Low-Energy Electron-Induced Reactions of Water

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Abstract

The radiation chemistry of water is of fundamental importance to fields as diverse as interstellar chemistry, waste remediation, radiation processing of food, nuclear reactors, medical diagnoses, and radiation treatment of cancer. The water radiolysis experiments in our laboratory were conducted in an ultrahigh vacuum (UHV) chamber in which nanoscale thin films of amorphous solid water (H₂O/D₂O), deposited on a Mo(110) single crystal substrate at 90 K, were irradiated with low- and high-energy electrons (5–1000 eV). To analyze products trapped in the thin films after irradiation, post-irradiation temperature programmed desorption (TPD) and infrared reflection absorption spectroscopy (IRAS) experiments were conducted, using a quadrupole mass spectrometer and a Fourier-transform infrared spectrometer, respectively. Following irradiation of condensed D₂O with 5 eV electrons with a fluence of 16.7 µC, TPD experiments demonstrated evidence for the production of D₂. The production of H₂O₂ was also observed after both high and low-energy (10–1000 eV) irradiation of H₂O. Our results are consistent with our hypothesis that the production of complex species in the interstellar media may result from low-energy electrons produced when condensed matter interacts with high-energy radiation.
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1. Introduction

1.1 Why study low-energy electron-induced reactions?

The chemical evolution of homochirality of terrestrial amino acids and sugars has fascinated scientists ever since Pasteur’s time.[1] Some theories suggest that specific enantiomers were selected from racemates during endogenous evolution of life on earth. One of the most prominent experiments that supports the endogenous origin of life is the Miller-Urey experiment: ammonia, hydrogen, water, methane and carbon monoxide were subjected to an electric spark for a week to form amino acids such as glycine and alanine.[2] Even though this experiment supported the endogenous theory, it had two major drawbacks: (1) the experiment was performed under reducing conditions (atmosphere with H₂) while primitive earth lacked hydrogen in its atmosphere, and (2) the amino acids formed were racemic mixtures. More recent RNA-based biotic theories hypothesize that the homochirality of amino acids was a consequence of D-RNA molecules stereo-selectively choosing L-amino acids during the aminoacylation of RNA.[3] On the other hand, exogenous theories attribute homochirality, single-handedness to prebiotic chemical evolution that occurred due to irradiation in the interstellar media. In fact, radiolysis experiments of butanol involving spin-polarized secondary electrons from a magnetic substrate have demonstrated chiral selective chemistry.[4] Our hypothesis is that even electrons that are not spin polarized may have contributed to the formation of complex organic molecules in space during radiolysis reactions.

Nineteen L-enantiomer amino acids were discovered in Murchison and Murray carbonaceous chondrite meteorites, a finding that is consistent with exogenous viewpoints.[5] Extraterrestrial organic compounds could have been sources for life on Earth because these alpha-methyl-alpha-amino alkanoic acids found in meteorites show resistance to racemization
and have the tendency to form chiral secondary structures.[5] With the recent advent of the Atacama Large Millimeter/submillimeter Array (ALMA) telescope, astrochemists have begun to actively explore the mechanisms by which interstellar prebiotic molecules are synthesized.[6]

The most widely accepted model for interstellar molecular synthesis involves energetic processing of cosmic ices by UV light. Prior to the formation of the solar system, molecular clouds at cold temperatures of around 10 K contained interstellar dust covered with ice, consisting of mainly water, and small amounts of carbon monoxide, methanol, ammonia and carbon dioxide.[7] UV light incident on these ices is thought to form internally because externally sourced UV light is not able to penetrate these dense, dark, molecular interstellar clouds.[8] UV light within these clouds is attributed to cosmic rays (10–100 MeV) which are thought to excite the Layman and Werner band systems of molecular hydrogen that then emit UV light.[9] The interaction between the UV light and the icy grain mantles leads to the formation of radicals like •H and •OCH₃ that in turn lead to the formation of complex organic molecules. Ice containing ammonia, carbon monoxide, and water, when irradiated with circularly polarized UV light (UV-CPL), demonstrated the formation of glycine, alanine and other amino acid precursors.[5] When R-UV-CPL was used, D enantiomers were produced in 0.44% excess while during irradiation with L-UV-CPL produced L-enantiomers in 0.65%.
In addition to UV light, we conjecture that cosmic ray induced low-energy secondary electrons initiate chemical reactions in cosmic ices. As shown schematically in Figure 1, most of these secondary electrons have energies below 20 eV.[10] Although dissociation probability increases with electron energy, most of the radiolysis yield is due to low-energy electrons. Hence, our studies focus on studying astronomically relevant ices using low-energy (< 20 eV) electrons because we hypothesize, based on work previously done in our laboratory, that “low-energy, electron-induced condensed phase reactions may contribute to the interstellar synthesis of “complex” molecules previously thought to form exclusively via UV photons”. [11]
1.2 Importance of studying water radiolysis

