Communication

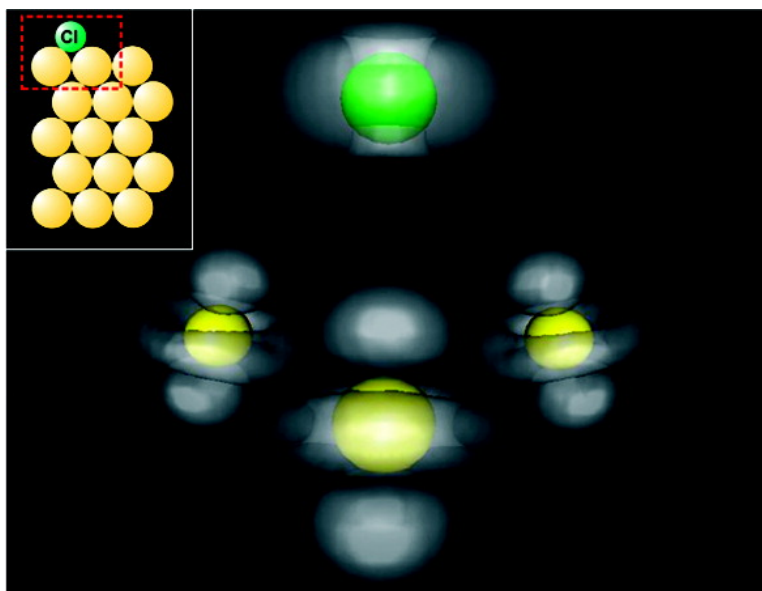# Nature of Cl Bonding on the Au(111) Surface: Evidence of a Mainly Covalent Interaction

Thomas A. Baker, Cynthia M. Friend, and Efthimios Kaxiras

More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Links to the 1 articles that cite this article, as of the time of this article download
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

View the Full Text HTML

Nature of Cl Bonding on the Au(111) Surface: Evidence of a Mainly Covalent Interaction

Thomas A. Baker,[†] Cynthia M. Friend,[†,‡] and Efthimios Kaxiras*[,‡,§]

Department of Chemistry and Chemical Biology, Harvard University, 12 Oxford Street, Cambridge, Massachusetts 02138, School of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts 02138, and Department of Physics, Harvard University, 17 Oxford Street, Cambridge, Massachusetts 02138

Bonding of strongly electronegative halogen atoms on metal surfaces is of fundamental importance in understanding surface adsorption and has been studied extensively with experimental[1−4] and theoretical[5−8] tools. A particularly interesting case is the interaction of chlorine on the Au(111) surface,[9−12] which has advantages for various applications: Gold(III) chloride is used as a homogeneous catalyst for several important organic reactions including intramolecular cyclizations and cross-cycloisomerization reactions.[13,14] In heterogeneous chemistry, chlorinating reagents with gold can be used, for instance, to remove mercury emissions from coal-fired boilers;[15] chlorine also increases the selectivity of styrene epoxidation on Au(111)[16] and acts as a poison for CO oxidation on supported gold particles.[17,18]

In this letter, we report theoretical evidence from first-principles density functional theory (DFT) calculations that the bonding between Cl and the Au(111) surface is primarily covalent in character. This is in contrast to the generally held view that the bonding of halogens to metal surfaces is ionic: Doll et al.[7] concluded from their theoretical studies that the interaction of Cl on Ag(111) is mainly ionic based on the finding that there is only a small overlap population between Cl and Ag and the chlorine charge is larger in the orbitals that are the most separated from silver. Bagus et al.[5] and Rubio et al.[8] used cluster calculations and found that a halogen atom on silver and mercury surfaces has a net charge of one electron. However, Quattrucci et al.[19] reported that they "do not observe significant charge transfer to the Cl [adsorbed on Au(111)]". Experimentally, the change in the work function can be used to measure the charge of an adsorbate.[20] Theoretical work predicts[21] a positive work function change (indicating a negatively charged adsorbate) for chlorine adsorption on the (001) surfaces of Cu, Ag, and Au and a negative change (indicating a positively charged adsorbate) on Rh, Pt, and Pd. While the general conclusion is chlorine ionically bonds on all of these metal surfaces, these theoretical results show that the experimental work function changes should be treated with caution in interpreting the adsorbate charge.

