

The Formation of Neutral Copper Clusters from Experimental Binding Energies and Reactivity Descriptors

Pablo Jaque and Alejandro Toro-Labbé*

Laboratorio de Química Teórica Computacional (QTC), Facultad de Química,
Pontificia Universidad Católica de Chile, Casilla 306, Correo 22, Santiago, Chile

Received: August 1, 2003; In Final Form: November 26, 2003

In this paper we study and rationalize the formation of neutral copper clusters from dimer to nonamer using the available experimental data of binding energies and electronic properties. A complete and consistent picture of the formation of copper clusters in terms of the changes in chemical potential and hardness emerges indicating that the one-atom growth reactions are mainly driven by changes in hardness. An analytic expression for the binding energy as a function of the cluster size is proposed and used to predict the growth pattern of copper clusters.

1. Introduction

The interest in the study of small metal clusters has grown considerably in recent years because new experimental and theoretical techniques have been developed allowing detailed characterizations of these types of systems.^{1,2} Much information is now available concerning clusters' spectroscopy, structure, and their chemical reactivity toward small molecules. Transition metal clusters are particularly interesting for their potential use in many processes such as heterogeneous catalysis, organometallic chemistry, or new electronic materials.^{1,3}

An interesting topic in clusters science is the study of the evolution of clusters' properties when increasing the number of constituent atoms. Neutral even-numbered copper clusters are closed-shell systems, whereas odd-numbered copper clusters are open-shell systems.^{4–10} In investigations on ion abundances,^{11–13} ionization potentials,^{14–18} electron affinities,¹⁹ and binding energies of neutral and charged copper clusters (Cu_n),^{20,21} a typical behavior known as even–odd alternation has been found. In this paper our main goal is to provide a new viewpoint to understand the formation reaction $\text{Cu}_{n-1} + \text{Cu} \rightarrow \text{Cu}_n$ ($n = 2–9$); in doing so, the observed even–odd alternation of binding energies will be analyzed in detail. Our approach consists of the rationalization of the available experimental data of binding energies through the use of reactivity descriptors calculated from experimental data of ionization potentials and electron affinities.^{14–21} As a result of this approach, correlations between energetic and electronic properties can emerge; such correlations are expected to be useful in understanding the formation reaction of copper clusters and may provide new elements to rationalize growth reactions of metal clusters.

In a recent paper¹⁰ we have characterized neutral copper clusters (Cu_n ; $n = 1–9$) in terms of calculated chemical reactivity descriptors defined within the framework of density-functional theory (DFT), usually used to study the reactivity pattern of molecules and molecular aggregates.^{10,22,23} The set of reactivity descriptors, electronic chemical potential (μ), chemical hardness (η), and electrophilicity index (ω), together with chemical reactivity principles such as the principle of

maximum hardness, define quite powerful tools to analyze and rationalize different processes experienced by complex systems.^{10,23–26}

A formation reaction can be seen as resulting from the combination and redistribution of atom's and fragment's electron densities, giving rise to a new electronic distribution from which the electronic descriptors of the new aggregate are derived. DFT²⁷ is quite well suited to describe such electronic reorganization processes as it provides the basis for rigorous mathematical definitions of reactivity descriptors such as chemical potential, electronegativity,²⁸ chemical hardness,²⁹ softness ($S = 1/\eta$), and so forth.; all these are well-established global quantities in chemical reactivity studies and will be used in this paper to study the formation process of copper clusters Cu_n ($n = 2–9$) in one-atom growth reactions.

The chemical potential characterizes the escaping tendency of electrons from equilibrium; on the one hand it is the Lagrange multiplier associated with the normalization constraint in DFT, on the other hand it is the negative of the electronegativity ($\chi = -\mu$).²⁸ Hardness represents the resistance to charge transfer, whereas softness is a measure of the propensity of the system to change its electronic distribution and has been qualitatively related to the polarizability α .^{27,29–31} The electrophilicity index measures the stabilization of a system when it acquires electronic charge from the surroundings.³²

A major focus of attention and discussion in the application of DFT to chemical reactivity is the principle of maximum hardness (PMH) proposed by Pearson.³⁰ The PMH asserts that molecular systems at equilibrium present the highest value of hardness; the PMH is a widely accepted electronic structure principle that in most cases complements the minimum energy criterion for molecular stability. The PMH provides an independent criterion to rationalize the behavior of chemical reactions.

In the next section we present a summary of the theoretical elements we use here; section 3 contains the results and discussion, and in section 4 we draw our conclusions.

2. Theoretical Background

In DFT, the chemical potential and molecular hardness for an N -electron system with total energy E and external potential $v(\vec{r})$ are defined as the following first and second derivatives

* Author to whom correspondence should be addressed. E-mail: atola@puc.cl.

of the energy with respect to N :^{27–29}

$$\mu = \left(\frac{\partial E}{\partial N} \right)_{v(\vec{r})} = -\chi \quad (1)$$

and

$$\eta = \frac{1}{2} \left(\frac{\partial^2 E}{\partial N^2} \right)_{v(\vec{r})} = \frac{1}{2} \left(\frac{\partial \mu}{\partial N} \right)_{v(\vec{r})} \quad (2)$$

In numerical applications μ and η are calculated through the following approximate versions of eqs 1 and 2, based upon the finite difference approximation, where these derivatives are calculated numerically as energy differences between systems with $(N - 1)$, N , and $(N + 1)$ electrons:²⁷

$$\mu \approx -\frac{1}{2}(\text{IP} + \text{EA}) \approx \frac{1}{2}[E(N + 1) - E(N - 1)] \quad (3)$$

and

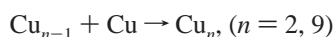
$$\eta \approx \frac{1}{2}(\text{IP} - \text{EA}) \approx \frac{1}{2}[E(N + 1) + E(N - 1) - 2E(N)] \quad (4)$$

$\text{IP} = [E(N - 1) - E(N)]$ is the ionization potential, and $\text{EA} = [E(N) - E(N + 1)]$ is the electron affinity. The electrophilicity index is in turn defined as³²

$$\omega = \frac{\mu^2}{2\eta} \quad (5)$$

When clusters or metallic surfaces are considered as binding environments, ω can be especially suited to analyze the interaction with small molecules in heterogeneous catalysis processes.