In addition to possibly explaining life’s origins, radiolysis of water has a wide range of applications relevant to sustaining human life. For example, radiation processing of food is used to preserve freshness and remove harmful pathogens.[12] In addition, irradiating contaminated water is useful for reducing the amount of environmental and biohealth hazards being released from wastewater treatment facilities.[13-15] Following irradiation of waste water, toxic compounds such Chromium(IV) have been reduced to less hazardous compounds, such as Chromium(III).[16]

To understand the formation of biologically relevant compounds observed in space, it is essential to study the mechanisms by which water radiolysis occurs because the cosmic ices, containing predominantly water, are continuously bombarded by high-energy particles such as cosmic rays. Water in our solar system was initially thought to have formed from the solar proplanetary disk that orbited the sun, but recent research shows that a significant fraction of the solar system’s water predates the sun.[17] Cosmic ices containing water are found in comets, icy planets (e.g., Neptune), icy moons, and also surrounding dust particles in the interstellar medium. Most recently, bright spots thought to be active ice were detected by the Dawn spacecraft on Ceres, the largest object in the asteroid belt between Mars and Jupiter.[18] Energetic processing of ices is prevalent on the surfaces of Europa, a Galilean satellite covered with water ice.[19] On Europa’s surface, hydrogen peroxide (H₂O₂) has been detected in an unusually high abundance of 0.13% in comparison to water ice.[20-22] Formation of hydrogen peroxide may be due to irradiation of water ice by UV photons.[23] In fact, the presence of peroxide, an oxidant may be critical for the possible formation of complex life in the oceans of Europa.[24]
Cosmic ices are found in the form of amorphous solid water (ASW), a water phase formed below 130K.[25] When ASW is gradually heated, it transforms into a crystalline state in an irreversible process; the exact heat of crystallization is dependent on experimental conditions.[26]

1.3 Electron-Induced Chemistry

Electron-induced chemistry may lead to the formation of compounds that are not formed through photochemistry.[11] Electrons have been shown to be more efficient than photons in inducing some condensed-phase chemical reactions.[27] Electron-induced singlet-to-triplet transitions are allowed because the incident electron can replace those of the molecule, while similar photon-induced transitions are nominally forbidden.[28] In addition, in contrast to photons, the parent molecule may gain a negative charge by capturing electrons. The negative ion may then fragment to produce species unique to electron-induced chemistry.

Electrons interact with molecules by one of three mechanisms: (1) electron impact excitation (EIE), (2) electron impact ionization (EII), and (3) dissociative electron attachment (DEA).[10] During EIE, the impact of the electron results in a molecule in its excited state. In the case of EII, the electron ionizes the molecule, forming a positively charged molecular cation. The DEA mechanism involves the formation of a temporary negative ion followed by dissociation if the anion is dissociative in the Franck-Condon region and one of the fragments has a positive electron affinity.[29] The initial electron-molecule interaction step during DEA may take only $10^{-15}$ seconds, after which the molecule may dissociate into negative ions and radicals. For DEA, anion formation is a resonant process.[30] The resonant peaks for the condensed and gas phases may be different due to the attractive polarization and image forces in the condensed phase.[30] The species formed from any of the three processes may combine to
form various detectable products. For water these products include H$_2$ and H$_2$O$_2$, which are the focus of this thesis (Figure 2).

**Figure 2:** Decomposition of water after irradiation. Electron Impact Ionization (EII) for H$_2$O occurs for electron energies greater than 11 eV.[31] Electron Impact Excitation occurs when water interacts with electrons with energies greater than 7.3 eV.[32] Dissociative electron attachment (DEA) occurs for electron energies less than the excitation energy of H$_2$O. Adopted from [33]

### 1.4 Techniques for investigating electron-induced radiolysis of water

Electron-induced radiolysis studies involve observation of both desorbed species (electron stimulated desorption) and remnant species trapped in the thin films (post-irradiation analysis). When used in combination, surface science techniques such as electron-stimulated desorption (ESD), post-irradiation temperature programmed desorption (TPD), and post-
irradiation infrared reflection-absorption spectroscopy (IRAS) can provide a comprehensive understanding of condensed phase radiolysis.

