Formation mechanisms of oxygen atoms in the O\(^{1}D\) state from the 157 nm photoirradiation of amorphous water ice at 90 K

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Vacuum ultraviolet photolysis of water ice in the first absorption band was studied at 157 nm. Translational and internal energy distributions of the desorbed species, O\(^{1}D\) and OH\(_{v}=0,1\), were directly measured with resonance-enhanced multiphoton ionization method. Two different mechanisms are discussed for desorption of electronically excited O\(^{1}D\) atoms from the ice surface. One is unimolecular dissociation of H\(_2\)O to H\(_2\)+O\(^{1}D\) as a primary photoprocess. The other is the surface recombination reaction of hot OH radicals that are produced from photodissociation of hydrogen peroxide as a secondary photoprocess.

II. EXPERIMENTAL

A. Apparatus and preparation of ice films

Experimental details are described elsewhere.\(^{22}\) ASW was prepared by backfilling deposition of water vapor onto a sapphire disc substrate sputter coated with a thin polycrystalline film of Au(111) at 90 K for 60 min by a pulsed nozzle (General Valve) at rate of 10 Hz and at 20 Torr stagnation pressure of water vapor. In order to spread water vapor all over the chamber, a flat plate was attached in front of the...
pulse nozzle. The exposure was typically 1500 L (1 L = 1 \times 10^{-6} \text{Torr}). This exposure resulted in formation of 500 monolayers (ML) of H$_2$O on the substrate if we adopt the reported experimental conversion factor of 1 ML deposition by 3 L exposure.\textsuperscript{23}

Unfocused 157 nm laser radiation with full width at half maximum duration of 10 ns was incident at an angle of about 80° to the surface normal on the ice surface at a fluence <0.1 mJ cm$^{-2}$ pulse$^{-1}$. O(\textsuperscript{1}D) atom products were subsequently ionized at a distance of 4 mm (2 mm for OH) from the substrate surface by the (2+1) REMPI transition via the O(\textsuperscript{1}F$_3$ ← \textsuperscript{1}D$_2$) transition at 203.8 nm,\textsuperscript{24} and collected with a small mass spectrometer aligned perpendicular to the ice surface. O(\textsuperscript{1}D) atoms were also observed via the O(\textsuperscript{1}P$_1$ ← \textsuperscript{1}D$_2$) transition at 205.5 nm.\textsuperscript{25} OH($v=0$ and 1) products were also detected by REMPI via the $D^2\Sigma^+(v'=0)←X^2\Pi(v''=0)$ at 243.5–245.0 nm and the $3^2\Sigma^+(v'=0)←X^2\Pi(v''=1)$ transitions at 237.5–237.7 nm, respectively. The REMPI transition strength data are obtained by Greenslade et al.\textsuperscript{20} The delay $r$ between the photolysis and REMPI laser pulses was varied with a delay generator to allow investigation of the flight times of the photoproducts. Three types of ice samples, fresh ASW, ASW after 157 nm photolirradiation for 30 min, and fresh H$_2$O$_2$ on ASW, were prepared. The surface of fresh ASW was kept fresh for laser irradiation by expanding water vapor to the ASW surface by a pulsed nozzle at rate of 10 Hz. The duration of the H$_2$O pulse was about one millisecond. During this exposure, the chamber pressure was increased up to 5 \times 10^{-7} \text{Torr}. For the concentrated H$_2$O$_2$ photolysis experiments, a commercially available H$_2$O$_2$ solution (30\%) was concentrated in a glass container by vacuum distillation and the H$_2$O$_2$ / H$_2$O vapor was deposited on the gold substrate. The exposure of the codeposited H$_2$O$_2$ / H$_2$O mixture on the ASW film was <8 L for 330 s duration at 90 K. Fresh surfaces of cocondensed H$_2$O$_2$ were prepared as described above. The photolysis experiments were performed at 90 K.

