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Electron-stimulated desorption of D^- (H^-) from condensed D_2O (H_2O) films

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Abstract

The electron-stimulated desorption (ESD) of D^- and H^- ions from condensed D_2O and H_2O films is investigated. Three low-energy peaks are observed in the ESD anion yield, which are identified as arising from excitation of 2B_1 , 2A_1 and 2B_2 dissociative electron attachment (DEA) resonances. Additional structure is observed between 18 and 32 eV, which may be due to ion pair formation or to DEA resonances involving the $2a_1$ orbital. The ion yield resulting from excitation of the 2B_1 resonance increases as the film is heated. We attribute the increase in the ion yield to thermally induced hydrogen bond breaking near the surface, which enhances the lifetimes of the excited states that lead to desorption. © 1997 Elsevier Science B.V.

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1. Introduction

Low-energy electron–molecule scattering results in the formation of transient negative ion resonances which decay via electron autodetachment and dissociative electron attachment (DEA). DEA usually involves multielectron core-excited resonances which consist of an excess electron temporarily bound by the positive electron affinity of an electronically excited target molecule. These are generally two-electron, one-hole configurations

that are classified as either Feshbach or core-excited shape resonances. Since the lifetimes of Feshbach resonances are typically $\sim 10^{-12}$ – 10^{-14} s, dissociation into stable anion and neutral fragments may result if the resonance is dissociative in the Franck–Condon region and if one of the fragments has a positive electron affinity.

Considerable attention has been focused recently on extending the current understanding of DEA in gas-phase molecules to explain the resonant behavior observed in the electron-stimulated desorption (ESD) of negative ions and neutrals from adsorbed molecules and from molecular solids [1–8]. DEA in condensed molecules can be described in terms of single-site scattering, as in

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the gas phase. However, condensation may affect the energy, width or lifetime of a scattering resonance [9]. To interpret the DEA resonances properly in condensed molecules one must consider additional factors such as (1) changes in the symmetry of the scattering problem, (2) the fixed orientation of the molecule with respect to the solid surface, (3) the polarization response of the medium, (4) short-range interactions between the molecules and image interactions with the substrate, (5) new decay channels, (6) inelastic scattering of the incident electron, and (7) post-dissociation interactions between the ion fragment and the surrounding medium [3–12].

The resonant structure observed in the H^- and D^- ESD yields from thin films of H_2O and D_2O is qualitatively similar to what is seen in the DEA of water vapor, indicating that the condensation does not fully quench the DEA process in water [3,8]. The anion ESD yield has a threshold at ~ 5.5 eV and peaks at ~ 7.4 eV with a shoulder at ~ 9 eV [3]. This structure in the anion yield is attributed to excitation of the $^2\text{B}_1$ (7.4 eV) and $^2\text{A}_1$ (9 eV) DEA resonances, which are ~ 1 eV higher in energy and broader than in water vapor. When D_2O is substituted for H_2O , the main ($^2\text{B}_1$) DEA resonance narrows in the same manner as is seen in the gas phase, suggesting that inelastically scattered electrons do not contribute significantly to the resonant structure [3]. The shift to higher excitation energy is attributed to perturbations of the electronic structure of water by short-range interactions between neighboring molecules. The broadening is also ascribed to condensation-induced changes in the potential energy surfaces involved in the dissociation process. At low incident electron energies E_i , the most probable kinetic energy of the desorbing anions increases linearly with E_i , with a slope close to that seen in the gas phase (0.4 eV eV^{-1}) [8]. However, the anion kinetic energy distributions are shifted down by ~ 0.5 eV and are noticeably broader. In addition, the measured angular distributions of the desorbing ions no longer reflect the symmetry of the transient anion states, as they do in the gas phase. Instead, they are peaked along the surface normal direction [8]. Finally, electron energy-loss measurements of H_2O multilayer films indicate that

condensation opens up an additional decay channel for the $^2\text{B}_1$ Feshbach resonance, which can decay via long-range dipole interactions into intermolecular vibrational modes of the surrounding film [12].

