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DOI:

[10.1063/1.4878658](https://doi.org/10.1063/1.4878658)

Document Version

Accepted author manuscript

[Link to publication record in Manchester Research Explorer](#)

Citation for published version (APA):

Petrik, N. G., Monckton, R. J., Koehler, S. P. K., & Kimmel, G. A. (2014). Electron-stimulated reactions in layered CO/H₂O films: Hydrogen atom diffusion and the sequential hydrogenation of CO to methanol. *Journal of Chemical Physics*, 140(20), 204710-1-204710-11. [204710]. <https://doi.org/10.1063/1.4878658>

Published in:

Journal of Chemical Physics

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Electron-stimulated reactions in layered CO/H₂O films: Hydrogen atom diffusion and the sequential hydrogenation of CO to methanol

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Abstract

Low-energy (100 eV) electron-stimulated reactions in layered H₂O/CO/H₂O ices are investigated. For CO layers buried in amorphous solid water (ASW) films at depths of 50 ML or less from the vacuum interface, both oxidation and reduction reactions are observed. However for CO buried more deeply in ASW films, only the reduction of CO to methanol is observed. Experiments with layered films of H₂O and D₂O show that the hydrogen atoms participating in the reduction of the buried CO originate in the region that is 10 – 50 ML below the surface of the ASW films and subsequently diffuse through the film. For deeply buried CO layers, the CO reduction reactions quickly increase with temperature above ~60 K. We present a simple chemical kinetic model that treats the diffusion of hydrogen atoms in the ASW and sequential hydrogenation of the CO to methanol to account for the observations.

I. Introduction

Non-thermal reactions in aqueous systems are important for a number of areas including radiation chemistry and nuclear technology,¹ radiation biology,² and photocatalysis.^{3, 4} When interacting with condensed matter, most forms of high-energy radiation (γ -rays, α , β , etc.) generate large numbers of low-energy secondary electrons, and these secondary electrons, which are chemically active, are responsible for many of the radiation-induced chemical reactions.³ Due to the high-scattering cross sections that lead to very short mean-free path lengths, the interactions of low-energy electrons with liquid water are difficult to study directly. To surmount this difficulty, many experiments have been performed with low-energy sources (electrons, ions and photons) on amorphous solid water (ASW) and crystalline ice films adsorbed on cold substrates in ultrahigh vacuum.⁵⁻³⁰

Non-thermal reactions in water ices, with or without other co-adsorbed molecules, are also of interest in astrochemistry and planetary sciences.³¹⁻³⁴ For example, dust grains in cold molecular clouds are coated with molecular ices for which water is typically the main component. Thermal and non-thermal

processing of these icy dust grains produces some of the complex molecules that have been observed in interstellar space.^{35, 36} Reactions in water ices are also important in comets and some of the moons of the gas-giant planets.^{31, 32, 34} In cold, dense molecular clouds, CO is an abundant component in icy grain mantles,³⁷⁻³⁹ and reactions in CO/H₂O ices contribute to the wide variety of organic molecules that have been observed in these environments. As a possible route to the production organic molecules, the non-thermal reactions in CO/H₂O ices have been investigated for photon, electron, and ion irradiation.^{17, 27, 37, 39-41}

Both reduction and oxidation reactions are observed in irradiated CO/H₂O ices.^{17, 27, 37, 40, 41} These reactions occur because the interaction of ionizing radiation with condensed water leads to water dissociation through a variety of channels producing both oxidizing and reducing species:^{1, 3}

The oxidation products of CO are typically the most abundant products observed.^{17, 37, 39, 40} For example, Hudson and Moore used 800 keV protons to irradiate mixed CO/H₂O ices, and found that the predominant reaction was the conversion of CO to CO₂.³⁷ However, small amounts of the formyl radical (HCO),^{27, 37, 40} formaldehyde (CH₂O),^{27, 37, 40, 41} methanol (CH₃OH),^{27, 37, 41} formic acid (HCOOH),^{27, 37, 41} and methane (CH₄)³⁷ are also observed.³⁷ Sequential reactions with hydrogen atoms are believed to convert CO to methanol (CH₃OH).^{37, 41-43}

The hydrogenation reactions can be initiated by gas-phase hydrogen atoms that strike the surface^{41, 42, 44-47} or from H atoms produced by non-thermal dissociation of water in the ice mantles.^{17, 37, 41, 42}

Yoshinobu and co-workers investigated the electron-stimulated reactions in CO/H₂O ice.¹⁷ In their experiments, CO was dosed on 5 nm thick water films, then capped with 30 nm thick water layers, and irradiated with 200 eV electrons. Similar to other experiments, they observed both oxidation products (e.g. CO₂) and reduction products (HCO, CH₂O and CH₃OH). However since the penetration depth of 200 eV electrons in condensed water is considerably less than 30 nm,⁴⁸ the mechanism by which these reactions occurred is not immediately clear. One possibility is that the CO diffused through the ASW cap layer to the region near the surface where it reacted with species produced by the energetic electrons.^{49, 50} Another possibility is that mobile species produced in the ASW (e.g. H, H₂O*, or H₃O⁺) diffused to the buried CO layer and subsequently produce the observed reactions.

We have previously studied electron-stimulated reactions in ASW films.^{6, 9-11, 16, 19, 51-53} Some of those experiments demonstrated that the non-thermal reactions and the electronic excitations that initiate those reactions do not necessarily occur at the same location in the ASW. For example, H₂ is preferentially produced at the ASW/substrate and ASW/vacuum interfaces.^{16, 19, 52} However, the energy that drives the reactions at the ASW/substrate interface is absorbed in the “bulk” of the ASW film.^{16, 19, 52} Molecular oxygen is also produced in electron-irradiated ices,^{12, 20} but the reactions that produce O₂ occur primarily at or near the ASW/vacuum interface.^{54, 55} Our previous research on the spatial distribution of electron-stimulated reactions in neat ASW films and the results of Yoshinobu and co-workers motivated us to investigate the spatial distribution of the electron-stimulated reactions in CO/ASW films.