Let us consider the following process, referred to as a one-atom growth reaction:



The overall energy change that corresponds to the binding energy is given by $\Delta E = E(\text{P}) - [E(\text{R1}) + E(\text{R2})]$, where $\text{P} = \text{Cu}_n$ is the product of the reaction and $\text{R1} = \text{Cu}_{n-1}$ and $\text{R2} = \text{Cu}$ are the reactants. When dealing with an electronic property, say Ω , we define $\Delta\Omega = \Omega(\text{P}) - S\{\Omega(\text{R})\}$, ($\Omega = \mu, \eta$) and $S\{\Omega(\text{R})\} \equiv \Omega_{\text{S}}(\text{R})$ is the Sanderson's average of the property associated with the reactants R1 and R2 . The Sanderson's average of the chemical potential of reactants is given by the geometric mean of the chemical potentials of R1 and R2 :^{23,25,33–35}

$$S\{\mu\} = -[\mu_{\text{R1}}\mu_{\text{R2}}]^{1/2} \equiv \mu_{\text{S}} \quad (6)$$

The Sanderson's average for the hardness of reactants is obtained by differentiating $S\{\mu\}$ with respect to N thus obtaining^{23,25,35,36}

$$S\{\eta\} = \left(\frac{\partial \mu_{\text{S}}}{\partial N} \right)_{v(\vec{r})} = \frac{\mu_{\text{S}}}{2} \left[\left(\frac{\eta}{\mu} \right)_{\text{R1}} + \left(\frac{\eta}{\mu} \right)_{\text{R2}} \right] \equiv \eta_{\text{S}} \quad (7)$$

The difference between the averaged values ($S\{\mu\}$ and $S\{\eta\}$) with respect to the actual values obtained using eqs 3 and 4 might be attributed to relaxation of the electron density after

TABLE 1: Experimental Values of Binding Energies for Cu_n ($n = 2–9$)^a

Cu_n	$-\Delta E^b$	$-\Delta E^c$	$-\Delta E$
Cu_2	2.04 ± 0.17	1.81 ± 0.14	1.93 ± 0.11
Cu_3	1.15 ± 0.20	0.76 ± 0.23	0.96 ± 0.15
Cu_4	2.72 ± 0.20	2.03 ± 0.76	2.38 ± 0.39
Cu_5	1.85 ± 0.17	1.59 ± 0.78	1.72 ± 0.40
Cu_6	2.56 ± 0.32	1.80 ± 0.77	2.18 ± 0.42
Cu_7	2.66 ± 0.44	1.05 ± 0.79	1.86 ± 0.45
Cu_8	2.98 ± 0.35	2.16 ± 0.79	2.57 ± 0.43
Cu_9		1.02 ± 0.50	1.02 ± 0.50

^a All values are in eV. ^b Values are from CID experiments on the anionic clusters.²⁰ ^c Values are from CID experiments on the cationic clusters.²¹

bonding; the quantification of this difference may help understand the reordering of the electron density as the reaction takes place.

3. Results and Discussion

3.A. Binding Energy, Ionization Potential, and Electron Affinity. Table 1 shows the experimental values of binding energies of the neutral copper clusters (Cu_n) recently reported by Spasov et al.²⁰ and Ingólfsson et al.²¹ These authors have performed collision-induced dissociation (CID) experiments to study stability and fragmentation pathways for anionic and cationic copper clusters, respectively. Experimental data of the bond energies for $\text{Cu}-\text{Cu}_{n-1}$ systems are therefore obtained from a thermodynamic cycle using the dissociation energy of one-atom loss from charged copper clusters and electron affinities,¹⁹ in the case of anionic clusters,²⁰ or ionization potentials,^{14–18} for cationic clusters.²¹ In our analysis we have considered the average values (ΔE) which are also given in Table 1.

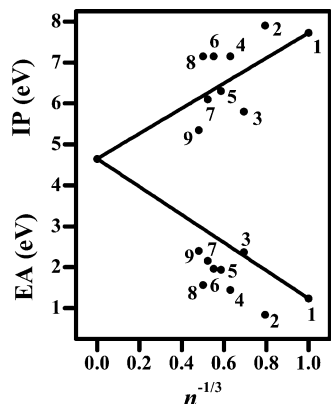
ΔE presents an oscillatory behavior: even-numbered clusters present higher values of binding energy than odd-numbered clusters, that is, chemical bonds in clusters with even n are stronger than in clusters with odd n . Therefore, in one-atom fragmentation reactions, clusters with an even number of atoms are more stable than clusters with an odd number of atoms. This is because clusters with even n present closed-shell electronic configurations that come along with an extra stability, whereas clusters with an odd number of atoms present open-shell configurations^{4–6,9,10} that make them more reactive; this is in agreement with recent studies where it has been observed that odd-numbered clusters exhibit a high reactivity in front of NO ³⁷ and O_2 .³⁸ On the other hand, in the limit of very large clusters the binding energy can approach the negative of the vaporization energy of the bulk solid; the experimental value for this property is 3.50 eV,³⁹ and it will be used as a reference value in the forthcoming discussion.

