Photoemission Studies of Inorganic (CO, O, NO) and Organic (C_2H_2, C_2H_4, C_6H_6) Adsorbates on Ni(111) and Surface Reactions

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Photoemission Studies of Inorganic (CO, O, NO) and Organic (C₂H₂, C₂H₄, C₆H₆) Adsorbates on Ni(111) and Surface Reactions*

D. E. EASTMAN and J. E. DEMUTH

IBM Thomas J. Watson Research Center
Yorktown Heights, New York 10598

We describe adsorption studies of serveral inorganic and organic species on single crystal Ni(111) using ultraviolet photoemission spectroscopy ($hv = 21.2$ eV). Adsorbate orbital ionization energies and line shapes have been measured and surface reactions have been studied. Ionization energies for chemisorbed unsaturated hydrocarbons (C_2H_2, C_2H_4, and C_6H_6) exhibit large surface-induced relaxation shifts (~ 1–3 eV) relative to their gas phase counterparts as well as π-orbital bonding shifts (~ 0.9–1.5 eV). We estimate these π-d bonding interaction strengths and chemisorption energies using Mulliken's donor-acceptor theory as described by Grimley for weak chemical bonds and show that an observed surface reaction, i.e. the dehydrogenation of chemisorbed ethylene (C_2H_4) to chemisorbed acetylene (C_2H_2) for $T \gtrsim 230$ K, becomes exothermic only for the chemisorbed species due to the π-d electron interaction.

§1. Introduction

A powerful approach to study the interaction of atoms or molecules with surfaces is via their valence electronic structure. One rapidly developing technique for probing the electronic structure of the surface is ultraviolet photoemission spectroscopy.[1-15] High intensity ultraviolet resonance lamps of He (21.2 and 40.8 eV) and Ne (16.8 eV) which excite electrons over a wide range (≥ 15 eV) of valence orbital energies and from within about 2–6 layers of the surface (i.e. high surface sensitivity) are particular useful for such studies.

Here, we present photoemission orbital energy spectra for several inorganic adsorbate systems, i.e. chemisorbed CO, O and NO on Ni (111), as well as for several organic adsorbate systems, i.e. chemisorbed and condensed (weakly bound) acetylene (C₂H₂), ethylene (C₂H₄) and benzene (C₆H₆) on Ni(111). These photoemission spectra permit the chemical state of the adsorbate to be readily determined and can be used to study surface reactions.

Adsorbate energy levels for both chemisorbed and condensed species are observed to be shifted in energy (and sometimes broadened) relative to their gas phase levels. These shifts are due both to surface-induced nonbonding relaxa-

tion effects (*e.g.* final-state image charge screening) as well as to chemical bonding effects. Adsorbed unsaturated hydrocarbons present us with an example where these relaxation and bonding shifts can be separated due to a wealth of both bonding and non-chemical-bonding orbitals that can be measured.[15] For these adsorbates we observed that bonding occurs via π-d orbital interactions. We have made estimates of π-d interaction strengths and chemisorption energies for chemisorbed C₂H₂, C₂H₄ and C₆H₆ on Ni (111) using Mulliken's theory[16] of donor-acceptor complexes as applied by Grimley[17] to the case of weak chemisorption.

An understanding of orbital energy shifts for chemisorbed CO, O and NO on Ni is complicated by non-negligible surface-induced relaxation shifts (*e.g.* corrections to Koopman's theorem) which are difficult to determine and are not involved in chemical bonding. Such relaxation effects have been previously studied for He autoionization processes,[18] for core levels,[19] and for implanted rare gases.[20] We discuss the relation of experimental orbital energies to several models of chemisorption.

§2. Experimental Procedures

Photoemission energy distributions were measured using a three-grid LEED optics system as a retarding field analyzer with a differentially pumped He resonance lamp mounted

nearly perpendicular to the axis of the LEED optics. Typical photocurrents were ~ 8nA (total) for Ni and signal to noise ratios of $\sim 120{:}1$ were obtained using synchronous detection with a 1 sec time constant. A single crystal Ni sample was oriented to the [111] plane within $\pm 1/4°$, cut into slabs $(5 \times 15 \times 0.5$ mm), and polished. Sample temperatures between 100 K and 1600 K could be achieved by liquid nitrogen cooling or resistive heating of the sample. Ion-bombardment, oxygen exposure and heat treatments were used to clean the sample in a fashion identical to those previously described.[21] "In situ" characterization of surface cleanliness was preformed via Auger spectroscopy while surface order and periodicity were examined via LEED. The single crystal (111) nickel sample was established to be a well-ordered (111) surface virtually free of surface contaminants (primarily carbon and sulfur).

The organic (O, CO and NO) and inorganic gases (C_2H_6, C_2H_4, C_2H_2, C_3H_8 and C_4H_{10}) used in this adsorption study were high purity ($>99.9\%$) reagent grade gases. Vapors of benzene and cyclohexane were obtained by vacuum distillation from reagent grade liquids. For both organic and inorganic gases, final analysis in the UHV system with the mass spectrometer confirmed their purity. We also observed that prolonged exposures (principally at higher pressures $\sim 10^{-7}$ Torr) substantially increased H_2, CO and CO_2 background pressures, particularly for the hydrocarbons.

