Adsorbate Ionicity and Surface-Dipole-Moment Changes: Cluster-Model Studies of Cl/Cu(100) and F/Cu(100)

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A cluster-model study of Cl and F chemisorbed at a fourfold site of Cu(100) shows that the halogen ionicity is essentially -1. The interaction and bonding arise, almost entirely, from the Coulomb attraction between the charged halogen and metal and from the polarization of the electrons associated with these units; covalent bonding makes a very small contribution. The polarization dramatically reduces the dipole moment from that given by the unpolarized ionic units. Thus, changes in the work function are not a measure of the adsorbate ionicity.

When an adsorbate layer forms on a metal surface, the work function, ϕ, of the system may change. Since ϕ depends on the surface dipole, this change in ϕ has been used[1,2] to estimate the ionicity of the bond between substrate and adsorbate. We studied the interaction between a halogen (F,Cl) and a square pyramidal Cu_5 cluster modeling the fourfold hollow site on the Cu(100) surface. Attention will be focused on the ionic character of the bonding and on the importance of polarization effects for the dipole-moment changes resulting from the bonding. The major polarization effect arises from the redistribution of the substrate electrons away from the negatively charged adsorbate.

It will be demonstrated below that the bonding in Cu_5X, $X = F$ or Cl, is nearly completely ionic and that both the Cu_5^+ and X^- ions polarize to a large extent. This intraunit polarization reduces the dipole moment from that due to the superposed and orthogonalized charge distributions of Cu_5^+ and X^-. The change in ϕ is related to the change in the surface dipole; however, because of the effects of polarization this change cannot be related in a simple way to the degree of ionicity of the adsorbate-substrate interaction.

The Cu_5 cluster used (see Fig. 1) models the fourfold hollow site on a Cu(100) surface[3]; this is the Cl chemisorption site determined from experimental data.[4,5] The Cu atom distances are fixed at their bulk values.[6] The halogen atom to surface distance in Cu_5X ($X = F$ or Cl) is varied along the C_{4v} symmetry axis (z axis); the distance of X from the surface plane is denoted by r. Self-consistent-field (SCF) wave functions[7] were obtained for these clusters with use of contracted Gaussian-type basis sets.

In order to facilitate the calculations, the He core of F and the Ne cores of Cl and Cu were replaced by effective core potentials (ECP). Cu is described with use of the frozen orbital ECP method of Pettersson *et al.*[8]; the $3s$ and $3p$ Cu shells are frozen at their free-atom (ECP) character in the cluster calculations. The orbitals occupied by the electrons arising from the Cu

$3d$ and $4s$ shells and the halogen valence s and p shells are varied in the cluster SCF calculations. The Cu basis set is large enough to permit a flexible description of the $3d$ and $4sp$, conduction-band, electrons; two diffuse p basis functions describe the hybridization of the atomic $4s$ shell. The basis set optimized for the neutral Cl atom was extended with diffuse functions of s, p, and d symmetry in order to obtain a good approximation for the SCF electron affinity (EA) of Cl and for the dipole polarizability, α_D, of Cl^-. The basis set optimized[9] for neutral F was extended only with a diffuse p function. Details of the basis sets and ECP parameters will be given elsewhere.[10] In order to test the Cu ECP, the Cu_5-cluster results obtained with the ECP were compared to those from an all-electron calculation[7]; the agreement was very good.[10]

For distances near the Cu-halogen equilibrium separation, the ground state of the Cu_5X clusters is $\dots 1a_1^2 2a_1^2 3a_1^2 1e^4 2e^2 (^3A_2)$; the halogen cores, $1s^2$ for F and $1s^2 2s^2 2p^6$ for Cl, as well as the Cu $1s^2$ to $3d^{10}$ cores are not explicitly given. This state arises by the combination of the ground state[7] of Cu_5, $a_1^2 e^3$, with the seven valence electrons of X in the configuration $a_1^2 a_1^2 e^3$. The main bonding effects are in the e shells and can be viewed as either covalent or ionic. In the covalent view, the open e shells of Cu_5 and X combine to form a filled, $1e^4$, bonding and a half-filled, $2e^2$, antibonding orbital. In the ionic view, the Cu_5 cluster is ionized to form $Cu_5^+ a_1^2 e^2 (^3A_2)$ and the electron is added to the halogen to form the closed shell
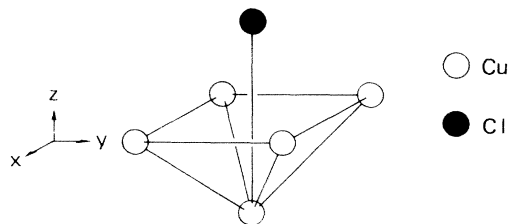

FIG. 1. Schematic representation of the Cu_5X, $X = F$ or Cl, cluster.

