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Structure and Bonding in Metal–Oxide Systems: The CuMgO and CuCaO Molecular Systems

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The molecular structure of the different isomers arising from the interaction of Cu and both MgO and CaO molecules has been determined from all-electron ab initio self-consistent field, SCF, and complete active space self-consistent field, CASSCF, wave functions. Only linear stable structures are found as characterized through the vibrational analysis. The dissociation energy with respect to the isolated molecules was obtained by explicitly considering the electronic correlation effects through second-order perturbation theory, MP2, or multireference configuration interaction calculations. The role of electronic correlation is very important due to the near degeneracies existing in the isolated MgO and CaO molecules where the SCF description is not adequate enough. A set of theoretical techniques has been used to analyze the chemical bond in these molecular complexes. All the results indicate that the bonding in the O- and M-bonded complexes is very different. This fact may be interpreted from the different behavior of the dipole moment curve and from simple arguments such as the importance of different valence bond resonating structures.

I. Introduction

A large number of industrial and technologically relevant chemical processes are carried out with the help of heterogeneous catalysts. An important class of heterogeneous catalysts is that of supported metals systems.¹ The supports are usually ionic materials and more generally metal oxides.^{1,2} Because of their technological importance, the metal–oxide interface has been extensively studied by means of the experimental techniques of modern surface science.² The purpose of these studies is to gain understanding about the chemical nature of the metal–oxide interaction as a necessary step to design more specific catalysts.

From a theoretical point of view, the nature of the metal–oxide interaction can be studied through the use of model systems and a given computational framework. Thus, cluster models have been very recently used in a preliminary study of the Ti/MgCl₂ Ziegler–Natta supported catalyst³ and, also, to investigate the chemisorption of CO on Ni clusters supported on alumina.⁴ However, there is almost no information concerning the direct interaction between a metal and an oxide. To the author's best knowledge, the first attempt to use the ab initio methods of quantum chemistry in the metal–oxide interface is due to Bacalis and Kunz.⁵ These authors deal with the interaction of a single Cu atom on a cluster model of MgO(100) and, based on unrestricted Hartree–Fock calculations, conclude that the interaction is very weak (≈ 0.04 eV) with a potential well rather far from the surface plane (≈ 8 bohr). This result contrasts with a very recent study on the same system by Li et al.⁶ who using the density functional formalism in the so-called local approach conclude that the interaction is indeed quite strong (≈ 1.42 eV) with the Cu atom sitting at 3.70 bohr from the surface. We must, however, point out that very recent calculations have shown that the large binding energy obtained in ref 6 is due to the use of the local approach and that a binding energy of about 0.3 eV is obtained from gradient-corrected density functional calculations.⁷

Apart from the different theoretical approach, Hartree–Fock versus density functional, both studies differ on the embedding

used to model the MgO substrate. Thus, Bacalis and Kunz include the Madelung potential through an array of point charges whereas Li et al. use a finite cluster of ≈ 50 atoms without any further embedding. Because of these differences it is not possible to decide which approach gives a better representation of the real system, although it has been shown that cluster atoms modeling MgO surfaces exhibit different reactivity depending on whether the Madelung field is or not explicitly included in the calculation.⁸

In order to understand the metal–oxide bonding it seems logical to start with the isolated molecular complexes and add the effect of the surroundings in a subsequent step. This will permit examination of the properties of the isolated molecules. This is precisely the aim of the present work. Hence, we will study the molecular structure and chemical bonding on the molecular complexes formed by Cu and either MgO and CaO. We will show that, in both cases, two stable structures with a very different bonding mechanism exist. Although our main goal is to understand the basic mechanisms governing chemical bonding in these molecular complexes rather than providing numerical benchmark calculations, we also report a reasonable estimate of the geometrical structure, vibrational frequencies, and bonding energies. Unfortunately, a direct comparison with experiment has not been possible because, to the authors surprise, and in spite of their considerable stability, there is no experimental (or theoretical) previous information.

II. Computational Approach

The molecular and electronic structures of the Cu–MgO and Cu–CaO complexes have been studied by means of ab initio methods. All-electron wave functions have always been considered where the one-electron basis functions or molecular orbitals, MO's, have been expressed in a rather large basis set of contracted Gaussian type orbitals, CGTO's. The basis sets used in the present work are as follows: For Cu we use a 8s,6p,4d contraction of the 14s,11p,6d primitive set of Wachters⁹ modified by Bagus et al.¹⁰ by adding two CGTO's to represent the Cu 4p atomic character and a diffuse d as recommended by Hay;¹¹ the final basis is indicated as [14s,11p,6d/8s,6p,4d]. For

