Observation of Resonant Photoemission in an Adsorbed Molecule

G. Loubriel
Sandia National Laboratories, Albuquerque, New Mexico 87815

and

T. Gustafsson
Department of Physics and the Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, Pennsylvania 19104

and

L. I. Johansson
Department of Physics and Measurement Technology, Linköping University, S-58183 Linköping, Sweden

and

S. J. Oh
Physics Department, Stanford University, Stanford, California 94305

(Received 19 March 1982)

The observation of resonant photoemission from CO chemisorbed on Pt(111) is reported. The resonance originates in excitation of a C 1*s* electron to the unoccupied $2\pi^*$ level and causes a giant enhancement of valence shakeup peaks in the emission spectra.

PACS numbers: 79.60.-i, 33.60.Fy, 73.90.+f

We report the first evidence for resonant enhanced photoemission from a chemisorbed molecule. We show in studies of the CO/Pt(111) system that a great increase in photoemission intensity is observed in the valence and near-valence energy region for a photon energy at the (bound to bound) transition from C 1*s* to CO $2\pi^*$. This new intensity is distributed in peaks that are very weak off resonance and cannot be associated with simple one-electron-hole states.

Resonant photoemission has been the subject of a great deal of work in recent years,[1-6] particularly since the discovery of the resonating 6-eV satellite in Ni.[2] In a general sense, such resonances are believed to be due to an excitation from a core level to an unoccupied valence level, followed by deexcitation. The identity of the intermediate state is, however, difficult to determine, especially in solids. In many cases questions remain about the importance, if any, of coupling between resonating and nonresonating ionization channels and about the relative weight of the main line and satellite on resonance. The data presented below, which constitute the first evidence for resonant photoemission in an adsorbed molecule, make what we believe to be an important contribution towards an understanding of these questions. The low symmetry of the adsorbed molecule makes it possible to use symmetry selection rules for the excitation event. These allow us experimentally to identify the intermediate state uniquely in a way not accomplished in most systems. We show that the nonresonant channel is quite unimportant for CO/Pt(111), making the question of channel interference a moot one. The spectral weight on resonance is (within the crude estimates possible) completely attributable to the satellite line, which we speculate is because of the specific screening mechanism operable in adsorbed CO. While quantitative data on other systems is hard to come by, it appears that the relative enhancement on resonance relative to off resonance is bigger than in any other system we are aware of. Finally, our data show strikingly a phenomenon that will be of importance for the emerging spectroscopy of the carbon *K* edge, one of the growth areas of the surface science in the coming years.

The basic principles in our experiment can be understood[4,6,7] from the schematic diagram in Fig. 1. An adsorbed molecule *M* has a core level *C* [in our case, the C 1*s* (2σ)], an occupied valence level (OV) (the 3σ, 4σ, 5σ, and 1π manifold), and an unoccupied valence level (UV) (CO 2π). (The Fermi level of the substrate is located between OV and UV.) On resonance, a photoelectron is excited from *C* to UV, leaving the molecule in a highly excited neutral state M^*. This state will now decay by one or more of three possible channels:

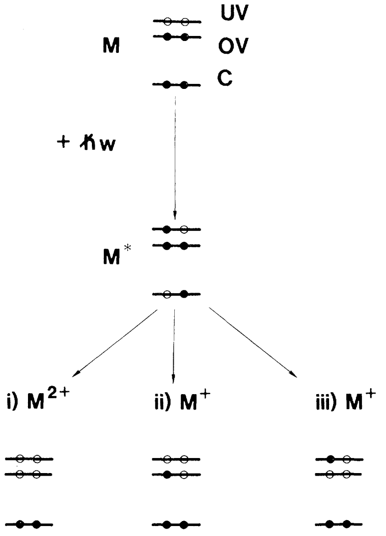

FIG. 1. Schematic illustration of three different deexcitation paths following a core (C) to unoccupied (UV) level excitation in a molecule M. OV is an occupied valence level and M^* signifies an excited molecular state.

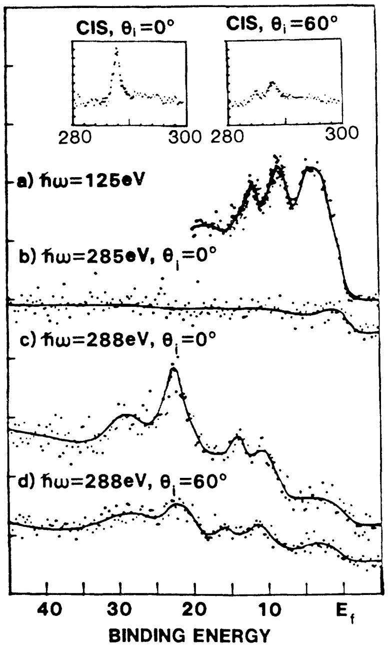

FIG. 2. Photoemission and CIS spectra from CO/Pt(111) as a function of photon energy and incidence angle of the light (θ_i). The insets show the intensity of the peak at 23-eV binding energy [(c) and (d)] as function of photon energy. In (b), (c), and (d) the electron take-off angle, θ, was 55°.

