Photodesorption from low-temperature water ice in interstellar and circumsolar grains

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Dust grains in the interstellar medium and the outer Solar System commonly have a coating of water ice, which affects their optical properties and surface chemistry. The thickness of these icy mantles may be determined in part by the extent of photodesorption (photosputtering) by background ultraviolet radiation. But this process is poorly understood, with theoretical estimates of the photodesorption rate spanning several orders of magnitude.

Here we report measurements of the absolute ultraviolet photodesorption yield of low-temperature water ice. Our results indicate that the rate of photodesorption is appreciable. In particular, it can account for the absence of icy mantles on grains in diffuse interstellar clouds, it exceeds solar-wind ion erosion and sublimation in the outer Solar System, and it is important in determining the lifetimes of icy mantles in dense molecular clouds.

The experiments were performed in an ultra-high-vacuum chamber (base pressure \( \sim 1 \times 10^{-10} \) torr) using a quartz crystal resonator microbalance (sensitivity 0.1 monolayers of water) and a quadrupole mass spectrometer. Ice films were grown by vapour deposition on the cooled gold electrode of the microbalance to a thickness \( \sim 5000 \) Å much larger than the attenuation depth of the 10.2-eV Lyman-\( \alpha \) photons \( \sim 350 \) Å.

Changing growth conditions to produce amorphous or crystalline cubic ice produced no detectable effect on photodesorption. Irradiation was done at normal incidence with light from a hydrogen microwave discharge which was shown to have negligible ultraviolet radiation outside the Lyman-\( \alpha \) region. Calibration of the optical spectrometer and photon detectors were done at the SURF-II metrology line (NIST, Gaithersburg, Maryland).

Once an ice film is grown, its mass remains essentially stable until it is exposed to the ultraviolet radiation. When the ultraviolet source is turned on, the mass of ice decreases steadily; from this mass loss and the measured photon dose, we calculate the desorption yield \( Y \) as the number of molecules desorbed per incident photon. Mass spectrometry shows that the desorption flux is mainly \( \text{H}_2\text{O} \), as expected, with small amounts of \( \text{H}_2 \) and \( \text{O}_2 \). The mass loss at large doses is proportional to the photon flux (Fig. 1), showing that desorption is not due to sublimation caused by absorbed heat. Furthermore, the mass loss dropped to unmeasurable levels when we used a window that blocked the Lyman-\( \alpha \) radiation, but let the visible and infrared pass unattenuated to the sample.

Figure 2 shows the dependence of \( Y \) on photon dose and ice temperature. The low-dose behaviour shows that photodesorption does not occur because of absorption of a single photon, as assumed previously, but requires that the ice be altered by previous photoabsorption events. This result can be related to those for fast, light ions where the desorption yield at low temperatures and low excitation densities is proportional to the square of the excitation density. The observed photon-dose dependence of \( Y \) at low doses confirms that single excitation events, like those leading to direct dissociation or dissociative attachment, do not produce significant desorption in pure water ice.

A mechanism for desorption can involve the formation of precursors (probably radicals) which directly absorb the radiation or react with a nearby, newly excited molecule, converting potential energy into kinetic energy of the reaction products. Thus the incubation stage which we observe at low temperatures, before we can measure significant photodesorption, may result from the need to achieve a sufficient density of radical precursors in the surface layers of the ice films, so that the formation of a new photolyised radical is likely to lead to a desorption event. The incubation dose of \( \sim 10^{18} \) photons cm\(^{-2}\) at 35 K decreased by a factor of about two in experiments in which a fresh 200-Å layer was deposited on a previously ultraviolet-saturated sample and then re-irradiated. Figure 2 also shows that incubation is shorter at higher temperatures, where radicals diffuse more easily and reactions are enhanced.

Figure 3 shows that the temperature dependence of the saturation photodesorption yield is similar to that of desorption yields under ion and electron bombardment. The temperature dependence of the yield is fitted by an expression \( Y(T) = Y_0 + Y_1 e^{-E/kT} \) where \( T \) is temperature, with an activation energy \( E \sim 0.03 \) eV. This value is in the range associated with hydrogen diffusion, and the sharp increase of \( Y \) occurs at temperature where OH becomes mobile. The accumulation of radicals in the ultraviolet-irradiated ice was confirmed by thermal desorption experiments. Mass spectrometry of the gas produced by heating the ice to 160 K at \( \sim 1 \) K min\(^{-1}\) showed peaks at mass 33 and 34, corresponding to H-deficient H\(_2\)O and H\(_2\)O\(_2\) species, consistent with hydrogen loss. The background at mass 17, caused by fragmentation of water molecules in the mass spectrometer, did not allow us to make inferences about the ejection of OH radicals. We also found that sublimation from irradiated ice at 80 K is orders of magnitude larger than from unirradiated ice.

