PHYSICAL REVIEW B

CONDENSED MATTER

THIRD SERIES, VOLUME 35, NUMBER 18 15 JUNE 1987-II

Inverse-photoemission studies of adsorbed diatomic molecules

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(Received 4 February 1987)

We present inverse-photoemission observations of the unoccupied 2π level for N_2, CO, and NO adsorbed on Ni(001) and CO adsorbed on Pd(111). We also present results from a study of the coadsorption system K and CO on Ni(001). We find that the position of the 2π level is deeper (higher binding energy) the stronger the chemisorption bond. This is opposite to expectations based on the conventional picture of σ donation and π back donation. We suggest that this is due to final-state screening. We also compare our inverse-photoemission studies with earlier near-edge x-ray-absorption fine-structure studies of the same systems and find that the principal screening of the core hole in the latter technique is determined by the occupation of the 2π orbital in the excited state. Finally, we find that for the coadsorbed system the 2π orbital is more occupied and that it lies at a higher binding energy: 2.8 eV rather than 4.0 eV above the Fermi level.

I. INTRODUCTION

The adsorption of diatomic molecules, particularly carbon monoxide, remains a problem of considerable interest in the many subfields of surface science.[1] In the majority of systems studied it has been found that carbon monoxide stands vertically on the surface with the carbon atom nearest to the surface. The bonding mechanism is generally thought to involve both the occupied 5σ orbital and the unoccupied 2π orbital of the molecule, both of these orbitals being concentrated on the carbon atom. Further, it is generally accepted that the predominant substrate orbitals involved in the bonding are the d orbitals,[2] although we note that certain theories favor a greater involvement of the unoccupied metallic p orbitals.[3]

With the emergence of inverse photoemission spectroscopy (IPES) as a technique capable of examining the unoccupied levels there have now been studies of the 2π level in several adsorption systems (e.g., Refs. 4–8). These studies have attempted to establish the role of this orbital in the metal-molecule bond from measurements of its binding energy. A further justification for the study of the unoccupied levels is their presumed involvement in the multielectron excitation spectra associated with photoemission from weak chemisorption systems.[9] Such systems include carbon monoxide adsorption on the noble metals and nitrogen adsorption on nickel.[10] In these systems the photoemission spectra contain satellite peaks which are thought to reflect different levels of charge transfer from the metallic substrate into the 2π level during the photoexcitation process.

Inverse-photoemission measurements of these unoccupied levels will be influenced both by initial-state shifts due to the bonding mechanism and by final-state relaxation effects, as previously noted in photoemission studies from the occupied molecular orbitals. The relative contribution of these different effects is still not fully understood for the IPES process. Indeed in recent experiments to determine the role of final-state relaxation due to image charge screening in physisorbed inert gas systems, two groups discussing similar results arrived at diametrically opposite conclusions.[11,12]

In this paper we examine these different questions by studying several molecular adsorption systems. In Sec. II we describe the experimental techniques and in Sec. III we compare IPES measurements from the strong chemisorption of CO on Ni(001) with the weak chemisorption of N_2 on Ni(001). We also examine the change in the IPES spectra as CO is adsorbed on Pd(111). For this adsorption system it is known that the CO moves from a threefold site to a twofold site as the coverage increases.[13] With the higher-energy resolution available in the present system we look for changes in the binding energy of the 2π level as the adsorption site changes. We also present inverse photoemission spectra from NO adsorbed on these two surfaces. The adsorption of NO is of interest in that unlike CO, the molecule already contains an electron in the 2π orbital in the gas phase. Finally, in this section we

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present results from the system carbon monoxide coadsorbed with potassium. It is well established that the coadsorbed alkali metals act as catalytic promotors. In particular, it has been shown that the presence of the potassium significantly alters the properties of the carbon monoxide including amongst other things a dramatic lowering of the C-O stretching frequency and enhanced dissociation.

In Sec. IV we discuss the binding energies observed in the present studies and compare them with earlier studies of other carbon monoxide adsorption systems. We examine the different factors that may influence these measured binding energies. The nitric oxide observations are discussed and again compared with earlier studies. We also compare the binding energies of the 2π orbital in the present IPES study with the binding energies observed in earlier near-edge x-ray-absorption fine structure (NEXAFS) studies of the same systems. Finally, in this section we discuss our results from the coadsorption system and the implications these observations have on the possible bonding of CO in alkali covered surfaces. In Sec. V we present our conclusions.

II. EXPERIMENTAL PROCEDURE

The experiments described in this paper were carried out using an experimental apparatus which has been described in detail elsewhere.[14] Briefly, photons emitted in the inverse-photoemission process were detected with a grating spectrograph operating in the range 10—30 eV. Combined with a custom-built electron source[15] this instrument was operated with an overall energy resolution of approximately 0.5 eV for most of the experiments reported in this paper. The incident beam has an included angle of 5°. Ni(001) and Pd(111) surfaces were cleaned by repeated cycles of argon bombardment and annealing. It was found that for the Ni(001) surface annealing in an oxygen atmosphere was necessary to fully ensure a clean surface. Surface cleanliness and order were monitored using Auger electron spectroscopy (AES) and low-energy electron diffraction (LEED). The clean surfaces were exposed to differing amounts of carbon monoxide, nitric oxide, and nitrogen either at room temperature or at liquid-nitrogen temperatures as indicated. For the coadsorption studies potassium was evaporated from a SAES getter source with the sample at either room temperature or liquid-nitrogen temperatures. In the figures presenting experimental spectra in this paper, dots indicate the raw data and solid lines indicate the same after smoothing to 0.5-eV resolution.