The experimental values of ionization potentials^{14–18} and electron affinities¹⁹ reported in the literature for the copper clusters considered in this work are quoted in Table 2. It should be noticed that both properties follow an even–odd oscillatory pattern which is again attributed to the change of spin multiplicity of the ground state of neutral copper clusters; even-numbered clusters present higher and lower values of IP and EA, respectively, with respect to their neighboring odd-numbered systems. Therefore, in the ionization process it is more difficult to remove an electron from the doubly occupied highest occupied molecular orbital (HOMO) than from a single occupied molecular orbital (SOMO) of an open-shell configuration cluster. In contrast to this, the electron attachment process will be more favorable in clusters with odd n because the electron will occupy

TABLE 2: Experimental Values of Ionization Potentials and Electron Affinities for Cu_n (*n* = 1–9)^a

Cu _n	IP	EA ^b
Cu	7.724 ^c	1.235 ± 0.005
Cu ₂	7.9042 ± 0.0008 ^d	0.836 ± 0.006
Cu ₃	5.80 ± 0.04 ^e	2.37 ± 0.01
Cu ₄	7.15 ± 0.75 ^f	1.45 ± 0.05
Cu ₅	6.3 ± 0.1 ^e	1.94 ± 0.05
Cu ₆	7.15 ± 0.75 ^f	1.96 ± 0.05
Cu ₇	6.1 ± 0.05 ^e	2.16 ± 0.1
Cu ₈	7.15 ± 0.75 ^f	1.57 ± 0.05
Cu ₉	5.35 ± 0.05 ^e	2.40 ± 0.05

^a All values are in eV. ^b Values are from ref 19. ^c Values are from ref 14. ^d Values are from ref 15. ^e Values are from ref 16. ^f Values are from ref 18.

**Figure 1.** Experimental values of IP and EA for copper clusters as a function of cluster size.

a half-filled orbital (SOMO), as is expected from the high values of EA of these systems.

3.A.1. Size Dependence of IP and EA. Metal clusters are aggregates that have different properties than a single atom or the bulk metal; in fact, these are the extremes that can be seen as infinitely small and infinitely large clusters. We have analyzed the evolution of IP and EA with the size of the clusters; both properties are expected to converge to the work function (Φ) in the limit as $n \rightarrow \infty$, that is, to the value of the polycrystalline copper, $\Phi = 4.65$ eV.⁴⁰ In this context, it has been shown that the evolution of a property P , such as IP and EA, as a function of the number of atoms n can be described through the following analytic form:⁴¹

$$P(n) = P(\infty) + A_P n^{-1/3} \quad (8)$$

where $P(\infty)$ corresponds to the property value in the limit of the bulk metal and A_P is a fitting parameter. Figure 1 displays the IP and EA values of the clusters; the straight lines are two-points reference lines defined from the following boundary conditions:

$$\begin{aligned} n^{-1/3} = \\ \left\{ \begin{array}{l} 0 \Rightarrow n \rightarrow \infty, \text{ bulk limit} \Rightarrow \text{EA} = \text{IP} = \Phi = 4.65 \text{ eV} \\ 1 \Rightarrow n = 1, \text{ atomic limit} \Rightarrow \text{EA} = 1.24 \text{ eV}; \text{IP} = 7.72 \text{ eV} \end{array} \right. \end{aligned}$$

From the above conditions, the two-points reference lines of IP and EA are given by

$$\text{IP}(n) = \text{IP}(\infty) + A_{\text{IP}} n^{-1/3} \quad (9)$$

and

$$\text{EA}(n) = \text{EA}(\infty) + A_{\text{EA}} n^{-1/3} \quad (10)$$

where $\text{IP}(\infty) = \text{EA}(\infty) = \Phi$; the values of the slopes are $A_{\text{IP}} = 3.07$ and $A_{\text{EA}} = -3.41$. These results will be used in turn to define reference lines for μ and η .

It should be noticed that all clusters, except Cu₃, present lower values of EA than what is expected from the reference EA line. On the other hand, the IP values of even- and odd-numbered clusters present different behaviors with respect to the reference IP line; even clusters present higher values than what is expected from the reference line, whereas odd clusters present lower values with respect to the reference IPs. This observation prompted us to conclude that the characteristic odd–even oscillatory behavior of electronic properties that depend on IP and EA should be mainly determined by the ionization potential rather than the electron affinity.

3.B. Electronic Global Properties. Using the values of IP and EA given in Table 2 in eqs 3 and 4, numerical values of chemical potential and molecular hardness are obtained; with these data the electrophilicity index for clusters from Cu to Cu₉ are estimated through eq 5, and the resulting numerical values are quoted in Table 3. Also included in this Table are the Sanderson's average of the electronic properties of reactants (μ_S and η_S) obtained using eqs 6 and 7 from the corresponding values of Cu_{n-1} and Cu. The use of Sanderson's average properties in eq 5 produces ω_S . It can be noticed that all DFT descriptors present the characteristic even–odd pattern already observed in other properties. This is also true for μ when excepting the reference Cu atom. This result is again attributed to the change in the spin multiplicity of the ground state along the series.

