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Low-energy electron-stimulated production of molecular hydrogen from amorphous water ice

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We have observed, via quadrupole mass spectrometry (QMS), stimulated production of D_2 (H_2) during low-energy (5–50 eV) electron–beam irradiation of D_2O (H_2O) amorphous ice. The upper limit for the D_2 (H_2) production threshold is 6.3±0.5 eV; well below the first excited state of condensed water at 7.3 eV. The D_2 (H_2) yield increases gradually until another threshold is reached at ~17 eV and continues to increase monotonically (within experimental error) up to 50 eV. We assign the 6.3 eV threshold to D^- $(H^-)+D_2O$ $(H_2O)\rightarrow D_2$ $(H_2)+OD^-$ (OH^-) condensed phase (primarily surface) reactions that are initiated by dissociative attachment. We associate the yield below ~11 eV with the dissociation of Frenkel-type excitons and attribute the yield above ~11 eV mainly to the recombination of D_2O^+, or D_3O^+, with quasifree or trapped electrons. Exciton dissociation and ion–electron recombination processes can produce reactive energetic D (H) atom fragments or D_2 (H_2) directly via molecular elimination. The importance of D^+ (H^+) interactions increases at ~17 eV (dipolar threshold) and at energies $\geqslant$21 eV where multihole and multielectron final states are energetically accessible.

I. INTRODUCTION

The fundamental mechanisms involved in radiation damage of molecules in the condensed phase are often probed by studying the interactions of high-energy radiation (i.e., x rays, gamma rays, electrons, etc.) with condensed molecular ices. Despite the importance of high-energy processes, it should be noted that energetic particles lose energy primarily via the production of low-energy secondary electrons. For example, thermalization of a (~600 keV) Compton electron produces $\sim 10^3-10^4$ low-energy (1–100 eV) secondary electrons[1] since the average energy lost per condensed phase ionization event is approximately 30 eV. These secondary electrons are produced with variable energy and spatial distributions and can stimulate condensed phase radical or ion (anion or cation)–molecule reactions. Low-energy electron-stimulated processes on or within multilayers are fundamentally important in many conventional areas of physics, chemistry, materials science, and radiation biology,[2] and are also relevant to understanding chemical transformations which occur in harsh radiation containment environments such as "mixed" (radioactive/chemical) waste storage facilities.

Because of the crucial role of water in biology and technology, the influence of ionizing radiation on ice has been the subject of many investigations.[3–9] Many of these studies involved irradiating ice with high-energy electrons (1 keV–5 MeV) and concentrated on understanding the subsequent bulk emission and luminescence spectra. Some studies of the interactions of low-energy electrons with thin films of amorphous ice have been carried out.[10–14] Prince *et al.*[10] reported on the electron (50–200 eV) induced fluorescence of H_2O (D_2O) ice at 77 K and presented some evidence for electron-stimulated desorption (ESD) of excited OH (OD) radicals ($A\ ^2\Sigma^+$). A detailed study of low-energy (15–50 eV) ESD of protons from water ice reported an H^+ ESD threshold of ~21 eV and a monotonic increase in the yield above threshold.[11] The ESD of H^+ has been assigned to two-hole two-electron excitations ($1b_1^{-2}4a_1^2$ and $1b_1^{-1}3a_1^{-1}4a_1^2$) by Noell *et al.*[11] These assignments differ slightly from the two-hole one-electron states ($1b_1^{-2}4a_1$ and $1b_1^{-1}3a_1^{-1}4a_1$) previously assigned by Ramaker.[15]

Recent work at lower electron energies (5–15 eV) reports the observation of the ESD of H^- (D^-) from amorphous thin films of H_2O (D_2O) via dissociative electron attachment (DA).[14] The H^- (D^-) desorption yield has a weak threshold at 5.5 eV, becomes appreciable at ~6 eV, reaches a maximum at ~7.4 eV, and is negligible for energies greater than ~11 eV. The DA resonances responsible for the ESD were assigned to the $^2B_1$ and $^2A_1$ states. The experimental kinetic energy distributions of the desorbing H^- (D^-) ions were peaked near 0 eV, indicating that post-dissociation interactions had occurred within the ice or on its surface. This implies that scattering processes which could lead to the production of neutral reaction products, such as molecular hydrogen, may have occurred.[14]

We present recent results on the stimulated production of molecular deuterium (hydrogen) during low-energy (5–50 eV), electron–beam irradiation of thin films of amorphous D_2O (H_2O) ice. We briefly address the role of dissociative electron attachment, dissociative excited states, electron-hole pair recombination, dipolar excitations, and multihole final states in the stimulated production of D_2 (H_2).