III. EXPERIMENTAL RESULTS

Inverse-photoemission spectra recorded from the clean Ni(001) surface and the same surface exposed to 50 L of N_2 [1 langmuir (L) $\equiv 10^{-6}$ Torr sec] and 20 L of CO are shown in Fig. 1. For adsorption the Ni surface was cooled to approximately 90 K. It will be seen from the figure that the clean-surface spectrum contains two features: the image state at 4.7 eV above the Fermi level[16] (0.5 eV below the vacuum level), and a peak immediately above the Fermi level associated with the unoccupied part

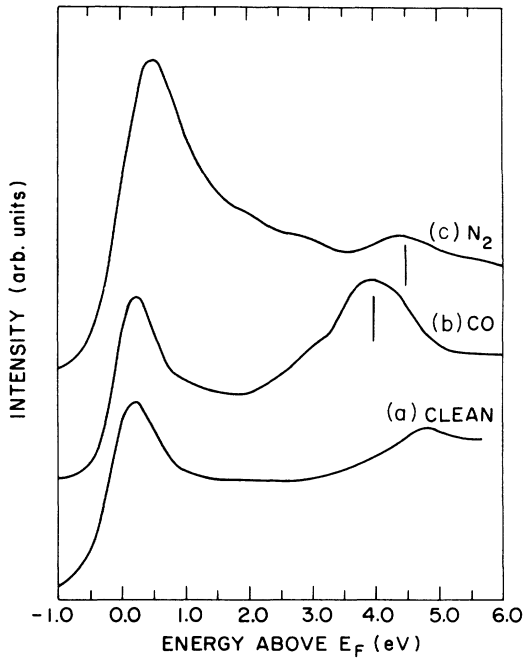

FIG. 1. Inverse-photoemission spectra recorded from the clean Ni(001) surface [curve (*a*)], the same surface with 20 L of CO adsorbed at 100 K [curve (*b*)], and following 50 L of N_2 at 100 K [curve (*c*)]. The incident electron beam energy and the angles of incidence were 17 eV and 0° in curves (*a*) and (*b*) and 21 eV and 30° in curve (*c*). The position of the 2π orbital is indicated by a vertical line in each spectrum. [1 langmuir (L) $\equiv 10^{-6}$ Torr sec.]

of the *d* band.[17] In this spectrum we are not clearly able to identify a surface resonance above the Fermi level, the equivalent of which has already been observed on Cu(001).[18,19]

Adsorption of the isoelectronic molecules CO and N_2 result in broad peaks centered at 4.0 and 4.5 eV above the Fermi level, respectively. The CO spectrum was recorded with a normally incident electron beam of energy 17.0 eV with respect to the Fermi level. Elsewhere we have reported in detail on the observed intensity of this CO 2π level as a function of incident electron beam energy.[20] The N_2 spectrum was recorded with a 21.0-eV incident electron beam energy 30° off normal. This latter change in the angle of incidence was required to clearly distinguish between the weak adsorbate-induced feature and the image state which disperses above the vacuum level as the angle of incidence increases. The reduction in the ratio of the intensity of the 2π peak to the *d* band on going from CO to N_2 is a reflection of the fact that the latter spectrum is recorded off normal and at a point where the intensity of the peak at the Fermi level has increased substantially.

In Fig. 2 we present the inverse-photoemission spectrum from the clean Pd(111) surface and a series of spectra following the adsorption of CO as a function of exposure at room temperature. The CO was observed to form a sharp $(\sqrt{3}\times\sqrt{3})$ $R30°$ structure at a coverage of ap-

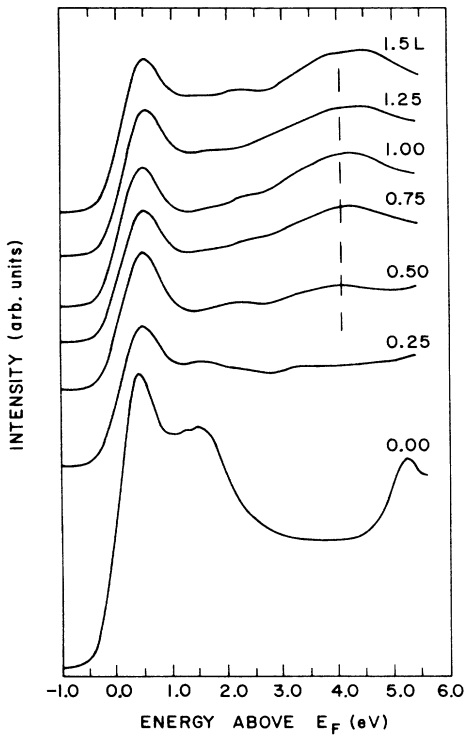

FIG. 2. Inverse-photoemission spectra recorded from Pd(111) as a function of carbon monoxide exposure at room temperature. The spectra are for normal incidence with the incident electron beam energy at 15.8 eV with respect to the Fermi level.

