

Another Look at Organic/Metal Interfaces: Correlation with Experiment

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ABSTRACT

The topological features of the electron density at the bond critical point (BCP), such as the Laplacian and ellipticity, were previously established as a determinative factor of the nature of a specific interfacial interaction. Herein, a general methodology for the determination of the nature of the interfacial interactions is proposed by investigating the changes of organic/metal BC parameters as consequences of both increasing the size and changing the shape of the metal surfaces. In particular, the adsorption of acrylonitrile (AN) on the model copper (Cu) clusters (Cu_n , $n = 9-14, 16, 18, 20$) simulating the actual Cu(100) surface is analyzed. Several statistical models with their goodness of fitting the data obtained by use of the topological analysis of the charge density at the AN/ Cu_n BCPs are reported. The calculated electron densities at the AN/ Cu_n BCPs are shown to be well-correlated with the experimentally determined electronic affinities (EAs) of the Cu_n clusters.

Keywords: electron density, quantum theory of atoms in molecules (QTAIM), bond critical point, organic/metal interfacial interaction, electronic affinity

1 INTRODUCTION

In our previous study [1] the quantum theory of atoms in molecules [2] was fundamentally established as a valuable means of investigating the nature of the interactions between organic molecules and metallic surfaces. The quantitative characteristics of the electron density at the organic/metal BCP contain an essential amount of chemical information on the nature of an interfacial interaction. The beauty is that the definition of a bonded interaction becomes free of any assumptions, fully physical, and convenient to be visualized by means of the topological features of the total electron density [1]. The fact that the size of transition metal clusters affects the chemisorption of an adsorbate to a great extent has been confirmed theoretically [3,4] and experimentally [5-7]. Because the shape and size of various metal clusters determine their electronic properties and reactivity, the cluster approach is physically justified as long as chemisorption is treated as a local phenomenon and long-range interactions are neglected. To explore the nature of the molecule/surface interaction, the advantages of the use of finite models of metal surfaces are versatile in terms of

both generating the adsorbate geometry reliably and having the limited size of the system involved in quantum-chemical computations at a sophisticated level. In this article, the nature of the AN/copper (100) surface interaction is extrapolated using the AN/ Cu_n ($n = 9-14, 16, 18, 20$) BCP parameters and, consequently, is correlated with the measured electronic affinities of the Cu_n clusters.

2 METHODOLOGY

The adsorption of AN on the (100) surface of the fcc copper crystal is investigated by use of several copper clusters having sizes between 9 and 20 atoms, as shown schematically in Fig. 1. The clusters have two layers of atoms and are denoted by $\text{Cu}_n(k,l)$. The subscript n denotes the total number of copper atoms in the cluster. The numbers k and l ($k + l = n$) within parentheses indicate the number of copper atoms located in the upper and bottom layers, respectively.

In a previous study [8], the adsorption of AN on $\text{Cu}_9(5,4)$ was shown to include two copper atoms, of which the first is the central atom (Cu1 in Fig. 1) and the second is an edge atom (Cu2 in Fig. 1) of the cluster. The central atom of the upper layer has the same number of nearest neighbors as an actual surface atom, while the edge atom is unsaturated with reference to one on the actual (100) surface. Hence, the $\text{Cu}_9(5,4)$ cluster has been enlarged to saturate the peripheral binding site by extending both the upper layer in $\text{Cu}_{10}(6,4)$, $\text{Cu}_{11}(7,4)$, and $\text{Cu}_{12}(8,4)$ and the bottom layer in $\text{Cu}_{13}(8,5)$ and $\text{Cu}_{14}(8,6)$. The $\text{Cu}_{14}(8,6)$ cluster has two central atoms possessing the same number of nearest neighbors as on the actual (100) surface. Denote the two central atoms by Cu1 and Cu2 in Fig. 1. $\text{Cu}_{16}(8,8)$, $\text{Cu}_{18}(9,9)$, and $\text{Cu}_{20}(10,10)$ have the same two central atoms too. Acrylonitrile was placed above the two central copper atoms before optimizing the complexes. There are indications that the copper atoms with the lowest spin density represent the most likely interaction sites [8]. In all the clusters, the concentration of the spin density is most pronounced in the vicinity of the peripheral Cu atoms of the upper layer. The unsaturated edge atoms having the lowest coordination number are not expected to simulate the copper surface (100) atoms as reliably as the central atoms of the upper layer. Thus, the interfacial interaction between C1 in AN and Cu1 in $\text{Cu}_n(k,l)$ is looked upon as being more physically realistic.