1.4.1 Electron Stimulated Desorption (ESD)

In ESD, during electron irradiation, a quadrupole mass spectrometer detects desorbing species, which are typically ions or radicals. These species have sufficient kinetic energy to leave the surface of thin films after being formed via dissociative electron attachment, ionization, or dissociative excitation.[34]

1.4.1.1 Hydrogen anion formation from water during ESD

The formation of hydrogen anions from condensed phase H$_2$O has been extensively studied. In the condensed phase, the formation of hydrogen anions has been shown to predominantly occur at the amorphous solid water (ASW)/vacuum and ASW/Pt (crystal) interphases.[35] Previous ESD studies of six monolayers of condensed H$_2$O/D$_2$O have detected hydrogen/deuterium anions desorbing at a threshold of 5.5 eV with resonance maximum yield at 7.4 eV, a finding that is consistent with a mechanism involving dissociative electron attachment.[29] For gas phase reactions, the DEA resonance peaks for hydrogen and deuterium anions are at 6.5eV. This finding suggests that the escape of anions in the condensed phase is impeded by the attractive polarization forces that is otherwise not present in gas phase.[36]

1.4.1.2 Hydrogen molecule formation during ESD

Past ESD studies have found the threshold energy for D$_2$ production to be 6.3eV, which is below the first excited electronic state (7.3 eV) of water.[32] The formation of D$_2$ below the threshold energy is attributed to D$^-$ that formed from dissociative electron attachment.[37] Even
though the $D^{-}$ yield decays after ~7.4eV, the $D_{2}$ yield continues to increase. The Frenkel exciton$^{1}$ excitations of $H_{2}O$ can form $H_{2}O^{+}$ and $H_{3}O^{+}$ that dissociate to form molecular hydrogen.[32]

1.4.2 Post Irradiation Analysis: Temperature Program Desorption

ESD is an important experimental method but does not give a complete understanding of electron-induced reactions. Post-irradiation analysis is essential for studying the products that remain trapped in the thin film after irradiation due to insufficient kinetic energy to desorb. In a typical post-irradiation TPD experiment, an irradiated sample (film adsorbed on a single crystal) is gradually heated and the products that desorb are analyzed by a quadrupole mass spectrometer. The mass spectrometer ionizes the products as they enter the ionizer; the resulting fragment ions enter the quadrupole region where they are subjected to an oscillating electric field that separates the ions by their mass-to-charge ratios ($m/e$). A peak in the mass spectrometer signal as a function of temperature indicates the desorption of the parent sample or its radiolysis product. We can differentiate between two products by using their different fragment mass-to-charge ratios and their different desorption temperatures.

1.4.2.1 Molecular hydrogen formation detected via post-irradiation TPD

An important product of water irradiation is molecular hydrogen. $D_{2}$ desorbed at 160 K in TPD from $D_{2}O$ thin films irradiated with 485 eV electrons.[38] $D_{2}$ was also seen with peaks that started at 90 K in experiments where thin $D_{2}O$ films were irradiated with 5 keV electrons.[39]

1.4.2.2 Hydrogen peroxide production detected via post-irradiation TPD

Desorption of hydrogen anions during ESD imply that OH radicals are left behind in the thin film. These OH radicals may combine to form a hydrogen peroxide. OD radicals are mobile

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$^{1}$ Exciton is a neutral particle with an excited electron in the conduction band that is attracted to the positively charged electron hole due to an electrostatic Coulomb Force.
at 90 K and can combine to form $\text{D}_2\text{O}_2$ if they are within a radius of 1–4.4 Å.[40] Past TPD studies have shown the production of $\text{H}_2\text{O}_2$ following irradiation of condensed water. For instance, $\text{H}_2\text{O}_2$ was seen to desorb at 160–170K after water thin film was irradiated by 200 keV electrons.[41] In a separate post-irradiation TPD study, the electron-induced production of $\text{D}_2\text{O}_2$ from $\text{D}_2\text{O}$ was found to increase with incident electron energy (5–50 eV).[22]

1.4.3 Post Irradiation Analysis: Infrared Spectroscopy

Infrared reflectance absorption spectroscopy (IRAS) is used to identify radiolysis products that remain trapped in the thin film. In contrast to TPD, this technique does not involve thermal processing of the thin film after the irradiation. After irradiation, the absorption of an IR beam reflected on the crystal is measured using Fourier Transform Infrared Spectroscopy (FTIR) to identify the products remaining in the thin film.