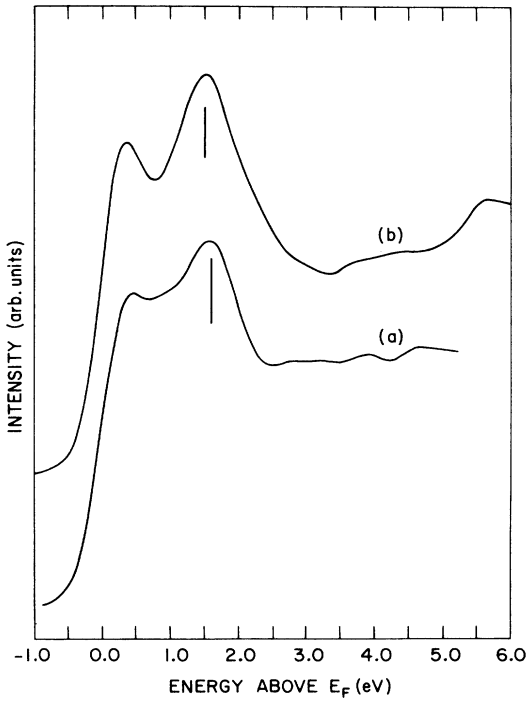

FIG. 3. Inverse photoemission spectra recorded from Pd(111) [curve (*a*)] and Ni(001) [curve (*b*)] following the adsorption of NO at room temperature and 100 K, respectively. The incident electron beam energies are 17.0 eV with respect to the Fermi level. The 2π orbitals are indicated by vertical lines.

proximately 0.3 monolayers in agreement with earlier studies.[13] In the present experimental system this coverage was obtained with an exposure of approximately 0.5 L. At higher coverages a (4×2) structure is known to form although this was never observed as a sharp LEED pattern in the present studies.

The spectrum from the clean Pd(111) surface has been described in detail elsewhere.[21] Briefly, the spectrum contains three features: the image state at 5.1 eV above the Fermi level, a surface state 1.3 eV above the Fermi level, and a peak associated with the unoccupied part of the *d* band. Following exposure to CO the surface features are quenched and a broad peak centered 4.0 eV above the Fermi level appears for the $(\sqrt{3}\times\sqrt{3})R30°$ structure. As the exposure is increased this peak broadens slightly and its center appears to shift to a marginally lower binding energy with respect to the vacuum level. A feature at a binding energy of 4.0 eV with respect to the Fermi level was observed in our earlier studies.[6]

In Fig. 3 inverse-photoemission spectra are shown following adsorption of NO on both the Ni(001) and Pd(111) surfaces. Again the Ni(001) studies were performed at 90 K. It will be seen from the figure that in both cases adsorption of NO results in a broad peak approximately 1.5 eV above the Fermi level, being 1.5 eV for Ni(001) and 1.6 eV for Pd(111).

Finally, in Fig. 4 we present the results of an inverse-photoemission study of the coadsorption of potassium and carbon monoxide on the Ni(001) surface. In Fig. 4 curve (*a*) we show again the spectrum recorded from the clean Ni(001) surface and in Fig. 4 curve (*b*) compare this with the spectrum recorded from the same surface with 0.1 monolayers of potassium coverage. The potassium was deposited from a SAES getter and the coverage was calibrated using AES and compared with an earlier calibration of Sun *et al.*[22] With the addition of potassium the image state on the clean surface is quenched and a new feature, which we associate with either the potassium 4*s* or 4*p* level, appears above the Ni *d* band at 1.2 eV with respect to the Fermi level.

In Fig. 4 curve (*c*) the IPES spectrum recorded from 20 L of CO coadsorbed with the 0.1 ML of potassium is compared with the spectrum recorded following CO adsorption alone, Fig. 4 curve (*d*). The principal observation is that coadsorption of potassium causes the 2π orbital of CO to move 1.2 eV closer to the Fermi level. A similar observation has previously been made for potassium coadsorbed on a Pt(111) surface.[23]

IV. DISCUSSION

A. CO adsorption

In Sec. III a number of inverse-photoemission spectra from different adsorption systems were presented. As noted in the Introduction the binding energy of the peaks

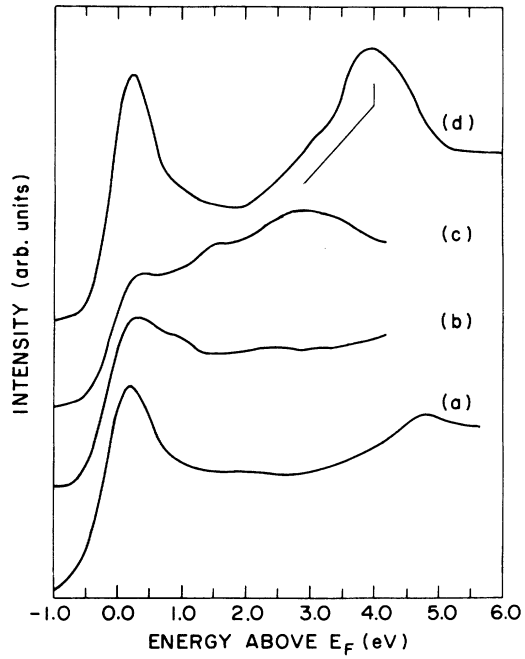

FIG. 4. Curve (*a*), inverse-photoemission spectrum from clean Ni(001). The normally incident electron beam has an energy of 17 eV with respect to the Fermi level E_F. Curve (*b*), IPES spectrum from the same surface with 0.1 monolayers of potassium. The incident beam energy is 15.5 eV with respect to E_F. Curve (*c*), the same surface as in curve (*b*) following exposure to 20 L of CO. The incident beam energy is 15.5 eV with respect to E_F. Curve (*d*), the clean surface exposed to 20 L of CO. The shift of the $2\pi^*$ orbital between curves (*d*) and (*c*) is indicated.

observed in these spectra will be influenced by both initial-state and final-state effects.