II. EXPERIMENT

The experiments were performed in two ultrahigh vacuum (UHV) systems: one at the Molecular Science Re-

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search Center of Pacific Northwest Laboratory (PNL) and the other at the University of Sherbrooke. The system at PNL is equipped with a low-energy electron gun, a quadrupole mass spectrometer (QMS), a cryogenically cooled platinum foil, an effusive gas doser, and a time-of-flight spectrometer for laser multiphoton ionization detection of neutrals. The electron gun has an energy spread of ~0.5 eV and approximately constant current (~8 μA) and beam size (~1–3 mm) over the entire energy range (5–50 eV) studied. Since the predominant background gas in the PNL instrument ($\sim 1-2\times 10^{-10}$ Torr) was molecular hydrogen, electron-stimulated production of D_2 from D_2O multilayers was studied to eliminate background problems. D_2O multilayers (~50–100 layers) were prepared by dosing at ~50 K under conditions that have been shown to produce amorphous ice.[16]

The Sherbrooke apparatus has been previously described in detail[2] and is equipped with two low-energy electron guns, a QMS, a cryogenically cooled platinum foil, and an effusive gas doser. An important feature of this apparatus is that the electron gun had a lower energy spread and higher current, which improved the accuracy of the H_2 threshold measurement. In addition, the main chamber was immersed in liquid nitrogen to reduce the background hydrogen signal. The H_2O multilayers were condensed on Pt foil at ~80 K under conditions that form amorphous ice.[16] The background pressure in this system was typically $\sim 5-8\times 10^{-10}$ Torr.

For the experiments performed on D_2O, the multilayer samples were irradiated with low-energy electrons at several fixed energies. (The incident electron energy is the voltage applied to the electron filament corrected for the work function difference between the filament and the surface.) The neutral D_2 desorbates were detected using a QMS system equipped with an electron-impact (70 eV) source which does not allow electrons to escape the ionization zone and irradiate the ice sample. To avoid problems associated with the buildup of reaction products and charge in the ice layer, the D_2 yield at each incident electron energy was measured on a newly deposited ice layer and a short electron–beam exposure time (0.10 s) was used. Though we have no direct measurements of the amount of charging that may have occurred, previous low-energy electron transmission studies[17] indicate that the ice films could charge up (negatively) by approximately 0.5 to 1.0 V. However, the dc conductivity of hexagonal ice at 263 K has been reported[18] to be $\sim 10^{-7}\ \Omega^{-1}\ \text{cm}^{-1}$, which suggests charging may reduce the incident electron energy by only several meV. Thus, the threshold energy of 6.3 eV discussed below should be considered an *upper* limit.

III. RESULTS AND DISCUSSION

The relative D_2 yield as a function of incident electron energy is shown in Fig. 1. The data is the average of several different measurements at each energy and is measured as the total counts, normalized by the incident electron current. The estimated yield is approximately one D_2 per 10^3 incident electrons. The yield of H_2 from H_2O as a function of incident electron energy (measured at Sherbrooke) is qualitatively similar to the results shown in Fig. 1. Since the D_2 and H_2 yields are similar, we will, for clarity, discuss the results primarily in terms of the D_2 production from electron irradiated D_2O. Similar arguments should apply for H_2 and we do not expect isotope effects to change the conclusions.