Here we investigate the electron-stimulated reactions in layered H₂O/CO/H₂O ices as a function of the position of the CO layer within the water films. For CO layers buried within the first 50 ML of the

vacuum/water interface, we find that both oxidation and reduction reactions occur as observed in earlier experiments.^{17, 27, 37, 40, 41} However when the CO layer is buried deeper within the water film, only reduction products (HCO, CH₂O and CH₃OH) are observed. For water cap layer coverages, θ_{Cap} , greater than 50 ML, the number of CO reactions per incident electron decreases as $1/\theta_{\text{Cap}}$. The hydrogen atoms, which are responsible for the CO reduction reactions, originate in the region between 10 ML and 50 ML below the vacuum interface and subsequently diffuse to the buried CO layer. For $\theta_{\text{Cap}} > 50$ ML, the number of CO reactions per electron decreases rapidly as the irradiation temperature decreases and is negligible for temperatures below 70 K. We present a simple kinetic model based on the diffusion of hydrogen atoms within the ASW film and the sequential hydrogenation of CO to methanol that qualitatively accounts for the observations.

II. Experimental Procedure:

The experiments were carried out in an ultrahigh vacuum (UHV) system that has been described previously.⁵⁶ The system is equipped with a molecular beam line for dosing water, CO and other adsorbates on the sample, a closed-cycle helium cryostat for sample cooling, a low-energy electron gun (Kimball Physics, model ELG-2), a quadrupole mass spectrometer (Extrel, model EXM720), and a Fourier-transform infrared spectrometer (Bruker, Vertex 70). Infrared spectroscopy of the CO/water films was performed in reflection mode at a grazing angle of incidence ($\sim 84^\circ$ with respect to the surface normal).

Water films were deposited on the Pt(111) using a calibrated molecular beam at normal incidence. Previous research has shown that this produces dense, smooth ASW films.⁵⁷⁻⁵⁹ The coverage of the water films is determined by the dosing time and checked by measuring the water temperature programmed desorption spectra. Here, the water coverage is reported in monolayers (ML), where $1 \text{ ML} = 1.14 \times 10^{15} \text{ \#}/\text{cm}^2$, which is the areal density of a bilayer of crystalline ice at 100 K. The thickness of the water films is not measured directly, but it is proportional to the water coverage.⁵⁹ Since the sticking coefficient for

CO on ASW is ~ 1 at $T < 30$ K,⁶⁰ the initial coverages of CO were determined from the dosing time using the known flux of the molecular beam line. [The CO flux was determined from our previous investigation of the adsorption of CO on TiO₂(110).⁶¹] Decreases in the CO coverages due to electron-stimulated reactions were then calculated from decreases in the integrated CO signals measured by infrared reflection absorption spectroscopy (IRAS).

An important aspect of the current work is to explore the electron-stimulated reactions between water and CO as a function of the depth of the CO within the water films. Therefore it is important to control and characterize the position of the CO within the water films.^{49, 50} The typical procedure used to produce a CO layer trapped at a known location within a water film involved several steps. First, a non-porous water film was deposited on the Pt(111) using a molecular beam at normal incidence at 100 K.⁵⁷⁻⁵⁹ The coverage of this “spacer” layer was usually 30 ML, which is sufficiently thick that the Pt(111) substrate was unlikely to influence the reactions. Several control experiments with thicker ASW layers confirmed this assumption (data not shown). Next, a layer of CO, typically with $\theta_{\text{CO}} \sim 4 \times 10^{14}$ molecules/cm², was adsorbed at $T < 30$ K. Finally, to bury the CO within the water film, ASW “cap” layers of varying coverages, θ_{Cap} , were adsorbed as follows: 10 ML of water was adsorbed at $T < 30$ K, then the temperature was set to 100 K and additional water was adsorbed to reach the desired θ_{Cap} . During the annealing of the initial 10 ML water cap to 100 K, unstable structures within the water relax effectively locking the CO in place.

The procedure described above for depositing the layered ASW/CO/ASW films was developed based on several control experiments that were conducted to determine the initial distribution of CO within the ASW films. For example, by measuring the amount of CO that desorbed upon subsequent heating as a function of the coverage of the water dosed at $T < 30$ K it was determined that a 3 ML H₂O film traps $\sim 50\%$ of the CO, while a 10 ML H₂O film traps essentially all the adsorbed CO (see Figure S1, supplemental information). Since investigations by Kay and co-workers have demonstrated that diffusion of atoms and small molecules in ASW is negligible below ~ 120 K,⁵³ the results in Figure S1 effectively

give the width of the CO layer within the ASW/CO/ASW films (see inset, Fig. S1). As described below, most of the results presented here will focus on experiments where $\theta_{\text{cap}} > 50$ ML. As a result, the width of the CO layer (full width at half maximum ~ 3 ML) is small compared to the width of the ASW cap layer. Experiments described below showing sequential reactions in two CO distinct layers of ^{13}CO and ^{12}CO separated by 10 ML of water also support the results shown in Figure S1.

For all the experiments reported here, the incident electron energy was 100 eV. As described previously, the electron beam was rastered over the surface to provide a uniform fluence of electrons.¹⁹ Typical instantaneous current densities were $\sim 1.5 \times 10^{15}$ #/cm²/s with a beam diameter of ~ 1.5 mm. Because electron-stimulated sputtering of the water films can be significant in the course of experiments involving large electron fluences,⁶² additional water was dosed during the experiments to maintain the thickness of the ASW cap layer. Therefore, the typical experimental procedure included preparing the layered ASW film with the trapped CO (as described above) and obtaining an IRAS spectrum prior to irradiating the film. Next, the films were irradiated with energetic electrons. After the irradiation, additional water was dosed to account for the amount sputtered during the irradiation, and an infrared spectrum for the irradiated film was obtained. The sequence of electron irradiation, water dosing and IRAS was then repeated the desired number of times to obtain a series of IRAS spectra for increasing electron fluences while maintaining an approximately constant water coverage. For example, for the results shown in Figure 4a, the amount of water sputtered during each irradiation cycle was ~ 8 ML. Thus for the experiment with a 60 ML cap, the coverage varied between 60 ML at the beginning of each irradiation cycle to ~ 52 ML at the end while the 200 ML cap varied between 200 ML and 192 ML. For several cases, we also repeated the experiments with smaller electron fluences (and thus less sputtering and redosing) per cycle and found similar results to those shown. Typically, the experiments depend on the electron fluence (i.e. #/cm²), but not the electron flux (#/cm²s) Also for the timescales of interest here, the reactions only occur when the electron beam is on. As a result, it is feasible to follow the progress of

the electron-stimulated reactions using this repeated cycle of electron irradiations followed by water redosing and IRAS.