The initial-state effects result from shifts in the 2π level associated with both the bonding mechanism through hybridization with the substrate orbitals and also the possible change in the molecular bond length on adsorption. The latter effect results from the fact that the 2π orbital, which is antibonding in the molecule, moves to a higher binding energy with respect to the vacuum level as the separation of the carbon and oxygen increases.[1] Within the standard Blyholder picture of carbon monoxide adsorption,[2] hybridization of the 2π level with the metallic *d* orbitals will result in a bonding-antibonding combination of levels, the antibonding level being the one observed in the present studies. From a simple perturbation analysis it would be expected that as the bond strength increased this antibonding level would move to lower binding energy or away from the Fermi level. In alternative models which favor the formation of a resonance between the unoccupied molecular 2π orbital and the continuum electrons[3] the interaction between the metallic *p* and 2π levels will tend to push the latter towards the Fermi level. The low-energy part of the resonance has bonding character while the high-energy part has antibonding character with respect to the metal-atom bond.

The final-state effect results from the fact that in the inverse-photoemission process from a molecule, an electron is added to a relatively localized orbital.[24] Coulomb repulsion between this electron and the other electrons will cause the measured binding energy of the excited state to be lower than the ground-state binding energy before the addition of the electron. This is equivalent to the electron-hole interaction in photoemission where the Coulomb interaction between the photoelectron and the hole results in the measured binding energy of the excited state being greater than the ground-state binding energy. However, it is thought that the latter interaction may be reduced by screening of the photohole due to either charge transfer in strong chemisorption systems or image charge screening in physisorbed systems.[25] Weak chemisorption systems are thought to involve some mixture of these screening mechanisms. Without more theoretical studies it is not easy to distinguish between initial-state and final-state effects. Some interesting comparisons may be made, however, between different adsorption systems.

Clean Ni(001) and Ni(111) have the same work functions to within 0.1 eV,[26] and thus the *d* bands have a similar binding energy with respect to the vacuum level. At 0.3 monolayer coverage the reported adsorption energy of 27 kcal/mol for CO in the twofold site on Ni(111) (Ref. 27) is less than the 30 kcal/mol for the 0.5 monolayer coverage with CO in the onefold site on Ni(001).[28] Thus one might simply argue that for these systems, with the IPES measured binding energy of the 2π orbital being 3.0 eV with respect to the Fermi level for Ni(111) (Ref. 4) and 4.0 eV for Ni(001) in the present study, the Blyholder model holds with the 2π orbital moving further from the Fermi level with increasing adsorption energy.

Another interesting comparison may be made between adsorption on the (111) and (001) surfaces of palladium. Again the clean surfaces have a similar work function within 0.1 eV.[29] Following adsorption an earlier study found the 2π level located 4.8 eV above the Fermi level on Pd(001),[30] whereas the present study of the (111) surface finds the level 4.0 eV above the Fermi level for 0.3 monolayer coverage increasing to approximately 4.5 eV at saturation. At 0.3 monolayer coverage the preferred site on the (111) surface is the threefold site with movement into twofold sites at saturation.[13] This latter site is also the preferred site on the (001) surface.[30] On the (111) surface we, therefore, find that (see Fig. 2) contrary to our comparison of the nickel surfaces, as the adsorption energy drops from 34 to less than 25 kcal/mol on moving from 0.3 to 0.5 monolayer coverage the 2π level moves slightly further from the Fermi level. However, we note that the movement is in the direction of the observed binding energy on the (001) surface, which has the same adsorption site. In a recent study of CO adsorption on a stepped Pd(111) surface Rojozik and co-workers[31] noted that the observed binding energy of the 2π level moved to lower binding energy (away from the Fermi level) with increased coverage. They attributed this movement to adsorption on terrace sites at low coverage and step sites at higher coverage. The present study would suggest that this movement could also simply reflect a change of binding site on the terraces.

Comparison of earlier studies of CO absorption on the low index planes of copper[7,8] with adsorption on the nickel surfaces does not reveal any obvious correlation between bonding strength and the observed binding energies referenced with respect to the Fermi level. Indeed, the measured binding energies appear to span a similar range being less for Cu(001) (Ref. 8) (2.5—3.8 eV) than Ni(001) (4.0 eV) but more for Cu(111) (Ref. 23) (3.9 eV) than for Ni(111) (Ref. 4) (3.0 eV).

In looking for some other form of correlation we plot in Fig. 5 the observed binding energies, referenced with respect to the vacuum level rather than the Fermi level, against the stretch frequencies measured in infrared absorption (IRAS) studies of the same systems. Obviously a plot such as this requires a knowledge of the clean work function of the metal substrate, the change in the work function upon adsorption of CO, and the ir stretch frequency of the adsorbed CO as a function of coverage. In compiling Fig. 5 we have obtained these different facts from Ref. 1 and references given therein. As a result the points obtained are not absolute and we would have to attach vertical error bars of the order of 0.5 eV to the different points in the figure. For the purpose of plotting Fig. 5 it is assumed that the stretch frequencies measured in IRAS may, to first order, reflect the change in the bond length of the adsorbed CO which in turn reflects change in bonding site[13] or bonding strength. We note that a similar correlation restricted to twofold adsorption sites has already been indirectly presented in a review by Dose.[23]

