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Translational and internal energy distributions of methyl and hydroxyl radicals produced by 157 nm photodissociation of amorphous solid methanol

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Methanol is typically observed within water-rich interstellar ices and is a source of interstellar organic species. Following the 157 nm photoexcitation of solid methanol at 90 K, desorbed CH3(ν=0) and OH(ν=0,1) radicals have been observed in situ, near the solid surface, using resonance-enhanced multiphoton ionization (REMPI) detection methods. Time-of-flight and rotationally resolved REMPI spectra of the desorbed species were measured, and the respective fragment internal energy and kinetic energy distributions were obtained. Photoproduction mechanisms for CH3 and OH radicals from solid methanol are discussed. The formation of O(1D) and 3P) atoms and H2O was investigated, but the yield of these species was found to be negligible. CH3 products arising following the photoexcitation of water-methanol mixed ice showed similar kinetic and internal energy distributions to those from neat methanol ice.

I. INTRODUCTION

Methanol is the smallest closed shell alcohol and has long served as a model for the dissociation of organic molecules. There is a comparably large body of literature on the vacuum ultraviolet (VUV) photolysis of methanol in the gas phase.1–6 The results of the gas phase methanol photolysis studies at 157 nm showed that the relative contribution of the atomic hydrogen elimination process is larger than that of the molecular hydrogen elimination process, i.e., the ratio is 1:0.21.2 C–O bond cleavage [reaction (1)] is another primary photoprocess following excitation of the 21A1→X1A1 transition in the 151–163 nm region, where it competes with the atomic and molecular hydrogen elimination processes,

\[
\text{CH}_3\text{OH} + h\nu \rightarrow \text{CH}_3 + \text{OH}. \tag{1}
\]

The relative contribution of the C–O bond cleavage channel in the gas phase photolysis at 157 nm has yet to be determined.2,3 Reaction (1) was also observed following the photoexcitation of CH3OH in various rare-gas matrices at 4 K and the photodissociation threshold energy for reaction (1) identified at λ ~ 175 nm.7 Since methanol is known to be a component of the icy mantle of interstellar grains, comets, and other solar system bodies,8–11 the effects of irradiating pure methanol ice by electrons, ions, and UV photons have each received much experimental study.12–16 Compared to the gas phase, however, the photochemical processes occurring in condensed phase samples of CH3OH are more complicated because of the many possible secondary reactions on/in solid CH3OH.15,16 UV absorption of methanol in the condensed phase is observed at wavelengths shorter than the ~185 nm threshold.17 Gerakines et al. reported VUV (λ > 110 nm) photolysis studies of solid CH3OH at 10 K. Hydrogen (H2), carbon monoxide (CO), carbon dioxide (CO2), formyl radical (HCO), formaldehyde (H2CO), methane (CH4), and methyl formate (CH3OCHO) were detected as products by in situ infrared (IR) absorption spectroscopy, but CH3 and OH radicals were not.16 CH4 production from VUV photolysis of solid methanol was reported to scale linearly with irradiation time.15,16 Unimolecular photodissociation,

\[
\text{CH}_3\text{OH} + h\nu \rightarrow \text{CH}_3(\text{X}^1\text{A}_1) + \text{O}(1\text{D}), \tag{2}
\]

is thus one plausible CH4 formation mechanism. As Gerakines et al. noted, however, further research is necessary since gas phase photolysis studies have failed to reveal any evidence of reaction (2).2,3,16

To obtain a more complete mechanism understanding of amorphous solid methanol (ASM) photolysis—including possible secondary reactions on/in ASM—it would be helpful to determine the kinetic and internal energy distributions of the photoproducts generated from the primary photodissociation of ASM. Hama et al. previously used sensitive resonance-enhanced multiphoton ionization (REMPI) methods to determine the translational and internal energy distributions of, and thus formation mechanisms for, photodesorbed H atoms and H2 molecules following VUV photolysis of ASM.18

In this paper, we investigate the mechanisms, the dynamics of production and the possible reactions of CH3 and OH...
products following 157 nm photodissociation of ASM at 90 K, using REMPI methods to determine their respective translational energy distributions and internal state population distributions. Possible secondary reactions on/in ASM are discussed in light of the obtained results. An attempt was also made to detect O(1D) and O(3P) atoms and H2O products.

