

Metastable hydronium ions in UV-irradiated ice

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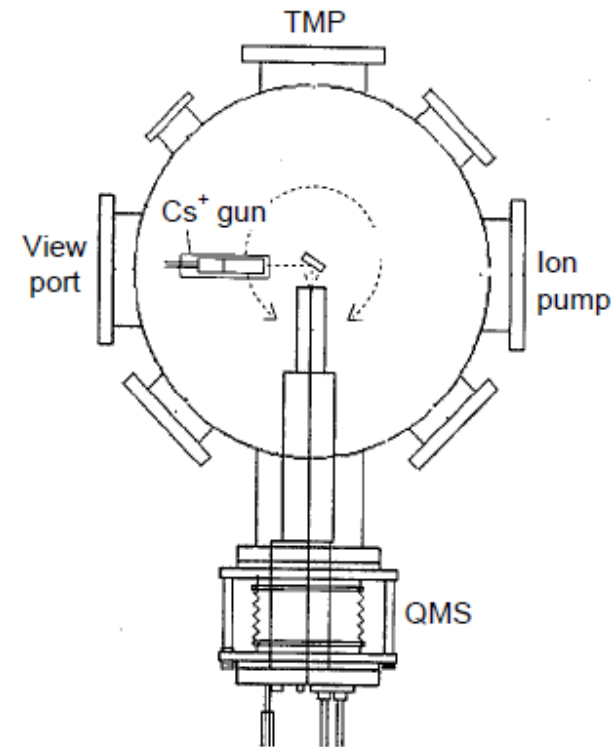
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Introduction:

1. Water-ice is one of the most abundant solid materials in planetary atmospheres, comet tails, and interstellar media (ISM).
2. There ice is usually under bombardment of energetic photons, ions, and electrons. Therefore, the interaction of high-energy radiation with ice surfaces is a subject of astrophysical relevance and also of fundamental interest in the physics and chemistry of ice.
3. Several studies have been conducted in the past decades to investigate the effects of energetic photons incident on ice surfaces.
4. These studies have revealed that UV irradiation can change the morphology of ice sample, induce photochemical reaction through which H atoms, OH radicals, H₂ and H₂O₂ molecules are produced.
5. Photodesorption studies have observed the emission of H atoms, H⁺ ions, and H₃O⁺ ions from water-ice samples subjected to UV irradiation at different photon energies.
6. So far formation of ionic products in ice by UV irradiation is not well understood compared to photofragmentation and radical recombination processes in ice.
7. The formation of H₃O⁺ in ice irradiated with UV light at an energy of 10–11 eV, which is less than the vertical ionization energy of free water molecules (12.6 eV).
8. In the present work, evidence of the UV-induced formation of H₃O⁺ in ice and examine the thermal and temporal stabilities and migration activity of the photogenerated H₃O⁺ species.

Experimental section:

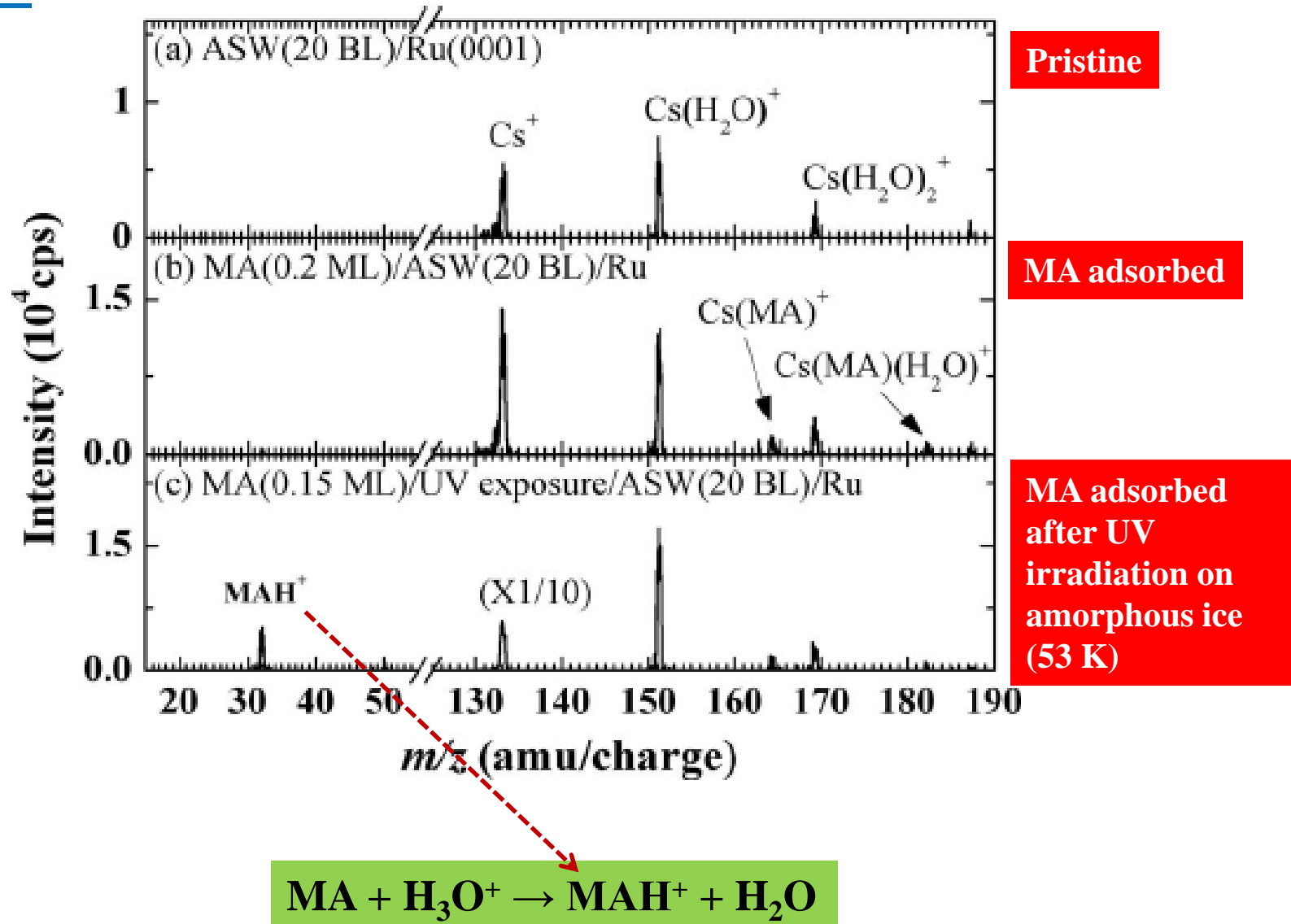
1. The experiment was carried out in an ultrahigh vacuum (UHV) surface analysis chamber equipped with instrumentations for LES (low energy sputtering), RIS (reactive ion scattering), TPD and RAIRS. The ice films were prepared on the (0001) face of a Ru single crystal. The thickness of the amorphous ice films was typically 9-20 bilayers (BLs, $1 \text{ BL} = 1.1 \times 10^{15} \text{ water molecules cm}^{-2}$) and crystalline ice thickness was $\sim 150 \text{ BL}$.
2. Neutral and ionic species present at the ice film surfaces were analyzed by the techniques of LES and RIS where 30 eV Cs^+ beam was used for amorphous ice (ASW) and 38 eV energy for crystalline ice (CI).
3. Methylamine (MA) gas was introduced onto the sample surface through a tube doser to deposit methyl amine on the ice surface.
4. The UV light source was a radio frequency (rf)-powered Kr lamp which produced photons with two sharp intensity maxima at energies of 10.03 and 10.64 eV . The photon flux (F) reaching the sample was estimated to be $\sim 2.1 \times 10^{13} \text{ photons cm}^{-2} \text{ s}^{-1}$.