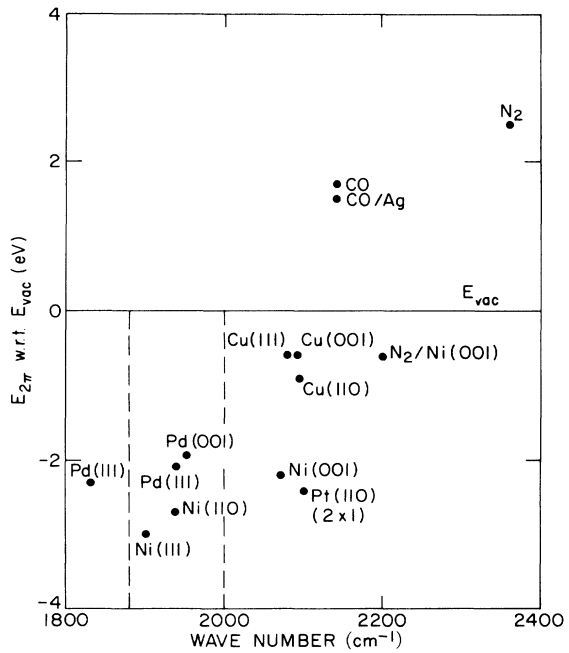

FIG. 5. Binding energies of the unoccupied CO 2π level, with respect to (w.r.t.) E_{vac}, observed in inverse photoemission plotted against the infrared stretch frequencies for the same adsorption systems. The sources are as follows: N_2 (Ref. 1), CO (Ref. 1), CO/Ag (Ref. 32), Cu(111) (Ref. 23), Cu(001) (Ref. 23), Cu(110) (Ref. 23), Pd(001) (Ref. 26), Ni(110) (Ref. 33), Pt(110) (Ref. 34), and Ni(111) (Ref. 4). The vertical dashed lines represent the division from the left-hand side into threefold, twofold, and onefold adsorption sites.

Examination of Fig. 5 shows that the observations clearly group into three categories: gas phase or physisorption, weak chemisorption, and strong chemisorption. Note that the gas phase and physisorption measurements in Fig. 5 represent resonant electron scattering studies rather than inverse-photoemission measurements. One may question whether the distribution of energies in Fig. 5 simply reflects the change in the interatomic distance between the carbon and oxygen. Some measure of the effect of the change in this bond length may be estimated if we follow others and assume that the change in the binding energy of the 2π orbital is of the order of approximately 11 eV/Å change in the interatomic distance.[35] Then in going from the gas phase to the CO adsorbed on Cu(001) we would expect this effect to account for a change in the binding energy of the order of 0.2 eV. The fact that the observed changes are much larger than this and also that the change in the binding energy increases on going to the stronger chemisorption systems such as CO on the Ni surfaces, for which the molecular interatomic distance is similar,[36] suggests that the observed binding energies are not solely determined by the bond-length change.

Figure 5 might well be interpreted as evidence for the model involving bonding between the 2π orbital and the metallic p electrons.[3] As noted earlier this interaction is expected to drive the 2π orbital to higher binding energy as the metal-molecule bond strengthens. However, it is difficult to distinguish possible ground- or initial-state shifts due to this interaction from the final-state image screening which also reflects an interaction between the electron in the 2π orbital and the continuum electrons. The experimental observation of two CO-induced features following absorption on the Cu(001) surface[8] has been cited as evidence for involvement of the substrate p electrons in the bonding, the two peaks being identified as the bonding and antibonding components. However, we note that the same observation has not been made in the present study of CO adsorbed on Ni(001). On both surfaces the CO occupies the atop site and the observed binding energy places the 2π within a band gap of the substrate. We further note that proponents[3] of this model have found that in the "ground state" the bonding was predominantly $d_\pi - 2\pi$.

We therefore have the possibility that the image screening of the final state plays a role in determining the details of Fig. 5. If we take as an example CO adsorbed on Cu(001) then LEED studies indicate that the copper carbon spacing is of the order 1.8 Å.[36] Lang and Kohn have performed an analysis of the image potential experienced by an electron outside of a jellium, $r_s = 2$, and find that the image plane is centered 1.6 a.u. beyond the jellium edge.[37] For Cu(001) this would place the image plane at 1.75 Å from the last row of copper atoms. Our own analysis of the binding energy of image states found that for Cu(001) the image plane was centered 1.3 Å from the last row of atoms.[38] Thus for an electron in the 2π orbital centered on the carbon atom adjacent to the surface, this image interaction could amount to several eV. Indeed it

has already been suggested that final-state screening determines the measured binding energy of the 2π for the weak chemisorption of CO on Cu(110) by Gumhalter.[39] However, it is well known that the image potential saturates near the surface and ultimately merges into the bulk potential. Analyses of surface barrier resonances in LEED studies of Cu(001) (Ref. 40) find that the transition region from saturating imagelike potential into bulklike potential is located approximately 1.88 Å from the last row of atoms. Thus for this weak chemisorption system, the large 2π orbital effectively spans this transition region with its charge density. This may explain the observation that while Fig. 5 appears to indicate the binding energy of the "affinity level" following the image potential, no change in the binding energy of the 2π level is observed as Ni(110) is exposed to CO,[33] even though the work function changes continuously up to saturation by 0.9 eV. Indeed in plotting the Ni(110) data point in Fig. 5 we are forced to choose the work-function change for some mid coverage, i.e., 0.5 monolayer.

