Observation of Neutral Atomic Fragments for Specific 1*s* Core Excitations of an Adsorbed Molecule

S. P. Frigo, P. Feulner, B. Kassühlke, C. Keller, and D. Menzel

Physik-Department E20, Technische Universität München, D-85748 Garching, Germany
(Received 9 April 1997)

We have succeeded in detecting a *neutral* atomic fragment produced by energy- and polarization-specific molecular core electron excitations, enabling a comparison of oxygen atom and oxygen ion yields from photon induced dissociation of chemisorbed CO molecules on the Ru(001) surface. Resonances in the O^0 atom yield are observed at 534 and 550 eV, but no enhancement is observed for higher-energy excitations which stepwise increase the O^+ yield. The mechanistic reasons for the similarities and differences in neutral and ionic fragment production are discussed, with emphasis on the influences of charge transfer and redistribution processes. [S0031-9007(98)05657-9]

Molecular photodissociation involves the interplay of both electrons and nuclei from the initial electronic excitation to final fragmentation products [1]. In the study of photodissociation dynamics, one type of electronic excitation, namely, that involving the creation of a core hole, is particularly interesting. This is because a core hole is a spatially well-defined charge vacancy which has a very short (1–10 fs in low Z atoms) lifetime.

Photodissociation driven by core excitation has been explored for both free and adsorbed molecules. In the gas phase, both electron emission [2] and fluorescence [3] from excited fragments have been detected. However, most studies to date, especially from surface systems, have focused for experimental reasons mainly on the detection of *ionic* fragments [4]. *Neutral* dissociation products, which may well constitute the majority, remain yet to be investigated.

Such measurements would be beneficial, because the charge of a dissociation fragment is very sensitive to both the nature of the molecule's electronic structure and its environment. For example, when a molecule is chemisorbed onto a metal surface, the adsorption bond provides an efficient charge conduit from the metal, greatly affecting ion production [5]. When the electronic structure leads to an extremely repulsive potential energy surface for the core hole state, the nuclei are accelerated. In some cases this leads to bond breaking in 5–10 fs [2], producing two neutral fragments, one of which contains the original core hole. These two examples illustrate that measurement of neutral fragments is required to better understand fundamental charge transfer and redistribution processes occurring during photodissociation.

We have recently constructed apparatus to detect neutral atom fragments from adsorbed molecules in order to study these important, yet poorly known aspects of photodissociation following core excitation. In this Letter, we present results from a model adsorption system, that of the simple diatomic CO adsorbed on the transition metal Ru. Our results illustrate that the photon energy- and polarization-dependent yield of neutral fragments following core level excitation provides, heretofore, unobtainable insights into surface-adsorbate bonding, as well as the excitation dynamics and molecular photodissociation in general.

The experiments were performed at HASYLAB, Hamburg, using beam line BW3 [6]. The photon energy resolution was set to ~1 eV, and the energy scale calibrated to ± 0.2 eV by recording the absorption features of a 20-layer thick O_2 film [7]. The soft x-ray beam was 7° incident with respect to the surface. The measurement geometry was such that the polarization vector was either fully within the surface plane (denoted A_{xy} [5]) or 7° off normal (A_z), while the detector axis was always positioned along the surface normal. The neutral particles were detected with a sensitive quadrupole mass spectrometer (QMS) fitted with a liquid helium cooled copper cap over the ionizer which was optimized for efficiency. Desorbing ions were detected with a separate QMS having no ionizer.

The residual gas molecules (except H_2) in the QMS ionizer region were effectively removed by condensation onto the cap's inner surfaces [8]. To further enhance the signal-to-background ratio, the soft x-ray beam was chopped and the QMS signal processed by a lock-in amplifier. A neutral CO photodesorption spectrum and the CO mass spectrum were used to determine and subtract the contribution to the O^0 signal from CO molecules cracking inside the QMS ionizer [8]. We also measured CO partial photoabsorption by monitoring the electron partial yield using a standard detector having a potential of -350 V applied to a retarding grid. This detector was oriented at a grazing exit angle for maximum surface sensitivity and operated in parallel with either the ion or atom detectors.

