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Adsorption of molecular nitrogen on nickel. II. Comparison of photoemission for N_2/Ni(100) to CO/Ni(100) and to theory

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Valence-level and core-level photoemission results are presented for N_2 molecularly adsorbed on a Ni(100) surface at 77 K. Comparison is made to the Ni(100)/CO system. Differences are interpreted in terms of differences in chemisorption bonding. The data are in agreement with theoretical calculations (ΔSCF Hartree-Fock) for NiCO and NiN_2 cluster models, provided the possibility of Ni $4p\pi$-$2\pi^*$ (adsorbate) backbonding is allowed for in those calculations. Certain features are explainable without inclusion of such backbonding, but the agreement with absolute ionization potentials (IP's) for the valence levels is worse and the core-level satellite structure effects become unexplainable. We conclude that the data demonstrate the existence of Ni $4p\pi$ to adsorbate π^* backbonding (stronger for CO) and also justifies the use of the cluster-model calculations to interpret adsorbate photoemission data. Implicit in these conclusions is the assignment of the main line N 1*s* (or C 1*s* and O 1*s*) IP's to a core-hole state in which an electron has been transferred from the Ni valence level to the adsorbate $2\pi^*$ level (shake-down process).

I. INTRODUCTION

In Part I (preceding paper)[1] we have presented MO calculations of the electronic structure and valence-level ionization potentials (IP's) for the ground state (GS) of the linear cluster NiN_2. In a comparison to the equivalent NiCO cluster it was found that the differences in *calculated* IP's could be understood in a reasonably straightforward fashion from the differences in the initial-state bonding and final-state relaxation of CO and N_2 bound to the Ni atom in the clusters. A second set of calculations on an excited state of NiN_2 [referred to as GS(π)] was performed to allow for the possibility of Ni $4p\pi \rightarrow N_2 2\pi^*$ backbonding. Such an interaction is excluded in the GS calculation because there is no Ni $4p\pi$ occupation. It was found that including the possibility of backbonding in this way increased the Ni$-N_2$ cluster bond strength and reduced all the calculated absolute IP's because of charge transfer to the N_2. The *relative* IP's did not change significantly, however. We wished to include such a possibility of backbonding interaction in the calculations because it had been suggested that the core-level x-ray-photoemission-spectroscopy (XPS) spectra for N_2/Ni(100), [2-4]N_2/ W(110),[2] and CO/Cu(100),[2,5] could only be explained[2] by the presence of such a backbonding interaction.

In this paper we present the experimental valence- and core-level photoemission spectra for Ni(100)/N_2 and compare to Ni(100)/CO, the free molecules N_2 and CO, and to the results of the NiN_2 and NiCO model cluster calculations of the preceding paper. We will show that the GS(π) calculations of the cluster satisfactorily explain most aspects of the valence- and core-level photoemission of the real surface situation. Besides justifying the use of such cluster models for simulating surface interactions[6] these results also mean that we may relate some of the differences between the Ni(100)/N_2 and CO photoemission spectra *directly* to differences in the chemisorption bond character. In particular we shall see that differences in the separation between adsorbate σ-level valence IP's and differences in the core-level satellite structure in the two systems are well-explained by the adsorbate-bonding interaction differences, as described by the model cluster calculations.

II. EXPERIMENTAL

All photoemission spectra [He II ultraviolet photoemission spectroscopy (UPS) and Al $K\alpha$ XPS] were obtained using a UHV electron spectrometer (VG Scientific, United Kingdom) which has been described elsewhere.[7] In addition to photoemission it has low-energy electron diffraction (LEED), Auger, and secondary ion mass spectroscopy (SIMS) capabilities. The Ni(100) sample was cut and polished to within 1° orientation and cleaned by combined ion sputtering and heating procedures. Once clean and annealed (less than 2% monolayer carbon and oxygen, as judged from the C 1*s*/Ni 2*p* and O 1*s*/Ni 2p ratios) the (100) integrity was checked by LEED, the XPS core-level and He II UPS spectra taken, and the crystal cooled to 77 K (N_2 will not adsorb on Ni at ambient temperatures). It was then checked by XPS for any adsorption of residual CO during the cooling by recording the He II and XPS spectra again. Figure 1 shows the spectra of the clean Ni(100) surface at ambient temperature and after cooling to 77 K. The crystal was then exposed to a 20-L dose of N_2 (admitted from a separate UHV gas-handling line) at a pressure of 5×10^{-7} Torr and all spectra re-recorded. The results are also shown in Fig. 1. Further exposure to N_2 did not increase the N 1*s* intensity, from which we assumed that saturation coverage had been reached. Figure 2 shows spectra for CO adsorbed to saturation at 77 K on the same Ni(100) crystal for comparison. The experimental valence- and core-level IP's are collected together in Table I. From the ratios O 1*s*/Ni $2p_{3/2}$: N 1*s*/Ni $2p_{3/2}$ (background subtracted as shown in Figs. 1 and 2), the known relative Al $K\alpha$ photoionization cross sections of O 1*s* and N 1*s*,[11] and the known saturation coverage of CO on Ni(100) at 77 K (0.69 monolayer[12]), the saturation N_2 coverage (assuming it to be all in molecular form, as discussed later) is about 0.6 monolayers. It is also clear from a comparison of Fig. 2 to 1 that a small amount of CO, about 0.04 monolayer, is adsorbed on the Ni(100) surface while cooling to 77 K prior to N_2 adsorption.

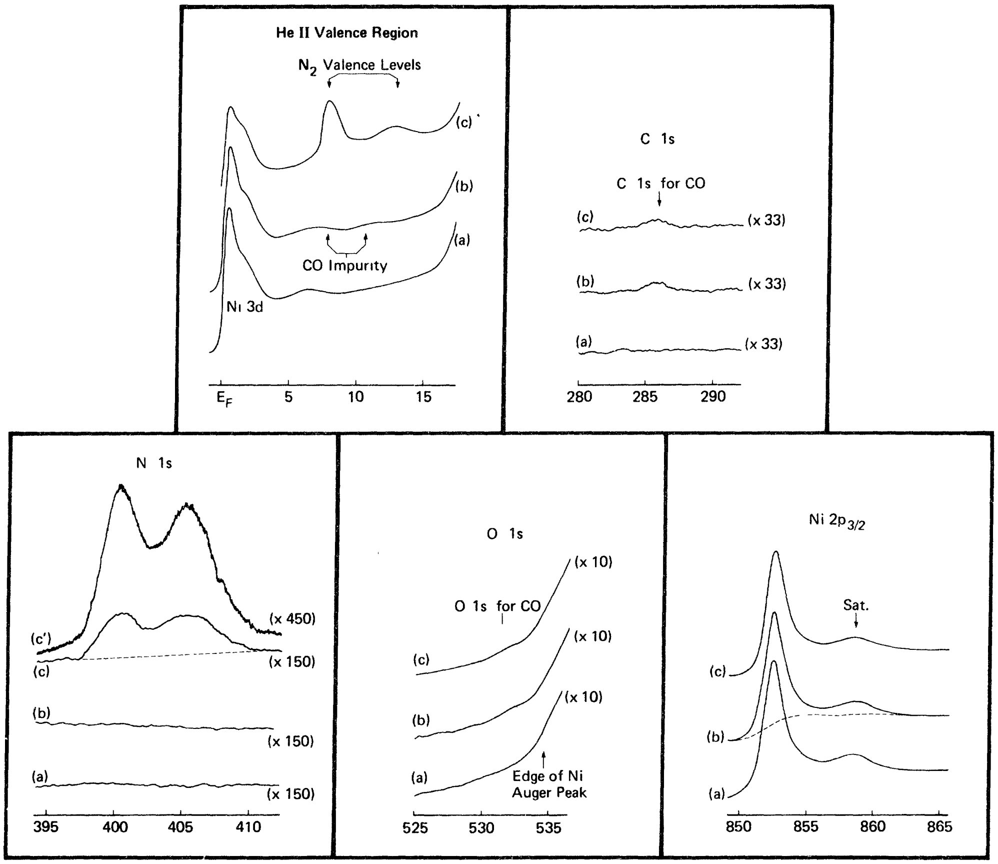

FIG. 1. He II UPS and XPS core-level spectra for (a) clean Ni(100) at room temperature; (b) Ni(100) cooled to 77 K at ambient residual pressure; (c) Ni(100) at 77 K plus saturation coverage of N_2. N 1*s* is recorded using Al $K\alpha$ radiation to avoid an overlapping Ni Auger signal in this energy region. All other XPS spectra are with Mg $K\alpha$.

