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Role of OH radicals in the formation of oxygen molecules following vacuum ultraviolet photodissociation of amorphous solid water

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Photodesorption of O2(3Σg−) and O2(a 1Δg) from amorphous solid water at 90 K has been studied following photoexcitation within the first absorption band at 157 nm. Time-of-flight and rotational spectra of O2 reveal the translational and internal energy distributions, from which production mechanisms are deduced. Exothermic and endothermic reactions of OH+O(3P) are proposed as plausible formation mechanisms for O2(3Σg−) and a 1Δg). To examine the contribution of the O(3P)+O(1P) recombination reaction to the O2 formation following 157 nm photolysis of amorphous solid water, O2 products following 193 nm photodissociation of SO2 adsorbed on amorphous solid water were also investigated. © 2010 American Institute of Physics.

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I. INTRODUCTION

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.1,2 Oxygen molecule is known to be a product when water ice is irradiated with photons, electrons, or with energetic ions.3–6 Westley et al.7,8 observed desorption of H2, O2, and H2O by a quadrupole mass spectrometer (QMS) during vacuum ultraviolet (VUV) irradiation of water ice at 35–100 K with mainly Lyman-α photons (λ ≈ 121 nm). Öberg et al.9 used a VUV lamp (118 nm ≤ λ ≤ 177 nm) to irradiate water ice at 18–100 K, and detected OH, H2, O2, and H2O as desorbing species by QMS. 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.

Various primary processes are energetically possible following photoexcitation of water ice at λ ≤ 130 nm,10–12 whereas photodissociation of H2O in the first absorption band of water ice (130–165 nm) involves mainly two primary processes,10,13,14

\[
\text{H}_2\text{O} + h\nu \rightarrow \text{H} + \text{OH},
\]

\[
\text{H}_2\text{O} + h\nu \rightarrow \text{H}_2 + \text{O}(1\text{D}).
\]

Measurements of the translational and internal energy distributions of the photoproducts generated from photodissociation of ASW allow the assessment of possible secondary reactions on/in ASW from reaction dynamics point of view. The translational and internal energy distributions of OH(v=0,1) radicals and O(1D) and 3P atoms were previously measured following 157 nm photodissociation of ASW.15–17 For the O(3P) production, two different formation mechanisms were proposed: the exothermic recombination reaction of OH and the photodissociation of OH on the ASW surface.17

\[
\text{OH} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{O}(3\text{P}), \quad \Delta H = -67 \text{ kJ mol}^{-1},
\]

\[
\text{OH(ads)} + h\nu \rightarrow \text{H} + \text{O}(3\text{P}).
\]

Thermodynamic data are calculated using solid phase data for the condensed or adsorbed species (“ads”) and the gas phase data for other species.18–20 From the fact that OH(v=0 and 1) and O(3P) are formed with large excess energy via reactions (1), (3), and (4),15,17 O2(3Σg−) and O2(a 1Δg) can be produced via subsequent reactions (5) and (6) in the 157 nm photolysis of ASW:

\[
\text{OH} + \text{O}(3\text{P}) \rightarrow \text{O}_2(3\Sigma_g^-) + \text{H}, \quad -68,
\]

\[
\text{OH} + \text{O}(3\text{P}) \rightarrow \text{O}_2(a 1\Delta_g) + \text{H}, \quad 26.
\]

Reaction (5) is a barrierless process in the gas phase.21 OH(v=1) has a sufficient vibration energy of 43 kJ mol−1 to proceed in reaction (6).22 In fact, Lunt et al.23 observed the formation of O2(a 1Δg) via the reaction of O(3P) and vibrationally excited OH(v≥1) in the gas phase by monitoring the near-infrared emission at 1.27 μm from the product O2(a 1Δg).

In the present work, we have investigated the kinetic and internal energy distributions of O2(3Σg−, v=0) and O2(a 1Δg, v=0) following 157 nm photodissociation of ASW at 90 K using the resonance-enhanced multiphoton ionization (REMPI) method. H2O2 photolysis experiments have also been performed at 157 nm to elucidate the role of OH in the O2 formation. In addition, we have also studied desorption of O2 following 193 nm photolysis of SO2 adsorbed on ASW to measure the kinetic and internal energy

\[\text{H}_2\text{O}+\nu\rightarrow\text{H}+\text{OH},\]

\[\text{H}_2\text{O}+\nu\rightarrow\text{H}_2+\text{O}(1\text{D}).\]
distributions of O₂ formed via highly exothermic recombination reaction of two O(³P), i.e., reaction (7), which was proposed as a source for O₂(X ³Σ₋₋) formation in VUV photon and electron irradiations of ASW,8,24

\[ \Delta H \text{ (kJ mol}^{-1} \text{)} = O(³P) + O(³P) + M \rightarrow O₂(X ³Σ₋₋) + M, \quad -498. \tag{7} \]

