Thermal and Photochemistry of Methyl Iodide on Ice Film Grown on Cu(111)

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Thermal and photochemistry of methyl iodide (CH_3I) adsorbed on D_2O ice film on Cu(111) at 100 K were studied using temperature-programmed desorption (TPD) time-of-flight mass spectrometry (TOF-MS), X-ray and ultra-violet photoelectron spectroscopies. On the basis of TPD, multilayer and monolayer CH_3I molecules desorb from D_2O ice layer at 120 and 130 K, respectively. Photo-irradiation at 100 K exhibits dramatic changes in the TPD and I $3d_{5/2}$ XPS of CH_3I on ice film, due to a dramatic dissociation of CH_3I. The dissociation is likely activated by solvated electrons transferred from the metal substrate during photo-irradiation. No other photo-initiated reaction products were found within our instrumental detection limit. During photo-irradiation, the CH_3I, CH_3 and I could be trapped (or solvated) in ice film by rearrangement (and self-diffusion) of water molecules. A newly appeared parent molecular desorption peak at 145 K is attributed to trapped CH_3I. In addition, the CH_3 and I may diffuse through ice and chemisorb on Cu(111), indicated by TPD and I $3d_{5/2}$ XPS taken with photo-irradiation time, respectively. No molecular ejection was found during photo-irradiation at 100 K. The work functions for $CH_3I/Cu(111)$, D_2O/Cu (111) and $CH_3I/D_2O/Cu(111)$ were all measured to be about 3.9 eV, 1.0 eV downward shift from that of clean Cu(111).

Key Words: Temperature-programmed desorption, X-ray photoelectron spectroscopy, Photo-dissociation, Solvated electron, Diffusion

Introduction

Understanding heterogeneous catalysis reactions of molecules on metal catalysts is of very importance fundamentally and industrially. Uncountable researches have been performed to elucidate specific or general reaction processes for molecules of interest.[1-4] Among the molecules, halocarbon compounds have been employed to understand reactions of alkyl groups adsorbed on a catalytic substrate from an industrial point of view,[1-3] also to tract reactions between stratospherically (or environmentally) important molecules and frozen water molecules.[5-8] Stratospheric ozone depletion has been understood through halogen radical-related (e.g., chlorofluorocarbons) reaction chemistry.[9,10] Environmentally, for the photo-initiated (e.g., by sunlight) chemistry of organic molecules the role of ice (or snow) has been studied deeper and broader.[11] This includes uptake of organic compounds by ice and release (or desorption) of the molecules (or other thermal and photo-induced reaction products) from ice by temperature rise. When organic molecules in (or on) ice are irradiated by UV photons it is known that solvated electrons in ice play a significant role in the dissociation of the molecules.

The aim of this research is to better understand the role of ice in the dissociation, desorption of halocarbon compounds, and the behaviors (e.g., diffusion and solvation) of the molecules including halogen radicals. Assisted by temperature programmed desorption, X-ray and ultra-violet photoelectron spectroscopies, we have studied CH_3I which has widely been

employed for understanding (heterogeneous) catalytic photochemical and thermal reaction processes of halocarbons adsorbed on a metal substrate.[12-17] Because the initial thermal or photo-dissociation channel is a breakage of C–I bond, and no reformation of C–I bond occurs it is possible to separately elucidate the behaviors of CH_3 and I.