1.4.3.1 Hydrogen peroxide production observed with IR

Many studies have used IRAS to study the photolysis and radiolysis of water. One of the main radiolysis/photolysis products of water is hydrogen peroxide, and the IRAS findings related to this radiolysis/photolysis product are summarized in Table 1. The symmetric bending ($1454$ cm$^{-1}$) and the asymmetric bending ($1389$ cm$^{-1}$) modes of $\text{H}_2\text{O}_2$ combine to form an IR absorption peak (~$2848$ cm$^{-1}$), which is easily detected.
Table 1: Previous publications that detected peroxide with IRAS

<table>
<thead>
<tr>
<th>Reference</th>
<th>Irradiated compound</th>
<th>Incident energy, irradiating particle</th>
<th>Temperature (K)</th>
<th>Peroxide IR peak Position (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gerakines et al. 1996 [42]</td>
<td>H(_2)O</td>
<td>1100 A UV flux</td>
<td>10</td>
<td>H(_2)O(_2) 2850 and 1457 cm(^{-1})</td>
</tr>
<tr>
<td>Moore 1999 [43]</td>
<td>H(_2)O</td>
<td>0.8 MeV protons</td>
<td>16–80</td>
<td>H(_2)O(_2) 2851 cm(^{-1})</td>
</tr>
<tr>
<td>Baragiola et al. 2006 [20]</td>
<td>30% H(_2)O(_2) in H(_2)O</td>
<td>150–173</td>
<td></td>
<td>H(_2)O(_2) 2852 cm(^{-1})</td>
</tr>
<tr>
<td>Zheng et al. 2006 [39]</td>
<td>Triply distilled water condensed on Ag substrate</td>
<td>5 keV electrons</td>
<td>12</td>
<td>H(_2)O(_2) 2852 cm(^{-1})</td>
</tr>
<tr>
<td>Carlson et al. 2011 [44]</td>
<td>Pure water</td>
<td>10 keV electrons</td>
<td></td>
<td>H(_2)O(_2) 2850 cm(^{-1})</td>
</tr>
</tbody>
</table>

2. Experimental

All experiments were performed in the same custom-designed UHV chamber apparatus described in previous publications (Figure 3). [45] The chamber has a base pressure of ~5×10\(^{-9}\) Torr maintained by an ion pump (Perkin Elmer 2070122), a titanium sublimation pump (TSP) (Perkin Elmer 2140411), and a cryoshroud (Perkin Elmer 1001241). A turbomolecular pump (Leybold TMP360V) and a rotary vane pump (Leybold D16B) are used for the initial pump down of the UHV chamber. Following a bakeout, the UHV chamber is isolated from these two pumps which are then used to pump down gas-handling system. The chamber contains a Mo(110) single crystal substrate (8 mm diameter) mounted on a manipulator capable of \(x\), \(y\) and \(z\) translation, as well as \(\theta\) rotation. Single crystal surfaces have a well-defined atomic arrangement that allows for studying surface reactions. [46] The number 110 refers to the exposed single crystal surface plane. The crystal is cooled to ~90 K with an attached liquid nitrogen cooling apparatus. Water vapor was deposited on the cryogenically cooled crystal.
surface via a precision leak valve (from Sapphire-sealed variable leak valve: 9515106). Film thickness was varied from 15 monolayers (ML) to 100 ML. Thickness of sample layers was calibrated by monitoring the drop in pressure reading of the Baratron capacitance gauge. Based on the results of temperature programmed experiments, a pressure drop of 0.0003Torr was found to correspond to 1 ML. A sample temperature below 130 K allows amorphous solid water, the ice phase found in cosmic ices, to form on the Mo(110) crystal. D$_2$O with isotopic purity of 99.9% was provided by Sigma Aldrich and nanopure water of 18.2 MΩ-cm purity was provided by Barnstead thermo scientific.

Following deposition, the sample was bombarded with quasi-monoenergetic electrons originating from an EGPS-1106A electron gun (Kimball Physics Inc.) with an incident current that was varied from 2 to 12 μA. The incident energy of electrons was varied from 5 eV to 1 keV (the energies have a spread of about 0.4 eV) and the duration of irradiation was varied from 30 s to 9.8 hrs. For control experiments involving high-energy electrons, the electron gun and the ion gauge were turned off. For control experiments involving low-energy (< 100 eV) electrons, the thin films were exposed to the electron gun with a negative bias of 100 V applied to the crystal. For short irradiation times, the crystal was not only turned away from the electron gun to stop irradiation, but a negative bias was also applied to the crystal directly before and after irradiation.

