Desorption of hydroxyl radicals in the vacuum ultraviolet photolysis of amorphous solid water at 90 K

Hama, Tetsuya; Yabushita, Akihiro; Yokoyama, Masaaki; Kawasaki, Masahiro; Andersson, Stefan


ISSUE DATE:
2009-08

URL:
http://hdl.handle.net/2433/109883

Copyright 2009 American Institute of Physics. This article may be downloaded for personal use only. Any other use requires prior permission of the author and the American Institute of Physics. The following article appeared in JOURNAL OF CHEMICAL PHYSICS 131, 054508 (2009) and may be found at http://link.aip.org/link/JCPSA6/v131/i5/p054508/s1
Desorption of hydroxyl radicals in the vacuum ultraviolet photolysis of amorphous solid water at 90 K

Tetsuya Hama, Akihiro Yabushita, Masaaki Yokoyama, Masahiro Kawasaki, and Stefan Andersson

Department of Molecular Engineering, Kyoto University, Kyoto 615-8510, Japan
Leiden Observatory, Leiden University, P.O. Box 9513, 2300 RA Leiden, The Netherlands and Gorlaeus Laboratories, Leiden Institute of Chemistry, Leiden University, P.O. Box 9502, 2300 RA Leiden, The Netherlands

(Received 16 January 2009; accepted 9 July 2009; published online 6 August 2009)

We have studied the desorption dynamics of OH radicals from the 157 nm photodissociation of amorphous solid water (ASW) as well as H$_2$O$_2$ deposited on an ASW surface at 90 K. The translational and internal energy distributions of OH were measured using resonance-enhanced multiphoton ionization methods. These distributions are compared to reported molecular dynamics calculations for the condensed phase photodissociation of water ice and also reported results for the gas phase photodissociation of H$_2$O at 157 nm. We have confirmed that OH radicals are produced from two different mechanisms: one from primary photolysis of surface H$_2$O of ASW, and the other being secondary photolysis of H$_2$O$_2$ photoproducts on the ASW surface after prolonged irradiation at 157 nm. © 2009 American Institute of Physics. [DOI: 10.1063/1.3191731]

I. INTRODUCTION

Experimental and theoretical studies on the effects of radiolysis by UV photons on pure or mixed water have been extensively reported because of its importance to reaction dynamics and kinetics, atmospheric chemistry, and astrophysics. The first absorption band of water ice (the $A^1B_1^+-X^1A_1$ transition) has significant cross section in the 130–165 nm range, and photodissociation of H$_2$O in the gas phase involves two primary processes in the first absorption continuum:

$$H_2O + h\nu \rightarrow H_2 + O(1D),$$

$$H_2O + h\nu \rightarrow H + OH.$$ (1)

The effects of irradiating pure water ice by UV photons have received much experimental study. Gerakines et al. observed OH, HO$_2$, and H$_2$O$_2$ as products in the condensed phase through infrared spectroscopy after amorphous solid water (ASW) at 10 K was exposed to UV light ($\lambda > 110$ nm). Ghormley and Hochanadel reported the formation of H, OH, and H$_2$O$_2$ in the condensed phase after Xe-discharge flash photolysis of crystalline ice at 263 K. Experimental works on photodissociation or electron-stimulated desorption of species from water ice were also reported. Westley et al. investigated the absolute desorption yield from water ice at 35–100 K under irradiation with Lyman-\(\alpha\) photons of 10.2 eV. Kimmel and co-workers used resonance-enhanced multiphoton ionization (REMPI) methods to study the electron-stimulated desorption of D and O atoms and D$_2$ molecules from amorphous D$_2$O. In addition to the dissociation of water molecules, secondary reactions at the ASW/vacuum interface are also important for the desorption from ASW. Petrik et al. found that electron-stimulated desorption of O$_2$ occurs via the secondary processes of OH, HO$_2$, and H$_2$O$_2$ products at the surface/vacuum interface of ASW. Yabushita et al. observed that the photodesorption of cold and hot H$_2$ from ASW is induced by the surface reactions of H atoms produced in reaction (2).