### B. Simulation of time-of-flight spectra of photoproducts

The measured time-of-flight (TOF) spectra were fitted with one or more flux-weighted Maxwell–Boltzmann (MB) distributions defined by a translational temperature $T_{\text{trans}}$. Details regarding the simulation of such TOF spectra have been reported previously.\textsuperscript{22} The TOF spectrum $S(a_i, t, T_{\text{trans}})$ was fitted with a combination of the MB distributions defined by the temperature $T_{\text{trans}}$. The coefficient $a_i$ is used for the relative population of each MB distribution,

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

$$S_{\text{MB}}(t, r) = r^3 e^{-r^2} \exp[-mr^2/2k_BT_{\text{trans}}^2],$$

$$P_{\text{MB}}(E_t) = (k_BT_{\text{trans}})^{-2}E_t e^{-E_t/k_BT_{\text{trans}}},$$

where $r$ is a flight length for the photofragment. The MB distribution $P_{\text{MB}}(E_t)$ as a function of translational energy $E_t$ is characterized by the averaged translational energy $\langle E_t \rangle = 2k_BT_{\text{trans}}$, where $k_B$ is the Boltzmann constant.\textsuperscript{27} Conversion from the energy distribution to the TOF distribution was performed using the Jacobian listed by Zimmerman and Ho.\textsuperscript{28}

### III. RESULTS

#### A. TOF spectra of O(\textsuperscript{1}D) atoms

Figure 1 shows TOF spectra of the O(\textsuperscript{1}F$_3$ ← \textsuperscript{1}D$_2$) transition from the photodissociation of (a) fresh ASW, (b) ASW after 157 nm photolirradiation for 30 min without intermisible dosing of water vapor, and (c) fresh H$_2$O$_2$ on ASW. These TOF spectra are reproduced by three MB distributions with $T_{\text{trans}} = 2250 \pm 250$ K ($\langle E_{\text{trans}} \rangle = 9.0 \pm 1.0$ kcal/mol), 800 $\pm 150$ K (3.2 $\pm 0.6$ kcal/mol), and 300 $\pm 100$ K (1.2 $\pm 0.4$ kcal/mol). For both cases (b) and (c), the stronger O(\textsuperscript{1}D) signals and the larger contributions of the O(\textsuperscript{1}D, $T_{\text{trans}} = 2250$ and 300 K) components were observed than those for case (a). Table I summarizes the results.

#### B. O(\textsuperscript{1}D) signal intensity change as a function of 157 nm photolirradiation time

Figure 2 shows the O(\textsuperscript{1}F$_3$ ← \textsuperscript{1}D$_2$) transition signal intensity change as a function of the 157 nm irradiation time for the O(\textsuperscript{1}D, $T_{\text{trans}} = 2250$ and 300 K) atoms. In Fig. 2, the pre-

### TABLE I. Contributions (%) of translational temperature ($T_{\text{trans}}$) components of O(\textsuperscript{1}D) atoms from the 157 nm photolysis of ASW and hydrogen peroxide (H$_2$O$_2$) at 90 K.

<table>
<thead>
<tr>
<th>Ice sample</th>
<th>$T_{\text{trans}}$ (K)</th>
<th>Relative integrated TOF signal intensity$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh ASW$^b$</td>
<td>2250 800 300</td>
<td>11 80 9</td>
</tr>
<tr>
<td>ASW after photoirradiation$^c$</td>
<td>49 22 29</td>
<td>3.5 $\pm$ 0.5</td>
</tr>
<tr>
<td>Fresh H$_2$O$_2$ on ASW</td>
<td>46 22 32</td>
<td>3.7 $\pm$ 0.3</td>
</tr>
</tbody>
</table>

$^a$Integrated TOF signal intensities are relative to the fresh ASW sample.

$^b$ASW stands for amorphous solid water at 90 K.

