

High-Resolution C 1s and O 1s Core-Excitation Spectroscopy of Chemisorbed, Physisorbed, and Free CO

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High-resolution soft-x-ray excitation spectra are reported for free CO, CO condensed on Au at ~ 20 K, and CO chemisorbed on Ni(111). Chemisorption increases dramatically the widths of the C and O $1s \rightarrow 2\pi^*$ transitions from < 0.2 to 2.2 eV for C 1s and from 1.15 to 3.5 eV for O 1s. Shifts of 0.3 eV (for C 1s) and 1.7 eV (for O 1s) towards lower energy are resolved for the first time and are explained in terms of the electronic distribution in excited CO.

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Core-level excitation spectroscopy probes unoccupied valence orbitals by making a transition from a core level to a valence state with soft x rays. Interesting new results have emerged since the C 1s and O 1s levels became accessible.¹ This technique has the capability to be site specific but the disadvantage to be affected by the electron-hole interaction. We have taken the CO molecule as a model system to get a better understanding of the electron-hole interaction for free, physisorbed, and chemisorbed molecules. Of particular interest are the valence orbitals of CO that are involved in the bonding to a surface. Current models emphasize two mechanisms: a charge transfer from the occupied 5σ orbital towards the surface and a back donation of charge from the surface into the unoccupied $2\pi^*$ orbital.² The orbital shifts associated with chemisorption and physisorption have been measured by use of photoemission and inverse photoemission for filled and empty orbitals, respectively. The chemical shift, however, is masked by a relaxation shift since the substrate screens the hole produced in photoemission (or the electron that is added in inverse photoemission). This difficulty calls for a different probe which leaves the molecule neutral and minimizes screening effects, such as core-level absorption or electron energy-loss spectroscopy.

Previous core-level absorption measurements of chemisorbed CO were not able to resolve any shift or broadening of a core-to- $2\pi^*$ transition that went beyond the experimental limits.^{3,4} Our high-resolution measurements show that there exist significant shifts when going from free CO to chemisorbed CO. The O $1s \rightarrow 2\pi^*$ transition is affected more strongly than the C $1s \rightarrow 2\pi^*$ transition despite the fact that CO bonds to the metal with the C end. We interpret these results on the basis of different electron distributions in ground state CO, C-1s-excited CO, and O-1s-excited CO. This can be

viewed as a new type of electron-hole interaction. We also propose a simple way of accounting for the Coulomb interaction between the electron and the hole for chemisorbed CO. The large width of the transitions for chemisorbed CO is dominated by the width of the $2\pi^*$ orbital which hybridizes with Ni $4s, p$ states.

The experiments were performed with a new high-resolution 6-m/10-m toroidal grating monochromator which is described elsewhere.⁵ We measured the yield of photoelectrons above ≈ 100 eV kinetic energy which is proportional to the absorption coefficient provided that the mean free path of the photoelectrons (or the sample thickness) is small compared with the absorption length. For gas-phase CO the transmission through a column of 3 m length was measured with use of a Na-salicylate phosphor with a photomultiplier. In order to assure reproducible photon energy and resolution settings compatible with the high resolution of the experiment we always used solid CO as a reference by moving a cryostat with condensed CO in and out of the beam.

Figure 1 shows the absorption coefficient for the core-to- $2\pi^*$ transitions of free CO, CO condensed on gold (≈ 10 layers at 20 K), and CO chemisorbed on Ni(111) (saturation exposure at room temperature). In going from free to condensed CO no changes are detected for the O $1s \rightarrow 2\pi^*$ transition within the experimental accuracy of 0.05 eV. We assume that there are no significant changes for the C $1s \rightarrow 2\pi^*$ transition, either. For CO chemisorbed on Ni(111) a substantial shift towards lower transition energies is observed (0.3 eV for C 1s and 1.7 eV for O 1s). The width increases dramatically from 0.1 eV^{6,7} for individual vibronic levels of free CO to 2.2 eV for the C $1s$ -to- $2\pi^*$ transition. The larger width of the O 1s gas-phase transition (1.15 eV^{6,7}) is due to unresolved vibronic structure and does not represent the intrinsic level width which is