3.B.1. Chemical Potential and Charge Transfer. When two systems are brought together, charge transfer occurs from a system with high μ to the system with a lower value of μ . From Table 3 it can be noticed that clusters with odd n (open-shell clusters) present high value of μ ; this indicates that open-shell systems have a more marked tendency to charge transfer than closed-shell configurations (even n). The tendency to close their electronic shell by losing one electron, as indicated in Figure 1, explains the relatively high reactivity presented by odd-numbered clusters; this is in agreement with some recent experimental studies.^{37,38}

In the context of the formation reaction of molecules and aggregates, when two components (in this case Cu and Cu_{n-1}) come into interaction, their μ 's tend to equalize, thus determining the direction of charge transfer. In all cases the transfer direction is from Cu_{n-1} to Cu; the only exception to this rule occurs in the formation of Cu₇. An estimation of the charge transfer (ΔN) involved in the formation process of a two-fragment reaction can be obtained through the following expression:^{27,28,30}

$$\Delta N = \frac{(\mu_1 - \mu_2)}{2(\eta_1 + \eta_2)} \quad (11)$$

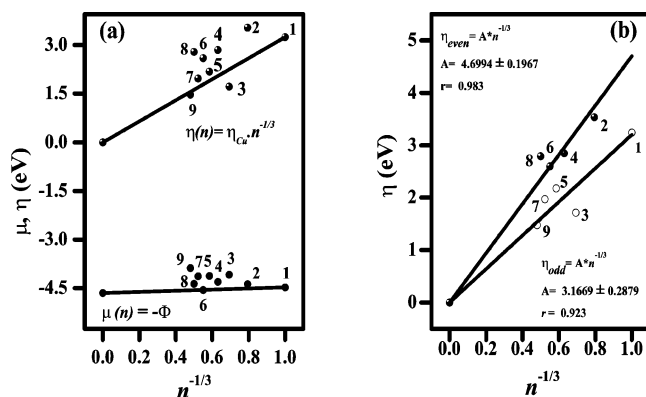
The values of ΔN as well as its two contributions are quoted in Table 4. It is interesting to note that in general ΔN is quite small although in the formation of even clusters it becomes large mainly as a result of the small value of the hardness term. Indeed, the difference of chemical potentials ($|\mu_1 - \mu_2|$) is almost constant along the series, the average value being 0.37 eV for even clusters (Cu₂ is not included in this analysis) and 0.12 eV for odd clusters, thus showing a dispersion of few tenths of an eV. The factor $2(\eta_1 + \eta_2)$ presents a clear difference in the formation of clusters with odd and even n ; the average value of $2(\eta_1 + \eta_2)$ is 11.04 eV for even clusters and 12.37 eV for odd clusters. This indicates that the formation of strong bonds

TABLE 3: Chemical Potential, Chemical Hardness, and Electrophilicity Index of Cu_n (n = 1–9)^a

Cu _n	−μ	−μ _s	η	η _s	ω	ω _s
Cu	4.4795 ± 0.0050		3.2445 ± 0.0050		3.0923 ± 0.0068	
Cu ₂	4.3701 ± 0.0061	4.4795	3.5341 ± 0.0061	3.2445	2.7019 ± 0.0071	3.0923
Cu ₃	4.0850 ± 0.0412	4.4245	1.7150 ± 0.0412	3.3914	4.8651 ± 0.1359	2.8862
Cu ₄	4.3000 ± 0.7517	4.2777	2.8500 ± 0.7517	2.4471	3.2439 ± 1.1727	3.7389
Cu ₅	4.1200 ± 0.1118	4.3888	2.1800 ± 0.1118	3.0438	3.8932 ± 0.2494	3.1641
Cu ₆	4.5550 ± 0.7517	4.2960	2.5950 ± 0.7517	2.6924	3.9977 ± 1.4871	3.4274
Cu ₇	4.1300 ± 0.1118	4.5171	1.9700 ± 0.1118	2.9226	4.3292 ± 0.2964	3.4908
Cu ₈	4.3600 ± 0.7517	4.3012	2.7900 ± 0.7517	2.5835	3.4067 ± 1.2379	3.5805
Cu ₉	3.8750 ± 0.0707	4.4193	1.4750 ± 0.0707	3.0145	5.0900 ± 0.2771	3.2394

^a All values are in eV.**TABLE 4: Estimation of Charge Transfer (ΔN) Associated with the Formation of Neutral Copper Clusters and Their Contribution in Terms of (μ₁ − μ₂) and 2(η₁ + η₂)**

Cu _n	(μ ₁ − μ ₂)	2(η ₁ + η ₂)	ΔN	ΔN _{max} ^a = −(μ/η)
Cu				1.3806
Cu ₂	0.0000	12.9780	0.0000	1.2366
Cu ₃	0.1094	13.5572	0.0081	2.3819
Cu ₄	0.3945	9.9190	0.0398	1.5088
Cu ₅	0.1795	12.1890	0.0147	1.8899
Cu ₆	0.3595	10.8490	0.0331	1.7553
Cu ₇	−0.0755	11.6790	−0.0065	2.0965
Cu ₈	0.3495	10.4290	0.0335	1.5627
Cu ₉	0.1195	12.0690	0.0099	2.6271

^a ΔN_{max} is the maximum electronic charge that can be acquired by copper clusters from their surroundings.**Figure 2.** (a) Experimental values of μ and η for copper clusters. (b) Dependence of η as a function of cluster size.

in even-numbered clusters is characterized by a high electronic charge transfer between the reactants (Cu and Cu_{n−1}) until their μ's are equalized.