(i) The UV electron may escape to the substrate, leaving a singly ionized molecule behind. This is equivalent to the starting point for conventional Auger decay. The core hole will then be filled, just as off resonance, by one OV electron. The excess energy will be absorbed by another OV electron. The spectrum of these emitted electrons will be the same as for off-resonance Auger electrons. (The two holes in the valence shell will subsequently be screened by substrate electrons.)

(ii) The UV (2π) electron will fill the core hole and the excess energy will be taken up by an OV electron (or vice versa). The energy of this electron will be *exactly* that of an electron excited *directly* from the OV level(s). This corresponds to an enhancement of the excitation strength of the OV electrons ("the main line").

(iii) One OV electron fills the core hole and another one is emitted. The UV (2π) electron remains a spectator in this event. The resulting state can be viewed as either a modified Auger or a modified photoemission spectrum. It is Auger-like since one has an Auger decay in the presence of the $2\pi^*$ electron. It is photoemissionlike in that the final state of the system is singly ionized although having two holes and one electron. This type of final state is referred to as a shakeup state. These shakeups are eigenstates of the ion and can, of course, be reached also by direct ionization from the molecular ground state off resonance. The intensity of the shakeup peaks is usually small relative to that of the main line, especially in chemisorbed molecules, where the strong background from the substrate usually obscures the weak shakeup peak in the valence-band region.

As the ions left behind in these three cases have different energies, one can separate these three possibilities by measuring the energies of the emitted photoelectrons.

The experiments were carried out at the Stanford Synchrotron Radiation Laboratory with a Vacuum Generators model ADES400 electron energy analyzer. The photon energy resolution was ~0.4 eV at 288 eV. Electrons were collected in the plane of incidence. The spectra are labeled in terms of θ_i, the angle of incidence of the light, and θ, the angle at which electrons were collected (both measured with respect to the sample normal). The CO exposure was 3 langmuirs (1 langmuir = 10^{-6} Torr sec) at room temperature. The CO molecular axis is parallel to the surface normal.[8]

Far off resonance [$\hbar\omega = 125$ eV, Fig. 2(a)], the photoemission spectra exhibit normal photoemission peaks at $\simeq 12.0$ eV (4σ) and $\simeq 9.0$ eV ($1\pi + 5\sigma$) binding energy in good agreement with previous work.[8,9] At photon energies from 280 to ~286 eV we find negligible CO-derived emission (the C 1*s* binding energy is ~285 eV with respect to the Fermi level). A spectrum in this energy range [Fig. 2(b), $\hbar\omega = 285$ eV] shows no peaks above the (large) noise level. Just above this energy the valence-band electron emission increases dramatically and peaks at 288 eV. This resonance emission [Fig. 2(c), $\hbar\omega = 288$ eV] exhibits peaks at ~28 and ~23 eV and substructures at ~11 and ~14 eV binding energy. To obtain the behavior of these peaks as a function of photon energy we recorded a series of constant-initial-state (CIS) spectra (in which the partial electron yield at a fixed binding energy is taken as the photon energy is swept). CIS spectra taken for a binding energy of 23 eV are shown in the insets in Fig. 2.[9,10] The small width of the resonance enhancement, ~1 eV full width at half maximum, is consistent with bound-to-bound transitions. *This line shape is quite symmetric, indicating negligible importance of the nonresonant shakeup channel.*[6]

Given that the axis of the adsorbed CO molecule is along the surface normal,[8] dipole selection rules predict that 2σ (C 1*s*) to $2\pi^*$ absorption should vary as $\cos^2\theta_i$, whereas a σ-to-σ transition yields a $\sin^2\theta_i$ dependence. In Figs. 2(c) and 2(d) the ratio of the intensity of the peaks at $\theta_i = 0°$ versus 60° is ~4. The CIS spectra also show this ratio. *We consequently attribute the resonance to electron emission following C 1s to* $2\pi^*$ *transitions.*

Figure 3 shows off-resonance and resonance spectra together with an x-ray-excited Auger spectrum from adsorbed CO.[11] It is clear that most of our peak binding energies at resonance do not match those of either Auger or off-resonance photoemission data. Consequently, mechanisms (i) and (ii) above can be excluded. We attribute the enhancement instead to *resonance enhancement of the shakeup states, mechanism (iii).* This assignment is given strong support by the work of Norton, Doodale, and Selkirk,[12] who observed for CO/Pt(111) very weak peaks at 11.5- and 14-eV binding energy at $\hbar\omega = 40.8$ eV, tentatively attributed to shakeup states. As a result of our poor signal-to-noise ratio, we cannot observe these weak peaks in our spectra off resonance.