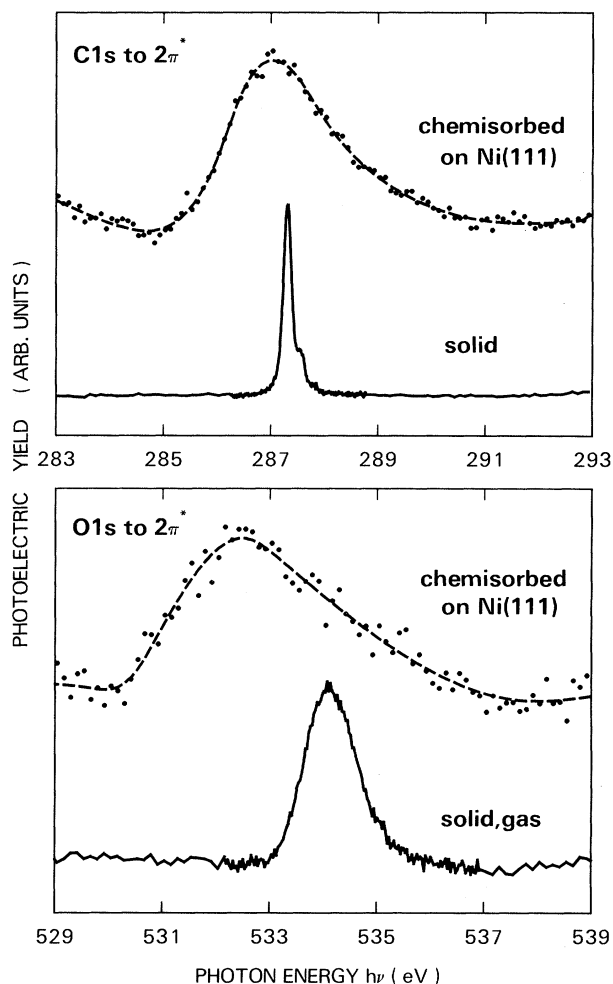


FIG. 1. Core-level excitation spectra for solid CO and chemisorbed CO on Ni(111). The shifts and the broadening are mainly due to changes in the $2\pi^*$ orbital upon chemisorption. Vibronic fine structure is resolved for the C $1s$ excitation in solid CO but unresolved for the O $1s$ excitation.

expected to be similar to the C $1s \rightarrow 2\pi^*$ transition.

We discuss first the excitation energy shifts and then the widths of the transitions. Compared with photoemission and inverse photoemission the relaxation energy associated with core excitation is very small since we are dealing with an essentially neutral entity.⁸ Through the mixing of the $2\pi^*$ orbital with the metallic states there will be a certain charge transfer (somewhat different than in the ground state) but the associated relaxation energy is smaller than the relaxation energy E_R of $2\pi^*$ in inverse photoemission by a factor $(\Gamma/W)^2$, where Γ is the $2\pi^*$ width and W is the bandwidth of the metal band.⁹ In general, then the relaxation energy will be < 0.5 eV.

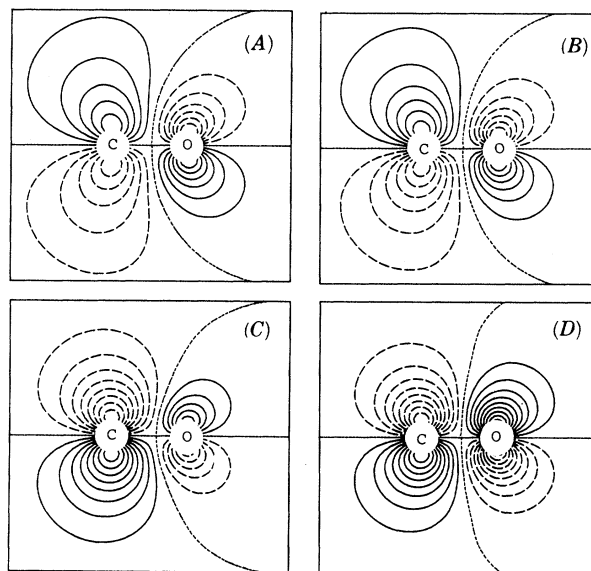


FIG. 2. Orbital plots for the $2\pi^*$ orbital of free CO: (a) the virtual $2\pi^*$ orbital of ground-state CO, (b) the $2\pi^*$ orbital of CO^- , (c) the $2\pi^*$ orbital of excited CO with an O $1s$ hole, and (d) the $2\pi^*$ orbital of excited CO with a C $1s$ hole. In the presence of an O $1s$ hole the $2\pi^*$ orbital has a larger charge density at the carbon end of the molecule (left-hand side) than in all other cases. This causes a large chemisorption shift (see Fig. 1).

