Ultraviolet photodesorption from water ice

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Abstract. The absolute desorption yield of low temperature (35–100 K) water ice under irradiation with Lyman-α (121.6 nm) photons, and its dependence on ice temperature and irradiation dose are measured. It is found that photodesorption can account for the absence of ice on grains in diffuse interstellar clouds, is an important factor determining the life of ice mantles in molecular clouds, and exceeds solar wind ion erosion and sublimation of ice grains in the outer solar system.

Introduction

Interest in the effects of ultraviolet radiation on water ice arises both from its significance as an analog for damage of biological materials and also from the need to understand the stability of ice grains or ice mantles on refractory grains in the interstellar medium (Sternberg et al., 1987) and in the solar system (Harrison and Schoen, 1967; Carlson, 1980). For instance, the rate of desorption of molecules from ice surfaces is needed to account for the balance between molecules in the gas and condensed phase in a molecular cloud or near Saturn’s tenuous E-ring, or to account for the erosion of cometary grains (Combi, 1987). In the past decades, it has been assumed that photodesorption (also called photosputtering) by background UV photons is an important desorption mechanism for low temperature ices in space. In the absence of experimental values, such studies relied on theoretical estimates, which span several orders of magnitude (∼10−5–0.1 H₂O/photon) (Draine and Salpeter, 1979; Hartquist and Williams, 1990). Therefore, we have measured the absolute yield for photodesorption of low temperature (35–100 K) water ice by Lyman-α (10.2 eV) photons. We find a pronounced dependence of the yield on both irradiation dose and ice temperature which is related to the storage of photolyzed radicals in the ice. These results contrast drastically with the assumptions that have been made in modeling photodesorption in the interstellar medium and the outer solar system.

Experimental details

Apparatus

The experiments were made in an ultra-high vacuum chamber (base pressure ∼1×10⁻¹⁰ Torr) equipped with a cooled quartz crystal resonator microbalance with sensitivity of 0.1 monolayers of water (Sack and Baragiola, 1993) onto which ice films were grown, a microwave-powered hydrogen flux lamp, calibrated UV detectors, a UV–visible spectrometer, and a quadrupole mass spectrometer. The light spectrometer and the UV detectors used to measure the photon flux during the experiments were calibrated at the National Institute for Standards and Technology (NIST). The UV light was generated by a hydrogen microwave discharge which was shown to consist of negligible UV radiation outside the Lyman-α line (Fig. 1).

Procedures

The ice films were grown by vapor deposition on the optically-flat gold electrode of the microbalance from vapor effusing from a microcapillary array. The growth rate was approximately 1.0 Å s⁻¹, and the growth temperature was between 30 and 100 K, conditions that produce mainly amorphous ice. Some experiments performed under conditions that produce cubic ice (Sack and Baragiola, 1993) produced no detectable effect of crystallinity on the photodesorption yields, as will be shown below. The film thickness was approximately 5000 Å for almost all of the measurements. This thickness is much larger than the penetration length of Lyman-α photons in ice,
\begin{figure}
\centering
\includegraphics[width=\textwidth]{fig1.png}
\caption{Spectra of the light reaching the ice target from the microwave-powered hydrogen lamp, corrected for analyzer transmission and detector sensitivity.}
\end{figure}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{fig2.png}
\caption{Fluence and temperature dependence of photodesorption yield. The growth and irradiation temperatures were the same.}
\end{figure}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{fig3.png}
\caption{Fluence dependence of the photodesorption yield at 50 K of ice that is mainly amorphous (grown at 50 K) and polycrystalline (grown at 140 K).}
\end{figure}

