2π⁺-derived states for CO on Ni(111) studied by uv bremsstrahlung spectroscopy

Th. Fauster and F. J. Himpsel
IBM T. J. Watson Research Center, Box 218, Yorktown Heights, New York 10598
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Angle-resolved and polarization-dependent uv bremsstrahlung spectroscopy (inverse photoemission) is used to determine the energy and symmetry of the 2π⁺-derived states for CO on Ni(111). We observe a 3-eV-wide band centered at 3 eV above the Fermi level. This shows that the electron-hole interaction for transitions C 1s → 2π⁺ is reduced from 10 eV in the gas phase to 1 eV for chemisorbed CO due to screening by metal electrons. Compared with physisorbed and gas phase CO, chemisorption on Ni(111) lowers the energy of the 2π⁺ orbital and increases its width.

We present the first angle-resolved study of empty adsorbate orbitals using uv bremsstrahlung spectroscopy (inverse photoemission). The adsorbate-induced features show strong intensity variations with polar angle of the incident electrons as expected from dipole selection rules for the 2π⁺ orbital of CO bonded normal to the surface. The determination of the one-electron energy of the lowest unoccupied CO derived state shows the effect of the electron-hole interaction on "two-electron-state" spectroscopies which promote an electron from a core or valence state into the 2π⁺ orbital. Here, energies measured with spectroscopies which involve only one excited orbital of the molecule, such as photoemission or bremsstrahlung spectroscopy, are referred to as one-electron energies, in contrast to spectroscopies such as optical-absorption or electron energy-loss spectroscopy which excite two molecular orbitals. The bondig of the molecule to the surface is studied by comparing our results with one-electron energies obtained by resonance electron scattering for gaseous and physisorbed CO. The 2π⁺ level is pulled down below the vacuum level for chemisorbed CO making it invisible to other techniques.

The system CO on Ni(111) has been investigated by a wide variety of surface-sensitive techniques such as low-energy electron diffraction, photoemission, work-function measurements, and vibrational-loss spectroscopies from which the following picture has emerged (see Ref. 1 and references therein): At room temperature, CO is bonded in a bridge position to the Ni substrate independent of coverage with a weakly ordered (√3 × √3)R30° overstructure at $\frac{1}{3}$ monolayer coverage which we have studied. The occupied valence levels for CO on Ni(111) have mainly been studied by photoemission,² whereas the available information on the empty adsorbate levels comes from optical-absorption measurements³ and electron energy-loss spectroscopies.⁴ However, these techniques measure the empty state in the presence of a core or valence hole, which is a large perturbation to the one-electron energy levels of molecules. uv bremsstrahlung spectroscopy or inverse photoemission detects the photons emitted when electrons are decelerated in the sample and is the time-reversed process of regular photoemission.⁵ By observing radiative transitions from free-electron-like states into empty states above the Fermi level of the sample only one orbital of the molecule is excited and we measure the one-electron energies without the distortion of an inner hole.

We have extended our recent angle-integrated inverse photoemission study of CO on Ni(111) (Ref. 6) to include angular resolution for the incident electrons and detection of the polarization of the light, and improved the energy resolution. The apparatus consists of a Pierce-type electron gun, a Seya Namioka monochromator, and a position-sensitive microchannelplate device for parallel detection of different photon energies and is described elsewhere.⁷ Standard techniques as Ar⁺ ion bombardment and annealing were employed to clean the Ni(111) single-crystal sample. The CO coverage of $\frac{1}{3}$ monolayer was controlled by measuring the work-function change which is a precise measure of the coverage via the current-voltage characteristic of the electron gun. The incident electron energy was chosen to 20 eV (relative to $E_F$) in order to avoid irreversible dissociation of CO on the surface, which has a threshold around 27 eV.⁸ The work-function change due to electron-stimulated desorption of molecular CO was less than 0.1 eV at a current density of 1 mA/cm² for $\frac{1}{2}$ h measurement time. After slight heating, the clean surface could be restored, indicating no dissociation of CO.

Figure 1 shows the experimental data for the clean (dashed line) and CO-covered (solid line) Ni(111) surface for various polar angles of the incident electron beam and three azimuthal orientations of the sample. The experimental geometry is sketched in the upper part of the left panel in Fig. 1. The indicated $p$ component of the electric-field vector (in the
plane of the drawing) is enhanced by a factor of 3 compared to the s component (perpendicular to the plane of drawing). The spectra for clean Ni are dominated by a peak just above $E_F$ arising from transitions into empty d states, which are quenched after CO exposure. Upon CO adsorption a broad peak centered $\sim 3$ eV above $E_F$ appears whose intensity increases with polar angle. We assign this peak to states derived from the lowest unoccupied $2\pi^*$ orbital of CO which are strongly broadened upon binding to the Ni substrate and pulled down from $\sim 1.5$ eV above the vacuum level in the gas phase\textsuperscript{10} to $\sim 3$ eV below the vacuum level in the chemisorbed phase.