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O we use a $[9s,5p/4s,3p]$ previously used by Broughton and Bagus¹² in their study of core-level shifts in bulk MgO and more recently used by Bagus et al. to describe excited states¹³ and excitons also in MgO.¹⁴ Finally, for Mg and Ca we use respectively the $[13s,8p/6s,3p]$ and $[15s,10p,1d/7s,5p,1d]$ sets with exponents and coefficients taken by Pacchioni et al.¹⁵ The reason for choosing these particular basis sets is to permit direct comparison with previous calculations for bulk oxides and with future studies focussing on interaction of Cu on MgO and CaO surfaces. This choice may result in a too limited basis set and it may be argued for instance that polarization functions in MgO may lead to significant changes in the calculated properties. To show that this is not the case, key calculations were carried out by adding two d functions to Mg previous basis set and a single d polarization function to the oxygen basis set. The exponents for these polarization functions were the same used in ref 16 and the interested reader may find extensive additional details in the list of references included in ref 16.

Using the atomic basis sets described above, different kinds of ab initio N -electron wave functions of increasing complexity were obtained depending on the property to be analyzed. Thus, the search of stable structures of the potential energy surface (minima) and their characterization (vibrational frequencies) by diagonalization of the Hessian matrix was carried out at the restricted open-shell Hartree–Fock, ROHF, level of theory. It is worth pointing out that all the molecular systems considered in this work contain an unpaired electron. Therefore, we find it convenient to investigate the electron spin density and this is done by using the unrestricted Hartree–Fock, UHF, wave function corresponding to the ROHF optimum geometries. Also, we have investigated the adequacy of the Hartree–Fock wave function to represent the electronic structure of these molecular complexes. To this end, we have used multiconfigurational self-consistent field, MCSCF, wave functions constructed in a complete active space, CAS (see ref 17). The particular CASSCF wave function used for a given structure will be described later on but here we would like to point out that in all cases the projection of the ROHF determinant in the CASSCF wave function is larger than 95%, thus indicating that the ROHF description of the chemical bond is qualitatively correct. Finally, because some of the stable compounds exhibit a markedly large ionic character, we have explicitly considered the effect of dynamical correlation. Dynamical correlation has been included in two different ways. In the first attempt we simply use the second-order perturbation theory and the framework of the Møller–Plesset partition of the electronic Hamiltonian. However, we must remark that here the ROHF wave function is taken as the zeroth order. Second-order perturbation on a ROHF may be considered as a particular case of multireference second-order perturbation theory in which the reference space contains a single configuration state function. From the many possible definitions of multireference second-order perturbation theory, we have chosen that of the CIPSI algorithm originally suggested by Huron et al.¹⁸ and reviewed in several recent publications.^{19–21} The second method used to introduce dynamical correlation is multireference configuration interaction, MRCI. In particular, we use a CAS as reference space and include all the single and double excitations on each determinant belonging to the CAS. The CAS determinants are constructed from a MO set where the occupied orbitals correspond to the ROHF wave function, and the valence virtuals are improved following the polarized hybrid orbital approach²² and further localized into the fragments. The localization procedure is carried out to ensure that the physical description of the electronic structure arising from the wave function at large and short distances is as close as

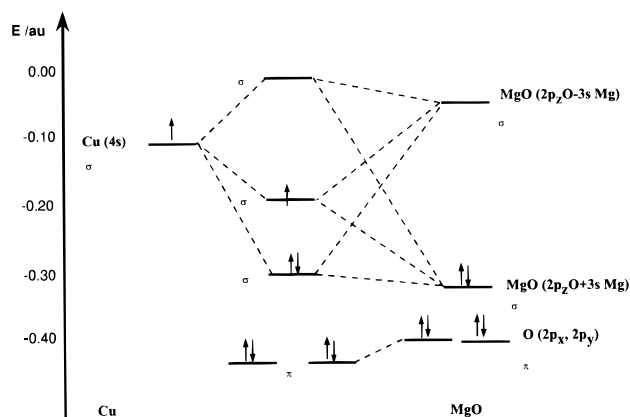


Figure 1. Schematic representation of the orbital interactions for the Cu–MgO molecule.

possible (see also refs 23 and 24). In all cases, the reference CAS includes three electrons in three orbitals. We will show that this CAS is enough to explain the relevant features leading to the final interaction energy. In fact, we will show that the qualitatively correct behavior can be found from a simple CASCI wave function. To avoid exceedingly large MRCI expansions some orbitals were kept doubly occupied in the MRCI wave function. The MRCI calculations were carried out using the three-class CIPSI algorithm²⁵ and always assuring that the perturbational contribution to the correlation energy was less than 10^{-4} hartree (see also ref 19).

