Electronic States of CO Adsorbed onto Ni

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I have calculated the electronic spectra of CO adsorbed onto Ni(001) in the $c(2\times 2)$ structure. The 4σ band is found 10.8 eV below E_F. The 1π and 5σ bands overlap to form one peak at -7.9 eV below E_F. This two-peak structure agrees with photoemission measurements. The results indicate that the chemisorbed CO molecular states are sufficiently extended so that dynamic final-state relaxation effects are negligible, and energy-level shifts are due to chemical bonding alone. Similar results are obtained for C_2H_4 and C_2H_2.

The linear combination of muffin-tin orbitals (LCMTO) energy-band method[1] is used to perform the first *ab initio* calculation of the energy bands of CO molecules adsorbed onto a Ni(001) thin film four layers thick. The surface structure[2] used was $c(2\times 2)$ with the CO in the fourfold hollow sites. The CO molecular rotation axis was perpendicular to the Ni surface and the C-Ni distance was chosen to be 3.87 a.u.[3] CO molecular orbitals give rise to two peaks centered near 10.8 and 7.8 eV below E_F in close agreement with photoemission experiments.[4] The 7.8-eV peak consists of overlapping 5σ and 1π bands whereas the 10.8-eV peak is due solely to the 4σ band.

This agreement between theory and experiment suggests that the molecular-orbital electronic states of chemisorbed CO do not undergo a dynamic (time-dependent) final-state relaxation on emission. To support this conclusion further, the charge densities of the molecular orbitals will be shown to be significantly delocalized (or relaxed) upon being chemisorbed by CO-CO and CO-Ni bonds. Such delocalization will reduce the final-state relaxation effects that are known to occur in gas-phase ultraviolet-photoemission spectroscopy (UPS).

The agreement between theory and experiment will be shown to be independent of the choice of α in the $X\alpha$ potential as nearly identical results are obtained for $\alpha = 1.0$ and $\alpha = 0.7$. Furthermore, *ab initio* calculations for infinite monolayers of C_2H_4, when properly referenced relative to E_F of Ni, indicate that the ionization potentials (IP's) of these two molecules do not undergo final-state relaxation when the molecules are chemisorbed onto Ni. This theory of relaxation will be compared to the view that the 2–3-eV difference in IP's of gas and chemisorbed molecules is due to extramolecular relaxation of the substrate electrons about the final-state hole.[4-6]

Previous *ab initio* treatments of adsorbed CO were limited to small clusters where E_F is not well defined and the Ni levels are not delocalized. Batra and co-workers,[3,7] who use overlapping muffin-tin spheres as adjustable parameters, place one CO on five Ni atoms at a C-Ni distance of 3.87 a.u. In the first calculation the 5σ level is located at ~ -10.9 eV and the 1π level at ~ -8.8 eV whereas in a second calculation, the 1π level is located at ~ -7.5 eV, the 5σ level at ~ 9.0 eV, and the 4σ level at ~ -12.0 eV. Furthermore, they suggested correctly that the 1π and 5σ levels could overlap to give a single peak in photoemission.

Waber *et al.*[8] used the discrete variational method[9] (DVM) to calculate the states of a CO molecule in the potential field of a similar cluster of Ni atoms. Their results for a (single) CO molecule agree reasonably with the present results for a single CO layer. However, they find that the 5σ level crosses the 1π level for a C-Ni distance of 4.48 a.u., instead of the 3.87 a.u. found here. Several factors such as their not allowing CO-CO interactions and also not allowing the Ni and CO orbitals to hybridize could account for the difference.

In the LCMTO method,[10] potentials are constructed by overlapping atomic charge densities[11] and using local exchange with $\alpha = 1.0$ or $\alpha = 0.7$. The molecular levels and the Ni levels are calculated relative to a common atomic zero. For ease of comparison, all energy levels will be given relative to the E_F of Ni, which is done by subtracting the Fermi energy (-8.6 eV for $\alpha = 1.0$ or -5.17 eV for $\alpha = 0.7$) from each energy level including the molecular levels. I chose a four-layer-thick Ni substrate because it reproduces both the bulk density of states (DOS) and the Fermi energy accurately.[10] The DOS was calculated by performing exact calculations at six symmetry points in the irreducible sector of the square Brillouin zone. Each of the 360 distinct levels was broadened by the Gaussian function $[1/(2\pi)^{1/2}\times\sigma]\exp[-(E-E_i)^2/2\sigma^2]$, where $\sigma=0.125$ eV. The fraction of the DOS associated with each layer is obtained from the electron probability distribution associated with that layer. This distribution is straightforward to calculate within the LCMTO approach[10] as all space is divided into nonoverlapping atomic Wigner-Seitz cells.