Figure 2a displays the values of μ and η together with their reference lines obtained from IP(n) and EA(n), eqs 9 and 10, respectively. The two-points reference line for μ is given by

$$\mu(n) \approx -\frac{1}{2}[\text{IP}(n) + \text{EA}(n)] \approx -\Phi + 0.17n^{-1/3} \approx -\Phi \quad (12)$$

that shows a very weak dependence of μ upon n, a result that is confirmed by the experimental data points that appear scattered around the reference line. The constancy of μ along n^{−1/3} indicates that η must be the property that drives the formation reactions of copper clusters.

The fact that the average of the experimental μ values is very close to the negative of the work function Φ indicates that chemical bonds in Cu clusters are expected to be similar to those in the bulk metal; this observation is in agreement with recent works on the topology of the electron density for face-centered cubic (fcc) copper⁴² and copper clusters. These results add evidence to validate the use of metallic clusters in heterogeneous

catalysis as adequate models. It is interesting to note in Figure 2a that Cu₃ and Cu₉ present the highest values of μ along the series; this can be explained in terms of the ability of these two clusters to lose an electron to close their electronic shell thus leading to systems with two and eight valence electrons, respectively, which are magic numbers in the jellium model. Their capacity to lose an electron is reflected in the low values of the ionization potentials of Cu₃ and Cu₉ (see Table 2). Although these clusters also present the highest values for electron affinity, thus showing their capacity to gain one electron, this process does not lead to products with extra stability associated with closed-shell systems in the jellium model.

3.B.2. Chemical Hardness. The chemical hardness has been established as an electronic quantity that in many cases may be used to characterize the relative stability of molecules and aggregates through the PMH.³⁰ From Table 3 it should be noted that clusters with even n are harder than their neighbor systems following an opposite trend to that of the binding energy (ΔE); this result is in agreement with the PMH.

Figure 2a also shows the experimental hardness data points together with the two-points reference line determined from eqs 9 and 10:

$$\eta(n) \approx \frac{1}{2}[\text{IP}(n) - \text{EA}(n)] \approx \eta_{\text{Cu}} n^{-1/3} \quad (13)$$

It should be noticed that η presents quite a strong dependence upon the size of the cluster with a slope that can approach the hardness of atomic copper. A close view of Figure 2a indicates that the η reference line fits correctly the values for odd clusters, whereas those of even clusters are systematically above the line. This indicates that the extra stability of even clusters due to the closing shell effect is accompanied by an increase of the hardness value. In this context, since the average η value of even clusters is above that of odd clusters by more than 0.8 eV, it is apparent that a simple model, such as that of eq 13, is not able to reproduce the hardness variation upon n^{−1/3} of both even and odd clusters in a unified way.

When the η values of odd and even clusters are fitted separately against n^{−1/3} under the common condition that η(∞) = 0, the reference straight lines displayed in Figure 2b are obtained; the correlation coefficients are r = 0.97 and 0.98, respectively. The slope of the even clusters (4.70 eV) is larger than that of the odd clusters (3.17 eV), which in turn is quite close to η_{Cu} = 3.25 eV of the η reference line that can describe correctly the growth pattern of odd clusters only. In summary, even clusters appear to be harder than odd clusters; this is evidence that the PMH holds for these systems.

3.B.3. Electrophilicity. Once the behavior of μ and η is discussed, a comment on the trend observed in the electrophilicity index is in order (see Table 3). In Cu_n the behavior presented by ω is mainly due to the term 2η since, as already

pointed out, μ remains quite constant along the series. Clusters with odd n are considerably softer than those with even n ; this leads to high values of ω . The quantification of the maximum electronic charge that can be acquired by the systems until it reaches a stabilization energy, $\Delta E = -\omega$, is given by $\Delta N_{\max} = -(\mu/\eta)$;³² these values are quoted in Table 4. Note that clusters with odd n will acquire more charge until saturation than clusters with even n which are more stable because they are already saturated. Therefore, the maximum electrophilic power presented by odd clusters is due basically to low values of η ; this result is in agreement with the expected capacity of odd clusters to reach a closed-shell electronic configuration by accepting electronic charge from their surroundings.

3.B.4. Relaxation Effects. The difference between the electronic property calculated using the Sanderson's average (eqs 6 and 7) with respect to the actual value determined from the IPs and EAs (eqs 3 and 4) allows one to quantify the effect of relaxation and redistribution of the electronic density due to the new bonding interactions between Cu_{n-1} and Cu. In the context of one-atom growth reactions, note that μ_S values are quite close to the actual values obtained using eq 3; this is due to the fact that $\mu(\text{Cu}_n)$ results from combination of $\mu(\text{Cu}_{n-1})$ and $\mu(\text{Cu})$ values that are quite close to each other. In contrast to this, comparison of η_S and η indicates that the formation of odd clusters is accompanied by stronger reordering than in even-numbered clusters, which can be attributed to structural and spin density polarization effects. These results confirm the statement that the stability of the even cluster is determined by the closed-shell electronic structure as a manifestation of the PMH.^{43,44}