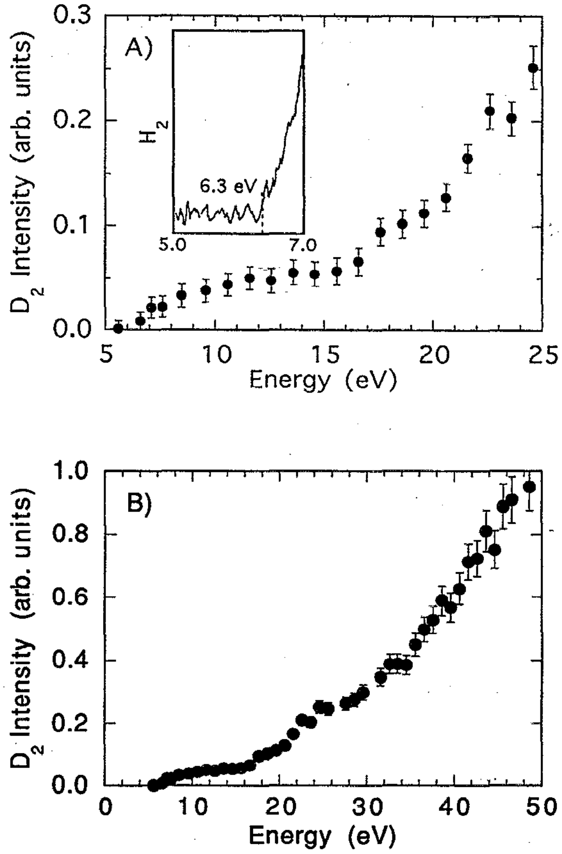

FIG. 1. D_2 yield from low-energy electron-irradiated amorphous D_2O ice as a function of the incident energy. (A) The D_2 yield shows a gradual increase above threshold and a noticeable increase above 17 eV. Inset: H_2 threshold (6.3 eV) from amorphous H_2O ice. (B) The D_2 yield as a function of incident electron energy from 5–50 eV.

Several features in the data are noteworthy. First, the D_2 (H_2) production threshold is below the threshold for electronic excitations. Second, D_2 is produced in the energy range from ~11 to ~21 eV, which is above the energies where DA occurs,[14] but below the threshold for ESD of protons from multilayers of water.[11] Third, the D_2 yield increases above ~17 eV. Finally, the D_2 yield increases monotonically (within the experimental uncertainty) from 17–50 eV. In order to understand the reactions associated with these features, we will briefly discuss the electronic structure of ice.

The ground state of the isolated water molecule is $(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^2(1b_1)^2\ {}^1A_1$ with two empty antibonding orbitals $(4a_1)$ and $(2b_2)$.[18] The $4a_1$ antibonding orbital is strongly coupled to the $3s$ Rydberg orbital leading to the designation $3s4a_1$. The electronic structure of ice has been extensively studied experimentally,[12,19–24] but only a few theoretical studies have been carried out due to the difficulty of treating the disorder in ice.[25,26] A qualitative diagram of the band structure of ice, which has been derived

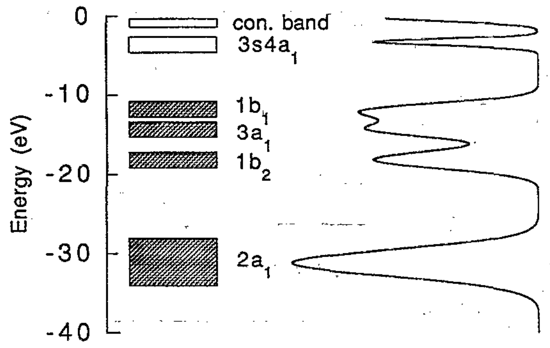

FIG. 2. Schematic representation of the band structure of water ice which has been constructed from the existing experimental (Refs. 19–24) and theoretical (Refs. 24 and 25) data. The vacuum level defines the zero for the energy scale and filled bands are indicated with shaded boxes. The density of states from photoemission experiments is estimated with solid lines.

from the available experimental[12,20–24] and theoretical information,[25,26] is presented in Fig. 2.

In amorphous, hexagonal, and cubic ice, the lowest energy electronic excitation of H_2O and D_2O has been measured with vacuum-ultraviolet (VUV) absorption spectroscopy[22–24] and electron energy loss spectroscopy[12] and has a threshold at 7.3 eV with a maximum at ~8.6 eV. This has been assigned as the ${}^{3,1}B_1(1b_1 \rightarrow 3s4a_1)$ transitions, which are ~1.2 eV higher in energy than the gas phase values.[12,22,23] The width of the transitions may be due in part to the dissociative nature of the $3s4a_1$ state, as well as interactions with neighboring molecules. The excited state is probably best described as a Frenkel exciton that lies below the conduction band.[23] The exciton radius is estimated to be 2.2 Å,[14] which is somewhat smaller than the distance between nearest-neighbor oxygen atoms (2.76 Å). Likewise, the $3a_1 \rightarrow 3s4a_1$ transition at ~10.2 eV is also likely to be a Frenkel-type exciton,[23] albeit with a more extended radius. Valence-to-conduction band transitions begin around 11 eV.[23] Optical reflectivity data, along with photoconductivity and photoemission data for solvated electrons, suggests that the bottom of the conduction band, V_0, lies ~0.8–1.0 eV below the vacuum level.[12,19,23]