II. EXPERIMENTAL

A. Apparatus and preparation of ice films

The apparatus has been described before, and only details relevant to the present experiments are given here.19 As shown in the schematic diagram of the experimental arrangement (Fig. 1), photodesorbed products were ionized at the focal point of the REMPI probe laser light, which was separated from the ice surface by a vertical distance of r. ASM was prepared by backfilling deposition of methanol vapor onto the gold substrate at 90 K for 60 min. The exposure was typically 1500 L (1 L = 1 × 10−6 Torr s) to exclude the influence of reactions at the ASM/substrate interface.

Since crystallization of solid methanol occurs at temperatures above 103.4 K, the morphology of the prepared solid methanol is amorphous.22 Unfocused 157 nm laser (Lambda Physik, OPTexPro) radiation with a pulse duration of 10 ns [full width at half maximum (FWHM)] was incident on the ice surface at an angle of −80° to the surface normal and at a fluence, F < 0.1 mJ (≈1014 photons) cm−2 pulse−1, which roughly corresponds to that in molecular clouds over ~104 yr.23 CH3 photoproducts were ionized at a distance of r = 2 mm from the substrate surface (4 mm for the case of OH products). CH3 products were detected by (2+1) REMPI via the 4p2 2A2(υ′ = 0) → X 2Π(υ″ = 0) transition in the wavelength range of 285.0–287.0 nm and collected with a small mass spectrometer aligned perpendicular to the ice surface.24 OH products were probed by (2+1) REMPI via the D 2Σ− (υ′ = 0) → X 2Π(υ″ = 0) transition at 243.5–245.0 nm and via the D 2Σ− (υ′ = 1) → X 2Π(υ″ = 0) and 3 2Σ− (υ′ = 0) → X 2Π(υ″ = 1) transitions in the wavelength range of 237.5–237.7 nm.25 PGOPHER, a program for simulating rotational structure, was used to simulate the measured spectra and thereby establish the product rotational temperatures. Detection of O(1D), O(3Pj=2,1,0) atoms and H2O molecules was attempted also by (2+1) REMPI via the O(1F3←1D2) transition at 203.8 nm, the O(3Pj=2,1,0) transition at 225.6–226.4 nm, and the C(000)-X(000) transition at 247.3–248.6 nm, respectively.27–29 but no signal was observed. Photodesorption of O(1D2), O(3Pj=2,1,0) atoms, and H2O molecules has been previously observed with the same REMPI setup following the 157 nm photolysis of H2O ice at 90 K.29–31

Recognizing that photoproducts might accumulate on the ASM surface after prolonged irradiation by 157 nm photolysis pulses, and that the photochemistry of these products might influence the measured product (state) distributions, the ASM surface was continually refreshed by intermissive exposure to CH3OH vapor. In the present experiments, the pulsed valve was opened after each laser shot so as to deposit a fresh layer of ASM.

For the CH3OH/H2O codeposited ice photolysis experiments, CH3OH/H2O (1:1 mixture) vapor was deposited on the gold substrate. As before, the exposure was typically 1500 L and, again, fresh surfaces of cocondensed CH3OH/H2O were prepared as described above. All of the present photolysis experiments were performed at a sample temperature of 90 K, and the chamber pressure was 5 × 10−7 Torr (due to the intermissive CH3OH or CH3OH/H2O vapor injection into the chamber).

B. Simulation of (2+1) REMPI spectra

CH3 products were monitored by (2+1) REMPI via the 4p2 2A2(υ′ = 0) → X 2Π(υ″ = 0) transition. Spectral simulation employed the program PGOPHER (Ref. 26) and the spectroscopic constants reported by Black and Powis.24 The 4p2 2A2(υ′ = 0) state predissociates with a level dependent efficiency.24 This affects the measured REMPI line intensities and linewidths such that the latter vary as {0.4+0.08[N(N+1)−K2]} (in cm−1), while the former declines by the square of this term. The measured spectra show evidence of power broadening also, which we accommodate by further broadening each transition with a Lorentzian function (3 cm−1 FWHM) and by reducing the relative weighting of the zero rank component of this two-photon transition. The two-photon transition probability is carried by two (a zero and a second rank) components. The former contributes only to the intense central Q branch (which is noticeably saturated under the present conditions), while the latter gives rise to O, P, Q, R, and S branches.

The REMPI features associated with OH products were also assigned and simulated using literature constants for the relevant electronic states.25,32 The two-photon absorption cross sections reported by Greenslade et al.25 allow estimation of the (υn=1)/(υn=0) branching ratio in the OH products.