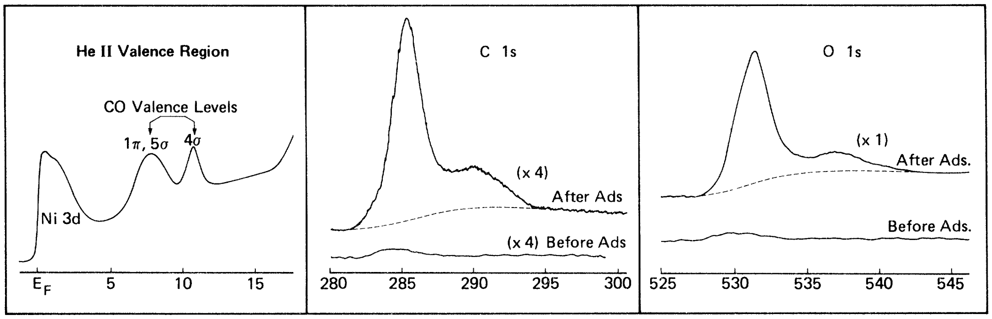

FIG. 2. He II UPS and XPS core-level spectra for saturation coverage of CO on Ni(100) at 77 K. XPS data recorded using Al*Kα* radiation to avoid an overlapping Ni Auger signal in the O 1*s* region.

III. DISCUSSION

A. Core-level features

The XPS N 1*s* spectrum for N_2 adsorbed on polycrystalline Ni was reported several years ago by one of the present authors.[13] The data was poor but the spectrum was essentially similar to that shown in Fig. 1 for Ni(100). At that time the presence of the two N 1*s* features was tentatively interpreted as implying *two* adsorptions states of *molecular* nitrogen. The possibility that one or both represented dissociated states was excluded because the N 1*s* value for atomic nitrogen on Ni was known to be several eV lower than the observed N 1*s* features for N_2/Ni. Since then it has become apparent that the two N 1*s* features represent different ionized final states of a *single* adsorption state of N_2.[2] Both core-level features grow at an equal rate during adsorption (we checked this in separate adsorption runs following the collection of the data in Fig. 1). Desorption data show no indication of the coexistence of two states. We also know from those situations where different molecular states of a given species *do* coexist [e.g., CO on W (Ref. 14), CO on Fe (Ref. 7)] that the core-level XPS chemical shifts between the states are small compared to the ~5.2 eV shift between the two N 1*s* lines reported here (Fig. 1). Finally N 1*s* spectra for N_2 on W(110) (Ref. 2) and N_2 on Fe (poly) (Ref. 15) at 77 K also show similar N 1*s* two-peaked structures. All these features help confirm our suggestion that the N 1*s* spectrum for molecular N_2 on Ni (W,Fe) represents a main line and a higher IP satellite (of unusually high intensity) similar in character to the main line and satellite observed in the O 1*s* and C 1*s* spectra of CO on Ni (Ref. 2) (see Figs. 1 and 2).

TABLE I. Experimentally determined valence- and core-level IP's (eV) for CO, N_2, Ni(100)/CO, and Ni(100)/N_2. nm denotes not measured.

Level	CO	N_2	Ni(100)/CO[d]	Ni(100)/N_2[d]
5σ	14.0[a]	15.5[b]	6.5	7.6
1π	16.9[a]	16.8[b]	7.9	7.6
4σ	19.7[a]	18.6[b]	10.9	12.4
3σ	38.9[b]	37.3[c]	nm	nm
C 1*s*	296.2[b]		285.6;290.8	
N 1*s*		409.9[c]		400.2;405.3
O 1*s*	542.3[b]		531.5;537.0	

[a] Reference 8.
[b] Reference 9.
[c] Reference 10.
[d] Referred to E_F. To make a direct comparison to the gas-phase values add a work-function correction of ~5.5 eV.

The general mechanism proposed for the generation of the satellite structure for adsorbate core levels has been discussed by the present authors[2-5] and others[16-19] and is represented schematically in Fig. 3. In essence, the formation of a core hole on the adsorbate pulls an empty MO lying near E_F (such as the $2\pi^*$ of CO or N_2) several eV below E_F. This situation, with the $2\pi^*$ orbital still remaining empty, is what might be termed the single-electron-transition final state of the N 1*s* ionization process, since there is no change in occupancy among valence-electron MO's. It is clearly not the lowest-energy final state of the system which would involve occupation of $2\pi^*$ by Ni valence-electron density and which could be termed a "shake-down" process. In the N 1*s* spectrum, therefore (O 1*s* or C 1*s* for CO adsorption), the high IP "satellite" represents the "normal" one-electron-transition final state (also designatable as the unscreened final state) and the lower IP "main

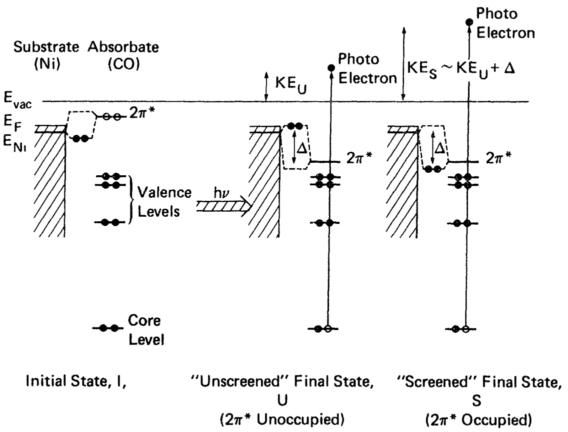

FIG. 3. Schematic representation of the photoemission process taking the adsorbate-substrate system from an initial state I to screened S or unscreened U adsorbate core-hole final states. The ratio of intensities into the two final states is given by the ratio of the overlap matrix elements

$$I_u/I_s = |\langle \phi_u | \phi_1^{n-1} \rangle|^2 / |\langle \phi_s | \phi_I^{n-1} \rangle|^2 ,$$

where ϕ_1^{n-1} is the electron wave function of the frozen initial-state configuration minus the photoelectron. ϕ_u and ϕ_s are the final ionized-state wave functions. Note: If ϕ_I has no $2\pi^*$ contribution I_s must be zero and I_u unity.

line" represents the shake-down final state (screened final state). The experimental photoemission relative intensities into the screened and unscreened photoemission final states for Ni(100)/CO and Ni(100)/N_2 are given in Table II. If one considers the extreme situation of ignoring any bonding effects between adsorbate and metal, i.e., the separated atom situations, it is immediately clear from equivalent core considerations,[20] that the above description of the final states is correct for CO adsorption. The equivalent core molecule for $C^*O^+$is NO^+. NO^+ has an electron affinity of ~10 eV whereas Ni metal has a work function of ~5 eV. Therefore the screened final state, Ni + C^*O, lies about 5 eV below the unscreened Ni + C^*O^+ state. The probability of producing the Ni^+ + C^*O final state would be zero, however, since for the separated atom situation there is no overlap between Ni and CO $2\pi^*$ orbitals, so the overlap matrix between the initial state I, Ni + CO, and the screened final state S, Ni^+ + C^*O, is zero (i.e., there is no mechansim for the Ni electron to be transferred to the CO molecule). Only the one photoemission C 1*s*/O 1*s* IP corresponding to the unscreened final state U, Ni + C^*O^+, would therefore be observable. For the real situation of adsorption Ni and CO orbitals *can* mix, however. In particular any overlap (orbital interaction) between Ni orbitals and CO $2\pi^*$ (or N_2 $2\pi^*$) orbitals provides a means of getting intensity into the screened core-hole final state S since the transition matrix between the initial state and the screened final state is now nonzero. The general effects of the chemisorption bond on the energy separation and relative photoemission intensities of the two final states were suggested originally by Schönhammer and Gunnarsson.[16,17] who used a model Hamiltonian to represent interaction between a surface and a molecule with an empty MO just above E_F. The model Hamiltonian calculations (not specific to Ni or CO, N_2) indicated that for a weak coupling between substrate and adsorbate empty MO, the unscreened final state should dominate; for a strong coupling the screened final state dominates, and for some intermediate value the states should have comparable intensities (see Fig. 4). It was this work that lead to the general interpretation of the N 1*s* and C 1*s*/O 1*s* core-level spectra in terms of screened and unscreened final states.[2] *Ab initio* HF (Hartree-Fock) core-hole calculations on the linear clusters NiCO (Ref. 21) and NiN_2 (Ref. 4) were subsequently carried out to establish whether the actual experimental energy separations and photoemission relative intensities of screened and unscreened final states of specific metal-adsorbate systems could be accounted for by simple finite cluster models. The first conclusion of these calculations[21] was that the main line-satellite relative intensities could not be accounted for using the ground state (GS) of the linear cluster[22] as the final state for photoionization. In the HF approximation, the GS for both NiN_2 and NiCO is (in $C_{\infty v}$ notation) a $^3\Delta$ state with configuration

$$\text{core } 8\sigma^2 9\sigma^2 10\sigma^2 11\sigma^2 12\sigma^1 3\pi^4 4\pi^4 1\delta^3 .$$

