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CO and CO$^+$ photodesorption from Pt(001) at 193 nm

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ArF excimer laser irradiation of CO adsorbed on Pt(001) at 80 K provoked photodesorption of both CO and CO$^+$. The neutral species was state-selectively detected and found to be rotationally cold (≈ 150 K) and vibrationally excited (≈ 800 K). The photodesorption yields of both species, CO and CO$^+$, exhibit a $F^{\sim 3}$ and $F^{\sim 1.8}$ dependence versus fluence (F), respectively. We propose that neutral-species desorption proceeds via three-photon ionization of the adsorbate followed by reneutralization without recapture, while CO$^+$ desorption results from a two-photon electronic excitation of the admolecule followed by its ionization due to the transfer of an electron to the metal and desorption before neutralization.

Photochemistry of adsorbates has long attracted the interest of the scientific community.[1] Much effort has been poured into investigations of the UV photostimulated desorption (PSD) process. This work provides insights into processes such as the transfer of substrate hole-electron excitation to the adsorbate[2] and of admolecule or surface-state electronic excitation[3] to the adbond vibration. State-selective detection provides worthwhile information for the prospect of elucidating the PSD mechanism[4] but its application has been limited to reactive systems consisting of NO adsorbed on various substrates.[5–10] In this paper we present a state-selective investigation of UV photodesorption of CO chemisorbed[11] on Pt(001), which is achieved by (2+1)-resonant multiphoton ionization (RMPI). The irradiation of the reactive system by relatively high-energy UV photons (193 nm = 6.41 eV) maximizes our chances of observing nonthermal processes.

We observe PSD of both neutral CO and CO$^+$ and a strong nonlinear dependence of the photodesorption yield (PDY) versus fluence (F) for both species. These observations contrast with the features presented by previous PSD experiments performed using similar nanosecond long UV laser pulses or continuous discharge lamp sources. As discussed below, we consider that desorption proceeds via the direct photoionization of the adsorbate for PSD of CO and via a two-photon valence electron excitation of the admolecule followed by the transfer of the electron to the metal for PSD of CO$^+$. Although these ionization mechanisms are already considered to be the first step of electron-stimulated desorption (ESD) processes,[12,13] as far as we know, this is the first observation when the desorption is photostimulated.

The 6-mm-diam Pt(001) sample preparation has been described elsewhere.[14] It is fixed on a liquid-nitrogen-cooled holder (sample temperature ≈ 80 K). A CO background pressure of 5×10^{-8} Torr is maintained in the chamber to ensure the monolayer adsorbate saturation (1.3×10^{15} molecules cm^{-2}) (Ref. 15) during the whole photodesorption experiment.

The pump beam, which is generated by an excimer laser (Lambda Physik EMG 150 MSC; pulse duration, 11 ns), irradiates a 1.8×1.8 mm^2 square on the sample at an incidence angle of 25° from the surface normal. The probe beam emanating from a frequency doubled (in a β-barium borate crystal) dye laser (Spectra Physics Quanta-Ray PDL-2; dye, Coumarin 460; line width, 0.2 cm^{-1}; pulse duration, 6 ns) has a diameter of ≈ 0.1 mm and is parallel to the sample surface. Both pump and probe beams are p-polarized and their axes contained in the same incidence plane. Unless otherwise specified, the probe-beam–sample distance is 1.5 mm and the pump pulses fired 4 μs before the probe pulses at a repetition rate of 10 Hz. The CO molecules photodesorbing at a speed of 375 m/s are thus positively ionized. These ions, along with photodesorbed CO$^+$, are accelerated towards the inlet of a flight tube, and deviated towards a microchannel plate.[6] The signals are averaged and stored as flight-time spectra by a transient recorder. The two signals corresponding to the CO and CO$^+$ PSD are discriminated using temporal windows. Unless otherwise specified, all the data points, presented in Figs. 1–3, result from an averaging over 128 laser shots, recorded with a probe beam power of 0.2 mW (0.02 mJ/pulse).