C. Simulation of time-of-flight spectra of photoproducts

Time-of-flight (TOF) spectra of the CH3 and 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 photoprod-

(a) 2 (2+1) REMPI excitation spectrum of CH3 radicals from the 157 nm photolysis of a fresh ASM sample at 90 K, recorded at t=6.0 μs. (b) Simulated REMPI excitation spectrum of CH3 radicals, resonance enhanced at the two photon energy by the 4p2 → 3A′ (υ′=0) level, assuming a Boltzmann distribution rotational state population distribution with Trot=150 K.

FIG. 2. (a) (2+1) REMPI excitation spectrum of CH3 radicals from the 157 nm photolysis of a fresh ASM sample, monitoring on the Q branch of the (2+1) REMPI spectrum shown in Fig. 2. The solid curves are fits to the data derived assuming two MB distributions with Ttrans=3000 K (10%) and 90 K (90%). The vertical flight distance used in these experiments is 2 mm.

products as shown schematically in Fig. 1. The measured TOF spectra, S(a1, t, Ttrans), of the CH3 and OH products were fitted to a sum of one or more flux-weighted Maxwell–Boltzmann (MB) distributions, SMB, each defined by a translational temperature, Ttrans. Details regarding the simulation of such TOF spectra have been reported previously.19 The coefficients, a1, define the relative population associated with each MB component,

$$S(a1, t, T_{trans}) = \sum a1S_{MB}(t, T_{trans}), \quad (3)$$

$$S_{MB}(t, T_{trans}) = r^2 - r^4 \exp[-m^2/2kBT^2], \quad (4)$$

where r is the flight distance. The MB distribution, PMB(E1), as a function of translational energy, E1, is characterized by the averaged translational energy, $\langle E_1 \rangle = 2kBT_{trans}$, where kT is the Boltzmann constant.

$$P_{MB}(E_1) = (kBT_{trans})^{-2}E_1 \exp[-E_1/k_BT_{trans}]. \quad (5)$$

Conversion from the E1 distribution to the TOF distribution was performed using the Jacobian listed by Zimmerman and Ho.34

In these calculations for details, we assume that signals come from a disk (VUV photoradiation area) with a radius of 6 mm. Hence, the effective flight length is given by $r^2 + R^2/2$ and the detection probability is proportional to $2\pi Rdr/(r^2 + R^2)^{1/2}$, where r=2 and 4 mm for the case of CH3 and OH products, respectively, and 0≤R≤6 mm.19 The variable R is the radius of the irradiation area which was defined in Ref. 19. For the angular distribution of the photofragments from the ice surface, cosθ, where θ is the surface polar coordinate, n=0 was adopted in the best-fitting procedures because the parent CH3OH molecules adsorb randomly on the ASM surfaces.19,35

III. RESULTS

A. Kinetic energy and rotational energy distributions of the CH3 radical

Figure 2(a) shows a rotationally resolved REMPI spectrum of CH3 (υ′=0) products formed following the 157 nm photolysis of freshly deposited ASM recorded at a fixed delay of t=6.0 μs. The spectrum is readily assignable to the 4p2 → 3A′ (υ′=0) ← X2A′ (υ′=0) transition.24,36 The best-fit simulation is shown in Fig. 2(b).

The rotational temperature, Trot, is estimated to be 150±50 K ($\langle E_{rot} \rangle = 1.2 \pm 0.4$ kJ mol$^{-1}$) by comparison with the spectral simulation. Figure 3 shows a typical TOF spectrum of the CH3 products monitored at a REMPI wavelength of 286.0 nm (i.e., in the congested Q branch), which is reproduced well by a sum of two MB distributions with Ttrans = 3000 ± 1000 K ($\langle E_{trans} \rangle = 49.9 \pm 16.6$ kJ mol$^{-1}$) and 90 ± 20 K ($\langle E_{trans} \rangle = 1.5 \pm 0.3$ kJ mol$^{-1}$). Table I summarizes these results. Changing the REMPI probe wavelength, e.g., to the S(2) line at 285.45 nm, led to no appreciable change in the TOF profile. We were unable to characterize the rotational resolved REMPI spectrum for the Ttrans=3000 K component in terms of a specific Trot because of the weak signal intensity.

