Enhanced photon stimulated ion-desorption yields from chemisorbed molecules through bond-selective core-electron excitation

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The photon-stimulated ion desorption from deuterated formic acid chemisorbed on Si(100) has been studied by bond-selective C 1s electron excitation. Each ion yield strongly depends on the excitation energy. It is found that the excitation to a particular antibonding orbital enhances ion yields, which follows a rupture of the bond to have been specified. The results show applicability of the two-hole one-electron mechanism for core-excited ion desorption in adsorbates. Also discussed are electronic relaxation via Auger processes and the neutralization effects of the substrate on ion desorption. [S0163-1829(96)05220-4]

Study of photon-stimulated ion desorption (PSID) can provide information concerning scientific issues such as the nature of the chemical bonding at the surfaces in both the ground and excited states, surface dynamical processes involving charge or energy transfer, and the conversion of electronic potential energy into nuclear motion.¹ At corelevel excitation, the Auger-stimulated desorption model was proposed to describe the PSID from covalent systems or adsorbates.^{2–4} In this model, Auger-induced two-hole (2h)states are the most important for the desorption if the effective hole-hole repulsion U^e is greater than some appropriate covalent interaction or bandwidth V (i.e., $U^e > V$). If $U^e < V$ two-hole one-electron (2h1e) states induced by resonant Auger decay become more important. In chemisorbed systems, it is known that the screening of 2h states by charge transfer from the substrate is so strong as to eliminate most of the localization induced by the hole-hole Coulomb interaction and the bonding to the surface leads to an enhanced bandwidth of the molecular levels (i.e., $U^e < V$). Thus, the 2h1e mechanism is more effective on the chemisorbed molecules than that of the 2h. In the 2h1e states, the expulsion of the ion usually results from occupation of a strongly antibonding orbital (i.e., 1e part) but may also result from the emptying of a bonding orbital (i.e., 2h part). Therefore, it is expected that the desorption process is governed by the antibonding character of the final orbital (corresponding to the 1e part). Then, it is interesting whether or not selective excitation of a core electron to a particular antibonding orbital (localized along a bond within an adsorbed polyatomic molecule) enhances yields of PSID, which follows a rupture of the bond to have been specified. In the present paper, we investigate the role of antibonding orbitals for desorption. As a model system, we consider the PSID from a formic acid chemisorbed on a silicon surface. This system is primarily chosen because the formic acid contains only one carbon atom involved in a number of different bondings such as

C—H, C—O, and C=O, which can be selectively excited at $\pi^*(C=O)$, $\sigma^*(C-H)$, $\sigma^*(C-O)$ and $\sigma^*(C=O)$ resonances in the C *K*-edge region.⁵ Furthermore, the following facts are convenient for the present study. The adsorption structure of this molecule is well understood, its sticking coefficient is relatively high.⁶ The C atom is not too close to the substrate and screening on the C atom is not so effective that 3h or even higher excited states reached by the primary core satellite state are needed for desorption.

This experiment demonstrates ion desorption in an adsorbed polyatomic molecule through bond-selective innershell excitation. Due to the small cross section of the phenomenon, the precise work in the present experiment requires the combination of the time-of-flight (TOF) detection using pulsed synchrotron radiation (SR) with a highintensity undulator beam. The TOF detection permits the highly efficient and simultaneous detection of several desorbing species, differing greatly from the conventional mass spectrometer. In the present study, it is found that enhanced productivity can be predicted by the repulsive nature of the final orbital (i.e., 1e part).

The experiment was conducted using the 10-m grazingincidence monochromator⁷ installed on the soft x-ray undulator beam line 2B at the Photon Factory. The energy width of the photon beam used was about 0.25 eV at 287 eV. The experimental details have been described elsewhere.⁸ Briefly, desorbing ions were detected and analyzed by the TOF mass spectrometer using a pulsed SR (624-ns interval and 100-ps width). The SR was directed incident to the sample at an angle of about 15° from the surface. To obtain information, for a photoabsorption cross section, an Auger electron yield (AEY) curve was measured using a double-pass cylindrical mirror electron-energy analyzer. The Si(100) crystal was constructed of *p*-type doped boron with 1000- Ω cm resistivity. The crystal was cleaned by several cycles of Ar⁺-ion bombardment and annealing. Deuterated formic acid

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FIG. 1. Auger electron yield and PSID yields of D⁺, CDO⁺, O⁺, and CD⁺ from the DCOO/Si(100) as a function of photon energy near the C *K* edge. The vertical lines across the figure indicate the positions of π^* and σ^* resonances in the AEY.

(DCOOD) was employed as an adsorbate gas in order to eliminate interference from residual H_2O and other impurities in the ultrahigh vacuum (UHV) chamber. The H_2O preferentially adsorbs to the clean surface before the adsorption of the sample gas and efficiently desorbs as H^+ ions. The DCOOD was exposed at room temperature. It is well known that HCOOH dissociates into an unidentate formate (HCOO) species and H adatoms on the Si(100)(2×1) surface at 300 K.⁶ The formate is bonded, via the hydroxyl oxygen atom, to the dangling bond of the surface Si atom. All measurements were performed at room temperature in the UHV chamber. The base pressure of the chamber was typically maintained at 2×10^{-8} Pa.