To understand the photolysis of ASW comprehensively, it is crucial to reveal the contribution of secondary photoproducts. By direct detection of photodesorbed species, the characteristic behavior of ice photolysis may be investigated. Since OH photoproducts are readily trapped in the ice matrix, H$_2$O$_2$ was produced on the water ice surface at 90 K presumably due to recombination of photolytically produced OH.

$$OH + OH \rightarrow H_2O_2.$$ (3)

H$_2$O$_2$ formed via reaction (3) could be subsequently photodissociated to generate OH as a secondary photoproduct,

$$H_2O_2 + h\nu \rightarrow 2OH.$$ (4)

Molecular dynamics (MD) calculations by Andersson and co-workers predicted the probabilities of H atom, OH, and H$_2$O desorption from the vacuum ultraviolet (vuv) photolysis of ASW. Öberg et al. used a vuv lamp emitting in the range of 7.0–10.5 eV to irradiate ices at surface temperatures in the range of 18–100 K and detected desorbing species such as H$_2$O, OH, H$_2$, and O$_2$. However, experimental results on the details of the mechanism of photodesorption and the kinetic and internal energy distributions of the OH products have not yet been reported. In the present study, we have investigated translational and internal energy distributions of photodesorbed OH radicals following the 157 nm photodissociation of ASW and H$_2$O$_2$ at 90 K to reveal the desorption dynamics of OH radicals.
H₂O(ads) + hν(157 nm) → H(i) + OH(i).  
(5)

H₂O₂(ads) + hν(157 nm) → 2OH(i).  
(6)

The available energies in units of kcal/mol for reactions (5) and (6) at 157 nm are \( E_{\text{avail}}(5) = 51.2 \) and \( E_{\text{avail}}(6) = 115.9 \) kcal/mol. In this work, 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. Based on the present results, we have proposed two OH formation mechanisms, reactions (5) and (6). Reaction (6) is appreciable after prolonged vuv irradiation on ASW.

II. EXPERIMENTAL

A. Apparatus and preparation of ice films

Surface photodissociation of ASW at 90 K was carried out in a high vacuum chamber, which was equipped with two turbo molecular pumps, a pulsed molecular beam, an excimer laser, and a dye laser. The experimental details are described elsewhere. In brief, a vacuum chamber was evacuated to a base pressure of \( 10^{-8} \) Torr using two turbomolecular pumps in tandem (Shimadzu, 800 and 50 L s\(^{-1}\)). A circular sapphire substrate sputter coated with a thin polycrystalline film of Au was supported in the center of the chamber by a liquid-nitrogen-cooled manipulator connected to an X-Y-Z stage. The temperature of the substrate was controlled to within 1 K. The controller was composed of an alumel-chromel resistance thermometer with cooling by liquid nitrogen and heating from a 0.35 mm diameter tantalum filament attached to the substrate. The ASW film was prepared by back-filling deposition of water vapor onto the substrate at 90 K for 60 min by a pulsed nozzle (general valve) at the rate of 10 Hz and at 30 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 1800 L for 330 s by a pulsed nozzle (general valve) at the rate of 10 Hz and at 30 Torr stagnation pressure of water vapor.

For the H₂O₂/H₂O co-deposited ice 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 H₂O₂/H₂O mixture on ASW was \( < 10 \) L for 330 s duration at 90 K. Fresh surfaces of H₂O₂ co-condensed on ASW were prepared as described above.

B. Simulation of time-of-flight spectra of OH products and REMPI transition factors

Time-of-flight (TOF) spectra of OH photoproducts were taken as a function of time \( t \) between the photolysis and REMPI laser pulses using a delay generator (Stanford Research) in order to investigate the flight times (and thus translational energies) of the desorbing OH photoproducts, as shown schematically in Fig. 1. Details regarding the simulation of such TOF spectra have been reported previously. The measured TOF spectra \( S(a_i,t,T_{\text{trans}}) \) of the OH products were fitted to a sum of one or more flux-weighted Maxwell–Boltzmann (MB) distributions \( S_{\text{MB}} \), each defined by a translational temperature \( T_{\text{trans}} \). The coefficients \( a_i \) define the relative population associated with each MB component.