In Fig. 1, excellent agreement is shown between the calculated DOS spectra for $\alpha = 1.0$ and the experimental photoemission spectra of Gustafsson *et al.*[4] The molecular orbital 4σ accounts for the peak at − 10.8 eV and overlapping 5σ and 1π states account for the peak at − 7.8 eV (5σ overlaps 1π). A straightforward explanation of this agreement between theory and experiment is that the electronic states of chemisorbed CO and Ni do not undergo a dynamic or time-dependent final-state relaxation, and the IP's are approximately equal to the $X\alpha$ eigenvalues. Such a relationship holds only for sufficiently broad or delocalized states.[12]

Figure 1 also includes the calculated spectra for a single CO layer using the $c(2\times 2)$ distances, i.e., infinite C-Ni distance. The 4σ and 1π levels shift by 0.5 eV whereas the 5σ level shifts by 5.3 eV. The similarity of the bandwidths (~ 0.33 eV for 4σ, ~ 0.58 eV for 5σ, and ~ 0.86 eV for 1π) to the chemisorbed monolayer bandwidths (~ 0.44 eV for 4σ, ~ 0.60 eV for 5σ, and ~ 0.88 eV for 1π) indicates that the CO-CO bond plays an important role in the broadening of the molecular levels.

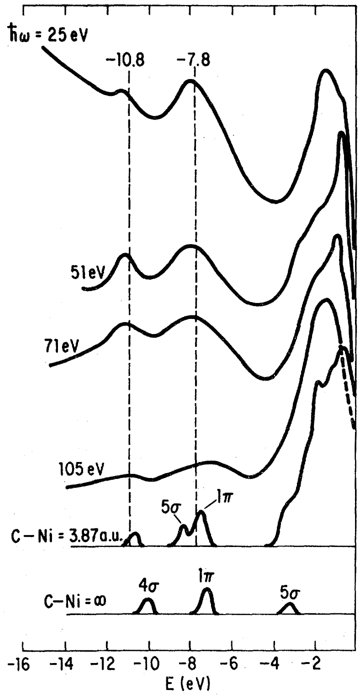

FIG. 1. Comparison of experimental photoemission spectra of Gustafsson *et al.* (Ref. 4) with the present theoretical spectra for C-Ni distances of 3.87 a.u. and ∞.

In the LCMTO method,[10] space is divided into atomic Wigner-Seitz (AWS) cells. Each electronic state then has a probability of being found in a given AWS cell, with the total probability being 1. In Table I, the eigenvalues and probabilities of being found within the O or C AWS cell are tabulated for the isolated monolayer and the chemisorbed monolayer. The eigenvalues E_i are given relative to $E_F = 8.6$ eV, as a common atomic zero is used for both calculations.

For a single monolayer, the 5σ level is primarily a C state, whereas the 4σ and 1π levels are O states. Upon chemisorption, the σ states suffer a large redistribution of charge so that the states are composed of nearly equal amounts of C and O character. In addition, the combined probability of being observed in the O and C AWS cells is reduced by 13% for 4σ and 2% for 5σ, thus indicating further delocalization. The 1π level remains primarily an O-like state but the combined probability of being within the C plus O AWS cells is reduced by 7.2%. About half of the redistribution or loss of charge within the O plus C sites goes to the Ni AWS cells with the other

TABLE I. Comparison of probability density and eigenvalue at symmetry points (00), ($\frac{1}{2}$0), and ($\frac{1}{2}\frac{1}{2}$).