Results:

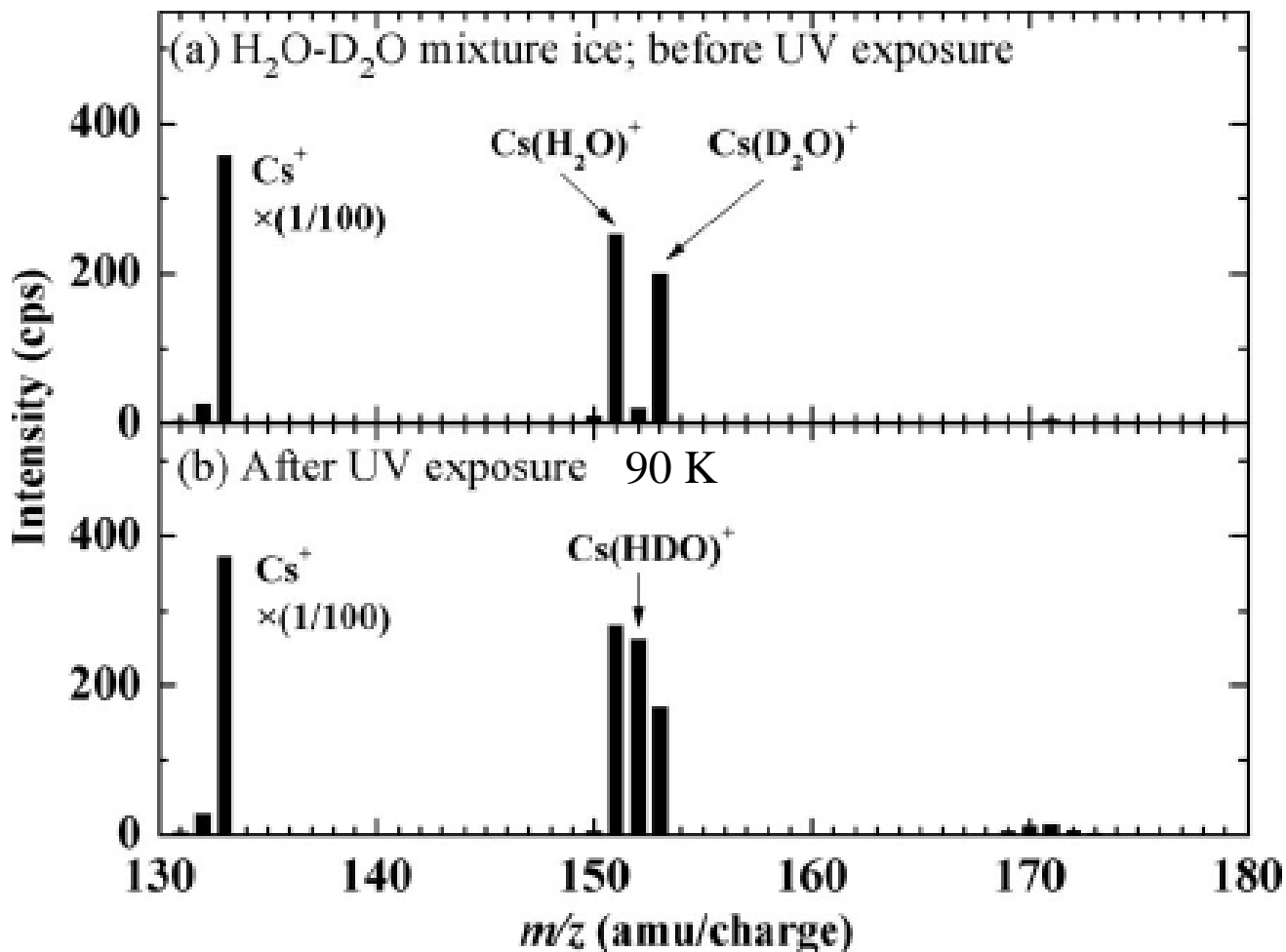
Evidence of hydronium ion formation induced by UV radiation

Experiment 1:



Intensity of MAH^+ is proportional to mobile proton on the surface

Experiment 2:

