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New analysis of lone-pair binding-energy shifts in photoemission from adsorbed molecules: CO and NH_3 on Cu(100)

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The origin of the differential ionization-potential shifts of the CO 5σ and NH_3 $3a_1$ lone pairs observed in the photoemission spectra of these molecules chemisorbed on transition-metal surfaces is identified. These shifts are unambiguously shown to arise largely from electrostatic, environmental potential effects. The consequences of interunit charge transfer, donation and back donation, and of intraunit polarization for these differential ionization-potential shifts have been determined using the constrained space orbital variation method. They are found to be smaller than the electrostatic shift due to the superposition of the unperturbed charge distributions of the separated, metal and ligand units. Thus, these differential shifts do *not* indicate the nature of the adsorbate-metal chemical bond; they may, however, indicate the adsorption geometry. *Ab initio* Hartree-Fock cluster-model studies of chemisorption at an on-top site for CO/Cu(100) and NH_3/Cu(100) have been made, but the results are expected to apply to metal surfaces in general.

I. INTRODUCTION

In valence photoemission spectra (PES) of chemisorbed lone-pair ligand molecules, one often observes a large differential shift of the ionization potential (IP) of the lone-pair derived orbital with respect to those of the other adsorbate valence orbitals. In gas-phase CO, the 1π IP is 2.9 eV larger[1] than the (C lone-pair) 5σ IP while for CO adsorbed on transition-metal surfaces [e.g., Ni(100)[2] and Cu(100)[3]] the resonances due to CO 5σ and 1π ionization are at almost the same energy.[2,3] Thus, one finds a differential shift of the 5σ IP by ~ 3 eV with respect to 1π when CO is adsorbed. In contrast, the 1π and 4σ IP separation does not change between chemisorbed and free CO.[2,3] In the case of NH_3, the $1e$ IP of the free molecule is larger by ~ 6.0 eV (Ref. 4) than the (N lone-pair) $3a_1$ IP; for NH_3 adsorbed on transition-metal surfaces [e.g., Fe(111)[5] and Fe(110)[6]], the $3a_1$-$1e$ IP splitting is smaller, ~ 4.5 eV. There is a differential shift of the NH_3 $3a_1$ IP by ~ 1.5 eV with respect to $1e$ when NH_3 is adsorbed.

The differential lone-pair IP shifts are usually interpreted as bonding shifts acting on the lone-pair orbital which, as a consequence, is assumed to make a major contribution to the chemisorptive bonding with the metal. This idea has been used for the interpretation of the valence PES of, e.g., the NH_3/Fe system[5,6] where the NH_3 is believed to adsorb with the N pointing towards the metal surface. Also, Allyn, Gustafsson, and Plummer[2] have concluded, from their PES studies on CO/Ni(100), that the CO—Ni bond arises primarily from a CO 5σ metal coupling; in this case, it has been established that CO adsorbs with its internuclear axis perpendicular to the surface and C closest to the metal.[7]

However, recent analyses of the lone-pair molecule-metal interaction,[8,9] based on the constrained space orbital variation (CSOV) method, have given strong evidence that the coupling of the lone-pair orbital with the metal does *not* make the dominant contribution to the interaction energy. For CO interacting with simple *sp* metals[8] and with Cu (Ref. 9) (which has a filled *d* band), donation and covalent bonding of CO σ electrons leads to a rather small energy contribution. In the case of metals with open *d* shells, the CO to metal σ donation can become somewhat more important for the interaction energy.[10,11] However, all CO/metal systems studied so far with the CSOV analysis show that metal to CO π donation is energetically more important than CO to metal σ donation (involving the lone-pair 5σ orbital). This is in strong contrast to the conventional picture of the CO-metal bonding.[2] For NH_3 interacting with simple *sp* metals[8] and Cu,[9] the binding energy arises largely from electrostatic contributions due to the large dipole moment of NH_3 and from polarization effects; NH_3 to metal $a_1(\sigma)$ donation, believed to involve the lone-pair $3a_1$ orbital,[5,6] is much less important.[8,9] Furthermore, cluster calculations on AlCO (Ref. 12) and $AlNH_3$ (Ref. 13) show that the lone-pair orbital, 5σ for CO and $3a_1$ for NH_3, Koopmans' theorem (KT) IP increases monotonically as the Al-ligand distance decreases. This occurs even though the interaction becomes more and more repulsive when the Al-ligand distance is decreased from its equilibrium value. This suggests[12] that the differential lone-pair IP shifts are evidence for the geometry of the molecular adsorption rather than for the nature of the bonding.