In order to understand the trend in our data we use the simple *equivalent-core* picture. In this picture, an atom with a core hole is considered equivalent to an atom with a unit-higher atomic number so that $\text{CO}^+(\text{C } 1s^{-1})$ is equivalent to NO while $\text{CO}^+(\text{O } 1s^{-1})$ is equivalent to CF. In the CO ground state, because of the electronegativity difference between C and O, the occupied 1π orbital has a higher amplitude on the O atom and the orthogonal $2\pi^*$ orbital has its highest amplitude on C. This trend is seen in orbital plots obtained by self-consistent-field calculations on CO [Fig. 2(a)]. Since N has higher electronegativity than C, the $2\pi^*$ amplitude in NO will be more evenly distributed between the two atoms than in CO and this trend is seen in the $2\pi^*$ orbital of C $1s \rightarrow 2\pi^*$ -excited CO [Fig. 2(d)]. Finally, since F has higher electronegativity than O, the $2\pi^*$ orbital of O $1s \rightarrow 2\pi^*$ CO will be concentrated heavily on the C atom [Fig. 2(c)]. The metal-CO interaction will be maximized when the overlap of the $2\pi^*$ orbital with the metal is highest. From the above discussion, this should happen in the O $1s \rightarrow 2\pi^*$ excited state which has high $2\pi^*$ amplitude on C (CO bonds to the metal with the carbon end), in agreement with our findings. The O $1s \rightarrow 2\pi^*$ transition shifts to lower en-

ergy for chemisorbed CO in qualitative agreement with theory.¹⁰

It is interesting that in a previous lower-resolution study of CO/Ni(100) no shifts in the excitation energies between the gaseous and chemisorption phases were found within the experimental limits of 0.5 eV.³ We speculate that the cause for the differences between CO/Ni(111) and CO/Ni(100) is due, at least partially, to the different extent of $2\pi^*$ involvement in the bonding to the two Ni surfaces. Under the conditions in which the two experiments were performed, CO on Ni(100) is terminally bonded¹¹ while CO on Ni(111) is predominantly bridge bonded.¹² The stronger involvement of charge back donation to the $2\pi^*$ orbital in the higher-coordination sites is

reflected in a larger reduction in the C-O stretch frequency^{11,12} and also suggested by cluster calculations.¹³ Such a sensitivity of the O $1s \rightarrow 2\pi^*$ transition to the adsorption site could be very useful for studying site-specific catalytic reactions and the influence of promoters such as K.

In Fig. 3 we summarize the orbital energies observed with photoemission ($\text{CO}^+ + e$), inverse photoemission and resonant electron scattering ($\text{CO}^- - e$), and photoabsorption (arrows $h\nu$) and compare them with the corresponding calculated excited-state orbital energies for a Cu_5CO cluster.¹⁰ The calculated ground-state orbital energies are also shown because they are often used to discuss the energetics of chemisorption but cannot be measured directly. One can see from Fig. 3 that the