The system base pressure was 3×10^{-11} mbar. The Ru(001) surface and well-ordered ($\sqrt{3} \times \sqrt{3}$) CO/Ru(001) overlayers were prepared using standard procedures [9]. At this CO coverage, the O^+ photodesorption (PSD) cross section is maximum, and the ion emission is peaked about the surface normal (see Ref. [4]). We dosed

$^{12}C^{18}O$ (99.8% purity) for easy discrimination against ambient CO.

The experimental results are shown in Fig. 1. They consist of the O^0 atom yield (AY), the electron partial yield (PY), and the O^+ ion yield (IY) as functions of photon energy in the O 1s excitation region. Since the CO molecules are oriented 90° to the surface, π-symmetry excitations are observed for A_{xy} geometry and those of σ symmetry for A_z. In order to determine the relative desorption efficiencies on a per excitation basis, we display the ratio AY/PY for both symmetries. The spectral assignments are from symmetry-resolved gas-phase absorption data [10], *ab initio* calculations [11], and previous ion desorption data [5].

The PY π-symmetry (PY$_\pi$) spectrum has two peaks at 534 and 550 eV. The first is the $[1\sigma]2\pi$ main resonance. The second is assigned to be mainly due to the $[1\sigma1\pi]2\pi2\pi$ two-hole–two-electron (2h-2e) shakeup process, but there may be some contribution from the $[1\sigma5\sigma^2]2\pi^3$ state [11]. The PY σ-symmetry (PY$_\sigma$) spectrum is dominated by the $[1\sigma]6\sigma$ shape resonance at 550 eV while the peak at 534 eV is likely residual PY$_\pi$ signal. Beyond 560 eV, the PY decreases similarly as the appropriate Ru partial absorption cross section.

As in the PY$_\pi$ spectrum, both the $[1\sigma]2\pi$ resonance at 534 eV and the $[1\sigma1\pi]2\pi2\pi$ shakeup at 550 eV appear in AY$_\pi$, although with different weights. Comparing peak widths, we find that the AY$_\pi$ maximum at 550 eV cannot be due to a residual 6σ shape resonance signal, in agreement with gas-phase data [10]. For A_z, the similarity between the PY and AY is less clear. At 550 eV, where the 6σ shape resonance appears as a well-defined, symmetric PY peak, we find a 10 eV broad AY feature which resembles a step rather than a maximum. Beyond 550 eV, the O^0 atom yield decreases uniformly, approaching 80% of the prethreshold signal at 625 eV.

In strong contrast to both the PY and the AY, O^+ IY increases stepwise in the same photon energy range until it is 20 times the prethreshold value. These data agree with earlier work [5], but show improved statistics, better photon energy resolution, and a higher degree of polarization. There are three distinct resonances at 534, 550, and 570 eV in the IY$_\pi$ spectrum and smaller features at 585 and 598 eV. The first peak ($[1\sigma]2\pi$) lies upon a flat background, but the remaining ones all lie near or partially over steps. These form a series of multielectron ionization thresholds corresponding to two-hole and three-hole configurations above 550 and 570 eV, respectively. The peaks are bound neutral shakeup excitations under each respective multi-ionization threshold. The excitation cross sections for the higher mh-ne excitations are much smaller than the 1h-1e channels and, hence, are not observed in absorption (PY), but they do appear in desorption due to the coupling of the molecule with the substrate which quenches the 1h-1e channel. The general loss of spectral structure with increasing hole number