\textbf{Results}

\textit{Photodesorption yield}

The measurements of the absolute photodesorption yield showed that the yield increased with irradiation time, eventually reaching a saturation after long irradiations. This behavior was hypothesized to be due to a dose dependence of the yield. Figure 2 shows the results of plotting the yield vs. dose of Lyman-\(\alpha\) photons at the five different irradiation temperatures from 35 to 100 K. The lowest temperature is limited by the experimental apparatus, and the highest temperature results from the need to avoid significant mass loss due to sublimation. Figure 3 shows that the structure of the ice has no discernible effect in the desorption yield.
To show that the mass loss of the film is not due to sublimation caused by surface heating during irradiation, we examined the dependence of the mass loss on lamp intensity. This comparison was made at $T = 100$ K, in the saturation region where the photodesorption yield does not depend on irradiation dose (Fig. 4). The linearity of the photodesorption yield with lamp intensity indicates that surface heating and sublimation is not a primary cause of the measured photodesorption yield. If this were not the case, the lower surface temperatures at lower intensities would have an exponentially lower sublimation rate, since sublimation rate depends exponentially on temperature.

The fluence dependence indicates that the photochemical processes that occur in the water ice sample before saturation are involved in determining desorption on a photon-by-photon basis. An incubation period of bond-breaking and diffusion of radicals is apparently required before species can start to desorb, since virgin ice does not desorb at low temperatures. The fact that the incubation period is shorter at higher temperatures hints that an activated process such as diffusion may be the limiting factor at lower temperatures. The radicals formed by photodissociation may be more likely to recombine at lower temperature since they cannot readily diffuse to interact with a species far from their formation point. In other words, at lower temperatures, the processes leading to desorption are more easily quenched or are bypassed. This would mean the larger threshold doses at lower temperatures are needed to create a large radical concentration, which initiates the photochemical processes that eventually lead to photodesorption.

**Species desorbed during irradiation**

The mass spectrometer was used to measure the partial pressures of relevant mass peaks during irradiation. These measurements were made at 50 to 100 K, 50 K representing a threshold region, and 100 K representing a temperature with a small or nonexistent threshold. Figure 5 shows the results of plotting the irradiation induced change in partial pressure of peaks at mass 2 (H) and 32 (O$_2$) as a function of dose, with the sample at 50 and 100 K, respectively. Other peaks not displayed in this figure did not show any significant changes due to irradiation. The data for H$_2$ and O$_2$ do not show the dose dependence observed for the total desorption yield. Since we calibrated the mass spectrometer, we can convert the partial pressure increases to fluxes of desorbed species to obtain the partial desorption yields given in Table 1.

After an irradiation experiment, the mass spectrometer was used to examine the species desorbed between 1 and 100 amu during heating and sublimation of the ice sample. Besides the peaks corresponding to masses 17 and 18, we saw significant desorption of several other species with masses of 19, 20, 33, and 34 amu for the previously irradiated samples. These last two peaks may represent HO$_2$ and H$_2$O$_2$, indications of photochemical changes induced by the UV irradiation.

In another set of experiments we looked at desorbing water molecules with the mass spectrometer using iso-
topically labeled H$_2^{18}$O ice. In this way, we could distinguish a pressure increase due to desorbed molecules from the large background of H$_2^{16}$O coming from the vacuum system walls. We made experiments at 35 and at 100 K which showed that the dependence of the signal at mass 20 (H$_2^{18}$O) with irradiation dose is the same as that of the total photodesorption yield, within experimental uncertainties. These data are consistent with the hypothesis that H$_2$O is the primary species desorbed from these ice samples when irradiated by Lyman-\(\alpha\) photons.

**Possible desorption mechanism**

Using the fact that the primary dissociation products are H, OH, H$_2$, and O, the reactions that are important for H$_2$ and O$_2$ production may include:

\[
\begin{align*}
\text{H} + \text{H} &\rightarrow \text{H}_2 & \Delta H &= -4.5 \text{ eV} \\
\text{O} + \text{O} &\rightarrow \text{O}_2 & \Delta H &= -5.1 \text{ eV} \\
\text{O} + \text{H}_2 \text{O}_2 &\rightarrow \text{H}_2 \text{O} + \text{O}_2 & \Delta H &= -3.7 \text{ eV} \\
\text{OH} + \text{H}_2 \text{O}_2 &\rightarrow \text{H}_2 \text{O} + \text{HO}_2 & \Delta H &= -1.4 \text{ eV}
\end{align*}
\]