Apart from the calculations described above, the electronic structure of the stable structures of the Cu–MgO and Cu–CaO complexes was studied by means of a series of methods of theoretical analysis. This includes the constrained space orbital variation,^{26–28} CSOV, the corresponding orbital transformation (ref 29; see applications in refs 30 and 31), the orbital projections,^{32–34} and the analysis of dipole moment curves.^{32–35}

The geometry optimization, UHF, and CASSCF calculations were carried out using the HONDO8.5 package³⁶ whereas ROHF-MP2 and MRCI calculations were carried out using the HONDO-CIPSI chain of programs.³⁷

III. Molecular Structure

The interaction of a Cu metal atom with either MgO or CaO can, in principle, lead to several stable structures exhibiting different symmetry point groups. Thus, it is possible to have the linear Cu–MO or Cu–OM structures ($M = \text{Mg, Ca}$) or the corresponding nonlinear C_s structure. Following the usual procedure, the search for stable structure has been carried out by total energy minimization in a given symmetry group and using analytical gradients. Two different kinds of wave functions were used to carry out the geometry optimization. First, we used the ROHF approach and the resulting geometries were refined at the CASSCF level to make it sure that the former description is free of artifacts arising from near degeneracies. The bonding of the Cu atom directly toward the metal atoms proceeds mainly through the interaction between the Cu (4s) orbital and the MgO (CaO) HOMO and LUMO of σ symmetry and dominated by the O $2p_z$ and Mg $3s$, respectively. For the Cu–MO structures, the minimal CAS could be defined by these three orbitals of σ symmetry and, hence, the CAS contains three active electrons in three active orbitals (see Figure 1). In the case of the Cu–OM structures the situation is very similar although the lowest bonding orbital of σ symmetry lies now below the nonbonding MgO orbitals of π character (Figure 2) and we include both in the CAS which thus contains seven active electrons in five active orbitals.

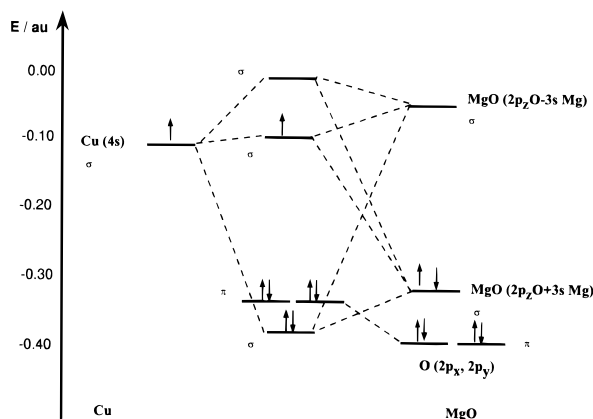


Figure 2. Schematic representation of the orbital interactions for the Cu–OMg molecule.

TABLE 1: Equilibrium Distances for Cu–MO and Cu–OM (M = Mg, Ca) Corresponding to Different Wave Functions of Increasing Complexity (ROHF and CAS; See Text)^a

structure	wave function	<i>R</i>	<i>R</i> _{MO}
Cu–MgO	SCF	4.834	3.504
	CAS	4.927	3.502
	CAS*	4.793	3.572
Cu–OMg	SCF	3.426	3.393
	CAS	3.458	3.395
	CAS*	3.453	3.363
Cu–CaO	SCF	5.635	4.087
	CAS	5.708	4.083
Cu–OCa	SCF	3.431	4.038
	CAS	3.466	4.051

^a The distances are given in atomic units and *R* stands for the distance from the Cu atom to either M in Cu–MO or O in Cu–OM compounds, *R*_{MO} is the distance between M and the O. CAS* stands for CASSCF results obtained by including polarization functions to both Mg and O (see text).

TABLE 2: Vibrational Frequencies (in cm^{−1}) for Cu–MO and Cu–OM (M = Mg, Ca) Corresponding to the ROHF Description^a

structure	$\nu(\Sigma^+)$	$\nu_{MO}(\Sigma^+)$	$\nu_b(\Pi)$
Cu–MgO	200.5	624.7	45.4
Cu–OMg	384.9	930.8	147.4
Cu–CaO	154.8	527.4	32.2
Cu–OCa	309.6	823.7	112.9

^a ν and ν_{MO} stand for the Cu–M and MO stretching, respectively, and ν_b is the corresponding bending mode.

