ kinetic energy does not exceed the threshold for D_3O^+ desorption. The remainder of these DPI events lead either to D_3O^+ , which is recaptured at the surface or to inelastically scattered D^+ , some of which desorbs as D^+ . Therefore based on simple statistical arguments, *if* hydrogen-bonded and free O-D bonds undergo DPI *with equal probability*, we would predict that the $D^+ : D_3O^+$ desorption ratio should *not be less than 1:1* at low coverage and should *decrease* with increasing coverage. Neither of these predictions are corroborated by the data.

To explain why the D_3O^+ signal exceeds the D^+ signal and why the $D^+ : D_3O^+$ ratio changes as it does with increasing coverage, we speculate that there is a propensity for the

hydrogen bonded O-D to break preferentially over the free O-D bond. In this sense, the observed photochemistry goes beyond surface-aligned photochemistry in that the hydrogen bonding not only directs the D^+ ion toward its reaction partner, but also it preferentially biases the photodissociation reaction toward the O-D bond that leads to reaction rather than toward a free O-D bond. While energetically a hydrogen bond is worth only ~ 0.25 eV, the question is how the presence of a hydrogen bond affects the transition state for photodissociation compared to photodissociation along a free O-D bond. Perhaps more important than the hydrogen bond itself is the presence of a highly exothermic product channel, leading to $D_3O^+ + OD$, which will be strongly favored over the less energetically favored $D^+ + OD$ channel. We suggest here that the barrier into the more exothermic $D_3O^+ + OD$ channel is lower than the barrier into the less exothermic $D^+ + OD$ channel, which leads to preferential photodissociation of the hydrogen-bonded O-D bond.

Another possible mechanism for the desorption of D_3O^+ is that a localized solid-state excitation creates a repulsive force between the D_3O^+ moiety and the remainder of the ice cluster to which it is bound. While it is easy to imagine how a Coulomb repulsion is manifested between the atoms partaking in a covalent bond, it is more difficult to envisage how a Coulomb repulsion arises along a hydrogen bond. We cannot rule out the possibility that this mechanism also contributes to the D_3O^+ desorption yield. However, there are several factors that militate against it being the majority channel. First, electronic excitations do not have an isotopomeric dependence. Large isotope effects in the yields of DIET processes are well known;^{64,65} however, these should favor a higher yield of the lighter isotopomer rather than the heavier one, contrary to our data for H_2O and D_2O . Second, such a localized excitation should be at least as effective at removing D_2O^+ from the surface since in this case D_2O^+ formation always precedes D_3O^+ formation. However, the yield of D_2O^+ is very small. Therefore, it would appear that the majority channel for the production of D_3O^+ is due to the ion-molecule reaction between D^+ and D_2O .

V. CONCLUSION

We have investigated the surface photochemistry of H_2O and D_2O adsorbed on graphite at 80 K. For 21 eV excitation, H^+ (or D^+) is the only ion detected in the desorbed flux. For 41 eV excitation, H_3O^+ (or D_3O^+) is also found to desorb. The yield of D_3O^+ is larger than the D^+ yield, whereas the opposite is true for H_3O^+ and H^+ . We have proposed that the hydronium ion desorbed from the surface is created in a two-step process. First, dissociative photoionization produces H^+ (D^+). Second, H^+ (D^+) collides with adsorbed H_2O (D_2O) to form hydronium in a surface-aligned ion-molecule reaction. The more massive D^+ transfers momentum more efficiently to D_3O^+ than H^+ can to H_3O^+ , which explains the isotopomeric dependence of the relative yields.

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