Two RMPI spectra of the neutral species desorbing at speeds of 375 and 750 m/s are presented in Fig. 1. The two peaks observed at 230.10 and 230.27 nm correspond to the Q heads of the $B\,^1\Sigma^+(v=0)\leftarrow X\,^1\Sigma^+(v=0)$ and $B\,^1\Sigma^+(v=1)\leftarrow X\,^1\Sigma^+(v=1)$ transitions, respectively. v is the vibrational quantum number. The $(v=1)$ Q head is considerably attenuated in the slow-velocity spectrum (375 m/s), which indicates that the vibrationally excited desorbing molecules propagate much faster than those in the vibrational ground state. The width of the Q head peaks results from the overlap of the $(\Delta J=0)$ rotational lines.

Two RMPI spectrum simulations of CO in thermal equilibrium are also presented in Fig. 1. These have been computed following the scheme proposed by Tjossem and Smyth[16] (the simulated RMPI spectra presented in this last reference are erroneously shifted by -0.04 nm), adopting the molecular constants given in Refs. 17 and 18, modeling the probe laser beam line shape by a Lorentzian of full width at half maximum 0.002 nm and taking the Franck-Condon factors and the rotational line strengths equal to unity and $(2J+1)$, respectively. As clearly illustrated in Fig. 1, the measured spectra differ considerably from the simulations for molecules in thermal equilibrium where the rotational and vibrational state population distributions correspond to a unique

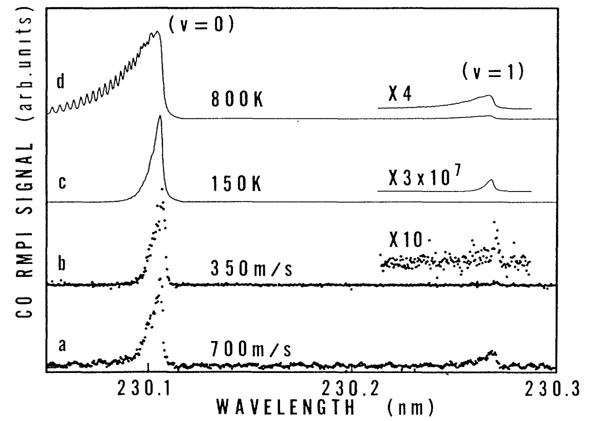

FIG. 1. RMPI spectra of the photodesorbing neutral CO molecules. *a*, *b*, experimental curves measured for a pump beam fluence of 11 mJ/cm^2. Curves *a* and *b* were measured with a probe-beam–sample distance of 0.375 and 1.5 mm, a probe pulse delay of 0.5 and 4 μs, respectively. *c*, *d*, RMPI spectrum simulations for CO molecules in thermal equilibrium at 150 and 800 K, respectively.

temperature. For a temperature of 150 K, the simulation generates two Q heads ($v=0$ and 1) of correct rotational broadening but their relative intensity (3.7×10^7) is far more prominent than the measured ones (curve *a*, ≈0.16; curve *b*, ≈0.02). A temperature of 1600 K (750 K) would give the correct relative intensity for the two Q heads of the curve *a* (*b*), but with too prominent Q head rotational broadening (as demonstrated by the 800-K simulation).

As shown in Fig. 2, we observe a strong supralinear dependence of both neutral CO and CO$^+$ PDY versus fluence (F). The $F^{\sim3}$ and $F^{\sim1.8}$ dependences could be inferred for CO and CO$^+$, respectively, the exponent accuracy being limited by a PDY measurement range of only one decade. Since the CO and CO$^+$ signals are comparable in intensity, the PDY of CO$^+$ must be several orders of magnitude lower than that of CO because of the low efficiency of the RMPI process ($\ll10^{-4}$).

