# Surface photochemistry of carbonyl sulfide adsorbed on Ag(111)

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The surface photochemistry of carbonyl sulfide (OCS) on Ag(111) at 100 K has been investigated using temperature programmed desorption and photoelectron spectroscopy. Adsorption of OCS at 100 K is molecular and lowers the work function by 0.6 eV. In TPD, adsorbed OCS molecules all desorb reversibly at 128 K with no detectable thermal decomposition. Photodissociation of OCS occurs readily at 100 K with photon energies higher than 3.0 eV. Surface S and gas phase CO are produced. There is no photon induced desorption of molecular OCS, but the desorption of CO can be readily monitored with a mass spectrometer during UV irradiation. The photodissociation cross section is  $\sim 4.4 \times 10^{-20}$  cm<sup>2</sup> at 254 nm and decreases with increasing wavelength. Compared to the gas phase photochemistry, the photodissociation of OCS on Ag(111) has a higher cross section and a lower threshold. The surface photochemistry is discussed in terms of direct excitation of the OCS–Ag complex and bulk substrate excitation.

### 1. Introduction

Photochemistry of molecules adsorbed at metal surfaces has received considerable attention in the last five years from an increasing number of investigators [1-31]. As a part of our continuing investigation of surface photochemistry at metal-adsorbate interfaces, we report in this paper on the photochemistry of OCS adsorbed on Ag(111) at 100 K.

The UV photochemistry of OCS in the gas phase has been well studied [32-34]. The near UV absorption spectrum starts at about 255 nm and is continuous. The absorption maximizes at 225 nm with a cross section of ~  $1 \times 10^{-19}$  cm<sup>2</sup>. Semiempirical molecular orbital calculations indicate that this absorption band corresponds to a  $\pi \rightarrow \pi^*$ transition and a  $^{1}\Delta$  excited state [33]. The radiative lifetime of the excited state is  $\sim 10^{-9} \text{ s}^{-1}$  and the time-scale for the decomposition is  $\leq 10^{-10} \text{ s}^{-1}$ [33]. In the  $\pi \to \pi^*$  transition, charge is transferred mostly from S to C with a relatively small effect on the C=O portion of the molecule [33]. Therefore, in the near UV region, the main photodissociation channel involves C=S bond cleavage, producing CO and S. Both <sup>1</sup>D and <sup>3</sup>P S atoms are produced, and they react with another OCS molecule to form CO and  $S_2$ . The quantum yield of CO formation is 1.81 at both 253.7 and 228.8 nm. In the vacuum UV region, the excitation channel involving charge migration from O toward C is open, producing CS and O.

Monahan and Walker [35] reported that the electronic spectra of solid OCS (0.26 and 0.77  $\mu$ m films at 53 K) exhibited two absorption continua at 4.3 and 4.7 eV, not observed in the gas phase, and were assigned to the  ${}^{3}\Sigma^{+}$  and  ${}^{3}\Delta$  excited states, respectively. They also showed that the  ${}^{1}\Delta$  absorption of solid OCS was enhanced by a factor of 12 over the gas phase spectra at equivalent densities and blue-shifted by 0.29 eV. The effects of solidification on the absorption of the OCS were attributed to the perturbation of the OCS electronic structure through an intermolecular potential, which blue-shifted the absorption continua and suppressed various selection rules.

Photodissociation of OCS adsorbed on LiF(001) at 222 nm has been reported by Polanyi and coworkers [36]. For OCS adsorbed directly on LiF(001), the photodissociation cross section (to S(g) and CO(g)), which decreases from  $3.3 \times 10^{-16}$  to  $2 \times 10^{-17}$  cm<sup>2</sup> with increasing dose from  $2 \times$ 

 $10^{-4}$  to 0.11 L, is much greater than for gas phase OCS (~ $1 \times 10^{-19}$  cm<sup>2</sup>). However, for OCS separated from LiF(001) surface by a layer of water (~100 L dosed at 110 K) the photodissociation cross section is reduced dramatically and the dissociation is undetectable at 0.04 L dose of OCS. The authors conclude that the surface is acting as a catalyst for the photodissociation and that proximity to the LiF surface is necessary for the enhancement effect.

In this paper, we demonstrate that the photochemistry of OCS adsorbed on Ag(111) is also different than for gas phase OCS. The photodissociation cross section at a given wavelength ( $\lambda \le$ 254 nm) is significantly higher and the photon threshold is much lower than in the gas phase.