\[ S(a_i,t,T_{\text{trans}}) = \Sigma a_i S_{\text{MB}}(t,T_{\text{trans}}), \]
\[ S_{\text{MB}}(t,T_{\text{trans}}) = r^3 \exp[-mr^2/2k_BT_{\text{trans}}^2], \]
\[ P_{\text{MB}}(E_i) = (k_BT_{\text{trans}})^2 E_i \exp[-E_i/k_BT_{\text{trans}}], \]
the detection probability is proportional to \(2B\) Boltzmann constant. ASW. The rotational temperature peak in the TOF profile from the 157 nm photolysis of fresh \(\text{H}_2\text{O}\) is the arrow is the best-fitting procedures because the parent \(\text{H}_2\text{O} \text{ or } \text{H}_2\text{O}_2\) molecules adsorb randomly on the ASW surfaces. PGO- 

Model calculations were performed as follows. First, \(P_{\text{MB}}(E)\) is converted from the energy distribution to the TOF distribution using the Jacobian listed by Zimmerman and Ho.29 In these calculations we assume that signals come from electronic states of OH.25,30

III. RESULTS

A. OH radical from the 157 nm photolysis of fresh amorphous solid water

Figure 2(a) shows a REMPI spectrum of OH\(\nu=0\) recorded at a fixed delay of \(t=1.5 \mu\text{s}\), corresponding to the peak in the TOF profile from the 157 nm photolysis of fresh ASW. The rotational temperature \(T_{\text{rot}}(\nu=0)\) is estimated to be \(400 \pm 100 \text{ K}\) by spectral simulation [Fig. 2(b)]. Figure 3(a) shows a mixed band REMPI spectrum of OH (\(\nu=0\) and 1) at \(t=1.5 \mu\text{s}\). Figure 3(b) is a simulated mixed band spectrum for \(T_{\text{rot}}(\nu=0)=400 \text{ K}\) and \(T_{\text{rot}}(\nu=1)=300 \text{ K}\). The rotational temperature \(T_{\text{rot}}(\nu=1)\) is estimated to be \(300 \pm 100 \text{ K}\) and the population ratio of \(\nu=1/\nu=0\) is \(0.2 \pm 0.1\) by spectral simulation. Figure 4(a) shows a typical TOF spectrum of OH\(\nu=0\) for the \(R(1)+R(5)\) line, which is reproduced by two MB distributions with \(T_{\text{trans}}(\nu=0)=7500 \pm 1000 \text{ K}\) (5% contribution) and \(1300 \pm 300 \text{ K}\) (95%). Figure 4(b) shows a typical TOF spectrum of OH\(\nu=1\) for \(R(2)\) line, which is reproduced with \(T_{\text{trans}}(\nu=1)=7500 \pm 1000 \text{ K}\) (10%) and \(1300 \pm 300 \text{ K}\) (90%). We found no clear evidence of the formation of vibrationally

FIG. 2. (a) REMPI excitation spectrum of the OH \(D^2\Sigma^+ \rightarrow X^2\Pi(\nu''=0, \nu''=0)\) transition from fresh ASW. TOF=1.5 \(\mu\text{s}\). (b) A simulated OH spectrum assuming a Boltzmann distribution with \(T_{\text{rot}}=400 \text{ K}\). The arrow is the \(R(1)+R(5)\) line used for TOF spectrum measurements.

FIG. 3. (a) REMPI excitation spectrum of OH \(D^2\Sigma^+ \rightarrow X^2\Pi(\nu''=0, \nu''=0)\) and \(3^2\Sigma^+ \rightarrow X^2\Pi(\nu''=0, \nu''=1)\). TOF=1.5 \(\mu\text{s}\). (b) A simulated spectrum assuming \(T_{\text{rot}}(\nu=0)=400 \text{ K}\) (blue line) and \(T_{\text{rot}}(\nu=1)=300 \text{ K}\) (red line). The experimental conditions are the same as for Fig. 2. The arrow is the \(R(2)\) line used for TOF spectrum measurements.

FIG. 4. (a) TOF spectrum of the \(R(1)+R(5)\) line in the OH \(D^2\Sigma^+ \rightarrow X^2\Pi(\nu''=0, \nu''=0)\) transition. (b) \(R(2)\) line in OH \(3^2\Sigma^+ \rightarrow X^2\Pi(\nu''=0, \nu''=1)\). The solid black curves are fits to the data derived assuming a MB distribution. (a) \(T_{\text{trans}}=7500 \text{ K}\) (5% contribution, dashed red line) and \(1300 \text{ K}\) (95%, dashed blue line) and (b) \(T_{\text{trans}}=7500 \text{ K}\) (10%) and \(1300 \text{ K}\) (90%). Other gray curves show the error bar ranges (see Table I). The experimental conditions are the same as for Fig. 2.
excited OH($v=2$) in the wavelength region of the $3 \Sigma^{-} (v'=0) \leftrightarrow X \Pi (v''=2)$ transition. Table I summarizes these results.