TABLE II. Experimentally determined relative intensities for the "main" and "satellite" peaks of the adsorbate core levels for Ni(100)/CO and Ni(100)/N_2

	Ni(100)/CO		Ni(100)/N_2	
Level	IP(eV)	Rel. Int.	IP(eV)	Rel. Int.
C 1*s* Main	285.6	0.74		
Sat.	290.8	0.26		
N 1*s* Main			400.2	0.50
Sat.			405.3	0.50
O 1*s* Main	531.5	0.83		
Sat.	537.5	0.17		

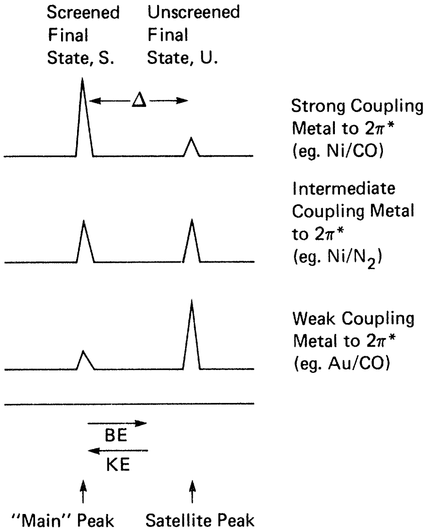

FIG. 4. Schematic representation derived from Fig. 3 of C 1*s*, O 1*s*, or N 1*s* core-level photoelectron spectra for adsorbed CO or N_2.

TABLE III. Sudden approximation relative photoionization intensities from the $^3\Delta$ GS of NiCO to C 1*s* and O 1*s* unscreened, U, and screened, *S*, final hole states as a function of Ni – CO bond distance *d* (Ref. 23).

	I_u/I_s	
d(bohr)	O 1*s* core-hole state	C 1*s* core-hole state
3.08	3.02	2.91
3.48	4.54	4.57
3.88	7.95	8.30
4.28	15.17	16.92
4.68	32.20	38.00
5.08	65.40	87.10
5.48	166	178

The 8σ, 9σ, 10σ, and 3π orbitals are the CO or N_2-like orbitals which retain much of their free-molecule character and may therefore be considered as $\tilde{3}\sigma$, $\tilde{4}\sigma$, $\tilde{5}\sigma$, and $2\pi^*$, respectively. 11σ, 4π, and 1δ are predominantly Ni 3*d*-like. 12σ is a Ni 4*s* 4*p* hybrid. The bonding is predominantly between Ni 3*d* and CO 5σ (for N_2, 5σ and 4σ) as discussed in detail in the preceding paper. The only occupation of the adsorbate $2\pi^*$ orbital (i.e., backbonding) is contained in the $4\pi^4$ cluster orbital which is largely Ni $3d\pi$ with a little adsorbate $2\pi^*$. The coupling is weak because Ni $3d\pi$ is rather corelike compared to $2\pi^*$ and can not form an effective overlap. Thus, with the $^3\Delta$ state as initial state for the core-level photoionization calculation it is not possible to generate much intensity into a screened final state (i.e., $2\pi^*$ occupied by metal $d\pi$ to ligand $2\pi^*$ charge transfer) at any reasonable $d_{\mathrm{Ni-C}}$ distance. To exemplify this point the calculated relative intensities I_u/I_s for ionization from the $^3\Delta$ GS to the unscreened and screened final states for NiCO are given in Table III.[22] Clearly the theoretical spectrum is restricted to a very small "main" peak and a dominant high IP satellite, which is not the experimental situation (Fig. 1 and Table II). The $^3\Delta$ GS state of the "single-atom cluster" thus clearly underestimates the coupling between the Ni surface and the adsorbate $2\pi^*$.

The slightly excited cluster photoionization initial state $^3\phi$, has the configuration

$$\text{core } 8\sigma^2 9\sigma^2 10\sigma^2 11\sigma^2 3\pi^4 4\pi^4 5\pi^1 1\delta^3$$

in which the Ni $4sp\sigma$ valence electron of the GS $12\sigma^1$ orbital has been promoted to Ni $4p\pi$ and contributes to the $5\pi^1$ orbital. $5\pi^1$ has a strong admixture of adsorbate $2\pi^*$ because of the latter's good overlap with the valence-like Ni $4p\pi$. Using this configuration [termed GS(π)] as the initial state for the core-level cluster calculations, Hermann and Bagus[4,21] calculated energy separations and relative intensities for main and satellite core levels and found them to be compatible with the experimental real surface results for Ni(100)/CO and Ni(100)/N_2 at a Ni-adsorbate bond distance slightly larger (~0.5 bohr) than the experimentally determined Ni(100)/CO distance (~3.5 bohr, with the CO taking up a linear head-on site arrangement[24]). Figure 5 shows the calculated adsorbate core-level IP's as a function of $d_{\mathrm{Ni-C}}$ and $d_{\mathrm{Ni-N}}$ for the GS(π) of the NiCO and NiN_2 clusters.[4,21] The results for GS NiCO (Ref. 23) (i.e., without any Ni $4p\pi$-adsorbate backbonding) are also shown for comparison. The experimental value for $d_{\mathrm{Ni-N}}$ is unknown, but since the atomic radii of C and N are very similar we might expect it to be close to 3.5 bohr or slightly longer, since the experimental bond strength is weaker. The points to note about Fig. 5 are (a) that the screened-unscreened final-state separations for the GS(π) calculations are rather insensitive to the choice of *d*; (b) the calculated separation is around 7.5 – 8.5 eV for all core levels compared to the experimental value of around 5 – 5.5 eV; (c) the calculated absolute IP's to the screened final state for the GS(π) calculations are rather close to the experimental values, allowing for a work-function correction of 5.5 eV to reference the latter to the vacuum level (Fig. 5). The C 1*s* – *O* 1*s* separation of the screened final states is calculated to be 245.8 eV, very close to the

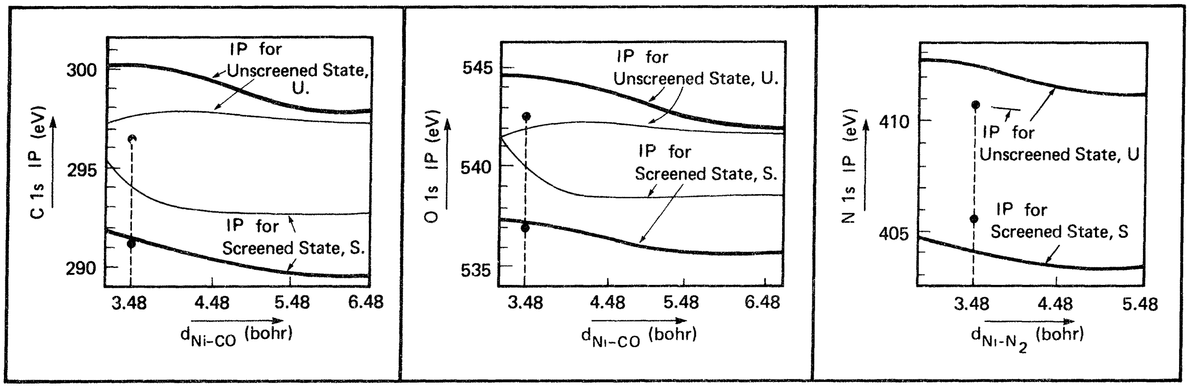

FIG. 5. Calculated adsorbate core-level IP's for NiCO and NiN_2 as a function of Ni-adsorbate distance d. Heavy lines: GS(π) initial state; faint line: GS initial state. Solid circles represent the experimentally determined values for CO and N_2 adsorption on Ni(100) (see Figs. 1 and 2 and Table I) at the experimentally found d value for CO/Ni(100) (Ref. 24).

experimental value of 245.9 eV (Table I). If one were to judge on the basis of core IP values alone, one would conclude that the GS(π) calculations are doing a reasonable job of describing the substrate—adsorbate bonding and the photoemission process. Figure 5 shows, however, that the GS calculations *also* do a creditable job, at least for $d > 3.5$ bohr. Therefore a *clear* distinction between the two calculations, which is critical in determining the real nature of the chemisorption bond since GS(π) includes substantial backbonding but GS does not, is not possible from the core-level IP values alone.