## 2. Experimental

The experiments were performed in a UHV chamber which has been described in detail previously [37]. The chamber was equipped with a double pass cylindrical mirror analyzer (CMA) with a coaxial electron gun, a dual anode X-ray source for X-ray photoelectron spectroscopy (XPS), a differentially pumped He discharge lamp for ultraviolet photoelectron spectroscopy (UPS), a quadrupole mass spectrometer (QMS) for temperature programmed desorption (TPD) and a sputtering gun for surface cleaning. The chamber was ion-pumped and had an auxiliary titanium sublimation pump and a 170  $\ell/s$  turbomolecular pump. The base pressure was (4–5) × 10<sup>-10</sup> Torr.

The crystal (~ 0.8 cm<sup>2</sup>) mounting and cleaning procedure has been reported previously [38]. The sample was cooled down to 100 K with liquid nitrogen. The temperature was measured with a chromel-alumel thermocouple, spot-welded to a Ta loop that was pressed into a hole drilled in the edge of the crystal. XPS was referenced to the Ag(3d<sub>5/2</sub>) binding energy of 367.9 eV [39] and utilized 1253.6 eV Mg K $\alpha$  incident radiation and a band pass of 50 eV on the CMA. UPS was referenced to the low binding energy inflection point of the Ag(4d) emission at - 3.9 eV [40] and was done with a band pass of 25 eV on the CMA. Work functions ( $\phi$ ) were measured from the threshold of the UPS secondary electron kinetic energy distributions.

OCS (> 96%, Linde) was dosed, with the Ag(111) surface at 100 K, through a multichannel array doser positioned about 7 mm from the sample. Before dosing,  $2 \times 10^{-10}$  Torr OCS was introduced into the chamber with the sample facing away from the doser. Turning the sample to the line-of-sight position initiated the dose. This dosing procedure is very reproducible, but the exposures in langmuirs are unknown.

The UV source was a focused 100 W high pressure Hg arc lamp, which generates photons broadly distributed from 230 to 900 nm. The light passed through a 1.2 cm diameter aperture to define the beam and then a quartz window at the chamber wall. Using the full arc (no filter), the incident power flux delivered to the crystal was 75 mW/cm<sup>2</sup> (measured outside the chamber with a power meter placed at the source-sample distance). The temperature rise during irradiation never exceeded 5 K. The incidence angle of the light was about 15° off the sample normal and cutoff filters were used to vary the incident photon energy distribution.

## 3. Results

## 3.1. Adsorption and desorption of OCS on Ag(111)

Before presenting our photochemistry data, we describe briefly the adsorption and desorption of OCS on Ag(111) studied using TPD, UPS, XPS and work function change measurements. Fig. 1 shows the TPD results and the inset the OCS TPD area versus dosing time. Adsorbed OCS desorbs molecularly at 128 K for all exposures, indicating first-order desorption kinetics. For low exposures (curves a and b), there is a higher temperature shoulder at about 135 K, probably from defects. The OCS TPD area increases with dosing time and saturates at about 120 s. These results indicate that no more than one monolayer OCS is formed at 100 K. It is significant that, after TPD, there was no detectable O, C or S in AES, indicating no thermal decomposition. At saturation coverage (1 monolayer (ML)), OCS lowers the work function



Fig. 1. TPD spectra of OCS after dosing at 100 K for (a) 15, (b) 30, (c) 50, (d) 75, (e) 100 and (f) 240 s. The inset shows the OCS TPD area versus dosing time. The temperature ramp rate was 2.5 K/s.

of Ag(111) by 0.6 eV, from 4.7 eV for clean Ag(111) [38] to 4.1 eV for 1 ML OCS.

Fig. 2 shows the UPS results. For a clean surface (curve a), the dominant feature is the Ag d-band between 3 and 8 eV below the Fermi level. With 1 ML OCS (curve b, with the clean Ag(111) spectrum subtracted), we observe three bands at 6.0 (A), 10.6 (B) and 13.3 eV (C), which correlate well with the gas phase spectrum (curve c) [41]. UPS indicates clearly that the adsorption of OCS on Ag(111) is molecular with little distortion from the gas phase electronic structure. According to the assignment of the gas phase spectrum, peak A is related to  $3\pi$ , B to  $2\pi$ , and  $9\pi$ , and C to  $8\sigma$  electrons [33,42].