II. EXPERIMENTAL

A. Apparatus and preparation of ice

A photodissociation study of ASW at 90 K was carried out in an ultrahigh vacuum chamber, which was equipped with two turbomolecular pumps in tandem, a pulsed molecular beam, an excimer laser, and a dye laser. Experimental details are described elsewhere.25 A vacuum chamber was evacuated to a base pressure of 10⁻⁶ Torr by turbomolecular pumps (800 and 50 L s⁻¹). ASW was prepared with the backfilling deposition of water vapor for 60 min onto an optically flat sapphire disk substrate, sputter coated with a thin polycrystalline film of Au(111) cooled by liquid nitrogen at 90 K. The exposure was typically 1500 L (1 L=1×10⁻⁶ Torr s). This exposure resulted in the formation of roughly 500 ML (monolayer) of H₂O on the substrate if we adopt the reported experimental conversion factor of 1 ML deposition by 3 L exposure,26 which is sufficiently thick to neglect the possible influence of reactions at the ASW/Au substrate interface and of any photoelectrons from the Au substrate.27 For the concentrated H₂O₂ photolysis experiments, a commercially available H₂O₂ solution (30%) was concentrated in a glass container by vacuum distillation, and the H₂O₂/H₂O vapor was deposited on ASW. The exposure of the codeposited H₂O₂/H₂O mixture on ASW was ~8 L at 90 K. For SO₂ photolysis experiments at 90 K, prepared ASW was exposed to a mixture gas of SO₂(5%) + N₂(95%) for 300 s, which resulted in net 8 L exposure of SO₂ on ASW. The surface of SO₂/water ice was kept refreshed by intermittent exposure of the SO₂ mixture gas to ASW during 93 nm photolysis experiments. In this experiment, a pulsed valve was opened after each laser shot so as to deposit a fresh layer of SO₂. The chamber pressure was 5×10⁻⁷ Torr during the intermittent deposition.

To photolyze water ice, unfocused 157 nm (or 193 nm) laser radiation was directed onto the ice surface at an angle of either ~80° or 45° to the surface normal. A suitable slit was used for the laser irradiation area to have the disk substrate with a radius of 6 mm. The incident fluence F was typically <0.1 mJ cm⁻² pulse⁻¹ at 157 nm in 15 ns pulse duration. The F value at 193 nm was <1.0 mJ cm⁻² pulse⁻¹. 193 nm irradiation of ASW produced no measurable REMPI signals of O₂(X ³Σ₋₋) and a ¹Δ g₁ and OH at such low incident intensities, although H atom photofragments from dimerlike water molecules on ASW surface were observed following 193 nm photodissociation of ASW.26,29

Photodesorbed O₂(X ³Σ₋₋) were ionized at a vertical distance of 2 mm from the ice surface by 2+1 REMPI process via the C ³Π°C(v′=2) → X ³Σ₋₋(v″=0) at 283–289 nm produced by frequency doubling the output of a Nd³⁺:YAG (yttrium aluminum garnet) pumped dye laser (Lambda Physik, Göttingen, SCANmate),30,31 and collected with a small mass spectrometer aligned perpendicular to the ice surface. Electronically excited O₂(ν ¹Δ g₁, ν=0) photodesorbed from ASW has also been observed with the same experimental setup via the d ³Π₅(ν′=1) → a ¹Δ g₁(ν″=0) REMPI transitions at 329–332 nm.32 Johnson III et al.31 suggested that the REMPI cross section for O₂(ν ¹Δ g₁) is at least an order of magnitude greater than that for O₂(X ³Σ₋₋). Photodesorbed O(³Pₖ=2,1,0) atoms were ionized by the 2+1 REMPI transition via the O(³Pₖ=2,1,0) transition at 225.6–226.4 nm.17 We tried to search for REMPI signals of oxygen molecules in the higher electronically excited states, i.e., b ³Σ⁺, c ³Σ₋₋, and ⁵Π using the REMPI transitions reported by Morrill et al.32 and Slinger and Copeland,33 but no evidence for these products was obtained.

### II. SPECTRAL ANALYSIS

#### A. Simulation of 2+1 REMPI spectra of oxygen molecules

1. O₂(X ³Σ₋₋, ν=0,1,2,3)

The spectra were simulated using the program PGOPHER,34 a program for simulating the rotational structure accompanying multiphoton electronic transitions. The simulated spectra were used to the estimate values of the rotational temperatures of the oxygen products. Spectroscopic parameters for the X ³Σ₋₋(ν″=0,1) and C ³Π₅(ν′=2) states of O₂ are summarized in Table I.30,35–39 For spectral simulations of 2+1 REMPI via the sequence bands of the