Figure 6 shows the computed relative intensities of the two final states, I_u/I_s as a function of d for GS(π) NiCO and NiN_2 and GS NiCO. The GS(π)

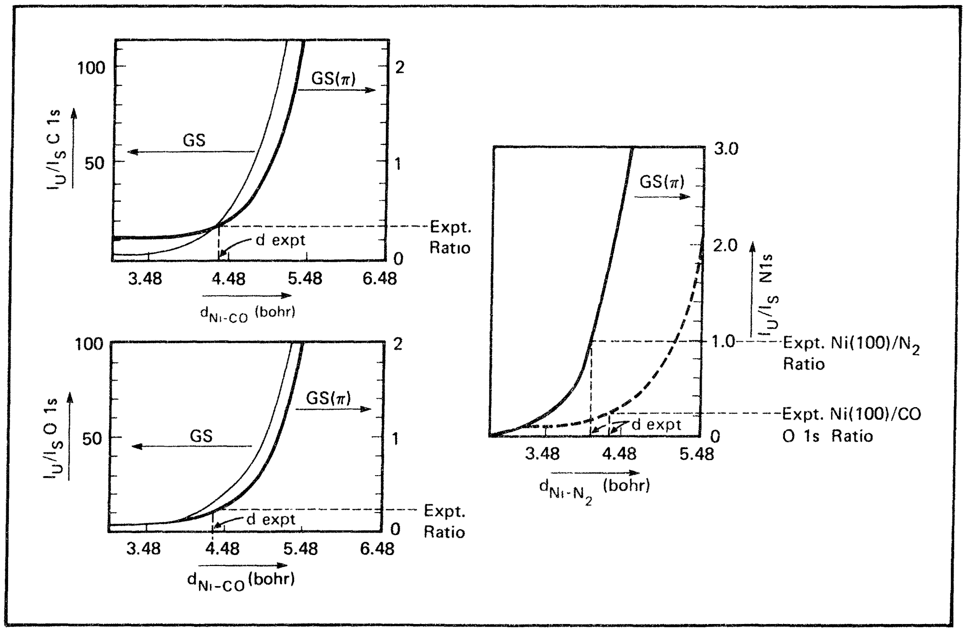

FIG. 6. Calculated relative photoionization intensity I_u/I_s into the unscreened and screened final states as a function of Ni-adsorbate distance d, for NiCO and NiN_2. Heavy lines: GS(π) initial state; faint lines: GS initial state. The O 1s ratio [GS(π)] for NiCO has been replotted (dashed line) on the N 1s graph of NiN_2 for easier comparison. The experimental ratios for the CO and N_2 on Ni(100) systems are indicated on the figure, together with the value of d that would be predicted from these ratios from the linear cluster theory.

and GS intensity curves differ dramatically, unlike the case for the IP's, and are also strong functions of *d*, thereby allowing a much stronger test of the calculations against experiment. One immediately recognizes, as stated earlier, that the GS calculations cannot reproduce the experimental I_u/I_s ratio even at impossibly short values of *d*. The predominant intensity is always into *U*. We therefore exclude the GS calculations as giving a true representation of the substrate-adsorbate interaction and examine the GS(π) results as a function of *d* in more detail.

For small *d* most of the intensity resides in the screened state; at large *d* most resides in the unscreened state; and at intermediate distances the relative distribution changes sharply. So far this merely confirms the model Hamiltonian calculations[16,17] and the general correctness of Fig. 4. The specific values of the intensity ratios versus *d* are rather different for C 1*s*, O 1*s*, and N 1*s*, however, thereby allowing a more critical test of the cluster model against the specific experimental data. For CO adsorption we see that theoretical ratio I_u/I_s is always larger for C 1*s* than O 1*s*. In fact $(I_u/I_s)^{\text{C}\,1s}:(I_u/I_s)^{\text{O}\,1s}$ is predicted to be approximately constant at around 2:1 for $d<3.8$ bohr and to decrease to $\sim 1.5{:}1$ between 3.8 and 4.5 bohr. The experimental values (Table II) do show the predicted larger value for $(I_u/I_s)^{\text{C}\,1s}$. The absolute values and the ratio $(I_u/I_s)^{\text{C}\,1s}:(I_u/I_s)^{\text{O}\,1s}$ are consistent with a $d_{\text{Ni}-\text{C}}$ of around 4.3 bohr. (Considering the difficulty in measuring the ratio accurately owing to the underlying scattered electron background, the error limits are $3.8-4.5$ bohr.) This is somewhat larger than the LEED-determined value (3.5 bohr), probably implying an overemphasis of the Ni $4p\pi-2\pi^*$ interaction in the cluster GS(π) model calculation relative to the true surface, which will reduce the slope of I_u/I_s versus distance. However, even at $d=3.5$ bohr predicted values are within a factor of 2 of the experimental ones, which must be considered a significant success for the cluster model.

For the N 1*s* of the NiN_2 cluster[25] the weaker bonding (see valence-level section and Ref. 1) causes I_u/I_s to increase rapidly at a smaller value of *d* than it did for NiCO. This is exactly what is found for the experimental Ni(100)/N_2 situation, where an I_u/I_s of ~ 1 is found (Table II). This ratio corresponds to a *d* value of ~ 4.1 bohr for the linear cluster theory, in close agreement with that predicted above for the NiCO case. Thus, the strong experimental difference in I_u/I_s observed for the two systems is reproduced quantitatively by the NiCO and NiN_2 cluster at an atom-adsorbate distance of $4.1-4.3$ bohr. The reason for the difference is that the Ni $4p\pi$-$2\pi^*$ coupling is weaker for N_2 than for CO. [The equilibrium values determined from the I_u/I_s ratios are greater than either the experimental Ni/CO distance of 3.5 bohr[24] or the GS(π) theoretical equilibrium distance, ~ 3.5 bohr, for NiN_2. This occurs because the Ni $4p\pi\rightarrow 2\pi^*$ backbonding is overemphasized in the GS(π); this overemphasis causes the I_u/I_s curves to rise too slowly with *d* in both NiCO and NiN_2.]

Our conclusions from this section are that whereas a simple comparison of core-level IP calculated values to experiment is unable to allow a correct assessment of the amount of backbonding involved between substrate and adsorbate, a comparison of calculated photoemission intensity ratios does allow such an assessment. There is clearly substantial backbonding, though the GS(π) model calculations overestimates this, resulting in quantitative agreement with experiment at too large a *d* value. Moreover the differences in relative intensities between the Ni/N_2 and Ni/CO cases are well reproduced by the calculations, showing that they are caused by a weakening of the backbonding interaction in the Ni/N_2 case.