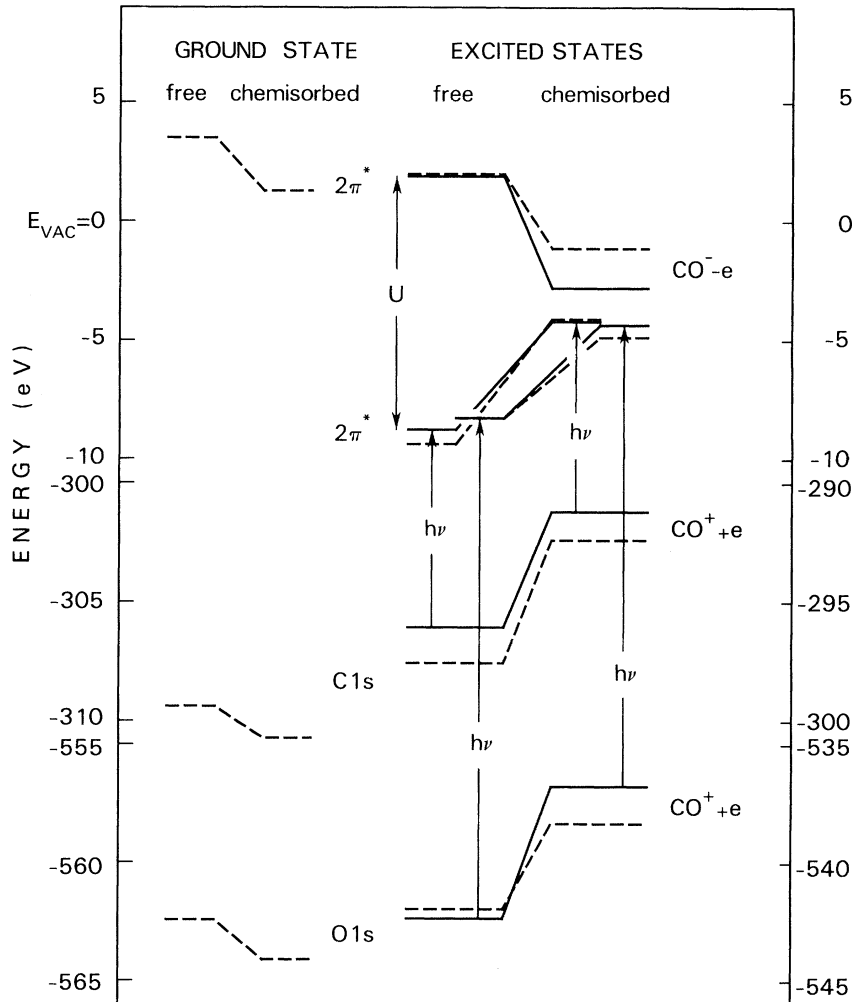


FIG. 3. Energy diagram showing orbital shifts in various states of free CO and chemisorbed CO. Full lines are from data for CO/Ni(111) (see Refs. 7, 14, and 15); dashed lines are from a first-principles self-consistent-field calculation for a Cu_5CO cluster (Ref. 10). The length of the arrows $h\nu$ represents the excitation energy in photoabsorption. U is the electron-hole interaction energy.

chemical shift of the ground state is almost unobservable because it is nearly cancelled when making a core-to- $2\pi^*$ transition and because it is obliterated by relaxation shifts in photoemission and inverse photoemission. It has been emphasized that the transition energy in photoabsorption should be lowered relative to the difference between the levels measured with inverse photoemission and photoemission (see Fig. 3) by the absent electron-electron repulsion energy, $U(1s, 2\pi^*)$ (or equivalently, lowered by an electron-hole attraction). We can therefore express the $2\pi^*$ energy as $\epsilon(2\pi^*) = \epsilon(1s) + E_{\text{exc}} + U(1s, 2\pi^*)$, where the orbital energies ϵ are experimental values and as such they contain relaxation energy (E_R) contributions. Upon chemisorption the relaxation effects raise the $1s$ level by $E_R(1s)$ while the $2\pi^*$ energy is lowered by $E_R(2\pi^*)$. Since the excitation energy for a transition between these two levels is not significantly affected by relaxation the effective electron-hole interaction U has to change. Here we follow a simple heuristic approach and write $\tilde{U} = U - 2E_R$ so that the excitation energy is unaffected by relaxation.⁸ The physical basis behind the expression for \tilde{U} lies on the fact that the electron-hole attraction is reduced by the repulsive interaction between the electron in $2\pi^*$ with the negative surface charge density induced by the $1s$ hole and by the analogous repulsion between the hole and the positive charge density induced by the electron. For free CO the electron-hole interaction is $U(C1s, 2\pi) = 10.6$ eV, for chemisorbed CO we find $\tilde{U}(C1s, 2\pi) = 1.4$ eV, and for solid CO we find $\tilde{U}(C1s, 2\pi) = 6.1$ eV.

The large width of the core excitations of chemisorbed CO is dominated¹² by the width of the $2\pi^*$ orbital, as one can see from the comparable width observed in inverse photoemission.¹⁴ The $2\pi^*$ orbital is broadened by hybridization with the Ni substrate (mostly $4s, p$) states. The extra broadening of the O $1s \rightarrow 2\pi^*$ excitation can be attributed to inhomogeneous broadening between bridge and on-top sites.

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