<table>
<thead>
<tr>
<th>State origins</th>
<th>Rotational constant B</th>
<th>Centrifugal distortion constant D</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>C ³Π₅(ν=2), F₃(Ω=0)</td>
<td>69 353</td>
<td>1.633</td>
<td>1.5</td>
</tr>
<tr>
<td>C ³Π₅(ν=2), F₃(Ω=1)</td>
<td>69 437</td>
<td>1.665</td>
<td>1.0</td>
</tr>
<tr>
<td>C ³Π₅(ν=2), F₃(Ω=2)</td>
<td>69 548</td>
<td>1.685</td>
<td>1.3</td>
</tr>
<tr>
<td>d ³Π₅(ν=2)</td>
<td>70 011</td>
<td>1.29</td>
<td></td>
</tr>
<tr>
<td></td>
<td>70 142</td>
<td>1.12</td>
<td></td>
</tr>
<tr>
<td>X ³Σ₋₋(ν=1)</td>
<td>1556.3</td>
<td>1.422</td>
<td>4.8402</td>
</tr>
<tr>
<td>X ³Σ₋₋(ν=0)</td>
<td>0</td>
<td>1.438</td>
<td>4.8390</td>
</tr>
</tbody>
</table>

*Second entry refers to the extra level H ³Π₅(ν=8) (see Ref. 35).*
C $^3\Pi_g(v'=v''+2) \leftrightarrow X^3\Sigma_g^-(v'')$ transitions for $v''=1, 2, \text{and } 3$, the literature constants for $C^3\Pi_g(v'=2)$ and $X^3\Sigma_g^-(v''=1)$ were adopted$^{35-39}$ since no information is available on the vibrationally excited levels. Although White and Beuhler$^{30}$ reported some assignments of the $2+1$ REMPI spectrum via the $C^3\Pi_g(v'=2) \rightarrow X^3\Sigma_g^-(v''=0)$ transition, the Rydberg-valence state interactions with the repulsive $H^3\Pi_g$ valence state resulted in highly perturbed rotational structures and large predissociation linewidths in the triplet manifold of the excited states. $O_2(X^3\Sigma_g^-, v=0)$ via the spin forbidden REMPI $d^1\Pi_g(v'=2) \rightarrow X^3\Sigma_g^-(v''=0)$ transition was also included in the spectral simulation,$^{31,35}$ and the contribution to the observed $O_2(X^3\Sigma_g^-, v=0)$ REMPI signals was found to be very small, less than 3%.

Rotational energy, $E_{\text{rot}}$, is characterized $\langle E_{\text{rot}} \rangle = k_B T_{\text{rot}}$, where $k_B$ and $T_{\text{rot}}$ are the Boltzmann constant and the rotational temperature, respectively.

2. $O_2(a^1\Delta_g, v=0)$

Morrill et al.$^{32}$ reported the complex rotational structures in the REMPI spectra via the five $d^1\Pi_g(v'=0–4)$ states due to the strong perturbations between $d^1\Pi_g$ Rydberg and $H^1\Pi_g$ valence states. The spectral segmenting is the result of avoided crossings between the rotational level manifolds of $d^1\Pi_g(v'=1)$ and $H^1\Pi_g(v'=5, 6, 7)$.$^{32}$ Unfortunately, we could not estimate the rotational temperature of the $O_2(a^1\Delta_g, v=0)$ products because of these strong interactions.

B. Simulation of time-of-flight spectra of desorbed oxygen molecules

Time-of-flight (TOF) spectra of photoproducts were taken as a function of time, $t$, between the photolysis and REMPI laser pulses using a delay generator (Stanford Research) to investigate the translational energies of desorbing photoproducts. The measured TOF spectra, $S(t, T_{\text{trans}})$, were fitted to a sum of flux-weighted Maxwell–Boltzmann (MB) distributions, $S_{\text{MB}}$, with coefficients $a_i$, which are defined by a translational temperature, $T_{\text{trans}}$. Details regarding the simulation of such TOF spectra have been reported previously,$^{25}$

$$S(t, T_{\text{trans}}) = \sum a_i S_{\text{MB}}(t, T_{\text{trans}}),$$

$$S_{\text{MB}}(t, T_{\text{trans}}) = r^3 t^{-4} \exp\left[-mr^2/2k_B T_{\text{trans}}^2\right],$$

where $r$ is the flight distance to the REMPI probe region. In these calculations we assume that signals come from a disk area (UV photolysis area) with a radius of 6 mm. The MB distribution, $P_{\text{MB}}(E_{\text{trans}})$, as a function of translational energy, $E_{\text{trans}}$, is characterized by the averaged translational energy, $\langle E_{\text{trans}} \rangle$.$^{40}$

$$P_{\text{MB}}(E_i) = (k_B T_{\text{trans}})^{-2} E_i \exp\left[-E_i/k_B T_{\text{trans}}\right].$$

Conversion from the $E_i$ distribution to the TOF distribution was performed using the Jacobian given by Zimmerman and Ho.$^{41}$ The angular distribution of the molecules photodesorbed from the ice surface was assumed to follow a cos$^2 \theta$ function, where $\theta$ is the surface polar coordinate. $n=0$ was adopted in the present best-fit procedures.$^{25,42}$

