State-Resolved Characterization of a Surface Reaction: Evidence for Concerted Dynamics

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State-resolved characterization is carried out for a photodissociation reaction in the monolayer region on a metal surface, $Cl_2CO/Ag(110)$. Contrary to common expectation based on quenching rates, both translational and rotational energies of CO (*g*) from monolayer photodissociation are much higher than those from multilayers. We take this as evidence for concerted reaction dynamics on the surface: The high exothermicity in the Cl-Ag bond formation on the surface exerts part of the energy to the Cl-CO coordinate, leading to higher energies in CO (*g*).

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State-resolved characterization has played a central role in surface dynamics studies. These activities were lured by the promise that the product energy distribution from a gas-surface interaction should reflect the nature and rates of energy flow in the transition state. Understanding at such a fundamental level may allow us not only to understand but also to predict surface reaction rates. This is perhaps one of the ultimate goals in surface chemistry. Past attempts in state-resolved characterization have concentrated on molecule-surface scattering [1], recombinative desorption [2], laser induced desorption [3], and photodissociation at multilayer coverages [4]. Despite the success of the state-resolved approach in surface dynamics, it is striking to note that few attempts [5–7] have been made in understanding surface dissociation reactions in the monolayer region, which are the most widely encountered processes in surface chemistry. It is the purpose of this Letter to investigate the state-resolved dynamics of a true dissociation reaction on a metal surface. The $Cl_2CO/Ag(110)$ system is chosen for the following reasons: (i) Previous studies showed that Cl_2CO readily dissociates on metal surfaces upon photon or electron irradiation, yielding CO as the only gas phase product [8]. State-resolved detection of CO using laser induced fluorescence (LIF) [9] or resonance enhanced multiphoton ionization (REMPI) [10] is well established. (ii) In the gas phase, it is generally accepted that the first step in the UV photodissociation [11] or the dissociative electron attachment (DEA) [12] of Cl_2CO yields the unstable ClCO radical, which promptly dissociates to CO and Cl:

$$Cl_2CO + h\nu \text{ (or } e^-) \longrightarrow ClCO + Cl \text{ (or } Cl^-), \quad (1)$$

$$ClCO \longrightarrow CO + Cl. \quad (2)$$

It is anticipated that the reactive ClCO radical should also be formed in the photodissociation of Cl_2CO on metal. The prompt dissociation of this ClCO intermediate on the surface may serve as a model system for understanding surface dissociation dynamics.

All experiments were performed in a UHV chamber discussed in detail elsewhere [13,14]. The Ag(110) sample was cleaned by standard procedures and verified by low energy electron diffraction (LEED) and Auger electron spectroscopy (AES). Dosing and photolysis experiments were carried out at a sample temperature of ~90 K. In time-of-flight (TOF) measurements, signal from a quadrupole mass spectrometer (QMS) channeltron was recorded by a PC-based multichannel scaler. The cross-beam ionizer of the QMS was located at surface normal and 7.6 cm away from the sample. The TOF spectra were fit with modified Maxwell-Boltzmann (MB) distributions [15]. The photolysis light was from one of the following sources: an excimer laser (193 and 248 nm, 20 ns pulse width), a Nd:YAG laser (1064, 532, and 355 nm, 5 ns pulse width), and a YAG pumped dye laser (650 nm). The laser output was expanded to ensure uniformity on the sample surface. Typical laser pulse energies of 0.1–1 mJ/cm^2 was employed for monolayers and 60 $\mu J/cm^2$ for multilayers. The tunable light at ~215 nm for REMPI was obtained by tripling the dye output at ~645 nm. The 215 nm (~2 mJ) light was focused ($f = 25$ cm) into the UHV chamber, with the focal point ~1.0 cm away from the sample. Ions were detected by a TOF mass spectrometer equipped with multichannel plates.

