

H atom formation from the photodissociation of ice at 193 nm

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【Introduction】

Several experimental studies on VUV photodissociation of water adsorbed on cold surfaces have been reported. However at around 200 nm there has been no experimental study because it has been believed that the ice is almost completely opaque for photons of longer than 160 nm. Dressler and Schepp reported in 1960 a region of weak and continuous absorption extended from 180 to 210 nm. In the present experiment we have investigated the UV photodissociation dynamics of water ice at 193 nm. Our purpose is directly to observe the formation of hydrogen atoms and estimate its influence on the mesosphere ozone depletion since there are appreciable amounts of small water-ice particles including the noctilucent clouds (NLCs) in the high-latitude mesopause region and the solar radiation at 200 nm is much stronger than at Lyman- α line in the VUV region

【Experimental】

Hydrogen atom formation from the photodissociation of ice was carried out in an ultrahigh vacuum chamber, which was equipped with two turbo molecular pumps in tandem, a pulsed molecular beam, an excimer laser, and a dye laser (Fig.1). Ice films were prepared on sapphire substrates, which is cooled with liquid N₂. The substrate temperature is about 90 K. The chamber pressure was 0.5×10^{-8} without sample molecules injection. Ice film was photodissociated at 193 nm with an ArF excimer laser (10 Hz, $0.5 \text{ mJcm}^{-2}\text{pulse}^{-1}$) and at 248 nm with a KrF excimer laser. YAG pumped dye laser pulse (0.2 mJpulse^{-1} at UV) was used to ionize the photofragment by (2 + 1) resonance-enhanced multiphoton ionization (REMPI) for hydrogen atoms. The subsequent REMPI signals of the hydrogen atoms were detected by a time-of-flight mass spectrometer. The distance, l , between the substrate and the detection region was set to 3 mm. TOF spectra were taken as a function of time delay, t , between photolysis and probe pulses, which correspond to the flight time between the substrate and the detection region.

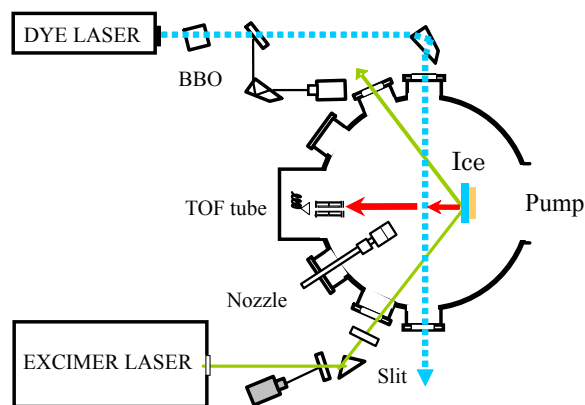


Fig.1 Schematic diagram of experimental setup

【Results and Discussion】

Hydrogen photofragments from the 193 nm photodissociation of ice were observed, which have both fast and slow components. Typical TOF spectra are shown in Fig.2. Channel **A** is the fast component which comes from the topmost water molecules and Channel **B** is the slow component which comes from the second, third and lower surface layers. For ASW channel **B** is dominant and becomes weaker for crystalline ice. Both components (channel A and B) are flux-weighted Maxwell-Boltzmann distributions. The fast component is characterized by $2k_B T_{\text{trans}} = 0.39 \pm 0.04 \text{ eV}$ ($2300 \pm 200 \text{ K}$). For the slow component, the energy distribution is characterized by $2k_B T_{\text{trans}} = 0.02 \text{ eV}$ ($120 \pm 20 \text{ K}$).

According to our theoretical calculation, the water molecules on ice surface may have a character similar to a water molecule attached to a $(\text{H}_2\text{O})_6$ that absorbs 200 nm photon. (Fig.3). Thus, surface water molecules can absorb 193 nm photons to produce H atoms.

About atmospheric implication of the present results, we have estimated relative contribution of the ice particle (NLCs) photodissociation to the hydrogen atom formation near the high-latitude mesopause region, comparing with that of water vapor photodissociation as shown in Fig.4.

$$\frac{H_{\text{ice}}}{H_{\text{vapor}}} = \frac{\int_{\lambda} d\lambda \sigma_i(\lambda) \times P_i(\lambda) \times \phi_i(\lambda) \times C_i}{\int_{\lambda} d\lambda \sigma_v(\lambda) \times P_v(\lambda) \times \phi_v(\lambda) \times C_v} \leq 0.5$$

where H stands for the amount of H, σ : absorption cross section, P: solar flux, ϕ : quantum yield = 0.01, C: concentration. Our estimate indicates that the photodissociation of NLCs could be another important source of H atoms by solar UV irradiation at around 200 nm.

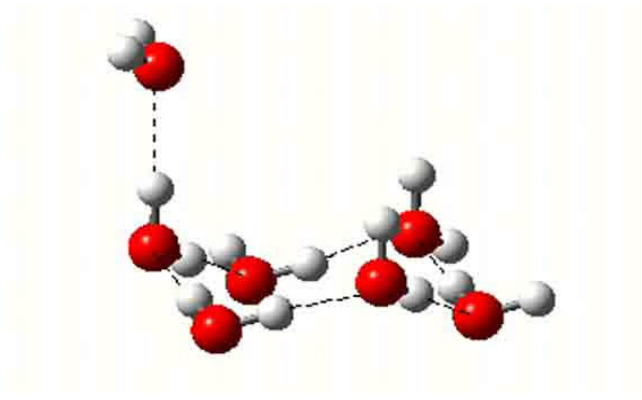


Fig.3 Optimized structure of the $(\text{H}_2\text{O})_{6+1}$ water cluster calculated at the HF/6-311++G(d,p) level. A water molecule is hydrogen-bonding to a model crystalline surface consisting of $(\text{H}_2\text{O})_6$.

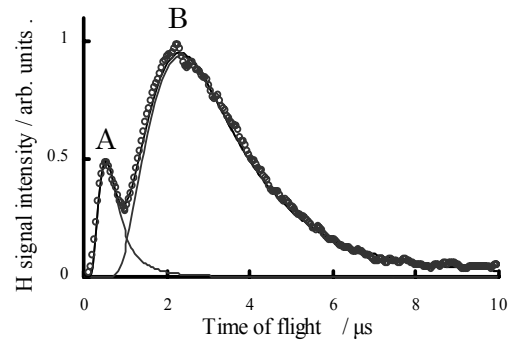


Fig.2 Time-of-flight spectra of H atoms from 193 nm dissociation of amorphous ice.

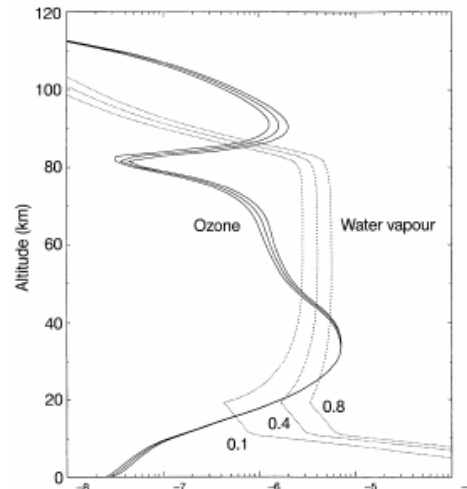


Fig.4 Model global mean diurnally averaged ozone profiles for different water-vapour profiles computed by setting the surface relative humidity equal to 0.8, 0.4 and 0.1, using channel a only for the reaction $\text{H} + \text{HO}_2$ and $\alpha = 1$