Formation mechanisms of oxygen atoms in the $O\left(^1D_2\right)$ state from the 157 nm photoirradiation of amorphous water ice at 90 K

Tetsuya Hamai,1 Akihiro Yabushita,1 Masaaki Yokoyama,1 Masahiro Kawasaki,1,a and Naoki Watanabe2
1Department of Molecular Engineering, Kyoto University, Kyoto 615-8510, Japan
2Institute of Low Temperature Science, Hokkaido University, Sapporo 060-0819, Japan

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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, $O\left(^1D\right)$ and $OH\left(v=0,1\right)$, were directly measured with resonance-enhanced multiphoton ionization method. Two different mechanisms are discussed for desorption of electronically excited $O\left(^1D\right)$ atoms from the ice surface. One is unimolecular dissociation of $H_2O$ to $H_2+O\left(^1D\right)$ 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. $H_2O_2$ is one of the major photoproducts in the vacuum ultraviolet photolysis of water ice. © 2009 American Institute of Physics.

[Intext citations]

I. INTRODUCTION

The chemical and physical processes following the photodissociation of water ice have been extensively studied because of its importance to reaction dynamics and kinetics, the upper atmospheric chemistry and astrochemistry. Photolysis in the first absorption band of water ice (130–165 nm) involves two primary processes,

$$H_2O + h\nu \rightarrow H_2 + O\left(^1D\right),$$  \hspace{1cm} (1)

$$H_2O + h\nu \rightarrow H + OH.$$  \hspace{1cm} (2)

$O\left(^1D\right)$ from primary reaction (1) could be an efficient reactant in formation of complex molecules on interstellar ices because of its high reactivity even though this reaction may be a minor channel. For example, the CO$_2$ molecule is one of main components of ice mantle observed toward interstellar molecular clouds and requires surface reactions to attain the observed abundances. Because a large amount of solid CO exist on/in interstellar water ice,\(^1\) one mechanism for CO$_2$ formation has been suggested to be the barrierless reaction of $O\left(^1D\right)$ and CO: $CO+O\left(^1D\right) \rightarrow CO_2$.\(^2\)–\(^6\) Another CO$_2$ formation mechanism is the reaction of OH and CO: $CO+OH \rightarrow CO_2+H$ by overcoming the barrier height in the gas phase, 2.7 kcal/mol.\(^4\)–\(^6\)

In the gas phase, Stief et al.\(^7\) reported the relative quantum yields for reaction (1) to be 0.11 for 105–145 nm and \(\approx 0.01\) for 145–185 nm, while Ung\(^8\) estimated it to be 0.08 at 147 nm. In the condensed phase the $O\left(^1D\right)$ formation reaction (1) has not been directly confirmed. In the photoysis of amorphous solid water (ASW) at the vacuum ultraviolet (vuv) region, the penetration depths are \(\approx 100\) and \(\approx 35\) nm for the first band at $\lambda =157$ and 140 nm, respectively, and \(\approx 50\) nm for the second band at $\lambda =122$ nm.\(^9\) Various photoproducts were detected in and on ice at 10 K.\(^10\) The main photoproducts, OH, H$_2$O$_2$, and HO$_2$, were the primary and secondary photoprocesses of reaction (2). In the condensed phase photolysis, not only the primary unimolecular reactions but also the secondary reactions would be the sources of photoproducts. Following the ultraviolet photolysis of H$_2$O$_2$ in various rare-gas matrices at 7.5 K, a (H$_2$O–O) complex was formed from the recombination of OH radicals, while the primary formations of H$_2$O+$O\left(^1D\right)$ or $O\left(^3P\right)$ have not been established from the photodissociation of gaseous H$_2$O$_2$ at 124–254 nm.\(^11\),\(^12\) Experimental works on photon- or electron-stimulated desorption (ESD) of species from water ice have also been reported,\(^13\)–\(^20\) and their results showed various desorbing species such as H, H$_2$, OH, H$_2$O, and O$_2$. For example, Kimmel and Orlando\(^21\) have used resonance-enhanced multiphoton ionization (REMPI) to study the ESD of O atoms in the $^1D$ and $^3P$ states from amorphous D$_2$O.