B. Valence-level features

In Figs. 1 and 2 the He II valence-level spectra for adsorbed N_2 and CO were presented. The information carrying part of the spectra extends to about 17 eV below E_F, at which point the He I β-induced photoemission begins to interfere with the He II spectrum. The adsorbate-resonance orbital assignments for CO on Ni are by now well established, the correct correlations between gas phase and adsorbate spectra being arrived at by a combination of comparisons to organometallics,[26] calculations on model clusters,[27] and angular and photon-energy-dependent UPS studies.[28,29] The assignments are as indicated in Fig. 2. References $26-29$ also help establish the adsorption geometry, end-on bonding with C attached to Ni, which was subsequently confirmed by LEED.[24] The main thrust of Sec. III A above was to show that the key to understanding the differences in the surface bonding of CO compared to N_2 from core-level spectra lay in a proper understanding of the satellite structure behavior in the two cases. One might anticipate, therefore, that satellite features should also be observed associated with the valence levels and that their energy separations and relative intesnities might also carry information on bonding characteristics. There are, however, no *obvious* satellite features observed (see Figs. 1 and 2). This does not exclude the possibility of these being present, but does impose some restrictions. For Ni(100)/CO any satellite associated with the $\tilde{1}\pi$, $\tilde{5}\sigma$ levels must either lie beyond ~ 17 eV ($> \sim 9$eV separation from the main line) or lie under the $\tilde{4}\sigma$ level (~ 3 eV separation from the main line) and be weak, or be so close to the main line as to be unresolved. The existence of $\tilde{5}\sigma$ satellite intensity in the $\tilde{4}\sigma$ region has been inferred recently from angle-dependent measurements for N_2/W(100).[30] Any satellite associated with the $\tilde{4}\sigma$ level must lie beyond 17 eV. Similar restrictions apply to the Ni(100)/N_2 spectrum. The theoretical treatment of valence-level satellites is also less well founded than for core levels. Though calculations can be done within the sudden approximation framework, it is not to be generally expected that the sudden approximation is valid for photon energies only 10's of eV above the ionization concerned (e.g., for He I and He II UPS). Since there are both experimental and theoretical difficulties in establishing the significance of valence-level He II UPS satellites, we will first examine how well we can understand the bonding differences between Ni(100)/N_2 and Ni(100)/CO on the basis of the observable IP's. We will see that a reasonably good understanding of the experimental results, in terms of initial and final-state bonding effects, can be achieved without considering possible satellite structure. This in itself may be an indication that valence-level UPS satellites have less significance than do core-level satellites.

The first point to consider is the orbital assignments for Ni(100)/N_2.[3] Intuitively, one would assume that the assignments parallel the CO case in that the 7.6 eV peak represents a combination of $\tilde{5}\sigma$ and $\tilde{1}\pi$ and the 12.4 eV peak represents $\tilde{4}\sigma$ (Fig. 1). Such an assignment requires some explanation, however, since the IP changes from the free molecule to the adsorbate are actually quite different from those for CO. This is illustrated in Fig. 7 where the valence IP's of gaseous CO and N_2 (Ref. 8) are compared to the adsorbate situation. In the case of CO the $\tilde{5}\sigma$ orbital is several eV deeper, relative to $\tilde{1}\pi$ and $\tilde{4}\sigma$, compared to the free molecule, resulting in a large *decrease* in $\tilde{5}\sigma - \tilde{4}\sigma$ separation. For N_2 the suggested adsorbate assignments imply that both $\tilde{5}\sigma$ and $\tilde{4}\sigma$ have moved deeper relative to $\tilde{1}\pi$ and in fact $\tilde{4}\sigma$ moves further, resulting in an *increase* in $\tilde{5}\sigma - \tilde{4}\sigma$ separation. To avoid any charges of circular arguments when comparing to the cluster calculations which, in fact, do predict these effects, it would be nice to have independent evidence of the validity of the intuitive assignments. The best way to do this would be angular and photon-energy-dependent studies, as was done for CO. These have not been done in sufficient detail yet for Ni(100)/N_2, but they have been done for the case of W(110)/N_2 (Ref. 30), which shows nearly identical UPS and adsorbate core-level spectra to those for Ni(100)/N_2. In that work it was demonstrated that the changes in relative intensity of the 7.6 eV and 12.4 eV peaks as a function of polar angle at He I photon energies were compatible only with N_2 bonded end-on to the surface with the 7.6 eV peak representing $\tilde{5}\sigma$ and $\tilde{1}\pi$, and the 12.6 eV peak representing $\tilde{4}\sigma$.

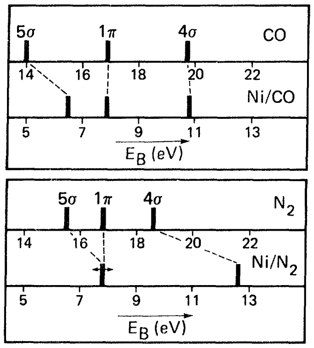

FIG. 7. Schematic comparison of the valence IP's of free and adsorbed CO and N_2. The free-molecule values are referenced to the vacuum level, the adsorbed values to E_F (Table I). The free-molecule and adsorbed-molecule energy scales are arbitrarily aligned at the 1π level since this orbital is not involved in the chemisorption bond for either CO or N_2.

Having established the validity of the experimental assignments we now compare the valence IP's in more detail to the model cluster calculation results of the preceding paper.[1] Recalling the conclusion from that paper we found that in the linear cluster NiCO (GS) the CO-to-Ni bonding was almost entirely through the 5σ lone-pair CO orbital, as judged by a population analysis. The CO orbital energies ϵ_n (Tables I and II of Ref. 1) changed on bonding in the manner depicted in Fig. 8. 5σ moves deeper by ~ 3.1 eV owing to the bonding effect, while the uninvolved 1π and 4σ levels move ~ 1.2 eV deeper, largely as a response to the

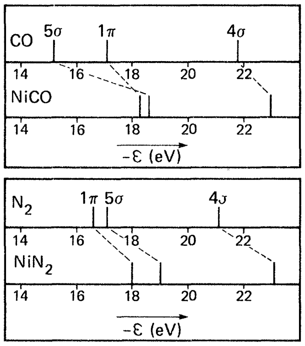

FIG. 8. Calculated eigenvalues for the valence orbitals of CO, NiCO(GS), N_2, and NiN_2(GS). The values are taken from Tables I and II of Ref. 1. The values of the Ni-molecule distance *d* used in the cluster calculations were 3.477 bohr for NiCO and 3.8 bohr for NiN_2.

change in potential in the cluster (chemical shift effect). For NiN_2, on the other hand, both the 5σ and 4σ orbitals of the homonuclear molecule are about equally involved in the bonding, which is weaker than for CO. The eigenvalue changes (Fig. 8) reflect this in that 5σ and 4σ each move ~ 1.9 eV deeper and the chemical-shift response of the 1π is ~ 1.4 eV.

If we first look for just intial-state bonding effects and simply compare the eigenvalue changes for the model clusters with the observed IP changes for the adsorption situations we already find some degree of agreement. (Note we are considering *changes*, not absolute values.) Examination of Fig. 7 in comparison to Fig. 8 shows that the eigenvalue changes for CO—NiCO semiquantitatively follow the IP changes for CO-Ni(100)/CO. The $5\sigma - 4\sigma$ separation gets smaller in both cases and the $1\pi - 4\sigma$ separation barely changes. For N_2 the agreement is much poorer. The $5\sigma - 4\sigma$ model cluster eigenvalue separation barely changes, whereas for Ni(100)/N_2 the $5\sigma - 4\sigma$ IP separation increases substantially. In addition, the 5σ and 4σ IP's both move substantially compared to 1π which does not happen for the eignevalues. We conclude from this that there are probably strong photoemission final-state bonding effects for Ni(100)/N_2 but not for Ni(100)/CO. This is borne out if we next compare the experimental IP's not to the cluster GS eigenvalues, but to the ΔSCF calculated IP's. In Table IV the free molecule and cluster eigenvalues, and the free molecule and cluster ΔSCF IP's, are listed. For NiCO the relative separation of the ΔSCF IP's differ from those in the eigenvalues by only ~ 0.3 eV, indicating no strong final-state effects. For NiN_2 the relative changes are much larger and the ΔSCF $\widetilde{5\sigma}$ and $\widetilde{4\sigma}$ IP's do move apart compared to the free N_2 ΔSCF 5σ and 4σ IP's. Thus the calculated 5σ and 4σ relative IP changes from free molecule to cluster do mimic the experimental changes from free molecule to adsorbate. This is best illustrated by comparison of Fig. 7 to Fig. 9. We suggest, therefore, that the reasons given for this behavior for the clusters, discussed in detail in the preceding paper,[1] are also the correct reasons for the adsorption-situation behavior. Thus, for Ni(100)/CO the predominant effect is the *initial-state* effect of the 5σ CO orbital forming a sigma bond with the Ni surface. For Ni(100)/N_2 both *initial* and *final-state* bonding effects are important. In the homonuclear N_2 the 5σ and 4σ orbitals are in-phase and out-of-phase combinations of the N 2*s* and 2*p* atomic orbitals. They have equal charge density at each end of the molecule and *both* can, and do, become involved in bonding to the Ni, leading to a similar initial-state bonding effect on each. For CO, as a consequence of the different nuclear charges on the carbon and oxygen atoms, the 5σ and 4σ orbitals are localized at the C and O ends of the molecule, respectively, and for C end-on bonding only the 5σ can be involved in bonding. The fact that final-state effects of adsorbate

TABLE IV. Calculated valence eigenvalues and calculated ΔSCF IP's for free molecules and GS clusters.