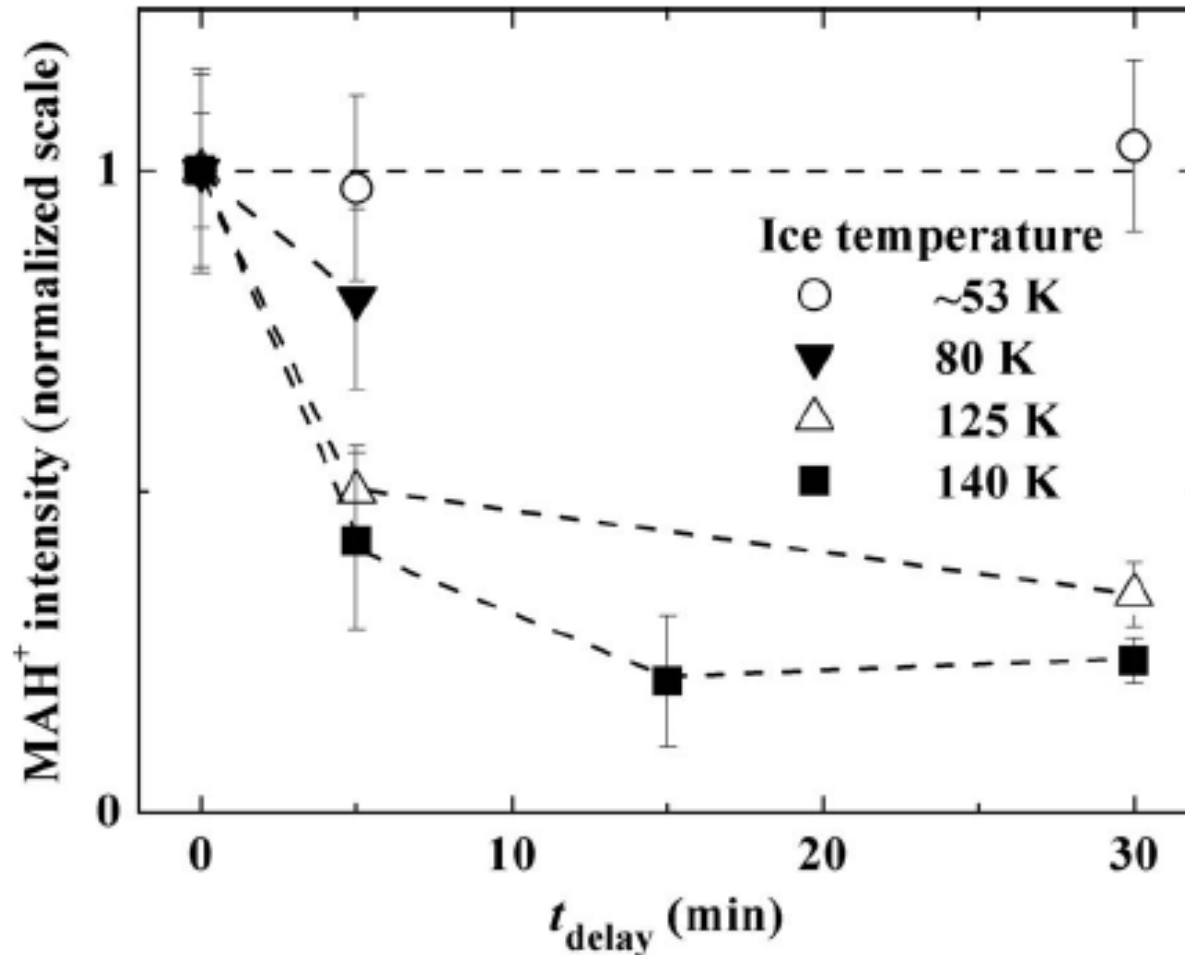


Careful ice layer deposition

The ice film (9 BL thickness) was prepared by codeposition of H_2O and D_2O vapor on Ru(0001) through separate dosing facilities. The bottom 6 BL of the film was grown in a crystalline phase at a temperature of 140 K, and the top 3 BL was grown in an ASW phase below 80 K. The low temperature employed for the growth of the upper film suppressed the thermal H/D exchange reaction of water.

Thermal and temporal stabilities of hydronium ions

Experiment 3:

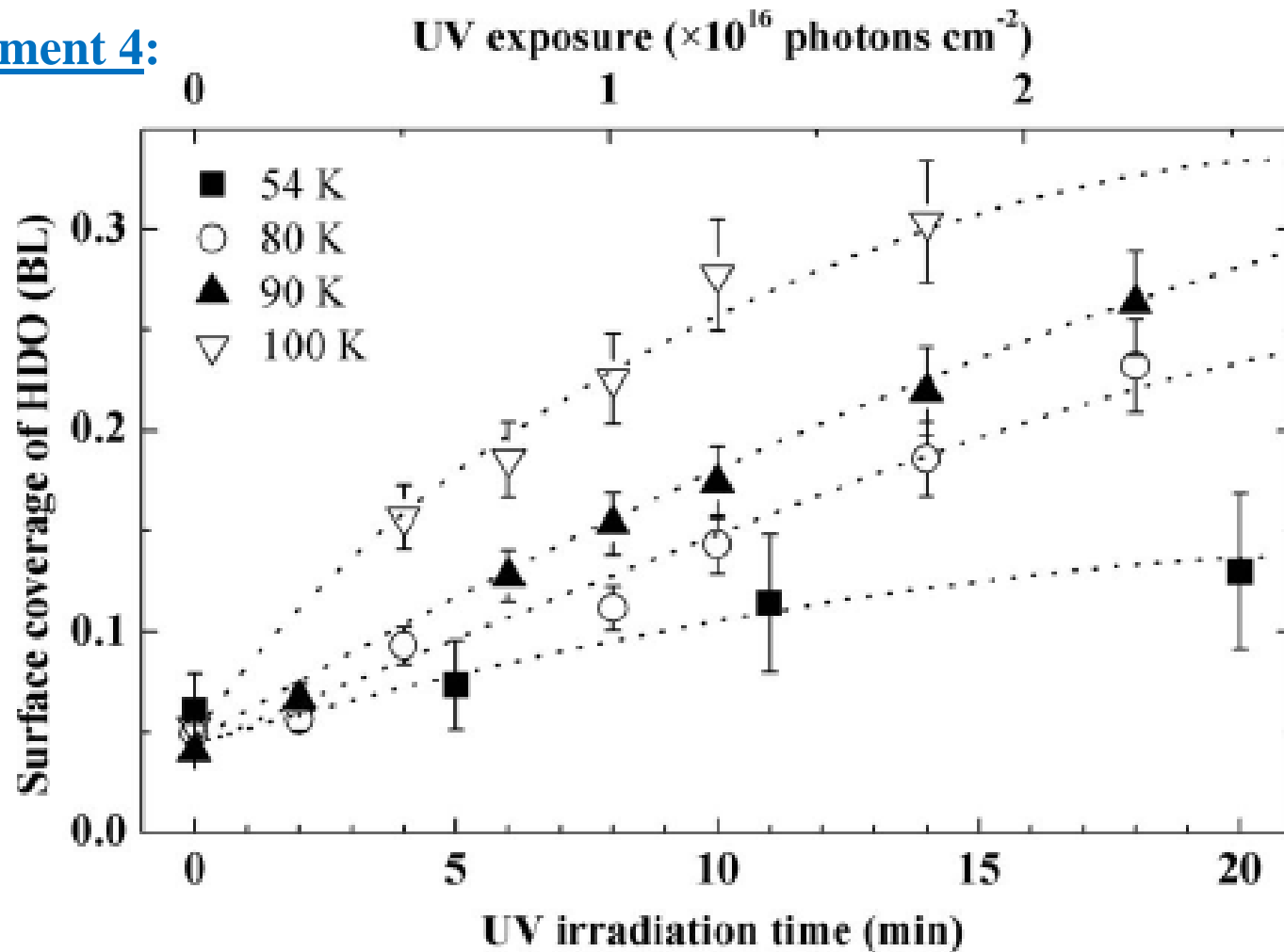


MAH⁺ signal intensity (displayed using a normalized scale) measured as a function of delay time (t_{delay}) from the termination of UV irradiation. The MAH⁺ intensity indicates the quantity of H₃O⁺ present in the ice film, as detected by MA titration experiments.

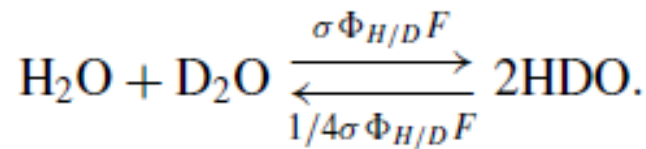
Control experiment: The stability of UV-generated hydroniums in the ice sample was examined by modifying the procedure of the MA adsorption experiment such that MA gas was adsorbed onto the ice film after a certain time delay (t_{delay}) following UV exposure. The sample was maintained at a specific temperature (T_{delay}) during the time delay.