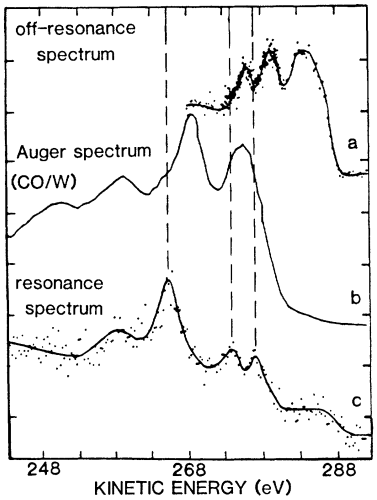

FIG. 3. (a) Nonresonant photoemission spectrum at CO on Pt(111), (b) the Auger spectrum of CO/W (Ref. 11), and (c) the photoemission spectrum at resonance. Spectrum (a) was shifted to align the Fermi level with that of spectrum (c).

Although the assignment of the valence shakeup peaks for chemisorbed CO may be expected to be very complicated,[13] one should in principle be able to assign every peak in our resonant spectra to two-hole, one-electron states of the system. The broad feature which extends from 20 to 33 eV is the easiest to interpret. In the C *KVV* Auger spectra of transition-metal carbonyls the most intense decays leave the molecule in a $5\sigma^{-1}1\pi^{-1}$ final state.[14,15] We postulate that the relative intensity of these features is not strongly perturbed by the presence of a $2\pi^*$ electron and assign the intense feature at ~23 eV to the $5\sigma^{-1}1\pi^{-1} \times 2\pi^{*+1}$ final state. A similar analysis suggests that the $5\sigma^{-2}2\pi^{*+1}$, $1\pi^{-2}2\pi^{*+1}$, $4\sigma^{-1}5\sigma^{-1}2\pi^{*+1}$, $4\sigma^{-1}1\pi^{-1}2\pi^{*+1}$ final states also contribute to the intensity between 20 and 33 eV. Calculations of their peak energies substantiate this statement.[16]

One can test our assumption that the extra $2\pi^*$ electron will not strongly influence the relative intensity of peaks by comparing intensities (not peak positions or the overall spectrum) of the N *KVV* spectrum of gas phase NO (Ref. 15) with the C *KVV* of CO.[17,18] One finds that all relative peak intensities are in rough agreement with the exception of the $1\pi^{-2}$. The reason for this is the strong configuration-interaction mixing of the 1π and $2\pi^*$ levels.[18] In general, our assumption is expected to be poor for peaks which admix with the $2\pi^*$ level. The lowest binding-energy peaks in the Auger spectrum of CO adsorbed on *nd* transition metal surfaces and for carbonyls are interpreted as $nd^{-1}5\sigma^{-1}$ and $nd^{-1}1\pi^{-1}$ final states. Using the previous analogy we tentatively assign the structures in the resonance spectrum at 11 and 14 eV to the $5d^{-1}5\sigma^{-1}2\pi^{*+1}$ and $5d^{-1}1\pi^{-1}2\pi^{*+1}$ states.

At off-normal incidence ($\theta_i = 60°$) a new feature arises at $\hbar\omega = 285$ eV in the CIS spectrum shown in the inset of Fig. 2. Symmetry selection rules show that this feature is caused by promotion of a C 1*s* electron to an unoccupied σ-derived orbital. We postulate that this orbital is the unoccupied part of the 5σ antibonding level. Its binding energy is in agreement with that found in calculations for CO on Ni(100).[19]