The values of \( Y \) at saturation are comparable to the probability of photoabsorption \( \sim 8 \times 10^{-14} \) in the first surface layer. This implies that photodesorption is very efficient, but not until the surface layers have been altered. Assuming the photoabsorption cross-section does not change significantly for...
the altered material, each molecule will have absorbed a photon and reformed (on average) a number of times, before contributing to a desorption event. This indicates that ice is very stable against radiation even at the highest doses of deposited energy used (~480 eV per molecule averaged over the penetration depth.)

Comparison of our results with existing estimates of $Y$ for ice is difficult because neither the dose nor the temperature dependence were anticipated earlier. Our yields at saturation are much lower than the value of $\sim 0.1$ estimated recently by Hartquist and Williams, but are much higher than earlier estimates of $\sim 4 \times 10^{-5}$ by Draine and Salpeter. The measured yield is close to Harrison and Schoen's estimate in the saturation region at low temperatures, an exceeds it by a factor of $\sim 3$ at 100 K.

In interstellar clouds, the expected fluxes of energetic ultraviolet photons are $F = 10^6$ cm$^{-2}$ s$^{-1}$ for the background photon field expected in diffuse and translucent interstellar clouds or on the outskirts of dense clouds. After a dose of $10^{18}$ photons cm$^{-2}$ (Fig. 3) or a time of $\sim 300$ years, the desorption rate from an ice mantle is then $> 2 \times 10^7$ molecules cm$^{-2}$ s$^{-1}$, several orders of magnitude larger than the gas adsorption rate in a diffuse cloud, implying rapid removal of a pre-existing ice mantle. This explains the puzzling absence of the characteristic infrared absorption at a wavelength of $3.1\mu$m (the 'ice signature') in these diffuse interstellar environments (visual extinction $<3.3$). Our measurements also imply that photodesorption is an important mechanism at the outskirts of dense molecular clouds, where the hydrogen density is $n_H = 10^2-10^3$ cm$^{-3}$, or in clumpy molecular clouds where the ultraviolet radiation can penetrate. At the core of dark clouds, the interstellar ultraviolet flux is attenuated, but a flux of a few thousand photons per cm$^2$ per s is believed to exist due to excitation of background H$_2$ by cosmic rays and shocked stellar winds. At these low levels, the photodesorption flux is $\sim 10^{-6}$ molecules cm$^{-2}$ yr$^{-1}$, sever orders of magnitude smaller than the accretion rate ($10^{10}$-10$^{12}$ molecules cm$^{-2}$ yr$^{-1}$). Therefore in the absence of additional processes, photodesorption cannot remove much of a water-ice grain mantle in a dense region of a molecular cloud, consistent with recent observations.

We now examine implications for circumstellar ice grains. Assuming that yields simply scale in the ultraviolet with the photoabsorption cross-section, we can scale estimates for photodesorption of ice in the outer Solar System using our Lyman-$\alpha$ data. At saturation, the calculated photodesorption rate, using the data in Fig. 2, exceeds the solar-wind sputtering calculated earlier and, beyond 5 AU, is larger than sublimation. Near Uranus ($\sim 70$ K) the photodesorption rate after $\sim 40$ years of exposure of an undisrupted ice surface is $\sim 50\%$ larger than estimated earlier, whereas near Saturn ($\sim 100$ K) it is about three times larger than the estimate after only $\sim 10$ years of exposure. This is close agreement, given the uncertainties in extrapolating laboratory data to astronomical conditions. For ice embedded in planetary magnetospheres, like Saturn's E-ring particles and the icy satellites, erosion by photons, although not negligible, is less important than by plasma ions.

These desorption rates are a lower bound because other processes can contribute synergistically to desorption. Sputtering of ice by magnetospheric ions may be enhanced because of precursor radicals produced by ultraviolet irradiation, possibly explaining the deficit between the observation of OH near Tethys and sputtering calculations. In addition, enhanced sublimation of photolysed ice may be triggered by a transient temperature increase produced by a grain-grain collision or a cosmic ray. This is supported in part by our observation of enhanced sublimation mentioned above; however, we did not find 'explosive' desorption in water ice because the back-reaction to reform water is apparently very efficient.