Ions consisting of D⁺, CD⁺, O⁺, and CDO⁺ were observed as the major products in the TOF measurement near the C K edge. The PSID yield curves of these ions from the DCOO/Si(100) substrate in the C 1s excitation region, along with the AEY curve, are shown in Fig. 1. The yield curves have been normalized to the incident photon flux measured with an Au mesh. The resonant peaks and structures observed in the AEY curve were assigned to transitions from the C 1s orbital to the $\pi^*(C=0)$ orbital at 288.6 eV, the $\sigma^{*}(C-D)$ orbital at 292.0 eV, the $\sigma^{*}(C-O)$ orbital at 297.5 eV, and the $\sigma^*(C=0)$ at 304 eV on the basis of near-edge x-ray absorption fine structure (NEXAFS) for condensed formic acid.⁵ Table I lists the energies for the resonant peaks and the assignments for the AEY and PSID yields, along with the data of the gas phase measurements. Each PSID yield exhibits a significant deviation in intensity from the corresponding AEY. This finding indicates that the PSID strongly depends on the initial excitation of the adsorbed formate. The PSID yields of the D^+ and the CDO^+ ions are largely enhanced at the $\sigma^*(C - D)$ and $\sigma^*(C - O)$ resonances, respectively. An increase in the O⁺ yield is observed at the $\sigma^*(C=0)$ resonance. These results suggest that selective excitation to an orbital, localized at a bond, induces desorption of a particular ion that is produced through the breaking of the specified bond. In other words, bond-specific ion desorption occurs. The D⁺ ions exhibit the highest yield among the measured ions over all photon energies. The order of the relative yields among these ions does not significantly change as the photon energy varies. This fact probably results from the following. The relative yields strongly depend on the mass of the particles leaving the substrate as shown by the classic Menzel-Gomer-Rendhead model9,10 and also on the number of bonds to be broken. The D⁺ ion can be generated through the rupture of one bond. The CDO⁺ ion is also produced through the breaking of one bond, although the bond to be broken is positioned closer to the surface than that of the D^+ ion. The O^+ ion results from the breaking of a double bond, while the generation of the CD⁺ ion requires the breaking of two bonds, namely, the CD-O and DC=O bonds.

TABLE I. Photon energies and proposed assignments for the peaks observed in the AEY and the PSID yields near the C K edge from the DCOO/Si(100) compared with those in the electron energy-loss spectroscopy of gas-phase HCOOH (Ref. 12).

	Photon energy (eV)					
AEY	D^+	CDO^+	O^+	CD^+	Assignment	(eV)
288.6	288.6	288.6	289	288.9	π* (C==O)	288.2
		291.7		291.5	3s Rydberg	
292.0	292.0	291.7	292		σ^* (C—D)	
					3s Rydberg/ σ^* (C—H)	292.0
					higher Rydberg	293.3
297.5		298.2			σ^* (C—O)	296.1
	298.8				Double excitation ^a	
				299.3	Double excitation ^a	
304			303		<i>σ</i> *(C==0)	303

^aSee text.

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When examining the dependence of each ion yield on the photon energy in greater detail, the dependence changes significantly with the ion yield. It is clearly seen that the CD⁺ yield is significantly enhanced at the $\pi^*(C=O)$ resonance, while the CDO⁺ yield is less at the $\pi^*(C=O)$ resonance than the $\sigma^*(C - O)$ resonance. Taking into account that the $\pi^*(C=O)$ orbital is an antibonding orbital, existing weakly along the C—O bond as well as strongly along the C=O bond,^{11,12} it is plausible that the enhanced CD⁺ yield originates from the antibonding character of the $\pi^*(C=O)$ orbital. When a spectator Auger process occurs after the core excitation, an excited electron remains in the antibonding orbital, producing the 2h1e final state having a steep repulsive potential. The 2h1e repulsive state decomposes at the chemical bond related to the antibonding orbital, which subsequently leads to the desorption of kinetic ions. The kinetic ions can easily survive neutralization and consequently produce the enhanced yields at the core-to-antibonding excitation. Here, it should be noted that a molecular orbital such as σ^* or π^* is not completely localized at one chemical bond and spreads to some degree.

Since the formate (DCOO) is bonded, via a hydroxyl oxygen atom, to the dangling bond of the surface Si atom, the probability of neutralization of the hydroxyl oxygen cation is expected to be much higher than that of the carbonyl oxygen. Generally, the PSID yields of atoms bonded to the surface exhibit delayed thresholds. That is, the yield spectra exhibit the onset at energies considerably above the ionization threshold, where multiple ionization begins to occur.^{8,13,14} Therefore, it is presumably concluded that the oxygen atoms found in the CDO⁺ and O⁺ ions are carbonyl oxygen atoms.

