We have determined the position of the lowest empty orbitals of CO and O chemisorbed on Ni(111) by using inverse photo-emission in the ultraviolet. The 2* orbital of CO is lowered by 4.5eV wide resonance centered 3.5eV above E_F in agreement with band calculations. This state disappears upon oxide formation.
Empty Orbitals of Adsorbates
Determined by Inverse UV-Photoemission

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Abstract: We have determined the position of the lowest empty orbitals of CO and O chemisorbed on Ni(111) by using inverse photo-emission in the ultraviolet. The 2\( \frac{1}{2}^+ \) orbital of CO is lowered by 4.5eV upon chemisorption and broadened to a 5.5eV wide resonance centered 3.5eV above \( E_F \). Chemisorbed oxygen has a sharp 2p state at 0.5eV above \( E_F \) in agreement with band calculations. This state disappears upon oxide formation.
It has been recognized for a long time that the electronic states of adsorbates play an essential role in surface chemical reactions including catalysis and corrosion. Occupied states have been studied extensively using mainly photoelectron spectroscopy. Very little is known about the empty states since the available probing techniques always create a hole when promoting an electron to an unoccupied state. This applies for optical spectroscopy, electron energy loss spectroscopy, appearance potential spectroscopy and partial yield photo-electron spectroscopy. The electron-hole interaction is a large perturbation to the one-electron energies in molecules. Inverse photoemission (or bremsstrahlung isochromat spectroscopy) avoids this complication by putting an extra electron into an empty state (see Fig. 1). The recent progress in extending this technique from the X-ray to the ultraviolet range opens prospects to observe electron states of adsorbates by increasing the surface sensitivity and reducing the electron-beam damage. Concurrent with experimental developments a theory of inverse photoemission has been developed which is analogous to the theory of photoemission.

We have used inverse photoemission with a tunable photon detector in the ultraviolet to determine the energy of empty adsorbate orbitals of CO and oxygen on Ni(111). There exist many theoretical and experimental studies of these adsorbate systems since they are often considered as models for catalysis and corrosion, respectively. For 1/3 monolayer CO on Ni(111) we find that the first empty $2\pi^*$ orbital lies about 2.5 eV below the vacuum level (pulled down from about 2 eV above the
vacuum level in the gas phase\(^{(19)}\). It is so strongly broadened (about 5.5eV full width half maximum) by interaction with the continuum of empty Ni4s,p states that the picture of a discrete orbital is not appropriate. For 1/4 mono-layer oxygen chemisorbed on Ni(111) sharp empty O2p states are found within 1eV of the Fermi level \(E_F\). Two layers of NiO formed by saturation exposure to oxygen exhibit a band of Ni4s,p states from 2 to 4eV above \(E_F\).

Figure 1 illustrates the measurement process. Our approach is somewhat different from previous setups\(^{(1-4)}\): We keep the incoming electron energy fixed and detect different photon energies. This corresponds to constant final state spectroscopy in photoemission. By taking spectra at different electron energies we rule out luminescence effects and are able to see cross section variations which help to identify the symmetry character of an orbital. The energy \(E\) of an empty state is determined relative to the Fermi level \(E_F\) which corresponds to the high energy cutoff of the photon spectrum. The experiments were performed in a triple-chamber vacuum system with a working pressure in the \(10^{-11}\) torr range. Electrons were produced by a pulse-heated tungsten filament at 1cm from the sample and the emerging bremsstrahlung photons were analysed by a Seya-monochromator (12Å band width) with a position sensitive detector. The work function change \(\Delta \phi\) of the sample upon gas adsorption was determined with \pm 0.05eV accuracy from the I(V) characteristic of the filament/sample diode. Since \(\Delta \phi\) is very sensitive to the coverage (\(\Delta \phi = +1.3eV\)\(^{(15)}\) for 1/2 layer CO and \(\Delta \phi = +0.5eV\)\(^{(18)}\) for 1/4 layer O) we could monitor surface contamination and e\(^{-}\)-beam damage effects
during data taking. During measurement no detectable work function change was found for clean Ni(111) and less that 0.2eV work function change for CO and O on Ni(111). The maximum e\textsuperscript{-}-beam dose was 200\mu A/cm\textsuperscript{2}\times30 min at about 20eV kinetic energy which is comparable to previous LEED (low energy electron diffraction) and Auger spectroscopy studies on these systems. As a further test for e\textsuperscript{-}-beam effects on CO/Ni(111) we desorbed CO thermally after data taking and obtained no remnants of cracked CO on the surface as judged by the inverse photoemission spectra and the work function.