In this study we investigate the ESD of H^- and D^- from condensed water (H_2O and D_2O) films. Two new features are observed in the energy dependence of the D^- yield from D_2O ice, which may be due to the excitation of additional DEA resonances. Also, the anion ESD yield arising from excitation of the $^2\text{B}_1$ DEA resonance in both H_2O and D_2O films is found to increase with the temperature of the film. The ESD signal begins to rise at roughly the same temperature at which pre-existing L defects (missing hydrogen bonds) become mobile in the films. Hence, we propose that the increased ion yield results from hydrogen bond breaking near the surface, which reduces the perturbation of the $4a_1$ antibonding level of the surface water molecules, thereby enhancing the lifetimes of the dissociative excited states that lead to ion desorption.

2. Experimental procedure

The experiments were carried out in two separate ultra-high vacuum (UHV) systems, one at Pacific Northwest National Laboratories (PNNL) and the other at the University of Sherbrooke. The PNNL apparatus consists of a UHV chamber (base pressure $\sim 2 \times 10^{-10}$ Torr) equipped with a pulsed low-energy electron gun, an effusive gas doser, a quadrupole mass spectrometer (QMS), a time-of-flight (TOF) detector and a Pt(111) crystal mounted on a liquid-nitrogen-cooled manipulator. The Pt crystal was cleaned by repeatedly heating it in O_2 (5×10^{-8} Torr) and then in UHV. Film temperature was measured using a K-type thermocouple, and has an estimated accuracy of ± 5 K. Ice films were grown via vapor deposition of ultrapure D_2O . Film thickness was determined by comparing D_2O temperature programmed desorption (TPD) spectra with published data [13–17], and has an estimated accuracy of $\sim 20\%$. Coverages are reported in monolayers (ML) of ice, where 1 ML is defined as the number of water molecules

in a complete bilayer of the (111) face of cubic ice ($\sim 10^{15}$ molecules cm^{-2}). D^- ions were generated by a monoenergetic electron beam, with an energy spread of ~ 0.3 eV full-width at half-maximum (FWHM), and collected in the TOF spectrometer. The incident electron beam was pulsed at 100 Hz, with a pulse length of $1 \mu\text{s}$ and an instantaneous current of $\sim 10^{-7}$ A in a spot size of $\sim 0.1 \text{ cm}^2$, resulting in a time-averaged current density of $\sim 10^{-10}$ A cm^{-2} . For the TPD and D^- temperature dependence measurements, the ice films were heated radiantly, at a rate of 0.133 K s^{-1} , using a tungsten filament mounted behind the Pt crystal.

The Sherbrooke apparatus and techniques have been described in detail elsewhere [3,4,11]. In brief, the system consists of a UHV chamber (base pressure $\sim 2 \times 10^{-10}$ Torr) containing a cryo-cooled polycrystalline Pt foil, a low-energy electron monochromator (80 meV FWHM), and a QMS. The Pt foil was cleaned by resistive heating. Doubly distilled H_2O was vapor deposited on the foil. Film thickness was estimated using a volumetric dosing technique [18], with an estimated accuracy of $\sim 50\%$. H^- ions were generated by the monochromatic electron beam (5×10^{-9} A in a 12 mm^2 spot) and detected using the QMS. Heating was achieved by turning off the cooling system and allowing the film to warm slowly, at a rate of $\sim 0.007 \text{ K s}^{-1}$ in the 100–140 K range.

3. Results and discussion

The resonant structure seen in the energy dependence of the D^- ESD yield from D_2O ice is illustrated in Fig. 1. The lower curve shows how the D^- yield varies with the incident electron energy from 3–36 eV. There are two intervals, 5–14 eV and 18–32 eV, in which the D^- signal rises significantly above the baseline. The baseline itself gradually increases with energy, which is attributed to D^- production via dipolar dissociation. The inset contains a more detailed scan of the region below 15 eV, which contains additional structure. The signal clearly peaks at ~ 7 eV, with a pronounced shoulder at ~ 9 eV and a slightly less intense feature at ~ 11 eV. As shown in the