m and electron number n in the initial excitation stems from an increased number of possible multiplet states *and* from increasingly repulsive excited state potential energy surfaces.
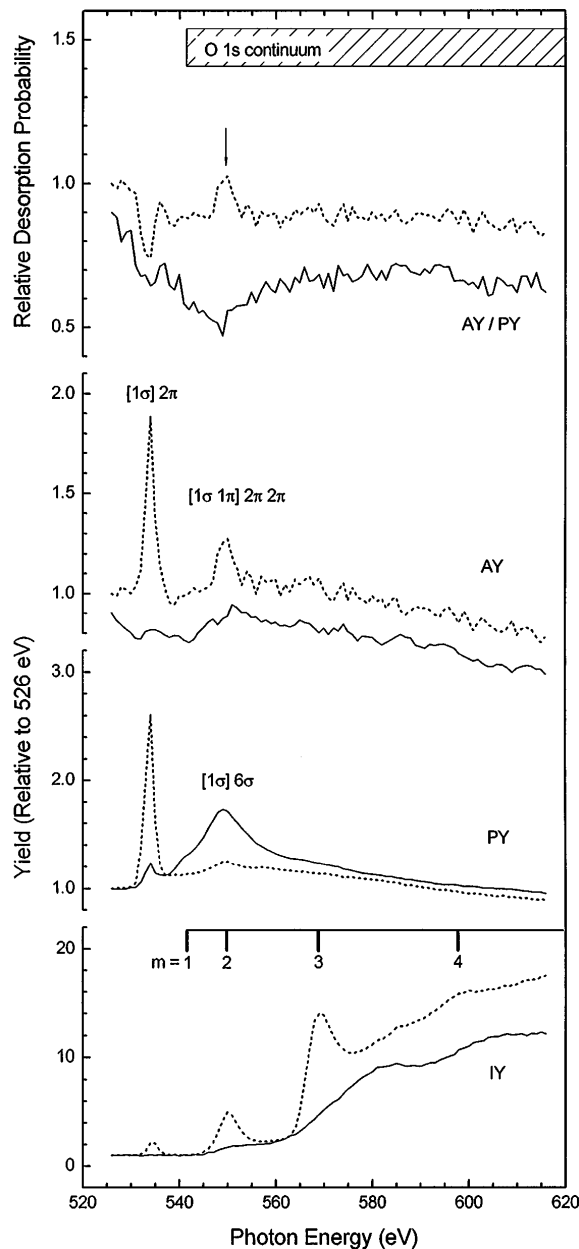

FIG. 1. From bottom to top: O^+ ion desorption yield (IY), partial absorption cross section from electron partial yield (PY), O^0 neutral desorption yield (AY), and relative O^0 desorption probability (AY/PY) as a function of photon energy from $(\sqrt{3} \times \sqrt{3})$ CO/Ru(001) in the O 1s excitation region. The dotted lines are for π-symmetry transitions and the solid lines for σ symmetry. The AY$_\sigma$ and (AY/PY)$_\sigma$ spectra have been shifted down by 0.1 for clarity and all spectra are rescaled to their prethreshold values at 526 eV. The O 1s ionization continuum (on top) and multiple ionization thresholds with respective hole number m (lower panel) are indicated. The O^0 enhancement from the neutral $[1\sigma1\pi]2\pi2\pi$ shakeup state is denoted by an arrow.

The markedly different spectral shapes of O^0 and O^+ yield curves shown in Fig. 1, and the previous results for O^{++} in Ref. [5], convincingly demonstrate the necessity of detecting neutrals to obtain a comprehensive picture of PSD. The AY is structureless beyond 550 eV and begins to decrease at the $2e$-$2h$ threshold while the O^+ IY then displays its most intense features. Emission of the doubly charged O^{++} fragment is extremely weak below the three-electron excitation threshold at 570 eV, indicating that at least three-hole excitations are necessary for PSD of O^{++} [5].

We note that the resonant peak structure in the AY and IY indicates that the photogenerated electrons originating from the Ru substrate are not a major channel for the production of fragments. In addition, our results show that the *maxima* in neutral and ionic desorption yields are clearly related to photoexcitation of core electrons into unfilled orbitals of valence type. Rydberg transitions between the 2π resonance and the O $1s$ ionization potential exhibit oscillator strength in the PY, but are not pronounced in desorption. As for the isolated molecule, excitations involving more diffuse Rydberg orbitals do not weaken the C—O bond as much as excitations into antibonding valence orbitals [12].