§3. Results

3.1 Chemisorbed inorganics

Photoemission energy distributions $N(E)$ for clean Ni(111) and for Ni(111) after exposure to 1.2×10^{-6} Torr-sec of CO (work function change $\Delta\phi = +0.6$ eV) are shown in Fig. 1a. In order to enhance adsorbate-induced features, it is useful to plot the adsorbate-induced change in emission $\Delta N(E)$, or difference curves, for chemisorbed CO as shown in Fig. 1b. Here the dashed "background" baseline estimates the contributions to $\Delta N(E)$ due to the attenuation of Ni d-band emission and increased inelastic secondary electron emission at low kinetic energies. We observe two CO-derived orbital levels, with a large asymmetric peak at 7.6 eV (IP = 13.6 eV) and a smaller peak at 10.7 eV
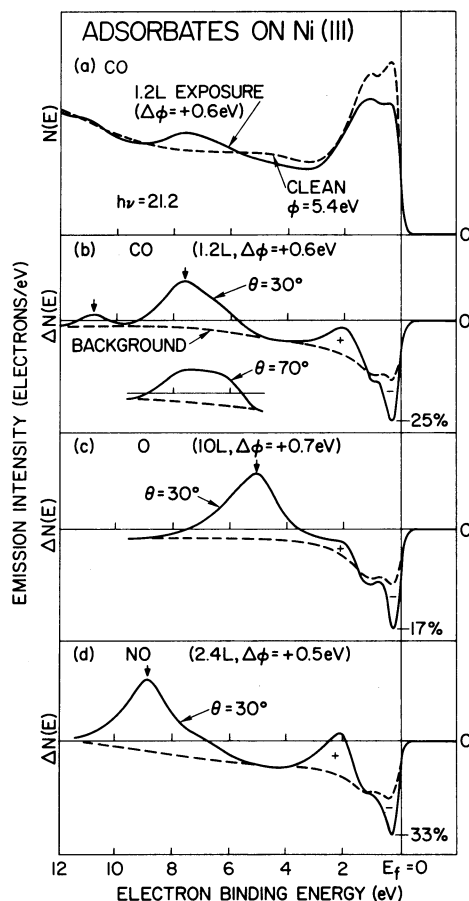

Fig. 1. (a) Photoemission spectra $N(E)$ for Ni(111) and after 1.2×10^{-6} Torr-sec exposure to CO at $T \sim 300$ K. Adsorbate induced difference in emission, $\Delta N(E)$, from the clean surface for (b) CO, (c) O, and (d) NO. The standard experimental configuration has the photon beam incident at an angle $\theta = 30°$ from the surface. For CO we observe an angular-dependent spectral shape as shown in (b).

(IP = 16.7 eV), which have been associated with the $5\sigma(\sigma 2p)$ and $1\pi(\pi 2p)$ orbitals of CO, respectively.[1] (The electron binding energies E_i used here are referred to the Fermi level and are related to ionization potentials (IP's) by IP = $E_i + \phi_{Ni} + \Delta\phi_{adsorbate}$). These CO levels are very similar to those previously seen for chemisorbed CO on Ni(100) and on polycrystalline Ni.[1,10] The difference curve $\Delta N(E)$ in Fig. 1b also shows a large asymmetric attenuation of d-band emission within ~ 2–3eV of the Fermi level E_F. This asymmetry, i.e. large attenuation of the 0.3eV peak and small attenuation near 2eV, is often seen for chemisorbed species on Ni and might be associated with adsorbate-induced

changes in surface *d*-orbitals.

The adsorbate-induced difference curve $\Delta N(E)$ for chemisorbed O (10×10^{-6} Torr-sec exposure to O_2, $\Delta\phi = +0.7$ eV) on Ni(111) is shown in Fig. 1c. In addition to attenuated *d*-band emission within $\sim$2–3 eV of E_F, we observe an O-derived level about 2eV wide centered at 5.3 eV (IP = 11.4 eV). This O-derived level for chemisorbed O on Ni(111) is quite similar to that previously reported for chemisorbed O on polycrystalline Ni (i.e. 5.5eV).[1]

The adsorbate-induced difference curve $\Delta N(E)$ for chemisorbed NO (1×10^{-6} Torr-sec exposure to NO, $\Delta\phi = +0.5$eV) on Ni(111) is shown in Fig. 1d. A broad asymmetric band of NO derived levels extending from binding energies of 6eV to 10eV with a peak at 8.8eV (IP = 14.7eV) is observed. We associate these NO-derived levels with the complex set of $\pi_u 2p$ and $\sigma_g 2p$ bands having IP's between 15.7 and $\sim$19.5 eV for gaseous NO (see ref. 22, p. 39) NO is more reactive than CO due to the presence of a single unpaired $\pi_g 2p$ electron (9.7 eV vertical IP). We do not observe this $\pi_g 2p$ level for chemisorbed NO on Ni(111). If unperturbed, this $\pi_g 2p$ level would lie just below the *d*-bands. However, we expect this orbital to be strongly involved in the chemisorption bond and as a result become degenerate in energy and strongly admixed with the Ni *d*-levels. This $\pi_g 2p - d$ level admixing could be responsible, at least in part for the strongly enhanced emission near $\sim$2eV in the *d*-band region.

For chemisorbed CO on Ni(111) the 7.6eV level is quite asymmetric in shape. A similar asymmetry is present in previous measurements for chemisorbed CO on Ni(100)[1,10] and polycrystalline Ni but has not been discussed experimentally. Penn[13] has discussed peak asymmetries, and has pointed out that an orbital peak as observed by photoemission spectroscopy can be shifted in position and rendered asymmetric by an interference between bulk and surface photoemission. Such an interference effect is not responsible for the observed asymmetry, as will be shown.