where direct production of H$_2$ by dissociation may also be important. Based on other photolysis research, the most important process in the production of O$_2$ is probably the O + O reaction although some evidence for the peroxide reaction has been observed. The production of H$_2$O$_2$ and HO$_2$ could also be important intermediate reactions, as was observed in some of the earlier photolysis and gamma ray experiments, since we observed a sizable pressure increase for mass 33 and 34 when heating the film. The production of H$_2$O$_2$ is most likely due to the reaction of two OH. There is a whole family of exothermic reactions involving intermediate OH, H$_2$O, and O which can lead to desorption if they occur near the surface (Westley, 1994). These reactions are probably the primary desorption mechanisms at low temperatures, where dose dependence is most pronounced. The dose and temperature dependence of the absolute photodesorption yield indicates that diffusion of radicals, atoms and molecules to the surface is probably the limiting rate factor at lower temperatures, where diffusion is slow. The diffusion coefficients of different species such as H, OH, and O in ice demonstrate that most species are not mobile. H$_2$ and O$_2$, once formed, probably have a higher probability of escaping, since they are still volatile, even at 35 K. The small dose dependence observed at 100 K could be due to photochemical mechanisms plus a constant yield due to a single photon ejection mechanism. The fact that the saturation yield is higher at higher temperatures may be due to the thermal activation of reactions involving radiolysis products or the activation of desorption channels for surface excited species.

**Astrophysical implications**

**Interstellar medium**

In diffuse interstellar clouds, the accretion rate for ice mantles on grains is very slow. The time for condensable species to be removed from the gas phase is $10^3 / n_{H}$ yr, where $n_{H}$ is the H density in the gas phase in atoms cm$^{-3}$. Since, on average, a grain stays $10^3$ yr in a molecular cloud phase and almost the same time in a diffuse phase, when a grain passes from a dense phase (molecular cloud) to an unsheilded phase (low density, 1–10 cm$^{-3}$), there must exist a mechanism which destroys the ice mantles since they are not seen in the diffuse phase (Draine and Salpeter, 1979). Several mechanisms have been proposed (Draine and Salpeter, 1979), including photodesorption. With the previously used photodesorption cross-section value: \(\sigma \sim 10^{-18} \text{ cm}^2\) (Draine and Salpeter, 1979), the process was negligible with respect to other destruction mechanisms (sputtering due to the shocks generated by supernova remnants) for low binding energy ice like water and methane. Using our data, \(\sigma \sim 8 \times 10^{-18} \text{ cm}^2\), which is three orders of magnitude greater than the previous ones gives, following Draine and Salpeter (1979), results in an erosion rate for water ice grains with initial radius of 0.1 \(\mu\)m of $3500 \times 10^{-8} \text{ yr}^{-1}$ instead of $4.5 \times 10^{-8} \text{ yr}^{-1}$. Therefore, photodesorption should be the main mechanism of erosion of ice grains both in diffuse clouds and in the intercloud medium. It should remove rapidly preexisting ice mantles thus explaining the puzzling absence of ice in these diffuse environments (visual extinction less than $\sim 3.3$) (Whittet, 1992), the outskirts of molecular clouds, \(n_{H} = 10^1-10^2 \text{ cm}^{-3}\) or in clumpy molecular clouds where the UV radiation can penetrate.

**Solar system**

For circumstellar ice, our results show that desorption yields for the Uranus satellites are 50% larger than estimated by Cheng and Lanzerotti (1978). For Saturn's rings, photodesorption is not the main desorption mechanism and it is likely that collisions between ring particles will disrupt their surfaces before the threshold dose is obtained. At distances larger than 5 AU, the photodesorption rate becomes larger than the solar-wind sputtering rate (Brown et al., 1982) and thermal sublimation. Other processes can contribute synergistically to desorption. Sputtering of ices due to energetic ion bombardment (Johnson, 1990) may be enhanced due to precursor radicals produced by UV irradiation, possibly explaining the deficit between the observation of OH near Tethys (Shemansky et al., 1993) and sputtering calculations (Johnson et al., 1993). This is currently being studied in our laboratory.

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**References**