All the geometry optimizations were done within LSDA [9,10] in conjunction with the DNP (double zeta numeric -

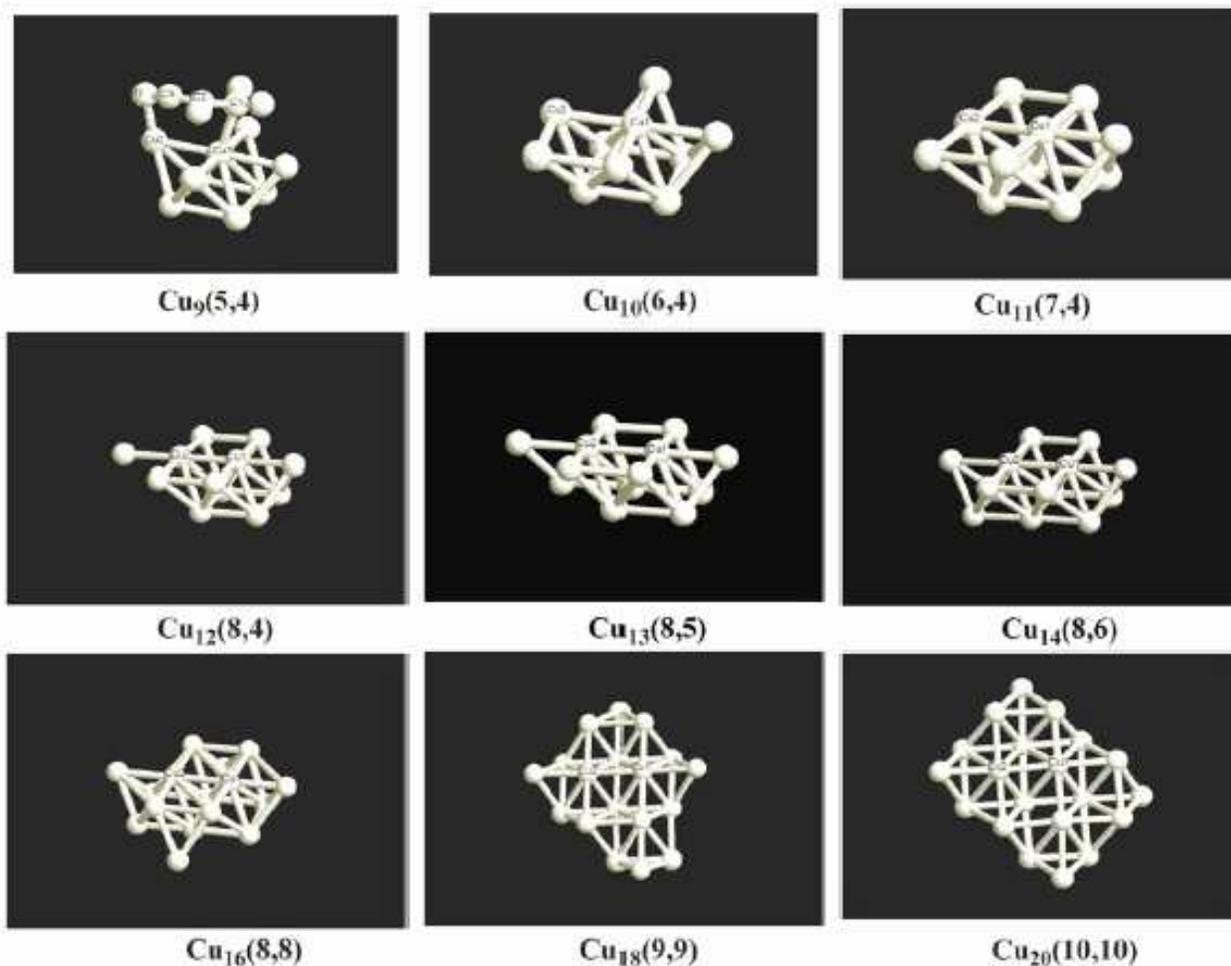


Figure 1: Clusters $Cu_n(k,l)$ simulating the Cu (100) surface. n – total # of atoms in clusters, k - # of atoms in the upper layer, l - # of atoms in the bottom layer. Acrylonitrile (AN) is bonded to Cu1 and Cu2 in all the complexes. Since Cu1 has the same # of nearest neighbors as an actual surface atom, we focus on the interfacial interactions between C1 in AN and Cu1 in $Cu_n(k,l)$.

with polarization) basis set were performed using the DMOL program [11-13]. The eigenvector-following algorithm of Baker [14] was improved to optimize the geometry in Cartesian coordinates [15] including constrains

via an efficient Lagrange multiplier algorithm [16,17]. During the optimization procedures, the distances between copper atoms in the clusters were fixed at the bulk crystal nearest-neighbor values (2.55 Å), neglecting reconstruction

Complex	d	x	ξ	ρ	∇^2	$\varepsilon_1(C1)^b$	$\varepsilon_1(Cu1)^b$	$\Delta\varepsilon_1^b$	$\varepsilon_2(C1)^c$	$\varepsilon_2(Cu1)^c$	$\Delta\varepsilon_2^c$	Δq^d
AN/Cu ₉	2.075	1.048	0.5038	0.559	2.141	-0.356	-0.894	0.538	-0.803	-0.016	0.787	0.0146