We have performed crude angular-dependent measurements for this CO-derived level which contribute additional information to this line shape question. Angular-dependent photoemission difference curves $\Delta N(E)$ for this CO-derived level are also shown in Fig. 1b.

Here $\theta = 30°$ is the grazing angle of incidence of photons, and electrons are analyzed predominantly at normal angles. With $\theta = 70°$, electrons are analyzed more predominantly at grazing angles. We observe that there are at least two structures in this orbital level (near 6.2 and 7.6 eV), with relative amplitudes that depend on the angle θ. One possible explanation is that there are two structural phases of chemisorbed CO on Ni(111).[24] Under our experimental conditions there exists no evidence to support this possibility.

Note added in proof—Recently we (in collaboration with J. L. Freeouf, E. W. Plummer and T. Gustafsson) have used synchrotron radiation to measure chemisorbed CO on Ni and find that the 6.2 eV and 7.5 eV structures are associated with the $5\sigma(\sigma 2p)$ and $1\pi(\pi 2p)$ levels, respectively, while the lower-lying 10.7 eV is associated with the $4\sigma(\sigma 2s)$ CO level, with all levels being shifted upwards by $\sim$3 eV relative to the gas phase due to relaxation effects. Thus previous assignments of the CO levels on Ni have been incorrect.

3.2 Adsorbed hydrocarbons

An interesting class of adsorbate systems are hydrocarbons adsorbed on group VIII metals (*e.g.* Ni, Pd, Pt). We present photoemission orbital energy levels for condensed (weakly bound) and chemisorbed phases of several simple unsaturated hydrocarbons (C_2H_2, C_2H_4, C_6H_6) adsorbed on Ni(111). These molecular adsorbate spectra are illuminating in that several π- and σ- orbital energies can be measured with 21.2eV photons and used to distinguish non-bonding π- and σ- orbital relaxation shifts and π-orbital bonding shifts.

Photoemission energy distributions $N(E)$ for clean Ni(111) and for Ni(111) after exposure to 2.4×10^{-6} Torr-sec of benzene (C_6H_6) are shown in Fig. 2a. We estimate that this exposure (work function change $\Delta\phi = -1.4$eV) results in a benzene coverage of $\sim$1/2 to 1 monolayer, i.e. 1/4 to 1/3 C_6H_6 molecule per surface Ni atom. The adsorbate-induced change in emission $\Delta N(E)$, or difference curve, for chemisorbed C_6H_6 is shown in Fig. 2b. The difference curve for several layers of weakly bound C_6H_6 condensed on top of the chemisorbed layer at $T \simeq 150$ K is shown in Fig. 2c. A useful reference is the spectra for gaseous C_6H_6 (Fig. 2d), which
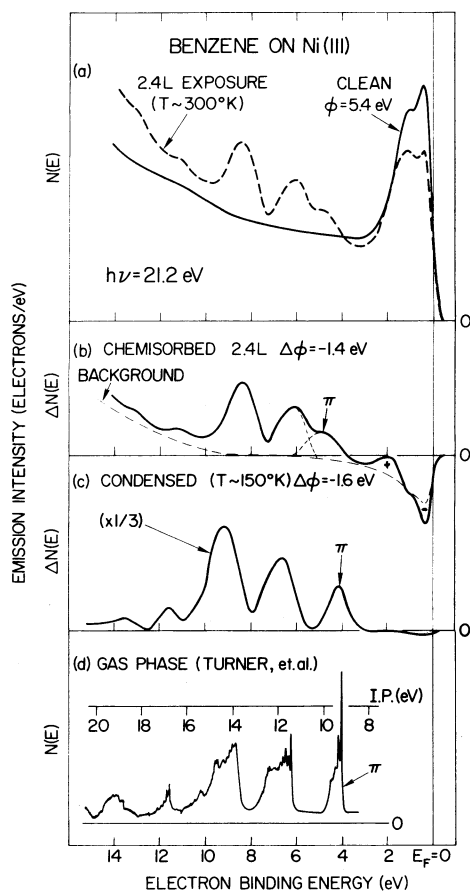
Fig. 2. (a) Photoemission spectra $N(E)$ for Ni(111) and with 2.4×10^{-6} Torr-seconds benzene exposure at $T \sim 300$ K, (b) adsorbate induced difference in emission, $\Delta N(E)$, from the clean surface for chemisorbed benzene, (c) $\Delta N(E)$ for a condensed benzene layer formed at $T \sim 150$ K with a benzene pressure of 2×10^{-7} Torr, (d) gas phase photoelectron spectra for benzene (ref. 22). Note that ionization energies ε_i (vacuum level reference) are given by $\varepsilon_i = E_i$ (binding energy) $+ \phi(Ni) + \Delta\phi$.

has been used to identify various π- and σ-orbital levels,[22] π-levels: vertical (center-of-gravity) IP $\simeq 9.4$ (2-fold degenerate) and 11.5 eV; σ-levels: vertical IP $\simeq 11.8$, 12.2, 13.9, 14.2, 14.8, 15.4, 16.9 and 19.2 eV). Orbital ionization potentials for chemisorbed and condensed C_6H_6 are summarized in Fig. 3.