**B. OH radical from the 157 nm photolysis of fresh H$_2$O$_2$ cocondensed on amorphous solid water**

Figure 5 shows the typical TOF spectra of (a) OH ($v=0$) and (b) OH($v=1$) from the 157 nm photodissociation of fresh H$_2$O$_2$ cocondensed on ASW. The OH signal intensities were 1.5–1.8 times stronger than those from fresh ASW.

**C. OH formation from the 157 nm photolysis of amorphous solid water after prolonged 157 nm irradiation**

Figure 8 shows the TOF spectra of (a) OH($v=0$) and (b) OH($v=1$) formed by 157 nm photolysis of ASW, which were measured after 1 h photoirradiation without the intermissive

![Figure 5](https://example.com/figure5.jpg)

**Figure 5.** (a) TOF spectrum of the $R(1)$+$R(5)$ line in OH $\Sigma^{-} \leftrightarrow \Pi (\nu'=0$, $\nu''=0)$ from fresh H$_2$O$_2$ cocondensed on ASW. (b) The $R(2)$ line in OH $\Sigma^{-} \leftrightarrow \Pi (\nu'=0$, $\nu''=1)$. The solid black curves are fits assuming $T_{\text{trans}}=7500$ K (30%) and 1300 K (70%) and $T_{\text{trans}}=7500$ K (40%) and 1300 K (60%). Other gray curves show the error bar ranges (see Table I).

![Figure 6](https://example.com/figure6.jpg)

**Figure 6.** REMPI excitation spectra of OH $\Sigma^{-} \leftrightarrow \Pi (\nu'=0$, $\nu''=0)$ of the fast OH signal (TOF=0.5 $\mu$s) from (a) fresh H$_2$O$_2$ (refer to Fig. 5). (b) After 1 h photolysis at 157 nm to ASW (refer to Fig. 8). (c) A simulated spectrum assuming $T_{\text{rot}}=500$ K.
The population ratio of species due to prolonged irradiation at 157 nm. Figure 9 also shows the REMPI excitation spectra of $D^2\Sigma^-\rightarrow X^2\Pi(v'=1, v''=0)$ and $3^2\Sigma^-\rightarrow X^2\Pi(v'=0, v''=1)$ of the fast OH signal (TOF=0.5 μs) from (a) fresh H₂O₂ (refer to Fig. 5). (b) After 1 h photoirradiation at 157 nm to an ASW film (refer to Fig. 8). (c) A simulated spectrum assuming $T_{\text{rot}}(v=0)=500$ K and $T_{\text{rot}}(v=1)=200$ K.

dosing of H₂O vapor. Without intermolecular deposition of water vapor on the ASW surface after each laser shot, photoproducts are accumulated on/in ASW, and hence, the secondary photolysis of the H₂O₂ photoproducts becomes appreciable in the OH formation. The OH signal intensity became about two times stronger than that from fresh ASW after prolonged photoirradiation because OH is produced from both the H₂O₂ and ASW photolysis. The contribution of the high translational temperature component ($T_{\text{trans}}=7500$ K) due to reaction (6) becomes appreciable. The results for translational temperatures and contributions are summarized in Table I.

To verify that the OH ($T_{\text{trans}}=7500$ K) component after prolonged 157 nm photolysis of ASW came from the photodissociation of the H₂O₂ photoprodut, time evolution curves of the OH($v=0$) and OH($v=1$) signal intensities were measured as a function of 157 nm irradiation time for the fast ($t=0.5$ μs) and slow ($t=2.5$ μs) TOF components. Figure 9 shows the results, in which OH signal intensities at $t=0$ are subtracted to show the increments caused by accumulated species due to prolonged irradiation at 157 nm. Figure 9 also includes the previously reported time evolution of H₂O₂ that was photolytically accumulated on the ASW surface by 157 nm irradiation. The two appearance curves correspond with each other, suggesting that the source of OH after prolonged 157 nm irradiation is photochemically produced H₂O₂.

