CARBON MONOXIDE ENTRAPMENT IN INTERSTELLAR ICE ANALOGS

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ABSTRACT

The adsorption and desorption of CO on and from amorphous H_2O ice at astrophysically relevant temperatures has been studied using temperature programmed desorption (TPD) and reflection-absorption infrared spectroscopy (RAIRS). Solid CO is able to diffuse into the porous structure of H_2O at temperatures as low as 15 K. When heated, a phase transition between two forms of amorphous H_2O ice occurs over the 30–70 K temperature range, causing the partial collapse of pores and the entrapment of CO. Trapped CO is released during crystallization and desorption of the H_2O film. This behavior may have a significant impact on both gas-phase and solid-phase chemistry in a variety of interstellar environments.

Subject headings: astrochemistry — infrared: ISM — ISM: lines and bands — ISM: molecules — line: profiles — methods: laboratory

1. INTRODUCTION

The two most abundant molecules in ice accreted on dust grains in dense interstellar clouds are H_2O and CO (Allamandola et al. 1999). H_2O ice has been detected in the infrared spectra of numerous astronomical sources, mainly through its O-H stretch absorption band at 3.07 μm. CO ice is detected in the infrared spectrum via its C-O stretch band at 4.67 μm. Two peaks are frequently co-evident in the CO stretch region—a broad flat peak centred at 4.681 μm and a sharper peak at 4.674 μm (Chiar et al. 1995). These two peaks are generally attributed to CO in hydrogenated (polar) and dehydrogenated (apolar) ice matrices, respectively, which are thought to form an "onion-like" structure, with an inner layer of a hydrogenated ice surrounded by an outer dehydrogenated layer (Allamandola et al. 1999). Hydrogenated ices are dominated by H_2O, with lower concentrations of species such as CH_3OH, NH_3, and CH_4. Dehydrogenated molecules may also be present in low concentrations, with CO observed at up to 10%. Dehydrogenated ices are dominated by species such as CO, CO_2, N_2, and O_2.

Laboratory experiments have shown that water accreted under the conditions prevalent in dark clouds—temperatures of roughly 10 K, low adsorption rates, and random trajectories of adsorbate molecules—will form with a highly porous, amorphous structure (Stevenson et al. 1999; Kimmel et al. 2001b). When warmed, this high-density form (I_{hda}) undergoes an irreversible phase change to a lower density, less porous amorphous structure (I_{lda}) between 38 and 68 K (Jenniskens et al. 1995). Although this phase change is not evident in the infrared spectra of water ice, it has been detected by several other techniques (Narten, Venkatesh, & Rice 1976; Jenniskens & Blake 1994; Lu et al. 2001). The formation of a cubic crystalline phase of water ice (I_c) from low-density amorphous ice occurs irreversibly

under ultrahigh vacuum (UHV) laboratory conditions at approximately 140 K (Smith et al. 1997). In light of these phase changes, we present a succinct qualitative description of the behavior of CO in and on the pores of water ice. The implications for CO adsorption and desorption under astronomically relevant conditions are discussed.

2. EXPERIMENTAL PROCEDURES

The experimental apparatus in use has recently been described in some detail (Fraser, Collings, & McCoustra 2002). Briefly, all experiments were performed in a UHV chamber operating with a base pressure of 1×10^{-10} mbar. A copper plate covered by a film of polycrystalline gold served as a substrate. This could be cooled to a base temperature of 8 K by a closed-cycle helium cryostat and radiatively heated by two halogen light bulbs to above room temperature while the cryostat was still operating. The sample temperature was measured by a KP-type thermocouple attached directly to the substrate. This was calibrated by comparison with an adjacent E-type thermocouple and the known desorption temperatures of several simple molecules from the solid state. This calibration method specifically assesses the temperature of the surface from which the molecules desorb. At the rates of temperature increase achievable (<0.1 K s^{-1}), temperature gradients across the substrate are insignificant.