In the present study, using pulsed 157 nm (181 kcal/mol) laser radiation the desorptions of electronically excited $O\left(^1D\right)$ atoms via the primary and secondary photoprocesses from ASW at 90 K have been directly confirmed by REMPI. Translationally and internally excited OH formation mechanisms were also discussed since hot OH is a plausible source for the oxygen atom.

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
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. 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.

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

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

$$ P_{\text{MB}}(E_i) = (k_BT_{\text{trans}})^{-2}E_i \exp[-E_i/k_BT_{\text{trans}}], $$

where $r$ is a flight length for the photofragment. The MB distribution $P_{\text{MB}}(E_i)$ as a function of translational energy $E_i$ is characterized by the averaged translational energy $\langle E_i \rangle = 2k_BT_{\text{trans}}$, where $k_B$ is the Boltzmann constant.

Conversion from the energy distribution to the TOF distribution was performed using the Jacobian listed by Zimmerman and Ho.

### III. RESULTS

#### A. TOF spectra of O(1D) atoms

Figure 1 shows TOF spectra of the O(1$^2$P $\rightarrow$ 1$^2$S) transition from the photodissociation of (a) fresh ASW, (b) ASW after 157 nm photolysis for 30 min without intermolecular water vapor, and (c) fresh H$_2$O$_2$ on ASW. These TOF spectra are reproduced by three MB distributions with $T_{\text{trans}} = 2250$ and 300 K. The weaker O(1$^2$D) signals and the larger contributions of the O(1$^2$D,$T_{\text{trans}} = 2250$ and 300 K) components were observed than those for case (a). Table I summarizes the results.

#### B. O(1D) signal intensity change as a function of 157 nm photolysis time

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

<table>
<thead>
<tr>
<th>Ice sample</th>
<th>$T_{\text{trans}}$ (K)</th>
<th>Relative integrated TOF signal intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh ASW$^b$</td>
<td>2250 800 300</td>
<td>1</td>
</tr>
<tr>
<td>ASW after photolysis$^c$</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 photolysis at 157 nm.
Panel, red open circles are reproduced by two MB distributions with diation for 30 min. The TOF spectra of OH following 157 nm photodissociation of ASW after photoirradiation on amorphous solid water are also plotted,29 which reflects the concentration of photogenerated product 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$_2$ photoproduced 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 photoirradiation for 30 min. The TOF spectra of OH are reproduced by two MB distributions with $T_{\text{trans}}$ =7500 ± 1000 (30 ± 4.0 kcal/mol) and 1300 ± 200 K (5.2 ± 0.8 kcal/mol). The population ratio of $v=1/v=0$ was estimated to be 0.2 ± 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. The TOF spectra of OH from fresh H$_2$O$_2$ on ASW were also measured, which were similar to those were obtained from the ASW after 30 min irradiation (not shown). For both cases, about two times stronger OH signal intensities and larger contributions of the OH($T_{\text{trans}}=7500$ K) component were obtained than those for the fresh ASW case. The maximum (kinetic+internal) energy of the observed OH formed by 157 nm photodissociation of ASW after photoirradiation for 30 min is about 55 kcal/mol.

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 photoirradiation 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 photoproducts such as H$_2$O$_2$, we propose that the primary unimolecular process (6) results in the formation of this component,

$$\text{H}_2\text{O(ad)s} + h\nu(157 \text{ nm}) \rightarrow \text{H}_2(i) + \text{O}^1D).$$  

(6)

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-
channal occurs on the ground state potential surface that fa-
states from an amorphous D²O film. O atoms in the

mechanical wavepacket calculations for the photodissociation of
water by van Harrevelt and van Hemert, the H₂+O¹(D) channel
occurs on the ground state potential surface that favors
dissociation to H⁺+OH. Based on the experimental results for fresh
ASW in Table I, most of the O¹(D) atoms have the MB component
with Ttrans=800 K and are not totally accommodated to the surface
temperature (90 K). These results suggest that the O¹(D) atoms
ejected from the surface would be produced on the ASW surface
and not from the bulk.