Experimental Section

The experiments were performed in an ultra-high vacuum chamber with a base pressure of about 4×10^{-10} Torr. The Cu (111) single crystal disc (13 mm diameter and 2.5 mm thick, MaTeck) was cleaned by several cycles of Ar^+ ion sputtering followed by annealing at 850 K. The cleanliness was checked using an Auger electron spectrometer or a X-ray photoelectron spectrometer (XPS). The crystal was resistively heated using a tungsten wire, or cooled to 100 K by contacting with a liquid nitrogen cooled holder. The temperature was measured using a chromel-alumel thermocouple. Methyl iodide (CH_3I, Aldrich) and D_2O (Cambridge Isotope, 99.9%) were degassed by repeated freeze-pump-thaw cycles. The adsorbates were dosed through a stainless steel tube connected to a leak valve at a substrate temperature of 100 K. The open end of the tube was about 4 cm away from the Cu(111) surface. In this paper, all the dosages were reported in langmuirs ($1 L = 1 \times 10^{-6}$ torr · s) without sensitivity correction of the ion gauge for the adsorbate. For $CH_3I(1.0 L)/D_2O(1.0 L)/Cu(111)$ sample, 1.0 L of D_2O was first dosed on Cu(111) at 100 K, and then 1.0 L of CH_3I was dosed on top of the D_2O layer. Temperature-programmed desorption (TPD) spectra before and after photo-

irradiation were taken using a time-of-flight mass spectrometer (TOF-MS) at a temperature ramp rate of 2 K/s. A 100 W Hg lamp (Oriel) was used for photo-irradiation to the sample at 100 K. The XPS measurements were carried out using a Perkin-Elmer system with a Mg Kα (1253.6 eV) X-ray source and a hemispherical energy analyzer. Ultraviolet photoelectron spectroscopy (UPS) spectra were taken using a photon energy of 21.2 eV (He I). A bias of -5.0 V was applied to the substrate during the UPS.

Results and Discussion

Figure 1 shows the 15 amu TPD profiles for $CH_3I(1.0$ L)/ $D_2O(1.0$ L)/Cu(111) at 100 K before and after 10 and 30 min photo-irradiation. Before the data is mentioned in detail, we will briefly discuss the TPD (not shown) of CH_3I dosed on a bare Cu(111) at 100 K. A broad 16 amu $(CH_4{}^+)$ peak at 460 K is attributed to a major thermal product, methane (CH_4). A broad 15 amu $(CH_3{}^+)$ TPD peak at 460 K with an intensity of $0.9 \times I_{16amu}$ is due to a fragmentation of CH_4. Two 15 amu TPD peaks were found at 120 and 140 K. The former is attributed to multilayer desorption of CH_3I. The latter is due to methyl radical ejection during the thermal dissociation of CH_3I into CH_3 and I at 140 K. The atomic iodine strongly chemisorbs on Cu(111) while the CH_3 radical either ejects into gas phase, or adsorbs on Cu when an empty adsorption site is available. The adsorbed CH_3 form mainly CH_4 and minor ethylene, or desorbs at 460 K. The chemisorbed I desorbs at above 950 K.[17] The details of thermal chemistry of CH_3I on Cu substrate are described in elsewhere.[16,17]

In Figure 1, two 15 amu peaks are seen at 120 and 130 K for the sample without photo-irradiation. The 142 (CH_3I^+) and 127 amu (I^+) TPDs (not shown) exhibit the same desorption profiles as the 15 amu TPD. The lower and higher temperature TPD peaks are attributed to multilayer and monolayer desorption of parent CH_3I from D_2O ice film, respectively. The multilayer desorption position at 120 K is the same as that observed for multilayer CH_3I on bare Cu(111) as expected. For the peak at 130 K, it is estimated that I_{15amu}/I_{142amu} $(CH_3{}^+/CH_3I^+) = 0.76$ and I_{127amu}/I_{142amu} $(I^+/CH_3I^+) = 0.5$, based on the relative TPD intensity. The 15 and 127 amu are mainly due to fragmentations of the parent molecule (142 amu). Other plausible desorption products were examined: CH_3OH (29, 31 and 32 amu), acetone (43 and 58 amu), acetic acid (43, 45 and 60 amu), formic acid (29 and 46 amu) and other I-containing species (e.g., I_2), but no clear evidence of these products was found within our instrumental detection limit. For the thermal desorption profile of D_2O (not shown), the desorption begins at around 140 K and shows a maximum intensity at 166 K. We assume that the ice film on Cu is amorphous because D_2O was dosed at 100 K.[18]