We observe that weakly bound condensed C_6H_6 and gaseous C_6H_6 are closely related in that all orbital energies and relative intensities are essentially unchanged, except that the magnitude of all ionization potentials measured relative to the vacuum level are reduced by a "relaxation" shift $\Delta\varepsilon^R \simeq 1.4$ eV. Such overall relaxation shifts, which include final-state
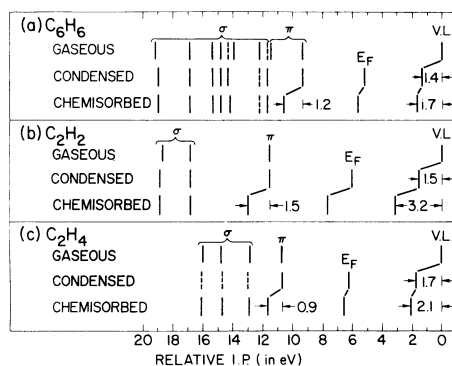

Fig. 3. Vertical ionization energies, Fermi (E_F) and vacuum levels (VL) for the gaseous,[22] condensed and chemisorbed phases of (a) benzene (b)acetylene and (c) ethylene, all plotted relative to σ-orbital gas phase levels. Relaxation shifts are given by the vacuum level shifts while bonding shifts are given for relevant π-orbital shifts. The dotted levels represent less certain orbital ionization energies.

image charge screening[20] as well as initial or final state changes associated with molecular polarization[18] and charge transfer from the molecule, have little to do with chemical bonding. In comparing chemisorbed C_6H_6 with condensed C_6H_6, we again observe that the binding energies of all lower-lying σ-orbitals are further reduced (a total relaxation shift from the gas phase IP's of 1.7 eV) while the binding energy of the uppermost two degenerate π-orbitals (9.4eV in the gas phase) is increased. We associate the latter shift with π-d chemical bonding. Emission features in the d-band region are also modified by chemisorbed C_6H_6, with relatively enhanced ($+$) emission near 2.5eV and relatively dimished ($-$) emission near E_F superimposed on an overall attenuation of d-band emission. This "downward" shift in d-band emission could be due to π-d bonding effects on the surface d-orbitals.

In general we have observed that the unsaturated hydrocarbons (C_2H_2, C_2H_4 and C_6H_6) exhibit such π-orbital bonding shifts as summarized in Fig. 3 while saturated hydrocarbons (C_2H_6, C_3H_8, C_4H_{10} and C_6H_{12}), which lack π-orbitals, only weakly adsorb ("physisorb") and show only relaxation shifts $\Delta\varepsilon^R$ of all orbitals such as seen for condensed C_6H_6.

Acetylene (C_2H_2) and ethylene (C_2H_4), which are the simplest hydrocarbons containing a triple and double carbon-carbon bond, respectively, exhibit the same general behavior as
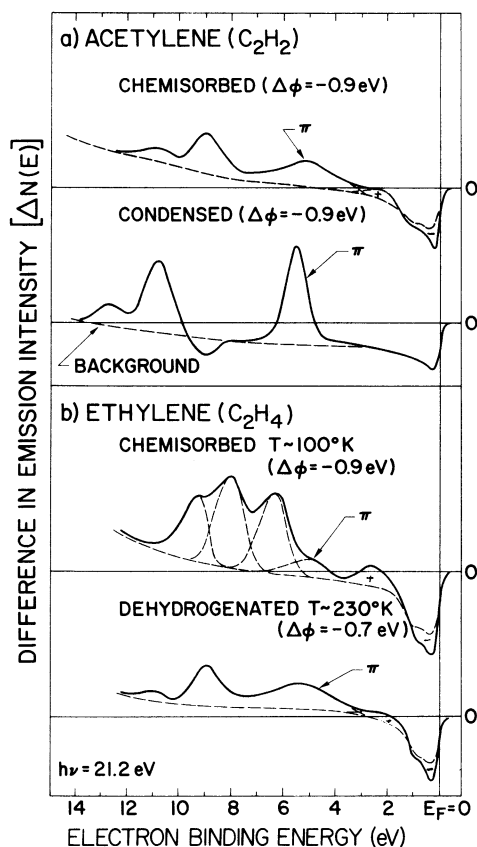
Fig. 4. (a) Difference in emission $\Delta N(E)$ for 1.2×10^{-6} Torr-seconds exposure to acetylene at $T \sim 300$ K (or at $T \sim 100$ K) and for condensed acetylene formed at $T \sim 100$ K with acetylene pressures of 6×10^{-8} Torr. (b) $\Delta N(E)$ for chemisorbed ethylene (exposure of 1.2×10^{-6} Torr-seconds at $T \sim 100$ K and for dehydrogenated ethylene (obtained by warming to $T \sim 230$ K or with an initial exposure at $T \sim 300$ K).

C_6H_6. In Fig. 4, we show adsorbate-induced difference curves $\Delta N(E)$ for chemisorbed and condensed C_2H_2 and for chemisorbed C_2H_4 on Ni(111). Vertical (non-adiabatic) ionization potentials for gaseous, condensed and chemisorbed C_2H_2 and C_2H_4 are also summarized in Fig. 3. Here we have plotted all energy levels relative to the σ-orbital levels of the gaseous species in order to illustrate the downward bonding shifts $\Delta \varepsilon^b$ of the uppermost π-levels, and the overall non-bonding relaxation shifts $\Delta \varepsilon^R$ for all levels. Exposures and work function changes are given Fig. 4. A (2×2) LEED Pattern was observed for either chemisorbed C_2H_2 or C_2H_4, but the exact coverages were not determined (estimated at $\sim 1/4$ to $1/2$ molecule per surface Ni atom).