In the present paper, we discuss the origin of the differential lone-pair IP shifts of CO and NH_3 upon adsorption on the Cu(100) surface. In previous work for CO/Ni(100), we have shown[14] that this differential shift arises almost entirely from initial-state effects. Thus, we focus on the changes of the orbital energies ϵ for the ligand-derived valence orbitals in Cu_5L, $L = CO$ or NH_3, clusters which we use to model the on-top site adsorption of CO and NH_3 on Cu(100). These clusters contain one Cu atom, the adsorption site atom, of the first layer of the Cu(100) surface and the four second-layer nearest neighbors of this atom; they are denoted $Cu_5(1,4)CO$ and $Cu_5(1,4)NH_3$, respectively.

At the on-top site, the molecules interact mainly with the adsorption site Cu atom while the second-layer atoms of $Cu_5(1,4)$ provide an environment for this atom and lead to a hybridization of its valence $4s$ electron into $4s$ and $4p$ character.[9,15,16] This results in a limited description of the 4*sp* conduction band of Cu metal. However, since the direct interaction between Cu(100) and the ligand largely involves the adsorption site Cu atom, the $Cu_5(1,4)L$ clusters give a reasonable representation of the main features of the interaction.[9,17–19] The specific values of particular adsorption properties obtained with larger clusters may be different from those obtained with Cu_5L, but the general features are the same. This is even true when a smaller, one metal atom, Cu*L* cluster is used.[9]

The electronic states and orbitals of the clusters are calculated using the *ab initio* Hartree-Fock self-consistent field (SCF), method. The orbital energies ϵ represent the frozen orbital, Koopmans' theorem, IP's and contain only initial-state effects. The changes of the ϵ's are followed through the various steps of the constrained variations.[8] First, we freeze the Cu_5 and L orbitals of the separated subunits and examine how the potential due to the Cu_5 subunit changes the orbital energies of the L subunit. Then we allow, in separate steps, the various intraunit and interunit charge rearrangements. For both CO and NH_3, the largest contribution to the differential shift of the lone pair ϵ arises at the initial, frozen orbital, CSOV step. This is a conclusive demonstration of the electrostatic, environmental potential origin of the differential shift.

II. COMPUTATIONAL DETAILS

For both CO/Cu(100) and NH_3/Cu(100), we consider adsorption at an on-top site directly above a Cu surface atom, with the molecular axis perpendicular to the surface and the C(N) atom nearest to the metal. The Cu(100) surface is modeled by the $Cu_5(1,4)$ cluster. For $Cu_5(1,4)$ and $Cu_5(1,4)L$, $L=$ CO, or NH_3, the geometry and interatomic distances of the Cu atoms are taken from the bulk fcc crystal.[20] The C-O distance $d_{\text{C-O}}=2.15$ bohrs, and the Cu-C distance $d_{\text{Cu-C}}=3.70$ bohrs, used in Cu_5CO, are very close to the equilibrium bond distances from a multiconfiguration self-consistent field study[17] on Cu_5CO and are within the errors of the distances obtained from a LEED analysis[7] for CO/Cu(100). For Cu_5NH_3, the NH_3 geometry $d_{\text{N-H}}=1.89$ bohrs and $< \text{HNH} = 107.2°$, are the optimized Hartree-Fock values for the free molecule,[8] and the Cu-N distance $d_{\text{Cu-N}}=4.30$ bohrs, has been optimized[9] for Cu_5NH_3. The electronic structure of Cu_5L is obtained from *ab initio* Hartree-Fock SCF calculations using contracted Gaussian basis sets to describe the molecular orbitals. For the four second-layer Cu atoms, a pseudopotential is used to describe the 28 "core" electrons, and only one electron 4*s* per atom is treated explicitly. The use of the pseudopotential for the peripheral Cu atoms does not significantly influence the Cu-*L* interaction; this has been confirmed by comparison with all-electron calculations.[16] Details of the basis sets and pseudopotential parameters are given elsewhere.[9,16]

The C_{4V} point group symmetry ground state of $Cu_5(1,4)$ is found[9,15] to be ^2E $(7a_1^2 1b_1^2 1b_2^2 4e^3)$, where the five 4*sp* valence electrons occupy orbitals $7a_1^2$ and $4e^3$. The addition of CO, with the ground-state configuration $^1A_1$ $(5a_1^2 1_e^4)$, yields a ^2E $(12a_1^2 1b_1^2 1b_2^2 5e^3)$ ground state for Cu_5CO.