		CO monolayer			CO on Ni		
		E_i	a	b	E_i	a	b
5σ	(00)	− 3.94	0.060	0.693	− 8.82	0.512	0.238
	($\frac{1}{2}\frac{1}{2}$)	− 2.91	0.051	0.814	− 8.22	0.283	0.580
	($\frac{1}{2}$0)	− 3.19	0.056	0.779	− 8.64	0.384	0.421
4σ	(00)	− 10.17	0.718	0.131	− 11.22	0.258	0.421
	($\frac{1}{2}\frac{1}{2}$)	− 10.49	0.775	0.147	− 10.79	0.544	0.332
	($\frac{1}{2}$0)	− 10.44	0.757	0.143	− 10.94	0.428	0.376
1π	(00)	− 7.41	0.793	0.083	− 8.16	0.661	0.164
	($\frac{1}{2}\frac{1}{2}$)	− 6.90	0.826	0.074	− 7.64	0.680	0.135
	($\frac{1}{2}$0)	− 6.89	0.786	0.075	− 7.72	0.674	0.131
	($\frac{1}{2}$0)	− 7.74	0.790	0.094	− 8.52	0.667	0.174

[a] Probability density within O AWS cell of volume 31.87 a.u.

[b] Probability density within C AWS cell of volume 25.32 a.u.

half going to the AWS cell between neighboring CO's.

Thus, the molecular orbitals are significantly perturbed and delocalized by the CO-Ni interaction in addition to the CO-CO interaction. It should be noted that the CO-Ni distance is rather large; as a result, the CO induces surface states that localize near the CO and do not broaden the molecular states.[13] Finally, the CO-Ni interaction results in delocalization perpendicular to the plane which is necessary for a small final-state relaxation.

Ab initio calculations were repeated for an infinite monolayer of CO in the $c(2\times 2)$ structure and for bulk Ni using $\alpha = 0.7$. The Ni Fermi energy is now 5.17 eV which is comparable to the experimental work function of 5.4 eV for clean Ni and 6.0 eV for CO on Ni.[4] The CO levels form bands centered at 2.94 (5σ), 9.93 (4σ), and 7.04 eV (1π) below E_F (5.17 eV). These positions compare well with those for $\alpha = 1.0$ in Fig. 1 (5σ at 3.16 eV, 4σ at 10.34 eV, and 1π at 7.2 eV). Thus, the CO levels and E_F of Ni for $\alpha = 0.7$ shift nearly uniformly by 3.5 eV from $\alpha = 1.0$. A chemisorption calculation was not repeated to investigate whether a C-Ni distance of 3.87 a.u. would lead to overlapping 1π and 5σ levels because of cost. However, on the basis of the $\alpha = 1.0$ calculations, chemisorption should shift the nonbonding 4σ and 1π levels by -0.5 eV which would provide excellent agreement with UPS for chemisorbed CO in Fig. 1.

UPS measurements[6] indicate that C_2H_4 π bonds to Ni when chemisorbed. Thus, the molecules lie flat on the surface and require large unit cells for a chemisorption calculation. Furthermore, no low-energy-electron-diffraction pattern has been reported for Ni(001). However, the CO results indicate that the energies of nonbonding orbitals are well approximated by a monolayer. Thus, a monolayer calculation can be performed for C_2H_4 and C_2H_2 and the molecular spectra referenced to E_F of Ni via a common atomic zero. The C_2H_4 molecules were placed perpendicular to the monolayer plane with lattice vectors $(\sqrt{2}a, 0)$ and $(0, \sqrt{2}a)$, where $a = 6.6519$ a.u., which is twice the unit cell area of $c(2\times 2)$.

In Fig. 2(a), the positions of the peaks of the molecular orbital distributions are plotted relative to E_F of Ni for $\alpha = 1.0$. The dashed lines in Fig. 2(b) indicate the approximate positions the orbitals would assume had a full chemisorption calculation been performed, except that the π would contain a chemical bonding shift.