At saturation coverage, XPS shows the binding energy to be 533.7 eV for O(1s), 164.6 eV for S(2p) (fig. 3) and 288.5 eV for C(1s) (not shown). By comparing the I(3d<sub>5/2</sub>) XPS area at 1 ML coverage of CH<sub>3</sub>I (4.6 × 10<sup>14</sup> molecules/cm<sup>2</sup> [43]) and adjusting for the relative XPS sensitivities [39], we calculate an absolute coverage for 1 ML OCS of  $(5.3 \pm 0.5) \times 10^{14}$  molecules/cm<sup>2</sup>.



Fig. 2. He(II) UPS spectra at 100 K of (a) clean Ag(111), (b) saturation OCS-covered Ag(111) with the clean Ag(111) spectrum subtracted and (c) gas phase OCS [41].

In metal–OCS complexes, the bonding between OCS and metal is through either the donation to the vacant metal orbitals of  $3\pi$  lone pair electrons residing mostly on S or the interaction of  $2\pi$  orbitals with the vacant metal orbitals; back donation of metal  $\sigma$ -electrons to the vacant OCS orbitals is also involved [34]. The latter forms C-metal and S-metal covalent bonds and weakens the C=S  $\pi$  bond. For the adsorption of OCS on Ag(111), the decrease of the work function and the weak interaction of OCS with Ag(111) (evidenced by the low desorption temperature of molecular OCS (fig. 1)) suggest that adsorption is most likely through the donation of OCS  $3\pi$  lone pair electrons to Ag(111).

#### 3.2. Photochemistry of OCS on Ag(111)

#### 3.2.1. XPS results

Fig. 3 shows the XPS results before and after irradiating 1 ML OCS with the full arc for various times at 100 K. After irradiation, a new S(2p)

peak at  $\sim 161 \text{ eV}$  appears. This peak is assigned to S atoms bound to Ag(111) and signals the photodissociation. While the 161 eV peak increases with increasing irradiation time, the S(2p) peak (~164.6 eV) of molecular OCS decreases. However, the total S(2p) peak area is nearly constant (fig. 4). For O(1s) (and C(1s), not shown), the peak shifts to lower binding energy while the peak area decreases with increasing irradiation time (fig. 4). These indicate that, while there is little or no desorption of OCS molecules during UV irradiation, C and O do photodesorb as CO (see section 3.2.3). These results are very similar to the photodissociation of phosgene (Cl<sub>2</sub>CO) on Ag(111) at 100 K, in which all Cl atoms remain on the surface and all the CO desorbs into the gas phase during UV irradiation [11].

#### 3.2.2. TPD results

*3.2.2.1. Time dependence.* Fig. 5 shows the TPD spectra of OCS after irradiating 1 ML OCS at 100



Fig. 3. S(2p) and O(1s) XPS spectra for saturation OCS adsorbed on Ag(111) at 100 K and then irradiated with the full arc for (a) 0, (b) 5, (c) 15 and (d) 60 min.



Fig. 4. XPS areas of S(2p) and O(1s) versus irradiation time (from fig. 3).

K with the full arc for various times. After short irradiations (curves b-d), OCS desorbs in two peaks at  $\sim 130$  and  $\sim 140$  K. The 130 K peak



Fig. 5. TPD spectra of OCS for 1 ML OCS irradiated with the full arc at 100 K for (a) 0, (b) 1.5, (c) 3, (d) 6, (e) 12, (f) 30 and (g) 60 min. The temperature ramp rate was 2.5 K/s. The dashed curve is for OCS on S/Ag(111) without irradiation.

decreases with increasing irradiation and disappears after 12 min (curve e). Above 12 min (curves e-g), the 140 K peak decreases and shifts to a slightly higher temperature. In the post-irradiation TPD, no independent CO desorption, except those tracking OCS, were observed. After TPD, surface S was readily detected by AES, but C and O were not. All these indicate that, after photodissociation of OCS, CO is not retained. This is consistent with the fact that CO does not stick to Ag(111) at 100 K [44]. TPD for OCS on S/Ag(111) surface without irradiation showed two desorption peaks (broken curve of fig. 5). Therefore, the higher temperature OCS peak in post-irradiation TPD is attributed to stabilization of OCS by surface S produced during photodissociation.

The lower panel of fig. 6 shows the post-irradiation OCS TPD area and surface S/Ag AES ratio (measured after TPD) versus irradiation time for 1 ML coverage irradiated with the full arc. The upper panel shows the photolysis yield and



Fig. 6. Lower panel: TPD area of OCS and S/Ag AES ratio as a function of irradiation time. 1 ML OCS was irradiated with the full arc at 100 K. Upper panel: photolysis yield and  $-\ln(l/l_0)$  versus irradiation time. The photolysis yield is defined as  $(l_0 - l)/l_0$ , where  $l_0$  and l are the OCS TPD areas before and after irradiation, respectively.