In order to chemisorb C_2H_4 and prevent spontaneous dehydrogenation to an acetylenic species, low substrate temperature ($\lesssim 175$–200 K) must be used. Upon warming to higher temperatures $T \gtrsim 230$ K, we observed that a surface reaction occurs, i.e. chemisorbed $C_2H_4 \rightarrow$ chemisorbed $C_2H_2 + H_2$ (gas). The occurrence of this surface reaction is clearly seen in Fig. 4 by comparing $\Delta N(E)$ in Fig. 4b for C_2H_4 warmed to 230 K (i.e. dehydrogenated C_2H_4) with the difference curve for chemisorbed C_2H_2 in Fig. 4a. The two spectra are identical, both in their π-orbital level (5.1 eV) and σ-orbital levels (9.1 eV and 11.0eV). It should be noted that this reaction did not appear to be photo-activated. An identical acetylenic species is also obtained by adsorbing ethylene on Ni(111) at $T \sim 300$ K. Chemisorbed C_2H_2 and C_6H_6 on Ni(111) are stable for $T \lesssim 470$ K, above which they completely dehydrogenate and form carbonaceous species. Also, we do not observe any other intermediate species, *e.g.* acetylene, during benzene decomposition.

§4. Discussion

4.1 *Surface reactions*

Knowledge of the chemical state of surface complexes is essential for many surface studies and has been the subject of much work. We have shown for several inorganic and hydrocarbon adsorbates on Ni that ultraviolet photoemission spectroscopy can give a direct unambiguous "picture", or "fingerprint", of the chemical state of the surface adsorbate. For example, we directly observe that at room temperatures CO and NO are adsorbed in a molecular state while oxygen is adsorbed in an atomic state (adsorbed molecular O_2 would have several observable orbital levels, which are not seen). Thus, various surface reactions can be monitored, such as the examples we have presented for $C_2H_4 \rightarrow C_2H_2 + H_2$ (gas) on Ni(111).

Adsorbed hydrocarbons present a particularly interesting and complex problem since many possible chemical states can exist due to hydrogenation, dehydrogenation, dimerization, etc. For example, the chemical state of C_2H_4 after adsorption on Ni has been controversial. Namely, acetylenic species for C_2H_4 adsorbed on polycrystalline Ni films at 300 K have been reported in kinetic and volumetric studies[25] while more recent infrared spectroscopy

studies[26,27] of C_2H_4 adsorbed on silica-supported polycrystalline Ni films at ~ 300 K have not identified a chemisorbed acetylenic species. For single crystal Ni(111), we observe a total conversion of chemisorbed C_2H_4 to a chemisorbed acetylenic species for temperatures $\sim 200 \lesssim T \lesssim 470$ K. Also, infrared spectroscopy studies[27] conclude that chemical bonding of C_2H_4 occurs via $\sigma\text{-}d$ bonding, in contrast with our observed $\pi\text{-}d$ bonding. There are of course difficulties in comparing with such infrared surface studies since the dissimilar substrates, exposure conditions and other experimental conditions could lead to different surface reactions.

From the close similarity of the ionization levels of chemisorbed benzene with those of gaseous and condensed benzene, the structural nature of the benzene molecule is obviously preserved in all states. Thus, opening of the benzene ring does not occur as has been suggested in previous flash desorption measurements on Ni(111).[28] Whether the aromatic character of benzene is lost upon adsorption as previously suggested[28,29] cannot be definitively answered from this work, however the small chemisorption-induced π-orbital modification that we observe argues for preservation of this aromatic character.

4.2 Screening effects, chemisorption bonding and chemisorption energies for hydrocarbon adsorbates

We now discuss observed photoemission ionization potentials for chemisorbed species in light of several recent theoretical treatments. Such discussions are difficult and tenuous because, as has been recently noted,[30] even in the simplest adsorbate systems current theoretical treatments are at best semiquantitative with many basic questions remaining to be answered.

One important message which is clearly illustrated by our results for chemisorbed hydrocarbons on Ni(111) is that there are important relaxation corrections to Koopman's theorem which must be considered when comparing measured ionization potentials with calculated adsorbate orbital energies.[15] Relaxation effects such as we have described for adsorbed hydrocarbons are likely to be important for all adsorbates although conceivably less important when "strongly bonded" (bulk-like) surface compounds are formed.

As summarized in Fig. 3, for a given hydrocarbon in either a condensed or chemisorbed state, all σ-levels experience the same reduction $\Delta\varepsilon^R$ in ionization energy (measured relative to the vacuum level of the gas phase), i.e. each set of σ-levels has the same relaxation shift $\Delta\varepsilon^R$. From this observation, we conclude that $\Delta\varepsilon^R$ has little to do with chemisorption bonding. For these chemisorbed species, we assume to first order that relaxation shifts of σ- and π-orbitals are equal $(\Delta\varepsilon_\pi^R = \Delta\varepsilon_\sigma^R)$. This tentative assumption is based on the observation that (a) the relaxation shifts of both π- and various σ-orbitals are seen to be identical for the condensed species, (b) that the chemisorption bonding is observed to be a weak perturbation on the molecule (the molecular configuration is virtually unaltered by this bonding) and (c) these species appear to adsorb in a planar configuration, i.e. lie parallel to the surface. (This assumption for $\Delta\varepsilon^R$ is of course not a general one). In the chemisorbed phase, uppermost π-orbitals are observed to have an additional increase $\Delta\varepsilon^b$ in ionization energy due to $\pi\text{-}d$ bonding. Thus to first order, the observed ionization levels ε_i for the chemisorbed hydrocarbons are related to their gas phase counterparts ε_i^g as follows:

$$\varepsilon_\sigma = \varepsilon_\sigma^g - \Delta\varepsilon^R$$

$$\varepsilon_\pi = \varepsilon_\pi^g - \Delta\varepsilon^R + \Delta\varepsilon^b$$

where $\Delta\varepsilon^R$ is the vacuum level shift for nonbonding σ-orbitals and $\Delta\varepsilon^b$ is the π-level bonding shift. These levels and level shifts are summarized for C_6H_6, C_2H_2 and C_2H_4 in Table I.