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, O¹(D) atoms generated
in the bulk easily react with water molecules to produce OH radicals or
H₂O₂ molecules by collisions and do not reach the surface.

Concerning the exciton mediated reaction, Orlando and
Kimmel have observed the ESD of O atoms in the ¹D and ³P
states from an amorphous D₂O film. O atoms in the ¹D and
³P states were produced at threshold electron energies be-
between 150 and 160 kcal/mol and desorbed with both the
nonthermal (1.4–2.0 kcal/mol) and thermal components.
They associated the ESD of O atoms in the ¹D and ³P states
from ice with dissociation of the Frenkel-type excitons of
4a₁ character, which are near the bottom of the ice conduction
band. The excitons formed in the bulk ice are trans-
ported 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, trimer, 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. Hahn et al. found that the
exciton in ice showed significant overlap with adjacent
sites. These calculations imply that exciton would be
prevented from dissociation within ASW, and in favor of disso-
ciation at the vacuum/ASW interface after the migration. In
fact, Petrlik and Kimmel found experimental support for mo-
bile excitons in ASW that initiate reactions at the ASW/
vacuum interface. This model could also be plausible for
our experimental results that the O¹(D) atom ejection oc-
curs at the vacuum/ASW interface, that is, the dissociation of
surface H₂O is the source of O¹(D) atom.

We will describe below the other mechanism for O¹(D)
atom formation via recombination of OH radicals.

B. O¹(D) formation mechanisms in ASW after 30 min
photolrradiation and fresh H₂O₂ on ASW

As shown in Fig. 1 and Table I, the strong O¹(D) signals
and the large contributions of the O¹(D), Ttrans =2250 and 300 K)
components were observed in ASW after 157 nm photolrradiation
for 30 min and fresh H₂O₂ on ASW. Figure 2 shows that
the appearance behaviors of O¹(D) signals at t=2 and 10 μs are
in accordance with the concentration of photogenerated H₂O₂ on the
ice surface. These results indicate that the O¹(D), Ttrans=2250 and
300 K) atoms come from photogenerated H₂O₂. For the cases of both
ASW after prolonged photolrradiation and fresh H₂O₂ on ASW,
there are additional mechanisms for formation of O¹(D) besides
reaction (6); the collisional recombination reactions
(11)–(14) of hot OH on the surface of ice,

\[ H₂O(ads) + hν(157 nm) \rightarrow H(i) + OH(i), \]  
\[ OH(i) + OH(i and ads) \rightarrow H₂O₂(ads), \]  
\[ H₂O₂(ads) + hν(157 nm) \rightarrow 2OH(i), \]  
\[ OH(i) + OH(i) \rightarrow H₂O(i) + O¹(D) \]  
\[ \rightarrow H₂O(ads) + O¹(D), \]  
\[ OH(i) + OH(ads) \rightarrow H₂O(i) + O¹(D) \]

TABLE II. Translational and rotational temperatures (Ttrans and Trot) of OH(v=0 and 1) radicals from three different ice samples.

<table>
<thead>
<tr>
<th>Ice sample</th>
<th>Ttrans (K)²</th>
<th>Trot (K)⁴</th>
<th>Relative integrated TOF signal intensity³</th>
<th>Vibrational level ratio ν=1/ν=0²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh ASW</td>
<td>7500 (5%)</td>
<td>1300 (95%)</td>
<td>400</td>
<td>1</td>
</tr>
<tr>
<td>ASW after photoirradiation</td>
<td>7500 (30%)</td>
<td>1300 (70%)</td>
<td>500</td>
<td>1.7 ± 0.1</td>
</tr>
<tr>
<td>Fresh H₂O₂ on ASW</td>
<td>7500 (30%)</td>
<td>1300 (70%)</td>
<td>500</td>
<td>1.6 ± 0.1</td>
</tr>
</tbody>
</table>