B. Kinetic energy and rotational distributions of the OH radical

Figure 4(a) shows a rotationally resolved REMPI spectrum of the OH (υ′=0) products recorded at t=2.0 μs, i.e., at the maximum of the single peak in their TOF spectrum. Spectral simulation [Fig. 4(b)] returns a best-fit rotational temperature Trot (υ′=0) = 300 K, and the rotational temperature Trot (υ′=0) is estimated to be 300 ± 100 K by spectral simulation ($\langle E_{rot} \rangle = 2.5 \pm 0.8$ kJ mol$^{-1}$). Figures 5(a) and 5(b) show typical TOF spectra of the OH (υ′=0) and OH (υ′=1) products.

TABLE I. Translational and rotational temperatures and energies of CH3(υ′=0) products.

\begin{tabular}{|l|l|l|l|}
\hline
Time-of-flight component, & Translational & Rotational & Rotational \\
contributions & energy & temperature & energy \\
 & (kJ mol$^{-1}$) & (K) & (kJ mol$^{-1}$) \\
\hline
CH3 (Ttrans=3000 K), 10% & 49.9 ± 16.6 & a & * \\
CH3 (Ttrans=90 K), 90% & 1.5 ± 0.3 & 150 ± 50b & 1.2 ± 0.4b \\
\hline
\end{tabular}

a The rotational spectrum could not be characterized by a specific Trot because of the weakness of the signal intensity.

b From spectra recorded at t=6.0 μs.
products monitoring, respectively, the $R_t(1)+R_t(5)$ line and the $R_t(2)$ line in the REMPI spectrum. Both are reproduced well by a single MB distribution with $T_{\text{trans}}=3000 \pm 500$ K ($\langle E_{\text{trans}}\rangle=49.9 \pm 8.3$ kcal mol$^{-1}$). No component with $T_{\text{trans}}=90$ K was detected, in contrast to CH$_3$ products. Figure 6(a) shows another portion of the OH REMPI spectrum which contains overlapping contributions from both OH($v=0$) and OH($v=1$) products, recorded at $t=2.0 \mu$s; the accompanying simulation [Fig. 6(b)] employs $T_{\text{rot}}(v=0)=300$ K and $T_{\text{rot}}(v=1)=200$ K. The rotational temperature $T_{\text{rot}}(v=1)$ is estimated to be 200 $\pm$ 50 K by spectral simulation ($\langle E_{\text{rot}}\rangle=1.7 \pm 0.4$ kJ mol$^{-1}$). The OH($v=1$)/OH($v=0$) population ratio is determined to be 0.2 $\pm$ 0.1. Table II summarizes these results.

**C. Additional 157 nm photolysis experiments involving ASM**

To assess possible contributions from secondary processes on the ASM surface and in the bulk, additional experiments were performed wherein TOF spectra of CH$_3$ and OH products formed by 157 nm photolysis of ASM were measured after 30 min photoradiation without the intermixture of CH$_3$OH vapor. No discernible differences were found in either the TOF spectra or the rotationally resolved REMPI spectra of the CH$_3$ or OH products recorded with the fresh or photoirradiated ASM samples. These results support the views that (a) the observed CH$_3$ and OH radicals are produced directly via the C–O cleavage reaction (1) and (b) secondary photoprocesses on/in ASM make no contribution to the formation of these desorbing species.

REMPI signals attributable to O($^1D$) and O($^3P$) atoms were sought in the TOF range 0.5 $\mu$s $\leq t \leq 30$ $\mu$s, but not observed. The primary formation of methane and O($^3P$) products is a spin-forbidden process, i.e.,

$$\text{CH}_3\text{OH} + h\nu \rightarrow \text{CH}_3(X^1A_1) + \text{O}(^3P).$$

O($^1D$) and O($^3P$) atoms have been successfully detected with the same REMPI setup following the 157 nm photolysis of H$_2$O or H$_2$O$_2$ ices films at 90 K. The lack of detectable O($^1D$) and O($^3P$) atoms in the present methanol experiments is in accord with the results of gas phase methanol photolysis studies at 157 nm (Refs. 2 and 3) and suggests that the primary formation of methane and O($^1D$) or O($^3P$) products via reactions (2) and (6) plays at most a minor role.