$X^- a_1^2 a_1^2 e^4$. The energies and the nonzero, z, component of the dipole moment, μ, of the Cu_5X cluster for X-to-surface distances near equilibrium, r_e, are given in Table I. The energies are relative to the energy of the cluster for the largest X-to-Cu separation given in Table I. The interaction curve is rather shallow; r_e is 4.16 bohrs (2.20 Å) corresponding to a Cu-Cl interatomic distance of 2.84 Å. This is somewhat larger than the R(Cu-Cl) value of 2.4 Å for Cl/Cu(100) deduced from experiment.[4,5] However, since the bonding curve is shallow, small errors could easily be responsible for the difference; our small cluster gives a Cu-Cl bond length reasonably consistent with experiment. The r_e for Cu_5F is 1.49 Å; this is consistent[11] with the smaller size of F but there are no experimental data.

It is tempting to use the nonzero z component of the cluster dipole moment, μ, to estimate the halogen ionicity in Cu_5X. For a simple view of the ionicity q of Cl in $Cu_5^{+q}Cl^{-q}$, we assume that the missing charge of Cu_5^{+q} is localized on the four surface-layer atoms and the excess charge of Cl^{-q} is spherical about the Cl nucleus; then $\mu \approx -qr$. [We neglect the small μ, -0.26 a.u. (1 a.u. = 2.54 D) of the bare Cu_5 cluster.] For Cl 4.08 bohrs above Cu_5 (near r_e), $\mu = -1.13$ a.u. and this would indicate a small charge, ≈ 0.3 electron. However, the change in μ for Cu_5Cl as r is varied is reasonably constant, and the slope suggests a large ionicity. With the assumptions described above, $\Delta\mu \approx -q\Delta r$ and $q \approx 1.5$. A Mulliken population analysis gives an intermediate value of $q \approx 0.6$, but this is an unreliable way to estimate ionicity.[12,13] As shown in Table I, there are similarly contradictory ionicity estimates from the magnitudes and slope of μ for Cu_5F.

An accurate evaluation of the ionicity is required and we use an approach based on the overlap of the Cu_5X cluster orbitals with those of free X^- illustrated with reference to Cu_5Cl. We make a unitary transfor-

mation of the orbitals of Cu_5Cl to form the corresponding orbitals[11,13,14] between Cu_5Cl and Cl^-; this transformation leaves the determinantal SCF wave functions unchanged. The overlap between the corresponding orbitals of the two systems, $\phi_i^f(Cl^-)$ and $\phi_i^f(Cl_5Cl)$, is diagonal:

$$\langle \phi_i^f(Cl^-)|\phi_j^f(Cu_5Cl)\rangle = \lambda_i \delta_{ij}. \tag{1}$$

The $\phi_j^f(Cu_5Cl)$ for which there is no counterpart in Cl^-, $j > 2(a_1)$ and $> 1(e)$, are orthogonal to the Cl^- orbitals. A reasonable measure of the charge associated with Cl in Cu_5Cl is made by summation of the squares of the nonzero overlap integrals of Eq. (1). This gives a Cl ionicity of -0.93 at $r = 4.08$ bohrs with similar values for nearby points; for Cu_5F, the F ionicity is -0.96 at $r = 2.83$ bohrs. The corresponding orbital analysis gives strong evidence that the halogen-metal interaction is essentially entirely ionic. We present additional evidence that the interaction is ionic and then address why the magnitude of the dipole moment is so small.

In order to understand the origin of the Cu-Cl interaction, we apply a constrained space-orbital variation (CSOV).[13,15] With the CSOV approach, it is possible to determine the importance of individual parts of the charge rearrangement which occurs when certain types of chemical bonds are formed between the constituent units of a system. The essence of the CSOV is that only a subset of the orbitals are varied while the remainder are held fixed. (However, the entire set of orbitals are required to be orthogonal so that a proper variational calculation is performed.) The CSOV is uniquely able to determine the respective energetic importance of intraunit polarization, e.g., formation of an image charge, and interunit covalent bonding and charge transfer. We start, CSOV step 0, with the superposed Cu_5^+ and Cl^- charge distributions; this gives the frozen-orbital (FO) interaction. Then we allow, CSOV step 1, the Cu_5^+ orbitals to vary