State-resolved detection of CO was achieved via the $E^1\Pi$-$X^1\Sigma^+$ (0,0) transition using a 2 + 1 REMPI scheme [10], which was used recently to record the spectrum for CO at 1000 K [16]. Boltzmann analysis of the published spectrum shows that this scheme accurately yields rotational state distribution of CO up to $J \leq 50$ [14]. However, due to the presence of a minor dissociation channel in the ionization step, following the CO^+ signal alone undercounts high J states. For a room temperature CO sample, this undercounting leads to −5% error in the rotational temperature [10,14]. This effect could not be accurately accounted for in our rotational analysis of CO from surface dissociation, since the signal level for C^+ and O^+ was near our detection limit in the whole spectrum region [14].

Cl_2CO adsorbs predominantly in molecular form on Ag(110) at 90 K [14]. TDS shows a monolayer (ML) desorption peak at 155 K and a multilayer peak at 120 K,

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similar to results on Ag(111) [8]. Photoirradiation of 1 ML Cl_2CO leads to dissociation, with Cl retained on the surface and CO desorbed into the gas phase. Panel (b) in Fig. 1 shows typical TOF spectra of CO from 1 ML Cl_2CO/Ag(110). The shape of the TOF spectrum was identical at all photon energies and was also found to be independent of the extent of photolysis. Each can be fit predominantly by a single modified MB distribution, with a minor slow tail. Since there is no evidence for bimodal distribution, we treat each as a single distribution. The flux-weighted mean translational energy of CO is $\langle E_{\text{trans}} \rangle = 0.26 \pm 0.2$ eV (or $\langle E_{\text{trans}}/2k \rangle = 1500 \pm 100$ K), independent of $h\nu$, panel (d). In contrast to $\langle E_{\text{trans}} \rangle$, the initial photodissociation cross section σ_{i} decreases by more than 2 orders of magnitude when $h\nu$ approaches the threshold (~1.9 eV), panel (c). There is no photodissociation at $h\nu = 1.2$ eV. For comparison, the TOF distribution of CO from the photodissociation of condensed Cl_2CO at $h\nu = 5.0$ eV is shown in panel (a) (see below).

The observation of photodissociation of monolayer phosgene at photon energies much lower than the gas phase threshold (~4.0 eV) and the independence of $\langle E_{\text{trans}} \rangle$ on $h\nu$ clearly establishes a substrate mediated excitation mechanism, one which most likely involves the attachment of a hot substrate electron to the absorbate. Support for the electron mechanism comes from the observation that the photodissociation cross section decreases significantly with the extent of reaction, due to the accumulation of Cl (a) which increases the local work function [14]. In the gas phase, the DEA level for molecular Cl_2CO is located at ~0 eV [12]. This level can be lowered by more than 1 eV when the molecule is adsorbed on the metal surface, a result of the stabilization of the anionic excited state by the charge-image potential. In addition, the adsorbate affinity level is also significantly broadened to a typical width of 1 eV due to its strong coupling to the metal conduction band [15,17]. In a hot electron mediated excitation process, photon absorption by the substrate creates nascent electrons, which quickly relax via scattering with electrons at the Fermi level to yield an overall hot electron distribution, whose upper limit is given by $h\nu + E_{\text{Fermi}}$. The observed photon energy dependence of σ_i can be accounted for by a DEA level located at >1.9 eV above the Fermi level.