$^c$After 30 min photoirradiation at 157 nm.
previously reported and presently measured time evolution data for the \(R(1)+R(5)\) line of OH\((v=0)\) due to the H\(_2\)O\(_2\) photoprod-uct on the 157 nm photoirradiated ASW surface are also plotted,\(^29\) which reflects the concentration of photogenerated H\(_2\)O\(_2\) on the ice surface. The appearance behaviors of the OH signal from the secondary photodissociation of H\(_2\)O\(_2\) photoprepared on the ASW surface and the O\(^{1}D\) signals in Fig. 2 were in agreement within the margin of error.

C. OH radical desorption in the 157 nm photodissociation on amorphous solid water

Translationally and internally excited OH radicals have been successfully detected with the same REMPI setup following 157 nm photolysis of H\(_2\)O or H\(_2\)O\(_2\) ices at 90 K, and the formation mechanisms were described before.\(^30\) Only details relevant to the present experiments are given here. The upper panels of Fig. 3 show (a) TOF spectra of the \(R(1)+R(5)\) line of OH\((v=0)\) and (b) the \(R(2)\) line of OH\((v=1)\) following 157 nm photodissociation of fresh ASW. The lower panels are for (c) the \(R(1)+R(5)\) line of OH\((v=0)\) at 244.25 nm and (d) the \(R(2)\) line of OH\((v=1)\) at 237.62 nm following 157 nm photodissociation of ASW after photodissciation for 30 min. The TOF spectra of OH are reproduced by two MB distributions with \(T_{\text{trans}}\) =7500 \pm 1000 and 1300 \pm 200 K (5.2 \pm 0.8 kcal/mol). The population ratio of \(v=1/v=0\) was estimated to be 0.2 \pm 0.1 by REMPI transition strength data by Greenslade et al.\(^26\) Observed rotational temperatures and vibrational level ratios of OH\((v=0\) and 1) are listed in Table II.

IV. DISCUSSION

A. O\(^{1}D\) formation mechanism in fresh ASW

As shown in Table I and Fig. 1, both the TOF spectra for ASW after photodissociation and fresh H\(_2\)O\(_2\) on ASW have similar translational distributions, that is, a smaller contribution of the middle temperature component \(T_{\text{trans}}=800\) K and higher total signal intensities than those for fresh ASW. The TOF spectrum for fresh ASW consists mostly of the middle temperature component. Since this middle temperature component comes from the fresh water surface and not from the secondary photoproduts such as H\(_2\)O\(_2\), we propose that the primary unimolecular process \(6\) results in the formation of this component,

\[ \text{H}_2\text{O}(\text{ads}) + h\nu(157 \text{ nm}) \rightarrow \text{H}_2(\text{i}) + \text{O}^{(1)D}. \]  

The available energy for reaction \(6\) at 157 nm is \(E_{\text{avail}}(6) = 7.9\) kcal/mol. In the present paper, the notation “ads” stands for condensed phase or adsorbed state, and the thermodynamic data for adsorbed species are taken from those for the solid phase. The notation “i” stands for species at the ASW/vacuum interface, and for these species we use the gas phase thermodynamics data.\(^31,32\) According to quantum me-
chemical wavepacket calculations for the photodissociation of water by van Harrevelt and van Hemert, the $H_2 + O(1D)$ channel occurs on the ground state potential surface that favors dissociation to $H + OH$.\(^\text{33}^\text{33}\) Based on the experimental results for fresh ASW in Table I, most of the $O(1D)$ atoms have the MB component with $T_{\text{trans}}=800$ K and are not totally accommodated to the surface temperature (90 K). These results suggest that the $O(1D)$ atoms ejected from the surface would be produced on the ASW surface and not from the bulk.

$$\text{surface} - H_2O(\text{ads}) + h\nu(157 \text{ nm}) \rightarrow H(i) + O(1D). \quad (7)$$