CO and H_2O were introduced effusively to the chamber by separate 6 mm glass dosing tubes that were directed at the substrate. However, the adsorption remains ballistic and results in water ice with the same structure as that accreted from the background, without any of the shadowing effects that are observed for H_2O films deposited by molecular beams (Kimmel et al. 2001b). Uptake of CO and H_2O by the substrate was calibrated by adsorption on a quartz crystal microbalance. This was performed separately from the desorption and infrared spectroscopy experiments to ensure that the quartz crystal and substrate had the same geometric position with respect to the glass dosing tubes during deposition. Analysis of the total integrated desorption of CO and H_2O detected by the mass spectrometer in desorption experiments showed less than 5% variation. The

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deposition rate of CO was 0.7 ng cm^{-2} s^{-1} for both desorption and infrared experiments; 0.07 μg cm^{-2} of CO was adsorbed for desorption experiments and 0.35 μg cm^{-2} for infrared experiments. Given the published value of the density of solid αCO (Ryberg 1984), 0.35 μg cm^{-2} of CO is equivalent to a thickness of 3.3 nm if adsorbed on a flat surface. Water was accreted at a rate of 57 ng cm^{-2} s^{-1} for desorption experiments and 114 ng cm^{-2} s^{-1} for infrared experiments, producing a 57 μg cm^{-2} film in both cases. From published values of density (Jenniskens & Blake 1994) and porosity (Kimmel et al. 2001a) of I$_{hda}$, the H$_2$O film thickness upon deposition at 8 K can be approximated at 0.6 μm. However, as porosity and density vary with the temperature-dependent structure of the ice, this thickness may be different for films that have been annealed or adsorbed at higher temperatures. Mass per unit area is therefore much more reliable than film thickness in quantifying the amount of ice present on the substrate.

Temperature programmed desorption (TPD) was performed at an average heating rate of 0.08 K s^{-1}, using a liquid nitrogen cooled line-of-sight quadrupole mass spectrometer. The desorption traces presented are corrected to account for the slight variation in ramp rate over the course of the experiment. Infrared experiments were performed in a reflection-absorption infrared spectroscopy (RAIRS) arrangement, with a resolution of 1 cm^{-1} and the co-addition of 1024 scans. All spectra were recorded at a temperature of 8 K. When the sample was annealed in a RAIRS experiment, it was held at the elevated temperature shown in Figure 2 for a period of 5 minutes, then re-cooled to 8 K before the RAIR spectrum was recorded. All changes observed in heated films are therefore irreversible, and the results are not complicated by temperature-dependent changes in the absorption intensity of transitions.

3. RESULTS AND DISCUSSION

In each of the TPD experiments displayed in Figure 1, H$_2$O and CO were adsorbed in separate exposures, under varied conditions. The H$_2$O desorption traces in each experiment (not shown) showed desorption characteristics consistent with those previously reported for clean H$_2$O films (Fraser et al. 2001). In Figure 1a, CO was adsorbed onto the sample at 8 K, then H$_2$O adsorbed as a second layer over it. Although this is unlikely to occur in any astrophysical environment, the experiment provides information regarding the structure of the amorphous H$_2$O film. The desorption observed in the 20–60 K range is consistent with CO desorption from the ice surface, given that the binding energy of CO to H$_2$O ice is approximately 10 kJ molecule^{-1} (1200 K; Allouche, Verlaque, & Pourcin 1998). Therefore, some CO is able to diffuse through the water film, which is unsurprising given its high porosity. There is evidence of at least two desorption features, suggesting that there are multiple adsorption sites of CO on the H$_2$O surface. The 140 and 160 K peaks are at a much higher temperature than can be reasonably expected for CO molecules bound to the H$_2$O surface, but they are coincident with the I$_{lda}$ → I$_c$ phase change and H$_2$O desorption, respectively. The entrapment of a volatile species beneath the less volatile layer of H$_2$O ice has been previously reported (Smith et al. 1997). New pathways to the surface are created during the nucleation and growth of the crystalline ice, allowing the abrupt desorption of the underlying volatile molecule in a desorption process
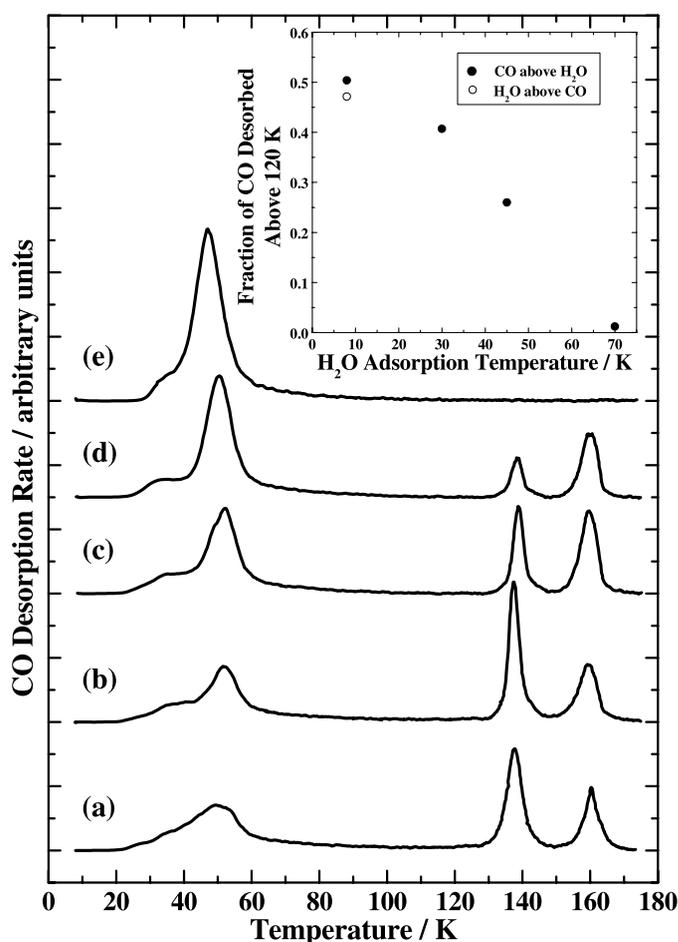
Fig. 1.—Temperature programmed desorption of CO (0.07 μg cm^{-2}) from H$_2$O (57 μg cm^{-2}). Trace a for H$_2$O adsorbed over CO, both adsorbed at 8 K; traces b–e for CO adsorbed at 8 K over H$_2$O adsorbed at 8, 30, 45, and 70 K, respectively. *Inset*: Fraction of the integrated area of desorption traces a–e attributable to trapped CO, as a function of H$_2$O adsorption temperature.