In all cases, the minimization procedure led to linear structures although the potential energy surface for bending is rather flat. Typically, a 10-degree distortion requires less than 0.5 kcal/mol. However, explicit diagonalization of the Hessian matrix shows that all eigenvalues are always positive or zero thus unequivocally showing that both Cu–MO and Cu–OM are local minima on the potential energy surface. The optimum geometrical parameters and vibrational frequencies are given in Tables 1 and 2, respectively, where CASSCF results for the largest basis including polarization functions on both Mg and O have been included. First, it is important to notice that both basis sets lead to essentially the same geometrical parameters. In fact, the deviation on the calculated equilibrium distances for the CuMgO and CuOMg molecular complexes is less than 3%. Notice that while experimental equilibrium distance for MgO is 3.305 bohrs, the calculated values are 3.466 and 3.486 bohrs at SCF and CASSCF (8,8) levels for the small basis sets and 3.351 and 3.426, respectively, when polarization functions

are included (similar results are found for CaO). This clearly indicates that calculated optimum distances are reasonable and that polarization functions are unimportant.

Results in Table 1 also show that the MO distance depends on whether the metal atom approaches the metal or the oxygen of the MO molecule. In the first case, the HOMO is slightly destabilized while the contrary holds for the attack through the oxygen atom (see diagrams in Figures 1 and 2). Therefore, the variations on the MO distances can be explained using simple orbital arguments. However, one must caution that these simple arguments seem to indicate a similar kind of bond for both orientations. Results in the forthcoming section will show that this is not the case. On the other hand, the Cu–M or Cu–O distances quite follow the sum of ionic radii. Notice, in fact, that for a given kind of wave function, the Cu–O distance is almost the same in Cu–OMg and Cu–OCa. With respect to the level of calculation, results in Table 1 show that the geometry has only a moderate dependence on the wave function. This is because in all the CASSCF calculations the ROHF configuration contributes by more than 95% to the final CASSCF wavefunction. The vibrational frequencies are quite difficult to interpret because the isolated MgO molecule cannot be described at the SCF level^{38–40} and a similar situation will occur for CaO. In any case we notice that the experimental vibrational frequency for isolated MgO is 785.1 cm^{−1}⁴¹ while with the present basis SCF gives 592.3 and a CASSCF calculation with eight electrons in eight orbitals gives 665 cm^{−1}. The difference between experimental and calculated value being due to the limited basis used in the present work, inclusion of polarization functions slightly improves the calculated values which are now 658.4 and 681.8 cm^{−1} at the SCF and CASSCF(8,8) level. In the best case, the calculated value is still in 13% error with respect to experiment. In fact, fairly large basis sets and extensive inclusion of electronic correlation has been shown to be necessary for a highly accurate description of the MgO stretching frequency.^{38–40} Here, the important point to stress is that both Cu–MgO and Cu–OMg orientations have very different values for the MgO stretching frequency. This is a first indication of different bonding mechanism in both orientations and shows that the strength of the MgO bond is, accordingly, modified in opposite directions depending on whether Cu approaches the metal or the oxygen atom. The same behavior has been found in the Cu–(CaO) complexes. Here, there is also a gap between our calculated frequency for CaO and the experimental one. The SCF frequency for CaO is 520.5 cm^{−1}, while CASSCF-(8,8) leads to 598.4 cm^{−1} and the experimental value is 650 cm^{−1}.⁴¹ Notice, however, that the differences between calculated and experimental values for CaO are smaller than that for MgO. This is simply because in MgO the multireference character of the electronic wave function is much more important than for CaO.

Finally, we will comment the energetic of the interaction. We will distinguish between interaction energy, *E*_{int}, and dissociation energy, *D*_e. The first is defined as the energy difference between that of the equilibrium geometry and the one where Cu is at infinite separation but where the MO (M = Mg, Ca) distance is maintained as in the equilibrium geometry of the molecular complex. The dissociation energy is defined as usual as the energy difference between that of the equilibrium geometry and that of the isolated fragments also at their equilibrium geometries. The fact that both values are very close is an indication that the energetic cost to form the molecule is quite small; i.e., the MO distance in the molecular complexes is almost unchanged with respect to the value for the isolated molecule (vide supra).

TABLE 3: Calculated Interaction Energy, E_{int} , and Dissociation Energies, D_e , (in eV) for Cu–MO and Cu–OM ($M = \text{Mg, Ca}$) Corresponding to Different Methods of Calculation of Increasing Complexity (See Section III)^a

structure	method of calculation	E_{int}	D_e
Cu–MgO	SCF	3.00	3.00
	MP2	1.62	1.58
	CASCI	1.78	1.80
	MRCI(CAS)	1.26	1.24
Cu–OMg	SCF	4.04	4.03
	MP2	1.99	2.04
	CASCI	2.71	2.64
	MRCI(CAS)	2.32	2.28
Cu–CaO	SCF	3.64	3.63
	MP2	0.29	0.28
	CASCI	1.93	2.00
	MRCI(CAS)	0.92	0.93
Cu–OCa	SCF	3.99	3.99
	MP2	2.40	2.41
	CASCI	2.37	2.38
	MRCI(CAS)	2.58	2.58

^a The interaction energy is defined as the energy difference between that of the equilibrium geometry minus the one corresponding to Cu at infinite separation whereas the dissociation energy is calculated with respect to the equilibrium geometry of the MO molecule.