Because the amount of CO is small compared to the water for most of the experiments, the new species created by the electron-stimulated reactions are typically difficult to discern in the raw spectra. However, the reaction products can be seen by taking the difference between the irradiated spectra and the spectra obtained prior to irradiation. Alternatively, experiments were repeated *without* CO and differential absorbance spectra were obtained from the irradiated ASW films with and without CO for the same electron fluence. This latter procedure is useful since electron irradiation leads to changes in the IRAS spectra of the ASW films that can make it difficult to observe the small signals associated with the CO-H₂O reaction products. However, qualitatively similar results were obtained using both methods.

For the results discussed below, the reaction probability refers to the number of reactions occurring per incident electron. The experiments do not measure the time-dependence of any of the electron-stimulated reactions, i. e. they do not measure the reaction rates. In addition, we will focus on experiments where the buried CO layer is spatially separated from the region near the ASW/vacuum interface where the energetic incident electrons create reactive species in the films. As a result of the spatial separation, simple kinetic models that assume the reactants are well-mixed are difficult to apply. Instead, the transport of reactants (H atoms in this case) needs to be addressed explicitly in any modelling.

III. Results

Figure 1a shows the IRAS spectra for a CO/ASW film prior to electron irradiation (black lines) and after irradiation at 90 K (red lines) with 100 eV electrons. The CO was deposited on a 100 ML ASW layer and was capped with a 30 ML ASW layer as described in the experimental section. For this electron fluence and H₂O cap layer thickness, the loss of the CO peak due to electron irradiation is readily apparent in the IRAS spectra, while other changes are more difficult to detect. Figure 1b shows a series of differential

absorption spectra from irradiated ASW films with and without trapped CO. As seen in the figure, the electron-stimulated reactions produce CO₂ (2343 cm⁻¹)³⁷ and methanol (CH₃OH). The top curve in Figure 1b (purple line) shows the differential absorbance spectra for a 75 ML ASW film with a buried layer of methanol for comparison with the irradiated spectra. All the main peaks observed in the methanol/ASW film (at 1018, 1126, 1430, 1450, 1462, 1478 and 2831 cm⁻¹)^{37, 41, 63} are also observed in the irradiated CO/ASW film. In the irradiated CO/ASW film, two small peaks at 1856 cm⁻¹ due to HCO^{37, 41, 64} and 1735 cm⁻¹ corresponding to CH₂O^{27, 41, 65} are also observed. For the largest electron fluence shown in Fig 1b, approximately 95% of the CO has been converted to other species (primarily CH₃OH) by the electron-stimulated reactions.

The results in Figure 1 show that for CO that is capped with a 30 ML ASW film, both reduction reactions leading to methanol and oxidation reactions producing CO₂ are observed, consistent with earlier experiments.^{17, 27, 37, 40, 41} The reduction of CO due to reactions with hydrogen is also observed for CO trapped much deeper in the ASW films. For example, Figure 2 shows several differential absorbance spectra for a CO layer that was capped with a 100 ML ASW film and irradiated with 100 eV electrons at 110 K. For this experiment, HCO, CH₂O and methanol (not shown) are observed. However, essentially no CO₂ is produced. The HCO peak increases quickly and is then approximately independent of electron fluence while the CH₂O peak increases in intensity for the range of fluences shown.

As the electron fluence increases, CO is converted to methanol. Figure 3 shows the integrated IRAS signals for CO and methanol versus electron fluence for a film where a ¹³CO layer was capped with a 60 ML ASW film and irradiated at 100 K. (Figure S3 shows a subset of the IRAS spectra for this experiment.) The amount of CO decreases approximately linearly (Fig. 3, black circles) while the amount of methanol increases linearly (Fig. 3, red triangles). The magnitude of the CO and methanol IRAS signals indicates that most, or all, of the CO is converted to methanol in this experiment. This result is in contrast to previous experiments where CO₂ production is an important pathway in the irradiation of mixed CO/water films.^{17, 27, 37, 39-41} As discussed below, the linear increase in the methanol signal without

any appreciable induction suggests that the reaction of CO with hydrogen atoms has the lowest probability of the hydrogenation reactions (reactions 2 – 5).

The number of reactions per electron for the CO depends on the thickness of the ASW film that is covering the adsorbed CO layer. Figure 4a shows the amount of CO remaining in the irradiated films versus electron fluence for $\theta_{\text{cap}} = 60, 100$ and 200 ML. For these experiments, the films were irradiated at 100 K. The loss of CO, measured by the decrease in its integrated IRAS signal, reflects the contributions from all the non-thermal reaction channels. As θ_{cap} increases, the reaction probability quickly decreases. For $\theta_{\text{cap}} \geq 60$ ML, the IRAS signal for CO decreases approximately linearly as the electron fluence increases. The solid lines in Fig. 4a show the best-fit lines for each coverage. For $\theta_{\text{cap}} < 50$ ML, the CO signal decreases approximately exponentially versus electron fluence, while for $50 \text{ ML} < \theta_{\text{cap}} < 60 \text{ ML}$, the data can be fit with a combination of linear and exponential decays (data not shown). The number of CO reactions per incident electron can be obtained from the best fit (exponential or linear) for each coverage (Figure 4b, circles). For $\theta_{\text{cap}} \geq 60$ ML, the reaction probability is inversely proportional to θ_{cap} (Fig. 4b, solid line). Because the probability for a particle to diffuse a distance L into a film falls as $1/L$, the results in Fig. 4b suggest that, for $\theta_{\text{cap}} \geq 60$ ML, reactants produced by the incident electrons near the ASW/vacuum interface diffuse into the ASW film and initiate the reactions with the buried CO layer.