Post-irradiation analysis of the bombarded thin film was conducted to investigate chemical species trapped in the thin film. Infrared Reflection Absorption Spectroscopy (IRAS) measurements were made using a TENSOR™ 27 FTIR spectrometer (Bruker Optics) equipped with a liquid nitrogen-cooled mercury cadmium telluride (MTC) detector. TPD experiments were conducted with a Hiden Ion Desorption Probe Series 500 Quadrupole Mass Spectrometer. During TPD experiments, the crystal was heated at ~ 15 K/s, using a KEPCO power supply
(ATE 6-10M) that heats a tungsten filament 1mm behind the crystal. Products are indicated by peaks whose areas correspond to relative yield of the products and were used to obtain quantitative data. Quantitative data (radiolysis yields) were obtained by integrating the corresponding TPD peaks.

Between experiments, the crystal face was cleaned by radiative and electron bombardment (TCR 600S1-1-OV DC Power Supply 600V 1A (Lambda America)) heating to 2200 K for 30 s, exceeding the desorption temperature of any possible remnant molecules.[47] After allowing the crystal to cool for six minutes to reach a temperature of ~ 90 K, sample gases were deposited on the crystal. At the end of all experiments for the day, the crystal was cleaned by dosing 5×10⁻⁶ Torr of oxygen while heating the crystal to ~1200 K for five minutes. Carbon monoxide, formed when oxygen reacts with a contaminant carbon, desorbs at 1200 K and the crystal is heated up to ~2200 K for 30 s to remove the remaining oxygen.
Figure 3: UHV chamber and experimental setup. A. Deposition: Molybdenum (110) crystal is cooled with liquid nitrogen to ~90K in a chamber at a pressure of ~5×10^{-9} Torr. H_2O or D_2O is deposited on the crystal facing the doser to form amorphous ice. B. Irradiation: The crystal is rotated to face the electron gun where the thin film is irradiated with electrons. Some products that are formed during irradiation escape the thin film. C. IR: Infrared light from FTIR spectrometer reflects off of the crystal and is detected by a liquid nitrogen cooled MCT detector. Products in the thin-film absorb IR with frequencies that match their bond vibrations. D. TPD: The products in the thin film are thermally desorbed when the tungsten filament heats the crystal. The desorbing species are detected by the mass spectrometer.
3. Results and Discussion

Post-irradiation infrared reflection-absorption spectroscopy (IRAS) and temperature programmed desorption (TPD) were used to monitor the electron-induced formation of molecular hydrogen/deuterium and hydrogen peroxide/deuterium peroxide from condensed H₂O/D₂O nanoscale thin films.

3.1 TPD Evidence for Production of Molecular Hydrogen at Low Incident Electron Energies (5 eV)

To investigate the production of molecular hydrogen (deuterium) from water radiolysis, 100 monolayer-H₂O/D₂O thin films were irradiated with low-energy (~5–20 eV) electrons, and subsequently analyzed through temperature programmed desorption (Figure 4). In the absence of electron irradiation, while monitoring the mass to charge ratio of 2(4) for H₂(D₂), three thermal desorption peaks for H₂(D₂) were consistently present. The first desorption peak that occurs around 90–100 K is attributed to water/hydrogen desorbing from the heating filament when the power is turned on. The second prominent peak is seen around 170 K, the temperature at which water desorbs. This peak is attributed to H₂⁺(D₂⁺) from H₂O(D₂O) that fragmented in the mass spectrometer. The third desorption peak is observed around 350 K and does not align with water peaks (H₂¹⁸O and D₂¹⁸O, mass to charge ratio of 20 and 22, respectively). This desorption peak is attributed to molecular hydrogen/deuterium (H₂/D₂) formed from hydrogen/deuterium atoms that combined on the surface of the crystal. These findings, pertaining to the surface chemistry of water on Mo(110) in the absence of radiation, are consistent with previously published data.[38]

In addition to the three aforementioned desorption peaks, a small thermal desorption peak appears at ~130 K in the temperature programmed desorption data for the irradiated H₂O
thin films (Figure 4). To verify that this fourth molecular hydrogen desorption peak was due to electron-irradiation, several control experiments with only photon exposure were conducted. Photon irradiation in the absence of electron irradiation was accomplished by negatively biasing the crystal in order to repel the electrons but not photons from the electron gun.

Figure 4: High-energy (900 eV) electron-induced production of H\textsubscript{2} observed during post-irradiation temperature programmed desorption. 100 ML-thick amorphous solid H\textsubscript{2}O films irradiated at 90 K. Molecular hydrogen (H\textsubscript{2}) was monitored (m/e = 2) before irradiation (blue) and after being irradiation with 900 eV electrons at 2 \( \mu \)A for 1 minute (red).