In the present work we use periodic slabs and GGA-PW91 to model the surface and electron exchange and correlation in the context of DFT calculations and examine the nature of Cl bonding on Au(111). Our choice of surface supercell is a $(\sqrt{3} \times \sqrt{3})R30°$ structure relative to the ideal bulk-terminated plane, with one adsorbed Cl atom per unit cell, which corresponds to Cl coverage of 0.33 monolayer (ML). The Cl atom is placed either on top of a surface Au atom or at the 3-fold hollow fcc site; in a previous report[12] we showed that the latter is the preferred binding site of Cl on this surface. Calculations were done at higher chlorine coverages, with similar results. One of the most important characteristics of a covalent bond is the localization of electronic

density between the two atoms participating in the bond,[22] whereas ionic character is assigned to a bond involving a transfer of electrons without localization between the atoms. We will employ electron density plots to examine the bonding between Au and Cl on the Au(111) surface.

To isolate the interaction between the Au surface and the adsorbed Cl atom, we calculate the difference in electronic density between the combined system (Cl adsorbed on the Au(111) surface) and the separate isolated components (free surface and free Cl atom) with atomic positions frozen at the optimized surface geometry with the adsorbate. This charge density difference for the two positions of the adsorbate is shown in Figure 1: there is an accumulation of electronic density in the region between the chlorine atom and its nearest neighbor Au atom in both cases. Since Cl is a highly electronegative atom, we can expect it to attract electrons from the Au substrate. A purely ionic interaction would result in an increase of the electronic density of chlorine in a symmetric fashion around the chlorine atom. Figure 1, in contrast, shows that electron density is removed from the region around the Cl atom and is added in the region between the chlorine and nearest neighbor Au atom. The degree of electron density accumulation between the chlorine and gold is more pronounced when Cl is bound on top of the gold atom (Figure 1a). When the coordination of chlorine decreases, the bond distance decreases (from 2.69 Å at the 3-fold hollow fcc site to 2.39 Å at the top site), and the electron density between Cl and the nearest Au neighbor increases (see the Supporting Information). Electron density is removed from the spherical region located around both the chlorine and the gold atom to contribute to the bond. This effect is reduced when Cl is situated at the hollow fcc site because of the higher coordination in this case. Figure 1 also shows a significant perturbation of the electronic density in the first layer of the gold substrate.

The degree of mixing between Au and Cl electronic states serves as another piece of evidence for covalent bonding between the Au substrate and the adsorbed Cl atom. Figure 2 shows the p electron partial density of states (p-PDOS) of Cl and Au as a function of energy for Cl at the hollow fcc site. The presence of common peaks in the Cl and Au p-PDOS suggests strong mixing of the two sets of electronic states characteristic of covalent bonding. The most pronounced feature in the Cl p-PDOS is a peak at ∼1.8 eV, which does not correspond to a major peak in the Au p-PDOS. To understand the nature of this peak, the electronic density of states around this energy value is shown in Figure 3. A significant covalent interaction between Au and Cl is evident, with electronic density extending over both the chlorine site and the top layer of the gold surface. The Cl orbital is a symmetric, ring shaped orbital parallel to the surface. The surface gold atoms participate in this bond through d_{z^2} atomic orbitals pointing toward the Cl position at the 3-fold hollow fcc site, in a different direction from their usual orientation on the clean surface, which is perpendicular to the