Fig. 7. TPD area of OCS and S/Ag AES ratio versus cutoff wavelength. 1 ML OCS was irradiated at 100 K for 30 min with various cutoff filters placed between the UV source and the sample.

 $-\ln(l/l_0)$  versus irradiation time. The yield is defined as  $(l_0 - l)/l_0$ , where  $l_0$  and l are the TPD areas of OCS before and after irradiation, respectively. The yield increases with irradiation time and tracks the S/Ag AES ratio. The initial slope of  $-\ln(l/l_0)$  versus time yields a photolysis rate of  $(5.8 \pm 0.5) \times 10^{11}$  molecules cm<sup>-2</sup> s<sup>-1</sup>. The departure from the linearity, as also observed for the photodissociation of alkyl halides on Ag(111) [30], indicates that the effective photodissociation cross section decreases.

3.2.2.2. Wavelength dependence. Fig. 7 summarizes the cutoff wavelength-dependent results of the photochemistry. 1 ML OCS was irradiated for 30 min with various cutoff filters placed between the UV source and the crystal. With increasing cutoff wavelength, the OCS TPD area increases and the S/Ag AES ratio decreases. From fig. 7, we conclude that the photon energy threshold for OCS dissociation on Ag(111) is ~ 420 nm (~ 3.0 eV). This is much lower than in the gas phase (~ 4.9 eV), indicating that the photodissociation threshold of OCS/Ag(111) is red-shifted. Such red-shifts have been observed for other adsorbate-metal systems [2,5,11,13,16,18,30].

#### 3.2.3. Estimate of photolysis cross section

As shown by XPS and post-irradiation TPD, photodissociation results in the loss of C and O. During irradiation of 1 ML OCS, we monitored, with the QMS, several possible desorbing species containing C, O and S. Only CO was detected and fig. 8 shows a typical time dependence. The CO pressure increases promptly when irradiation commences and then decreases with time. Similar spectra have been reported for the photodissociation of phosgene (Cl<sub>2</sub>CO) on Ag(111) [10], Fe(CO)<sub>5</sub> on Si(100) [45] and Mo(CO)<sub>6</sub> on Rh(100) [21]. It is significant that no CO pressure change was observed when a clean surface was irradiated [10].

Since all the CO in photodissociated OCS desorbs during irradiation, the desorption rate of CO is proportional to the photolysis rate. Therefore,  $\Delta P$  in fig. 8 represents the initial photolysis rate. We measured  $\Delta P$ 's while irradiating 1 ML OCS with various cutoff filters. Using the values of  $\Delta P$ and the initial photolysis rate (( $5.8 \pm 0.5$ ) × 10<sup>11</sup> molecules cm<sup>-2</sup> s<sup>-1</sup>) for the full arc, we can calculate the initial rates at different cutoff wavelengths from  $\Delta P$ . The results, along with the power fluxes, are shown in table 1. As an approximation, we attribute the rate difference,  $\Delta R$ , between two sequential cutoff filters to the photons distributed between them. The values of  $\Delta R$  and photon flux, n, between sequential cutoff filters are also listed



Fig. 8. Photodesorption spectrum of CO during irradiation of 1 ML OCS at 100 K with the full arc.



Fig. 9. Photodissociation cross section as a function of wavelength. See text for the method of calculating the cross sections.

in table 1. Between the full arc and the 285 nm cutoff, the photon flux is calculated using 254 nm since it dominates [46]. Between the other sequential cutoff wavelengths, median wavelengths are

used. The cross section is given by  $\sigma = \Delta R/nC_0$ , where  $C_0$  is the initial OCS coverage of  $(5.3 \pm 0.5) \times 10^{14}$  molecules cm<sup>-2</sup>. The values of the photolysis cross section are shown in fig. 9.  $\sigma$  is  $\sim 4.4 \times 10^{-20}$  cm<sup>2</sup> at 254 nm and decreases with increasing wavelength. Compared to the optical absorption cross section of gas phase OCS, the photolysis cross section on the surface in the wavelength region investigated is much higher.