IV. RESULTS

A. Kinetic and rotational energy distributions of $O_2$ following 157 nm photodissociation of ASW

1. $O_2(X^3\Sigma_g^-, v=0)$

Figure 1(a) shows a 2+1 REMPI spectrum following 157 nm photodissociation of ASW at a fixed delay $t=1.5$ $\mu$s that corresponds to the peak TOF, as shown in Fig. 2. Highly perturbed rotational structures were observed in Fig. 1(a). By comparison with the spectral simulation for $O_2(X^3\Sigma_g^-, v=0)$ shown in Fig. 1(c), $T_{\text{rot}}$ was estimated to be ~2000 K at $t$ = 1.5 $\mu$s. Figure 2 shows a typical TOF spectrum at 286.127 nm, which is characterized by $T_{\text{trans}} = 4500 \pm 1000$ K and 500 $\pm$ 200 K. These results are summarized in Table II. Changing the REMPI probe wavelength to other wavelengths, no discernible change in the TOF profiles was ob-

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FIG. 1. 2+1 REMPI spectra of $O_2$ (a) following 157 nm photodissociation of ASW. Time-of-flight is 1.5 $\mu$s; (b) following 193 nm photodissociation of SO$_2$/ASW mixed ices. Time-of-flight is 1.5 $\mu$s. [(c)-(f)] Spectral simulation $C^3\Pi_g(v'=v''+2) \rightarrow X^3\Sigma_g^-(v'')$ transition, (c) $v''=0$ assuming a Boltzmann rotational state population distribution with $T_{\text{rot}}=2000$ K, and (d) $v'=1$, (e) $v'=2$, and (f) $v'=3$ assuming $T_{\text{rot}}=8000$ K. (g) Accumulated spectrum of (c), (d), (e), and (f) with the relative ratios of 0.05:0.2:1:1.

FIG. 2. Time-of-flight spectrum of $O_2(X^3\Sigma_g^-, v=0)$ at a REMPI wavelength of 286.127 nm following 157 nm photodissociation of ASW. The solid curves are fits to the data derived with $T_{\text{trans}}=4500$ and 500 K.
TABLE II. Translational and rotational temperatures of oxygen molecules following 157 nm photolysis of ASW and 193 nm photolysis of SO₂ on ASW at 90 K.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Translational temperature $T_{\text{trans}}$ (K)</th>
<th>Averaged translational energy $\langle E_{\text{trans}} \rangle$ (kJ mol⁻¹)</th>
<th>Rotational temperature $T_{\text{rot}}$ (K)</th>
<th>Averaged rotational energy $\langle E_{\text{rot}} \rangle$ (kJ mol⁻¹)</th>
<th>Reaction mechanism</th>
</tr>
</thead>
<tbody>
<tr>
<td>$O_2(X^3\Sigma_g^-, v=0)$ from ASW</td>
<td>4500 ± 1000 (70%)</td>
<td>75 ± 17</td>
<td>−2000 b</td>
<td>−17 d</td>
<td>OH+O(³P)</td>
</tr>
<tr>
<td></td>
<td>500 ± 200 (30%)</td>
<td>8 ± 3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$O_2(a^1\Delta_g, v=0)$ from ASW</td>
<td>2500 ± 500 c</td>
<td>42 ± 8</td>
<td></td>
<td></td>
<td>OH+O(³P)</td>
</tr>
<tr>
<td></td>
<td>250 ± 100</td>
<td>4 ± 2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$O_2(X^3\Sigma_g^-, v=1-3)$ from SO₂ on ASW</td>
<td>3000 ± 1000 (55%)</td>
<td>50 ± 17</td>
<td>−8000 b</td>
<td>−67 d</td>
<td>O(³P)+O(³P)</td>
</tr>
<tr>
<td></td>
<td>500 ± 200 (45%)</td>
<td>8 ± 3</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1 Percentage in the parenthesis is a contributions of each temperature component.
2 Measured at time-of-flight=1.5 μs.
3 Each contribution depends on REMPI wavelength. See text for details.
4 Not estimated. See text for details.
5 With the relative ratios of 0.2: 1: 1 for $v=1: 2: 3$.

We were unable to estimate a rotational temperature for the $T_{\text{trans}}=500$ K component because of weak REMPI spectrum intensity.

2. $O_2(a^1\Delta_g, v=0)$

Figures 3(a) and 3(b) show REMPI spectra following 157 nm photolysis of ASW, which were recorded at (a) $t=2.0$ μs and (b) 10.0 μs. Figure 4 shows TOF spectra at the two different REMPI wavelengths, (a) 329.965 nm for a high rotational level, and (b) 331.215 nm for a low rotational level. The TOF spectra are reproduced by two MB distributions with $T_{\text{trans}}=2500 \pm 500$ K and 250 ± 100 K with different contributions: (a) 80% and 20% at 329.965 nm and (b) 15% and 85% at 331.215 nm, respectively.