Table I. Summary of chemisorption information for C_6H_6, C_2H_2 and C_2H_4 on Ni(111).

	C_6H_6	C_2H_2	C_2H_4
$\varepsilon_d(a)$	7.1	7.1	7.1
$\varepsilon_F(a)$	5.4	5.4	5.4
$\varepsilon_\pi^g = I(a, b)$	9.2	11.6	10.7
$\varepsilon_{\pi^*} = A(a)$	0.5	~ 0.5	~ 0.5
$\Delta\varepsilon^R$	1.7	3.2	2.1
$\Delta\varepsilon^b$	1.2	1.5	0.9
$N_\pi = N_{\pi^*}$	4	4	2
$\langle n_\pi \rangle$	0.98	0.98	0.96
V(in eV)	1.6	2.6	1.8
$-\Delta E^c$(in eV)	1.7	4.2	1.0

a) All level positions are referred to the vacuum level (in eV).

b) π-ionization levels exclusive of bonding and relaxation effects, i.e. gas phase π-levels (ref. 22).

We now make spectroscopic estimates of π-d bonding strengths and chemisorption bond energies in terms of $\Delta\varepsilon^b$, etc, based on Mulliken's[16] theory of donor-acceptor complexes as applied by Grimley[17] to weak chemisorption bonds. A perturbation theory approach appears to be valid to first order since we observe that (a) the molecular nature of a chemisorbed hydrocarbon is essentially preserved, (b) orbital energy shifts are small ($\Delta\varepsilon^b \ll I$ and I-ε_d, where I is the ionization potential and ε_d the center of the filled d-band), and (c) based on observed work function changes, orbital occupancies $\langle n \rangle$ are only slightly changed, e.g. $\langle n_\pi \rangle$ is reduced from 1.0 to $\sim$0.96 to 0.98 for C_6H_6, C_2H_2 and C_2H_4* (see Table I).

As described by Grimley[16] in his application to chemisorbed CO on Ni, an approximate wave function for the system is given by superimposing the unperturbed wave function of the "no-bond" state (M, Ni), where M denotes molecule, and the unperturbed wave functions for the lowest-order excited "charge-transfer" states (M$^-$, Ni$^+$) and (M$^+$, Ni$^-$). In the simplest approximation, we have the unperturbed orbital ionization energies $\varepsilon_\pi = I$ and $\varepsilon_\pi^* = A$ (affinity level) for M($|\pi^n\rangle$)$\rightarrow$M$^+$($|\pi^{n-1}\rangle$) and for M$^-$($|\pi^n\pi^*\rangle$)$\rightarrow$M($|\pi^n\rangle$) respectively, the unperturbed energies ε_d and ε_F (Fermi level) for the filled and empty d- states of Ni, and a π-d perturbation interaction V between each π-electron all ten d-states. For simplicity, we assume the same V for ground state π-electrons and excited state π^*-electrons.

Applying such a model to our case of chemisorbed hydrocarbons, the interaction strength V can be written in terms of spectroscopically observable energy levels and the bonding shift $\Delta\varepsilon^b$:

$$V^2 \simeq \Delta\varepsilon^b |\varepsilon_\pi - \varepsilon_d|$$

where we have neglected second-order terms in $\Delta\varepsilon^b$. The π-d interaction V causes the molecular ground state π-level to be shifted downwards in energy by $\Delta\varepsilon^b$ (π-d repulsion) while the d-state

energies are essentially unchanged due to the symmetric π-d and π^*-d interactions. Grimley[17] has evaluated the chemisorption energy ΔE^c, or heat of adsorption, for such a model, and application to our case yields

$$-\Delta E^c = V^2(N_{\pi^*}N_d/|\varepsilon_d - \varepsilon_{\pi^*}^g| + N_\pi(1 - N_d)/|\varepsilon_\pi^g - \varepsilon_F|)$$

where N_π and N_{π^*} are the number of π and π^* electrons per molecule and N_d is the fraction of filled d-states. The first term in ΔE^c corresponds to the (π^{*-}, Ni$^+$) contribution and is predominant because the surface d-bands are nearly full ($N_d \simeq 0.9$).