The H_2 production threshold is ~6.3 eV and is shown in detail in the inset in Fig. 1(A). The threshold for D_2 production, measured with the larger incident energy spread, also lies between 6–7 eV. Since the 6.3 eV threshold for D_2 (H_2) production is below the onset of electronic excitations, it seems likely that the D_2 (H_2) production is related to the DA process, at least at the lowest energies. As we discussed in Sec. I, D^- (H^-) is the only DA fragment observed from amorphous ice and has an appreciable yield above ~6 eV and a peak yield at ~7.4 eV.[14] The exothermic (ΔH_g=gas-phase reaction enthalpy) proton transfer reaction:

$$D^- \ (H^-) + D_2O \ (H_2O) \rightarrow D_2 \ (H_2) + OD^- \ (OH^-),$$
$$\Delta H_g = -0.45 \ \text{eV} \qquad (1)$$

has been studied in the gas phase[27,28] and is assumed to proceed via the formation of a proton-bound intermediate complex.[27] The reaction rate coefficient for the H^- reaction is 3.7×10^{-9} cm^3 molecule^{-1} s^{-1} at 297 K, which is approximately half the rate expected from the average dipole orientation theory.[27] Evidence for this reaction has also been presented in studies of low-energy electron attachment to $(D_2O)_n$, $(H_2O)_n$ van der Waals clusters.[28,29] The cluster ion distributions observed using 6–12 eV electrons were interpreted in terms of DA initiated intracluster ion–molecule half-reactions such as $(H^-)(H_2O)_{n-1} \rightarrow (OH^-)(H_2O)_{n-2} + H_2$.[28] It is very reasonable to expect similar interactions to occur in the condensed phase. The reaction may be enhanced in the condensed phase due to the large number of collision partners and the increased exothermicity resulting from ion solvation. Although DA initiated reactions may occur within the bulk, this experiment is primarily sensitive to events which occur on the surface or within the first few ice layers. In addition, the D_2 (H_2) production via the proton transfer reaction *above* the ice surface (i.e., in the gas phase) is negligible due to the low D^- (H^-) and D_2O (H_2O) desorption yields and the very low water background pressure.

In Fig. 1, the D_2 yield *increases* monotonically above threshold, whereas the DA yield of D^- decreases at energies greater than ~7.4 eV. Therefore, we suggest that the Frenkel excitons mentioned above are important in D_2 production for energies that are above the threshold for electronic excitations (~7.3 eV) but below the conduction band edge (~11 eV). [Note that the inelastic scattering cross section for electrons is too small to shift many higher energy electrons to energies where D^- (H^-) production via DA is likely.[12,13]] In the gas phase, the first excited singlet and triplet states of D_2O dissociate mainly into $D({}^2S) + OD(X\ {}^2\Pi)$.[30] In the ice, the energetic atomic fragments produced from the decay of the corresponding "excitonic" states of D_2O may react directly with surrounding D_2O to form D_2 via the well studied[31] endothermic hydrogen abstraction reaction:

$$D \ (H) + D_2O \ (H_2O) \rightarrow D_2 \ (H_2) + OD \ (OH),$$
$$\Delta H_g = 0.64 \ \text{eV}. \qquad (2)$$

The absolute reaction cross section for this reaction, which has a ~0.94 eV vibrational adiabatic reaction barrier[31] in the gas phase, increases substantially with collision energy.[31] Some of the energetic D (H) atoms may eventually thermalize due to inelastic scattering in or on the ice. Since D atoms are open shell radicals, they are also very reactive at low kinetic energies. For example, D_2 could be produced via the reaction $D + D \rightarrow D_2$. At the temperature of this experiment (50 K), the D atom diffusion rate is expected to be very low (i.e., a few hops per second),[32] precluding significant D_2 formation by this channel within 0.10 s. This is consistent with the low hydrogen atom loss rate measured in previous gamma-irradiated ice studies at 50 K (Ref. 33) and is also consistent with the conclusion by Smoluchowski[34] that H atom trapping on low-temperature amorphous ice surfaces occurs within nanoseconds.

An alternative decay channel for the excitonic states described above is deexcitation via molecular elimination to form D_2 directly since $O({}^1D) + D_2(X\ {}^1\Sigma_g^+)$ and $O({}^3P) + D_2(X\ {}^1\Sigma_g^+)$ are symmetry and energetically allowed singlet and triplet dissociation channels, respectively.[30] The branching ratio between the D (H) atom and D_2 (H_2) channels, which is 9:1 in the gas phase,[30] is unknown in the condensed phase.