[†] Department of Chemistry and Chemical Biology.
[‡] School of Engineering and Applied Sciences.
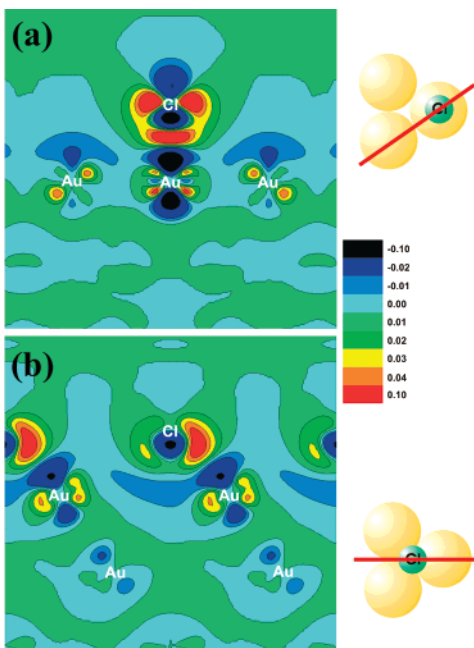[§] Department of Physics, Harvard University.

Figure 1. Charge density difference between the adsorbate system and the isolated components (gold surface and Cl atom), for Cl at (a) the top position and (b) the hollow fcc site (shown in the geometries on the right, with a red line indicating the plane of the charge difference plot). Positive values indicate accumulation of electronic charge; negative values correspond to depletion of charge. Each plot is 100 Å^2.
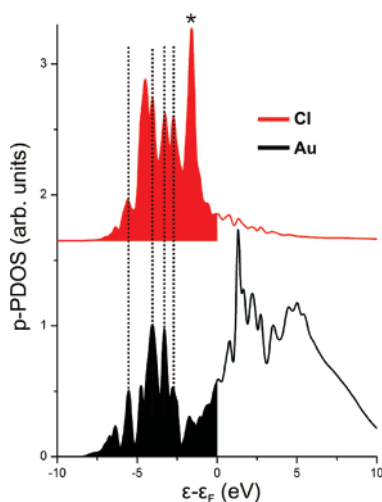

Figure 2. Density of states as a function of energy for p-electrons of Cl and Au for Cl adsorbed at the hollow fcc site on the Au(111) surface. The zero energy is the Fermi level, and filled states have shading below curve. The electron density corresponding to the states in the largest peak of the Cl p-PDOS (identified by the asterisk) is shown in Figure 3.

surface plane. The directionality of these orbitals and the mixing of Au and Cl states at this energy is strong evidence of the covalent nature of the Cl−Au interaction. Our results are at variance with the generally accepted view concerning the adsorption of halogens on metal surfaces. In general, the interaction of chlorine with metals is indeed ionic in nature, but the Au/Cl system appears to be an exception. The adsorption of chlorine on gold is unusual because gold has the highest Pauling electronegativity[23] of all transition metals, making it the most likely to form a covalent bond with the highly electronegative halogens. The difference in electronegativity between Au and Cl is 0.76, apparently small enough to lead to formation of covalent bonds. Our results do not contradict previous theoretical studies,[5−8] which concerned the interaction of chlorine
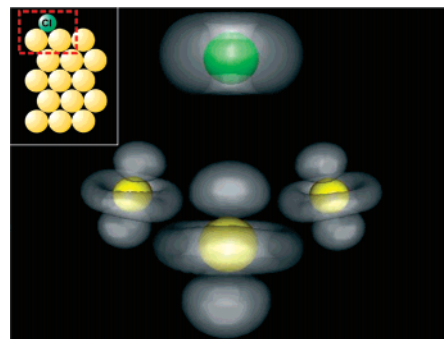

Figure 3. Electron density at the energy indicated by the asterisk in Figure 2 for Cl adsorbed at the hollow fcc site on Au(111). The inset shows a side view of the surface and the adsorbed Cl atom, with the area of the larger figure indicated by the red dotted line.

with the surfaces of other noble metals, such as silver and mercury. For example, the electronegativity difference between chlorine and silver or mercury is 1.23, considerably larger than that for the Cl− Au pair, justifying the more ionic character of the Cl−Ag and Cl− Hg interactions. Our results are particularly interesting in the context of olefin oxidation reactions, suggesting that the bonding and functionality of Cl used as a promoter is different on Ag and on Au surfaces; specifically, the degree of charge separation in the two cases may lead to a smaller perturbation in the bonding of oxygen on the Au surface vs on the Ag surface.