Since the optical depth of ASW at 157 nm is about 100 nm, the 157 nm photons are primarily absorbed in the ASW bulk, and could induce several other possible mechanisms, including the diffusion of atoms, radicals, and molecules. However, $O(1D)$ atoms generated in the bulk easily react with water molecules to produce OH radicals or $H_2O_2$ molecules by collisions and do not reach the surface.\(^\text{34,35}^\text{34,35}\)

Concerning the exciton mediated reaction, Orlando and Kimmel have observed the ESD of O atoms in the $^1D$ and $^3P$ states from an amorphous $D_2O$ film. O atoms in the $^1D$ and $^3P$ states were produced at threshold electron energies between 150 and 160 kcal/mol and desorbed with both the nonthermal (1.4–2.0 kcal/mol) and thermal components.\(^\text{36}^\text{36}\) They associated the ESD of O atoms in the $^1D$ and $^3P$ states from ice with dissociation of the Frenkel-type excitons of $4a_1$ character, which are near the bottom of the ice conduction band. The excitons formed in the bulk ice are transported to the near-surface region, and then, the reduced forces in this region allow dissociation. There are both theoretical and experimental works which support the existence of mobile excitons in water ice. In the high-level electronic structure calculations, the lowest excited states of hydrogen-bonded water clusters (dimer, trimmer, and pentamer) have the barrier for dissociation, and these results contrast with that of an isolated water molecule, in which the lowest excited state is well known to be dissociative.\(^\text{37,38}^\text{37,38}\) Hahn et al. found that the exciton in ice showed significant overlap with adjacent sites.\(^\text{39}^\text{39}\) These calculations imply that exciton would be prevented from dissociation within ASW, and in favor of dissociation at the vacuum/ASW interface after the migration. In fact, Petrik and Kimmel found experimental support for mobile excitons in ASW that initiate reactions at the ASW/vacuum interface.\(^\text{40,41}^\text{40,41}\) This model could also be plausible for our experimental results that the $O(1D)$ atom ejection occurs at the vacuum/ASW interface, that is, the dissociation of surface $H_2O$ is the source of $O(1D)$ atom.

We will describe below the other mechanism for $O(1D)$ atom formation via recombination of OH radicals.

### B. O(1D) formation mechanisms in ASW after 30 min photolysis and fresh $H_2O_2$ on ASW

As shown in Fig. 1 and Table I, the strong $O(1D)$ signals and the large contributions of the $O(1D), T_{\text{trans}}=2250$ and 300 K) components were observed in ASW after 157 nm photolysis for 30 min and fresh $H_2O_2$ on ASW. Figure 2 shows that the appearance behaviors of $O(1D)$ signals at $t=2$ and 10 $\mu$s are in accordance with the concentration of photogenerated $H_2O_2$ on the ice surface. These results indicate that the $O(1D), T_{\text{trans}}=2250$ and 300 K) atoms come from photogenerated $H_2O_2$. For the cases of both ASW after prolonged photolysis and fresh $H_2O_2$ on ASW, there are additional mechanisms for formation of $O(1D)$ besides reaction (6); the collisional recombination reactions (11)–(14) of hot OH on the surface of ice,

$$H_2O(\text{ads}) + h\nu(157 \text{ nm}) \rightarrow H(i) + OH(i), \quad (8)$$

$$OH(i) + OH(\text{ads}) \rightarrow H_2O_2(\text{ads}), \quad (9)$$

$$H_2O_2(\text{ads}) + h\nu(157 \text{ nm}) \rightarrow 2OH(i), \quad (10)$$

$$OH(i) + OH(i) \rightarrow H_2O(i) + O(1D) \quad (11)$$

$$\rightarrow H_2O(\text{ads}) + O(1D), \quad (12)$$

$$OH(i) + OH(\text{ads}) \rightarrow H_2O(i) + O(1D) \quad (13)$$

### Table II. Translational and rotational temperatures ($T_{\text{trans}}$, $T_{\text{rot}}$) of OH($v=0$ and 1) radicals from three different ice samples.