termed a "molecular volcano." It is evident here that some of the CO remains trapped after crystallization and is retained until desorption of the H$_2$O. The TPD traces of CO from a co-deposited mixture of CO and H$_2$O (not shown) are qualitatively similar. Given that CO is known to diffuse into a water film adsorbed above it (Palumbo & Strazzulla 1993), the experiment shown here is probably an accurate representation of TPD of intimate mixtures of CO and H$_2$O.

When the order of adsorption at 8 K was reversed, creating a simple model of a layered hydrogenated/dehydrogenated ice mantle, peaks corresponding to both desorbed and trapped CO are again present in the TPD trace (Fig. 1, *trace b*). Since no physical barrier trapping CO exists at the time of its adsorption, a structural change in the amorphous ice film must occur at some temperature prior to the completion of CO desorption at 60 K. This is confirmed by the desorption traces of CO adsorbed onto H$_2$O films grown at 30, 45, and 70 K (Fig. 1, *traces c–e*). A gradual reduction in the fraction of trapped CO (Fig. 1, *inset*) is observed over this range of water ice adsorption temperatures. It is clear that the structural change responsible for the CO entrapment occurs over a range very similar to that reported for the I$_{hda}$ → I$_{lda}$ phase change. The profile of the peaks

corresponding to CO desorption from the ice surface also changes as the adsorption temperature of H_2O is varied. It is possible that this results from a change in the diffusion rate of CO within the changing porous structure of the H_2O film. However, the reduction in desorption temperature of the higher temperature component suggests that a reduction in the binding strength of CO in this site is a more likely explanation. Further experimentation is required to clarify this issue, and a more detailed analysis of these peaks will be presented in future publications.

Infrared spectroscopy allows an indirect probe of this structural change. Figure 2 compares the CO stretch region of CO/H_2O films under varying conditions of adsorption and subsequent thermal processing. In Figure 2a, CO was adsorbed at 8 K onto an I_{hda} film also grown at 8 K. In Figure 2b, the CO was deposited at 8 K onto an I_{lda} film adsorbed at 80 K. The presence of multilayer (solid) CO is indicated in both experiments by the two sharp features at 2143.3 and 2138.6 cm^{-1}, which did not saturate with increasing exposure (not shown). They are attributable to the transverse and orthogonal C-O stretching vibrations, respectively, of polycrystalline solid CO (Chang, Richardson, & Ewing 1988). Since this splitting is not observed in IR transmission experiments unless a p-polarised infrared source is used, these two features have not generally been reported for laboratory work in the astronomy literature. Annealing in the 15–20 K range causes a reduction in the intensity of the solid CO features, which may be associated with desorption of multilayer CO. However, the growth of a new feature at 2153 cm^{-1} is evident in both experiments. This feature is associated with CO in a hydrogenated ice environment, indicating that solid CO is also diffusing into the pores. Diffusion of CO into the pores of I_{hda} at temperatures above 26 K has been reported previously (Devlin 1992; Palumbo 1997).