Finally in this section we comment on the observation of the unoccupied 2π orbital for the N_2/Ni(001) adsorption system. It is well established that the adsorption of N_2 on Ni(001) represents a weak chemisorption system and that photoemission spectra of both the nitrogen $1s$ core level[41] and the molecular valence levels show additional peaks attributed to multielectron excitations. Such satellite structure is also observed for the adsorption of CO on Cu(001),[42] but not CO on Ni(001).

As noted in the Introduction the basis for the difference is generally considered to reflect different degrees of charge transfer from the substrate into the unoccupied 2π level during the photoionization process. This charge transfer, which serves to screen the photohole, is more efficient for the strong chemisorption case than the weak chemisorption case where peaks characteristic of both screened and unscreened holes are observed. For this mechanism to occur the 2π level must be below the Fermi level and the overlap of the metallic electrons with this level must be sufficient to allow charge transfer. Clearly all of the observations of the CO and N_2 2π level reported in this paper indicate a level well displaced from the Fermi level and totally unoccupied. The ordering of the levels shows that the 2π for chemisorbed CO on Ni(001) appears further displaced from the Fermi level than the level for weakly chemisorbed CO on Cu(001).[8] The 2π level for N_2 on Ni(001) is farther from the Fermi level than that for CO on Ni(001). However, these represent measurements of the binding energy of the 2π on the negative ion, and in fact we have already noted in Fig. 5 that referencing the binding energies with respect to the vacuum level groups together the weak chemisorption systems. These levels will be pulled down following the creation of a core hole in x-ray photoemission spectroscopy (XPS) but the level of screening will be determined by the overlap of the 2π level with the metallic substrate. We note, from Figs. 1 and 2, that the observed width of the 2π level, after subtracting a Lorentzian width appropriate to the overall experimental resolution, increases from 0.8 eV for the weak chemisorbed system N_2/N(001) to typically 1.4 eV for the strong chemisorbed systems. This increase in width indicates a stronger overlap with the metallic s-p conduction electrons for the latter systems and suggests therefore that the screening should be more efficient.

B. NO adsorption

In Fig. 3 it was shown that inverse-photoemission studies of adsorbed NO generally indicate an unoccupied 2π level centered approximately 1.5 eV above the Fermi level. A similar result was reported earlier for the adsorption of NO on the Pd(001) surface.[30] As noted in the Introduction NO differs from CO and N_2 in that the 2π orbital is already partially occupied before adsorption. Indeed there have already been several photoemission studies of the occupied component of the 2π level following adsorption.

A photoemission study of NO adsorbed on Pd(111) (Ref. 43) suggested that the 2π orbital was located 2.6 eV below the Fermi level. The present inverse-photoemission studies locate the unoccupied 2π level at 1.6 eV above the Fermi level. An earlier photoemission study of NO adsorbed on Ni(001) under the same conditions as the present study indicated that the 2π level was located 2.1 eV below the Fermi level.[44] The present experiments identified the unoccupied 2π level 1.5 eV above the Fermi level. Are these results consistent?

In order to gain a better understanding of the NO adsorption systems we have compared $X\alpha$ SW calculations of the linear molecules NiCO and NiNO. Such calculations have been described in detail elsewhere.[45] The only change in moving from one linear chain to another has been the replacement of the carbon atom by a nitrogen atom; all bond lengths and radii remain the same, being set equal to the bond lengths determined from a LEED study of the adsorption of CO on Ni(001).[36] For both chains the bonding mechanism appears to involve the standard σ donation with π back donation. However, we note that in moving from CO to NO, π back donation appears to play a stronger role with an increase in the relative $d\pi$ component of this orbital.

The ionization potential or affinity level appropriate to photoemission and inverse photoemission, respectively, are calculated by removing or adding 0.5 electrons to the 2π orbital. Slater has shown that ionization potentials can be related to the orbital energy parameter for the half occupied level; this is known as the transition state.[45] We have simply extended this concept to the affinity level as has previously been done by Davenport *et al.*[46] in the calculation of inelastic electron scattering from oriented molecules. The results of these calculations are shown in Fig. 6, where for each linear chain, we show on the left, the orbital energy parameters for the ground state and on the right, the transition-state level of the excited state. From the figure it will be seen that for NO the partially filled 2π orbital is located right at the Fermi level in the ground state. On adding 0.5 electron (IPES) this level moves to a lower binding energy while the removal of 0.5 electron (PES) results in the level falling to the bottom of the d band. We assume that the transition-state level of the metallic d bands would coincide with the orbital energy parameter for the equivalent ground-state level in these diagrams. All of the experimental observations discussed

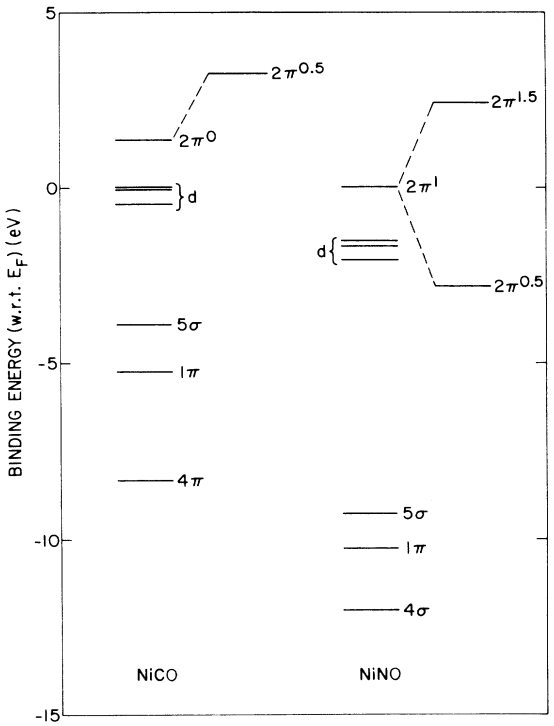

FIG. 6. Comparison of $X\alpha$ SW calculations of the linear chains NiCO and NiNO. The results of transition-state calculations representing the addition or removal of electrons from the 2π orbital are also indicated.

earlier in this section are consistent with the picture in Fig. 6 if we assume that the experimental observations are indeed of the same level.