TABLE I. Relative energies, ΔE, in electronvolts, and dipole moments, μ, in atomic units (1 a.u. = 2.54 D), for Cu_5X clusters as function of separation r in atomic units. Only the z component of the dipole moment is nonzero by symmetry. r_e denotes the calculated equilibrium distance.

| | Cu_5F | | | | Cu_5Cl | | |
r^a	ΔE	μ	$\Delta\mu$	r^b	ΔE	μ	$\Delta\mu$
3.33	-0.00	-1.14	$\cdots$	4.33	0.00	-1.52	$\cdots$
3.08	-0.09	-0.82	$+0.32$	4.08	-0.01	-1.13	$+0.39$
2.83	-0.13	-0.51	$+0.31$	3.83	$+0.04$	-0.74	$+0.39$
2.58	-0.10	-0.23	$+0.28$	3.58	$\cdots$	$\cdots$	$\cdots$
				3.33	$+0.40$	-0.01	$+0.73$

$^a r_e = 2.82.$ $^b r_e = 4.16.$

with those arising from Cl^- held fixed; this step permits the Cu_5 charge to rearrange, polarize, as a result of the presence of Cl^-. In principle, charge transfer from Cu_5^+ to Cl^- is possible but this is very small; Cl^- is not an electron acceptor. For CSOV step 2, the Cu_5^+ orbitals are fixed as determined at step 1 and the Cl^- orbitals are allowed to vary. This variation is limited to the virtual space of Cl^- and only intra-Cl^- charge polarization is allowed. For CSOV step 3, the Cl^- orbitals are varied in the full, Cl and Cu, basis-set space (excluding the occupied Cu_5 orbitals in Cu_5Cl). In this step Cl^- to Cu_5^+ charge transfer as well as Cl^- polarization is possible. In CSOV step 4, the covalent mixing between the valence e orbitals, $1e^4(Cl^-3p_\pi)$ and $2e^2(Cu_5^+e^2)$, is allowed; all other orbitals are fixed as determined at step 3. The results of step 4 are compared to the full, unconstrained, SCF results; if they are nearly the same, all important bonding effects are included in the series of CSOV steps. For each step, we consider the interaction energy, E_{int}, with respect to separated ions, Cu^{5+} and Cl^-, and the dipole moment μ. The E_{int} is defined as

$$E_{int} = E(Cu_5^+) + E(Cl^-) - E(Cl_5Cl),$$

where $E_{int} > 0$ indicates attraction.

For Cu_5Cl at $r = 4.08$ bohrs, near r_e, the values of E_{int} and μ and the changes between successive CSOV steps, ΔE_{int} and $\Delta\mu$, are given in Table II. There is already a strong electrostatic attraction of 2.9 eV between the Cu_5^+ and Cl^- FO ions at step 0. At step 1, this attraction is increased 1.3 eV by the polarization of Cu_5^+ charge which $\Delta\mu$ shows is away from Cl^-. This polarization reduces the repulsive contribution to the interaction due to the interpenetration of the FO Cu_5^+ and Cl^- charge distributions (a Pauli repulsion); it also enhances the electrostatic attraction between the (polarized) Cu_5^+ and Cl^- units. The step-2 intra-Cl^- charge polarization further increases the attraction by a

smaller amount, 0.5 eV. The full space variation of the Cl^- charge in step 3 gives a 0.3-eV contribution to E_{int} from the Cl^--to-Cu_5^+ charge transfer. (This small value is an upper bound because of basis-set superposition artifacts.[12]) Clearly this is small and consistent with the corresponding orbital Cl ionicity of -0.93; since Cl in Cu_5Cl is largely Cl^-, there is not very much charge transfer from Cl^-. Again, as expected from the large Cl^- ionicity, the $1e^4$-$2e^2$ covalent interaction leads to small changes in E_{int} and μ at CSOV step 4. The near agreement between the full SCF and step-4 E_{int} and μ shows that no important bonding effects have been neglected. This analysis clearly shows that there are two main contributions to the ionic interaction of Cl and Cu. The first is the FO Coulomb attraction and the second is the polarization of the Cu_5^+ and, to a lesser extent, of the Cl^- units; charge transfer from Cl^- to Cu and covalent bonding effects are small. Similar results are found for Cu_5F.