Upon 5 min photo-irradiation, the desorption peak at 130 K is reduced by 17%. Upon 30 min photo-irradiation, the peak is dramatically reduced by about 92%. In addition, a new peak appears at 145 K. It is estimated that I_{15amu}/I_{142amu} $(CH_3/CH_3I) = 1$ and I_{127amu}/I_{142amu} $(I/CH_3I) = 0.54$ for the two peaks at 130 and 145 K. Compared to CH_3I without photo-irradiation, the I_{15amu}/I_{142amu} ratio is increased from 0.76 to 1. This indicates
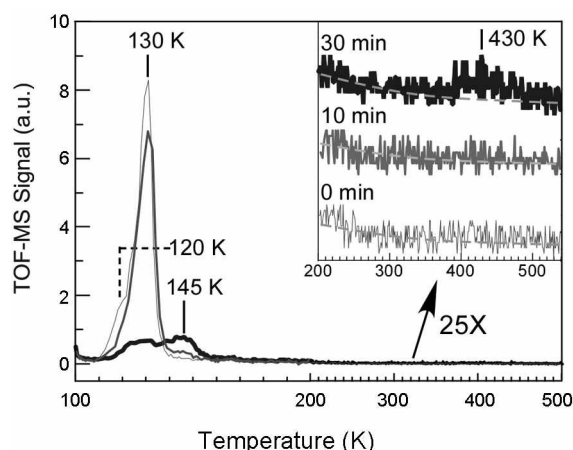

Figure 1. 15 amu TPD profiles with UV photo-irradiation time (0, 10, and 30 min) for $CH_3I(1.0$ L)/$D_2O(1.0$ L)/Cu(111) at 100 K. Inset shows magnified TPD profiles, ranging from 200 to 540 K.

that CH_3 radical ejection is enhanced relative to the parent molecule desorption. It seems that CH_3 radicals formed by photo-dissociation of CH_3I are trapped (or solvated) in ice, and they desorb during TPD, discussed further later.