A summary of results for the interaction and dissociation energies is reported in Table 3 and, before entering into the discussion, it is worth pointing out that ROHF basis set superposition error is ≈ 0.2 eV for Cu–OMg, ≈ 0.05 eV for Cu–MgO, and ≈ 0.1 eV for either Cu–CaO or Cu–OCa. The first striking feature of Table 3 is the large SCF value for both E_{int} and D_e which would suggest a very large interaction. More surprising is the fact that explicit introduction of the correlation energy through the MP2 method largely decreases these values. This means that the importance of electronic correlation effects is larger for the isolated systems than for the stable molecular complex. Clearly such a behavior has no physical sense and the only explanation is that some kind of artifact is present on the SCF wave function. However, the CASSCF wave function clearly shows that the contribution of the SCF determinant to the final CASSCF wave function is larger than 0.96. In fact, this is the smallest contribution and corresponds to Cu–MgO; in the other cases the contributions are larger: 0.97 for Cu–CaO, 0.98 for Cu–OMg, and 0.99 for the Cu–OCa molecular complex. Therefore, the only possibility seems to be that the SCF approach is not valid at the asymptote; we will show that this is indeed the case. In fact, if a simple CASCI wave function is constructed from the SCF MO's, and including as active the three orbitals of σ symmetry and three electrons, one can find that the contribution of the SCF determinant is dominant at equilibrium geometry but is only $\approx 60\%$ of the wave function for the separated systems. This is because, as shown in refs 37–39, the electronic structure of the MgO molecule cannot be described by a single configuration. Hence, while the chemical bond and molecular structure of the Cu–(MO) complexes studied in this work can be qualitatively described by the SCF approach, the calculation of either E_{int} or D_e requires a multireference wave function. Taking the above CAS as reference space and correlating 19 electrons we have calculated the E_{int} and D_e values at the MRCI level. The final results show that the molecules are stable but that the SCF asymptote is artificially too high, leading to too large E_{int} and D_e values.

Unfortunately, there is no previous information about geometries, vibrational frequencies, or dissociation energies concerning these isolated molecules. Hence, the present work predicts, for the first time, the existence of these stable molecular complexes and the calculated frequencies albeit not highly

accurate may be useful to assign the IR bands of possible experiments to monitor CuMgO and CuCaO in inert matrices. In any case the aim of the present paper is not to predict highly accurate numerical values but to understand chemical bonding on these complexes as a first step toward understanding the metal–oxide interface. The analysis of the chemical bond in these molecular complexes is the subject of the next two sections.

III. Bonding in Cu–OM and Cu–MO ($M = \text{Mg, Ca}$) Complexes

In the previous section we have shown that explicit inclusion of electronic correlation is necessary to achieve even a qualitative description of the energetic of the interaction between a metal atom such as Cu and a diatomic alkaline-earth oxide molecule. However, the analysis of the CASSCF, CASCI, and MRCI wave functions clearly shows that the need for electronic correlation is just to describe the near-degeneracy effects of the isolated MgO and CaO molecule. However, if one wishes to describe the properties of the molecular complexes, the SCF approach appears to be adequate. This is specially true if the main interest is the understanding of the chemical bond in these kind of systems. In fact, we will show that depending on whether Cu approaches the MO molecule toward the metal or oxygen atom the resulting chemical bond is completely different. Accordingly, we will discuss the different complexes separately.

Let us begin with the Cu–OM interaction which is quite simple to understand. Mulliken population analysis is often used to characterize the ionicity of a chemical interaction and even knowing that this analysis suffers from well-known artifacts⁴² it is used so often that it merits to be mentioned. For both Cu–OMg and Cu–OCa molecules the net charge on Cu atom is large and positive (≈ 0.9 and $0.7e$, respectively). This first qualitative result suggest an ionic interaction where the Cu electron is transferred to the MO molecule. We will show that this is in fact a good description of the interaction. Now, if the interaction is ionic one may wonder if the unpaired electron is localized. To answer this question, we have studied the spin density as arising from an UHF calculation at the RHF optimum geometry. In both cases, the UHF wave function exhibits a very small spin contamination ($\langle S^2 \rangle = 0.753$ and 0.751 for Cu–OMg and Cu–OCa, respectively) and the unpaired electron appears to be localized mainly around the metal atom. This behavior may be understood from very simple and naive arguments. Both MgO and CaO exhibit near degeneracies that from the point of view of valence bond theory can be understood as the interaction between four dominant resonant structures, namely (see Figure 3) where the diagrams that we have used to represent the resonant forms follow the ideas originally developed by Malrieu et al.^{43–47} and used extensively by them to interpret the physical meaning of electronic correlation.^{48–50} Notice that each resonating form corresponds to an instantaneous electronic situation and that the resonance is equivalent to a configuration interaction built on an atomic basis; the diagrams used in Figure 3 are an attempt to represent such configuration interaction in a simple way.