For CO coadsorbed with water, previous research^{37, 41, 42} and the results presented here suggest that sequential hydrogenation reactions lead to the formation of HCO, CH₂O and CH₃OH. For the experiments where the CO is located below the typical penetration depth of the energetic electrons, the reaction mechanism is not immediately clear. One possibility is that hydrogen atoms produced by electronic excitations within the penetration depth of the energetic electrons subsequently diffuse through the ASW, producing the observed reactions. However, previous experiments investigating the electron-stimulated reactions that produce molecular hydrogen at buried ASW/Pt(111) interfaces have indicated that hydrogen atom diffusion is not the dominant mechanism in that case.^{16, 19} To test for hydrogen atom diffusion, we performed experiments where the isotopic composition of the ASW cap layer was varied.

For the experiments shown in Figure 5, a 30 ML D₂O film was deposited on Pt(111) at 100 K, and CO was dosed at $T < 30$ K. The CO was then covered with a layer of D₂O followed by an H₂O layer where the total cap layer coverage was fixed at 100 ML, but the amount of each isotope was varied (see schematic in Fig. 6a). Figure 5 shows the IRAS spectra for various amounts of H₂O in the 100 ML cap.⁶⁶ For a pure H₂O film, positive peaks at 1856 cm⁻¹ and 1734 cm⁻¹ are observed corresponding to HCO and CH₂O. For a pure D₂O film, there is a peak at 1688 cm⁻¹ due to CD₂O, but no peak for DCO. (However, a previous matrix isolation experiment found that the C-O stretch in DCO was considerably weaker than in HCO.⁶⁴) As the fraction of H₂O in the cap layer increases, the 1856 cm⁻¹ peak for HCO quickly increases. Figure 6a shows the integrated intensity of the HCO peak normalized to the signal for a pure H₂O film versus the H₂O coverage in the cap layer. The HCO signal is approximately zero for $\theta(\text{H}_2\text{O}) \leq 10$ ML and then smoothly increases to its maximum value for $10 \text{ ML} < \theta(\text{H}_2\text{O}) < 60 \text{ ML}$. These results with layered H₂O/D₂O films indicate that hydrogenation of the buried CO is most likely associated with the H (or D) atoms primarily produced in the region from ~10 to 50 ML below the ASW/vacuum interface. Subsequent diffusion can transport the H atoms to the buried CO layer, leading to the observed hydrogenation reactions. The current results are distinct from earlier experiments investigating the electron-stimulated production of molecular hydrogen in layered H₂O/D₂O films.^{18,19,35} In those experiments, molecular hydrogen produced at interface between the substrate and the ASW films was not due to diffusion of H (or D) atoms through the ASW. Instead, a species that moved through the ASW without long range transport of the hydrogen atoms, such as hydronium ions or excitons, was implicated.^{16, 19, 52}

As a further test for diffusion of H atoms within the ASW films, we performed experiments with two spatially separated and isotopically labeled layers of CO within the ASW films (Figures 7 and 8). For these experiments a 60 ML ASW film was deposited on Pt(111) followed by a ¹³CO layer, a 10 ML ASW layer, a ¹²CO layer, and finally a 60 ML ASW layer (see schematic in Fig. 8). The films were then irradiated with 100 eV electrons at 110 K. The experiments were repeated with various coverages for the

^{12}CO and ^{13}CO layers. When no ^{12}CO is present, the ^{13}CO IRAS signal quickly decreases as the electron fluence increases (Fig. 7, dotted lines). With ^{12}CO present (Fig. 7, solid lines), the ^{13}CO signal initially decreases slowly while the ^{12}CO signal quickly decreases. Once a substantial fraction of the ^{12}CO has reacted, the ^{13}CO signal then decreases more quickly. Figure 8 (symbols) shows the integrated ^{13}CO and ^{12}CO IRAS signals versus electron fluence for several different coverages of the ^{12}CO and ^{13}CO layers. The number of reactions per electron for the ^{12}CO layer, which is closer to the vacuum, is independent of the coverage in the ^{13}CO layer. For example, the solid red and open red circles in Figure 8 show the ^{12}CO coverage versus electron fluence for $\theta(^{13}\text{CO}) = 0$ and $4 \times 10^{14} \text{ \#}/\text{cm}^2$, respectively. In contrast, the reaction probability for the more deeply buried ^{13}CO layer is sensitive to $\theta(^{12}\text{CO})$: As $\theta(^{12}\text{CO})$ increases, the onset for appreciable reactions in the ^{13}CO layer increases (Fig. 8). These results also show that the H atoms come from the region near the vacuum interface and preferentially react with the first CO layer they encounter within the ASW film.

The experiments in Figures 7 and 8 show that for $\theta(^{12}\text{CO}) > 1 \times 10^{14} \text{ \#}/\text{cm}^2$, almost none of the hydrogen atoms can initially pass that layer to react with the deeper ^{13}CO layer. One possible explanation for these results is that the ^{12}CO layer physically blocks H atom diffusion to the deeper ^{13}CO layer. However when the ^{12}CO layer is replaced with a Kr layer ($\theta(\text{Kr}) \sim 4 \times 10^{14} \text{ \#}/\text{cm}^2$), the ^{13}CO decreases at the same rate as when no Kr or ^{12}CO is present (Fig. 8, black circles). Therefore, physical blocking does not appear to explain the results, and instead reactions with the first CO layer consume the hydrogen atoms.