With further annealing of the CO/I_{hda} to 20 K (Fig. 2a), two broad CO stretch features at 2153 and 2139 cm^{-1} are evolved. This profile is typical of co-deposited CO/H_2O mixtures, as is evident in Figure 2c and as has been observed previously by many researchers (Sandford et al. 1988; Schmitt, Greenberg, & Grim 1989; Palumbo & Strazzulla 1993; Leto, Palumbo, & Strazzulla 1999; Palumbo 1997; Allouche et al. 1999). While the nature of the bonding site for the 2139 cm^{-1} peak remains uncertain, the 2153 cm^{-1} peak is generally assigned to CO molecules bound to dangling OH bonds (Schmitt et al. 1989; Devlin 1992; Palumbo 1997; Allouche et al. 1999). Such dangling bonds occur at the surface of amorphous water ice. The porous nature of such ices presents within its three-dimensional structure a much larger surface area, and hence a larger number of dangling bonds, than would be expected given the geometric (two-dimensional) area of the film. Annealing of the mixture (Fig. 2c) results in a gradual reduction in the intensity of the 2153 cm^{-1} peak between 30 and 70 K. This indicates that the number of dangling OH bond sites available for CO adsorption is reduced, behavior that is entirely consistent with pore collapse during the $I_{hda} \rightarrow I_{lda}$ phase change known to occur over this temperature range. For CO adsorbed on I_{lda} (Fig. 2b), the intensity of the 2153 cm^{-1} peak remains very low when the ice is heated beyond 15 K, reflecting the small number of dangling bond sites in the less porous water ice grown at 80 K. In Figures 2a and 2c, the
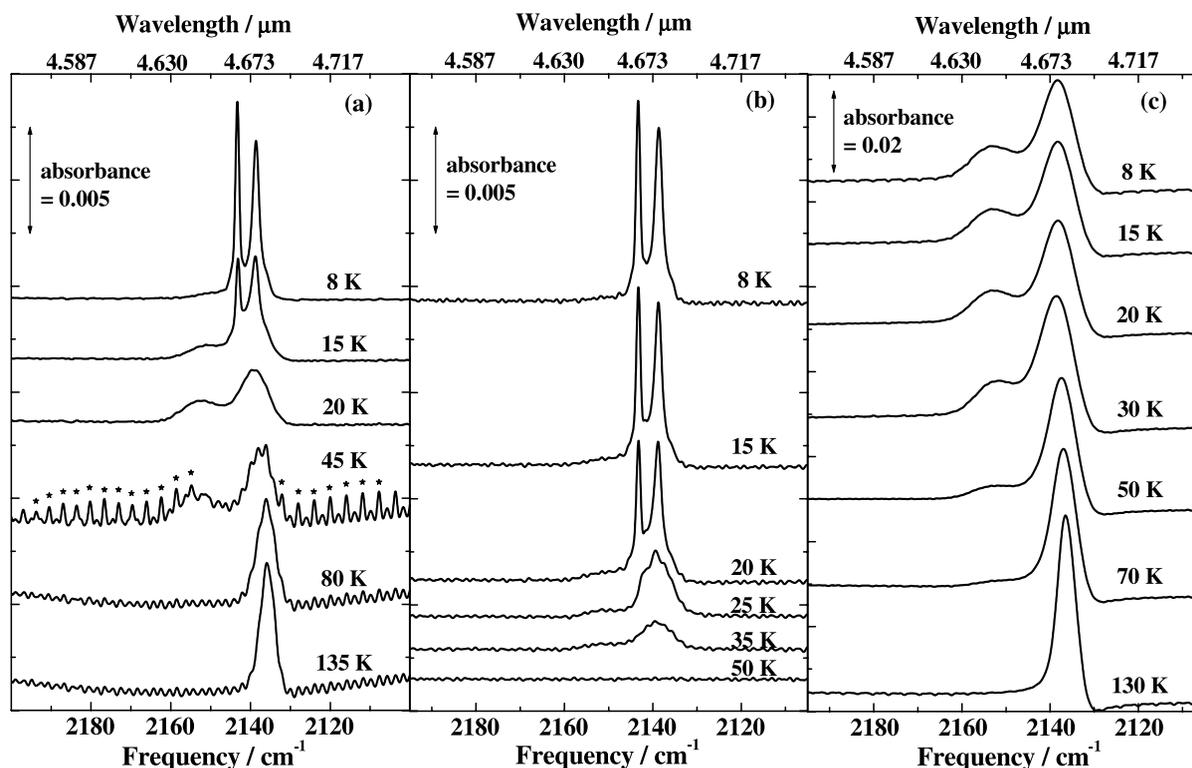
FIG. 2.—RAIR spectra of the CO stretch region of (a) 0.35 μg cm^{-2} CO adsorbed over 57 μg cm^{-2} H_2O at 8 K, (b) 0.35 μg cm^{-2} CO adsorbed at 8 K over 57 μg cm^{-2} H_2O at 80 K, (c) 57 μg cm^{-2} of a $\sim 5:100$ mixture of $CO:H_2O$ gas mixture adsorbed at 8 K. The samples have been annealed for 5 minutes at the temperatures indicated. Features marked with an asterisk in the 45 K spectrum of panel a are due to gas-phase CO transitions, resulting from contamination of the dry air in the purge of the IR optics. The increased baseline noise in the 45, 80, and 130 K spectra in panel a result from a slight mismatch between sample spectrum and background spectrum used in data processing.