AN/Cu ₁₀	2.100	1.052	0.5009	0.534	2.310	-0.356	-0.378	0.022	-0.856	-0.021	0.835	0.0272
AN/Cu ₁₁	2.150	1.079	0.5019	0.483	2.212	-0.356	-0.158	0.198	-0.823	-0.022	0.801	0.0188
AN/Cu ₁₂	2.120	1.068	0.5038	0.505	2.327	-0.356	-0.175	0.181	-0.826	-0.033	0.793	0.0218
AN/Cu ₁₃	2.140	1.074	0.5018	0.495	2.204	-0.356	-0.130	0.226	-0.833	-0.046	0.787	0.0178
AN/Cu ₁₄	2.116	1.060	0.5000	0.522	2.218	-0.356	-0.091	0.265	-0.855	-0.152	0.703	0.0171
AN/Cu ₁₆	2.140	1.075	0.5023	0.493	2.159	-0.356	-0.166	0.190	-0.832	-0.096	0.736	0.0187
AN/Cu ₁₈	2.160	1.092	0.5055	0.471	1.971	-0.356	-0.149	0.207	-0.778	-0.112	0.666	0.0204
AN/Cu ₂₀	2.080	1.053	0.5062	0.553	2.091	-0.356	-0.220	0.136	-0.831	-0.086	0.745	0.0149

^aBCP = the C1-Cu1 bond-critical point, $d = d(C1-Cu1)$, $x = d(Cu1-BCP)$, $\xi = x/d$, $\rho = \rho(BCP)$, $\nabla^2 = \nabla^2\rho(BCP)$.

^b $\Delta\varepsilon_1 = |\varepsilon_1(Cu1) - \varepsilon_1(C1)|$; $\varepsilon_1(C1)$, $\varepsilon_1(Cu1)$, natural charges on C1 and Cu1 before complexation.

^c $\Delta\varepsilon_2 = |\varepsilon_2(Cu1) - \varepsilon_2(C1)|$; $\varepsilon_2(C1)$, $\varepsilon_2(Cu1)$, natural charges on C1 and Cu1 after complexation.