Quantum yield of H/D exchange reaction

Experiment 4:



Variation in surface population of HDO as a function of UV exposure time at different ice film temperatures [54 K (■), 80 K (○), 90 K (▲), and 100 K (▽)]. HDO is formed by the H/D exchange reaction on the $\text{H}_2\text{O}/\text{D}_2\text{O}$ mixture ice film.



σ stands for UV absorption cross section of water molecule ($8 \times 10^{-18} \text{ cm}^2$)

$\Phi_{\text{H/D}}$ stands for quantum yield for a proton (deuteron) exchange process under water molecule, F is the photon flux ($2.1 \times 10^{13} \text{ photons cm}^{-2} \text{ s}^{-1}$).

$$\frac{1}{2} \frac{d\theta_{\text{HDO}}(t)}{dt} = \sigma \Phi_{\text{H/D}} F \theta_{\text{H}_2\text{O}}(t) \theta_{\text{D}_2\text{O}}(t) - \frac{1}{4} \sigma \Phi_{\text{H/D}} F \theta_{\text{HDO}}(t)^2. \quad \text{---- 1}$$

$\theta_X(t)$ denotes the surface coverage of species X (X = H₂O, HDO, or D₂O) and $\theta_{\text{H}_2\text{O}}(t) + \theta_{\text{HDO}}(t) + \theta_{\text{D}_2\text{O}}(t) = 1$

The above equation can be rewritten in terms of f_Y (Y = H or D) where

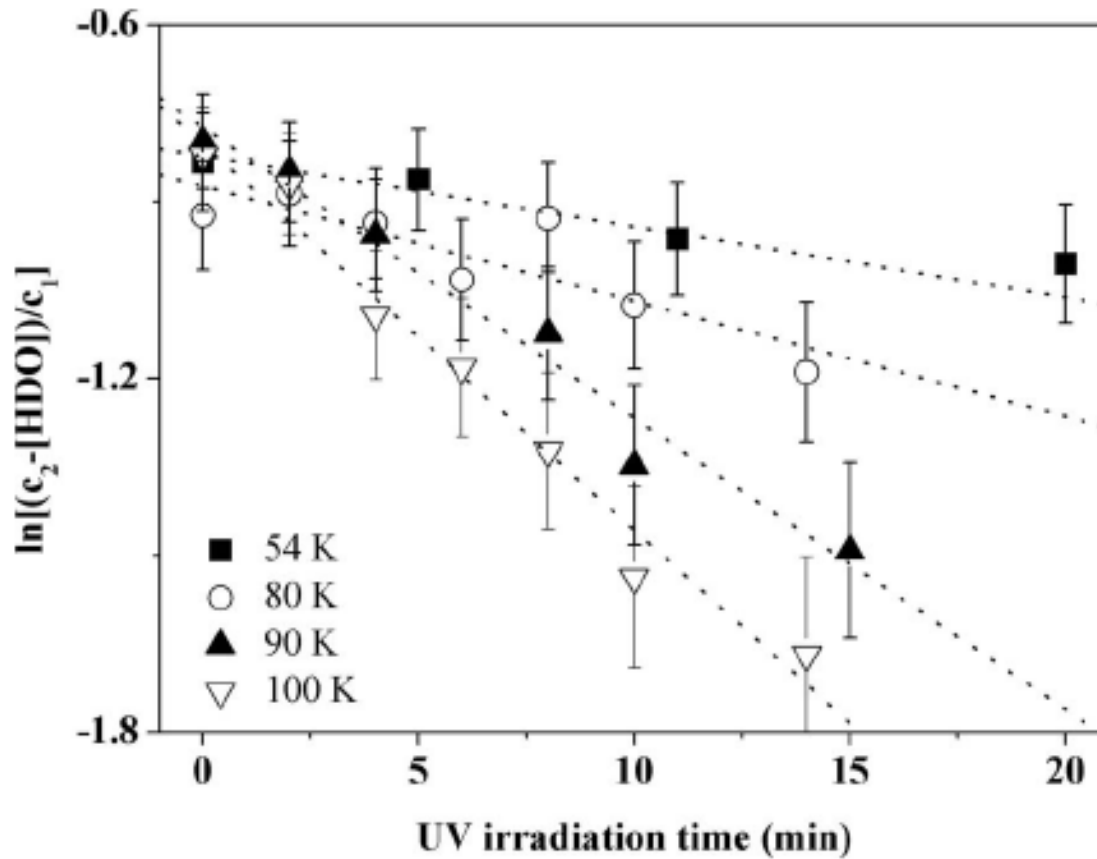
$$f_Y = \theta_{\text{Y}_2\text{O}}(t) + \theta_{\text{HDO}}(t)/2:$$