The reaction probability for CO depends on the irradiation temperature. Figure 9 shows the CO reactions per electron for experiments at several temperatures with $\theta_{\text{Cap}} = 100 \text{ ML}$. The CO reaction probability was determined from the decrease in the CO IRAS signal versus electron fluence at each temperature. For temperatures below $\sim 70 \text{ K}$ and $\theta_{\text{Cap}} = 100 \text{ ML}$, the reaction probability is small and difficult to measure. For $T > 70 \text{ K}$, the CO reaction probability increases approximately exponentially as the irradiation temperature increases with an apparent activation energy of $\sim 5.4 \text{ kJ/mol}$. Experiments with

H₂O and D₂O did not show an appreciable isotope effect, and the results shown in Figure 9 include both isotopes. Several processes could contribute to the temperature dependence of the reactions including the production of hydrogen atoms, their diffusion rate, and changes in the reaction probability (per encounter) with CO or its hydrogenation products. As a result, it is difficult to assign the measured activation energy to a single process. For example, previous research has found that non-thermal reactions in ASW, producing species such H, H₂ and O₂, increase rapidly above 70 K.^{8, 54, 62, 67, 68} However, the probability of overcoming the H + CO reaction barrier (~4.4 kJ/mol⁴⁶) on any given encounter also increases as the temperature increases. This could also lead to increases in the overall reaction probability.⁶⁹ Thus, both increased production of H atoms and increases in the reaction probability per encounter are likely to contribute to the results shown in Figure 9. Note that the results suggest that H/D isotope effects were not significant for the experiments with layered D₂O and H₂O films (Figs. 5 and 6).

One possible explanation for the reduced reaction probability at low temperatures shown in Figure 9 is a decrease in H (or D) diffusion rate. In that scenario, the CO reaction probability would decrease at lower temperatures because the H atoms do not have sufficient time to reach the buried CO layer (i.e. the H atoms become “frozen” in the ASW). If that were the case, introducing a time delay between the electron irradiation and subsequent measurement of the IRAS signal should affect the results, particularly at temperatures where the reaction probability first becomes appreciable (~70 – 80 K in our experiments). However experiments where such a delay time was introduced did not affect the results (data not shown), suggesting that a decrease in the H or D atom diffusion rate at lower temperatures was not primarily responsible for the decreasing CO reaction probability seen in Figure 9.

Estimates of the time required for an atom to diffuse to the buried CO layer as a function of the temperature also indicate that changes in the H or D diffusion rate are not primarily responsible for the results in Figure 9. The key point is that once the particles can diffuse far enough to reach the buried layer on the timescale of the experiments, further increases in the diffusion rate will not result in more reactions per incident electron. Using the diffusion rates measured by Bartels and co-workers⁷⁰ we can estimate the

time required for an H atom to diffuse from the region near the surface to the CO layer 100 ML below the surface: Since the hopping rate for both H and D in crystalline ice is $\sim 10^4$ jumps/s at 70 K,⁷¹ the time to diffuse to the CO layer should only be ~ 1 s, which is already fast on the timescale of our experiments. Thus at temperatures above ~ 70 K, the H and D atoms are already sufficiently mobile to reach the buried CO layer on the timescale of our experiments, and further increases in the diffusion rate will not lead to more reactions. This supports the observation that adding a waiting time after the irradiation did not change the results in Figure 9. The activation energy for the results in Figure 9 is approximately half the activation energy measured by Bartels et al., for the diffusion of H or D atoms in crystalline ice.⁷⁰ If the activation energy for H diffusion in ASW is lower than in crystalline ice, then the H and D atoms will become mobile at even lower temperatures, and thus will also not explain the observations.

Previous research has investigated the diffusion of H atoms on the surface of ASW at low temperatures (e.g. $T \leq 20$ K).^{42, 44, 46} Calculations suggest that H diffusion in ASW is slow enough that it does not play a role in the hydrogenation reactions for $T \leq 20$ K. Instead it was suggested that surface diffusion, including on the surfaces of cracks in the ASW, is important.⁴⁶ The H atom diffusion rate estimated above also suggests that any H atoms produced by the energetic electrons at temperatures below $\sim 40 - 50$ K, will be frozen in the ASW in our experiments. However since the reaction probability is small for $T < 70$ K, the results in Figure 9 provide no further information on the mobility of the H atoms at these lower temperatures.

IV. Discussion and Random Walk Model

Several species are detected in the irradiated films. For $\theta_{\text{Cap}} > 50$ ML, HCO, CH₂O and CH₃OH are all observed in the IRAS spectra while little or no CO₂ is observed. For $\theta_{\text{Cap}} < 50$ ML, both reduced and oxidized reaction products are observed. The separation of the CO reactions into regions with both oxidation and reduction for $\theta_{\text{Cap}} < 50$ ML and only reduction for $\theta_{\text{Cap}} > 50$ ML probably results from different mobilities for the reducing species (primarily H atoms) versus the oxidizing species within the

ASW films. As a result, the CO reactions provide a method for investigating the distribution of water dissociation events versus distance within the ASW films. The oxidation reactions occurring for CO trapped near the vacuum interface, and the distribution of water dissociation events will be the subject of a future publication. Here, we will concentrate on the CO reduction occurring in films with $\theta_{\text{Cap}} > 50 \text{ ML}$.

As discussed in the introduction, previous research suggests that the production of methanol during the irradiation of mixed $\text{H}_2\text{O}/\text{CO}$ ices proceeds by the sequential hydrogenation of CO (reactions 2 – 5),^{37, 41, 42} and the experiments reported here are generally consistent with this hypothesis. In the gas phase, the calculated barrier for the reaction, $\text{CO} + \text{H} \rightarrow \text{HCO}$, is $\sim 17 \text{ kJ/mol}$.^{72, 73} Therefore, it has been assumed that the reaction occurs when energetic H atoms, produced from H_2O dissociation, collide with a CO. However, the current results show that thermalized H atoms diffusing through the ASW react efficiently with trapped CO. Recent experiments where H and CO were co-deposited in a neon matrix at $T < 10 \text{ K}$ have also demonstrated that thermalized H can react with CO.⁴³ Calculations suggest that tunneling can result in relatively efficient reactions even at temperatures where above-barrier reactions would be slow.⁷⁴ For CO trapped in ASW films, cage effects - which keep the H + CO next to each other for longer times – should promote the reaction by allowing sufficient time for tunneling to occur. Because we do not detect any appreciable difference in the reaction probability for CO trapped in H_2O or D_2O (Fig. 9), isotope effects do not appear to be important for these experiments.