The time-of-flight (TOF) distributions of CO in the ($v=0, J\approx5$) and ($v=1, J\approx3$) states, measured by varying the delay between the pump and probe pulses, while the probe beam frequency is adjusted at one of the Q head maximum positions (230.105 and 230.268 nm, respectively), are presented in Fig. 3. The molecules in the ($v=1$) state propagate significantly faster than those in the ($v=0$) state. The maximum of the two TOF distributions correspond to kinetic energies of ≈0.15 and ≈0.023 eV.

The RMPI spectra and TOF distributions have been found to be independent of fluence. The relative intensity of the two Q heads of curve *a* (or *b*) in Fig. 1, divided by the relative value of the normalized TOF distributions of Fig. 3 at 4 μs (or 2 μs), gives an estimation of the ratio of vibrationally excited molecules. The latter ratio is $\approx2.5\%$ (or 2.8%) and corresponds to a "vibrational temperature" of 800±40 K. This value contrasts with the low "rotational temperature" of 150±50 K, corresponding to Q head broadening.

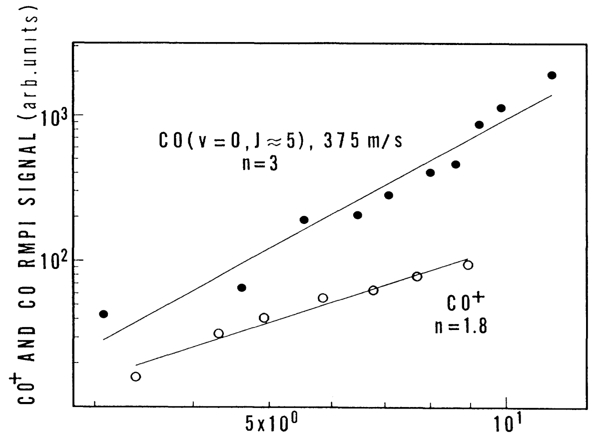

FIG. 2. Dependence of the CO (black circles) and CO$^+$ (open circles) PDY vs fluence [probe beam tuned at the center of the ($v=0$) Q head, 230.105 nm]. Solid lines show linear fits by least-squares method.

Finally, we emphasize that 5×10^{-8} Torr is the minimum background pressure needed for preventing the RMPI signal decay versus irradiation time for the maximum fluence used in this work. This corresponds to an exposure of 5×10^{-3} L (1 L$=10^{-6}$ Torr s) between laser shots. Comparing this value to that entailing a one monolayer coverage [≈4 L (Ref. 19)], the photodesorption probability for a fluence of 20 mJ/cm^2 can be estimated to be of the order of 10^{-3}.

Using the formalism developed by Bechtel,[20] the Pt direct heating by the pump beam is computed to be 7.5 K by 1 mJ/cm^2 of fluence for a reflectivity of 0.3 at 193 nm.[21] For the maximum fluences used in this work (20 mJ/cm^2), the surface temperature reaches a maximum value of 230 K. This prevents laser-induced thermal desorption which occurs above 350 K during slow heating of a thermal desorption scan.[19] The nonthermal char-

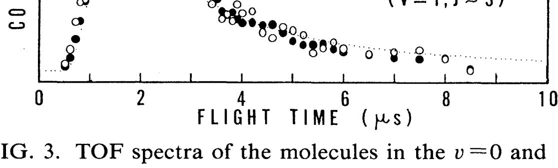

FIG. 3. TOF spectra of the molecules in the $v=0$ and 1 vibrational state. Black square: ($v=0$, $J\approx5$), probe at 230.105 nm, $F=29$ mJ/cm^2; open square: the same but $F=12$ mJ/cm^2. Black circle: ($v=1, J\approx3$), probe at 230.268 nm, $F=6$ mJ/cm^2; open circle: the same but $F=3.7$ mJ/cm^2. The distribution maximum heights have been normalized and do not represent relative detection sensitivity factor.

acter of the photodesorption process is indeed corroborated by the out-of-thermal equilibrium distribution of the desorbing molecule mechanical energy in the vibrational, rotational, and translational degrees of freedom.