B. Evolution of $O_2$ signal intensity as a function of 157 nm photoirradiation time in the ASW photolysis

1. $O_2(X^3\Sigma_g^-, v=0)$

The solid black line in Fig. 5(a) shows the time evolution of the $O_2(X^3\Sigma_g^-, v=0)$ signal intensity at 286.127 nm recorded at $t=1.5$ μs as a function of 157 nm irradiation time on ASW. For comparison purpose, Fig. 5(a) includes the time evolution of photodesorbed O(³P₂) signal intensity that was recorded at the peak of TOF, i.e., $t=4.5$ μs. The behaviors of $O_2(X^3\Sigma_g^-, v=0)$ and O(³P₂) signals are in accordance to each other. Previously reported time evolution of the OH signal due to the H₂O₂ photoproduct on the 157 nm photoirradiated ASW surface was also included in Fig. 5(a), which reflects the concentration of photogenerated H₂O₂ on the ice surface. 15,43 The $O_2(X^3\Sigma_g^-, v=0)$ REMPI signal increases faster than that of the H₂O₂ accumulated photolytically on the water ice surface.

2. $O_2(a^1\Delta_g, v=0)$

Figures 5(b) and 5(c) show time evolution curves of $O_2(a^1\Delta_g, v=0)$, which were recorded at (b) $t=2.0$ μs for $O_2(T_{\text{trans}}=2500$ K) at a high rotational level REMPI wavelength of 329.965 nm, and (c) $t=10.0$ μs for $O_2(T_{\text{trans}}=250$ K) at a low rotational level REMPI wavelength of 331.215 nm. Figures 5(b) and 5(c) also show the time evolution of the secondary photoproduction H₂O₂. 15,43 The curve for $O_2(T_{\text{trans}}=2500$ K) matches to that for H₂O₂. In addition, $O_2(T_{\text{trans}}=2500$ K) signals were observed promptly after 157 nm irradiation of H₂O₂/H₂O mixed ices, suggesting that the source of $O_2(T_{\text{trans}}=2500$ K) is photochemically produced H₂O₂ by 157 nm irradiation on ASW.

On the other hand, the $O_2(T_{\text{trans}}=250$ K) component appeared promptly upon 157 nm irradiation of ASW, as shown in Fig. 5(c). These results suggest that the source of the
Oxygen molecules following photolysis of ice


FIG. 5. (a) Time evolutions of O$_2$(X $^3\Sigma^-$, v=0) (black line) at t=1.5 $\mu$s at 286.127 nm and O($^3P_g$) (gray line) from ASW as a function of 157 nm irradiation time. The O($^3P_g$) signal was recorded at the peak time-of-flight of signal, t=4.5 $\mu$s. (b) and (c) Time evolutions of the O$_2$(a $^1\Delta_g$, v=0) at (b) t=2.0 $\mu$s (red line) at 329.965 nm and (c) t=10.0 $\mu$s (blue line) at 331.215 nm from ASW as a function of 157 nm irradiation time. Open circles in (a)–(c) represent the time evolution of H$_2$O$_2$ photoproducts accumulated on ASW (Refs. 15 and 43). (d) Expanded time evolution curves of the O$_2$(X $^3\Sigma^-$, v=0) (black line), O$_2$(a $^1\Delta_g$, v=0) (blue line), and O($^3P_g$) (gray line) signal intensity as a function of 157 nm irradiation time on ASW. The signal intensity of O$_2$(a $^1\Delta_g$, v=0) is adjusted for comparison.

FIG. 6. Time evolution curve of the vibrationally excited O$_2$(X $^3\Sigma^-$) REMPI signal at 285.038 nm as a function of SO$_2$ exposure time at 157 nm at t =1.5 $\mu$s.

FIG. 7. Time-of-flight spectrum of O$_2$ following 193 nm photolysis of SO$_2$/H$_2$O mixed ice

C. O$_2$ products following 193 nm photolysis of SO$_2$/H$_2$O mixed ice

193 nm irradiation of neat ASW produced no measurable REMPI signals of O$_2$(X $^3\Sigma^-$, v=0) and O$_2$(a $^1\Delta_g$, v=0). However, as SO$_2$ was deposited on ASW, m/z=32 signal was observed at 285.038 nm and its intensity increased, as shown in Fig. 6, i.e., O$_2$ was photodesorbed via reaction (7) following 193 nm photolysis of adsorbed SO$_2$ on ASW. Figure 1(b) shows a REMPI spectrum of O$_2$ following the 193 nm photolysis time at t=1.5 $\mu$s that corresponds to the peak TOF of O$_2$ in Fig. 7. The TOF spectrum in Fig. 7 is characterized by $T_{\text{trans}}=3000 \pm 1000$ K and 500 $\pm$ 200 K. These results are summarized in Table II. O$_2$(a $^1\Delta_g$, v=0) failed to be detected at 329–332 nm.