To check the origin of the desorption peaks at 130 and 145 K, TPD for $D_2O(1.0$ L)/$CH_3I(1.0$ L)/Cu(111) at 100 K was performed. For the sample, CH_3I was dosed first on top of a bare Cu(111) substrate, and then D_2O was dosed to cover CH_3I. The 142 amu TPD profile (not shown here) exhibits two peaks at 136 and 150K, with an intensity ratio of $I_{136K}/I_{150K} = 4/6$. The desorption positions are very similar to the two peaks (Figure 1) observed after 30 min photo-irradiation. For $D_2O/CH_3I/Cu(111)$, three plausible geometries of CH_3I are i) chemisorbed directly on Cu(111), ii) covered by D_2O, iii) and exposed on the surface of D_2O ice film. Because chemisorbed CH_3I do not desorb from Cu surface[16,17] the two TPD peaks correspond to the latter two plausible geometries (covered by and exposed on the ice film). It is more appropriate that the higher temperature peak at 150 K is assigned to CH_3I covered by ice film. The peak at 136 K—close to 130 K seen in Figure 1— is then attributed to CH_3I on the ice film. Because the peak at 145 K—observed after 30 min photo-irradiation—is very close to 150 K the adsorption geometries of CH_3I for the two peaks seem to be very similar. In other words, for $CH_3I/D_2O/Cu(111)$ CH_3I diffuses into ice film by rearrangement (and self-diffusion) of water molecules during photo-irradiation, and desorbs at 145 K during TPD. It was found that the desorption position of CH_3I depends on the crystallinity of ice film.[19] However we have no evidence of change in the crystallinity of the ice film before and after photo-irradiation. Interestingly, for CH_3I on 5 monolayers (mL) of amorphous D_2O grown on Ru(0001) at 50 K.[6] Perry *et al.* found that CH_3I desorption dominates at 130 K for 0.3 mL coverage of CH_3I while at 145 K for higher coverages (> 1 mL) of CH_3I. For 3.0 mL CH_3I on D_2O ice film with increasing electron beam irradiation time, they found that the dominant peak at 145 K becomes weaker while the peak at 130 K becomes stronger and broadens. Further irradiation makes the peak at 130 K disappear. Their results are in contrast with our TPD shown in Figure 1.
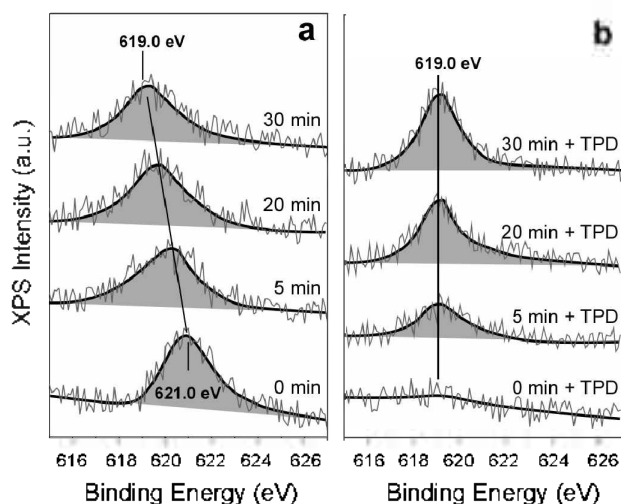
Figure 2. I 3d$_{5/2}$ XPS for CH$_3$I (0.4 L)/D$_2$O(1.0 L)/Cu(111) with (a) photo-irradiation (at 100 K) time, (b) photo-irradiation at 100 K followed by TPD from 100 to 800 K.
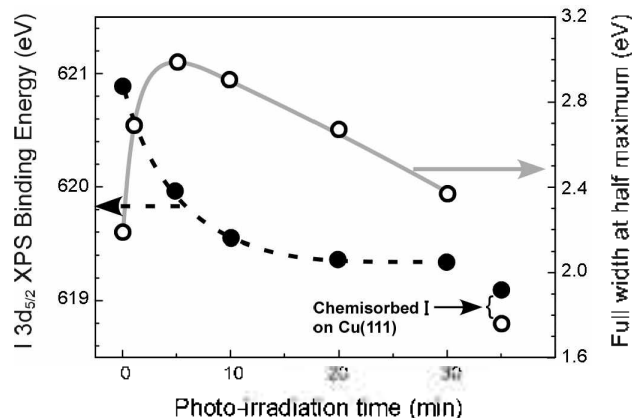

Figure 3. Binding energy and fwhm of I 3d$_{5/2}$ XPS with photo-irradiation time for CH$_3$I (0.4 L)/D$_2$O(1.0 L)/Cu(111) at 100 K. The BE and the fwhm of I 3d$_{5/2}$ XPS for chemisorbed I on Cu(111) are also displayed.

In the inset of Figure 1, for the 30 min photo-irradiated sample a broad 15 amu TPD signal is seen at 430 K. Although the peak is not strong it clearly appears above the background. Because the water desorption is completely finished below 300 K, the 15 amu peak could be due to desorption of CH$_4$ and/or CH$_3$ from bare Cu.[16,17] No 127 and 142 amu peaks were found at 430 K, indicating no desorption of parent CH$_3$I at 430 K. Because the peak at 430 K is due to chemisorbed CH$_3$ on Cu, some CH$_3$ radicals should diffuse into ice to chemisorb on Cu during photo-irradiation at 100 K and/or TPD. Because the peak at 430 K is weak we could assume that CH$_3$ diffusion is not that significant, but detectable.