To verify that the measured CH$_3$ product state distributions are not affected by possible contamination from back-

---

**TABLE II. Translational and rotational temperatures and energies of OH($v=0$) and 1) products.**

<table>
<thead>
<tr>
<th></th>
<th>OH($v=0$)</th>
<th>OH($v=1$)$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Translation</strong></td>
<td>Rotation</td>
<td>Translation</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>3000 $\pm$ 500</td>
<td>3000 $\pm$ 500</td>
</tr>
<tr>
<td>Energy (kJ mol$^{-1}$)</td>
<td>49.9 $\pm$ 8.3</td>
<td>2.5 $\pm$ 0.8</td>
</tr>
</tbody>
</table>

$^a$Population ratio OH($v=1$)/OH($v=0$)=0.2 $\pm$ 0.1.

$^b$From spectra recorded at $t=2.0 \mu$s.
ground water vapor, the ASM sample was changed to a 1:1 mixture of CH3OH/H2O ice. The intensities of the $T_{\text{trans}}$ = 3000 and 90 K components of the CH3 radical TOF signal from the mixed sample were both reduced, and the majority of the CH3 products are accommodated to the substrate temperature (90 K) which was similar to that from pure, fresh ASM samples.

A similar check is not possible for the OH products because of the contribution from other OH products formed by simultaneous photolysis of H2O.

### IV. DISCUSSION

The C–O bond cleavage has been observed as a primary process following photolysis of CH3OH both in the gas phase and in solid rare-gas matrices,

$$\text{CH}_3\text{OH}(\text{ads}) + h\nu \rightarrow \text{CH}_3(i) + \text{OH}(i),$$  

wherein we determine an average center of mass translational energy distribution of the CH3 and OH products resulting from reactions on/in ASM and thus remain undetected. In the following sections, possible secondary reactions of CH3 and OH products on/in ASM are proposed.

#### A. CH3 radical formation in the 157 nm photolysis of fresh ASM

Two MB components, characterized by $T_{\text{trans}}$ = 3000 and 90 K and with respective relative yields of 10% and 90%, are required to fit the TOF spectrum of CH3 products measured at 157 nm. The CH3 rotational temperatures for the $T_{\text{trans}}$ = 90 K component are almost thermally equilibrated with the substrate temperature (90 K), as shown in Table I. Since 90% of the CH3 fragments are almost thermally equilibrated in the ASM bulk and are subsequently relaxed by collisions within the ASM, they may be considered as formed in the ASM ensemble. Only a small fraction (10%) of the CH3 products are produced at the exposed ASM surface and retain a high translational temperature, i.e.,

$$\text{CH}_3\text{OH} + h\nu \rightarrow \text{CH}_3(T_{\text{trans}} = 3000 \text{ K}) + \text{OH},$$

$$\text{CH}_3(3000 \text{ K}) \rightarrow \text{CH}_3(90 \text{ K}).$$

CH3 photoproducts may also be removed by reactions within the bulk and thereby remain undetected by IR absorption spectroscopy. For example, hydrogen abstraction from methanol by CH3 radicals, reactions (14) and (15), are known in the gas phase.

$$\text{CH}_3(i) + \text{CH}_3\text{OH}(\text{ads}) \rightarrow \text{CH}_4(i) + \text{CH}_2\text{OH}(i),$$

$$\Delta H = 4.2, \quad E_a = 58.6 \text{ kJ mol}^{-1},$$

$$\text{CH}_3(i) + \text{CH}_3\text{OH}(\text{ads}) \rightarrow \text{CH}_4(i) + \text{CH}_3\text{O}(i),$$

$$\Delta H = 33.5, \quad E_a = 56.9 \text{ kJ mol}^{-1}.$$
Other possible removal processes for CH$_3$ include (generally barrierless) reaction with other radical photoproducts, e.g., reaction with H-atom photoproducts to form methane,

$$\text{CH}_3(i) + \text{H}(i) + \text{M} \rightarrow \text{CH}_4(i) + \text{M},$$  
$$\Delta H = -439.3 \text{ kJ mol}^{-1}. \quad (16)$$

Compared to the gas phase, we might anticipate a significant enhancement in the rate of reaction (16) in ASM since H atoms are very mobile, even at low temperature, and reaction (16) is a highly exothermic, three-body reaction. H atoms are known to be present in high density following pulsed 157 nm laser excitation of ASM at 90 K, and H$_2$ molecule formation from H atoms has also been reported,\textsuperscript{15} i.e.,

$$\text{CH}_3\text{OH} + h\nu \rightarrow \text{CH}_2\text{OH}/\text{CH}_3\text{O} + \text{H},$$  
$$\text{H} + \text{CH}_3\text{OH} \rightarrow \text{CH}_2\text{OH}/\text{CH}_3\text{O} + \text{H}_2(v = 0 \text{ and } 1),$$  
$$\text{H} + \text{H} \rightarrow \text{H}_2(v \geq 2).$$  