Table 3 shows that the chemical potential and hardness values using the Sanderson's formulas lead to the opposite trend with respect to the experimental one; this does not mean that the use of Sanderson's method is not right to estimate electronic properties of copper clusters from isolated fragments, but it suggests that the expected trend might be obtained through a combination of other fragments. There are many possible reactions that lead to Cu_n from a combination of different size clusters; in this paper we chose $\text{Cu} + \text{Cu}_{n-1} \rightarrow \text{Cu}_n$, and from the numerical viewpoint, these fragments lead to correct results for the formation of even-numbered clusters, whereas for odd clusters μ_S and η_S do not match the reference values. On the other hand, by use of the values of μ and η given in Table 3, it can be verified that when different fragments are used to produce Cu_n , thus leading to different formation reactions, for example, $\text{Cu}_2 + \text{Cu}_{n-2} \rightarrow \text{Cu}_n$, then the correct trend of the even-odd oscillation is obtained. Although not shown here, the experimental trend of μ and η is reproduced when the combinations $\text{Cu} + \text{Cu}_{n-1}$ and $\text{Cu}_2 + \text{Cu}_{n-2}$ are used. Different formation and fragmentation pathways in neutral copper clusters can be discussed in light of the above considerations; this point will be treated in a forthcoming study.

3.C. Rationalization of Growing Reactions. The $\{\mu, \eta, E\}$ Representation. The connections between energy and electronic descriptors is of considerable theoretical interest since the change in electronic properties is related to the reaction mechanism; therefore, the relation between energy and electronic properties allows one to connect the energetic and mechanistic aspects of a formation process. There are few interesting and useful attempts to relate electronic descriptors to reaction energies.^{24,36,45} In this context, Gázquez et al.⁴⁵ have established a relationship between energy and hardness differences, whereas in more recent papers^{24,36} we have shown that different aspects of a chemical event are well described in a representation where the chemical potential and molecular hardness are taken as

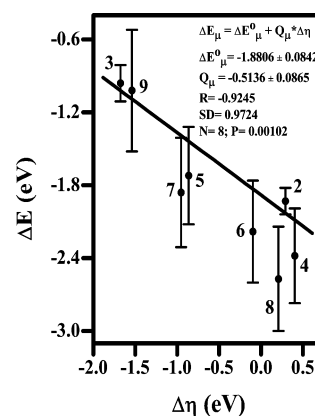


Figure 3. Relation between binding energies and chemical hardness in the one-atom growth reaction of Cu_n .

independent variables. In this context we write $E \equiv E[\mu, \eta]$, with total differential

$$dE = Q_\eta d\mu + Q_\mu d\eta \quad (14)$$

where

$$Q_\eta = \left(\frac{\partial E}{\partial \mu} \right)_\eta; \quad Q_\mu = \left(\frac{\partial E}{\partial \eta} \right)_\mu \quad (15)$$

The parameters Q_η and Q_μ are related to the charge redistributed among the atoms in the molecule during the chemical reaction. Therefore, within this model and in the context of one-atom growth reactions it is possible to write the binding energy (ΔE) in terms of two contributions, namely, ΔE_η and ΔE_μ , where the index is indicating that either the hardness or the chemical potential has been held constant during the stepwise process:

$$\Delta E = \Delta E_\eta + \Delta E_\mu \quad (16)$$

Each contribution can be written as

$$\Delta E_\eta = \Delta E_\eta^0 + Q_\eta \Delta\mu \quad (17)$$

and

$$\Delta E_\mu = \Delta E_\mu^0 + Q_\mu \Delta\eta \quad (18)$$

where ΔE_η^0 , ΔE_μ^0 , Q_η , and Q_μ are parameters that are determined through linear regressions; $\Delta\mu$ and $\Delta\eta$ are defined using the Sanderson's average as $\Delta\Omega = \Omega(\text{P}) - S\{\Omega(\text{R})\}$ ($\Omega = \mu, \eta$; see section 2). It is interesting to note that within this framework one can write the energy change through eqs 17 or 18 that depends only on two parameters each, when the chemical process is mainly driven by μ or η , respectively. Combination of eqs 17 and 18 is adequate when both electronic properties are driving the reaction.²⁴ On the other hand, note that a necessary condition for the principle of maximum hardness to be satisfied is that Q_μ must be negative. A decreasing ΔE_μ (higher stability) should be accompanied by increasing values of $\Delta\eta$.

It has been already pointed out that since μ remains quite constant when going from one cluster to another, hardness drives the formation processes and eq 18 should help rationalize them. In Figure 3 we display ΔE versus $\Delta\eta$; it can be noticed that there is an inverse relation between these properties, in agreement with the PMH. Values of $Q_\mu = -0.514$ and $\Delta E_\mu^0 = -1.881$ eV were determined through linear regression. Note that the linear regression procedure has been performed considering the experimental error of the binding energies.

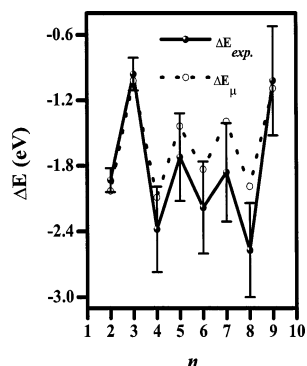


Figure 4. Comparison of the binding energies (ΔE_μ) obtained through eq 18 with the experimental data (ΔE).

To test the consistency of our model, we have recalculated the binding energies of Cu_n from Cu_{n-1} and Cu putting $\Delta\eta$, calculated from data given in Table 3, into eq 18 and using the fitting parameters of Figure 3; this gives the values displayed in Figure 4 that are compared with the experimental data of binding energies. It is interesting to note that the binding energies obtained through our approach reproduce the correct tendency, showing a fairly good agreement with the experimental values. Therefore, it is possible to estimate reasonably good binding energies of clusters only from their IP and EA values through the use of the two-parameter model, eq 18. We conclude that hardness is the key property that drives the reactions.