Eigenvalues (eV)[a]				ΔSCF IP's (eV)				
CO	NiCO	N_2	NiN_2	CO[b]	NiCO[b]	N_2[c]	NiN_2[c]	Orbital
15.2	18.6	17.1	19.0	13.5	15.4	15.9	16.4	$\widetilde{5\sigma}$
17.1	18.3	16.6	18.0	15.0	16.0	15.3	16.2	$\widetilde{1\pi}$
21.8	23.0	21.1	23.1	19.9	21.0	20.2	21.4	$\widetilde{4\sigma}$

[a] Taken from Tables I and II of Ref. 1.
[b] Taken from Tables II and III of Ref. 22(b).
[c] Taken from Tables IV and V of Ref. 1.

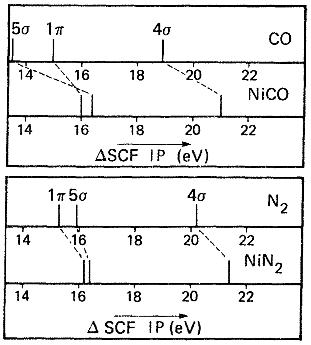

FIG. 9. Schematic comparison of the calculated ΔSCF valence IP's of free CO and N_2 to the values for the GS clusters NiCO and NiN_2. Values are taken from Table IV.

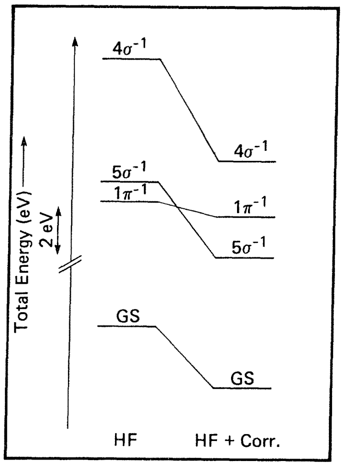

FIG. 10. Schematic total-energy diagram illustrating the effect on the hole-state energies of adding correlation corrections to the HF results (see also Ref. 1).

bonding are more important for N_2 than CO is actually also a consequence of the differences in initial-state bonding. Because of the already highly localized nature of the 5σ and 4σ orbitals for CO, not much change is possible in their orbital character in the ionized final states. For NiN_2, however, in the $\tilde{5}\sigma^{-1}$ final state the formerly delocalized bonding $\tilde{5}\sigma$ orbital, now singly occupied, becomes localized (and nonbonding) on the N atom furthest away from the Ni atom and the doubly occupied $\tilde{4}\sigma$ orbital becomes localized between Ni and the nearest N atom and constitutes all the σ bonding. This rearrangement in the $\tilde{5}\sigma^{-1}$ ionized state lowers its energy (because the 5σ orbital becomes nonbonding), causing the $\tilde{5}\sigma$ IP to be lower than it would otherwise be. Therefore, the separation between $\tilde{5}\sigma$ and $\tilde{4}\sigma$ IP's for the adsorbate situation *increases* compared to the free molecule, instead of remaining the same as predicted just by the eigenvalue (initial-state) changes.

At first sight, therefore, it seems as though we have a pretty good correspondence between the calculated valence photoemission behavior of the clusters and the acutal behavior for the real adsorbate situation. We might be tempted to conclude that the cluster (GS) calculations adequately describe the bonding of the molecule to a real surface. Several points should cause us concern about such a conclusion. First, the calculated behavior of the $\tilde{1}\pi$ IP relative to the $\tilde{\sigma}$ levels does *not* closely follow the experimental behavior, particularly for N_2 adsorption (see Figs. 7 and 9); second, the absolute IP's are too high by ~3 eV; and third, we *know* from the discussion of core levels given in Section III A that the GS state of the cluster is *inadequate* to represent bonding in the real-surface situation because it does not include Ni $4p$-adsorbate $2\pi^*$ backbonding.

The first point above is related to a problem with the HF calculations though is also provides information relevant to the necessity of including $2\pi^*$ backbonding. A study of Figs. 7 and 9 shows that the incorrect calculated behavior of the 1π IP changes (N_2 to NiN_2) relative to the σ changes is due to a problem in the free-molecule calculation rather than the cluster calculation. The HF calculated relative π and σ IP's for free N_2 are incorrect. The reason for this is well understood; there are large differential correlation errors in the HF calculations of the final states.[1] This is best explained by reference to Fig. 10, where the initial- and final-state total energies are schematically represented with and withough the correlation-energy correction. Generally, one expects a HF calculation for a small molecule to give IP's which are too low since the correlation energy lowering in the initial state should be larger than in the final state (the number of electron pairs is one less than in the initial state). For N_2 and CO, however, the low-lying unoccupied $2\pi^*$ orbital complicates matters. In the $5\sigma^{-1}$ and $4\sigma^{-1}$ final states the mixing of configurations which involve the $2\pi^*$ orbital leads to a lowering of the total energy by a large amount. In the $\tilde{1}\pi^{-1}$ final state this configuration interaction is less effective because there are only three 1π electrons instead of four. The result for HF plus correlation correction (and therefore the true situation for the free molecule) is that the 5σ and 4σ IP's are pulled down and 5σ actually drops below 1π for N_2 (Figs. 10 and 7). The HF calculated relative π and σ IP's for the NiN_2 cluster are in much better agreement with the adsorbate experimental results than is the case for free N_2. Why is this so? The differential final-state correlation effects are still present for the cluster and therefore the NiN_2 HF cluster calculation should have π and σ IP relative errors similar to those in the free N_2 calculation. In fact it probably has, but we are comparing the HF cluster results not to the experimental IP's of an NiN_2 molecule, but to a Ni *surface* bound to N_2. We know that the $2\pi^*$ adsorbate orbital is partially occupied by backbonding in the real surface situation, and in a screened final state is completely occupied. It is therefore less available for correlation and there will be no (or much reduced) strong final-state correlation effects. There are, therefore, no discrepancies between the HF calculated NiN_2 cluster IP's and the Ni(100)/N_2 IP's due to the final-state correlation errors of the HF calculation. We therefore end up with the somewhat paradoxical situation that the NiN_2 (GS) calculations by their agreement with the experimental results of Ni(100)/N_2 for relative $\tilde{\pi}$ and $\tilde{\sigma}$ IP's indicate that the real-surface situation involves $2\pi^*$ backbonding even though such bonding is not included in the GS calculation.