This interpretation is supported by the observed angular dependence of the intensity of this adsorbate-induced feature: We note that the molecular $2\pi^*$ orbital of CO has mainly $p_u$ symmetry and that the CO molecule is bonded normal to the surface.\textsuperscript{1,2} Using the selection rules for photoemission from adsorbates given by Grimley,\textsuperscript{11} which apply also for the time-reversed process of inverse photoemission, we expect an intensity variation proportional to $\sin^2 \theta$ in qualitative agreement with the observed behavior. More refined theories incorporating bonding of the CO to the surface, electron wave-function matching, and multiple scattering of the electrons are not available to date, but we do not expect these refinements to change the simple molecular model qualitatively. In order to support our interpretation, we show that the observed adsorbate-induced structures cannot be satisfactorily explained by surface umklapp processes, wave-function matching, or secondary electron effects: Surface umklapp processes induced by the extra reciprocal lattice vectors of the ($\sqrt{3} \times \sqrt{3}$) $R$30° overlayer could fold Ni-derived states from other parts of the Brillouin zone onto the sampled points of $k$ space. In the energy range of $\sim 3$ eV above $E_F$ only Ni s,p bands exist such as the extra peak in the 48° spectrum of clean Ni in the right-hand column of Fig. 1. However, Ni s,p states have strong energy dispersion as one can see from the adjacent $\theta = 34°$, 60° spectra where the s,p band feature is missing. This excludes the explanation of the dispersionless CO-induced feature as induced by surface umklapp processes. The CO overlayer could change the coupling of the incoming free-electron wave to the Bloch wave functions of the sample, but the different wave-function matching can only enhance or suppress structures of the bulk bands—as seen for the Ni d bands—and not produce new peaks as seen in Fig. 1. The observed peak at 3 eV cannot be explained by secondary electron processes either, where electrons have lost part of their energy before making the radiative transition of the bremsstrahlung process. A well-pronounced structure could only be produced by a characteristic energy loss (e.g., a plasmon) which replicates the Ni d-band peak near the Fermi level. However, in the electron energy-
loss data of Rubloff and Freeoul there is no indication of a CO-induced characteristic energy loss around 3 eV. In addition, we would not expect to observe any angular dependence for structures produced by secondary electrons. Therefore, we are led to the conclusion that the adsorbate-induced peak at 3 eV is related to the empty 2π* orbital of the CO molecule, pulled down and broadened by the chemisorption bond to the Ni surface. The observed angular intensity dependence of this peak is consistent with the accepted vertical bonding geometry of CO on Ni(111).1,2

Having established the one-electron energy of the empty 2π* orbital of chemisorbed CO, we can get information about the electron-hole interaction in core-level transitions from the carbon 1s level. The energy for a bound-state transition from the carbon 1s core level into the 2π* orbital for CO on Ni(100) is 287.5 eV,3 and similar values are found for CO on Pt(111) (288 eV) (Ref. 12) and for gaseous CO (287.4 eV).13 In the gas phase the C 1s ionization potential is ~296.1 eV (relative to the vacuum level $E_{\text{vac}}$).13,14 and the energy of the 2π* orbital measured with resonance electron scattering is $E_{\text{vac}}$ +1.5 eV.10 These values give an electron-hole interaction of ~10 eV for gas-phase CO. Using the C 1s binding energy of 285.6 eV (relative to $E_F$) for CO on Ni (Refs. 15 and 16) and $E_F$ +3 eV for the energy of the 2π* orbital we estimate the electron-hole interaction for chemisorbed CO to ~1 eV. The mixing of the CO orbitals with the Ni states in the strong chemisorption bond allows for charge transfer from the metal to the adsorbate, so that the core hole on the adsorbate can be screened almost completely.

In Fig. 2, we summarize the available information on the one-electron energy of the 2π* orbital of free and bound CO. The solid curve is the average of the difference spectra for clean and CO-covered Ni(111) shown in Fig. 1 (except the spectra for $\theta = 48^\circ$ and $\phi = -90^\circ$). The broad peak due to the 2π* level 3 eV below the vacuum level is clearly seen. The attenuation of the Ni d states gives rise to a negative dip at ~6 eV below $E_{\text{vac}}$. This makes it impossible to determine, whether the 2π* states extend below the Fermi level and are partially filled due to backbonding as postulated by chemisorption theory15 and possibly observed with photoemission18 and electron emission induced by metastable helium atoms.19 Whereas bremsstrahlung spectroscopy is the only technique which can provide information about one-electron energies of states between the Fermi level and the vacuum level, states above the vacuum level can be measured also by other techniques such as resonance electron scattering. Figure 2 shows data taken with this technique for gas phase CO (Ref. 10) and physisorbed CO condensed on a polycrystalline Ag film,20 which put the 2π* level 1.5–2 eV above the vacuum level. It is clearly seen that with increasing bonding strength the CO 2π* level goes to lower energy and is broadened by the CO-CO or CO-Ni interaction, respectively. It would be interesting to extend the present study to weak chemisorption systems such as CO on Cu or to physisorbed CO in order to verify these trends and to see whether bremsstrahlung spectroscopy and resonance electron scattering yield the same information. Indeed, it appears that an electron-scattering study of CO chemisorbed on Pt(111) (Ref. 21) does not find a 2π* resonance above the vacuum level as we would expect.

In conclusion, we have used angle-resolved, polarization-dependent inverse photoemission to measure the energy and symmetry of the 2π*-derived states of CO on Ni(111). The determination of the one-electron energy of this level enabled us to estimate the electron-hole interaction in core-level spectroscopies, which is reduced to ~1 eV due to the screening of the metal electrons compared to the value of ~10 eV for gas phase CO. The observed trends of energy and width of the 2π* in going from the gas phase over physisorbed CO to strongly chemisorbed CO would make it desirable to study physisorption or weak chemisorption systems with uv bremsstrahlung spectroscopy.

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**FIG. 2.** Energy of the empty 2π* level for gas phase (dashed curve) and physisorbed (circles) CO measured with resonance electron scattering compared to strongly chemisorbed CO on Ni(111) measured with uv bremsstrahlung spectroscopy (average over all difference spectra from Fig. 1). Increasing bonding strength shifts the 2π* orbital to a lower energy and broadens it.