The alternative suggestion might be that the photoemission studies are observing the bonding component being principally d_π with a smaller admixture of molecular 2π. Indeed this appears to be the picture proposed by Batra and Brundle[47] in an earlier cluster calculation of NO adsorbed on Ni(001). However, we note that the equivalent orbital in CO adsorption systems has never been conclusively identified.

Thus our picture of the photoemission and inverse photoemission of the NO 2π orbital is one of either removing or adding an electron to the same orbital. We, therefore, have a measure of an effective electron-electron interaction U_{eff} in the presence of a metallic substrate. U represents the difference between the ionization potential and affinity potential of the molecule. For Ni(001) and Pd(111) we find values of 3.6 and 4.2 eV for U_{eff}, respectively, whereas in the gas phase U has the value of 9.5 eV.[48] The difference, of course, results from the increased screening in the presence of the metallic substrate.

Finally, we note that the observations in this section regarding NO adsorption will also apply to systems showing strong chemisorption of CO. Thus, the present studies indicate that for a strong chemisorption system the measured binding energy of the unoccupied 2π orbital can be shifted by at most but probably less than 1.5 eV from the ground-state binding energy due to final-state effects.

C. Comparison of IPES with NEXAFS

In this paper we have discussed the observation of the 2π orbital in a number of absorption systems using the technique IPES. An alternative observation of this orbital may be made using the technique NEXAFS or near-edge adsorption fine structure.[49] In the latter technique electrons are excited from some core level to the unoccupied levels by absorption of photons of the appropriate energy. It has been noted elsewhere that the two measurements, IPES and NEXAFS, differ through the presence of the core hole in the near-edge experiment.[4,5,50]

In Fig. 7 the IPES measurements on the adsorption of CO, NO, and N_2 on Ni(001) reported in the present study are compared with the measured binding energies for the same systems in an earlier NEXAFS study.[49] In the figure the binding energy measured following excitation from the $1s$ core level of the atom adjacent to the surface is indicated by a solid line; excitation from the $1s$ core level of the atom further removed from the surface is indicated by a dashed line. It should be noted that the binding energies observed in the NEXAFS studies require a prior knowledge of the threshold energy for excitation of the core level to the Fermi level determined from another experiment. Thus, all of the indicated binding energies are subject to the uncertainty in calibration of a number of different experiments. Considering only the excitation

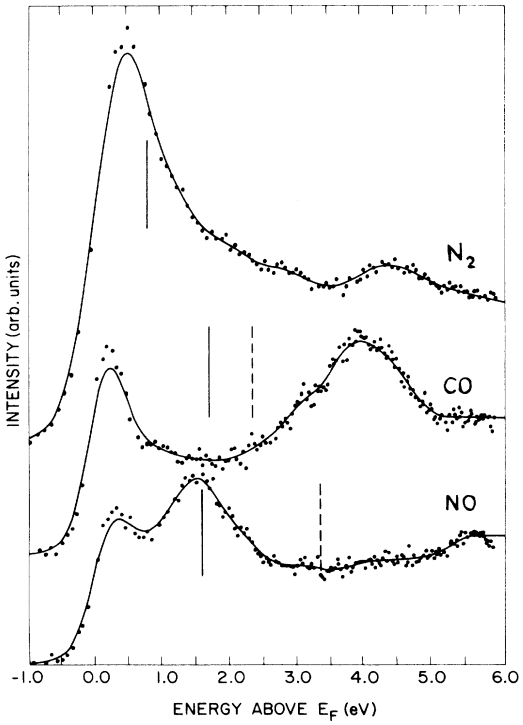

FIG. 7. Comparison of the 2π orbitals observed in IPES studies of N_2, CO, and NO adsorbed on Ni(001) with binding energies of the same orbitals observed in NEXAFS studies. Excitation from the core levels of atoms adjacent to the surface is indicated by solid lines; excitation involving atoms further removed from the surface is indicated by dashed lines.