Having got as far as we can with a comparison to the GS calculations, let us now consider a comparison to calculated cluster IP's using the GS(π) initial state; i.e., with inclusion of the $2\pi^*$ backbonding. The ΔSCF calculations have proven rather difficult owing to convergence problems in the $\widetilde{5\sigma}^{-1}$, $\widetilde{4\sigma}^{-1}$, and $\widetilde{1\pi}^{-1}$ final states. For this reason only GS(π) valence eigenvalues for NiN_2 were reported in the preceding paper. They were found to be almost uniformly about 2.5 eV lower than for the GS, owing to the charge transfer Ni $4p \rightarrow N_2\, 2\pi^*$. The nature of the $\widetilde{5\sigma}$, $\widetilde{4\sigma}$, and $\widetilde{1\pi}$ orbitals changed very little, however, so that the only significant difference in the initial-state electronic structure was the presence of the backbonding interaction. Since completing the preceding paper some scattered GS (π) ΔSCF IP's have been obtained for NiN_2.[31] The only bond distance for which all three valence IP's have been obtained is 4.2 bohr. As was the case for the core levels, both screened, S, and unscreened, U, final states exist, separated by some 6.5 eV. These IP's are compared to the GS valence ΔSCF IP's at 3.8 bohr (the trends with variation of d suggest only about 0.2 eV changes at 4.2 bohr) in Table V. The significant factor in the comparison is that the *relative* positions of the IP's are almost the same for the GS, GS(π) screened, and GS(π) unscreened IP's. This implies that it really is not possible to distinguish between the validity of the GS or GS(π) representation of the electronic structure of the Ni to N_2 bond on the basis of relative IP's. Neither is it possible to be very confident on the basis of absolute IP's. Compared to the experimental Ni(100)/N_2 results the GS(π) screened IP's are too low by 2–3 eV, and the GS IP's too high by 3–3.5 eV. The situation is therefore very similar to the core-level situation; relative intensities into screened and unscreened final states must be considered as well as IP's to distinguish GS from GS(π) characteristics. The sudden approximation calculated U/S GS(π) photoemission ratio for $\widetilde{5\sigma}^{-1}$ (the only valence IP calculation available[31]) is less than the calculated core-level ratio but it still predicts substantial intensity into the unscreened state. For the GS initial state, all the photoemission intensity would go into the unscreened final state, of course. For He II photon energies, however, the sudden approximation may not hold, so no comparison to the present experimental data for which no satellite structure is observed (see, however, Ref. 30), can be made. In addition, the predicted position of the $\widetilde{5\sigma}^{-1}$ unscreened satellite is close to the $\widetilde{4\sigma}^{-1}$ screened main IP and so it is possible that a moderate intensity would not be distinguishable.

To summarize this section, then, we have shown that the differences in the Ni(100)/CO to Ni(100)/N_2 He II UPS spectra can be clearly correlated, via the linear cluster calculations, to the differences in σ bonding character in the two cases (5σ only for CO; 5σ and 4σ equally for N_2). It is not so easy, however, to verify the importance of the Ni $4p$-adsorbate $2\pi^*$ backbonding from the valence-level data. Calculations with and without backbonding do a qualitatively similar job on

TABLE V. Calculated ΔSCF valence IP's for the NiN_2 cluster in the GS and GS(π).

	GS[a]		GS(π)[b]	
Orbital	S	U	S	U
5σ		16.4	10.4	17.1
1π		16.2	10.5	16.8
4σ		21.4	15.7	21.9

[a] From Ref. 1, $d(\mathrm{Ni-N_2})$ = 3.8 bohr.

[b] References 31, $d(\mathrm{Ni-N_2})$ = 4.2 bohr.

reproducing the observed $\tilde{5}\sigma$, $\tilde{4}\sigma$, and $\tilde{1}\pi$ IP's for Ni(100)/N_2 (the calculation with backbonding is closer by 1 − 2 eV), and the required relative intensity data is not yet available. The one *strong* suggestion we have from the valence IP's that $2\pi^*$ backbonding must be involved is that there appears to be no large differential correlation effects between the $\tilde{1}\pi^{-1}$ and $\tilde{5}\sigma^{-1}$ final states for Ni(100)/N_2. We believe this implies that $2\pi^*$ is occupied in the final state and unavailable for correlation.

IV. COMPARISON WITH OTHER STUDIES

So far we have based all our discussions on a comparison of the core and valence photoemission spectra to the linear cluster HF theory with and without the inclusion of $2\pi^*$ backbonding and with the appropriate allowances for the known correlation errors. The subject of the bonding characteristics of CO to surfaces and also to metal atoms in organometallic molecules has been the subject of a lot of other experimental and theoretical activity in the last few years. It would be remiss of us not to make comparison to some of this work, particularly as there are some basic disagreements in interpretation.

The experimental situations for metal carbonyls can be summarized as follows:

(1) C 1*s* and O 1*s* core levels exhibit very similar main satellite structures, both in terms of energy separation and relative intensities to CO−metal-adsorbate situations. Plummer *et al.*[32] have shown that there are subtle differences between carbonyls with 1, 2, and 3 or more metal atoms and that they converge on the adsorbate results for the higher numbers of metal atoms. The high-resoultion gas-phase studies of Bancroft *et al.*[33] have shown that there are several weaker satellites to higher energy in addition to the main features for the series $Mo(CO)_6$, $Cr(CO)_6$, and $W(CO)_6$.

(2) The valence level relative 5σ, 1π, and 4σ derived orbital main IP's are very similar to those for CO adsorption, again with a convergence as the number of metal atoms is increased.[32]

(3) The valence level satellite situation is in some cases clearer for the carbonyls than for the adsorbate case. For these cases, both in the He II UPS and the XPS, a satellite band is observed ~5 eV above the 5σ, 1π main IP (slightly above and overlapping the 4σ main IP) and ~5.5 eV above the 4σ main IP.[32] The structures become weak or unobservable when the number of metal atoms reaches three or four. This again seems to converge on the adsorbate situation where, as reported here, it is difficult to observe satellite structure (there is one exception to this; CO/Cu, see later).

The interpretation of these data is not agreed upon. Plummer *et al.* originally explained both the core- and valence-level satellites[32] for the carbonyls in the same phenomenological manner as given by us (following Schönhammer and Gunnarson)[16,17] for the adsorbate situation. They considered the main (lower) IP's to represent screened final states with $2\pi^*$ occupied and the shake-up satellites to represent the unscreened states. They had no detailed calculations of screened-unscreened IP separations or relative intensities, and the question of whether *d* or *p* backbonding from the metal atom was dominant was not considered. Bancroft *et al.*[33] interpreted the $Mo(CO)_6$, $Cr(CO)_6$ and $W(CO)_6$ C 1*s* core-level results also as involving metal-to-$2\pi^*$ charge transfer but in a completely different manner. They assign the main line as normal "one-electron transition" final states and the satellites as metal→$2\pi^*$ charge transfer shake up. This assignment is therefore a reversal of the ordering of final states given by us. It was based on semi-empirical calculations of orbital ordering in the initial states only, so the possibility of $2\pi^*$ being pulled below the metal levels in the presence of a core hole was not considered. There was, therefore, no possibility for assigning the metal-to-$2\pi^*$ charge transfer photoelectron peak as having a lower IP than the "single-electron transition" peak. Recently, however, an $X\alpha$-scattered-wave cluster calculation on $Ni(CO)_4$ (Ref. 34) performed within the transition-state approximation, which attempts to take into account final-state effects, was reported. In this calculation the CO core-level satellite peaks are assigned as ligand π to $2\pi^*$ shake up. This calculation then does not have $2\pi^*$ falling below the metal levels in the presence of a core hole.

It is *possible* that the metal-ligand bonding in carbonyls is substantially different from that in the adsorbate situation and that the satellite structures observed in each case have different explanations. Given the close similarity between the two sets of spectral data we are reluctant to believe this and suggest rather that if the description we have given for the adsorbate systems is correct, then it also describes the organometallics. At present we do not understand the reason for the large discrepancy in explanation of core-level satellite structure in $Ni(CO)_4$ given by the $X\alpha$ results[34] compared to that for our model NiCO given by the HF cluster calculation. An HF calculation on $Ni(CO)_4$ on a similar footing to the Ni-CO calculation is being pursued in an attempt to find the answer.

Other recently published calculations are aimed more directly at the adsorbate situation rather than organometallics. Saddei *et al.*[19] have published an interpretation of many-body effects for valence-shell photoionization of adsorbates by performing Green's-function calculations on the same linear clusters, NiCO and NiN_2. Single-particle wave functions are needed as input to these calculations, which then provide IP's and relative intensities of all satellites arising from final-state many-body effects. The technique is very powerful in its ability to provide these many-body effects, but since CNDO wave functions were used as input, it is not to be expected that absolute IP's or even relative positions of $\tilde{5}\sigma$, $\tilde{4}\sigma$, and $\tilde{1}\pi$ IP's will be given well. The most sensible comparison to experiment and to the HF calculations on the linear clusters is in the phenomenological description, energy separations, and relative intensities of the satellite features. The phenomenological description is the same as given by us, namely the "main" IP peaks are screened final states with metal-to-$2\pi^*$ charge transfer, the satellites representing unscreened final states. There are many of these, as opposed to one for the HF calculation, because of all the possible intraligand excitations. (These extra final states will exist, of course, in the HF ΔSCF scheme, but have not been explicitly calculated.) The satellite states carrying significant intensity are calculated to spread between 3 – 11 eV above the "main" $\tilde{5}\sigma^{-1}$, $\tilde{1}\pi^{-1}$, and $\tilde{4}\sigma^{-1}$ IP's. The total intensity into satellites in the NiN_2 cluster is higher than in the NiCO cluster. These general features are quire compatible with our own HF calculations which predicted valence-level satellite structure.