V. DISCUSSION

The 157 nm photolysis involves two primary processes; reactions (11) and (12),

H$_2$O(ads) + hv(157 nm) → H + OH(v = 0 and 1), (11)

H$_2$O(ads) + hv(157 nm) → H$_2$ + O($^3P$). (12)

In the case of 157 nm photolysis ($E_{\text{photon}}$=762 kJ mol$^{-1}$), the available energies for reaction (11) is $E_{\text{avail}}$(11) =220 kJ mol$^{-1}$ for OH(v=0), and $E_{\text{avail}}$(12)=38 kJ mol$^{-1}$. O($^3P$) atoms via reaction (12) were successfully detected following 157 nm photolysis of ASW, but would play only a minor role in the present study, considering the small quantum yields ($\leq$0.01 for 145–185 nm) in the gas phase, and high reactivity of O($^3P$) with parent H$_2$O molecules by collisions with ASW to produce OH or H$_2$O$_2$.

Our previous study showed that O($^3P$) atoms were photodesorbed immediately after 157 nm irradiation started, and are mainly formed by recombination of two OH radicals moving on the ASW surface, i.e., reaction (13),

OH + OH → H$_2$O + O($^3P$), $\Delta H = -67$ kJ mol$^{-1}$. (13)

Considering reactions (11) and (13), we will discuss three possible O$_2$ desorption mechanisms; exothermic and endo-
thermic reactions of OH with O(3P), i.e., reactions (14) and (15), and two O(3P) recombination reaction, i.e., reaction (16),

\[ \Delta H \text{ (kJ mol}^{-1} ) \]

\[ \text{OH} + \text{O}(3P) \rightarrow \text{O}_2(3\Sigma^-_g) + \text{H}, \quad -68, \quad (14) \]

\[ \text{OH} + \text{O}(3P) \rightarrow \text{O}_2(a^1\Delta_g) + \text{H}, \quad 26, \quad (15) \]

\[ \text{O}(3P) + \text{O}(3P) + \text{M} \rightarrow \text{O}_2(3\Sigma^-_g) + \text{M}, \quad -498. \quad (16) \]

A. \( \text{O}_2(3\Sigma^-_g,v=0) \) formation mechanisms

Figure 5(a) shows that the temporal signal behaviors of O\( _2(3\Sigma^-_g,v=0) \) and O(3P) are in fair agreement to each other, while OH signal intensity due to the H\( _2\text{O}_2 \) photoproducts on the 157 nm photoirradiated ASW surface increased slowly. These results indicate that O\( _2(3\Sigma^-_g,v=0) \) are not produced from the accumulated H\( _2\text{O}_2 \) photoproducts on the ASW surface.

On the assumptions that (a) a large amount of OH radicals are produced on the ASW surface after 157 nm laser shots on ASW, allowing successive surface reactions on the ASW surface to occur efficiently, and (b) the concentration of OH on ASW fed by primary photodissociation reaction (11) is much higher than that of O(3P) formed via secondary reaction (13), the appearance behavior of O\( _2(3\Sigma^-_g,v=0) \) signal intensity in Fig. 5(a) can be explained if the reaction schemes (17)–(21) proceeds on ASW,

\[ \text{H}_2\text{O} + h\nu(157 \text{ nm}) \rightarrow \text{H} + \text{OH}(v = 0 \text{ and } 1), \quad (17) \]

\[ \text{OH} + \text{OH} \rightarrow \text{H}_2\text{O}_2, \quad (18) \]

\[ \text{OH} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{O}(3P), \quad (19) \]

\[ \text{OH} + \text{O}(3P) \rightarrow \text{O}_2(3\Sigma^-_g,v = 0) + \text{H}, \quad (20) \]

\[ \text{H}_2\text{O}_2 + h\nu(157 \text{ nm}) \rightarrow 2\text{OH}(v = 0 \text{ and } 1). \quad (21) \]

Furthermore, after successive 157 nm irradiation on ASW, OH radicals are accumulated on ASW since they can exist on/in water ice at 90 K.\(^3\) These adsorbed OH on ASW can be additional sources for O(3P) via reactions (19) and (22),\(^17\) and contribute to the O\( _2(3\Sigma^-_g,v=0) \) production, as shown in Fig. 5(a).

\[ E_{\text{avail}} \text{ (kJ mol}^{-1} ) \]

\[ \text{OH(ads)} + h\nu(157 \text{ nm}) \rightarrow \text{H} + \text{O}(3P), \quad 278. \quad (22) \]

The translational temperature of O\( _2(3\Sigma^-_g,v=0) \) is much higher than the substrate temperature of 90 K, as shown in Table I. These results suggest that observed O\( _2(3\Sigma^-_g,v=0) \) originate only from the ASW surface, not from the bulk. Kimmel and their co-workers\(^8\) suggested that O\( _2 \) formation occurred at or near the ASW/vacuum interface in the low-energy electron-stimulated desorption experiments. The electron-stimulated migration of OH or OH\(^-\) to the vacuum interface, where they react and produce O\( _2 \), occurs via transport through the hydrogen bond network of the ASW.\(^4,5\)