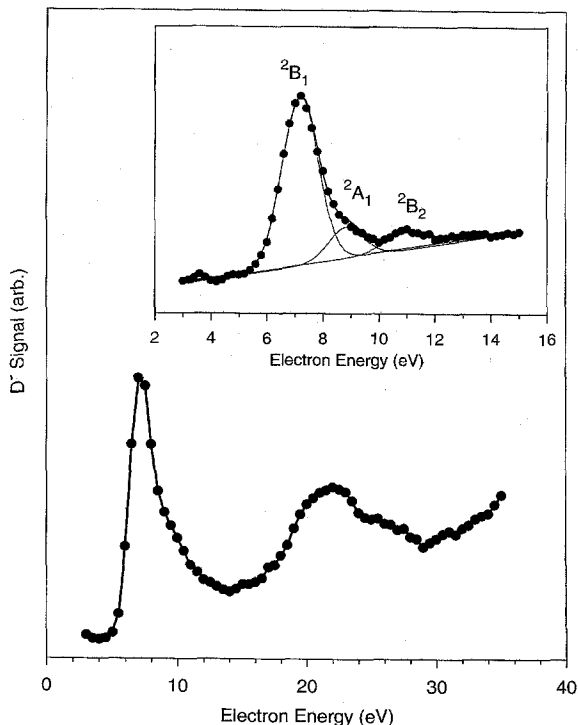


Fig. 1. D^- ESD signal vs. incident electron energy, collected at 120 K from a 5 ML film of amorphous D_2O ice, which was grown at 90 K. The inset contains a more detailed scan in the energy range 3–15 eV, along with a fit to the data (see text).

figure, a sum of three Gaussian peaks and a linearly increasing background fits this data reasonably well.

The low-energy structure in the ESD yield is attributed to DEA resonances in water. The ground state electronic structure of an isolated water molecule is $(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^2(1b_1)^2$ [19], where the $1a_1$ orbital is essentially the O(1s) core level, the $2a_1$ and $1b_2$ orbitals are primarily involved in O–H bonding, and the $3a_1$ and $1b_1$ are non-bonding lone-pair orbitals [20]. The lowest-lying unoccupied orbital is the $4a_1$ [19]. This strongly antibonding orbital mixes with the 3s Rydberg state [21], and hence is denoted as $(3s:4a_1)$. The 2B_1 , 2A_1 and 2B_2 resonances, which correspond to states having two $(3s:4a_1)$ electrons and a hole in the $1b_1$, $3a_1$, or $1b_2$ orbital respectively, have been observed in water vapor [22,23]. The ratio of their cross-sections for H^- production

is about 600:120:1 respectively [22,23]. The anti-bonding nature of the ($3s:4a_1$) orbital makes these excited states highly dissociative. Much of the Rydberg character of this level appears to be lost upon condensation due to short-range interactions between neighboring molecules, yet it retains its dissociative nature since both the 2B_1 and 2A_1 resonances have been observed to generate measurable ion yields in the ESD of condensed water films [3,8].

The energies and intensities of the two lowest-energy peaks in Fig. 1 are consistent with these earlier ESD measurements, and are assigned as the 2B_1 and 2A_1 DEA resonances. The third feature, at ~ 11 eV, is only resolvable at very low current densities and has not been observed previously in ESD from multilayer water films. A similar feature has been observed, however, in DEA measurements of water vapor and ascribed to excitation of the 2B_2 Feshbach resonance [22]. Maintaining a correspondence between gas-phase and condensed-phase results, we tentatively assign this feature to the 2B_2 resonance.

We consider two possibilities for the broad feature between ~ 18 and 32 eV. Since studies of negative ion resonances are often limited to electron energies below ~ 20 eV, there is no report of such a high-energy feature in the H^-/D^- yield from water vapor with which to compare. However, similar structure was observed at ~ 22 – 38 eV in the O^- yield arising from the electron bombardment of H_2O vapor, where it was attributed to the onset of ion pair formation [24,25]. The energies required to generate D^- from D_2O vapor via ion pair formation are estimated to be ~ 22 and 36 eV, but these values may be somewhat lower for condensed water because of dielectric screening. Thus, ion pair formation could lead to the structure in the D^- signal at ~ 18 – 32 eV. It is also possible that it arises from negative ion resonances associated with a hole in the $2a_1$ orbital. Kimmel and Orlando recently observed nearly identical structure in the D_2 yield vs. E_i during the electron bombardment of D_2O ice [2]. The production of D_2 in the ($J=0$, $v=0,2$) states increases noticeably between 18 and 32 eV, but no corresponding change is seen for the ($J=0$, $v=1$) state. This propensity to occupy only

