Energetic ballistic deposition of volatile gases into ice

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The trapping of volatile gases within ice plays a key role in the formation of heterogeneous icy planetesimals and is the primary method for preconcentration of reagents in the formation of complex molecules in the extraterrestrial environment [1–3]. Moreover, because volatile species trapped in ice play a central role in determining the composition of planetary atmospheres, a thorough understanding of the microscopic steps in their formation is necessary for the development of accurate models of atmospheric and extraterrestrial systems [4–8]. In general, volatile species are trapped in an ice when they adsorb to the surface and are subsequently buried by further adsorption of gas. Low surface temperatures, where the surface residence time of the gas is long, are needed to permit burial. Here, we demonstrate a new mechanism, energetic ballistic deposition, which has not been previously reported. Transitionally energetic xenon atoms penetrate the ice surface and become stably embedded within the ice well above the xenon desorption temperature. This new mechanism for gaseous incorporation warrants consideration in models that seek to accurately describe the trapping and concentration of volatile gases in molecular solids.

The xenon embedding process depends strongly on the incident energy collision, rather than first being adsorbed and percolating through the matrix. The xenon embedding process as an important mechanism for the formation of heterogeneous icy species under conditions relevant to those found in interplanetary space. There is some precedent for this process, Daschbach et al. implanted helium into ultrathin ice films at 25 K [16], but those results were for unique ice structures on Pt(111) at exceedingly low temperatures. Argon and other low-boiling gases can be trapped in highly porous amorphous solid water. The condensed gases may then diffuse into the bulk of the ice [17]. There are two key distinctions between these previous experiments and the results presented herein. The collision energies of the incident species studied here using a supersonic beam source cover the range between 1.7 and 6.5 eV, whereas in the previous work a thermal source was used, leading to gas-surface collision energies of at most a few tenths of an eV. Moreover, we found that xenon is directly injected into the ice as a consequence of the high energy collision, rather than first being adsorbed and percolating into pores or being buried by the condensation of additional water. The xenon embedding process depends strongly on the incident angle ($\Theta_i$) of the xenon atoms and their translational energy ($E_i$).
Additionally, we present data that show that the xenon that did not embed, but rather scattered from the ice surface, has lost most of its initial translational energy.

The experiments were performed using a precision ultra-high vacuum (UHV) gas-surface scattering instrument (base pressure \(1 \times 10^{-10}\) Torr) that is capable of having up to three independent molecular or atomic beams impinging simultaneously on a target Rh(111) crystal [18]. The Rh(111) was resistively heated and cooled with liquid nitrogen. The sample mount could be rotated with respect to the incident beams allowing for a range of different \(\Theta_i\) to be studied. The angular dependencies of the final energy \(E_f\) and intensity of xenon scattered from the surface were measured with a doubly-differentially pumped quadrupole mass spectrometer (QMS) that could be independently rotated around the target crystal.

Molecular beam techniques were used to prepare intense beams of xenon atoms with a narrow (c.a. 10% \(\Delta E_i\)) distribution of translational energy. High velocity beams of xenon atoms were formed through a supersonic expansion of dilute mixtures of xenon (1% Xe) in lighter carrier gases. Under these conditions, the heavier xenon atoms have nearly equivalent velocities as the lighter carrier gas, either He or H2. The energy of the xenon atoms in the beam was tuned between 1.1 and 6.5 eV by varying the carrier gas and the nozzle temperature (323–673 K). The xenon beams were made by expanding the gas mixture through a heatable nozzle with a 20 μm pinhole at a few hundred psi backing pressure. Time-of-flight analysis of the incident xenon beams determined the energy distribution and relative flux. The absolute xenon fluxes on target were on the order of \(10^{15} \text{Xe cm}^{-2} \text{s}^{-1}\) at normal incidence [19].