The comparison of the PSID yields with the AEY curve in Fig. 1 indicates that the peak position for each ion yield is close to that of the AEY. The peak positions of the D^+ and CD^+ yields (298.8 and 299.3 eV) at the $\sigma^*(C - O)$ resonance, however, deviate considerably to a higher energy from that of the AEY, while the peak position of the CDO⁺ ion is shifted slightly from the AEY peak. The shifts in the peaks of the D^+ and CD^+ yields suggest that other excitation channels are open at the energy of the production of the D^+ and CD⁺ ions, being more effective than the $\sigma^{*}(C - O)$ excitation having a large photoabsorption cross section. According to the intermediate neglect of differential overlap/ S-configuration interaction (INDO/S-CI) calculations¹¹ for a formic acid molecule, K-shell ionized shakeup states, C $1s^{-1}n^{-1}\sigma^*(C-D)^{+1}$ (*n* denotes the nonbonding orbital), and C $1s^{-1}\pi(C-O)^{-1}\pi^*(C-O)^{+1}$ exist at 10.90 and 11.67 eV above the ionization threshold, respectively. As shown in Fig. 1, the peaks of D^+ and CD^+ yields (around 299 eV) are close to this threshold, with values of 10.90 and 11.67 eV nearly equal to the energy deviations from the $\pi^*(C=O)$ resonance to the third peaks of D^+ (11.2 eV) and CD^+ (11.7 eV) yields, respectively. Therefore, two excited electron states such as $C 1s^{-1}n^{-1}\pi^*(C=0)^{+1}\sigma^*(C=D)^{+1}$ and $C 1s^{-1}\pi(C=O)^{-1}\pi^*(C=O)^{+2}$ are presumed to exist at 298.8 and 299.3 eV, respectively. The former state is probably repulsive for the C-D bond, due to one electron occupying the antibonding $\sigma^*(C-D)$ orbital, resulting in the desorption of D⁺ ions. The latter is strongly repulsive for the C=O bond due to one π (C=O) hole and two π^* (C=O) electrons, resulting in the generation of CD⁺ ions. Based on



FIG. 2. Closeup of the D⁺, CDO⁺, and CD⁺ yields at the $\sigma^*(C-D)/3s$ orbital resonances in Fig. 1. ΔE : photon energy width.

the consideration described above, the D⁺ yield peak at 298.8 eV and that at 299.3 eV in the CD⁺ yield possibly originate from the production channel consisting of the two excited electron states. It should be also noted that the slight shift in the peak CDO⁺ yield near the $\sigma^*(C-O)$ resonance may be caused by double electron excitation.

Figure 2 shows that the peak positions of the D^+ , CDO^+ , and CD⁺ yields differ from each other at the σ^* (C—D) resonance, where the structure of the peak AEY is similar to that of the D⁺ yield. Considering that the second peak is assigned to the mixed 3s Rydberg $\sigma^*(C-H)$ orbital in the gas phase of formic acid,¹² the 3s Rydberg and $\sigma^*(C-D)$ orbitals are not presumed to sufficiently overlap each other in the adsorption system of DCOO/Si(100). The peak in the D^+ yield probably corresponds to the $\sigma^*(C-D)$ excitation. Another peak can be assigned to the 3s Rydberg orbital excitation. Rosenberg et al.¹⁵ observed an enhancement in the production of electronically excited fragments following core-to-Rydberg excitation in the gas phase of both $SiCl_4$ and SiF_4 . They concluded that the reason for this enhancement was related to a greater probability of decaying of the coreexcited Rydberg state to unbound 2h1e states than other excitations. In the present work, therefore, it is suggested that the CD^+ ions at the 3s Rydberg excitation may be formed through a similar decay process, which possibly produces electronically excited fragments. One possible explanation for the broad structure of the CDO⁺ yield is that the CDO⁺ ions desorb easily at both resonances, owing to one single bond scission. Actually, CDO⁺ ions have been observed, even at valence orbital ionization in the gas phase of formic acid,¹⁶ while the CD⁺ ions were not observed.

Contrary to instances of free molecules, most of the ionic species produced through core electron excitation in adsorbed molecules are easily neutralized. The substrate has a significant capability for neutralizing products derived from 1h or 2h final states. The effective excitation in PSID processes then produces highly repulsive states that possess an electron distribution strongly localized on a particular bond. For core-electron excitation, Auger final states consisting of two holes on bonding orbitals and one electron on the antibonding orbital (2h1e) are effective in breaking the chemical bond, and in the production of a kinetic ion surviving reneutralization or image forces. Thus, it is expected that the

enhanced yields of desorbing ions mainly originate from the kinetic ions produced through the 2h1e states having steep repulsive potentials.

In conclusion, the present paper has shown that the PSID yield enhancement for each ion is related to the antibonding character of the excited molecular orbitals. The obtained results demonstrate that the characteristic ion desorption forms in the adsorbate of DCOO/Si(100) through bond-selective C 1s electron excitation. The results also indicate that the PSID yields can provide information on the local property of the unoccupied molecular orbital around the chemical bond to be

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broken. Thus, enhanced productivity can be predicted by the repulsive nature of the final orbital. It is foreseen that PSID can be applied for the assignment of initially excited states in a complicated NEXAFS spectrum of an adsorbed polyatomic molecule.

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