For Cu_5NH_3, which has C_s symmetry, there are two almost degenerate low-lying states, $^2A'$ and $^2A''$; these are the two C_s components of the C_{4v} ^2E state. We have obtained the variationally optimum orbitals and energies for the average of the $^2A'$ and $^2A''$ states. The Cu_5L orbitals retain much of their subunit, Cu_5 or ligand, character, hence, the free molecule notation will be used for the orbitals which have dominantly ligand character.

We have used the changes in the ligand-derived orbital energies ϵ of Cu_5L to estimate the origin of the IP shifts. For a closed-shell system, $-\epsilon$ is the Koopmans' theorem IP where final-state effects due to charge relaxation and screening[14] are neglected. For the ionization of open-shell systems, there are different space and spin coupled final ionic state multiplets. In this case, $-\epsilon$ gives the unrelaxed IP to a multiplet weighted average of the different final states.[14,21] Since the open-shell ^2E character of Cu_5 does not represent a feature of the Cu(100) surface, it is reasonable to use the $-\epsilon$ values for the KT IP's.

The CSOV analysis provides a way to determine the energetic importance of intraunit and interunit charge rearrangements[8,9] for the chemisorption of closed-shell, lone-pair molecules where the covalent bonding is dative.[22] The analysis is performed in several steps. For Cu_5L, it starts from the interaction of the fixed orbitals of the separated units, Cu_5 and L, placed at the geometry of Cu_5L. In step *A*, denoted FO (frozen orbital), the orbitals of the L subunit are fixed from the free ligand and the Cu_5 orbitals, orthogonalized to those of L, are also fixed (frozen). In step *B*, denoted FD (frozen density), the densities of both L and Cu_5 are kept fixed, but the closed-shell occupied orbitals within each subunit are allowed to mix with each other. The Cu_5L total energies of steps *A* and *B* are identical, but the orbital energies can be different. In step 1, denoted $V(Cu_5;Cu_5)$, the ligand density is fixed while the orbitals arising from Cu_5 are allowed to vary in the space of the Cu centered virtual orbitals. This step describes the polarization of the metal charge within the metal space in response to the presence of the (frozen) ligand. In step 2, $V(Cu_5;\text{all})$, the ligand density is still fixed, but the variational space of the Cu_5 orbitals is increased to include the ligand virtual orbitals. Charge donation from Cu_5 to L, and the formation of dative covalent bonds is now possible. In step 3, $V(L;L)$, the (polarized) Cu_5 charge density of step 2 is fixed, and the ligand-derived orbitals are allowed to vary in the ligand virtual space. Thus, the ligand charge can polarize in response to the presence of the (polarized) Cu_5 subunit. Finally, in step 4, $V(L;\text{all})$, the variational space of the ligand orbitals is increased to include the virtual Cu_5 orbitals, and ligand to metal charge donation is allowed. The similarity of the CSOV step 4 results with those from an unconstrained Cu_5L wave function shows the extent to which the important bonding effects have been included (for further details of the CSOV method, see Refs. 8 and 9). Limited tests[23] have been performed for the constrained variation first of the orbitals arising from the CO unit followed by the variation of the orbitals arising from the metal atoms; in effect, CSOV steps 3 and 4 are performed before steps 1 and 2. The contribution of any particular CSOV step to the interaction energy between metal and CO is very similar for both sequences of steps. It is reasonable to expect that this will also be true for the contributions of the CSOV steps to the Koopmans' theorem IP's.

III. RESULTS AND DISCUSSIONS

In earlier cluster model studies[14] of CO/Ni(100), the initial- and final-state contributions to the IP shifts of chemisorbed CO have been obtained. Among the CO 4σ, 5σ, and 1π orbitals, the contribution to the final-state relaxation energy due to the presence of the metal varied by ≈ 0.25 eV. In contrast, the FO IP shift for the 5σ orbital was larger by ≈ 2.0 eV compared to the 4σ and 1π shifts. Cluster-model studies[24] of NH_3 on Ni and Fe show a similar behavior. The final-state, relaxation, contributions to the IP shifts for the $2a_1$, $3a_1$, and $1e$ orbitals differ by only ≈ 0.1 eV, whereas the initial-state, frozen-orbital, contribution to the $3a_1$ IP shift is larger by ≈ 1.0 eV with respect to those of $2a_1$ and $1e$. Obviously, the differential lone-pair IP shifts are mostly due to initial-state effects and we can use the changes in the KT IP's, $-\epsilon$, to determine their origin.