certain vibrational states seems inconsistent with ion pair formation. Instead, the existence of a negative ion resonance associated with excitation of the $2a_1$ orbital was proposed to explain these results, with the width of the peak resulting from satellites associated with decay of the deep $2a_1$ valence level [2]. The production of D^- through similar excitations can also explain the higher-energy structure observed in the ESD yield.

Since DEA involves localized scattering events, excited-state lifetimes (and hence DEA cross-sections) are expected to be sensitive to the local potential which, in turn, will vary with the film's morphology and temperature. This should be most evident in water films, where short-range interactions between neighboring molecules strongly perturb their electronic structure. To investigate this, we measured the temperature dependence of the negative-ion ESD yield from crystalline and amorphous water films. Fig. 2 shows two cases: (a) the H^- signal from a thin amorphous film of H_2O , and (b) the D^- yield from a thick polycrystalline film of D_2O . In each case the signal rises with increasing temperature up to a point, from where it then drops to zero. The onset for the increase in signal occurs at a much lower temperature for the amorphous H_2O film (~ 100 K) than for the crystalline D_2O film (~ 120 – 130 K). This illustrates a general trend in the data: the ESD yield increases with temperature for both H_2O and D_2O , and it occurs at lower temperatures for amorphous films than for crystalline films.

TPD spectra are shown in Fig. 2 as continuous lines. The D_2O TPD spectrum was obtained experimentally. The H_2O spectrum, on the other hand, is simulated using the desorption rate parameters and kinetic model described in Refs. [16,17] and is presented only as a first-order estimate of the thermal desorption behavior of the H_2O film. Note that, from the simulation, which calculates the degree of crystallization as part of the desorption kinetics, it was determined that the H_2O film remained amorphous throughout the experiment. For both H_2O and D_2O , comparison of TPD and ESD data indicates that the drop in ESD signal generally corresponds with the thermal desorption of the films. The increase in the ESD signal,

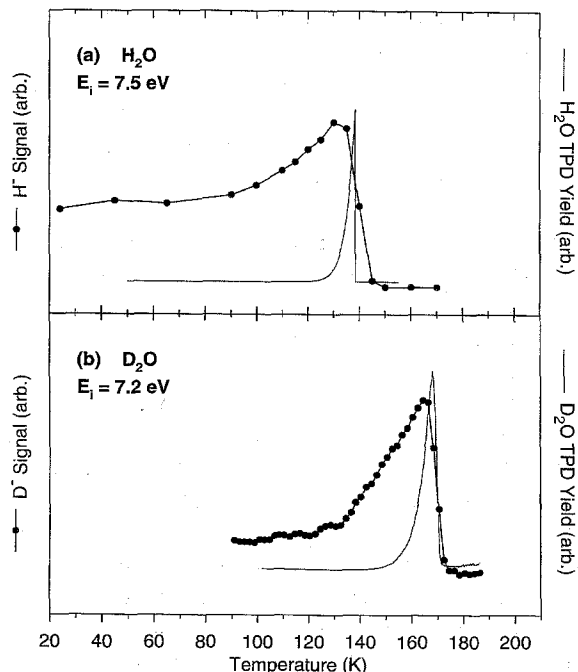


Fig. 2. (a) H⁻ signal vs. temperature (filled circles) for an incident electron energy of 7.5 eV, collected from ~3 ML of amorphous H₂O ice grown at ~20 K. Also plotted in the figure is a simulated TPD spectrum from this film (solid line), which was calculated for the same heating rate (0.007 K s⁻¹) using the desorption rate parameters and kinetics model given in Refs. [16,17]. (b) D⁻ signal vs. temperature (filled circles) for an incident electron energy of 7.2 eV, collected from a 60 ML polycrystalline D₂O ice film grown at 155 K. Also plotted in the figure is an experimentally obtained TPD spectrum, collected using the same heating rate (0.133 K s⁻¹).

however, begins at temperatures well below the onset of significant thermal desorption.