## 4. Discussion of photochemistry

In the near UV region, the photodissociation of gas phase OCS produces CO and S [33]. In terms of molecular orbitals, the excited electron occupies the  $4\pi^*$  antibonding orbital, which is dominated by atomic orbitals of C. The same products, perhaps the result of a different excitation process, are observed for the photodissociation of OCS on Ag(111). OCS is most likely bound to Ag(111) through the donation of its  $3\pi$  lone pair electrons centered on S (see section 3.1). In the excited state, the interaction between S and Ag will be strengthened by mixing of Ag and  $4\pi^*$  orbitals and this interaction can assist C=S bond cleavage. Considering the ground state, the C=S bond (3.12)eV) is weaker than the C=O bond (6.81 eV) [34]; thus, dissociation of an electronically quenched

Table 1					
Values for	estimating photolysis	cross section	of 1 ML	OCS on	Ag(111)

Cutoff wavelength (nm)	Initial rate $(10^{11} \text{ mole-} \text{cules cm s}^{-1})$	Power flux ((±0.5) mW/cm)	Wave- length (nm)	$\Delta R (10^{11})$ molecules cm <sup>-2</sup> s <sup>-1</sup> )	$n (10^{15})$ photons cm <sup>-2</sup> s <sup>-1</sup> )	
Full arc	5.8 ±0.5	75	······		·····	
285	25 102	64	254	$3.3 \pm 0.2$	14.1	
200	2.3 ±0.3	04	295	0.8 +0.1	5.8	
305	$1.7 \pm 0.2$	60		_		
325	11 + 01	56	315	$0.6 \pm 0.1$	6.3	
525	1.1 ± 0.1	50	337.5	0.4 + 0.05	6.0	
350	$0.7 \pm 0.1$	52.5		_		
200	0.25 + 0.05	47	365	$0.45\pm0.05$	10.1	
300	$0.25 \pm 0.05$	47	400	$0.25 \pm 0.05$	10.1	
420	0	42		5.20 <u>T</u> 0.00	****	

but vibrationally excited OCS to S(a) (or AgS) and CO(g) is thermodynamically preferred. By way of comparison, thermally activated bond breaking in OCS-metal complexes occurs exclusively through the C=S bond [34]. While the photoproducts, CO and S, are the same in the gas phase and on Ag(111), the wavelength dependence of the photodissociation is very different. In the following, we discuss briefly the possible photodissociation mechanisms and processes of OCS/Ag(111). Detailed discussion can be found elsewhere [31].

If adsorbed and gas phase OCS had the same optical properties, we would expect no photodissociation using photons from a high pressure Hg arc lamp. The observed photochemistry on Ag clearly demonstrates the important role of the substrate. In terms of photoexcitation, an adsorbate-metal system can be arbitrarily divided into three parts: (1) bulk metal, (2) adsorbatemetal complex containing the chemisorbed monolayer adsorbate and at least the first layer of metal, and (3) bulk adsorbate (physisorbed multilayer). Many systems, even physisorbed multilayers, which do not interact directly with the metal substrate, have different (longer) wavelength-dependent photochemistry than in the gas phase [2,4,16,30]. This difference has been attributed successfully to the attachment of photoelectrons from the substrate to the multilayer adsorbates [16,30]. Here, we do not need to consider the multilayer case since only monolayer OCS from on Ag(111) at 100 K.

Because the adsorbate-substrate complex is optically thin, most of the absorption occurs in the bulk metal. Relaxation (thermalization) of the excited electron-hole pairs in the substrate is rapid, but a small fraction of them can, with a certain probability, migrate to the surface, excite the  $4\pi^*$ -derived orbital of the adsorbate-substrate complex by electron attachment, and promote adsorbate dissociation. The subvacuum electrons could transfer, by tunneling through the potential barrier at the surface dipole layer, to the  $4\pi^*$ -derived antibonding orbital. The holes may be filled by the  $3\pi$  electrons of OCS. If both occur, the excited state is indistinguishable from that formed via direct excitation  $(3\pi \rightarrow 4\pi^*)$  of OCS molecules. If only energetic electrons are involved, a

process analogous to electron-molecule interactions (electron attachment processes) in the gas phase [47], is expected to form OCS<sup>-</sup>. This would involve the lowest unoccupied molecular orbital,  $4\pi^*$  (electron affinity level), which for gas phase OCS is 0.46 eV [34]. The excitation probability of adsorbates (or adsorbate-substrate complexes) by the photon-excited electron-hole pairs (hot carriers) in the substrates is unknown. However, a number of evidences of surface photochemistry activated by hot carriers have been reported [14,16,19,48]. Since the photodissociation threshold  $(\sim 3.0 \text{ eV})$  of OCS/Ag(111) is much lower than the work function (4.1 eV), photoelectrons may contribute but are not required for the dissociation. When excited electrons are involved in the photodissociation, the threshold is expected to move to longer wavelengths than in the gas phase since the electron density of Ag(111) extends well above the OCS  $3\pi$  orbital level (fig. 2).