CO stretch remains clearly evident up to crystallization temperatures due to CO trapped in the amorphous H_2O ice. Figure 2b shows that CO is completely desorbed from I_{lda} below 50 K, as no mechanism exists to trap CO during heating of the ice. The absorption intensities of transitions have different values in RAIRS and transmission experiments, therefore band-strength calculations based on these results cannot be applied to astronomical spectra. For this and a variety of other reasons, the value of a quantitative analysis of the RAIRS results is questionable, so such an analysis has not been attempted. The combination of TPD and RAIRS provides a better understanding of the system than either technique alone; however, TPD remains a more accurate and useful technique for quantifying the trapping of CO.

The fraction of the CO overlayer trapped during thermal processing that we report in Figure 1 relates specifically to the experimental conditions that we have applied. Changes in the degree of CO entrapment are expected as the heating rate and thickness of both the H_2O ice and CO overlayer are varied. To accurately predict the extent of CO entrapment under given conditions requires a detailed knowledge of the kinetics of desorption of CO from both its multilayer and the ice surface, the kinetics of CO diffusion into the pores, and the kinetics of the phase transition to I_{lda}. Such an analysis is extremely complex and well beyond the scope of this paper. Kinetic analysis and a more detailed examination of CO bonding sites will be presented in future publications. Various other factors may complicate the kinetics of individual processes in the astrophysical environment, including the nonhomogeneous nature of the hydrogenated and dehydrogenated ice layers, irradiation and ion bombardment of the ice, and the formation of ice by reaction rather than accretion. Entrapment of other species is expected and has been observed for N_2 (Kimmel et al. 2001b).

It is frequently assumed that the volatile components of the dehydrogenated ice layers on interstellar dust grains sublime below 30 K. Our results demonstrate that this assumption may be a gross oversimplification of the behavior of such ices. A substantial proportion of such volatile species may be desorbed into the gas phase at much higher temperatures as a result of adsorption on the extensive surface of the porous amorphous ice or entrapment within the hydrogenated layer until it also desorbs. The release of material into the gas phase at higher temperatures than previously thought may have a significant impact on the gas-phase chemistry. Such effects should be particularly prominent in hot cores in star-forming regions, especially if the warming of the dust occurs over a finite period so that the chemical composition of the gas changes markedly with temperature (Viti & Williams 1999). Models of hot cores incorporating the effects described here, and additional experiments, will shortly be reported. The presence of trapped volatiles in solid-phase materials may also significantly influence the solid-state synthesis of complex molecules, especially the conversion of CO to CO_2 and CH_3OH. Consequently, these results may impact substantially on numerous astrophysical environments where H_2O ice is accreted at low temperatures. Our results also demonstrate the importance of thermal history on the behavior of ice layers. The temperature at which the hydrogenated layer is formed, or heated to, prior to the growth of the dehydrogenated layer is the dominant factor in determining the extent

of trapping of volatiles during subsequent heating. Thermal history must also be considered when interpreting the infrared spectra of astronomical ices, as our results show that it is not possible to distinguish between CO adsorbed in the hydrogenated ice layer and diffusing into it when subsequently warmed.