Araya et al. performed molecular dynamics simulations of the UV photodissociation of ASW at 10–90 K. They reported that OH desorbs into the vacuum only when they were generated from the top 3 ML of ASW at 90 K and its probability is <0.05 per absorbed UV photon, whereas most of OH are trapped on/in ASW.\(^6\) Andersson et al.\(^7,8\) predicted that OH radicals in bulk ASW formed following photodissociation of ASW move only less than 0.5 nm, while OH radicals formed in the top 3 ML of ASW were able to move up to more than 6 nm until they were trapped. This large mobility of OH on the top ASW makes secondary reactions of OH with adsorbed species possible. These models support our proposed reaction schemes.

B. \( \text{O}_2(a^1\Delta_g,v=0) \) formation mechanisms

The time evolution curve for O\( _2(a^1\Delta_g,T_{\text{trans}}=250 \text{ K}) \) recorded at t=10.0 \( \mu\text{s} \) appears promptly, as shown in Fig. 5(c). Furthermore, Fig. 5(d) shows that O\( _2(a^1\Delta_g,v=0), \) O\( (3P) \), and O\( _2(3\Sigma^-_g,v=0) \) were photodesorbed immediately after the 157 nm irradiation started. Since vibrationally excited OH\( (v=1) \) are produced from primary photodissociation of H\( _2\text{O}_2 \),\(^15\) O\( _2(a^1\Delta_g,T_{\text{trans}}=250 \text{ K}) \) can be produced via reaction of vibrationally excited OH\( (v=1) \) and O\( (3P) \), as Lunt et al. observed in the gas phase, i.e., reaction (23),\(^23\)

\[ \Delta H \text{ (kJ mol}^{-1} ) \]

\[ \text{OH}(v = 1) + \text{O}(3P) \rightarrow \text{O}_2(a^1\Delta_g,v = 0) + \text{H}, \quad -17. \quad (23) \]

On the other hand, Fig. 5(b) shows that O\( _2(a^1\Delta_g,T_{\text{trans}}=250 \text{ K}) \) was not observed immediately after 157 nm photoirradiation, and the appearance behavior is in accordance with the concentration of photogenerated H\( _2\text{O}_2 \) on the ice surface. Furthermore, the O\( _2(a^1\Delta_g,T_{\text{trans}}=250 \text{ K}) \) was observed promptly after 157 nm irradiation of the H\( _2\text{O}_2/H_2\text{O}_2 \) mixed ices. These results suggest that H\( _2\text{O}_2 \) photoproduce on ASW is a source for the O\( _2(a^1\Delta_g,T_{\text{trans}}=250 \text{ K}) \) formation. Hama et al.\(^15\) previously reported that OH\( (v=0 \text{ and } 1), T_{\text{trans}}=7500 \text{ K} \) are produced from the secondary photodissociation of H\( _2\text{O}_2 \) that photolytically accumulated on the ASW surface by 157 nm irradiation, i.e., reaction (24),

\[ \text{H}_2\text{O}_2(\text{ads}) + h\nu(157 \text{ nm}) \]

\[ \rightarrow 2\text{OH}(v = 0 \text{ and } 1), T_{\text{trans}}=7500 \text{ K} \], \quad (24) \]

where \( E_{\text{avail}}(24) \) is 493 kJ mol\(^{-1}\). These OH\( (v=0 \text{ and } 1), T_{\text{trans}}=7500 \text{ K} \) can proceed in endothermic reactions on ASW surface.\(^6\) Thus, O\( _2(a^1\Delta_g,T_{\text{trans}}=250 \text{ K}) \) can be produced from the hot photoproducts such as OH from H\( _2\text{O}_2 \) via reaction (25),

\[ \text{OH}(v = 0 \text{ and } 1), T_{\text{trans}}=7500 \text{ K} \] + O\( (3P) \)

\[ \rightarrow \text{O}_2(a^1\Delta_g,T_{\text{trans}}=250 \text{ K}) + \text{H}, \quad (25) \]