XPS measurements were performed for both quantitative and more qualitative analyses. Figure 2 displays I 3d$_{5/2}$ XPS for CH$_3$I(0.4 L)/D$_2$O(1.0 L)/Cu(111) at 100 K with (a) photo-irradiation time at 100 K and (b) photo-irradiation time followed by TPD to 800 K. Figure 3 displays the XPS BE and the full width at half-maximum (fwhm) of CH$_3$I(0.4 L)/D$_2$O (1.0 L)/Cu(111) with photo-irradiation time at 100 K. The
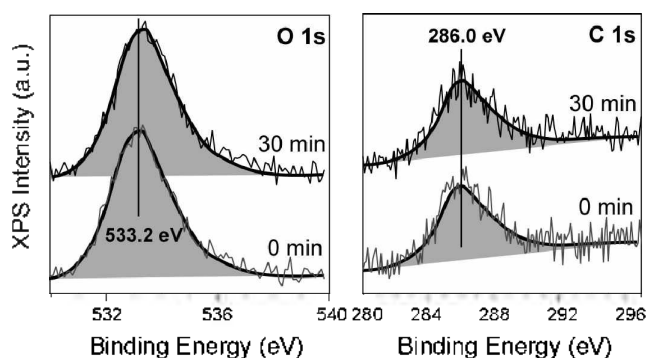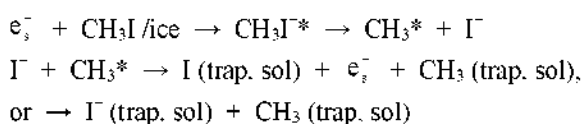

Figure 4. O 1s and C 1s XPS for CH$_3$I (0.4 L)/D$_2$O(1.0 L)/Cu(111) before and after 30 min photo-irradiation at 100 K.

I 3d$_{5/2}$ XPS BE and the fwhm for chemisorbed I on Cu(111) are 619.0 eV and 1.7 eV, respectively. The chemisorbed I on Cu(111) was achieved by annealing of 1.0 L CH$_3$I on Cu(111) to 800 K.[16,17] In Figure 2a, before photo-irradiation, the I 3d$_{5/2}$ XPS peak is positioned at about 621.0 eV with a fwhm of 2.2 eV. Upon 5 min photo-irradiation, the XPS peak is dramatically changed; the BE is decreased by 1 eV and the fwhm is broadened to 3.0 eV. As the photo-irradiation time increases further the BE is further decreased to near 619.0 eV while the fwhm becomes narrower. Because CH$_3$I dissociates to CH$_3$ and I by photo-irradiation the increase in fwhm of I 3d$_{5/2}$ XPS is due to XPS signals from both un-dissociated and dissociated CH$_3$I. Upon further photo-irradiation, the dissociated CH$_3$I becomes dominant to decrease in fwhm. The decrease in BE of I 3d$_{5/2}$ XPS with increasing photo-irradiation time could be due to an increase in solvated I, I radical, and/or chemisorbed I on Cu. Figure 2b contains some information on how the I radicals (or solvated I) behave. Without photo-irradiation, CH$_3$I completely desorbs from Cu, and no I 3d$_{5/2}$ XPS peak is seen after TPD to 800 K. After 5 min photo-irradiation at 100 K followed by TPD to 800 K, a I 3d$_{5/2}$ XPS peak appears at 619.0 eV, with a fwhm of 1.7 eV. As the photo-irradiation time increases the I 3d$_{5/2}$ XPS peak becomes stronger, with no change in BE. The BE and the fwhm are nearly the same as those for chemisorbed I on Cu(111). This indicates that the I radicals (or solvated I) do not desorb, instead they chemisorb on the Cu surface. For chemisorption, they should diffuse into ice film toward Cu surface during photo-irradiation at 100 K and/or TPD. The behavior of iodine diffusion is indicated by the gradual decrease in BE to 619.0 eV (the I 3d$_{5/2}$ XPS BE for chemisorbed I on Cu) with increasing photo-irradiation time at 100 K (Figure 2a).