<table>
<thead>
<tr>
<th>Ice sample</th>
<th>$T_{\text{trans}}$ (K)</th>
<th>$T_{\text{rot}}$ (K)</th>
<th>Relative integrated TOF signal intensity</th>
<th>Vibrational level ratio $v=1/v=0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh ASW</td>
<td>7500 (5%) 7500 (10%)</td>
<td>400 300 1 1</td>
<td>0.2 ± 0.1</td>
<td></td>
</tr>
<tr>
<td>ASW after photoirradiation</td>
<td>7500 (30%) 7500 (40%)</td>
<td>500 200 1.7 ± 0.1 1.8 ± 0.1 0.2 ± 0.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fresh $H_2O_2$ on ASW</td>
<td>7500 (30%) 7500 (40%)</td>
<td>500 200 1.6 ± 0.1 1.7 ± 0.1 0.2 ± 0.1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$The percentage in parenthesis is a contribution of each temperature component. $^b$The level ratios were measured at TOF=1.5 $\mu$s for fresh ASW and at TOF=0.5 $\mu$s for other two ice samples.

$^c$Integrated TOF signal intensities are relative to the fresh ASW sample.
that the recombination of OH occurs more readily at the surface of ASW compared to the bulk. In fact, Yabushita et al. reported in their vuv photolysis experiments that H2O2 was subsequently produced on the water ice surface at 90 K presumably due to recombination of photolytically produced OH.

As for reaction (8), because of the momentum conservation between the H and OH photofragments, the OH radical is slowly moving. In addition, the vibrational state distribution \( v = 1 \leftrightarrow v = 0 \) of OH(\( v = 0 \) and 1) is \( \approx 0.2 \) in the condensed phase, which is much lower than the gas phase results of \( \approx 1,1 \) reported by Lu et al.47 Hwang et al.48 and Yang et al.49 The vibrational energy of OH(\( v = 1 \)) is 10.2 kcal/mol.50 Andersson et al.45,46 reported that the energy of the electronically excited state of H2O was dissipated by the surrounding water molecules in the condensed phase, and this would lead to product energy distributions different from those if the excited molecule were unperturbed in the gas phase. Hence, reaction (9) mainly takes place from these low-energy OH radicals following the photolysis of H2O.

The large contribution (80%) of O(\( ^1D \), \( T_{\text{trans}} = 800 \) K) in fresh ASW shows that the O(\( ^1D \)) atoms are mainly formed via the primary unmolecular reaction (7) in fresh ASW. Table I shows the results of relative signal intensities of the O(\( ^1D \), \( T_{\text{trans}} = 800 \) K) component for three ice samples. For fresh ASW, we have the relative O(\( ^1D \)) intensity 80% \( \times 1 = 80 \). For ASW after 157 nm photoirradiation and fresh H2O2 on ASW, we have the intensities 22% \( \times 3.5 = 77 \) and 22% \( \times 3.7 = 81 \), respectively. These results imply that the signal intensity of the O(\( ^1D \), \( T_{\text{trans}} = 800 \) K) component did not change. Instead, the other components increased due to the bimolecular reactions (11)–(14) of hot OH radicals from the secondary photolysis of H2O2. A small contribution of the O(\( ^1D \), \( T_{\text{trans}} = 2250 \) and 300 K) atoms in fresh ASW may be attributable to photogenerated H2O2 on ice because the intermissive water vapor deposition during the experiment did not perfectly cover the surfaces.