The overall probability of photodesorption is the product of the primary excitation cross section and a desorption probability [4]. In this simple two-step framework, the atom desorption probability can be judged from the ratio AY/PY in Fig. 1. The quantity IY/PY is essentially the same as the IY spectrum and is not shown. This indicates that excitation dependent resistance to quenching governs the overall ion desorption probability. In the AY/PY ratio, however, we observe contrasting behavior for the $[1\sigma]2\pi$ $1h$-$1e$ and the $[1\sigma 1\pi]2\pi 2\pi$ $2h$-$2e$ bound double excitations. For the first, this ratio *drops*, indicating $[1\sigma]2\pi$ is the least efficient O $1s$ π-symmetry resonant excitation for O^0 production. The $[1\sigma 1\pi]2\pi 2\pi$ excitation, on the other hand, *increases* this ratio, making it the most efficient.

The result for the $[1\sigma]2\pi$ state is to be expected because of its one-electron character and vibrational fine structure in gas-phase absorption [12]. A large primary absorption cross section is paired with a relatively low desorption probability. The $[1\sigma 1\pi]2\pi 2\pi$ excitation, on the other hand, efficiently creates O^0 for two reasons. The first is because the molecular potential energy surface of the shakeup state is very repulsive, reflected by an intrinsic 3 eV natural peak width in absorption [10]. Second, electron correlation acts to localize the excitation and prevent it from diffusing into the substrate, as is the case for ions [5]. For the other symmetry (σ), the decrease in the AY/PY ratio in the 6σ shape resonance region shows how inefficient short-lived states are for neutral production, where instead of a maximum the broad $2e$ ionization threshold is seen. The AY/PY ratio in Fig. 1 is the first core excitation-induced desorption spectrum to illustrate both

efficient delocalization *and* localization of the molecular excitation in a *single* spectrum.

Despite a great deal of experimental effort, two fundamental questions regarding desorption from surfaces remain. First, what is the relative abundance of neutrals and ions? Second, to what extent are outgoing ions neutralized and appear as neutrals? Our data show a crossing point at 550 eV, whereafter neutral production falls off and that of ions increases. From this, we conclude that excitations with three or more holes ($m > 2$) do not effectively produce neutrals. This may not be surprising, but at least we have determined that multielectron charge transfer in a single step from the metal is unlikely. Admittedly, ion and neutral emission are two such complicated and interdependent processes that a single measurement of a model system cannot hope to fully answer all questions. But our results show it will now be possible to begin to answer these questions for well-localized core excitations by future application of the neutral yield measurement technique.

Photodissociation studies employing electron emission have measured fragments that undergo core hole decay, and thus can directly observe an ionic fragment [2]. Our method measures a neutral fragment which initially contained a core hole, produced through two possible scenarios. The first entails core decay of an intact molecule, charge redistribution, and subsequent fragmentation of the decay state. The second is charge redistribution and fragmentation before decay. By the very nature of the measurement, the neutral yield technique provides a new type of information which is complementary to that obtained via electron emission studies. Our model system illustrates this point. Partial filling of the 2π orbital by donation of electrons from the metal along with donation of CO 5σ electrons to the metal is responsible for the Ru—CO bond. Core deexcitation spectra of CO on a variety of transition metals show effective charge transfer into the 2π orbital from the metal before core hole decay [13]. Calculations for a related system, CO/Cu(100), show dramatic charge transfer for the $[1\sigma]$ state where the net CO charge is $Q = -0.48$, compared to $Q = +1$ in the gas phase [14]. Intramolecular charge redistribution also occurs. In the equivalent core model, O $1s$ core ionized CO is treated as CF [12]. An O^0 atom leaving the molecule as $(O^-)^*$, which is core equivalent to F^-, can become neutral via participator decay and emission of an electron. An electron in the 2π orbital is available to be captured by such a process. Significantly, the $[1\sigma 1\pi]2\pi 2\pi$ excitation has two such electrons.