To conclude, we have shown that resonant photoelectron emission near the C 1*s* threshold exists and we assign this resonance to process (iii):

$$(\mathrm{C}\ 1s^2)X^{20}2\pi^{*0} \rightarrow (\mathrm{C}\ 1s^1)X^{20}2\pi^{*1} \rightarrow (\mathrm{C}\ 1s^2)X^{18}2\pi^{*1},$$

where X represents the 3σ, 4σ, 5σ, 1π and $5d$, $6s$ manifold of levels. These final states can be understood as photoemission shakeup states or as Auger final states where the $2\pi^*$ electron is present as a spectator. Channel interference is not important, just as in the case of atomic copper.[6] To understand why process (iii) dominates will require further study. It is known that creation of a C 1*s* hole (removal of an electron to infinity) induces screening through charge transfer to the $2\pi^*$ level.[13] In the experiments above, we simultaneously create the hole and its screening charge. Hence, process (i) should not be strong. It is interesting to note that in the electron-excited gas-phase CO spectrum,[7] mechanisms (ii) and (iii) have comparable strength. The reason why (iii) dominates for chemisorbed CO is likely due to changes in the $2\pi^*$ level that are known to modify the screening of the C 1*s* hole.

We thank D. R. Jennison, I. Lindau, and R. R. Rye for useful support and discussions. This work was supported by the U. S. Department of Energy under Contract No. DE-AC04-76-DP00789, by the Gas Research Institute and by the National Science Foundation under Contract No. DMR-79-13102. We also acknowledge support from the National Science Foundation Materials Research Laboratory program under Grant No. DMR-79-23647. The experiments were performed at the Stanford Synchrotron Research Laboratory which is supported by the National Science Foundation under Grant No. DMR 77-27489 in cooperation with the U. S. Department of Energy. Sandia National Laboratories in a U. S. Department of Energy facility.

---

[1] G. J. Lapeyre, A. D. Baer, J. Hermanson, J. Anderson, J. A. Knapp, and P. L. Gobby, Solid State Commun. 15, 1601 (1974).

[2] C. Guillot *et al.*, Phys. Rev. Lett. 39, 1632 (1977).

[3] J. W. Allen, L. I. Johansson, R. S. Bauer, I. Lindau, and S. B. M. Hagstrom, Phys. Rev. Lett. 41, 1499 (1978).

[4] M. Iwan, F. J. Himpsel, and D. E. Eastman, Phys. Rev. Lett. 43, 1829 (1979).

[5] T. C. Chiang and D. E. Eastman, Phys. Rev. B 21, 5749 (1980).

[6] A. Zangwill and P. Soven, Phys. Rev. B 24, 4121 (1981).

[7] W. E. Moddeman, T. A. Carlson, M. O. Krausse, B. P. Pullen, W. E. Bull, and G. K. Schweitzer, J. Chem. Phys. 55, 2317 (1971).

[8] D. A. Shirley, J. Stohr, P. S. Wehner, R. S. Williams, and G. Apai, Phys. Scr. 16, 398 (1977).

[9] Similar CIS data were obtained for CO/Ni(100) by J. Stohr, K. Baberschke, R. Jaeger, R. Treichler, and S. Brennan, Phys. Rev. Lett. 47, 381 (1981).

[10] The CIS spectra in Fig. 2 are not normalized with respect to incident photon flux and light-source stability. This is justified as we are only concerned with relative cross sections and as carbon contamination on the optical elements in the monochromator was not a problem. This was demonstrated by taking CIS spectra on the CO-covered surface at a binding energy of 5 eV (in the Pt *d* band) as well as on the clean surface at $E_B \simeq 11$ and 14 eV. These spectra showed no structure between 285- and 300-eV photon energy.

[11] E. Umbach, to be published. The angle-integrated Auger spectra of molecularly adsorbed CO are only very weakly substrate dependent; cf., e.g., the CO/Ni(100) case (B. E. J. M. White and G. M. Loubriel, to be published).

[12] P. R. Norton, J. W. Doodale, and E. B. Selkirk, Surf. Sci. 83, 189 (1979).

[13] H. J. Freund and E. W. Plummer, Phys. Rev. B 23, 4859 (1981).

[14] D. R. Jennison, G. D. Stucky, R. R. Rye, and J. A. Kelber, Phys. Rev. Lett. 46, 911 (1981).

[15] G. D. Stucky, R. R. Rye, D. R. Jennison, and J. A. Kelber, to be published.

[16] G. Loubriel and D. R. Jennison, J. Vac. Sci. Tech. 20, 901 (1982).

[17] J. A. Kelber, D. R. Jennison, and R. R. Rye, J. Chem. Phys. 75, 652 (1981).

[18] D. R. Jennison, J. A. Kelber, and R. R. Rye, Chem. Phys. Lett. 77, 604 (1981).

[19] A. Rosen, E. J. Baerends, and D. E. Ellis, Surf. Sci. 82, 139 (1979).