We have evaluated the interaction strengths V and chemisorption energies ΔE^c using the above expressions with our observed bonding shifts $\Delta\varepsilon^b$ and energy levels (where we have taken account of relaxation effects) and obtain $V = 1.6$, 2.6 and 1.8 eV and $-\Delta E^c = 1.7$, 4.2 and 1.0 eV per molecule for C_6H_6, C_2H_2 and C_2H_4 respectively (see Table I). Unfortunately, we have been unable to find relevant thermochemical measurements of ΔE^c to compare with our spectroscopic estimates. ($-\Delta E^c$ for C_2H_2 adsorbed on a polycrystalline Ni film is $\sim$3 eV[31]). We expect that these calculated values for V and ΔE^c tend to overestimate the interaction strength and chemisorption energy due to neglect of correlation effects (both inter- and intra-molecular) and overlap of the π- and d-wave functions.[32]

Changes in orbital occupancies found using the above model are small ($\lesssim 10\%$), consistent with our use of perturbation theory. However, these changes correspond to an increase in work function ($\langle n_\pi \rangle + \langle n_\pi^* \rangle$ slightly larger than unity), while a decrease in work function is observed. While this could indicate that this model is wrong, we believe this behavior signifies that the surface dipole determined from the orbital occupancies in such simple models cannot be meaningfully compared to experimental work function changes. Charge redistribution in the real system can occur through occupancy changes as well as spatial modification of the ground state wave functions due to the interaction. The latter are neglected in such simple models.

The dehydrogenation of chemisorbed C_2H_4 to chemisorbed C_2H_2 on Ni(111) plus H_2(gas) for $T \gtrsim 230$ K is consistent with our spectro-

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* The orbital occupancy changes are based on the charge transfer associated with the surface dipole where the number of dipoles/cm^2 is based on a 2×2 LEED pattern (observed), the dielectric constant $\varepsilon = 1$, and the dipole distance $d = 1.5$Å. These numbers are only approximate since exact coverages are not known, in addition to uncertainties in distance d, etc.

scopically determined chemisorption energies ΔE^c. In the gas phase, this reaction is unfavorable, that is, endothermic with a heat of reaction $\Delta H_r^g = +1.8$ eV/molecule (41.9 kcal/mole)[33]) and an activation energy at least as large as ΔH_r^g. For the chemisorbed phase, we predict that the heat of reaction for the dehydrogenation of chemisorbed C_2H_4 to chemisorbed C_2H_2 plus H_2(gas) is $\Delta H_r^c = \Delta H_r^g - \Delta E^c(C_2H_4) + \Delta E^c(C_2H_2) = -1.4$ eV/molecule. That is, we predict an exothermic surface reaction, which we observe to be easily activated at ~ 230 K.

4.3 Chemisorbed CO, O and NO on Ni(111).

Any description of photoionization orbital energies for chemisorbed CO, O or NO on Ni in terms of theoretical models is complicated by relaxation shifts $\Delta \varepsilon^R$. Because only one or two orbital energies can be determined using 21.2 eV photons, the shifts in these orbitals due to nonbonding relaxation shifts cannot be easily determined. As we have seen for adsorbed hydrocarbons, these shifts can be comparable to chemical bonding shifts $\Delta \varepsilon^b$. Thus, while definitive interpretations of photoemission orbital energy shifts (e.g. predicted chemisorption energies) cannot yet be made for these adsorbates, some insight can be gained by discussing them in terms of existing theoretical models.

Of the inorganic adsorbates we have studied, molecularly adsorbed CO is weakly bound (chemisorption energy $\Delta E^c \simeq -1.8$ eV/molecule[35]), and is the simplest to theoretically consider. This case has been discussed by Grimley using both Mulliken's theory[16] as well as a surface compound approach.[17] Grimley considered orbital interaction strengths and orbital occupancies and their relation to the chemisorption energy based on available thermochemical data.[34] Molecular CO has a $5\sigma(\sigma 2p)$ donor level (vertical IP $= 14.1$ eV), a $1\pi(\pi 2p)$ level (IP $= 16.9$ eV) a $4\sigma(\sigma 2s)$ level (IP $= 19.8$ eV) and a $2\pi(\pi 2p)$ acceptor level (affinity level ~ 0 eV). Grimley estimated σ-d and π-d interaction strengths of $V_{5\sigma} = 2.7$ eV and $V_{2\pi} = 1.6$ eV for the donor and acceptor levels, respectively. Using Mulliken's theory, he then calculated a chemisorption energy in good agreement with experiment.

As a test of this model, we have calculated bonding shifts for the $5\sigma(\sigma 2p)$ and $1\pi(\pi 2p)$ levels

Table II. Data for chemisorbed CO, NO and O on Ni (111).

CO on Ni (111)	NO on Ni (111)	O on Ni (111)
$\varepsilon_{5\sigma}^g = 14.1$ eV[a]	$\varepsilon_m^g \simeq 17.5$[a]	$\varepsilon_{2p}^g = 13.55$[a]
$\varepsilon_{1\pi}^g = 16.9$	$\varepsilon_m(\text{Ni}) \simeq 14.7$	$\varepsilon_{2p}(\text{Ni}) = 11.4$
$\varepsilon_{5\sigma}(\text{Ni}) = 13.6$	$\Delta\varepsilon_m = -2.8$	$\Delta\varepsilon_{2p} = -2.2$
$\varepsilon_{1\pi}(\text{Ni}) = 16.7$	$\Delta\phi = +0.5$	$\Delta\phi \simeq +0.7$
$\Delta\varepsilon_{5\sigma} = -0.5$		
$\Delta\varepsilon_{1\pi} = -0.2$		

a) All energies are referred to the vacuum level (in eV).