Figure 4 shows O 1s and C 1s XPS for 0.4 L CH$_3$I adsorbed on D$_2$O ice film before and after 30 min photo-irradiation at 100 K. The intensities and the BE positions of the O 1s (BE = 533.2 eV) and the C 1s (BE = 286.0 eV) XPS show negligible changes even after 30 min photo-irradiation. This indicates that no other chemical species form and/or desorb from the surface during photo-irradiation at 100 K. For tert-butyl iodide adsorbed on ice film, Sohn et al. found that the C 1s XPS peak of the sample was significantly decreased by about 40% after only 5 min photo-irradiation at 100 K. They attributed this to facile ejection of reaction products (e.g., isobutene and iso-

butene) at 100 K.[20] In Figure 1, the 15 amu (CH_3^-) TPD peak is dramatically decreased after 30 min photo-irradiation at 100 K. If the decrease in intensity is solely due to molecular ejection during photo-irradiation, the C 1s XPS peak should be decreased, but the peak shows no change. This indicates that the dissociated products stay on (or in) the ice film by trapping and solvation. For 0.4 L CH_3I on bare Cu(111), the intensities and the BE positions of C 1s (BE = 288.0 eV) and I $3d_{5/2}$ (BE = 620.0 eV) XPS (not shown) show no change before and after photo-irradiation. The results indicate that CH_3I on bare Cu(111) is nearly intact by photo-irradiation, compared to CH_3I on ice.

It has been known that solvated electrons (e_s^-) play a crucial role in the dissociation of halocarbon compounds adsorbed on ice.[6,11,21] For the dissociation of CH_3I on ice film by photons with energies up to ~ 5 eV, the following reaction is proposed.

$$e_s^- + CH_3I /ice \rightarrow CH_3I^{-*} \rightarrow CH_3^* + I^-$$

$$I^- + CH_3^* \rightarrow I \text{ (trap. sol)} + e_s^- + CH_3 \text{ (trap. sol)},$$

$$\text{or} \rightarrow I^- \text{ (trap. sol)} + CH_3 \text{ (trap. sol)}$$

In the reaction, the C–I bond of transient CH_3I^{-*} breaks into CH_3 and I^- *via* dissociative electron capture process of CH_3I.[6,21] The I^- anion either back-transfers an electron into ice or not, and then the I anion (or radical) is solvated(sol)/trapped (trap) in ice film.[6,21] The CH_3 radical may also be trapped/solvated in ice film. During the time a structural rearrangement (and self-diffusion) of water molecules may also occur.[22,23] The water molecules should rearrange to minimize the energy potential when the environments of water molecules are changed upon forming new species (e.g., CH_3 and I from CH_3I) on ice film. Because the thickness of 1.0 L D_2O is not that thick (about 2.5 monolayers)[20] if the I^- anion (or I radical) moves further toward Cu during the water rearrangement and the solvation process, and is in the range of electronic coupling with Cu, the I^- anion (or I radical) is driven to chemisorb on the surface. The I $3d_{5/2}$ XPS BE shift (Figure 2a) with photo-irradiation time could indicate chemisorption of iodine on Cu. For $CH_3I:H_2O$ mixed matrix, Perry *et al.* found a similar I $3d_{5/2}$ XPS BE shift to a lower BE position from 624 to 622.5 eV after 3 hour X-ray irradiation. They proposed that the BE shift to a lower BE was due to solvated I^- anion.[6] In addition to adsorption of residual water molecules on CH_3I at 100 K, we also checked diffusion of the molecules by self-diffusion of water molecules at 100 K without photo-irradiation. However, we found no indication of these phenomena.