Figure 6(b) shows the REMPI spectrum of OH($v=0$) at $t=0.5$ μs and $T_{\text{trans}}=500±100$ K by spectral simulation [Fig. 6(c)]. Figure 7(b) shows a mixed band REMPI spectrum of OH ($v=0$ and 1) at $t=0.5$ μs with $T_{\text{rot}}(v=1)=200±100$ K. The population ratio of $v=1/v=0$ was 0.2±0.1 by spectral simulation [Fig. 7(c)]. These results are almost the same as for H₂O₂ cocondensed on ASW described in Sec. III B, suggesting again that the source of OH after prolonged 157 nm irradiation is photochemically accumulated H₂O₂.

IV. DISCUSSION

A. Translational and internal energies of OH radicals from fresh amorphous solid water

The translational energies of OH($v=0$) and OH($v=1$) from fresh ASW are mostly fitted with a temperature $T_{\text{trans}}=1300±300$ K. This temperature (translational energy=5.2±1.2 kcal/mol) is in accordance with ~1600 K that was reported in the gas phase photodissociation of water at 157 nm by Mikulecky et al. and the MD calculations (4.5–6.0 kcal/mol) by Andersson and co-workers. A small contribution (5%–10%) of the fast ($T_{\text{trans}}=7500$ K) component would be due to the secondary photoprocess from the H₂O₂ products on ASW since the ASW surface was not completely covered with fresh H₂O vapor even with intermolecular H₂O deposition. The rotational temperatures $T_{\text{rot}}(v=0)=400$ K and $T_{\text{rot}}(v=1)=300$ K are not thermally equilibrated with the ice film temperature of 90 K. Mikulecky et al. reported $T_{\text{rot}}(v=0)=620$ K and $T_{\text{rot}}(v=1)=460$ K for OH formed from the gas phase photodissociation of H₂O. These results suggest that we observed nascent OH photofragments originated from the ASW surface.
Andersson and co-workers\textsuperscript{18,19} calculated the desorption probabilities for OH radicals from water ice per absorbed vuv photon in the top 6 monolayers (ML). This gave the OH desorption probability as function of the monolayer in which H\textsubscript{2}O was excited. Only a small fraction of OH radicals from the top 3 ML can desorb with desorption probability less than 3\% per ML, while most OH products are trapped in/on the ice at 10 K. The lack of a surface accommodated TOF component in the present results indicates that OH formed in the ice bulk is readily trapped or reacts with water molecules in the ice bulk. In addition, the rotational distribution is essentially the same as those observed and calculated for gas-phase H\textsubscript{2}O photolysis. We conclude that the dominant fraction of OH desorbed into vacuum is released from the topmost monolayer(s) of ASW.

Our present observation of vibrational distribution \(v=1/u=0\sim0.2\) is in fair agreement with the molecular dynamic calculations at 10 K by Andersson and co-workers,\textsuperscript{18,19} which predicted that desorbed OH has a maximum population at \(v=0\) and that the amount of vibrational excitation drops only by about 30\%–50\% from one excited level to the next. The fractions of the total available energy partitioned into the different degrees of freedom in the dissociation products have also been determined. Using the translational, vibrational, and rotational distributions, it was found that 8\%–12\% of the available energy (51.2 kcal/mol) was partitioned into translation, 5\%–7\% into vibration, and 1\% and 2\% into rotation. The remainder presumably has been partitioned into the ASW matrix and translational energy of the H atom.

It is interesting to note the difference between the gas phase and solid phase photodynamics for H\textsubscript{2}O at 157 nm. Hwang et al.\textsuperscript{32} and Yang et al.\textsuperscript{33} showed that OH\((v=1)\) was populated by 10\% more than OH\((v=0)\), and OH\((v\geq2)\) populations dropped below the detection threshold. This vibrational state distribution is different from the condensed phase results as presented in this paper. Reasons for this can be found in differences in the excited state potentials, dissipation of energy, and/or the dynamics of the photodissociation process. The two first cases were already discussed in some depth by Andersson and co-workers.\textsuperscript{18,19} In short, there is evidence that the surrounding water molecules affect the electronically excited state of H\textsubscript{2}O by lowering the intramolecular part of the excitation energy. This was also found in the high-level electronic structure calculations by Chipman,\textsuperscript{34,35} which showed that the first excited state potential energy surface of H\textsubscript{2}O is significantly affected by neighboring H\textsubscript{2}O molecules. This would lead to somewhat different product energy distributions.