Upon interaction with Cu, the resonant forms appear to be (Figure 4) and as a result of the ionic interaction described above the only significant contribution to the wave function is that described by the 4c resonant structure and one can understand why the SCF approach is now qualitatively correct while a few configurations are necessary to describe the separate systems.

Now we will use the CSOV decomposition of the SCF energy to show that the bonding of Cu to OM is in fact well described as an ionic bond. As usual, we start the CSOV decomposition

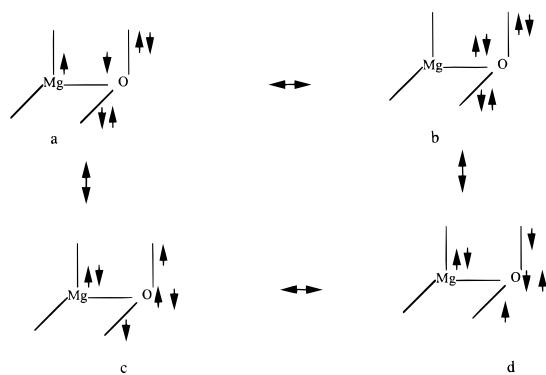


Figure 3. Schematic representation of the more important valence bond resonating structures of MgO. Parts c and d correspond to the neutral $\text{Mg}^0\text{--O}^0$ structure, and parts a and b are the ionic $\text{Mg}^+\text{--O}^-$ and $\text{Mg}^{2+}\text{--O}^{2-}$, respectively.

by obtaining a frozen orbital, FO, wave function as the superposition of the frozen densities of Cu and MO. The expectation value of the Slater determinant corresponding to this FO description is taken as our reference energy. This FO interaction is purely repulsive and commonly referred to as Pauli or steric repulsion. The initial Pauli repulsion may be reduced by different bonding mechanisms such as intraunit polarization or interunit charge donation. In a first step we allow the orbitals of Cu to vary from the FO shape but using the Cu virtual orbitals only. This variation accounts for Cu polarization, is represented by $V(\text{Cu};\text{Cu})$, and is significant for both Cu–OMg and Cu–OCa (see Table 4). Next, charge donation from Cu to MgO is allowed by enabling the Cu orbitals to vary in the whole virtual space. This is by far the largest contribution in both molecules and it clearly shows that the bond may be described as ionic. We must point out that at this step the only charge transfer allowed is that from the Cu closed shell, mainly 3d, to the MgO molecule but with the open-shell orbital still fixed and, hence, with the open-shell electron mainly located near the Cu atom. The following step accounts for the polarization of MgO due to the presence of Cu. This contribution is smaller than that of Cu but still significant. The charge donation from MgO to Cu is allowed in the next CSOV step and is rather small, thus indicating that MgO has no tendency to back-donate charge density to Cu. Finally, we allow the open-shell orbital to mix with the closed-shell orbitals of MgO. At first sight, one may think that this will result in a modest covalent contribution. However, from the UHF spin density we know that the open shell is located in the MgO moiety and more specifically close to the alkaline-earth metal atom. Therefore, the mixing of the open- and closed-shell orbitals does in fact reflect a new ionic contribution corresponding to the charge transfer of the open shell density from Cu to the alkaline-earth metal atom. This contribution is also important; in fact, it is the second largest contribution after charge donation from Cu to MO. At this point all the important physical mechanism should be included and the difference to the SCF energy indicates that some coupling between different bonding mechanisms. In the present case this difference is ≈ 0.5 eV; it is not meaningless but it is only $\approx 10\%$ of the total interaction and does not merit a second CSOV cycle that will only contribute to refine the contributions but will not change their relative importance.