Although our data showed that the saturation $Y$ was independent of photon flux in the range $10^{14}-10^{15}$ cm$^{-2}$ s$^{-1}$, this does not hold for lower fluxes. For lower fluxes, the saturation $Y$ is enhanced, and the yield is described by $Y(T) = Y_0 + Y_1 e^{-E/T}$, where $Y_0 = 0.035 \pm 0.002$, $Y_1 = 0.13 \pm 0.10$, $E = (29 \pm 6) \times 10^3$ eV.
not necessarily imply that situation will hold in photon fluxes of 10^4–10^5 cm^{-2} s^{-1} expected in the astrophysical environments of icy grains. It is possible that, in this case, the radicals may recombine in the time of 10^8 years between photon impacts in a region of molecular dimensions (10^{-15} cm). To elucidate this effect, which would result in smaller Y values than those reported here, detailed modelling based on the photon flux and the measured activation energy will be performed.

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A structural phase transition induced by an external magnetic field

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A vast number of compounds are known that exhibit structure transformations in response to changes in temperature, pressure and/or composition. One such example is the family of perovskites, La$_x$Sr$_{1-x}$MnO$_3$; for a limited range of compositions ($x$), they undergo a structural phase transition from an orthorhombic to a rhombohedral form with increasing temperature. These compounds are also ferromagnetic, a property that arises from coupling between the charge carriers and localized spin moments of the manganese ions. Here we show that, through careful tuning of the composition, the local spin moments and the charge carriers can in turn be coupled strongly to changes in the structure. For $x=0.170$, the crystal structure of the compound can be switched— reversibly or irreversibly, depending on the temperature—by application of an external magnetic field.

The ferromagnetic ground state of metallic La$_{1-x}$Sr$_x$MnO$_3$ is caused by the so-called “double-exchange interaction” between the Mn$^{3+}$ and Mn$^{4+}$ ions. The parent antiferromagnetic insulator LaMnO$_3$ contains Mn$^{3+}$ ions with $t_{2g}^4$ (spin quantum number $S=2$) configuration. The $t_{2g}$ electrons are localized and so can be viewed as local spins with $S=3/2$. In contrast, the $e_g$ electrons are strongly hybridized with the oxygen $2p$ states and change from a localized to itinerant character with oxidation of the MnO$_2$ lattice. An important feature is that strong intra-atomic ferromagnetic (Hund) coupling acts between the $t_{2g}$ spins and $e_g$ electrons, which gives rise to a parallel alignment of their spins. Chemical substitution of La$^{3+}$ by Sr$^{2+}$ introduces holes into the $e_g$ orbitals, that are mobile and mediate an interatomic ferromagnetic interaction between the Mn atoms; the $e_g$ electrons gain kinetic energy through this double-exchange interaction. This scheme was proposed by de Gennes as a microscopic origin of the ferromagnetic metallic states in the hole-doped La$_2$Mn$_2$O$_7$ perovskites. Very recently, such a strongly spin–charge coupled state has been extensively revisited in light of the observation of a colossal negative magnetoresistive effect. Near the ferromagnetic ordering temperature ($T_c$), an external magnetic field can align more or less ordered local spins ferromagnetically. The forced spin-polarized conduction electrons (holes) then suffer less from the scattering by local spins and become more itinerant.

In addition to strong spin–charge coupling, changes in the crystal structure can also couple strongly to the electronic states. The lattice of La$_{1-x}$Sr$_x$MnO$_3$ undergoes a structural phase transition between the orthorhombic form (low-temperature phase, $Pbnm$) and the rhombohedral form (high-temperature phase, $R3c$) with a change of the composition x and/or the temperature. We show in Fig. 1 the schematic crystal structure

![FIG. 1. Schematic crystal structures of La$_{1-x}$Sr$_x$MnO$_3$ ($x=0.170$) in the orthorhombic phase ($Pbnm$) and the rhombohedral phase ($R3c$). The lattice parameters for the orthorhombic phase (measured at 290 K) are $a = 5.475$ Å and $c = 8.097$ Å, giving a volume of 59.290 Å$^3$ per Mn atom. For the orthorhombic phase (measured at 280 K), the lattice parameters are $a = 5.502$ Å, $b = 5.547$ Å, and $c = 7.790$ Å. The corresponding volume is 59.445 Å$^3$ per Mn atom.](image-url)