The small μ for this ionic interaction is also explained by the CSOV analysis. The FO μ is nearly that expected from placement of a point charge above Cu_5^+. When the Cu_5^+ charge is allowed to polarize, the Cu_5^+ electrons move away from Cl^- and dramatically reduce the magnitude of the dipole moment. This charge motion leaves the Cu_5^+ more positively charged near the surface, an "image charge" formed by moving the Cu_5 electrons further away from the surface. The polarization of Cl^- charge toward the positive surface further enhances the decrease of $|\mu|$. This charge polarization explains the apparent disagreement between small changes in ϕ and large adsorbate ionicity. In particular, it explains why Westphal and Goldmann[2] deduce an effective negative charge on Cl of only 0.1 electron from changes in ϕ, while our calculations show that the Cl charge is ≈ -1.

A Cu surface is more polarizable than the Cu_5 clus-

TABLE II. CSOV analysis for Cu_5Cl at $r = 4.08$ a.u. Interaction energies, E_{int} in electronvolts given relative to the separated ions (see text) and μ in atomic units.

Step	E_{int}	ΔE_{int}	μ	$\Delta\mu$
0. Frozen orbital interaction	+2.88	⋯	−4.42	⋯
1. Cu_5^+ polarization, full basis	+4.16	+1.28	−2.41	+2.01
2. Cl^- polarization, Cl basis only	+4.62	+0.46	−1.66	+0.75
3. Cl^- polarization, full basis	+4.90	+0.28	−1.44	+0.22
4. Covalent e-symmetry interaction	+4.94	+0.03	−1.37	+0.07
Full SCF	+4.98	+0.04	−1.13	+0.24

ter and there will be a larger effect due to the motion of electrons at Cu surface in response to the presence of a chemisorbed halogen anion. The cluster provides a limited representation of the image charge formed at the surface.[16] The additional polarization at a metal surface will lead to an even larger decrease in the $|\mu|$ than we have found with our Cu_5 cluster; see Table II. The quantitative effect of the metal intraunit polarization is larger than we find with the Cu_5 cluster. This may be why Westphal and Goldman[2] conclude from work-function changes that Cl on Cu(100) has a charge of $-0.1e$ while a simple analysis of the Cu_5Cl dipole moment indicates a larger charge of $\sim -0.3e$. The critical fact is that the changes in ϕ and in the cluster dipole moment both are much less than would be expected from the large adsorbate ionicity. The qualitative cluster result that the origin of the small change in the surface dipole is due to metal polarization away from the halogen anion clearly applies to an extended metal surface.

In addition, the adsorption bonding energy of a halogen anion on a Cu surface will be larger than that obtained with the cluster. The metal polarization at a Cu surface will give a larger contribution to E_{int} than the 1.3 eV for the Cu_5Cl cluster; see Table II. The SCF wave function also underestimates electron affinities; our calculated EA's are 1.3 eV (F) and 2.6 eV (Cl) which are 2.1 and 1.0 eV smaller, respectively, than experiment.[17] (The Cu_5-cluster SCF ionization potential, 4.4 eV, is slightly smaller than the Cu work function.[18]) The EA and cluster-size limitations make the calculated bonding energy too small; on an extended metal surface, the halogen anionicity will be even more energetically favorable. Even so, the halogens are essentially fully anionic for the Cu_5X cluster.

Our CSOV analysis shows that dipole-moment changes due to the metal charge rearrangements can be viewed as arising from two canceling effects: first, the transfer of charge from the metal to the adsorbate which leads to a negative dipole moment, and second, the polarization of the metal charge away from the negatively charged adsorbate which, to a large extent, cancels the first effect. All metal surfaces are easily polarized. Thus, we expect this cancellation to occur generally and not just for Cu surfaces. The energetic cost of removing an electron from the metal,[18] work function, to form the halogen anion is similar for many metals. Thus, halogen adsorption is likely to be generally anionic.

For chemisorbed halogens, the adsorbate is at a relatively large distance above the surface; see Table I. For the much shorter distances appropriate, for example, to O chemisorption, it will be interesting to determine if the metal polarization has a similar impor-

tance. Lang[19] has focused on somewhat different aspects of the charge rearrangement associated with the ionic chemisorption of O.

In conclusion, the bonding of F and Cl on Cu is almost entirely ionic. With the CSOV analysis, we have, for the first time, rigorously separated the contribution of intraunit polarization from other, charge transfer and covalent hybridization, charge rearrangements. This analysis shows that the dipole moment does not directly reflect the ionicity of the cluster-adsorbate bond because of important polarization effects both in the substrate and the adsorbate. Thus, the measured change in ϕ due to adsorption cannot be used to determine the ionicity of the adsorbate.

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