The picture of the interaction emerging from the CSOV analysis can be confirmed by the analysis of the wave function. In particular, we have analyzed the corresponding orbitals²⁹ to find out which is the linear combination of the SCF orbitals that most resembles the orbitals of the separated interacting units [see also refs 30 and 31]. The corresponding orbital analysis

shows that the Cu 4s AO has almost no correspondence on the SCF wave function of either Cu–OMg or Cu–OCa (the equivalent eigenvalue of S^+S or SS^+ , S , being the overlap matrix between the Cu and MO occupied molecular orbitals in the molecular basis, is ≈ 0.25 whereas a value of 1.000 is found for orbitals that have exact correspondence between the unit and the supersystem). Moreover, the Cu 3d orbitals of σ and π symmetry show a noticeable change with respect to those of isolated Cu and the open shell of the molecule has no equivalent orbital in the space corresponding to the reunion of the occupied spaces of each unit. This is in agreement with the formation of an ionic bond.

Finally, we will describe the variation of the dipole moment with respect to the Cu–O distance. As earlier suggested by Bagus et al. the dipole moment curve is an excellent measure of the ionicity of a given bond.^{32–35} For a given interaction represented by a distance r , the idea is simply to compute the dipole moment as a function of $r - r_e$ and then to use a Taylor expansion such as

$$\mu = M_0 + M_1(r - r_e) + M_2(r - r_e)^2 + \dots$$

In the present case, the dipole moment curve is almost linear and the large slope ($M_1 \approx -1.0$) is typical of an ionic interaction (see also ref 16), (Figure 5).

In conclusion, the interaction of Cu with MgO and CaO through the oxygen atom leads to an ionic bond. In the following discussion, we will see that the interaction through Mg or Ca is completely different. In fact, while the arguments used to explain the role of electron correlation effect in Cu–OM are also applicable to Cu–MO, the final interaction energy is much less than for the corresponding Cu–OM isomers and the vibrational frequencies seem to indicate a different bonding mechanism. Similar indications are brought up by the Mulliken population analysis which suggest that the net charge in Cu is ≈ 0.03 for Cu–MgO and 0.27 for Cu–CaO. As for O-bonded isomers we have studied the spin density using the UHF description. In the case of Cu–MgO the UHF description gives $\langle S^2 \rangle = 0.77$ and the open shell appears to be localized near the oxygen atom. However, for Cu–CaO we find $\langle S^2 \rangle = 1.79$ and the UHF description is not reliable, although we believe that in Cu–CaO the open shell will also be located close to the oxygen atom; this is supported by the orbital analysis reported in Figure 1.

That the bonding in the Cu–MO complexes is different than in the O-bonded complexes can also be deduced from the CSOV analysis and the dipole moment curves. If the CSOV analysis is carried out following the same sequence of steps as in the O-bonded species, the energy difference between the SCF description and that resulting from the $V(\text{op};\text{cl})$ variation is 2.66 eV for Cu–MgO and 3.38 eV for Cu–CaO. In both cases this difference overwhelms the total interaction energy. To avoid this inconvenience, we have tried to carry out the variations in the reverse order but the same behavior was found. Therefore, we decided to carry out two CSOV cycles and found that after the second cycle the difference is reduced to about 0.5 eV. The fact that two CSOV cycles are needed to recover the SCF energy simply means that there is no leading term and, indeed, that the different contributions are strongly coupled. Accordingly, we will not report the different contributions and will simply extract the idea that here bonding is different than in the O-bonded species. To further prove that this is the case we now examine the dipole moment curves for the Cu–MgO and Cu–CaO as a function of the Cu–M distance. The corresponding plots are reported in Figure 6. The dipole moment curve is again linear but the slope is only a fraction of that

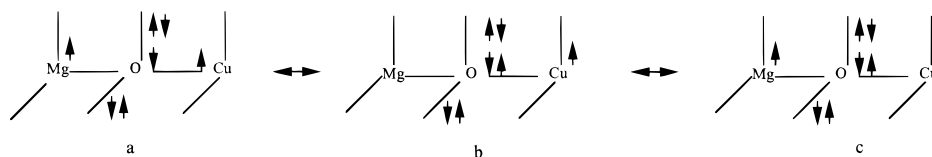


Figure 4. Schematic representation of the more important valence bond resonating structures of MgO-Cu. Part a represents the interaction between form Figure 3a and neutral Cu; Figure 4b corresponds to Figure 3b also plus neutral Cu and finally part c corresponds to the electron transfer from Cu to 3a.

TABLE 4: CSOV Decomposition of the SCF Energy for Cu-OMg and Cu-OCa Molecules^a

variation	bonding mechanism	Cu-OMg	Cu-OCa
V(Cu;Cu)	Cu polarization	0.67	0.89
V(Cu;all)	Cu to OM donation	2.33	1.89
V(MO;MO)	MO polarization	0.57	0.48
V(MO;all)	MO to Cu donation	0.14	0.24
V(op;cl)	open-shell relaxation	0.89	1.00
full SCF	remaining contributions	0.54	0.50

^a The energy decrease at each step accounts for a given bonding mechanism. Results are in eV.