^d Δq —ellipticity

Table 1: The B3LYP/6-31+G* parameters at the C1-Cu1 BCP in the AN/Cu_n ($n = 9-14, 16, 18, 20$) complexes.^a

phenomena. The single-particle density matrices needed for the investigation of the topology of the electron density were constructed with the B3LYP/6-31+G* hybrid DFT method using the GAUSSIAN 98 suite of programs [18]. A combination of Becke's three-parameter hybrid exchange functional [19], as implemented in GAUSSIAN 98 [20], and the Lee-Yang-Parr correlation functional [21] gives the B3LYP functional. The natural charges were computed at the same level of theory by GAUSSIAN 98. The natural charges obtained in this way were shown to be both sufficiently stable to computational parameters [22] and insensitive to the particular basis set [23]. The calculations pertaining to the topological features of the electron density were carried out using the program EXTREM [24].

3 RESULTS

The nature of the AN/copper (100) surface interfacial interaction is determined by extrapolating the AN/Cu_n (*n* = 9-14, 16, 18, 20) bond-critical parameters from a statistical standpoint. The AN/Cu_n (*n* = 9-14, 16, 18, 20) bond-critical parameters are given in Table 1. The interatomic distances *d* in this paper are given in Å, the electron density $\rho = \rho(\text{BCP})$ is in e/Å³, the Laplacian $\nabla^2 = \nabla^2\rho(\text{BCP})$ is in e/Å⁵, and the net (natural) atom charge on C1 in AN or Cu1 in Cu_n, $\varepsilon(\text{C1})$ or $\varepsilon(\text{Cu1})$, is expressed in e. The standard deviations σ_f of a fit (for *f* degrees of freedom) are quoted as a percent of the observed range of the dependent variable, for example, $\sigma_g = 0.0033 \sim 3.7\%$.

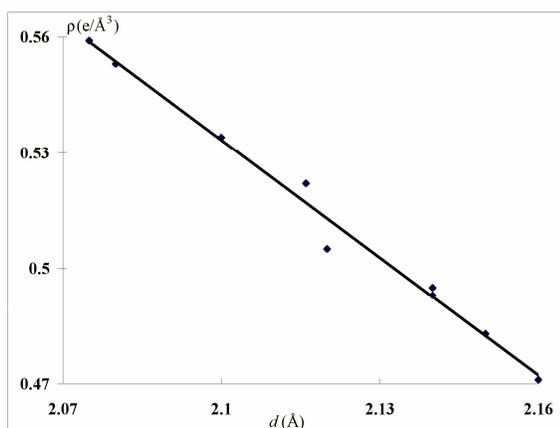


Figure 2: Correlation of *d* and ρ .

ρ increases monotonically with decreasing *d* in Fig. 2. This dependence can be represented by a linear, or a logarithmic, or a power, or an exponential function. The observed range of ρ is 0.088. A linear regression yields

$$\rho = -1.017 \cdot d + 2.669 \quad (1)$$

($r^2 = 0.987$, $\sigma_g = 0.0033 \sim 3.7\%$), a logarithmic regression yields

$$\rho = -2.152 \cdot \ln(d) + 2.129 \quad (2)$$

($r^2 = 0.987$, $\sigma_g = 0.0033 \sim 3.7\%$), a power regression yields

$$\rho = 11.753 \cdot d^{-4.171} \quad (3)$$

($r^2 = 0.986$, $\sigma_g = 0.0034 \sim 3.8\%$), and an exponential regression yields

$$\rho = 33.449 \cdot \exp(-1.971 \cdot d) \quad (4)$$

($r^2 = 0.986$, $\sigma_g = 0.0034 \sim 3.8\%$). Although eqs. (1) and (2) have a slightly smaller σ than eqs. (3) and (4), the correlations are quite satisfactory with respect to the observed range of the dependent variable. As all values of the electron density at the BCPs hover around 0.5 that is typically associated with weak donor-acceptor bonds, a value of the *d* coordinate of 2.624 at which ρ approximated by eq. (1) is equal to 0 has no a particular physical meaning.