A. Random Walk Model

To further explore the reaction of CO trapped in ASW with H atoms, we have developed a simple Monte Carlo diffusion model. The model is based upon the assumption that H atoms are produced by the interactions of the energetic electrons with water molecules in the ASW films (e.g. reaction 1), and once produced, these atoms can then diffuse through the film until they react. The possible reactions included in our model are 1) sequential hydrogenation of CO (i.e. reactions 2 – 5), 2) desorption from the film if the H atom reaches the ASW/vacuum interface, or 3) adsorption on the Pt(111) if it reaches the ASW/Pt

interface. In the model, the diffusion of the H atoms takes place on a simple cubic lattice, where each layer of the ASW film, i , is represented by a plane ($z = i$) in the lattice, and the system has periodic boundary conditions in the x and y directions. The CO layers are assumed to occupy a plane that is parallel to the ASW/Pt interface at a position corresponding to θ_{Cap} for the experiment of interest (see Figure S2, supplemental information).

In the model, lateral coordinates (i.e. x and y) are randomly chosen for the CO adsorption sites until a desired CO coverage is obtained. The CO and its reaction products are assumed to be immobile. Initial lateral coordinates for the H atoms are also chosen at random, while the initial z , z_0 , can be chosen from a specified distribution, $P_{\text{init}}(z_0)$. H atom trajectories are run sequentially and the atoms perform a random walk on the lattice until they react. If the atom encounters a site occupied with CO, HCO, CH₂O, or CH₃O, it reacts with a specified probability. If the atom does not react, it continues the random walk. The reaction sequence is assumed to stop at methanol. If an H atom reaches either interface of the film, it reacts (i.e. desorbs into vacuum or adsorbs on the Pt) with unit probability. H atom trajectories are run until all the CO is converted to CH₃OH. An advantage of this model over a mean-field chemical kinetics model is that it allows us to explicitly treat the position of the CO layer (or layers) relative to the source of the H atoms.

We have used this simple model to investigate several of the experimental observations: i) the $\sim 1/\theta_{\text{Cap}}$ decrease in the CO reaction probability (Fig. 4b), ii) the distribution of the initial positions for the H atoms that participate in the hydrogenation reactions (Fig. 6a), iii) the nearly linear decrease in the CO signal versus electron fluence (Figs. 3 and 4a), and iv) the delay in the loss of the more deeply buried CO layer in the two CO layer experiments (Figs. 7 and 8). Some of these observations depend sensitively upon the assumption of sequential hydrogenation reactions and their reaction probabilities, while others are largely independent of these details. For example, the model reproduces the $1/\theta_{\text{Cap}}$ dependence for the CO reaction probability seen in Fig. 4b because for any given $P_{\text{init}}(z_0)$ that is localized near the vacuum

interface, the probability of the atoms randomly walking to a depth of z in the film is proportional to $1/z$ (results not shown).

B. Initial Distribution of H atoms

The experiments shown in Figures 5 and 6a provide information on the distribution of the initial positions of H atoms within the ASW films that subsequently react with the CO layer, $P_{\text{react}}(z_0)$. Specifically, the results in Figure 6a correspond to the normalized integral of $P_{\text{react}}(z_0)$ versus z_0 :

$$I(z_0) = \int_0^{z_0} P_{\text{react}}(z') dz'. \text{ Note however that } P_{\text{react}}(z_0) \text{ is different than } P_{\text{init}}(z_0) \text{ because atoms that are created}$$

closer to the vacuum interface are more likely to reach that interface and desorb from the film, while those that are created deeper in the film are more likely to reach the CO layer. The probability for an atom created at a depth, z_0 , to diffuse to a CO layer buried at θ_{cap} , $P_{\text{diff}}(z_0)$, is $P_{\text{diff}}(z_0) = z_0/\theta_{\text{Cap}}$. Therefore, $P_{\text{react}}(z_0) = z_0 P_{\text{init}}(z_0)/\theta_{\text{cap}}$.⁷⁵ Previous simulations of the interaction of 100 eV electrons with water suggest that the initial excitations have an approximately exponential distribution, $P_{\text{init}}(z_0) = \alpha e^{-\alpha z_0}$, with $1/\alpha \sim 7$ ML (i.e. about 2.7 nm).⁴⁸ With this distribution of initial positions, the simulation does not reproduce the results (Fig. 6a, dashed line). Specifically, in the experiments essentially none of the H atoms that react with the buried CO layer originate from the first 10 ML of the film, while almost half the H atoms come from that region in the simulation. Thus the simulations suggest that the H atoms that react with the buried CO layer originate deeper within the film.

A distribution of initial positions, $P_{\text{init}}(z_0)$, that peaks in the near surface region can better reproduce the experimental results in Figure 6a. For example, Figure 6b shows $P_{\text{react}}(z_0)$ (black triangles) for a simulation where $P_{\text{init}}(z_0)$ is assumed to be a Gaussian distribution, $P_{\text{init}}(z_0) = \exp(-(z_0 - \mu)^2 / 2\sigma^2) / (\sigma\sqrt{2\pi})$, with $\mu = 18$ ML and $\sigma = 17$ ML (red circles). $P_{\text{react}}(z_0)$ is also approximately Gaussian but the maximum is shifted deeper within the film ($\mu \sim 28$ ML). $I(z_0)$

obtained with this form of $P_{\text{init}}(z_0)$ reproduces the experimental results reasonably well (Fig. 6a, solid line).