Then the reaction (1) will become

$$\frac{1}{2} \frac{d\theta_{\text{HDO}}(t)}{dt} = \sigma \Phi_{\text{H/D}} F \left(f_{\text{H}} f_{\text{D}} - \frac{1}{2} \theta_{\text{HDO}}(t) \right)$$

The solution for this differential equation is

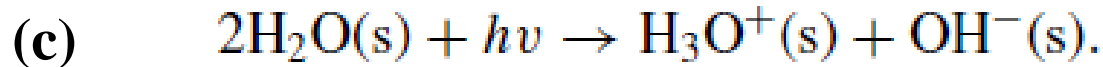
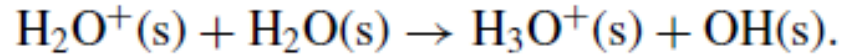
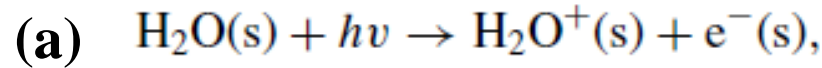
$$\begin{aligned} \theta_{\text{HDO}}(t) &= \overbrace{2f_{\text{H}}f_{\text{D}}}^{\text{Constant}} - [2f_{\text{H}}f_{\text{D}} - \theta_{\text{HDO}}(0)] \exp(-\sigma \Phi_{\text{H/D}} F t) \\ &= c_2 - c_1 \exp(-\sigma \Phi_{\text{H/D}} F t), \quad \text{---- 2} \end{aligned}$$



Kinetic plots for the change in HDO surface coverage with UV irradiation time.

Discussion:

Several channels may be responsible for the production of H_3O^+



Quantum yield of H/D exchange reaction

$$\Phi_{\text{H/D}} = N_{\text{hop}} \Phi_{\text{hyd}} \longleftarrow \text{Quantum yield of } \text{H}_3\text{O}^+$$

Quantum yield of surface water $\Phi_{\text{H/D}}^{\text{app}}$

$$\Phi_{\text{H/D}}^{\text{app}} \approx N_{\text{hop}} \Phi_{\text{hyd}} \times (\text{proton migration depth}) \approx N_{\text{hop}}^2 \Phi_{\text{hyd}}$$

Φ_{hyd} yield can be calculated from the yield of MAH^+ ion Φ_{MAH^+}

$$\Phi_{\text{MAH}^+} = \Phi_{\text{hyd}} \times (\text{proton migration depth})$$

$$\approx \Phi_{\text{hyd}} \times (\text{ice film thickness}).$$

Approximation holds when
film thickness is less like ~5
BL

Summary and conclusion:

1. UV photolysis of an ice film at photon energies of 10– 11 eV produces metastable hydroniums in the ice.
2. Evidence for the presence of hydroniums includes the formation of MAH⁺ by the acid-base reaction with MA adsorbates and the occurrence of the H/D exchange reaction in the ice.
3. The photogenerated hydroniums survive for a long time at low temperatures due to the efficient trapping of protons at defect sites as H₃O⁺.
4. A sizable portion of hydroniums survive for an extraordinarily long time even at 140 K, probably due to the deficiency of OH⁻ in comparison to H₃O⁺ in the ice sample.
5. It is suggested the possibility that metastable hydroniums play an important role in the acid-base chemistry of ice in UV-irradiated environments. For example, metastable hydroniums formed in the ice mantle of interstellar dust particles may protonate base molecules in the ice, even when the ice does not originally contain acids.

Thank you

1. Here it is not described that during the deposition of MA, mechanism of dissipation of the excess energy released by the MA vapor before it comes solid. This may increase the proton hopping on the surfaces hence the kinetics data may be misleading.
2. UV irradiation followed ion scattering (low energy H^+ or CH_2^+) may be a good experimental procedure at a particular temperature to confirm it that H/D exchange has taken place.