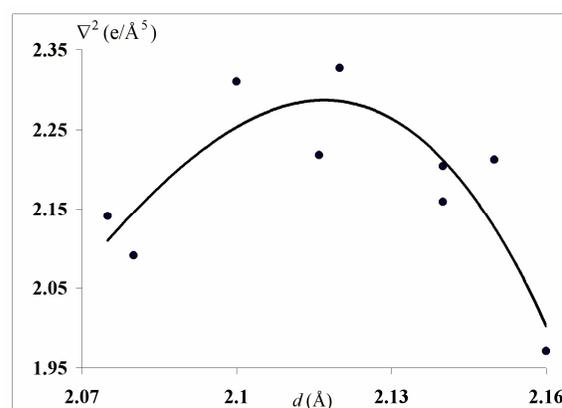


Figure 3: Correlation of *d* and ∇^2 .

The observed range of ∇^2 is 0.356. The variation of ∇^2 with *d* is approximated by a cubic polynomial (Fig. 3)

$$\nabla^2 = -629.15 \cdot d^3 + 3869.2 \cdot d^2 - 7923.2 \cdot d + 5404 \quad (5)$$

($r^2 = 0.739$, $\sigma_g = 0.0668 \sim 18.7\%$). The regression line has a maximum of 2.29 at *d* = 2.12 and crosses the $\nabla^2 = 0$ line at *d* = 2.05 and *d* = 2.17. The ∇^2 vs. ρ plot is of the

type observed for the correlation of d and ∇^2 . A cubic correlation over the entire ρ , ∇^2 data range is

$$\nabla^2 = 818.73 \cdot \rho^3 - 1385.3 \cdot \rho^2 + 775.26 \cdot \rho - 141.38 \quad (6)$$

($r^2 = 0.735$, $\sigma_g = 0.0538 \sim 15.1\%$), with a ∇^2 maximum

of 2.28 at $\rho = 0.515$ and $\nabla^2 = 0$ at $\rho = 0.468$ and $\rho = 0.587$.

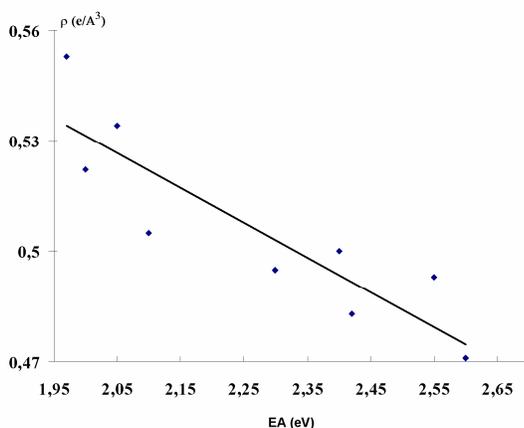


Figure 4: Correlation of measured EA and ρ .

Experimental EA values for the Cu_n clusters were taken from the literature [25]. The ρ vs. EA dependence (Fig. 4) is well-fitted with a linear regression

$$\rho = -0.0944 \cdot EA + 0.721 \quad (7)$$

($r^2 = 0.782$, $\sigma_g = 0.0262 \sim 29.8\%$), while a cubic polynomial over the entire range of ρ gives a slightly higher r^2 value of about 0.874.

4 SUMMARY

Because all chemical and physical properties of atoms and molecules are rooted in the electron density, the interfacial interactions are herein given physical definitions, free of any assumptions, and can be visualized using the topological features of the total electron density, as shown in [1]. One of the key beauties of this novel strategy is that, in getting these results essentially associated with the electronic properties and reactivity of various copper clusters, no reference to orbitals, being pure theoretical constructs, has been invoked. As the proposed methodology is independent of the scale and size of particular molecular components, its potential applications in changing and tuning the finest details of charge transfer taking place in the donor-acceptor complexes at the nanoscale is quite certain.

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