The difference between the distribution of initial electronic excitations expected from theory and the $P_{\text{react}}(z_0)$ that fits the data could have several causes. As illustrated in Fig. 6b, part of the difference is likely due to the preferential desorption of H atoms created near the vacuum interface. However, this effect does not appear to be responsible for most of the difference. Another possibility is that H atoms can react with other species created in the ASW film by the energetic electrons. For example, H atoms can recombine with OH's created by the dissociation of H_2O . Since the concentration of OH's should be highest near the vacuum interface, the recombination probability should also be higher there, decreasing the chance that H atoms escape that region. A third possibility is that the initial excitation produces a mobile species that moves prior to creating a hydrogen atom. For example, H_2O^+ quickly reacts to form H_3O^+ which can move through the film via proton hopping.^{3, 76} Subsequent reactions with an electron can then produce an H atom in a different location from the initial excitation. Mobile excitons, H_2O^* ,^{77, 78} produced by the energetic electron in the ASW can also dissociate to produce H and OH.^{51, 67, 79, 80} Interestingly, the form of $P_{\text{react}}(z_0)$ that fits the experimental results presented here is qualitatively similar to previous experiments investigating the production of molecular hydrogen in electron-irradiated ASW films adsorbed on Pt(111) or $\text{TiO}_2(110)$.^{16, 19, 52} Those experiments also indicated that the location of the initial electronic excitations was different from the subsequent reactions that caused hydrogenation of the substrate. For both the current and the previous experiments, the length scales characterizing the processes are similar (i.e. ~ 10 nm), while the specific reactions are different.

C. Reaction Probabilities

In the random walk model, the reaction kinetics (i.e. amounts of CO, HCO, etc. versus electron fluence) are largely determined by the reaction probabilities for the H atoms with each species, but are relatively insensitive to the assumed form for $P_{\text{init}}(z_0)$. Experimentally, the amount of CO in a single layer

decreases approximately linearly and the amount of methanol increases approximately linearly as the electron fluence increases (see Fig. 3), while the amount of the intermediate species is always small. Within the random walk model, this behavior can be reproduced if the reaction probability for H atoms with CO, P_{CO} , (equation 2) is significantly smaller than the reaction probability for the other hydrogenation steps, P_{HnCO} , (equations 3-5). The solid lines in Figure 3 show an example where $P_{CO} = 0.02$, and $P_{HnCO} = 1$ for $n=1,2$ and 3. However, a very low reaction probability for H with CO is problematic for two reasons. First, it is inconsistent with the experiments with two CO layers where the CO layer closest to the vacuum reacts preferentially with the H atoms (see Figs. 7 and 8). Specifically, if P_{CO} is too small, then the first CO layer becomes “transparent” to the H atoms and both CO layers decrease at nearly the same rate in the simulations. Second, the calculated gas-phase barriers for $H + CO$ and $H + CH_2O$ are comparable,⁸¹ suggesting that their reaction probabilities should be similar.⁸² In that case, we should expect that the amount of CH_2O will be comparable to the amount of CO in the irradiated films at intermediate electron fluences. This is not observed however: The amount of CH_2O in the irradiated films is always small during the experiments (see e.g. Figure 2), which suggests that $P_{CO} < P_{H2CO}$. To further investigate this issue, we performed experiments where we deposited a buried CH_2O layer in ASW and measured the loss of the CH_2O IRAS signal versus electron fluences (see Figure S4). Compared to a CO layer buried at the same depth, the CH_2O signal decreases with an initial rate that is ~ 7 times greater than the CO signal, indicating that the reaction probability for $H + CH_2O$ is much larger than for $H + CO$.

The dashed lines in Figures 3 and 8 show the simulations for the one and two layer experiments where $P_{CO} = 0.1$, and $P_{HnCO} = 1$ for $n=1,2$ and 3 (for both ^{12}CO and ^{13}CO). These probabilities represent a “best fit” for the experimental results in Figures 3 and 8.⁸³ These best-fit probabilities are also consistent with results in Figure S4 and the expectation that the radical reactions – $H + HCO$ and $H + CH_3O$ – are very efficient. In Fig. 3, the simulation is similar to the experiments, but the methanol signal has a short induction period before it starts increasing that does not appear in the data, and the decrease in the

simulated CO signal is not as linear as the experimental result. However, with these reaction probabilities and simulations with two CO layers, the initial rate of decrease for the deeper CO layer is larger than is observed in the experiments (Fig. 8, dashed lines). An even larger value for P_{CO} results in a slower initial reaction rate for the second CO layer, but the larger induction period before methanol appears is inconsistent with the experiments (Fig. 3). Despite these short-comings, the model qualitatively reproduces the experimental results.

The random walk model presented here is too simple to capture all the processes that might be relevant for the experiments. For example, the energetic electrons produce a variety of reactive species within the ASW and any possible reactions between these species have not been included in the model. As mentioned above, such reactions could influence the form of $P_{ini}(z)$ that fits the data in Figure 6. Likewise, the model does not include several alternative reactions, such as $H + HCO \rightarrow H_2 + CO$ and $H + CH_2O \rightarrow H_2 + HCO$, that may also occur.⁸¹ To get some idea of the sensitivity of the model results, we have tested several variations of the model including different reaction sequences, back reactions, possible blocking effects of the reactants on the H diffusion, the effect of broadening the CO layer(s) within the ASW, etc. Most of the model variants produce qualitatively similar results to the simplest model presented above. However, lacking specific data to motivate and constrain more complicated models, we feel that more detailed investigations of such models are not currently justified.

V. Summary

We have investigated the electron-stimulated reactions of CO in amorphous solid water. For CO buried within 50 ML of the ASW/vacuum interface, both oxidation and reduction of the CO are observed. However for CO buried more deeply in the film, only reduction reactions are observed. For films with CO buried under more than 50 ML of ASW, the observations are consistent with the sequential hydrogenation of CO to methanol due to hydrogen atoms. The H atoms are produced by electron-stimulated reactions in the ASW from $\sim 10 - 50$ ML and subsequently diffuse through the ASW where they can react with

trapped CO (or one of its reaction products). A simple kinetic model which treats the diffusion of H atoms through the ASW film and the sequential hydrogenation of CO to methanol accounts for most of the observations.