C. Transition state and reaction mechanism for the formation of O(\( ^1D \)) atoms via recombination reactions of OH radicals

Mousavipour and Saheb42 performed theoretical calculations for the transition state of H2O+O(\( ^1D \)) formation. According to them, in the kinetics and reaction mechanism of a hydroperoxyl radical (HO2) with a H atom, reactions (15) and (16) proceed on a singlet surface to produce H2O+O(\( ^1D \)) via the formation of intermediate oxywater (H2OO),

\[
H + \text{HO}_2 \rightarrow \text{H}_2\text{OO},
\]

(15)

\[
\text{H}_2\text{OO} \rightarrow \text{H}_2\text{O} + \text{O}(^1D),
\]

(16)

\[
\text{net } H + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}(^1D).
\]

(17)

Thermodynamic data in units of kcal/mol are \( \Delta H_{\text{trans}} = -38.3 \), \( \Delta H(16) = 36.0 \), and \( \Delta H(17) = \Delta H(15) + \Delta H(16) = -2.3 \).

H2OO is a proposed structural isomer of hydrogen peroxide (HOOH), which may serve as a transient intermediate.
in oxidation reactions initiated by hydrogen peroxide.\textsuperscript{51,52} \(\text{O}^{(1)}(D)\) atom can be produced without the barrier via the endothermic recombination reactions of hot OH radicals through the formation of HOOH and H2OO, 

\[
\text{OH} + \text{OH} \rightarrow \text{HOOH}, 
\]

\[
\text{HOOH} \rightarrow \text{H}_2\text{OO}, 
\]

\[
\text{H}_2\text{OO} \rightarrow \text{H}_2\text{O} + \text{O}^{(1)}(D), 
\]

\[
\text{net} \ \text{OH} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{O}^{(1)}(D). 
\]

Thermodynamic data in units of kcal/mol are \(\Delta H(18) = -42.2\), \(\Delta H(19) = 46.2\), and \(\Delta H(20) = 36.0\) and \(\Delta H(21) = \Delta H(18) + \Delta H(19) + \Delta H(20) = 40.0\).\textsuperscript{42} The barrier height for reaction (19), \(E_{\text{barrier}}(19)\), was calculated to be 52.2 kcal/mol.\textsuperscript{42} Recently, Franz \textit{et al.} reported an energy of 21 kcal/mol for the lowest electronic singlet states of H2OO along dissociation of the oxygen-oxygen bond into H2O and \(\text{O}^{(1)}(D)\), reactions (16) or (20), with quantum chemical calculations.\textsuperscript{53} When their value for \(\Delta H(20) = 21.0\) kcal/mol is adopted, \(\Delta H(21)\) is calculated as \(\Delta H(21) = \Delta H(18) + \Delta H(19) + \Delta H(20) = 25.0\) kcal/mol, that is, much lower than the above listed value of 40.0 kcal/mol. In either case, this endothermic value is less than the maximum available energy, \(E_{\text{av}}(10)/2 = 58\) kcal/mol, for hot OH radical formation from the 157 nm photodissociation of H2O2. Actually the maximum (kinetic+internal) energy of the observed OH products from photogenerated H2O2 on ASW is about 55 kcal/mol.

We cannot identify particular mechanisms for the \(\text{O}^{(1)}(D)\) formation. The two components of \(\text{O}^{(1)}(D)\) atoms imply at least two reactions in reactions (11)–(14) can occur. Based on the fact that (a) the higher reactant energy from two hot OH and (b) the lowest value of \(\Delta H(12)\), reaction (12) is the most plausible process.

D. Other mechanisms for \(\text{O}^{(1)}(D)\) formation

One of the other possible mechanisms for \(\text{O}^{(1)}(D)\) formation is the recombination reaction of H and OH, 

\[
\text{H}_2\text{O} + h\nu(157 \text{ nm}) \rightarrow \text{H}(i) + \text{OH}(i), 
\]

\[
\text{H}(i) + \text{OH}(i) \rightarrow \text{H}_2(i) + \text{O}^{(1)}(D), 
\]

\[
\text{H}(i) + \text{OH} \rightarrow \text{H}_2 + \text{O}^{(1)}(D), 
\]