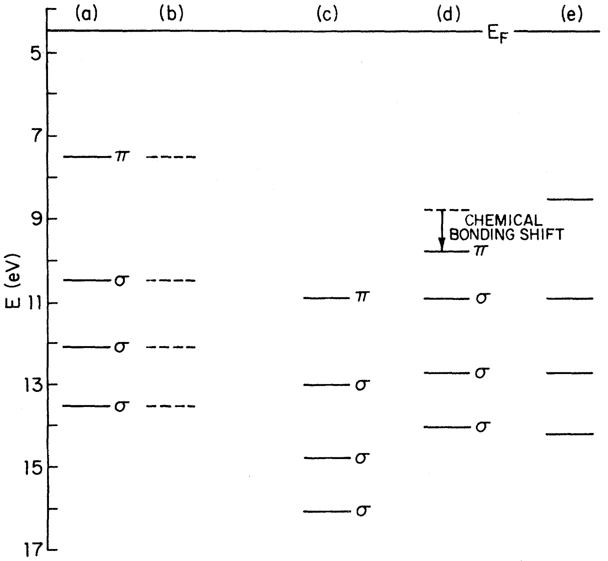

FIG. 2. Comparison of (a) calculated energy levels of a single-layer film of C_2H_4 and (b) the predicted energy levels of C_2H_4 chemisorbed onto Ni with the experimental IP's for (c) gas-phase C_2H_4 and (d) C_2H_4 chemisorbed onto NI(001). (e) Calculated energy levels of the single layer, $\alpha = 0.7$.

The experimental data consist of the UPS gas-phase spectra [Fig. 2(c)] and the chemisorption spectra [Fig. 2(d)].[6] The assumed chemical bonding shift of the π orbital is also designated. The agreement between theory [Fig. 2(b)] and experiment [Fig. 2(d)] indicates that final-state relaxation is far less than the 2.1-eV difference between the gas and chemisorbed IP's.

Finally, the spectra for a monolayer of C_2H_4 using $\alpha = 0.7$ in the $X\alpha$ potential is presented in Fig. 2(e). Again the agreement between the theoretical and experimental spectra is independent of α. Similar agreement between theory and experiment has been obtained for C_2H_2.[12]

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COMMENTS

Anomalous Angular Distributions and the Unique Structure of the $l = 1$ Transition Amplitude*

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The anomalous $l=1$ angular distributions found in heavy-ion-induced single-particle transfer reactions have been studied. The existence of a simple but special form of the $l=1$ transition amplitude is pointed out. The sensitivity of this transition amplitude to the geometry of the exit-channel distorting potential is demonstrated and a possible explanation of the observed anomalies in terms of this sensitivity is discussed.

Recently several experimental angular distributions observed in heavy-ion reactions for transitions from the $1p$ orbit in projectiles to $\frac{1}{2}^+$ states in residual nuclei have been reported[1-4] where the data showed oscillations which were completely out of phase with theoretical predictions. In some instances, similar transitions to $\frac{3}{2}^+$ states have also been observed.[5] These anomalies in all cases correspond to the unique $l=1$ transfer at certain incident energies or for the predominant $l=1$ transfer in the case of Ref. 5 if the recoil effect could be neglected. Attempts have been made to explain them in terms of coupled-inelastic-channel effects[6] for specific cases. However, it is not clear that these effects are the sole cause of the anomalies in all cases reported. In particular, in the mass-13 nuclei, the core-polarization effect with ^{12}C in the 2^+ configuration should contribute more to the ground state than the $\frac{1}{2}^+$ state in question,[7] while no evidence of anomalies was observed in the ground-state transitions.[1-3,8] The coupling in the exit channel is also difficult to justify, because the transitions carry, at most, single-particle transition strengths. It may be, however, different for the transitions; for example, in the ^{40}Ca region core-polarization effects are known to be very important. In fact, a coupled-channel Born-approximation calculation has shown a promising indication of such an effect.[6]

In this short Comment, we would like (1) to point out the particular form of the exact full-recoil distorted-wave Born-approximation (EFR-DWBA) amplitude for $l=1$ transfer which tells us that the $l=1$ angular distribution can be very sensitive to the DWBA parameters, and (2) to demonstrate in specific instances how this sensitivity can result in drastic phase shifts in the calculated angular distributions.

On the left-hand side of Fig. 1, some of the $l=1$ transitions observed are shown. The reactions ^{12}C(^{7}Li,^{6}Li)^{13}C($\frac{1}{2}^+$) at 36 MeV[8] and ^{26}Mg(^{11}B,^{10}Be)^{27}Al($\frac{1}{2}^+$) at 114 MeV[9] are reproduced well by the EFR-DWBA calculation[10] (shown by the heavy solid curves). Their wave numbers are $k_a = 2.2$ and 5.4 fm^{-1}, respectively, for the incident channel. The other four cases[1-4] show anomaly and their wave numbers are between these for the above two reactions. The dashed and thin solid curves show partial differential cross sections, $\sigma_{m=0}$ and $\sigma_{|m|=1} \equiv \sigma_{m=1} + \sigma_{m=-1}$, respectively. Here