Further experiments involving irradiation of D\textsubscript{2}O with low-energy (5–20 eV) electrons were conducted to investigate the lowest energy required to form molecular deuterium (Figure 5).
Figure 5: Temperature programmed desorption evidence for the production of D₂ from low-energy electron irradiation of D₂O. 100 ML-thick amorphous solid deuterium oxide films at 90 K were irradiated and D₂ was monitored with m/e = 4. The desorption peak at 130 K is attributed to the formation of molecular deuterium due to irradiation (grey highlight). D₂ production is seen at energies as low as 5eV with electron dose of 16.7 μC (blue).

The observation of the 130 K molecular deuterium desorption peak following irradiation of D₂O at incident electron energy of 5 eV represents a new finding. Production of D₂ at this incident energy eliminates two mechanisms, electron impact excitation and electron impact ionization, suggesting a role for dissociative electron attachment (DEA). This conclusion is based on the observation that 5 eV is less than the electron excitation threshold (7.3 eV [32]) and the electron impact threshold (11 eV [31]) for water. The formation of D₂ via dissociative attachment is consistent with previous studies which demonstrated the formation of H⁻ and D⁻ with a threshold of 5.5 eV [32]. Past ESD experiments have found that the minimum energy
required for the formation of D₂ to be 6.3 ± 0.5 eV.[32] The formation of D₂ was also attributed to dissociative electron attachment to produce D⁻ followed by an ion-molecule reaction:[32]

\[ D^- + D_2O \rightarrow D_2 + OD^- \]

The lower electron energy threshold observed in our post-irradiation studies indicates that D₂ formed at these energies may not have had enough kinetic energy to desorb from the thin film to be detected by ESD experiments. Other studies have attributed D₂ to be directly formed from core-excited\(^2\) negative resonances of D₂O that decay to form D₂.[48] The detection of molecular hydrogen/deuterium following low-energy irradiation of amorphous water ice further supports the hypothesis that low-energy electrons may contribute to the production of various species in the interstellar media during high-energy irradiation involving cosmic rays and gamma rays.

### 3.2 TPD Evidence for the electron-induced production of atomic hydrogen (deuterium) from water ice

Results of post-irradiation temperature programmed desorption experiments demonstrated the production of atomic H (D) following electron irradiation of H₂O (D₂O) ice. This conclusion is based on the increased yield of H₂ (D₂) observed at ~ 350 K following electron irradiation (Figure 6). Control experiments were done to account for the production of H₂ (D₂) due to surface chemistry and photochemistry. Such control experiments involved placing a negative bias on the crystal to repel electrons from the electron gun. As previously discussed, the H₂ (D₂) desorption peak results from the combination of H (D) atoms adsorbed on the Mo(110) surface. Therefore, our results indicate the formation of H (D) atoms following electron-irradiation of condensed H₂O (D₂O).

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\(^2\) Core-excited resonances are formed when two electrons occupy empty molecular orbitals to form temporary negative anions.
Figure 6: Temperature programmed desorption evidence for the production of D$_2$ via recombination following low-energy electron irradiation of D$_2$O. 10 ML-thick amorphous solid deuterium oxide film at 90 K was irradiated by 10eV electrons with currents of 13.8 µA (red). D$_2$ production was monitored by observing the fragment $m/e = 4$. A negative bias was applied to the crystal to prevent electron irradiation but allow for photon irradiation during control experiment (black). D$_2$ yield is higher following electron irradiation.

The yield for the recombination peak of D$_2$ after electron irradiation was 13% larger than the yield of D$_2$ in the control experiment with photon exposure of equal time length.

For experiments corresponding to low incident electron fluence, the yield of D$_2$ desorption at ~ 350 K increases with increasing irradiation time, providing additional evidence for the electron-induced production of hydrogen atoms from condensed water (Figure 7).
Figure 7: D₂ yield via combination of D as a function of electron dose observed during post-irradiation temperature programmed desorption. 100ML D₂O films were irradiated with 900 eV electrons with currents of 2 μA. A. Mass spectrometer signal versus time shows evidence for D₂ formation with peaks around 300–350 K. B. D₂ versus irradiation time shows the area of the desorption peak (300–350 K) increases and then decreases with increasing irradiation time.
The yield of D₂, due to combination of D atoms on the surface, increases until irradiation times of 90 seconds, after which the yield decreases. The peaks however become more defined and sharp with increased irradiation time. Similarly, past experiments of the electron-induced dissociation of water on Zirconium(0001) have shown that D₂ desorption at ~320 K during TPD experiments increases with higher coverage (thicker films) and irradiation.[38]

The mechanism of electron-induced D₂ and D₂O₂ formation is illustrated in Figure 8. D₂ formed in the film due to irradiation desorbs at low temperatures, ~130 K. The water thin film desorbs ~170–180 K.[41] The D atoms that are formed due to irradiation and left on the surface of the crystal can recombine to form D₂ that desorbs at high temperatures, ~ 350 K.
Figure 8: Mechanisms for the formation of D₂ and D₂O₂: Deuterium atoms form molecular deuterium in the film and desorb at 130 K. OD radicals react to form deuterium peroxide which desorbs at 170 K. Deuterium atoms recombine on the surface of the crystal to form D₂ at 350 K.