Finally, in the system studied here, the solvated electrons in ice film are likely the electrons transferred from the Cu metal substrate during photo-irradiation.[23,24] The work function for $D_2O/Cu(111)$ was measured to be 3.9 eV, in good agreement with the literature.[23] For $CH_3I/D_2O/Cu(111)$ and CH_3I/Cu (111), the work functions were also measured to be all 3.9 eV (± 0.1 eV). The work function was measured using the shift in secondary electron emission cutoff, relative to that of clean Cu (Φ = 4.95 eV),[25] as shown in Figure 5. Because the band gap of ice is ~ 8 eV[23,26] much higher energy than the energies
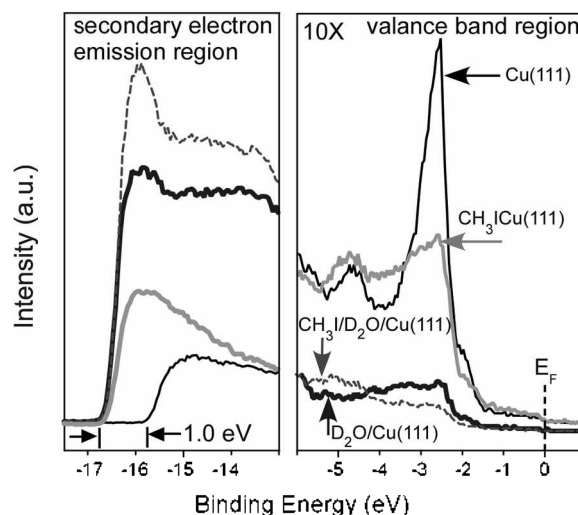

Figure 5. UPS for bare Cu(111), $CH_3I(1.0$ L$)/Cu(111)$, $D_2O(1.0$ L$)/Cu(111)$, and $CH_3I(1.0$ L$)/D_2O(1.0$ L$)/Cu(111)$ taken at 100 K. The binding energy is referenced to the Fermi level (E_F). The valance band (amplified by 10×) region is not discussed in this paper.

(up to ~ 5 eV) of photons generated from Hg lamp, it appears that the electrons photoexcited from the valance band of Cu transfer to the conduction band of ice to generate solvated electrons in the ice film. The solvated electrons then quickly transfer to CH_3I to precede the cleavage of C–I bond. Ryu *et al.* found that the lifetime of solvated electrons in H_2O ice film was a few hundred femtoseconds, and the lifetime was dramatically decreased upon adsorption of $CFCl_3$ on the ice film.[27] They attributed the lifetime decrease to dissociative (scission of C–Cl bonds) electron transfer of the electrons to the adsorbate $CFCl_3$.

Summary

Thermal and photochemistry of CH_3I dosed on D_2O ice film grown on Cu(111) at 100 K were studied by temperature-programmed desorption (TPD) time-of-flight mass spectrometry (TOF-MS), X-ray and ultra-violet photoelectron spectroscopies. On the basis of TPD, CH_3I desorbs from D_2O ice layer at 120 and 130 K, attributed to multilayer and monolayer desorptions, respectively. No other reaction products were detected within our instrumental sensitivity. CH_3I on ice film is dramatically dissociated by photo-irradiation at 100 K. We attribute the enhanced dissociation to solvated electrons in ice film. The electrons are likely the photoexcited electrons transferred from the Cu substrate. During photo-irradiation at 100 K, the dissociated products (CH_3 and I) seem to diffuse into ice film by rearrangement (and self-diffusion) of water molecules. The parent CH_3I may also diffuse into ice film to be solvated (or trapped), indicated by a newly appeared TPD peak at 145 K. No molecular ejection was found during photo-irradiation at 100 K, indicated by no change in C 1s, O1s, and I $3d_{5/2}$ XPS intensities. The CH_3 and I chemisorb on Cu(111) during photo-irradiation and/or TPD, indicated by a 15 amu TPD peak at 430 K and change in I $3d_{5/2}$ XPS, respectively. For the I $3d_{5/2}$ XPS of CH_3I on D_2O ice film at 100 K, the XPS BE shifts to

lower BEs and the fwhm dramatically changes with increasing photo-irradiation time. For all $CH_3I/Cu(111)$, $D_2O/Cu(111)$ and $CH_3I/D_2O/Cu(111)$ studied systems, the estimated work function was 3.9 ($\pm$ 0.05) eV, -1.0 eV shift from that of Cu (111).

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