A nearly identical temperature dependence was observed in the ESD yield of low-kinetic-energy D⁺ from D₂O ice [26]. The similarity in the D⁺ and D⁻ temperature dependence suggests that the changes observed in the cation and anion ESD yields have a common origin. Sieger et al. attribute the rise in D⁺ ESD yield with temperature to thermally activated reduction in surface hydrogen bonding which increases the lifetimes of the excited states responsible for ion desorption, especially those excited states that involve the a₁ bands of ice [26]. Rosenberg et al. also showed that excitations involving the lowest-lying (4a₁) Rydberg

orbital survive at the surface due to the reduced coordination of the surface molecules, and that these excitations lead to enhanced ion desorption [27]. Since the excitations that lead to D⁻ and low-energy D⁺ desorption both involve occupation of the 4a₁ level [26], it is likely that thermally induced changes in the lifetimes of excited states involving the 4a₁ level are responsible for the similarity in the temperature dependence D⁺ and D⁻ ESD yields. Moreover, based on the arguments of Sieger et al. [26], we suggest that the excited-state lifetimes are enhanced as a result of hydrogen bond breaking near the surface, which reduces the coordination of surface molecules, thereby enabling excitations to remain localized for a longer period of time.

One possible mechanism for thermally induced hydrogen bond breaking near the surface is the mobilization of pre-existing L defects (i.e. missing hydrogen bonds). The energy required to directly break a hydrogen bond (~0.5 eV) is too high for significant bond breaking to occur spontaneously at the temperatures where the ESD yield begins to rise. However, in a typical ice film there are a large number of pre-existing L defects that form as the film is grown [28]. The volume density of these defects can be as high as ~10¹⁹ cm⁻³ near the surface [29], yielding an area density of 10¹²–10¹³ cm⁻² (roughly one defect for every 10²–10³ surface molecules). Using infra-red absorption spectroscopy techniques, Devlin and coworkers observed that the onset for L defect mobility occurs at around 100 K for amorphous ice but at about 130 K for cubic crystalline ice [30,31], which is consistent with the onsets we observe for the increase in ESD yield (see Fig. 2). The mobilization and transport of these defects to the surface would temporarily break hydrogen bonds there, thus reducing the degree of perturbation on the 4a₁ orbitals of the surface molecules. If this reduced perturbation increases the lifetimes of the excited states that lead to ion desorption, as expected, then the ESD yield would increase with temperature.

Note that, although this L defect model is consistent with our data, it is not unique. Other explanations, such as a decrease in the density of ice with increasing temperature, could also be used

to explain these results. The basic argument would remain the same, however. As the temperature of the films is increased, molecules near the surface feel a reduced perturbation of their electronic structure which leads to an enhanced lifetime for occupying the states that lead to ion desorption.

4. Summary

In this study we investigate anion ESD from condensed water (H_2O and D_2O) films. The energy dependence of the ion yield exhibits structure which arises from excitation of the $^2\text{B}_1$, $^2\text{A}_1$ and $^2\text{B}_2$ DEA resonances of water at ~ 7 eV, 9 eV and 11 eV respectively. Additional structure is observed between ~ 18 and 32 eV, which results from either ion pair formation or DEA resonances associated with a hole in the $2a_1$ orbital. To our knowledge, this higher-energy structure has not been reported in studies of DEA in water vapor. The negative-ion yield generated by exciting the $^2\text{B}_1$ DEA resonance in both H_2O and D_2O films is found to increase as the film is heated. These results are consistent with the mobilization of pre-existing L defects in the ice films, which lead to hydrogen bond breaking at the surface. The reduced coordination of surface molecules that results from this softening of the hydrogen bonding network leads to an enhanced ESD yield. Additional investigations of the complex dependence of the ESD yield on the film thickness and morphology, including the effects of charging, are presented elsewhere [26,32].

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