A nonthermal UV photodesorption is usually described in the framework of the Menzel-Gomer-Redhead model[22] where desorption takes place during the admolecule relaxation from an excited state adsorption potential. The primary excitation can result from a direct one-photon excitation either of the admolecule or of a surface state [e.g., CO/Ni(111)-O $\approx$ 300 nm (Ref. 3)], or indirectly, because of the transfer to the adsorbate of electron-hole pair excitations resulting from the UV pump beam absorption by the substrate [e.g., CH_3Cl on Ni(111)-248 nm,[23] CCl_4/Ag(111)-193 nm,[24] NO/Pt(111)-355 nm,[5] NO/Pd(111)-620 nm,[8] CO/Cu(111)-620 nm (Ref. 2)].

A supralinear dependence of the PDY versus fluence, as measured in this work, is difficult to reconcile with a mechanism involving hole-electron excitations except in two cases. First, supralinearity may result from the substrate electronic system being driven out of thermal equilibrium with the phonon bath. However, this can only be achieved by ultrashort (<ps) pulse irradiation,[8,2] with a peak irradiance that is 5 orders of magnitude higher than that of this work. Second, Prybyla, Tom, and Aumiler[2] proposed that photodesorption can occur following femtosecond pulse irradiation, by multiple noncoherent transfer of the hole-electron excitations to the admolecule during the adbound vibration lifetime. The corresponding cross section of admolecule excitation with respect to the incident photons has been estimated for NO/Pt(111) (Ref. 25) to be $\approx 10^{-20}$ cm^2. For an incident photon flux of $\approx 10^{18}$ photon s^{-1} cm^{-2}, as used in this work, the excitation rate would be $\approx 10^{-2}$ Hz, much too low for multiple excitations to occur during the adbound vibration lifetime or pump pulse duration. Even if the cross section of hole-electron excitation capture for CO differs from that of NO, photodesorption via this mechanism is improbable.

Hole-electron excitation transfer being ruled out, the primary step must be direct optical excitation of the adsorbate. The supralinear dependences indicate that the PSD of CO and CO^+ proceed via the adsorption of three and two UV photons, respectively. The desorption mechanisms for both species are thus different and must be discussed separately.

Because three-photon energy (3×6.41 eV) exceeds the CO ionization potential (14 eV), the direct adsorbate photoionization is likely to be the first excitation step of the neutral CO PSD process, desorption occurring after reneutralization. This mechanism has indeed already been suggested, in the case of ESD experiment, for example, in the work of Feulner, Treichler, and Menzel[13] who studied the ESD of CO from Ru(001). It is also worth noticing that irradiation of gaseous CO at 193 nm essentially yields photofragmentation ($CO \rightarrow C+O$).[26,27] However, the photoionization channel (which would proceed via the resonant $a^3\Pi \leftarrow X^1\Sigma^+$ transition for gas phase molecules) can be enhanced because of the energy gained by the transfer of the electron to the substrate. Anyhow, we cannot discard the occurrence of some photofragmentation because neutral fragments cannot be detected by our experimental setup. Our state-selective data provide information concerning the ion adpotential. The excitation of the admolecule frustrate rotation, leading to rotational excitation of the desorbing molecule, arises because the ion evolves in a potential different from that of the admolecule ground state. Therefore, the fact that the desorbing molecules are poorly rotationally excited (broadening of the Q heads corresponding to a rotational temperature of 150 ± 50 K, Fig. 1) suggests that both potentials have a similar admolecule bending angle dependence. This supports the proposition of an excited adsorption potential being the ground-state potential modified only by the image charge force on the adion perpendicular to the surface,[25] to the detriment of the photodesorption mechanism proposed by Ferm *et al.*[9] [NO/Ni(001)-O], which involves the reorientation of the admolecule parallel to the surface while being in the excited state. The adion lifetime can be inferred from the CO vibrational excitation, the latter resulting from the contraction of the molecule while ionized. From the desorbing molecule ($v=1$) state population of $\approx 2.5\%$, taking a difference in interatomic equilibrium length between CO and CO^+ equal to 0.0131 Å (Ref. 28) and using the formulation given by Gadzuk *et al.*[25] [Eq. (23)], we obtain a reasonable CO^+ lifetime of ≈ 5 fs. We also note that correlation between the translational and vibrational excitation of the desorbing molecules, as observed in Fig. 3, may be expected because both excitations of the adbond and of the CO molecular vibration are correlated and increase for longer adion lifetime.