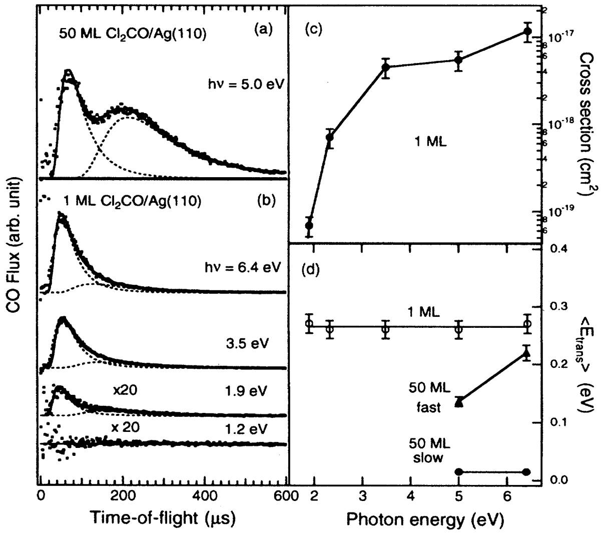

FIG. 1. (a) TOF spectrum of CO from the photodissociation of 50 ML Cl_2CO/Ag(110) at $h\nu = 5.0$ eV; (b) TOF spectra of CO from the photodissociation of 1 ML Cl_2CO/Ag(110) surface at 90 K. In both (a) and (b), the dashed curves are fits by modified MB distributions and each solid curve is the sum of two dashed curves. (c) The initial photodissociation cross section for 1 ML Cl_2CO/Ag(110) as a function of photon energy. (d) The dependence of $\langle E_{\text{trans}} \rangle$ of CO from 1 ML Cl_2CO (open circles) as a function photon energy. For comparison, those for the fast (solid triangles) and slow (solid circles) channels from 50 ML Cl_2CO are also shown.

We believe the observed independence of $\langle E_{\text{trans}} \rangle$ on $h\nu$, particularly when it is near the threshold, indicates that CO is not a product of the primary DEA reaction. Past studies on hot electron mediated photodesorption on metals have shown that $\langle E_{\text{trans}} \rangle$ is insensitive to $h\nu$ when $h\nu + E_{\text{Fermi}}$ is much higher than the adsorbate DEA level, but decreases significantly when $h\nu$ approaches the threshold [15,18]. For example, when the photon energy approaches threshold, $\langle E_{\text{trans}} \rangle$ decreases by 35% for the photodesorption of NO from Pt(111) [19] and (25–50)% for the photodesorption of SO_2 from Ag(111) [20]. Intuitively, when $h\nu$ approaches threshold, only the most energetic hot electrons can populate the lower end of the broadened electron affinity level, thus decreasing the available energy to the product [21]. The unusual finding in Fig. 1 can be rationalized when we assume that reactions (1) and (2) are also operative for the surface DEA reaction. The translational energy distribution of CO (g) is determined by the dynamics of ClCO dissociation on the Ag surface, independent of the electron excitation energy. Difference in the energetics resulting from reaction (1) is lost, probably due to quenching by the metal substrate or the dominance of energy transfer during the surface dissociation reaction, as discussed below.

Further insight into this surface reaction can be gained when we compare the results to those of the photodissociation in the condensed phase. For 50 ML phosgene, the initial excitation must be due to direct photon absorption by Cl_2CO, since (i) the TOF spectra do not change with adsorbate thickness (30–200 ML) or the preparation of the Ag surface (clean or CI covered), (ii) $\langle E_{\text{trans}} \rangle$ of the fast channel is positively related to photon energy, and (iii) no direct photodissociation is observed below the gas phase threshold. A low laser pulse energy (60 μJ/cm^2) was used avoid thermal or other collective effects, which were observed at much higher pulse energies [14]. The spectrum from multilayer Cl_2CO, panel (a) in Fig. 1, is bimodal and can be deconvoluted into two modified MB distributions. The translational temperature of the slow channel, $T_{\mathrm{trans}} = \langle E_{\mathrm{trans}}/2k \rangle = 84 \pm 5$ K, is independent of $h\nu$ and is close to the substrate temperature ($T_{\mathrm{sub}} \sim 90$ K). As shown more convincingly later, this channel corresponds to thermalized CO, which probably originates from dissociation below the top layer. Unlike the slow channel, the fast channel is positively correlated with $h\nu$: $\langle E_{\mathrm{trans}}/2k \rangle = 790 \pm 50$ K at $h\nu = 5.0$ eV and increases to 1300 ± 80 K at 6.4 eV [14]. These CO molecules are evidently not thermalized.

