Formation of oxygen molecules following vacuum ultraviolet photodissociation of amorphous solid water

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The effect of radiation on water ice has intrigued many scientists in the fields of interstellar chemistry and planetary ice science as well as reaction dynamics, since water is the predominant component of interstellar icy grain mantles in dense molecular clouds and small solar system bodies such as comets. Oxygen molecule is known to be a product when water ice is irradiated with photons, electrons, or with energetic ions. These experimental studies indicate that VUV photodissociation of amorphous solid water (ASW) leads to secondary reactions that result in molecular oxygen formation on or in ASW. Photodissociation of H_2O in the first absorption band of water ice (130–165 nm) involves mainly two primary processes.

$$H_2O + h\nu \rightarrow H + OH(v=0 \text{ and } 1) \quad (1)$$
$$H_2O + h\nu \rightarrow H_2 + O(^1D) \quad (2)$$

For the electronically ground $O(^3P)$ production, two different formation mechanisms were proposed: the exothermic recombination reaction of OH, and the photodissociation of OH on the ASW surface.[1]

$$OH + OH \rightarrow H_2O + O(^3P) \quad \Delta H = -67 \text{ kJ mol}^{-1} \quad (3)$$
$$OH + h\nu \rightarrow H + O(^3P) \quad (4)$$

From the fact that OH(v=0 and 1) and $O(^3P)$ are formed with large excess energy via reactions (1), (3) and (4), $O_2(X^3\Sigma_g^-)$ and $O_2(a^1\Delta_g)$ can be produced via subsequent reactions (5) and (6) in the 157 nm photolysis of ASW.[2]

$$OH + O(^3P) \rightarrow O_2(X^3\Sigma_g^-) + H \quad \Delta H = -68 \text{ kJ mol}^{-1} \quad (5)$$
$$OH + O(^3P) \rightarrow O_2(a^1\Delta_g) + H \quad \Delta H = 26 \text{ kJ mol}^{-1} \quad (6)$$

Measurements of the translational and internal energy distributions of the photoproducts generated from photodissocaiton of ASW allow assessment of possible secondary reactions on/in ASW from reaction dynamics point of view. In the present work, we have investigated the kinetic and internal energy distributions of $O_2(X^3\Sigma_g^-, v=0)$ and $O_2(a^1\Delta_g, v=0)$ following 157 nm photodissociation of ASW at 90 K using the resonance-enhanced multiphoton-ionization (REMPI) method.[3]

References

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