For incident electron energies greater than ~11 eV, which are above the valence-to-conduction band edge,[23] electron-hole pairs (D_2O^+ and quasifree electrons) are produced. In the condensed phase, D_2O^+ can rapidly react ($\sim 10^{-14}$ s)[9] with surrounding water molecules to form hydronium ions, D_3O^+. The D_2O^+ and D_3O^+ can subsequently recombine with quasifree or trapped electrons forming D_2O^* and D_3O^*, respectively. Previous workers have shown that excess electrons decay via recombination with mobile holes on the nanosecond time scale.[8] Detailed information concerning the decay pathways of the excited states produced via recombination in amorphous ice is lacking. However, the H_2:H branching ratios for the dissociative recombination reactions: $H_2O^+ + e^-$ and $H_3O^+ + e^-$ have been studied recently in the gas phase[35,36] and are reported to be ~1:4 and 1:1.5, respectively. Similar dissociative recombination events in the condensed phase can lead to desorption of atomic[37] and molecular fragments of the initially excited species when the excess energy available exceeds the intermolecular coupling interactions with the surface or matrix.

The D_2 yield increases rapidly above $E_i = 17$ eV, suggesting a threshold for one or more additional channels. Noell *et al.*[11] reported H^+ ESD at energies as low as 17 eV, although with much lower intensities than above the 21 eV "threshold." We note that the thermodynamic threshold for dipolar dissociation of the D_2O molecules into OD^- and D^+ is ~16.9 eV and we therefore suggest that dipolar excitations are responsible for the increase in D_2 yield above 17 eV. The dipolar surfaces are accessible in the gas phase mainly via curve crossings with highly excited Rydberg states since the Franck–Condon factors for a direct transition are unfavorable. In the condensed phase, the dipolar surfaces could be more accessible due to changes in the Franck–Condon factors resulting from hydrogen bonding. The D^+ fragments produced from dipolar excitation can react via the charge exchange reaction $D^+ + D_2O \rightarrow D + D_2O^+$, or proton transfer reaction $D^+ + (D_2O)_n \rightarrow D_3O^+ + (D_2O)_{n-1}$. These ions ($D^+$, D_2O^+, and D_3O^+) can all be neutralized by quasifree or trapped electrons leading to D_2 via the mechanisms already described above.

As the incident electron energy increases and additional ion-pair, single-hole, and multihole excited states become energetically accessible, the total D_2 yield increases as seen in Fig. 1(B). The proton yield also increases as a function of energy.[11,15] As mentioned previously, the multihole final states involved in ESD of protons have been assigned as either two-hole two-electron excitations ($1b_1^{-2}4a_1^2$, $1b_1^{-1}3a_1^{-1}4a_1^2$) or two-hole one-electron ($1b_1^{-2}4a_1$, $1b_1^{-1}3a_1^{-1}4a_1$) excited states. These assignments were partially based on the fact that the H^+ ions were emitted with relatively high translational energy distributions that became bimodal above electron energies of ~30 eV. These multihole final states are also assumed to have increased lifetimes since they do not involve orbitals which participate in hydrogen bonding. It is reasonable to suspect that similar multihole excitations are also involved in D_2 production since they lead to the production of reactive (energetic) D^+ species.

IV. CONCLUSIONS

We have measured the electron-stimulated production of D_2 (H_2) from amorphous D_2O (H_2O) in the energy range from 5 to 50 eV. Below the electronic excitation threshold (~7.3 eV) for D_2O (H_2O), D_2 (H_2) production can be attributed to reactions that are initiated by dissociative electron attachment. This finding strongly supports the hypothesis that some of the unscavenged H_2 yield in water radiolysis[38] must be due to the fast proton transfer process $H^- + H_2O \rightarrow H_2 + OH^-$. The D_2 (H_2) yield above the DA resonance but below the valence-to-conduction band edge (~11 eV) is associated with excitations that can be described as Frenkel excitons. Above ~11 eV, dissociative recombination of molecular ions [D_2O^+ (H_2O^+) and D_3O^+ (H_3O^+)] with quasifree or trapped electrons creates excited states that can decay to produce D_2 (H_2) directly via molecular elimination or indirectly via reactive scattering of energetic D (H) atom fragments. Dipolar excitations and curve crossings to ion-pair states become important at energies $\gtrsim$~17 eV, whereas multihole, multielectron final states become important above ~21 eV. These results suggest that the study of the neutral products are important in understanding nonthermal reactions in molecular ices since several types of electronic excitations which are not directly observable in the ion channels are important. Further work on measuring the yields and quantum state distributions of the D atom and D_2 (H_2) desorption products is underway. This information should help elucidate the nature of the excited states and dynamics involved in these nonthermal condensed phase reactions.

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