The observation that $\langle E_{\mathrm{trans}} \rangle$ of CO from direct photodissociation in the condensed phase is lower than that from the DEA process on the surface is unexpected. Previous surface photochemical studies have often shown the reverse [18]. For example, in the photodissociation of CH_3Cl on Ni(111), $\langle E_{\mathrm{trans}} \rangle$ of CH_3 from direct photodissociation in multilayers is 2–3 times higher than that from the DEA process on the surface [22]. These results can be rationalized by the presence of efficient quenching channels on the metal surface which take away much of the excitation energy. In addition, some of the initial photon energy is also lost during substrate excitation in the DEA mechanism. We believe the explanation for the surprising result in Fig. 1 lies in reaction (2). For monolayer dissociation, the surface is not a bystander during Cl-CO bond cleavage. It is known that Cl adsorbs strongly on metal and Cl-Ag bond formation should be highly exothermic (81 kcal/mole or 3.5 eV in the gas phase). We believe the high $\langle E_{\mathrm{trans}} \rangle$ from the surface reaction is evidence for concerted reaction dynamics on the surface: The high exothermicity in the Cl-Ag bond formation on the surface exerts part of the energy to the Cl-CO coordinate, leading to the observed high translational energy in CO (*g*). In a related study, Polanyi and co-workers reported that the yield of Cl^- (*g*) from the photodissociation of chloromethanes (RX) on Ag(111) showed a sharp maximum at the completion of the first layer, an effect which was attributed to the high exothermicity of *R*-surface bond formation [23].

One can argue that the lower CO translational energy from multilayers might result from the much higher partitioning of excess energy into the internal coordinate. To address this concern, we have measured the REMPI spectra of photodesorbed CO from both monolayer and multilayer Cl_2CO. Figure 2 shows the *R* and *S* branches of the CO REMPI spectra taken at a dissociation laser wavelength of 248 nm, with the delay time between the pump and probe laser pulses chosen to coincide with the peak positions in the TOF spectra. Since the TOF distribution from multilayers is bimodal, REMPI spectra for both fast and slow channels are presented. The following two observations can be made: (i) the rotational state distributions of CO from the slow multilayer channel is much colder than that from the fast multilayer channel and (ii) the rotational distribution in the monolayer spectrum is peaked at higher *J* levels than that in the fast multilayer spectrum. These conclusions are more obvious in Boltzmann plots shown below.

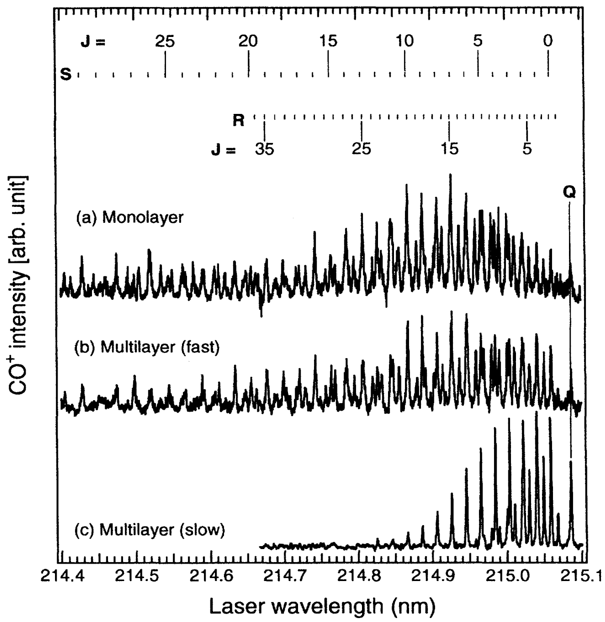

FIG. 2. REMPI spectra of CO from the photodissociation ($h\nu = 5.0$ eV) of 1 ML (a) and 50 ML (b),(c) Cl_2CO adsorbed on the Ag(110) surface at 90 K. The time delays between the pump and probe laser pulses were 10, 12, and 38 μs, for spectra (a), (b), and (c), respectively. These delays correspond to the peak TOF positions in Fig. 1. Variations in the CO flux in each measurement have been accounted for [24].