3.3 IRAS Evidence for Production of hydrogen peroxide due to high-energy (900 eV) electron irradiation

Infrared reflection absorption spectroscopy (IRAS) data indicates the production of hydrogen peroxide due to high-energy electron irradiation of condensed water (Figure 9). The IR absorption peak at ~2848 cm⁻¹ is the combination of the symmetric bending (1454 cm⁻¹) and the asymmetric bending (1389 cm⁻¹) modes of H₂O₂.[19]
Figure 9: High-energy (900 eV) electron-induced production of H₂O₂ observed during post-irradiation infrared reflection absorption spectroscopy. 100ML H₂O thin film irradiated with 900 eV electrons with current of 2 μA. The appearance of the well-known IR absorption at 2850 cm⁻¹ following irradiation is clear evidence for the production of H₂O₂ by high-energy electron irradiation of condensed H₂O at 90 K.

The H₂O₂ peak around 2850 cm⁻¹ was observed in past experiments where nanoscale films of pure water were irradiated with 10 keV and 5 keV electrons. [39,49] IRAS experiments of 30% H₂O₂ at 150–173 K showed the presence of an absorption peak at 2852 cm⁻¹, verifying the identification of this peak.[20]

The IR peak for the hydrogen peroxide became larger when the electron irradiation time was increased, as shown in Figure 10. The H₂O₂ peak increases linearly with increasing irradiation time, as seen in Figure 10B.
Figure 10: $\text{H}_2\text{O}_2$ yield as a function of electron dose observed in post-irradiation Infrared Reflection Absorption Spectroscopy. 100 ML of H$_2$O thin films at 90 K were irradiated with 900 eV electrons, with currents of 2 $\mu$A. 

A. The IRAS data show that the absorption band at 2850 cm$^{-1}$ becomes larger with the increase in irradiation time.

B. The yield versus irradiation time plot shows the increase in peak area is approximately linear with irradiation time.
However, the characteristic H$_2$O$_2$ IR peak was not observed during low-energy, 20 eV, electron irradiation of H$_2$O thin films for four hours (Figure 11).

![Graph showing absorbance vs. wavenumber with time points from 0 min to 240 min for 100 ML of H$_2$O with $E_i = 20$ eV and $i = 2 \mu$A.]

**Figure 11:** H$_2$O irradiation with low-energy electrons in post-irradiation IRAS. 100 ML of H$_2$O thin films at 90 K were irradiated with 20 eV electrons, with currents of 2 $\mu$A. The IRAS data do not show evidence for the formation of H$_2$O$_2$.

### 3.4 TPD Evidence for Production of hydrogen peroxide due to low- and high (10 – 1000 eV) electron irradiation of condensed water

The post-irradiation IRAS experiments presented clear evidence for the production of hydrogen peroxide following high-energy but not low-energy electron irradiation. Therefore, the production of hydrogen peroxide by both high- and low-energy electrons was studied using post-irradiation TPD. First by irradiating 150 ML of H$_2$O with 1 keV energy electrons, the effect of high-energy electron irradiation on the production of H$_2$O$_2$ is shown in Figure 12.
Figure 12: H$_2$O$_2$ yield as a function of electron dose observed in post-irradiation temperature programmed desorption. 150 ML-H$_2$O thin films were irradiated with 1 keV electrons with currents of 2 μA. A. TPD plots of mass spectrometer signal versus temperature. B. H$_2$O$_2$ yield versus irradiation time.

Our results are consistent with previous TPD experiments that demonstrated desorption of H$_2$O$_2$ at 170 K after irradiating crystalline water ice with 4.3 keV energy electrons.[39]

Amorphous water ice irradiated with 200 keV electrons for 1 minute also produced H$_2$O$_2$ at 170
As shown in Figure 12, the yield of H$_2$O$_2$ that desorbs at 170 K increases for irradiation times below 60 s. Longer irradiation times produce slightly less H$_2$O$_2$ yield. Irradiation with high-energy electrons for longer periods of time may have destroyed some of the H$_2$O$_2$.