Table I lists our results. For Cu_5CO [Table I(a)] and Cu_5NH_3 [Table 1(b)], the changes between the KT IP's of the valence-level ligand-derived cluster orbitals in Cu_5L and those of the free molecule $\Delta\epsilon$ are listed for all CSOV steps. The change for the $n\lambda$ orbital is defined as

$$\Delta\epsilon(n\lambda) = -\epsilon(Cu_5L,n\lambda) + \epsilon(L,n\lambda) \ , \qquad (1)$$

where $\Delta\epsilon > 0$ corresponds to a larger KT IP for the cluster than for the free molecule. The differences between the KT IP's for CO 1π and 5σ, and for NH_3 $1e$ and $3a_1$ are given for comparison. The interaction energy, E_{int}, between Cu_5 and L is defined as

$$E_{\text{int}} = E_{\text{SCF}}(Cu_5) + E_{\text{SCF}}(L) - E_{\text{SCF}}(Cu_5L) \ , \qquad (2)$$

where $E_{\text{SCF}}(X)$ is the total SCF energy of unit X. Positive values of E_{int} correspond to bonding, and negative values to repulsion.

For free CO, the 1π KT IP is 2.3 eV larger than the 5σ IP; this is somewhat different from experiment due to the neglect of electron correlation and final-state relaxation.[14] When the frozen CO and Cu_5 orbitals are placed together, step A, the CO IP's shift to larger values. While the 4σ and 1π shift is 0.9 eV, the 5σ shift is dramatically larger, 4.6 eV. This leads to the 5σ IP being larger than the 1π IP by 1.4 eV, while the 4σ-1π separation is not changed significantly from free CO. These changes in the ϵ's are of purely electrostatic origin; the rigid CO orbitals "see" the potential of the (rigid) Cu_5 charge distribution. Covalent chemical bonds cannot be formed at this CSOV step. Since the CO 5σ orbital is directed toward the nucleus of the adsorption site atom, it signficantly overlaps and interpenetrates the Cu charge; to a lesser extent, this also occurs for the other CO orbitals. Thus, the CO ϵ's become smaller, more negative, because their penetration of the Cu charge means that the Cu nucleus is not fully screened; the effect is largest for the 5σ orbital. The charge interpenetration also leads to a repulsion between CO and Cu_5 of $E_{\text{int}} = -0.52$ eV. In the frozen density step B, a mixing of the occupied CO σ orbitals is allowed and results in a small 0.4 eV change of the 4σ and 5σ ϵ's, which leaves the 5σ KT IP larger than the 1π IP.

The Cu_5 charge polarization in $V(Cu_5;Cu_5)$ does not

TABLE I. Results of the CSOV analysis for (a) Cu_5CO and (b) Cu_5NH_3. For the definition of the interaction energies, E_{int}, and IP shifts, $\Delta\epsilon$, see text. The IP separations are given for comparison. All energies are in eV.

(a) Cu_5CO results

	E_{int}	$\Delta\epsilon(4\sigma)$	$\Delta\epsilon(1\pi)$	$\Delta\epsilon(5\sigma)$	$-\epsilon(1\pi)+\epsilon(5\sigma)$
Free CO calc.	· · ·	21.71[a]	17.48[a]	15.19[a]	+2.29
Step A, FO	−0.52	0.93	0.89	4.60	−1.42
Step B, FD	−0.52	1.30	0.89	4.22	−1.05
Step 1, $V(Cu_5;Cu_5)$	−0.28	1.26	0.83	4.21	−1.09
Step 2, $V(Cu_5;\text{all})$	+0.07	0.59	0.14	3.54	−1.12
Step 3, $V(CO;CO)$	+0.27	0.96	0.66	3.60	−0.66
Step 4, $V(CO;\text{all})$	+0.42	1.06	0.76	3.70	−0.64
Cu_5CO SCF	+0.45	0.92	0.87	3.15	+0.01
CO/Cu(100) expt.	~0.7[b]	· · ·	· · ·	· · ·	~0.0[c]
Free CO expt.	· · ·	· · ·	· · ·	· · ·	2.9[d]