Lunt et al.\(^23\) reported 0.025 for the yield of O\( _2(a^1\Delta_g) \) formation via reaction of OH\( (v \geq 1) \) with O\( (3P) \) in the gas phase, and the majority of the products are O\( _2(X^1\Sigma^-_g) \). Lique et al.\(^21\) pointed out a possibility of the nonadiabatic transition for the OH+O reaction. The potential energy surface of OH+O reaction corresponding to the electronically excited 2\( ^A \) state correlates only with the O\( _2(a^1\Delta_g)+\text{H} \) product channel through the electronically excited state of the
The available energy for reaction $\text{H}_2\text{O}(a^1\Sigma_g^+, v=0)$ suggested that the observed $\text{O}_2(X^3\Sigma_g^-, v=0)$ and $\text{O}_2(a^1\Delta_g, v=0)$ fragments originate only from the ASW surface, not from the ice bulk. The exothermic barrierless reaction of OH and O$^3(\Pi)$ is proposed as the most plausible source for $\text{O}_2(X^3\Sigma_g^-, v=0)$ formation. The reaction of translationally and internally excited OH with O$^3(\Pi)$ plays a key role in the $\text{O}_2(a^1\Delta_g, v=0)$ formation. The contribution of recombination reaction of two O$^3(\Pi)$ to O$_2$ formation was found to be negligible. O$^3(\Pi)$ would react with OH much more frequently than they encounter another O$^3(\Pi)$ to produce O$_2$ since concentration of primary product OH on ASW is much higher than that of O$^3(\Pi)$ formed via secondary reaction on ASW.

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C. Other possible O$_2$ formation mechanisms

To consider a contribution of highly exothermic recombination reaction of two O$^3(\Pi)$, we measured the translational and internal energy distributions of O$_2$ following 193 nm photoexcitation of SO$_2$ adsorbed on ASW since O$^3(\Pi)$ were efficiently produced from the 193 nm photolysis of SO$_2$.

As shown in Figs. 1(b), 6, and 7, 193 nm photolysis of SO$_2$ on ASW yielded O$_2$ products via subsequent reactions (26) and (27) and they were desorbed into the vacuum, $E_{\text{avail}}$ (kilojoule mol$^{-1}$)

$$\text{SO}_2(\text{ads}) + h\nu(193 \text{ nm}) \rightarrow \text{SO} + \text{O}^3(\Pi), \quad 43 \text{kJ mol}^{-1} \quad (26)$$

$\Delta H$ (kilojoule mol$^{-1}$)

$$\text{O}^3(\Pi) + \text{O}(^3\text{P}) + \text{M} \rightarrow \text{O}_2(X^3\Sigma_g^+) + \text{M}, \quad -498. \quad (27)$$

The available energy for reaction (26) at 193 nm ($E_{\text{photon}} = 620 \text{ kJ mol}^{-1}$) was calculated using dilute solution phase thermodynamic data for the adsorbed SO$_2$(ads). The REMPI spectrum of Fig. 1(b) may be simulated by a sum of the sequence bands of the $C^3\Pi_v(v''=v'+2) \rightarrow X^3\Sigma_g^+(v')$ transitions mainly for $v''=2$ and 3 (Fig. 1(g)). In addition, O$_2(a^1\Delta_g, v=0)$ was failed to be detected at 329–332 nm. These results indicate that highly exothermic reaction (27) yields mainly vibrationally excited O$_2(X^3\Sigma_g^-, v=2$ and 3), and plays only a minor role in the formation of O$_2(X^3\Sigma_g^-, v=0)$ and O$_2(a^1\Delta_g, v=0)$ from neat ASW photolysis at 157 nm.

Hydroperoxyl radical, HO$_2$, is known to be photodissociated to OH and O$^1(D$ or $^3\text{P})$ at excitation wavelengths of 248–147 nm in the gas phase. Our previous studies showed no contribution of HO$_2$ photoproducts on ASW to production of OH and O$^1(D$ or $^3\text{P})$ following 157 nm photolysis of ASW, suggesting that the amount of HO$_2$ photoproducts on the ice surface was negligible at 90 K. Therefore, the O$_2$ formation following reactions of HO$_2$+H or HO$_2$+OH are considered to be unlikely sources for the observed O$_2$ ejection from the ASW surface in the present experiments.

VI. CONCLUSION

We have measured time-of-flight and rotational spectra of the photodesorbed O$_2(X^3\Sigma_g^-, v=0)$ and O$_2(a^1\Delta_g, v=0)$ following pulsed 157 nm irradiation of ASW at 90 K, and the translational and internal energy distributions were obtained. Measured translational energies of O$_2(X^3\Sigma_g^-, v=0)$ and O$_2(a^1\Delta_g, v=0)$ suggested that the observed O$_2(X^3\Sigma_g^-, v=0)$ and O$_2(a^1\Delta_g, v=0)$ fragments originate only from the ASW surface, not from the ice bulk. The exothermic barrierless reaction of OH and O$^3(\Pi)$ is proposed as the most plausible source for O$_2(X^3\Sigma_g^-, v=0)$ formation. The reaction of translationally and internally excited OH with O$^3(\Pi)$ plays a key role in the O$_2(a^1\Delta_g, v=0)$ formation. The contribution of recombination reaction of two O$^3(\Pi)$ to O$_2$ formation was found to be negligible. O$^3(\Pi)$ would react with OH much more frequently than they encounter another O$^3(\Pi)$ to produce O$_2$ since concentration of primary product OH on ASW is much higher than that of O$^3(\Pi)$ formed via secondary reaction on ASW.