Direct excitation, as discussed elsewhere [2,4, 11,30], may also contribute. To account for the red-shift, this model assumes that the excited states of the adsorbate-substrate complex involve large metal orbital components. Compared to the isolated excited adsorbates in the gas phase, this strong coupling between excited adsorbate and substrate stabilizes, and thus lowers the potential energy of the excited state. As a result, the required photon excitation energy is lowered and a red-shift from the gas phase photodissociation is observed. For the OCS-Ag complex, this could involve electron transfer either from Ag valence orbitals or the highest occupied molecular orbital (HOMO,  $3\pi$ ) of OCS to an excited state involving, as described above, both the lowest unoccupied molecular orbital (LUMO,  $4\pi^*$ ) of OCS and Ag metal orbitals. The former is analogous to metal-ligand charge transfer in organometallics [49].

For an OCS molecule in a weak external potential field, the Hamiltonian is written as  $H = H_0 + V$ , where  $H_0$  represents the isolated molecule and V the perturbation due to the external field. For the gas phase OCS, V equals zero, and for condensed solid OCS, it is the molecular crystal field potential which blue shifts the electronic absorption spectra [35]. At 100 K, OCS does not condense (physisorb) on Ag(111). Furthermore, for chemisorbed OCS, TPD (fig. 1) indicates that intermolecular interactions are weak compared to OCS-Ag interactions. Thus, V for chemisorbed OCS on Ag(111) is mainly a contribution of the bonding interaction between OCS and the Ag surface and we anticipate that the effects of chemisorption on the UV optical properties of OCS cannot be ignored.

Conceptually, the direct excitation description differs from the indirect bulk excitation model in the following ways: for direct excitation, the electromagnetic field of the incident radiation interacts directly with the adsorbate-substrate complex; the cross section for dissociation is, thus, governed by the optical properties of the complex which, assuming a structure, have predictable angular and polarization dependences. In the indirect process, the electromagnetic field couples to the metal, independent of the adsorbate; adsorbate excitation is a separable event. For this process, the angular and polarization dependence of the substrate absorption are predictable from the optical constants of Ag and differ from those describing the direct excitation. Such angular and polarization dependent studies would be very helpful in distinguishing these mechanisms. We are configuring another system which will permit these measurements.

Regardless of the excitation channel, the final excited electronic state can be quenched to the ground electronic state before bond dissociation. Metal substrate quenching is generally believed to occur on a time-scale of a few fs (resonant charge transfer) or  $\sim 100$  fs (Auger neutralization) [50]. The gas phase photodissociation of OCS occurs in the order of  $10^{-10}$  s<sup>-1</sup> [33]. If this is the operative time scale on the surface, direct dissociation is not expected. However, the surface could act as a catalyst to assist the dissociation of OCS and reduce the time-scale of the photodissociation significantly. Therefore, the photodissociation on the surface is very competitive with the substrate quenching. Even after electronic quenching, the resulting vibrationally excited ground state may still dissociate if, before quenching, sufficient kinetic energy is accumulated in the C=S bond by the assistance of the surface.

## 5. Summary and conclusion

At 100 K, OCS adsorbs molecularly on Ag(111) with little distortion from the gas phase electronic structure. The work function is lowered; the maximum is 0.6 eV. The OCS desorbs molecularly at 128 K with no detectable decomposition. UV photolysis of adsorbed OCS occurs readily; the C=S bond is broken, producing surface S and gas phase CO. Desorption of CO during irradiation is readily monitored. The photodissociation cross section of OCS on Ag(111) is  $\sim 4.4 \times 10^{-20} \text{ cm}^2$  at 254 nm. It decreases with increasing wavelength and has a threshold of  $\sim 3.0$  eV. Compared to the gas phase optical absorption spectrum, the photodissociation of OCS on Ag(111) extends to much longer wavelengths. The photodissociation is attributed to direct excitation of the OCS-Ag complex involving electron transfer from Ag to OCS and/or indirect excitation through the interaction of adsorbed OCS with photoexcited substrate electron-hole pairs.

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