(b) Cu_5NH_3 results

	E_{int}	$\Delta\epsilon(2a_1)$	$\Delta\epsilon(1e)$	$\Delta\epsilon(3a_1)$	$-\epsilon(1e)+\epsilon(3a_1)$
Free NH_3 calc.	· · ·	31.27[a]	17.17[a]	11.40[a]	+5.78
Step A, FO	+0.55	1.12	1.05	2.60	+4.23
Step B, FD	+0.55	1.14	1.05	2.58	+4.25
Step 1, $V(Cu_5;Cu_5)$	+0.70	1.55	1.45	3.09	+4.14
Step 2, $V(Cu_5;\text{all})$	+0.72	1.55	1.44	3.09	+4.13
Step 3, $V(NH_3;NH_3)$	+0.80	1.50	1.46	2.85	+4.38
Step 4, $V(NH_3;\text{all})$	+0.91	1.69	1.64	2.97	+4.45
Cu_5NH_3 SCF	+0.92	1.77	1.74	3.21	+4.30
NH_3/Cu(100) expt.	~0.7[e]	· · ·	· · ·	· · ·	~4.5[f]
Free NH_3 expt.	· · ·	· · ·	· · ·	· · ·	6.0[g]

[a] Koopmans' theorem IP's, $-\epsilon(n\lambda)$, for the free molecule.

[b] See Ref. 28.

[c] See Ref. 3.

[d] See Ref. 1.

[e] See Ref. 29.

[f] Experiments for NH_3/Fe; see Refs. 5 and 6.

[g] See Ref. 4.

modify the ϵ's significantly, although the repulsion between Cu_5 and CO is decreased by 0.23 eV. When charge transfer from Cu_5 to CO is allowed in $V(Cu_5;all)$, the Cu_5-CO interaction increases by 0.35 eV and becomes attractive; this is mainly due to Cu_5 to CO π donation.[9] The π charge transfer leads to an effective negative charge on the CO. All CO valence-level IP's, $-\epsilon$, decrease by 0.7 eV. It is easier to remove an electron CO^{x-} than from neutral CO. However, the change in the IP separations is small at this CSOV step. In $V(CO;CO)$, the CO charge polarizes to respond to the presence of the (polarized) Cu_5. As a result, the CO ϵ's become more negative by 0.1–0.5 eV; the 5σ FO IP is still larger than the 1π IP, but only by 0.7 eV. In the final CSOV step, $V(CO;all)$, charge transer from CO to Cu_5, almost entirely σ donation,[9] is included and leads to a rather small increase in E_{int}; the FO IP's of 4σ, 5σ, and 1π are uniformly increased by 0.1 eV. The results of this step are rather close to those of the unconstrained Cu_5CO SCF calculation. E_{int} differs by only 0.03 eV which confirms that the CSOV sequence contains the major contributions to the Cu_5-CO interaction. There are somewhat larger differences in the ϵ's 0.1–0.5 eV, between the last CSOV step and the full SCF. In part, these differences arise because the orbital energies are more sensitive to small changes in the charge distribution than is the total energy. They also arise because in the full SCF there is a mixing of the occupied orbitals of the Cu_5 and CO subunits with each other;[12,25] this mixing is not allowed in our sequence of CSOV steps. It is not important for the total energy of the neutral Cu_5CO cluster as is clearly shown by the near agreement of E_{int} for the $V(CO;all)$ CSOV step and for the full SCF. However, preliminary results from a study of final, ionic, state effects[25] show that this mixing does contribute to the IP's. The difference between the 5σ and 1π IP shifts changes somewhat for the various CSOV steps, from 3.7 eV at the FO superposition, CSOV step A, to 2.3 eV for the unconstrained SCF calculation. However, the large FO value clearly shows the dominant electrostatic origin of the differential shift.