which can be compared to measured values; $\Delta\varepsilon_\sigma^b = V_\sigma^2 / |\varepsilon_\sigma - \varepsilon_d| = 1.1$ eV and $\Delta\varepsilon_\pi^b = V_\pi^2 / |\varepsilon_\pi - \varepsilon_d| = 0.3$ eV. Here we have used Grimley's V_σ and have assumed the same interaction strength V_π for the occupied $\pi 2p$ level that Grimley estimated for the $\pi 2p$ affinity level. As previously mentioned in the added note, the observed shifts in the occupied 5σ, 1π and 4σ orbital energies for chemisorbed CO are $\Delta\varepsilon_{5\sigma} = \varepsilon_\sigma - \varepsilon_\sigma^g = -1.9$ eV, $\Delta\varepsilon_{1\pi} = \varepsilon_\pi - \varepsilon_\pi^g = -3.3$ and $\Delta\varepsilon_{4\sigma} = -3.1$ eV, where $\varepsilon_{\sigma,\pi}$ and $\varepsilon_{\sigma,\pi}^g$ are vertical IP's for the chemisorbed and gas phases, respectively. In the above, vertical ionization potentials rather than adiabatic IP's have been used for gas phase values since molecular vibrational broadening appears to be retained for the chemisorbed species, in addition to solid state broadening. Also, orbital ionization energies for a "saturation" CO coverage on Ni(111) have been used since the ionization energies are independent of coverage.[10] The above shifts are similar to those observed for chemisorbed CO on Ni(100) and on polycrystalline Ni[1,10] when the above IP definitions are used.

In analogy with our results for chemisorbed hydrocarbons, we assume that the observed shift of the 4σ level, which presumably is not strongly involved in bonding, is a rough measure of the nonbonding relaxation shifts of the valence orbitals, i.e. $\Delta\varepsilon^R \sim 3.1$ eV. Note that this crude assumption can not be exactly correct, since the 5σ orbital is spatially very different from the 1π and 4σ orbitals. Orbital dependent relaxation effects remain an interesting question. Nonetheless, using this assumption, we estimate $\Delta\varepsilon_{5\sigma}^b \sim +1.2$ eV and $\Delta\varepsilon_{1\pi}^b \sim -0.2$ eV, values which are qualitatively similar to the above values calculated ($+1.1$ and $+0.3$ eV) using Grimley's interaction strengths.

Grimley has also discussed a "surface compound" model[17] which fits the chemisorption energy about as well as the above-described model using the same interaction strengths V_σ and V_π. However, this model does not fit our observed orbital energies for chemisorbed CO on Ni. Namely, Grimley has calculated an upwards bonding shift $\Delta\varepsilon_{5\sigma}^b \simeq -1.6$ eV for the 5σ level using this model. Thus the total 5σ orbital shift would be $\Delta\varepsilon_\sigma = \varepsilon_\sigma - \varepsilon_\sigma^g = -\Delta\varepsilon_\sigma^R + \Delta\varepsilon_\sigma^b = -\Delta\varepsilon_\sigma^R - 1.6$ eV, where we $\Delta\varepsilon_\sigma^R$ (~ 3 eV) is positive. We observe a much smaller shift $\Delta\varepsilon_\sigma \simeq -1.9$ eV, inconsistent with the above. This discrepancy appears to be due to the use of Coulomb interaction energies ($Un_\sigma n_\pi$, etc) in the model which are too large. In addition, this model also tends to overestimate changes in orbital occupancies n_σ, n_π.

Other interesting descriptions of chemisorption include Hartree-Fock treatments[32,35,36] and the self-consistent field SCF-Xα "scattered-wave" method.[37] These models, to our knowledge, have not been applied to CO chemisorption or to organic adsorbates. The inclusion of configuration interaction in the Hartree-Fock scheme as described by Newns[35] appears to be essential to understand organic adsorbates.

Chemisorbed NO and O on Ni are strongly bound and are more complicated than chemisorbed CO on Ni or the organic adsorbates we have discussed. We simply summarize adsorbate orbital energies e_m and energy shifts $\Delta\varepsilon_m$ for these adsorbates (relative to gas phase IP's) in Table II. For chemisorbed NO on Ni(111), $\varepsilon_p(\text{Ni}) \simeq 14.7$ eV is the center-of-gravity of several unresolved $\pi 2p$ and $\sigma_g 2p$ orbital IP's.[22] The observed upwards shift in these levels relative to their gas phase values is quite large: $\Delta\varepsilon_m = \varepsilon_m - \varepsilon_m^g(\text{gas}) \simeq -2.8\text{eV}$.

For chemisorbed O on Ni(111), the ~ 2eV wide O-derived level is shifted upwards by $\Delta\varepsilon_{2p} \simeq -2.2$ eV relative to the first IP for atomic oxygen. Johnson and Messmer[38] have treated the case of a nickel oxide cluster (a very approximate model of chemisorbed oxygen) using the SCF-Xα method and obtain qualitative agreement with the observed O-derived level on Ni.

In summary, our photoemission studies of inorganic (CO, O and NO) and organic (C_2H_2, C_2H_4 and C_6H_6) adsorbates on Ni(111) suggest many interesting chemisorption and catalysis

studies in which valence orbital spectra can be used not only to monitor the chemical state of adsorbate complexes but to determine particular orbital bonding interactions and chemisorption energies involved in various surface reactions. As we have discussed, although quite basic chemical information is available from the orbital ionization energies of chemisorbed species, a detailed theoretical interpretation of such orbital energies requires an understanding of relaxation and image change screening effects. For molecules which have several accessible π- and σ- orbitals, such effects can be experimentally separated with UV photoemission spectroscopy as we have shown.

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