Acknowledgement:

NGP and GAK were supported by the US Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences & Biosciences. RJM and SPKK were supported by the Dalton Cumbrian Facility program in part funded by the Nuclear Decommissioning Authority. The work was performed using EMSL, a national scientific user facility sponsored by the Department of Energy's Office of Biological and Environmental Research and located at Pacific Northwest National Laboratory (PNNL). PNNL is a multiprogram national laboratory operated for DOE by Battelle under Contract DE-AC05-76RL01830.

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83. We simulated the reactions with various combinations of reaction probabilities.

Figure Captions:

Figure 1. IRAS spectra for electron-irradiated CO/ASW films with $\theta_{\text{cap}} = 30$ ML and $T_{\text{irr}} = 90$ K. a) Absorbance spectra before and after electron irradiation (fluence = 2.6×10^{16} #/cm²). b) Differential absorbance spectra for ASW films with and without CO for electron fluences of 0, 0.65, 1.3, 1.95 and 2.6×10^{16} #/cm² for the black, orange, green, blue and red curves, respectively. The top curve (purple) shows the spectrum for a non-irradiated methanol/ASW film for comparison.

Figure 2. Differential absorbance spectra for a CO/ASW with $\theta_{\text{cap}} = 100$ ML irradiated at 110 K for electron fluences of 0, 1.3, 2.6, 3.9, 5.2 and 6.5×10^{16} #/cm² for the black, orange, green, blue, red and purple curves, respectively. For this cap layer coverage, reduction products (HCO and CH₂O) are observed but very little oxidation products (CO₂). To obtain reasonable signal to noise for the small HCO and H₂CO peaks, the results shown are the average of 6 individual experiments.

Figure 3. Integrated CO (black circles) and CH₃OH (red triangles) IRAS signals versus electron fluence for $\theta_{\text{cap}} = 60$ ML and $T_{\text{irr}} = 100$ K. The solid and dashed lines are simulated CO and CH₃OH concentrations for two different sets of reactions probabilities (see text).

Figure 4. a) Remaining CO coverage versus electron fluence in irradiated CO/ASW films for $\theta_{\text{Cap}} = 60$, 100 and 200 ML and $T_{\text{irr}} = 100$ K. b) CO reactions per incident electron (the reaction probability) versus θ_{Cap} . For $\theta_{\text{Cap}} \geq 60$, the reaction probability is inversely proportional to θ_{Cap} .

Figure 5. Differential IRAS spectra for electron-irradiated CO/ASW films with various isotopic compositions for the water. For each spectrum, the thickness of the H₂O cap layer is listed with the spectra. The schematic in Fig. 6a illustrates the isotopic layering used for these experiments. Each film was irradiated at 90 K with an electron fluence of 6.5×10^{15} #/cm². For a CO/D₂O film (bottom curve), deuterated formaldehyde (D₂CO) is observed. For a CO/H₂O film (top curve), both HCO and formaldehyde (H₂CO) are observed. For films with increasing amounts of H₂O in the 100 ML cap layer, the amount of HCO gradually increases.

Figure 6. a) Integrated HCO IRAS signal (circles) versus the amount of H₂O in the 100 ML ASW cap. The films were irradiated at 100 K. The solid and dashed lines show integrated reaction probabilities for models with two different initial spatial distributions of hydrogen atoms (see text). The schematic illustrates the isotopic composition of the ASW films. b) $P_{\text{init}}(z)$ (red circles) and $P_{\text{react}}(z)$ (black triangles) show the probability distributions of initial positions for all the hydrogen atoms and those that subsequently react with the buried CO layer, respectively. Because most of the H atoms diffuse to the ASW/vacuum interface and desorb, $P_{\text{react}}(z)$ is smaller than $P_{\text{init}}(z)$ and its maximum is shifted deeper into the ASW (see text for discussion).

Figure 7. Differential IRAS spectra for electron-irradiated ASW films with one (dashed lines) or two (solid lines) buried CO layers. For the experiments with two CO layers, the ¹²CO and ¹³CO layers were separated by 10 ML of ASW and capped with 60 ML of ASW (see inset of Fig. 8 for a schematic). The electron fluences (#/cm²) for each experiment are shown in the figure. When two CO layers are present, the layer that is closer to the vacuum interface (i.e. ¹²CO) reacts first, while the deeper (¹³CO) layer is initially unchanged.

Figure 8. ¹²CO and ¹³CO coverages versus electron fluence for experiments with two CO layers separated by 10 ML (see schematic). Bottom curves: Solid red and open red circles show the ¹²CO signals for $\theta(^{13}\text{CO}) = 0$ and 4×10^{14} #/cm², respectively. Middle curves: ¹³CO signals versus fluence for $\theta(^{12}\text{CO}) = 0$, 0.8, 2.8 and 4×10^{14} #/cm² (green, orange, purple and blue symbols, respectively). When the ¹²CO layer is replaced with a Kr layer (with $\theta(\text{Kr}) \sim 4 \times 10^{14}$ #/cm²), the ¹³CO signal promptly decreases when irradiated (black circles). The solid lines are added to guide the eye. Top curves: Simulated ¹²CO (red) and ¹³CO signals (green, orange, purple and blue dashed lines) versus electron fluence for various initial ¹²CO coverages. For ease of viewing, the bottom and top set of curves have been offset from 0 by -1.5×10^{14} #/cm² and 3.0×10^{14} #/cm², respectively.

Figure 9. CO reactions per electron versus irradiation temperature. CO layers capped with 100 ML H₂O (black circles) or D₂O (red triangles) films were irradiated at various temperatures and the depletion of the CO signal versus electron fluence was measured using IRAS. The initial CO coverages were 3.4×10^{14} #/cm². The results for H₂O and D₂O films are the same within the uncertainty.

Figures:

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9