3.D. A Model for the Binding Energy. The above results open the way to characterize the binding energy as a function of the size of the cluster by introducing the size dependence through the already established equations relating η with n . Figure 2b indicates that $\eta_{\text{even}} = 4.70n^{-1/3}$ and $\eta_{\text{odd}} = 3.20n^{-1/3}$; therefore, $\Delta\eta = \pm^{3/2}n^{-1/3}$, where the plus sign applies when an even-numbered cluster is being formed and the minus sign is appropriate for formation of odd-numbered clusters. Now putting $\Delta\eta = \pm^{3/2}n^{-1/3}$ in eq 18 and using the fact that the value of $\Delta E_\mu^\circ \sim -1.88$ eV (see Figure 3) is approximately equal to half of the negative of the experimental vaporization energy of bulk copper ($\Delta E_{\text{bulk}}^\circ = 3.50$ eV), that is to say, $\Delta E_\mu^\circ \cong -1/2\Delta E_{\text{bulk}}^\circ$, then

$$\Delta E(n) \cong \frac{\Delta E_{\text{bulk}}^\circ}{2} \pm \frac{3}{2} Q_\mu n^{-1/3} \quad (19)$$

In Figure 5 is displayed the evolution of binding energy with n as obtained through eq 19; note the expected oscillatory behavior that allows one to extrapolate to large systems. It is remarkable that a simple two-parameter equation determined from data in the small clusters region is able to produce the correct trends and be semiquantitative in the region of large clusters and the bulk limit. When $n \rightarrow \infty$, $\Delta E(n) \rightarrow \Delta E_{\text{bulk}}^\circ/2$ (-1.88 eV), which should be compared with the experimental vaporization energy of bulk copper (-3.50 eV); the observed difference can be attributed to the simplicity of the model used here and to structural relaxation effects that are not considered in our approach. However, the values of binding energies produced for the reference clusters (Cu_n , $n = 2-9$) are quite close to the experimental values given in Table 1, thus validating the qualitative extrapolation displayed in Figure 5. It is worth pointing out that rationalization of the experimental binding energies achieved here through eqs 18 and 19 opens a new way to estimate the energy involved in the formation processes when only the electronic properties are available.

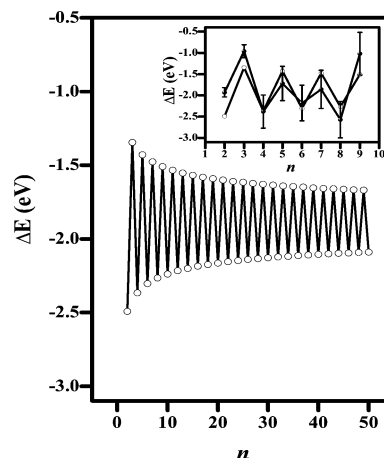


Figure 5. Binding energy as a function of cluster size predicted by eq 19. The inset compares the predicted data (○) with the available experimental data (●) of Table 1.

4. Concluding Remarks

In this work reactivity descriptors have been used to characterize and rationalize the growth of neutral copper clusters. Available experimental data of binding energies, ionization potentials, and electron affinities have been used to rationalize the formation reactions. It has been shown that the characteristic even-odd oscillatory behavior of electronic properties that depend on IP and EA is mainly due to fluctuations of the ionization potential.

It has been found that the one-atom growing reaction of copper clusters is mainly driven by changes in hardness. Chemical potential was found to be quite independent of the clusters size, thus indicating that chemical bonds do not change their nature when going from discrete systems to the bulk material. This adds evidence to validate the use of metallic clusters in heterogeneous catalysis as adequate prototype models.

Analytic relationships between energy and electronic properties were shown to be useful to gain insights into the reaction mechanism. This makes it possible to estimate binding energies of clusters only from their monoelectronic properties such as IP and EA. Relationships to estimate binding energy in terms of electronic properties and/or cluster size work very well in the regime of small or medium sizes where binding energy varies strongly.

On the other hand, the theoretical tools presented here can be very useful to predict growing and trends for electronic properties in the study of complex systems such as those found in heterogeneous catalysis and cluster fragmentation reactions.

Acknowledgment. This work was supported by FOND-ECYT through Projects 2000050 and 1020534.

References and Notes

- (1) Morse, M. D. *Chem. Rev.* **1986**, *86*, 1049.
- (2) Alonso, J. A. *Chem. Rev.* **2000**, *100*, 637.
- (3) Zacarias, A. G.; Castro, M.; Tour, J. M.; Seminario, J. M. *J. Phys. Chem. A* **1999**, *103*, 7692.
- (4) Balbuena, P.; Derosa, P.; Seminario, J. M. *J. Phys. Chem. B* **1999**, *103*, 2830.
- (5) Calaminici, P.; Koster, A. M.; Russo, N.; Salahub, D. R. *J. Chem. Phys.* **1996**, *105*, 9546.
- (6) Calaminici, P.; Koster, A. M.; Vela, A. *J. Chem. Phys.* **2000**, *113*, 2199.
- (7) Massobrio, C.; Pasquerello, A.; Dal Corso, A. *J. Chem. Phys.* **1998**, *109*, 6626.
- (8) Jackson, K. A. *Phys. Rev. B* **1993**, *47*, 9715.
- (9) Jug, K.; Zimmermann, B.; Calaminici, P.; Koster, A. M. *J. Chem. Phys.* **2002**, *116*, 4497.