The translational energy distribution of the desorbing H atoms seemed to be affected by this effect, possibly combined with the dissipation of excess energy.\textsuperscript{14} This dissipation of energy will most likely proceed through energy transfer to vibrational modes of water molecules in the ice and/or through reaction of energetic H atoms with H\textsubscript{2}O\textsubscript{2}.\textsuperscript{14–16}

\begin{equation}
\text{H + H}_2\text{O} \rightarrow \text{H}_2 + \text{OH}.
\end{equation}

The good agreement between the classical MD calculations and experiments could be fortuitous or there could be a more fundamental reason for this. Generally, full quantum dynamics calculations are required to obtain reliable product quantum state distributions. This has been done for the case of gas-phase photodissociation of H\textsubscript{2}O by van Harrevelt and van Hemert.\textsuperscript{36} However, in the case of multidimensional systems such as a liquid or a solid the most important quantum effects are often "static," i.e., inclusion of zero-point energy, rather than dynamic interference effects.\textsuperscript{37,38} The reason for this is the rapid loss of coherence that is common in condensed phases.

B. OH radical formation by the secondary photoprocess of H\textsubscript{2}O\textsubscript{2}

In their MD calculations, Andersson and co-workers\textsuperscript{18,19} studied the mobility of OH radicals following the photolysis of water ice. The OH radicals formed in the ice move only at a maximum distance of 5 Å at 10 K. However, OH radicals formed from photodissociation in the top 3 ML are able to move up to more than 60 Å. This indicates that the OH radicals that have diffused along the surface and have dissipated some of their internal energy to the surface in the process are likely trapped at the surface site but not desorbed. On the other hand, Petrik et al.\textsuperscript{13} reported the low-energy electron-stimulated production of molecular oxygen from thin ASW films and proposed that the electron-stimulated migration of OH or OH\textsuperscript{+} to the vacuum interface, where they react and produce molecular oxygen, occurs via transport through the hydrogen bond network of the ASW. In either case, it is speculated that the recombination of OH to form H\textsubscript{2}O\textsubscript{2} occurs more readily at the surface of ASW compared to the bulk. In fact, Yabushita et al.\textsuperscript{17} reported in their vuv photolysis experiments that H\textsubscript{2}O\textsubscript{2} was subsequently produced on the water ice surface at 90 K presumably due to recombination of photolytically produced OH.

Figure 9 shows the appearance behavior of OH signals mainly due to reaction (6), the secondary photodissociation...
of surface-bound H$_2$O$_2$ formed via reaction (3). The higher-translational temperature ($T_{\text{trans}}=7500$ K) of Figs. 5(a) and 5(b) is attributed to the larger $E_{\text{avail}}$ in reaction (6) than reaction (5). In addition, the translational and internal energies for the OH radicals from H$_2$O$_2$ directly condensed on ASW are in good accordance with those for the OH radicals following the prolonged 157 nm irradiation of ASW. Therefore, the contribution of OH radicals from other by-products such as HO$_2$ formed as follows would be small, since (a) 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) HO$_2$ disappears at elevated temperatures.\(^7\)

\[
\begin{align*}
\text{H}_2\text{O}_2 + h\nu & \rightarrow \text{H} + \text{HO}_2, \\
\text{H}_2\text{O}_2 + \text{OH} & \rightarrow \text{H}_2\text{O} + \text{HO}_2, \\
\text{HO}_2 + h\nu & \rightarrow \text{O} + \text{OH}.
\end{align*}
\]

V. CONCLUSION

In the 157 nm irradiation experiments on ASW at 90 K, we have measured the translational and rotational temperatures and vibrational distributions for OH (\(v=0\) and 1) that are the products from surface H$_2$O of ASW as well as the products from H$_2$O$_2$ that is photochemically produced on the surface of ASW. OH from H$_2$O$_2$ is characterized by a translational temperature of 1300 K, while that of OH from H$_2$O$_2$ is 7500 K. We found that the contribution of the secondary photolysis of accumulated photoproducts is appreciable in the condensed phase photoprocesses of water ice.

ACKNOWLEDGMENTS

This work is supported by a grant in aid from JSPS (Grant No. 20245005).


\(^{29}\) C. M. Western, Porphyr, a program for simulating rotational structure, University of Bristol, http://pgophernet.bris.ac.uk.