The second calculation is a brief description of $X\alpha$-scattered-wave results on a Cu_5CO cluster.[35] Core-level and valence-level satellite IP's are calculated relative to the main lines within the transition-state procedure. The calculated energy spread of the (many) satellites is compatible with the experimental results (Fig. 11) for Cu(100)/CO, but again the $X\alpha$ results do not describe the main peaks as screened metal to $2\pi^*$ shake-down final states, but as "normal" states. All the satellites are described as ligand-to-ligand shake-up transitions. Bagus and Seel[5] have performed HF calculations on Cu_5CO identical in spirit to the linear-cluster HF calculations. They find, in disagreement with the $X\alpha$ results, that the character of the final states, and therefore the satellites for Cu(100/CO, is the same as found for the linear cluster, i.e., screened "main" IP's involving metal *sp*-to-ligand $2\pi^*$ charge transfer. There are two additional important features compared to the linear-cluster calculations. First, the *ground state* of the cluster now has substantial metal *sp*-to-$2\pi^*$ bonding, i.e., it is no longer necessary to "fake" this interaction by using an excited GS(π). This merely demonstrates that our use of GS(π) for the linear cluster to simulate the experimental surface-adsorbate situation was justified and that a Cu_5 cluster is large enough and of the right symmetry to qualitatively reproduce this bonding feature of a real extended surface directly. Secondly, the calculated I_u/I_s ratios for O 1*s* and C 1*s* are considerably higher at a given *d* value than for NiCO and the ratio is higher for C 1*s* than O 1*s*. This is in agreement with experiment [Fig. 11(a)] and with the general trend expected for the screened-unscreened assignment scheme since Cu(100)/CO has a weaker bond strength than Ni(100)/CO and therefore a weaker metal-to-adsorbate $2\pi^*$ coupling strength. Since a high-satellite intensity is predicted and found for the core levels of the Cu(100)/CO system, one might expect satellites to be more easily observable in the valence-level spectrum. This is born out by experiment which shows clear satellite structure[36] [Fig. 11(b)], some of which has been well characterized as such by photon, angle, and polarization-dependent UPS studies.[37]

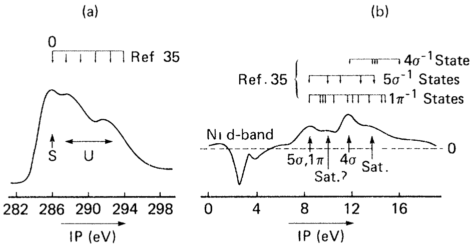

FIG. 11. (a) C 1*s* spectrum for Cu(100)/CO (Ref. 36), (b) He II UPS difference spectrum for Cu(100)/CO (Ref. 36). Our assignments would make the main (lowest) IP peaks screened final states *S*, with metal-to-$2\pi^*$ charge transfer, and the satellite structure unscreened states with $2\pi^*$ unoccupied. In Ref. 35 the satellite assignments (given at the top of the figure) are all in terms of ligand-to-ligand shake-up structure.

V. CONCLUSIONS

We have demonstrated that the core- and valence-level photoemission spectra of Ni(100)/CO and Ni(100)/N_2 are well explained by the ΔSCF HF calculations on the GS(π) electronic states of the linear clusters. The changes with respect to the free molecule spectra and the strong differences between the two systems are reproduced by the cluster calculations. We have clearly shown that if any statement on the details of the surface-adsorbate bonding characteristics is to be made by comparison of the HF cluster calculations to the experimental data, it is absolutely essential to consider the satellite structure. Comparing relative IP's in both core and valence regions does not suffice since different initial-state electronic structure configurations in the linear clusters can give comparable fits to such data. When the core-level satellite structure is considered as well, it becomes clear that, within the framework of the HF results, only an electron structure including significant Ni $4p$ to adsorbate $2\pi^*$ backbonding is capable of explaining the data. Inclusion of such bonding also explains why the ΔSCF HF valence-level-calculated IP's for the cluster more accurately predict the adsorbate results than do equivalent calculations on the free molecules predict the free-molecule values. (In the latter case the unoccupied $2\pi^*$ is available for correlation causing large differential correlation effects in the final state, whereas in the former case $2\pi^*$ is occupied in the final state and unavailable for correlation.)

The phenomenological interpretation of the main peak and satellite structure is consistently explained in terms of a screened final state with $2\pi^*$ occupied by Ni $4p$ charge transfer lying at a *lower* energy than an unscreened state. There is a large experimental difference in the screened-unscreened final state relative core-level photoemission intensities between Ni(100)/CO and Ni(100)/N_2 which is well reproduced by the sudden approximation calculations. The differences come about because the Ni $4p$ — adsorbate $2\pi^*$ coupling is weaker in the N_2 case than the CO case. Calculations on the larger cluster Cu_5CO[5] also predict a large difference in relative intensities for Cu/CO compared to Ni/CO for the same reason; the backbonding to Cu being much weaker. The predicted differences are indeed found in practice. We conclude, therefore, on the basis of comparison to the HF calculations that metal-adsorbate backbonding is important; that it comes about largely through metal p (or rather for an extended surface an sp band) interaction with adsorbate $2\pi^*$, with metal d interaction being of lesser importance; that the strength of the backbonding varies from system to system; and that this variation has its most obvious signature in the photoemission as a change in the screened to unscreened final-state intensities in the adsorbate core-level spectra. The σ bonding also differs substantially between CO adsorption and N_2 adsorption, this difference showing most clearly in the valence-level adsorbate IP shifts compared to the free molecules. For CO, the bonding is entirely through 5σ (lone pair on C), resulting in an intial-state shift in this level in the UPS. For N_2 the σ bonding is weaker (c.f. the backbonding) and involves 5σ and 4σ orbitals (delocalized over the whole molecule) almost equally. The effects show up as both initial- and final-state shifts in the UPS.

We believe the same general description of the bonding and the same interpretation of the major satellite structure is appropriate for organometallics since their spectra are so similar. We are, however, in disagreement with two $X\alpha$ calculations, one on $Ni(CO)^4$ (Ref. 34) and one on a cluster related to a surface-adsorbate situation, Cu_5CO,[35] in terms of the phenomenological description of the satellite structure. These calculations interpret the satellite structures as ligand-to-ligand charge transfer shake up. This makes the whole subject controversial since our arguments concerning backbonding depend on our assignment of main and satellite peaks as screened and unscreened final states. We do not, as yet, understand the reason for the discrepancies between the $X\alpha$ and HF results. a strong point in favor of our present interpretation is that the HF results produce a consistent behavior in satellite intensities with change in metal — ligand distance or bond strength. Thus, as the ligand becomes more uncoupled from the metal, the adsorbate spectra approach those of the free molecule. It is not clear how this could be achieved for satellite assignments of ligand-to-ligand shake up. Experimentally, the satellite intensities *increase* as the adsorbate bonding gets weaker, yet for the limit of free CO or N_2 intense ligand-to-ligand satellites do not exist in the region of the adsorbate induced satellites.

Some suggestions can be made to further test the ideas presented in this paper. Valence-level satellite structure has not yet been observed for Ni(100)/N_2 or Ni(100)/CO, though it is predicted by both HF and Green's-function calculations. For the W(110)/N_2 system it has been suggested[30] that an apparent discrepancy between the calculated relative intensities (angular resolved) of the $\tilde{5}\sigma+\tilde{1}\pi$ peak to the $\tilde{4}\sigma$ peak compared to experiment indicates $\tilde{5}\sigma$ satellite structure superimposed on the $\tilde{4}\sigma$

peak. This should be looked for carefully for the Ni(100) system using the appropriate combination of angle, photon, and polarization variations. The whole interpretation in terms of screening orbitals requires the presence of a low-lying empty adsorbate orbital which is pulled below E_F in the hole state. Adsorbates which have no such low-lying level would therefore not be expected to show the same type of satellite structure. None is found for atomic oxygen, for instance, but it would be very instructive to examine molecular cases where there are no low-lying empty levels.

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