Supporting Information Available: Details of the calculations, results for chlorine bound to different sites, charge density plot for Cl adsorption on Ag(111), and work function results. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Shard, A. G.; Dhanak, V. R. *J. Phys.Chem. B* **2000**, *104*, 2743−2748.
(2) Shard, A. G.; Dhanak, V. R.; Santoni, A. *Surf. Sci.* **2000**, *445*, 309−314.
(3) Shard, A. G.; Dhanak, V. R.; Santoni, A. *Surf. Sci.* **1999**, *429*, 279−286.
(4) Kadodwala, M. F.; Davis, A. A.; Scragg, G.; Cowie, B. C. C.; Kerkar, M.; Woodruff, D. P.; Jones, R. G. *Surf. Sci.* **1995**, *324*, 122−132.
(5) Bagus, P. S.; Pacchioni, G.; Philpott, M. R. *J. Chem. Phys.* **1989**, *90*, 4287−4295.
(6) Doll, K.; Harrison, N. M. *Chem. Phys. Lett.* **2000**, *317*, 282−289.
(7) Doll, K.; Harrison, N. M. *Phys. Rev. B* **2001**, *63*, 6.
(8) Rubio, J.; Ricart, J. M.; Casanovas, J.; Blanco, M.; Illas, F. *J. Electroanal. Chem.* **1993**, *359*, 105−113.
(9) Spencer, N. D.; Lambert, R. M. *Surf. Sci.* **1981**, *107*, 237−248.
(10) Kastanas, G. N.; Koel, B. E. *Appl. Surf. Sci.* **1993**, *64*, 235−249.
(11) Lemoine, D.; Quattrucci, J. G.; Jackson, B. *Phys. Rev. Lett.* **2002**, *89*, 4.
(12) Gao, W. W.; Baker, T. A.; Zhou, L.; Pinnaduwage, D. S.; Kaxiras, E.; Friend, C. M. *J. Am. Chem. Soc.* **2007**, in press.
(13) Hashmi, A. S. K.; Schwarz, L.; Choi, J. H.; Frost, T. M. *Angew. Chem., Int. Ed.* **2000**, *39*, 2285−2288.
(14) Stephen, A.; Hashmi, K.; Frost, T. M.; Bats, J. W. *J. Am. Chem. Soc.* **2000**, *122*, 11553−11554.
(15) Zhao, Y. X.; Mann, M. D.; Pavlish, J. H.; Mibeck, B. A. F.; Dunham, G. E.; Olson, E. S. *Environ. Sci. Technol.* **2006**, *40*, 1603−1608.
(16) Pinnaduwage, D. S.; Zhou, L.; Gao, W. W.; Friend, C. M. *J. Am. Chem. Soc.* **2007**, *129*, 1872.
(17) Broqvist, P.; Molina, L. M.; Gronbeck, H.; Hammer, B. *J. Catal.* **2004**, *227*, 217−226.
(18) Oh, H. S.; Yang, J. H.; Costello, C. K.; Wang, Y. M.; Bare, S. R.; Kung, H. H.; Kung, M. C. *J. Catal.* **2002**, *210*, 375−386.
(19) Quattrucci, J. G.; Jackson, B.; Lemoine, D. *J. Chem. Phys.* **2003**, *118*, 2357.
(20) Lang, N. D.; Kohn, W. *Phys. Rev. B* **1971**, *3*, 1215.
(21) Migani, A.; Sousa, C.; Illas, F. *Surf. Sci.* **2005**, *574*, 297−305.
(22) Pauling, L. *The Nature of the Chemical Bond and the Structure of Molecules and Crystals; An Introduction to Modern Structural Chemistry*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960.
(23) *CRC Handbook of Chemistry and Physics*, 77th ed.; Lide, D. R., Ed.; CRC Press: New York, 1996.

JA7109234