¹The percentage in parenthesis is a contribution of each temperature component.
²Trot and the vibrational level ratios were measured at TOF=1.5 μs for fresh ASW and at TOF=0.5 μs for other two ice samples.
³Integrated TOF signal intensities are relative to the fresh ASW sample.
The schematic illustrations of reactions (11)–(14) are shown in Fig. 4. Thermodynamic data in units of kcal/mol are $E_{\text{avail}}(10)=115.9$, $\Delta H(11)=28.3$, $\Delta H(12)=17.6$, $\Delta H(13)=41.2$, and $\Delta H(14)=30.5$. Reactions (11)–(14) are endothermic and barrierless processes. The translational and internal energies of the OH radicals from ASW after protracted 157 nm irradiation on ASW are in good accordance with those of the OH radicals from fresh H$_2$O$_2$ on ASW as shown in Table II. The translationally hot OH($v=0$ and $T_{\text{trans}}=7500$ K) from H$_2$O$_2$ would produce the O($^1D$) atoms via reactions (11)–(14). The energy available for the H$_2$O+O pair gains kinetic energy from the hot OH radicals and the O atom is provided with enough energy to be excited electronically. Figure 4 shows that the hot OH radicals that can produce O($^1D$) atom could be formed from reaction (10). The large available energy in reaction (10) could accelerate O($^1D$) formation. Khriachtchev et al. reported in their ultraviolet photolysis of H$_2$O$_2$ in low temperature Ar matrix that (a) the excess energy provides enough kinetic energy for, at least, one OH to exit the Ar matrix cage with some probability, and (b) a considerable part of the OH pairs that remain in the cage recombine to produce the H$_2$O–O van der Waals complex. The backreaction, H$_2$O + O($^1D$) → H$_2$O$_2$ was found in the matrix photolysis of a water-ozone mixture. Andersson et al. performed classical molecular dynamics calculations for photodissociation and photodesorption efficiencies of amorphous water ice at 10 K and predicted that the mobility of OH radicals is low within the ice. However, OH radicals formed in the top 3 ML are quite mobile on top of the surface and have an increased probability of reactions with other species in or on the ice. On the other hand, Petrik et al. reported the low-energy electron-stimulated production of molecular oxygen from ASW and proposed that the electron-stimulated migration of OH or OH$^-$ to the vacuum interface where they react and produce molecular oxygen occurs via transport through the hydrogen bond network of the ASW. Both models support 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 H$_2$O$_2$ 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 $v=1/0$ of OH($v=1$ and $v=0$) is $\Delta H(15)=-38.3$, $\Delta H(16)=36.0$, and $\Delta H(17)=\Delta H(15)+\Delta H(16)=-2.3$. H$_2$O$_2$ is a proposed structural isomer of hydrogen peroxide (HOOH), which may serve as a transient intermediate.

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

Mousavipour and Saheb performed theoretical calculations for the transition state of H$_2$O+O($^1D$) formation. According to them, in the kinetics and reaction mechanism of a hydroperoxyl radical (HOO$_2$) with a H atom, reactions (15) and (16) proceed on a singlet surface to produce H$_2$O + O($^1D$) via the formation of intermediate oxywater (H$_2$OO),

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

(15)

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

(16)

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

(17)

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

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

(16)
in oxidation reactions initiated by hydrogen peroxide.\textsuperscript{51,52} 
\( O(^1D) \) atom can be produced without the barrier via the endothermic recombination reactions of hot OH radicals through the formation of HOOH and H$_2$O,

\[
\begin{align*}
\text{OH} + \text{OH} &\rightarrow \text{HOOH}, \\
\text{HOOH} &\rightarrow \text{H}_2\text{O}_2, \\
\text{H}_2\text{O}_2 &\rightarrow \text{H}_2\text{O} + O(^1D), \\
\text{net } \text{OH} + \text{OH} &\rightarrow \text{H}_2\text{O} + O(^1D).
\end{align*}
\]

(18) (19) (20) (21)

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 \( \Delta H(21) = \Delta H(18) + \Delta H(19) + \Delta H(20) = 40.0. \) The barrier height for reaction (19), \( E_{\text{bar}}(19) \), was calculated to be 52.2 kcal/mol.\textsuperscript{42} Recently, Franz et al. reported an energy of 21 kcal/mol for the lowest electronic singlet states of H$_2$O$_2$ along dissociation of the oxygen-oxygen bond into H$_2$O and O($^1D$), 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, \( E_{\text{avail}}(10)/2 = 58 \) kcal/mol, for hot OH radical formation from the 157 nm photodissociation of H$_2$O$_2$. Actually the maximum (kinetic+internal) energy of the observed OH products from photogenerated H$_2$O$_2$ on ASW is about 55 kcal/mol.