- (10) Jaque, P.; Toro-Labbé, A. *J. Chem. Phys.* **2002**, *117*, 3208.
- (11) Katakuse, I.; Ichihara, Y.; Fujita, Y.; Matsuo, T.; Sakurai, T.; Matsuda, H. *Int. J. Mass Spectrom. Ion Processes* **1985**, *67*, 229.
- (12) Zheng, L. S.; Kraver, C. M.; Brucat, P. J.; Yang, S. H.; Pettiette, C. L.; Craycraft, M. J.; Smalley, R. E. *J. Chem. Phys.* **1986**, *85*, 1681.
- (13) Leopold, D. G.; Ho, J.; Lineberger, W. C. *J. Chem. Phys.* **1987**, *86*, 1715.
- (14) Moore, C. E. *Atomic Energy Levels*; National Standard Reference Data Series; U.S. Government Printing Office: Washington, D.C., 1971; Vol. II.
- (15) James, A. M.; Lemire, G. W.; Langridge-Smith, P. R. *Chem. Phys. Lett.* **1994**, *277*, 503.
- (16) Knickelbein, M. B. *Chem. Phys. Lett.* **1992**, *192*, 129.
- (17) Powers, D. E.; Hansen, S. G.; Geusic, M. E.; Michalopoulos, D. L.; Smalley, R. E. *J. Chem. Phys.* **1983**, *78*, 2866.
- (18) Winter, B. J.; Parks, E. K.; Riley, S. J. *J. Chem. Phys.* **1991**, *92*, 8618.
- (19) Ho, J.; Ervin, K. M.; Lineberger, W. C. *J. Chem. Phys.* **1990**, *93*, 6987.
- (20) Spasov, V. A.; Lee, T.-H.; Ervin, K. M. *J. Chem. Phys.* **2000**, *112*, 1713.
- (21) Ingólfsson, O.; Busolt, U.; Sugawara, K. *J. Chem. Phys.* **2000**, *112*, 4613.
- (22) Chattaraj, P. K.; Fuentealba, P.; Jaque, P.; Toro-Labbé, A. *J. Phys. Chem. A* **1999**, *103*, 9307.
- (23) Gutiérrez-Oliva, S.; Jaque, P.; Toro-Labbé, A. *J. Phys. Chem. A* **2000**, *104*, 8955.
- (24) Toro-Labbé, A. *J. Phys. Chem. A* **1999**, *103*, 4398.
- (25) Jaque, P.; Toro-Labbé, A. *J. Phys. Chem. A* **2000**, *104*, 995.
- (26) Crispin, X.; Bureau, C.; Geskin, V.; Lazzorini, R.; Brédas, J.-L. *Eur. J. Inorg. Chem.* **1999**, 349.
- (27) Parr, R. G.; Yang, W. *Density Functional Theory of Atoms and Molecules*; Oxford University Press: New York, 1989.
- (28) Parr, R. G.; Donnelly, R. A.; Levy, M.; Palke, W. E. *J. Chem. Phys.* **1978**, *68*, 3801.
- (29) Parr, R. G.; Pearson, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 7512.
- (30) Pearson, R. G. *Chemical Hardness: Applications from Molecules to Solids*; Wiley-VCH: New York, 1997.
- (31) Simón-Manso, Y.; Fuentealba, P. *J. Phys. Chem. A* **1998**, *102*, 2029.
- (32) Parr, R. G.; von Szentpaly, L.; Liu, S. *J. Am. Chem. Soc.* **1999**, *121*, 1922.
- (33) Sanderson, R. T. *Chemical Bond and Bond Energy*, 2nd ed.; Academic Press: New York, 1976.
- (34) Sanderson, R. T. *Science* **1955**, *121*, 207.
- (35) Sengupta, S.; Toro-Labbé, A. *J. Phys. Chem. A* **2002**, *106*, 4443.
- (36) Gutiérrez-Oliva, S.; Jaque, P.; Toro-Labbé, A. *Reviews of Modern Quantum Chemistry: A Celebration of The Contributions of Robert G. Parr*; Sen, K. D., Ed.; World Scientific: London, 2002; p 966.
- (37) Holmgren, L.; Andersson, M.; Rosen, A. *Chem. Phys. Lett.* **1998**, *296*, 167.
- (38) Gronbeck, H.; Rosen, A. *Chem. Phys. Lett.* **1994**, *227*, 149.
- (39) Wagman, D. D.; Evans, W. H.; Parker, V. B.; Schumm, R. H.; Halow, I.; Bailey, M.; Charney, K. L.; Nuttall, R. L. *J. Phys. Chem. Ref. Data, Suppl.* **1982**, *11* (SI), 1.
- (40) Kittel, C. *Introduction to Solid-State Physics*, 4th ed.; Wiley: New York, 1971.
- (41) Müller, H.; Fritsche, H. G.; Skala, L. Analytic Cluster Models and Interpolation Formulae for Clusters Properties. In *Clusters of Atoms and Molecules I*; Haberland, H., Ed.; Springer-Verlag: Berlin, 1995; p 114.
- (42) Aray, Y.; Rodríguez, J.; Vega, D. *J. Phys. Chem. B* **2000**, *104*, 4608.
- (43) Parr, R. G.; Zhou, Z. *Acc. Chem. Res.* **1993**, *26*, 256.
- (44) Harbola, M. K. *Proc. Natl. Acad. Sci. U.S.A.* **1992**, *89*, 1036.
- (45) Gázquez, J. L.; Martínez, A.; Méndez, F. *J. Phys. Chem.* **1993**, *97*, 4059.