As shown in Fig. 3, the rotational state distribution of CO from the slow multilayer channel can be well represented by a straight line, corresponding to a Boltzmann temperature of $T_{\mathrm{rot}} = 96 \pm 3$ K, nearly identical to T_{trans} or T_{sub}. This result firmly establishes a completely thermalized origin for CO in the slow TOF channel. The distributions from both the fast multilayer channel and the monolayer are non-Boltzmann in nature. Both are characterized by a fast decay at low *J(s)* and a slower decay at higher *J(s)*. To facilitate quantitative comparison, we have fit each distribution with the sum of two Boltzmann distributions. These fits yield bimodal rotational temperatures of $T_1 = 700 \pm 100$ K and $T_2 = 7000 \pm 1000$ K for the monolayer and $T_1 = 210 \pm 40$ K and $T_2 = 2200 \pm 300$ K for the fast multilayer channel. In passing, we note that an overlapping (1,1) hot band is also present in REMPI spectrum (a) or (b) in Fig. 2. Analysis of this hot band yields a relative vibrational population of $N_{\nu=1}/N_{\nu=0} = 0.3$ for CO from both the monolayer and the fast multilayer channels [14].

The observation of much higher energies of CO in both translational and rotational coordinates from the surface than those from the condensed phase is consistent with the proposed mechanism involving concerted reaction dynamics. Energetically, breaking two Cl-C bonds in Cl_2CO in the gas phase requires 3.6 eV [11]. The threshold photon energy of 1.9 eV for surface dissociation

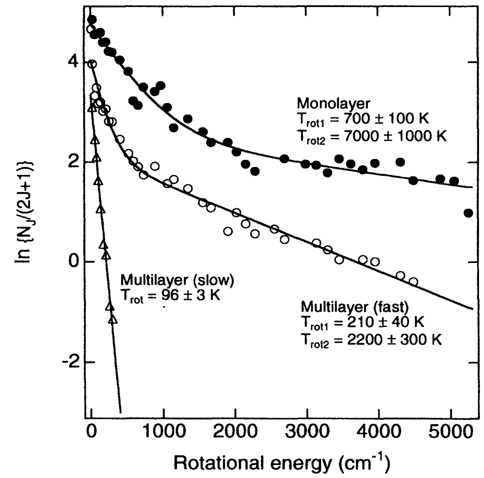

FIG. 3. Boltzmann plots of the rotational state distribution of CO obtained from the REMPI spectra in Fig. 2. The data points were from the *R* branch only, taking into account the two photon rotational line strength. Results from other branches were similar. The solid curves are fits to the data, which yield the indicated rotational temperatures.

is much lower than this energy requirement, let alone the excess energy in CO. The exothermic Cl-Ag bond formation has to be an integral part in the dynamic process. The exact bonding geometry of Cl_2CO on the surface is not known. Previous studies on other surfaces favored bonding to the surface via Cl [8]. This seems to be consistent with the observation that all Cl remained on the surface in electron or photon induced dissociation. Therefore we expect the breaking of the first Cl-CO bond to result in a transiently adsorbed ClCO radical, probably with Cl attached to the surface. In a simple picture, during the dissociation of Cl-CO on the surface, if the exothermic Ag-Cl bond formation imparts a force to the C end of the diatomic CO, additional rotational excitation is also expected as long as the molecular axis of CO is not in line with the Ag-Cl bond. Vibrational excitation is, on the other hand, determined by the C-O bond length at the transition state for Cl-CO bond cleavage and can well be the same in both monolayer and multilayers. The "bimodal" rotational distribution of CO perhaps reflects the orientational distribution of Cl-CO.

To conclude, we provide dynamics evidence for what is commonly believed in surface science: Adsorbate-surface bond formation can assist intra-adsorbate bond breaking. The substrate mediated photodissociation of Cl_2CO on Ag(110) yields CO (*g*), probably via a reactive intermediate, ClCO. The high exothermicity in the Cl-Ag bond formation can exert part of the energy to the Cl-CO coordinate, leading to much higher translational and rotational energies in CO (*g*) from monolayer dissociation than those from multilayers.

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[24] The fluxes of CO were determined in separate experiments at fixed probe laser wavelengths. The flux was constant for multilayer, but decreased with the extent of photolysis for monolayer. The monolayer spectrum was obtained in ten measurements, each starting with a freshly prepared surface and ending with more than 50% of Cl_2CO remaining on the surface. These measurements were for small overlapping wavelength intervals, with each spectrum normalized to the CO flux. Within experimental uncertainties, the flux-normalized spectrum was independent of the extent of photolysis.