We cannot identify particular mechanisms for the O($^1D$, \( T_{\text{trans}} = 2250 \) and 300 K) atom formation. The two components of O($^1D$, \( T_{\text{trans}} = 2250 \) and 300 K) 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 O($^1D$) formation

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

\[
\begin{align*}
\text{H}_2\text{O(ads)} + h\nu(157 \text{ nm}) &\rightarrow \text{H}(i) + \text{OH}(i), \\
\text{H}(i) + \text{OH}(i) &\rightarrow \text{H}_2(i) + O(^1D), \\
\text{H}(i) + \text{OH}(\text{ads}) &\rightarrow \text{H}_2(i) + O(^1D), \\
\text{H}(\text{ads}) + \text{OH}(i) &\rightarrow \text{H}_2(i) + O(^1D).
\end{align*}
\]

(22) (23) (24) (25)

Thermodynamic data in units of kcal/mol are \( E_{\text{avail}}(22) = 51.2 \), \( \Delta H(23) = 43.3 \), \( \Delta H(24) = 47.4 \), and \( \Delta H(25) = 56.2. \) There has been no direct measurement of O($^1D$) 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 H$_2$O 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 et al. reported the evolution of spectral features in vuv photoirradiation on H$_2$O ice and found that OH was the first photoproduct observed in ice at 10 K, and then, after OH, accumulation of H$_2$O$_2$ and HO$_2$ started.\textsuperscript{10} In the present experiment, the contribution of the photolysis of OH(ads) for O($^1D$) formation, reaction (26), would be small in fresh ASW and H$_2$O$_2$ 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{18,54} and also the surfaces of ice were kept fresh for laser irradiation by exposing them with water or H$_2$O$_2$/H$_2$O vapor to suppress the secondary photolysis of the accumulated products formed on the ice surface during the photolysis,

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

(26)

O($^1D$) atoms would not be formed from the secondary photolysis of OH(ads) in ASW after prolonged photoirradiation because the TOF spectrum of O($^1D$) for ASW after 30 min photolysis has the similar translational distribution to that of fresh H$_2$O$_2$ on ASW. Van Dishoeck and Dalgarno performed theoretical calculations of the photodissociation of the OH by ab initio calculations and predicted that the vuv photodissociation of OH at 152–190 nm would not lead to O($^1D$)+H but only to O($^3P$)$_J$ + H.\textsuperscript{55,56} In fact, the secondary photolysis of OH(ads) is attributed to O($^3P$)$_J$ formation in the 157 nm photolysis of water ice where the TOF spectra of O($^3P$)$_J$ for ASW after prolonged photolysis have a different translational distribution from those of fresh ASW and fresh H$_2$O$_2$ on ASW. These results will be described in the following paper for our separate experiments.

The contribution of HO$_2$ would also be small since (a) the time evolution data of O($^1D$) in Fig. 2 are quite similar to those of H$_2$O$_2$ on the ice surface while HO$_2$ is produced from a three-step reaction of OH+H$_2$O$_2$ where H$_2$O$_2$ is produced from OH+OH, and (b) the concentration of HO$_2$ on/in ice disappeared or decreased at elevated temperatures such as 90 K.\textsuperscript{10,57}

V. SUMMARY

We have demonstrated that electronically excited O($^1D$) 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 photoproduct H$_2$O$_2$. In fresh ASW, the main part of O($^1D$) comes from the primary unimolecular reaction. In ASW after prolonged 157 nm photolysis, the contributions of unimolecular reaction become smaller, and the bimolecular reactions of hot OH radicals from the photoproduct H$_2$O$_2$ become dominant.
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