It is remarkable that CO^+ PSD requires the absorption of only two photons compared with three for CO PSD. Since direct ionization requires more energy, the initial step of the CO^+ PSD process must be an admolecule valence electron excitation and ionization will follow as a result of the excited electron transfer to the substrate, as proposed by Burns, Stechel, and Jennison[12] who studied ESD of NO and CO from Pt(111). The CO^+ desorption can proceed from this ion resonance before reneutralization. A good candidate for the initial excitation is the promotion[12] of an electron from the 4σ to the antibonding $2\pi_a$ orbital. UV photoelectron and inverse photoemission spectroscopy place the two states at -12 and $+5$ eV from the Fermi level, respectively, for CO/Pt(011).[29] Taking account of a screened core-hole potential correction of ≈ 5 eV,[30] the corresponding photoabsorption frequency should be close to the two UV photon energy. The electron transfer from the $2\pi_a$ resonance of width 3 eV to the metal would occur rapidly (<fs). Desorption following this ionization process is considered to be inefficient for the ESD of CO from Pt(111), in agreement with our observation that CO^+ PDY is several orders of magnitude smaller than that of CO.

We cannot discard the fact that some neutral CO PSD occurs following reneutralization from this ion resonance; this two-photon PSD signal could be obscured by that of the CO three-photon PSD process. Correspondingly, the CO^+ three-photon PSD signal of the ions, which would directly desorb from the adion state before its reneutralization, may be obscured by that of the above discussed CO^+ two-photon PSD process.

The validity of the proposed mechanisms must be further experimentally confirmed. Wavelength dependence measurement of PDY should show a resonance or a threshold behavior[25] in the case of admolecule optical excitation or substrate hole-electron mediated photodesorption process, respectively. The few lines of the excimer lasers may hamper this measurement. PDY dependence versus the incident beam polarization can also help to determine the initial excitation step.[5] These experiments are in progress in our laboratory.

In summary, both neutral CO and CO^+ desorb from Pt(001) when irradiated by 193-nm laser pulses. The neutral species has been investigated by state-selective detection technique. We propose that the first step of the CO photodesorption process is the direct three-photon ionization of the admolecule. The low rotational excitation of CO supports the proposition that the ion and ground-state molecule adpotentials differ only by the image charge effect. The CO would then desorb after reneutralization. We consider that CO^+ photodesorption proceeds via a two-photon electronic excitation followed by the transfer of the excited electron to the substrate. CO^+ would desorb from the ion resonance before reneutralization. These processes could not have been observed in previous CO UV photodesorption experiments [CO/Ni(111)-O,[3] CO/W,[31] CO/NiO,[32] CO/Cu(111)-620 nm (Ref. 2)] presumably because of the use of UV sources of lower intensities or longer wavelengths (> 250 nm).

This work constitutes a step in the state-selective investigation of the CO photodesorption process from various substrates. The ionization scheme adopted in this work offers the advantage of detection sensitivity but the rotational lines of the Q heads overlap each other. Therefore the information available from this RMPI of CO is still limited compared with that from NO RMPI.[5-10] Other probe beam polarization conditions and frequency ranges, allowing the measurement of O, P, R, or S bands, where the rotational lines are easily resolved,[16,33] may also be tried.

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