of the core levels on the atoms adjacent to the surface which results would appear to be consistent with earlier observations. On moving from the weak chemisorption system N_2/Ni(001) to CO/Ni(001) the difference in the measured binding energy from the two techniques is reduced from approximately 4.0 to 2.0 eV. This is consistent with the trend suggested in Refs. 4 and 50, where it was shown that the electron-hole interaction is reduced as the metal-molecule bond increases. For the NO/Ni(001) system the difference is reduced to approximately zero, probably reflecting the increased occupation of the 2π orbital. However, if we consider the O $1s \rightarrow 2\pi$ transition for NO/Ni(001) the measured binding energy is now lower than that observed in the IPES experiment. Further, for the CO/Ni(001) system the binding energy measured in the O $1s \rightarrow 2\pi$ transition is closer to the IPES observation than the equivalent higher-resolution experiment on the CO/Ni(111) system[50] where excitation from either the carbon core level or the oxygen core level produced an approximately equal binding energy for the 2π level. It seems unlikely that CO/Ni(001) should be so different from CO/Ni(111) and, therefore, suggests the possibility of an error in the calibration of one of the experiments determining the NEXAFS binding energy. We are clearly not able to specifically identify the source of such an error and we are left with the conclusion that, allowing for small shifts, the level of screening is principally determined by the occupation of the 2π orbital in the excited state. We would further make the observation that the difference in measured binding energies is greater for CO/Ni(001) than for CO/Ni(111) consistent with increased back bonding into the 2π orbital for higher coordination sites.[51,52] The assumption of an error may, of course, be incorrect, in which case one would have to appeal to different degrees of charge transfer during the excitation from the different core levels as has been discussed elsewhere for NO/Cu cluster calculations.[3] More light may be shed on this interesting dilemma with both further theoretical calculations and new experiments.

D. The coadsorption system K/CO

In Fig. 4 we presented spectra recorded from coadsorbed potassium and carbon monoxide. The main observation was that the presence of 0.1 monolayers of potassium causes the 2π orbital of the carbon monoxide to move by 1.2 eV to the higher binding energy of 2.8 eV above the Fermi level. Indeed such a shift has been predicted in theoretical studies of these systems. In an $X\alpha$ *SW* cluster calculation MaClaren *et al.*[53] find that coadsorption of Li and CO on a Ni(001) surface causes the 2π orbital of CO to be pulled down to the Fermi level through an interaction with the lithium *sp* orbitals. In a slab calculation of coadsorbed K and CO on Ni(001) Wimmer *et al.*[54] find that the 2π orbital moves towards the Fermi level by approximately 1.5 eV. Similar observations have already been made in an experimental IPES study of coadsorption on Pt(111).[23]

For the coverage of potassium and exposure to carbon monoxide in the present experiment the work function is reduced by approximately 0.2 eV.[55] Thus, the binding energy of the 2π orbital with respect to the vacuum level would be 2.2 eV. However, we would emphasize that without any *in situ* measurement of the work-function change this binding energy can only be considered approximate. With reference to Fig. 5 this binding energy would fall within the range of those found for the transition metals or chemisorption systems. We are not aware of any measurement of the IRAS stretch frequency for this system but we assume that it would show the same reduction to a frequency of the order of 1500 cm^{-1} found for other coadsorption systems. The fact that the binding energy of the 2π with respect to the vacuum level remains similar would imply from Fig. 5 that there is not a large change in the bonding strength between the molecule and the surface. This is different from the conclusion of Dose.[23] It is interesting to compare the typical changes in the binding energy of the 2π measured in NEXAFS following coadsorption with those indicated here for IPES studies. In fact the published changes in binding energy observed in NEXAFS experiments[56,57] are typically much less than the change observed in the present IPES study. This results in the difference in the binding energies observed in the two techniques being reduced, and thus from our earlier discussion is an indication of an increased filling of the 2π in coadsorption systems. Thus our picture is of an increased filling of the 2π but not necessarily an increase in the bonding strength of the CO to the substrate. This suggests that models such as those discussed by, for example, Heskett *et al.*[58] where the CO π bonds to the adsorbed potassium may indeed prove to be reasonable descriptions of the coadsorption systems.

V. SUMMARY

We have presented inverse-photoemission observations of the unoccupied 2π orbital for a number of different molecular adsorption systems. We find that the binding energies observed in these studies are not simply explained by the Blyholder model of CO adsorption, and by comparing with earlier studies we have attempted to establish the different initial- and final-state effects which contribute to the observations. We find that the energy of the 2π orbital is further from the vacuum level but not necessarily closer to the Fermi level as the bond strength to the substrate increases. We believe that this is an indication that final-state effects play a role in distinguishing between the typical binding energies observed in weak chemisorption systems and those observed for strong chemisorption systems. Thus, we have a picture that suggests that the effect of the Coulomb repulsion resulting from the addition of an electron to the system is reduced as the bond strength increases, due to increased screening.

By comparing inverse-photoemission observations of the binding energy of the 2π orbital for NO adsorbed on Ni(001) and Pd(111) and comparing these values with earlier observations of the same systems we believe that we are able to determine U_{eff}, the electron-electron interaction, for a relatively localized orbital in the vicinity of a metallic substrate. We find that this is substrate dependent with a value of 3.6 eV for Ni(001) and 4.2 eV for Pd(111).

We have also compared the binding energies observed

in IPES with the binding energies observed in NEXAFS. It would appear that the principal screening of the core hole in the latter technique is due to the occupation of the 2π orbital itself. Thus, the screening of the N $1s$ hole in NO is nearly complete due to the increased occupation of the 2π level in the ground state. The screening is less effective in N_2 than CO because in the former molecule the 2π orbital is evenly distributed between the two atoms rather than being centered on the atom next to the surface.

Our studies of the coadsorption system K/CO show that the 2π orbital is closer to the Fermi level than the equivalent orbital following CO adsorption on clean Ni(001). While comparisons with NEXAFS imply an increased filling of the 2π orbital, we do not find that this necessarily implies an increase in the bonding strength to the substrate.

ACKNOWLEDGMENTS

We would like to acknowledge many useful discussions with J. W. Davenport and R. H. Gaylord. This work was supported by the Division of Materials Sciences U. S. Department of Energy under Contract No. DE-AC02-76CH00016.

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