Evidence for the formation of hydrogen peroxide after irradiating 150 ML of H$_2$O with 1 keV electrons led to further investigations of hydrogen peroxide production induced by low-energy electron irradiation. In such experiments, one concern was that thick water films might become negatively charged, repelling low-energy electrons. Hence, preliminary experiments were performed to determine minimum film coverage required to produce hydrogen peroxide after irradiation with electrons (Figure 13).

![Figure 13: H$_2$O$_2$ yield versus film thickness observed in post-irradiation temperature programmed desorption. H$_2$O thin films were irradiated with 1 keV electrons with 2 μA of current for 30 seconds. H$_2$O$_2$ is produced in films thicker than 30ML.](image-url)
In Figure 13, at our mass spectrometer setting, evidence for the formation of hydrogen peroxide is detected for water thin films ~30 ML thick and above.

To compare the production of hydrogen peroxide as a result of high- and low-energy electron irradiations, first 35 ML of H₂O are irradiated with 1 keV electrons for 30 seconds. Irradiation peaks attributed to hydrogen peroxide were visible at ~170 K (Figure 14). When a 35 ML water thin film was irradiated with 10 eV electrons (current of 11.7 μA for 4 hours), a small H₂O₂ desorption peak (m/e = 34) was observed at ~ 160 K during post-irradiation temperature programmed desorption experiments (Figure 14: red curve). During the control experiments, smaller desorption peaks, corresponding to hydrogen peroxide, were detected for a water thin film that was not irradiated (black curve) and that was exposed to photons for 4 hours (magenta curve).

While the H₂O₂ peak at ~170 K for the 10 eV irradiation experiment is small, it can be attributed to hydrogen peroxide because it does not appear in the control experiment in which the water thin film was not irradiated with electrons but was irradiated with photons. The above data is a key preliminary experiment for continuing investigations into the low-energy electron-induced formation of hydrogen peroxide from water ice. Previously published data has shown that the formation of D₂O₂ occurs when 5–8 ML of water is irradiated with electrons with energies as low as 5 eV.[22]
Figure 14: H$_2$O$_2$ yield versus incident electron energy observed in post-irradiation temperature programmed desorption. 35 ML of H$_2$O at 90 K were irradiated with 1 keV electrons with current of 2 µA for 30 seconds (blue and green), 35 ML of H$_2$O at 90 K were irradiated with 10 eV electrons with current of 11.7 µA for 4 hours (red), and 35 ML of H$_2$O at 90 K were irradiated with 10 eV photons with current of 10.4 µA for 4 hours (magenta). The production of H$_2$O$_2$ in the water film is seen at incident electron energies as low as 10 eV.

The H$_2$O$_2$ is hypothesized to form via the combination of two OH radicals as illustrated in Figure 8. OH radicals diffusing to the reactive Mo(110) surface and undergoing decomposition may explain the lower yield of H$_2$O$_2$ in our experiments compared to previously published work.

4. Conclusion

The radiolysis of condensed water as a function of incident electron energy, film thickness, and irradiation time was studied using both the post-irradiation temperature programmed desorption and infrared reflection-absorption spectroscopy. The desorption of
molecular hydrogen and deuterium was observed at ~ 130 K during TPD experiments following irradiation at incident energies ranging from 5 eV to 900 eV. The production of molecular hydrogen at 5 eV was attributed to dissociative electron attachment, because 5 eV is below the electronic excitation threshold of water. To look for conclusive evidence, future experiments should involve a range of incident electron energies (2 to 20 eV) characteristic of DEA. Such experiments should be done at constant incident fluence to search for resonances representative of DEA. The formation of D₂ due to combination at the Mo(110) surface of the crystal was observed during low- and high-energy irradiation of water ice. In the future, additional experiments will be conducted to obtain the cross-section for the production of D₂ as a function of incident electron energy. The formation of molecular hydrogen during electron irradiation may provide fundamental information related to the hydrogen explosion at the Fukushima nuclear reaction in 2010 since it is believed that the vessel exploded due to internal pressure form hydrogen buildup due to water irradiation.[50]

Evidence for hydrogen peroxide formation was seen in IRAS data and TPD experiments. The formation of hydrogen peroxide is attributed to the combination of two hydroxide radicals. Further studies using low-energy irradiation need to be conducted to identify the threshold energy for the formation of hydrogen peroxide using post irradiation TPD experiments. The formation of H₂O₂ via low-energy electron-induced reactions of water ice may explain the observation of H₂O₂ on the surface of Europa.

The observation of radiolysis products following both low-energy and high-energy electron irradiation of condensed water is consistent with the hypothesis that low-energy electrons play a significant role in these electron-induced processes.
5. References