The results for ammonia ionization are qualitatively very similar to those for CO. The $1e$ KT IP of free NH_3 is 5.8 eV larger than the $3a_1$ IP; this is close to the experimental difference, ≈ 6.0 eV (Ref. 4). The superposition of the frozen NH_3 and Cu_5 orbitals, CSOV step A, leads to an increase of the NH_3 IP's which is about the same for the $2a_1$ and $1e$ orbitals, 1.1 eV, but considerably larger for $3a_1$, 2.60 eV. As a consequence, the $1e$-$3a_1$ IP splitting of the free molecule is reduced by 1.5 eV. The change is due to different electrostatic effects for the $3a_1$ orbital compared to $1e$ or $2a_1$. The $3a_1$ N lone pair is directed towards the absorption site Cu atom and penetrates into the Cu charge to a much larger extent than the NH_3 $2a_1$ and $1e$ orbitals, which are localized between N and H in the molecule. In contrast to Cu_5CO, the charge superposition of NH_3 and Cu_5 results in an attraction, $E_{int} = +0.55$ eV, which can be explained by the large NH_3 dipole moment and its orientation $(N^-H_3^+)$ with respect to Cu_5.[8,9,26] When mixing of the occupied NH_3 a_1 orbitals is allowed, step B, the $2a_1$ and $3a_1$ KT IP values are only very slightly modified.

The Cu_5 charge polarization at step $V(Cu_5;Cu_5)$ leads to an increase of all NH_3 derived valence IP's by about the same amount, 0.4–0.5 eV. These shifts are considerably larger than the corresponding shifts for Cu_5CO, which is explained by the increased Cu_5 charge rearrangement[9] in the presence of the large NH_3 dipole moment. However, the binding-energy contribution due to Cu_5 polarization is found to be somewhat smaller in Cu_5NH_3, 0.15 eV, than in Cu_5CO, 0.24 eV. Charge transfer from Cu_5 to NH_3, included in $V(Cu_5;all)$, has only a minor influence on both E_{int} and the NH_3 IP shifts; this is expected since there is no significant metal to ammonia donation.[9] Polarization of the NH_3 in response to the (polarized) Cu_5, $V(NH_3;NH_3)$, which increases the binding by 0.08 eV, results in changes of the $\Delta\epsilon$ values by very small amounts for $2a_1$ and $1e$, 0.02–0.05 eV, while the effect on $\Delta\epsilon(3a_1)$ is larger, 0.24 eV, but still small. The last CSOV step, $V(NH_3;all)$, includes, in addition, NH_3 to Cu_5 donation involving the lone-pair $3a_1$ orbital.[9] This increases the binding by 0.11 eV; the NH_3 derived valence IP's increase by 0.1–0.2 eV. The Cu_5NH_3 binding energy at the last CSOV step is, as in Cu_5CO, very close to the unconstrained SCF result which confirms the validity of the energy decomposition. The differential lone-pair $3a_1$ IP shift of ≈ 1.5 eV in NH_3, which arises already in the frozen orbital superposition (step A), varies by less than 0.2 eV among the CSOV steps. This confirms its electrostatic origin.

IV. CONCLUSION

The present study on $Cu_5(1,4)CO$ and $Cu_5(1,4)NH_3$ clearly demonstrates the dominant electrostatic contribution to the observed differential lone-pair IP shifts for chemisorbed CO and NH_3. The separations between the CO derived valence orbital IP's in Cu_5CO, computed in the KT approximation, reproduce the experimental findings;[3] the 1π-4σ IP separation remains almost constant between free CO and the adsorbed molecule, while the 5σ-1π IP separation is drastically reduced. Preliminary results[27] for a much larger $Cu_{29}CO$ cluster give essentially identical changes in the CO ϵ's for CSOV steps 1–4. The similarity in the $\Delta\epsilon$ results for Cu_5CO and $Cu_{29}CO$ is very strong evidence that our conclusions are indeed valid for chemisorbed CO. For NH_3, the differential $3a_1$ IP shift is also of dominantly electrostatic origin. The separations between the KT IP's of the NH_3 derived valence orbitals in Cu_5NH_3 are consistent with experimental results for NH_3 on transition metals, e.g., iron.[5,6] The $3a_1$-$1e$ separation is reduced by ≈ 1.5 eV between free NH_3 and the adsorbed molecule, while the $1e$-$2a_1$ separation remains constant. Even though the importance of the electrostatic potential effect has been demonstrated for Cu(100), it should also be important for other metals.[12,13] In the case of open d-shell metals, where the ligand to metal σ donation is somewhat more important,[10,11] there may also be shifts due to dative 5σ-d bonding. However, these will occur in addition to the electrostatic effects which we have shown to be important.

Our results unambiguously show that the differential lone-pair IP shift does *not* measure the nature of the dative covalent bonding. On the other hand, the shift does show that the adsorption geometry has the lone-pair orbital directed toward the surface.[12] The magnitude of the shift may be a measure of the distance between the adsorbate and the metal surface.[12,13]

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