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

Thermodynamic data in units of kcal/mol are \(E_{\text{av}}(22) = 51.2\), \(\Delta H(23) = 43.3\), \(\Delta H(24) = 47.4\), and \(\Delta H(25) = 56.2\).\textsuperscript{31,32} There has been no direct measurement of \(\text{O}^{(1)}(D)\) formation via the recombination reaction of H and OH in the gas phase. Since these reactions are largely endothermic and not three-body reactions, large rate reduction in these reaction rates would be expected on the surface. Classical molecular dynamics calculations for the condensed phase showed that a H2O molecule was formed via H and OH recombination reaction following the photolysis of water ice.\textsuperscript{45,46} Thus, the contribution of these reactions should be negligible.

Gerakines \textit{et al.} reported the evolution of spectral features in vuv photoirradiation on H2O ice and found that OH was the first photoproduce observed in ice at 10 K, and then, after OH, accumulation of H2O2 and HO2 started.\textsuperscript{10} In the present experiment, the contribution of the photolysis of OH(ads) for \(\text{O}^{(1)}(D)\) formation, reaction (26), would be small in fresh ASW and H2O2 on ASW because it is unlikely that multiphoton process occurred with this low laser intensity of unfocused 157 nm laser at a fluence \(<0.1\) mJ cm\(^{-2}\) pulse\(^{-1}\).\textsuperscript{18,34} and also the surfaces of ice were kept fresh for laser irradiation by exposing them with water or H2O2/H2O vapor to suppress the secondary photolysis of the accumulated products formed on the ice surface during the photolysis, 

\[
\text{OH}(\text{ads}) + h\nu(157 \text{ nm}) \rightarrow \text{H} + \text{O}^{(1)}(D). 
\]

\(\text{O}^{(1)}(D)\) atoms would not be formed from the secondary photolysis of OH(ads) in ASW after prolonged photoirradiation because the TOF spectrum of \(\text{O}^{(1)}(D)\) for ASW after 30 min photoirradiation has the similar translational distribution to that of fresh H2O2 on ASW. Van Dishoeck and Dalgarno performed theoretical calculations of the photodissociation of the OH by \textit{ab initio} calculations and predicted that the on the photodissociation of OH at 152–190 nm would not lead to \(\text{O}^{(1)}(D)\) but only to \(\text{O}^{(3)P_J}\) + H.\textsuperscript{55,56} In fact, the secondary photolysis of OH(ads) is attributed to \(\text{O}^{(3)P_J}\) formation in the 157 nm photolysis of water ice where the TOF spectra of \(\text{O}^{(3)P_J}\) for ASW after prolonged photoirradiation have a different translational distribution from those of fresh ASW and fresh H2O2 on ASW. These results will be described in the following paper for our separate experiments.

The contribution of HO2 would also be small since (a) the time evolution data of \(\text{O}^{(1)}(D)\) in Fig. 2 are quite similar to those of H2O2 on the ice surface while HO2 is produced from a three-step reaction of OH+H2O2 where H2O2 is produced from OH+OH, and (b) the concentration of HO2 on/in ice disappeared or decreased at elevated temperatures such as 90 K.\textsuperscript{10,57}

V. SUMMARY

We have demonstrated that electronically excited \(\text{O}^{(1)}(D)\) atoms are formed via two processes: The unimolecular reaction on the surface of low temperature ASW at 90 K in the 157 nm photoirradiation and the bimolecular reactions of translationally and internally hot OH radicals on the surface of water ice. The hot OH radicals on ASW are produced from secondary photolysis of the photoproduce H2O2. In fresh ASW, the main part of \(\text{O}^{(1)}(D)\) comes from the primary unimolecular reaction. In ASW after prolonged 157 nm photoirradiation, the contributions of unimolecular reaction become smaller, and the bimolecular reactions of hot OH radicals from the photoproduce H2O2 become dominant.
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