(17)  
(18)  
(19)

Earlier VUV photolysis studies of solid methanol at 10 K found the yield of CH$_4$ to depend linearly on the irradiation time, but no IR absorption signal attributable to CH$_3$ was observed,\textsuperscript{15,16} probably because these radicals were efficiently consumed by reaction with H atoms, i.e., via reaction (16).

In the mixed CH$_3$OH/H$_2$O ice experiment, the TOF signal intensity of the CH$_3$ radicals was reduced. This may be due to (a) the reduction in CH$_3$OH density on the surface, or (b) the reaction of CH$_3$ products with H atoms or OH radicals formed from photolysis of H$_2$O. The reaction of CH$_3$ with water molecules is unlikely: the TOF profile of CH$_3$ radicals produced from the mixed ice showed a similar behavior to that from the fresh ASM samples, i.e., the majority of the CH$_3$ products are accommodated to the substrate temperature (90 K). This implies that the CH$_3$ products desorb without reaction with solid water, as would be expected given the large activation energy of reaction (20),

$$\text{CH}_3(i) + \text{H}_2\text{O}(\text{ads}) \rightarrow \text{CH}_4(i) + \text{OH}(i),$$  
$$\Delta H = 104.6, \quad E_a = 138.1 \text{ kJ mol}^{-1}. \quad (20)$$

The activation energy or reaction (20) was estimated from theoretical calculations for the reverse process, CH$_4$+OH $\rightarrow$ CH$_3$+H$_2$O, by Bravo-Pérez et al.\textsuperscript{42}

The translational temperatures of the photodesorbed H or OH products following the 157 nm photolysis of water ice have been previously observed with the same REMPI setup.\textsuperscript{38,43,44} The previous results showed that the majority of the photodesorbed H atoms were relaxed by collisions within the water ice and the translational temperature was accommodated to the substrate temperature. The photodesorbed OH radicals, on the other hand, were not thermally equilibrated with the substrate temperature but were likely formed near the water ice surface, whereas collisionally cooled OH products were either efficiently trapped in the bulk or reacted with water.\textsuperscript{38,43,44}

B. OH radical formation in the 157 nm photolysis of fresh ASM

The translational energies of OH($v=0$ and 1) products from the 157 nm photolysis of fresh ASM are described by a single temperature $T_{\text{trans}}=3000 \pm 500 \text{ K}$ ($\langle E_{\text{trans}} \rangle = 49.9 \pm 8.3 \text{ kJ mol}^{-1}$). The OH rotational temperatures, $T_{\text{rot}}(v=0) = 300 \pm 100 \text{ K}$ and $T_{\text{rot}}(v=1) = 200 \pm 50 \text{ K}$, are not thermally equilibrated with the substrate temperature of 90 K, as shown in Table II. These results suggest that (a) the observed OH($v=0$ and 1) fragments originate from the ASM surface, not the bulk, and (b) OH($v=0$ and 1) radicals formed in the ASM bulk are either efficiently trapped or react in the bulk as described before in the 157 nm photolysis of H$_2$O.\textsuperscript{37,38} i.e.,

$$\text{CH}_3\text{OH} + h\nu \rightarrow \text{CH}_3 + \text{OH}(T_{\text{trans}} = 3000 \text{ K}),$$  
$$\text{OH}(3000 \text{ K}) \rightarrow \text{trapped or react with ASM.} \quad (21)$$

Possible H abstraction reactions from methanol by OH radicals are

$$\text{OH}(i) + \text{CH}_3\text{OH}(\text{ads}) \rightarrow \text{H}_2\text{O}(i) + \text{CH}_2\text{O}(i),$$  
$$\Delta H = -50.2, \quad E_a = 3.8 \text{ kJ mol}^{-1}, \quad (23)$$

$$\text{OH}(i) + \text{CH}_3\text{OH}(\text{ads}) \rightarrow \text{H}_2\text{O}(i) + \text{CH}_2\text{O}(i),$$  
$$\Delta H = -25.1, \quad E_a = 14.6 \text{ kJ mol}^{-1}. \quad (24)$$

The activation energies quoted are for the corresponding gas phase reactions, estimated by Jodkowski et al.\textsuperscript{41} Reaction (23) has been proposed previously in methanol-water condensed phase systems.\textsuperscript{45} Recalling Table II, the OH products from the 157 nm photolysis of ASM have ample energy to overcome the barriers for reactions (23) and (24), and thus OH radical initiated hydrogen abstraction is likely to occur on/in ASM.