Figure 2a shows spectra for clean and CO-covered Ni(111). Clean Ni(111) exhibits a sharp peak near E\textsubscript{F} due to the ~0.3eV-wide empty 3d-band and a continuum of 4s,p electrons and "secondary photons" produced by electrons which have created an electron-hole pair before falling into an empty 3d-state. Upon CO-adsorption the emission intensity increases over a wide range of photon energies which is seen in the difference spectrum in Fig. 3a. From our measured work function change \( \Delta \phi = +0.8eV \) we obtain a CO-coverage of 1/3 layer which corresponds to a \( \sqrt{3} \times \sqrt{3} \) superlattice (see Ref. 15). The lowest empty orbital of CO is an antibonding \( 2\pi^* \) \( (p_{x,y}-\text{symmetry}) \). In the gas phase it is found as a ~2eV wide resonance centered around 2eV above the vacuum level, i.e. the free CO-molecule has negative electron affinity. The highest occupied orbital \( (5\sigma) \) of free CO lies 14eV below the vacuum level. Note that the energy to promote an electron from \( 5\sigma \) to \( 2\pi^* \) is about 6-9eV\textsuperscript{(16,19)} which is only half as much as the difference in the one-electron energies of these orbitals. This discrepancy of
up to 8eV is due to electron-hole interaction and makes optical and energy loss spectroscopies inadequate for determining one-electron energies of empty molecular states. When CO is chemisorbed on a Ni surface the occupied orbitals exhibit well understood chemical and relaxation (image charge screening) shifts.\(^6\)\(^-\)\(^{13}\) The empty \(2\pi^*\)-orbital will be lowered by an eV or two due to a positive image charge but even stronger chemical effects could pull it partially below the Fermi level thus enabling "back donation" of negative charge (see Refs. 6, 17). Cluster calculations\(^9\),\(^10\),\(^12\),\(^13\) place the \(2\pi^*\) orbital of adsorbed CO at various energies between the Fermi level and the vacuum level. However, their accuracy is questionable because they place the \(2\pi^*\) orbital in free CO below the vacuum level resulting in a wrong sign for the electron affinity. Our finding of a very broad (~5.5eV full width half maximum) \(2\pi^*\) resonance for chemisorbed CO suggests that a delocalized band picture may be more appropriate than the description in terms of a discrete orbital of a cluster. This will influence the interpretation of charge transfer in chemisorption and surface chemical reactions.

In contrast to chemisorbed CO we find a sharp empty orbital for chemisorbed oxygen on Ni(111) as shown in Figs. 2b and 3b. For a work function change \(\Delta\phi = +0.6\) eV an ordered p(2\(\times\)2) structure is observed\(^{18}\). The empty orbital is centered at 0.5eV above \(E_F\) and is 0.6eV broader than the empty Nickel d-bands. Oxygen-induced states just above \(E_F\) have been predicted by a band calculation for a p(2\(\times\)2) oxygen layer on Ni(100) (Ref. 14). The calculation shows that the O2p states gain substantial Ni 3d\(z^2\)
character through bonding with Ni surface atoms. Little energy is needed to
transfer electrons from Ni to these empty O2p states, i.e., to form the more
ionic nickel oxide. Saturation oxygen exposure at room temperature is known
to form two layers of NiO on Ni(111) with a reversal in the work function
change (see Ref. 18 and references therein). The empty states of oxidized
Ni(111) are quite different from those for chemisorbed O (Fig. 2b). Extra
emission is seen between 2 and 4eV above EF which we assign to the Ni4s,p
bands according to cluster(20) and band(21) calculations. A previous inverse
photoemission study of NiO has come to a similar conclusion4. We find that
the Ni4s,p states increase their cross section rapidly with increasing photon
energy relative to the Ni3d and O2p states. Emission near EF is weak in NiO
since there are no more empty O2p states. Remaining emission above EF can
be assigned to the two empty 3d-states of NiO. These d-states are related to
the particular properties of NiO as antiferromagnet and Mott-insulator.

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Figure Captions:

Fig. 1: Schematic description of inverse photoemission. The work function $\phi$ is 5.2eV for clean Ni(111).

Fig. 2: Inverse photoemission spectra for adsorbates on Ni(111). (a) 1/3 monolayer CO/Ni(111) and clean Ni(111), (b) 1/4 monolayer chemisorbed O, clean Ni(111), and the saturation coverage of two layers NiO (dots). The kinetic energy of the incident electrons was 26eV and 18eV for curves (a) and (b), respectively.

Fig. 3: Difference spectra (covered minus clean) for adsorbates on Ni(111). For 1/3 monolayer CO a broad resonance is seen due to the CO 2π* orbital hybridized with the Ni 4s,p bands. For 1/4 monolayer Oxygen sharp empty O2p states exist near $E_F$. 
INVERSE PHOTOEMISSION

ELECTRON ENERGY (eV)

\[ E^F = 0 \]

\[ \phi \]

\[ 10 \]

\[ 20 \]

\[ 30 \]

\[ 40 \]

\[ \text{EMPTY STATE} \]

\[ \text{EMITTED PHOTON} \]

\[ \text{INCIDENT ELECTRON} \]

\[ e^- \]
INVERSE PHOTOEMISSION SPECTRA

(a) + 6 L CO; ΔΦ = 0.8 eV

(b) + 100 L O₂; ΔΦ = 0.0 eV

+ 1.5 L O₂; ΔΦ = 0.6 eV

clean Ni (111)

PHOTONS PER INCIDENT ELECTRON

ENERGY OF EMPTY STATE (eV relative to E₀)
DIFFERENCE SPECTRA

(a) Ni (111) + 6 L CO
   \( \Delta \phi = 0.8 \text{ eV} \)

(b) Ni (111) + 1.5 L O\(_2\)
   \( \frac{1}{4} \) Monolayer
   \( \Delta \phi = 0.6 \text{ eV} \)

ARBITRARY UNITS

ENERGY OF EMPTY STATE (eV relative to \( E_F \))