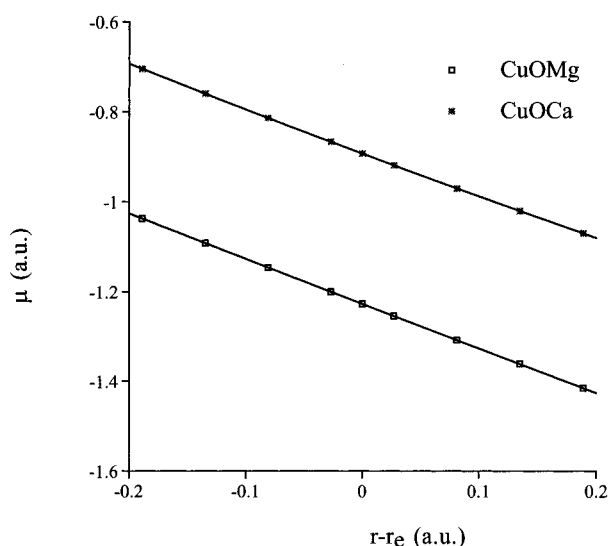


Figure 5. Dipole moment curves for the Cu-OMg and Cu-OCa molecules.

corresponding to the O-bonded species, -0.2 for Cu-MgO and $+0.05$ for Cu-CaO. The small values of the slopes univocally show that the bond in the O-bonded and M-bonded species is different. From the point of view of valence bond theory this difference only implies that the leading term is now not the ionic but the neutral one. Again, this can be understood from Figure 1 that clearly shows that Cu 4s orbital interacts with the largely Mg 3s σ LUMO of MgO to form a quite typical covalent bond while the largely O 2p_z σ HOMO of MgO is destabilized and possesses the unpaired electron.

IV. Conclusions

For the first time, the molecular structure of the different isomers arising from the interaction of Cu and both MgO and CaO molecules has been determined from all electron ab initio SCF and CASSCF wave functions. The only stable structures are the linear O- and M-bonded and both have been characterized as minima of the electronic ground state potential energy surface through the proper vibrational analysis. Likewise, the dissociation energy with respect to the isolated molecules has been obtained at several levels of theory going from the simple MP2 to quite accurate MRCI calculations. The role of electronic correlation is very important but it is mainly due to the near

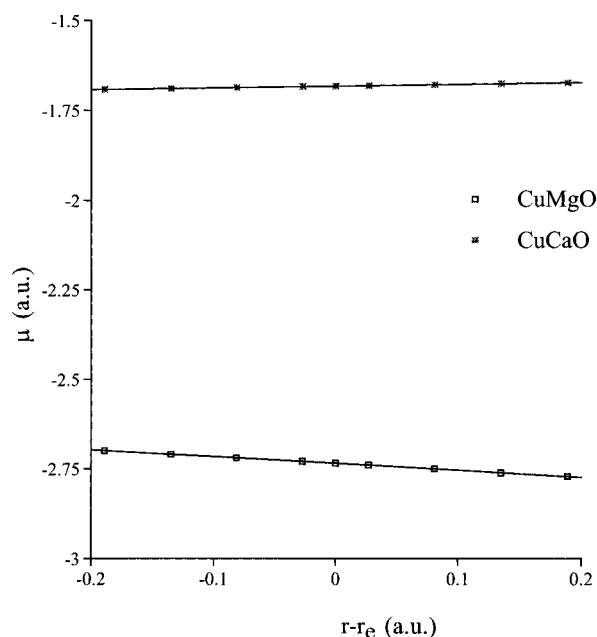


Figure 6. Dipole moment curves for the Cu-MgO and Cu-CaO molecules.

degeneracies existing in the isolated MgO and CaO molecules where the SCF description is not adequate enough.

Also, a set of theoretical techniques has been used to analyze the chemical bond in these molecular complexes. These techniques includes the analysis of the interaction energy through the constrained space orbital variation method, the analysis of the SCF wave function based in the corresponding orbital transformation and the analysis of the interaction through the study of the dipole moment curves. All these techniques give compelling evidence that the bonding in the O- and M-bonded complexes is very different. This fact may already be seen from the different behavior of the dipole moment curve and can be rationalized using simple arguments such as the importance of different resonating structures.

In summary, we predict that stable Cu-MgO, Cu-CaO, Cu-OMg, and Cu-OCa molecules exist and we give reasonable values of the structural parameters for these systems that may be used to help in their experimental determination. Our error estimate for these properties is about 5–10%; this gives a precision that is sufficient to distinguish among different compounds and geometries.

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