However, neither photodesorption nor production of H$_2$O was observed in either the present or earlier VUV photolysis studies on ASM.\textsuperscript{15,16} These results imply that the yield of OH production via the C–O bond cleavage reaction (7) on the surface is small and that the secondary H$_2$O formation via reactions (23) and (24) does not proceed efficiently.

C. Other possible secondary reactions

After photolysis of a CH$_3$OH molecule in bulk ASM, the probability of reaction (25) is expected to be high since the photogenerated CH$_3$ and OH radicals are effectively caged by the ASM matrix.\textsuperscript{17,46,47} i.e.,

$$\text{CH}_3(i) + \text{OH}(i) + \text{M} \rightarrow \text{CH}_3\text{OH}(\text{ads}) + \text{M},$$  
$$\Delta H = -422.6 \text{ kJ mol}^{-1}, \quad (25)$$

the bimolecular reaction between gas phase CH$_3$ and OH radicals has been studied extensively, both theoretically and experimentally.\textsuperscript{48} The calculations of Jasper et al. show a number of reactive radicals and molecular products from this
reaction, e.g., CH₃OH, HCOH+H₂, and CH₂+H₂O. In the condensed phase, Hodys et al. reported a UV (130–335 nm) photolysis study of CH₃-H₂O ice mixtures at 20 K. Their analysis assumes that OH radicals formed by the photodissociation of water react with methane to form CH₃ radicals, which then recombine with OH radicals to form methanol.

Ethane formation, from the recombinational reaction of two CH₃ radicals [reaction (26)], was also reported in the photolysis of CH₃-H₂O ice mixtures,

\[
\text{CH}_3(i) + \text{CH}_3(i) + \text{M} \rightarrow \text{C}_2\text{H}_6(i) + \text{M},
\]

\[
\Delta H = -376.6 \text{ kJ mol}^{-1}.
\] (26)

No IR absorption attributable to C₂H₆ was observed in the earlier VUV photolysis studies of solid CH₃OH at 10 K, however. This finding is understandable if CH₃ photo-products react with other species (e.g., H, OH, or CH₃OH) much more frequently than they encounter another CH₃ radical.

Hodys et al. proposed that the presence of CH₄ in CH₃-H₂O ice mixtures inhibited the formation of H₂O₂ (from the combination of two OH radicals) by serving as a trap for OH radicals, since the C–H bonds are also attacked by OH radicals. In fact, no IR absorption features attributable to H₂O₂ or OH were observed in the VUV photolysis of solid CH₃OH at 10 K. Our previous experimental work has confirmed that OH radicals are formed following the 157 nm photolysis of H₂O₂, and that the translational energy of OH radicals from H₂O₂ was much larger than that from H₂O. There are no discernible differences in the TOF spectra, or the rotational resolved REMPI spectra, of the OH radicals from the 157 nm photolysis of fresh or photolized ASM samples, i.e., the OH radicals detected in the present study are produced directly, via reaction (7), and not from secondary photolysis of photogenerated H₂O₂.

V. CONCLUSION

The translational and rotational temperatures of CH₃(υ =0) and OH(υ=0 and 1) radicals (i.e., the products from the primary C–O bond cleavage) have been measured following pulsed 157 nm irradiation of ASM at 90 K. Most of the detected CH₃ species have low translational and internal energies, implying that these photoproducts accommodate to the ASM bulk temperature and desorb from the ASM surface without reaction in the bulk near the solid/vacuum interface. The detected OH fragments, in contrast, are deduced to originate exclusively from the ASM surface; any OH radicals formed in the ASM bulk phase are readily trapped or react in the bulk phase. The equivalence of the TOF spectra of CH₃ fragments from ASM and from a mixed CH₃OH–H₂O ice sample indicates that the reactivity of solid water with CH₃ products is small.

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26 C. M. Western, PGOPHER, a program for simulating rotational structure, University of Bristol, available at http://pgopher.chm.bris.ac.uk.