Ultrafast dissociation (UFD) processes entail appreciable nuclear motion on strongly repulsive potential curves during the very brief core hole lifetime, up to and including complete bond breaking [2,4]. Bond breaking can also continue after core decay. Although most fragments might stem from dissociative spectator decay states, we believe that the AY peak at 550 eV most probably has

an ultrafast dissociation contribution. Using the reflection method [1], we estimate the $[1\sigma 1\pi]2\pi 2\pi$ potential curve to have a gradient of 3 eV/0.15 Å $= 20$ eV/Å in the Franck-Condon region. Under a constant acceleration from this gradient during the O $1s$ core lifetime (5 fs), an O atom would travel 0.15 Å, which is almost 15% of the ground state equilibrium CO bond length. Although this is an upper bound, it shows that the atom likely travels a significant distance before core decay.

In summary, we have demonstrated the feasibility of detecting neutral atomic fragments created by energy- and polarization-specific molecular core excitations. Results from a model adsorption system show the necessity of such measurements for the understanding of desorption from surfaces. The strong differences between neutral and ion yields emphasize the importance of charge transfer processes. The study of dissociation dynamics, the behavior of electronic and nuclear coordinates during fragmentation, will benefit from the measurement of neutral atomic fragments. A total yield measurement alone cannot decisively discern whether a fragment originates from UFD or a core decay product. In conjunction with either time-of-flight or coincidence methods, however, a wealth of dynamical information will be obtainable. For these reasons, we feel that the technique has the potential to be the basis of extremely powerful probes of photodissociation.

[1] R. Schinke, in *Photodissociation Dynamics: Spectroscopy and Fragmentation of Small Polyatomic Molecules,* Cambridge Monographs on Atomic, Molecular, and Chemical Physics Vol. 1 (Cambridge University Press, Cambridge, 1993).

[2] A. Menzel, B. Langer, J. Viefhaus, S. B. Whitfield, and U. Becker, Chem. Phys. Lett. **258**, 265 (1996).

[3] R. A. Rosenberg, C.-R. Wen, K. Tan, and J.-M. Chen, in *Desorption Induced by Electronic Transitions: DIET IV*, edited by G. Betz and P. Varga (Springer-Verlag, Berlin, 1990), p. 97.

[4] P. Feulner and D. Menzel, in *Laser Spectroscopy and Photochemistry on Metal Surfaces: Part II*, edited by H.-L. Dai and W. Ho, Advanced Series in Physical Chemistry Vol. 5 (World Scientific, Singapore, 1995), pp. 627–684.

[5] R. Treichler, W. Wurth, W. Riedl, P. Feulner, and D. Menzel, Chem. Phys. **153**, 259 (1991).

[6] C. U. S. Larsson, A. Beutler, O. Björneholm, F. Federmann, U. Hahn, A. Rieck, S. Verbin, and T. Möller, Nucl. Instrum. Methods Phys. Res., Sect. A **337**, 603 (1994).

[7] P. Kuiper and B. I. Dunlap, J. Chem. Phys. **100**, 4087 (1994).

[8] S. P. Frigo *et al.* (to be published).

[9] P. Hofmann, J. Gossler, A. Zartner, M. Glanz, and D. Menzel, Surf. Sci. **161**, 303 (1985), and references therein.

[10] E. Shigemasa, T. Hayaishi, T. Sasaki, and A. Yagishita, Phys. Rev. A **47**, 1824 (1993).

[11] H. Ågren and R. Arneberg, Phys. Scr. **30**, 55 (1984).

[12] M. Domke, C. Xue, A. Puschman, T. Mandel, E. Hudson, D. A. Shirley, and G. Kaindl, Chem. Phys. Lett. **173**, 122 (1990).

[13] W. Wurth, C. Schneider, R. Treichler, D. Menzel, and E. Umbach, Phys. Rev. B **37**, 8725 (1988).

[14] L. G. M. Pettersson, H. Ågren, O. Vahtras, and V. Carravetta, Surf. Sci. **365**, 581 (1996).