Icy particles are formed in space through aggregation of gas-phase species and thus are likely a mixture of small domains of amorphous solid water and crystalline ice [3]. Amorphous solid water (ASW) is a molecularly disordered, metastable phase of ice formed by vapor deposition at temperatures below 120 K. Crystalline ice (CI) is the ordinary hexagonal ice phase and is formed at temperatures of 140 K or higher. To avoid any influence on the ice morphology by the underlying metal substrate, ice films of at least 1000 layers thickness were grown. D2O was used in these studies because the background signal in the detector at m/e = 20 (D2O) was much smaller than at m/e = 18 (H2O), leading to greater sensitivity for detecting sputtered molecules, a related experiment not discussed here [20]. Both the crystalline and amorphous ices grown lack any long range order at these thicknesses and the Rh(111) substrate does not affect the nature of the ice film [21]. To further ensure this lack of long-range order, the Rh(111) surface was precoated with O2 to create an ordered 0.5 monolayer O structure [22]. Ice films were then grown by dosing the prepared substrate with D2O from a molecular beam produced by bubbling He through a D2O filled reservoir. The ice was deposited at a rate of 0.5 layers s\(^{-1}\) (1 layer = 1.07 \(\times 10^{14}\) D2O cm\(^{-2}\)). The use of D2O from a molecular beam minimizes background accumulation typically encountered when backfilling a vacuum chamber with water vapor and allows for the deposition of high-purity ice films of known morphology; the morphology of the ice (ASW or CI) depends on the temperature of the Rh(111) substrate during deposition. Film thickness was determined by temperature programmed desorption (TPD), where the surface temperature was ramped while monitoring the D2O signal. The coverage calibration was done by comparing the post-exposure TPD signal with that of a monolayer of D2O [22]. The shape of the TPD spectra verified whether the ice overlayer was CI or ASW, where the desorption of crystalline ice is a smooth peak and there is a small bump in the desorption peak near 160 K for amorphous solid water [23].

The angular distribution of the intensity of xenon scattered via the fast channel (red) and the trapping-desorption channel (blue). The solid line through the trapping-desorption data is a cos(\(\Theta_i\)) least squares fit, and the solid line through the fast data is simply to guide the eye. The inset shows an example of the time of flight distribution. The data are open circles, and the total fit is the solid green line. The fits for the fast and TD channels are shown in red and blue, respectively. The conditions were: \(E_i = 6.5 \text{ eV}, \Theta_i = 25^\circ\), and ASW ice at \(T_s = 115 \text{ K}\).
scattered xenon atoms’ initial energy was dissipated to the ice lattice, their final energy was still significantly greater than the scattered atoms from the trapping-desorption channel. Figure 1 shows the relative intensity of the two scattering channels at various final scattering angles for 6.5 eV xenon atoms impinging at 25° on ASW. The scattering was qualitatively similar for CI under the same conditions. Each data point was derived by integrating the energy distribution (as shown in the inset of Figure 1) of the scattered xenon at a given exit angle (\(\Theta_f\)). As \(\Theta_f\) becomes more glancing, the faster scattering component becomes more energetic and intense relative to the slower trapping-desorption channel. Under all conditions, an appreciable trapping-desorption scattering component was observed.

After exposing the ice sample to a beam of energetic xenon, TPD experiments that measured both the desorbing xenon (\(m/e \approx 132\)) and D$_2$O were performed on the resultant ice film. Figure 2 shows plots of post-exposure TPDs comparing xenon desorption from either ASW (blue) or CI (red) after exposure to 6.5 eV xenon atoms at normal incidence. For the TPD plots, the ordinate scaling is the measured TPD signal divided by the relative xenon flux of the incident beam (as measured by TOF spectra), the exposure time, and \(\cos(\Theta_f)\). This is called the exposure weighted xenon TPD signal. The total exposure was nearly 8% larger for the ASW than for the CI. As shown in the figure, there are unmistakable xenon desorption peaks nearly 100 K above the expected desorption temperature (55 K) for xenon on ice [9,11,12]. Furthermore, the desorption temperature is different for each ice morphology. On crystalline ice, xenon desorbs as a single peak near 140 K and desorption of xenon begins before any significant desorption of the ice occurs; crystalline D$_2$O desorption is shown by the thin dashed line in Figure 2. Xenon desorption from ASW has a more complicated profile comprised of two separate xenon desorption peaks. The first peak is qualitatively similar to desorption from CI, but shifted about 15 K higher. The second is a sharp peak near 160 K. ASW irreversibly converts to CI around 160 K [23], and is evident as a hump in the D$_2$O desorption indicated by the thin solid black line in Figure 2.