4. CONCLUSIONS

The adsorption and desorption of a solid CO overlayer on and from I_{hda} water ice at astronomically relevant temperatures has been studied, enabling us to produce a succinct qualitative model of its behavior, as summarized in Figure 3. Following adsorption of CO at less than 10 K, heating of the film to 15–30 K results in some desorption of solid CO but also some diffusion of CO into the porous bulk of the H_2O film. Heating over the 30–70 K temperature range allows desorption of CO from the surface of the water ice. The $I_{hda} \rightarrow I_{lda}$ phase change also occurs over this temperature range, causing partial pore collapse that seals off many pathways to the surface from pores in the bulk. Thus, CO entrapment competes with CO desorption. Between 70 and 140 K, no CO is desorbed. At 140 K, the $I_{lda} \rightarrow I_c$ trans-
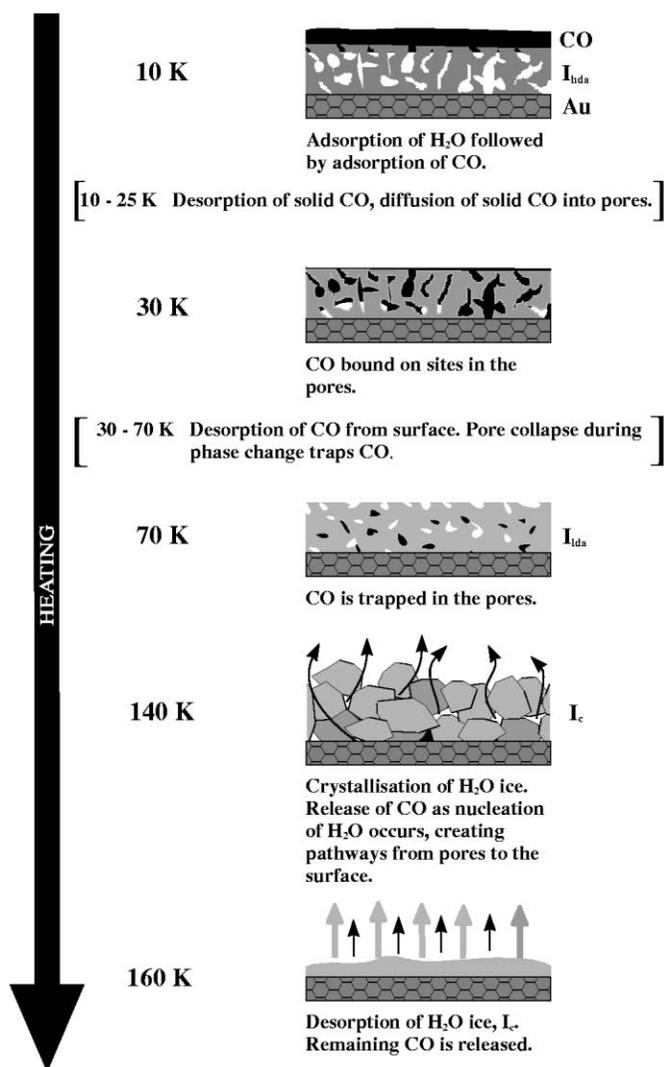
FIG. 3.—Cartoon summarizing the behavior of CO adsorbed on amorphous H_2O under laboratory conditions (not to scale).

formation in H_2O ice opens new pathways to the surface and allows some of the trapped CO to desorb in a molecular volcano. At 160 K, the H_2O film desorbs, releasing the remaining CO.

Note added in manuscript.—Following the initial submission of this paper, a publication by Ayotte et al. (2001) became available to us. It reports TPD analysis of the trapping of CO and other species in water ice. The extent of CO entrapment reported was less than we observed here; how-ever, the deposition temperatures were lower in our experiments and other deposition parameters are different, so we do not consider these results contradictory to ours or to the interpretation presented here.

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