A significant amount of the desorbing xenon came off as a sharp feature at the transition, which we attribute to long-range diffusion followed by the expulsion of the xenon as the ice crystallizes [27].

Figure 3 shows the exposure weighted xenon TPD spectra from ASW after exposure to beams of xenon atoms of different incident energies and angles. The total xenon fluences for each exposure were within a factor of 1.5, and this small deviation in total exposure had no apparent effect on the TPD peak shape or intensity. As can be seen in the figure, at the lowest \(E_i\) and glancing incidence, no xenon was measured in the TPD. As \(E_i\) increased at 25° incidence, a sharp desorption feature grew near 160 K. Finally, at the greatest \(E_i\) studied, a second, broader peak developed below 155 K. Taken together, these results show that the amount of xenon adsorbed increases with greater \(E_i\) and more normal incidence.

The data in Figure 3 suggest that embedding is increasingly favored with higher incident energy, and therefore higher incident momentum. One consequence of this trend would be that embedding of heavy atoms would be favored over light atoms having the same energy (and commensurately lower momentum). The effect that momentum has on embedding of the incident gas atoms will be discussed in an forthcoming publication.

The presence of the trapping-desorption channel in the scattering (Figure 1) suggests that the xenon has a significant residence time on the ice surface. While adsorbed to the surface, it is possible that the xenon could diffuse into the ice bulk. Because xenon was observed to embed under the gentlest conditions (low \(E_i\) and glancing incidence), there is an appreciable TD component, diffusion from the surface into the bulk is not an important contribution to the embedded xenon observed after more vigorous exposures.

It is important to explain why the ordinate is scaled by the xenon exposure rather than just showing the absolute signal. The xenon is trapped within the ice, so it is reasonable that there be a limit to how much xenon can be adsorbed at any depth below the ice surface. The penetration and embedding involve the breaking and reformation of many intermolecular D$_2$O bonds, which

**Figure 2.** Exposure weighted TPD spectra (10 K min$^{-1}$ ramp rate) for xenon desorbing from either crystalline ice (CI, red) or ASW (blue). Both substrates were exposed to a 6.4 eV xenon beam at normal incidence for nearly the same xenon exposure (about 8% difference). The scaled (divided by 20) D$_2$O desorption spectra are shown for CI (dashed) and ASW (solid). The ASW to CI transition is shown by the hump in the ASW desorption around 160 K which is coincident with the second xenon desorption.

**Figure 3.** Exposure weighted TPD spectra (10 K min$^{-1}$ ramp rate) for xenon desorbing from ASW after several different dose conditions. The 6.4 eV, normal incidence data are the same as shown in Figure 2 and the dashed vertical line corresponds to the ASW-CI transition near 160 K. The xenon TPD spectrum for 1.7 eV at 65° incidence (gray line) establishes the background xenon signal, as no xenon was observed.
have an energy of about 0.3 eV per bond [28]. Higher energy xenon can penetrate deeper into the ice, leading to a larger quantity of xenon incorporated in the ice matrix. At more glancing incident angles, the impinging xenon atom would encounter many more D$_2$O molecules to reach a given depth below the surface than if it struck the surface at 0°. The incident xenon loses energy with each encounter, so it would be expected that for a given $E_i$, less would be adsorbed with increasing $\Theta_i$. With this interpretation, there should be a saturation limit for any given $E_i$ and $\Theta_i$; the amount of xenon adsorbed should at first increase with continued exposure, but eventually reach a limit. The experiments discussed in this Letter do not address the uptake kinetics of the embedding process, but we are presently conducting experiments that will, and these will be presented in a future publication.

In conclusion, we have shown that xenon atoms can be embedded in amorphous and crystalline ice at hyperthermal incident energies and near-normal incident angles. Most importantly, the gas embedding occurs at temperatures (120 K) well above the normal desorption temperature of xenon adsorbed on the ice surface (55 K). These results demonstrate a new mechanism for the incorporation of gaseous moieties in the surface region of both amorphous solid water and crystalline ice. This uptake mechanism has not been previously considered as a route by which icy planetesimals in interplanetary or interstellar space can acquire new material in the astrophysical environment.

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References