Electronic Structures and Energetics in the CuX and Cu_2X Series (X = O, S, Se, Te, Po)

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The CuX and Cu_2X series (X = O, S, Se, Te, Po) have been investigated using a standard pseudopotential and a correlation-corrected pseudopotential for copper. Using the latter pseudopotential leads to cheaper but nevertheless accurate results in comparison to standard high-level ab initio methods. The spectroscopic parameters also compare favorably with the available experimental data. These calculations constitute the first theoretical study of Cu_nTe and Cu_nPo (n = 1, 2). Trends in structural and energetic properties for the whole series are discussed, in particular the $d^{10}-d^{10}$ "metallophilic interaction" between the copper atoms.

I. Introduction

Since the beginning of the 1990s, there has been a marked interest, through both experimental and theoretical studies, for the so-called "aurophilicity". This phenomenon, which occurs in organometallic compounds with two or more gold atoms (numerous examples can be found in the literature[1−3]), originates from attractive $d^{10}-d^{10}$ dispersion type interactions, also called "aurophilic interactions". Other metals show a similar behavior, e.g. Rh,[4] Pd,[5] Pt,[4,5] Hg,[6] and Tl.[7] A more general name, "metallophilic attraction", was therefore proposed.[8]

These weak but nonnegligible interactions lead to short intra- or intermolecular metal−metal contacts and unusual molecular geometries and coordination numbers (for example, there is a hypercoordination[9] of X in $(LM)_nX^{m+}$, where L = ligand, M = metal, and X = main group element). Sometimes, steric effects originating from the ligands are critical as they compete with the metal−metal interactions.[10−13] Moreover, the ligands also play a significant role through electronic effects.[8,11,12] Finally, the number of d electrons is also important, as it can be observed that the metallophilic interaction typically occurs for atoms located at the right side of the transition metal series.

A rich variety of gold compounds showing metallophilic interactions have been studied (see the references above), but relatively few copper-containing molecules.[12,14−16] Nevertheless, some interesting applications exist for molecules involving short Cu−Cu interactions. For example, Cu−S−Cu units have been recently found in an active site of some metalloproteins like cytochrome c oxidase.[17] The short Cu−Cu distance (∼2.5 Å) and small Cu−S−Cu bond angle (∼70°) are believed to play an essential role in the electron transport made by this protein. Cu_2S is also used, among other things, in solar cells.[18] Furthermore, Roof and Kolis,[19] in an excellent review article, emphasize the importance of selenium and tellurium, in particular in proteins, semiconductors, photovoltaics, etc.

It is therefore worthwhile to investigate the electronic structures and energetics of small model compounds, in order to understand the mechanism of the copper−copper dispersion type interaction.

Kölmel and Ahlrichs[20] have performed a theoretical study for some compounds showing short Cu−Cu distances. Recently, Schäfer and co-workers[13,21] have presented theoretical results for $(Cu_2Se)_n$ and $(Cu_2Se)_n(PR_3)_m$ ($n \leq 6$ and R = H, CH_3), in coordination with Fenske et al.,[14,15] who managed to synthesize stoichiometric copper selenium clusters $(Cu_2Se)_n(PR_3)_m$ ($n \geq 6$). Cu−Se−Cu angles of about 70° and again short Cu−Cu distances are characteristic of the latter clusters. We note that Li and Pyykkö[22] have performed calculations for the equivalent heavier compounds Ag_2Se, $(AgPH_3)_2Se$, Au_2Se, $(AuPH_3)_2Se$, and Au_2Te, while Alemany et al.[23] considered only Ag_2Se and Au_2Se.

The new research direction opened by the previously mentioned groups incited us to study systematically the whole Cu_nX series (n = 1, 2 and X = O, S, Se, Te, Po), in order to have an insight into the evolution of the structure and stability of these molecules with the nature of the chalcogen atom. Our study gives the trends for the geometries, vibrational frequencies, and energetics for the ground states of the CuX and Cu_2X species. These small model compounds should give some insight into the properties of the previously mentioned molecules. One important guideline along this article is the Cu−Cu distance and the Cu−X−Cu bond angle in Cu_2X, since these parameters are somewhat a measure of the magnitude of the metallophilic interaction. The copper atoms are formally not bonded, but present a "bond" distance around 2.540 Å, while the experimental bond length is 2.219 Å in the gaseous copper molecule[24] and the next-neighbor distance is 2.56 Å in metallic copper. Moreover, we try to analyze more thoroughly the correlation effects responsible for this interaction. This study is also useful to validate our computational method (by comparison with experimental data for the CuX molecules), since we employed a new correlation-corrected pseudopotential for copper.[25]

The Quantum Chemistry Literature Data Base[26] indicates the lack of theoretical studies on the CuX and Cu_2X molecules, in particular the heaviest compounds. Although the main interest of this paper is the behavior of Cu_nTe and Cu_nPo (n = 1, 2), we included Cu_nO, Cu_nS, and Cu_nSe in our study, in order to have a coherent level of calculation available for the whole series. Considering theoretical works, CuO[27−38] has been frequently studied, whereas CuS,[32,36,38] Cu_2O,[36,39,40] and Cu_2S[36] have been given only little interest.

II. Computational Details

Two pseudopotentials were used for copper. The complete theoretical presentation and generation procedure of these pseudopotentials are described in a previous article.[25] The first one is a Hartree−Fock pseudopotential (named HF-PP), which

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TABLE 1: Exponents of Diffuse (s and p) and Polarization (d) Functions for O, S, Se, Te, and Po

	ζ_s	ζ_p	ζ_d
O	0.108 151	0.070 214	0.73
S	0.053 458	0.037 851	0.36
Se	0.042 691	0.035 105	0.32
Te	0.037 304	0.030 303	0.29
Po	0.047 199	0.046 595	0.24

has been optimized to reproduce the HF atomic spectrum of copper. The second pseudopotential is correlation-corrected, since it has been designed to take into account part of the atomic correlation effects and reach experimental accuracy for the atomic spectrum at the MP2 level using a small basis set. Indeed, an accurate description of the lowest part of the atomic spectrum (for example the $d^{10}s^1$, d^9s^2, and d^{10} states of copper) is necessary to well describe the molecular situation, as several states can contribute to the bonding (see for example ref 32). We expect this correlation-corrected pseudopotential, named MP2-PP, to give more accurate results for molecules than the HF pseudopotential, at the same level of calculation. In other words, the correlation-corrected pseudopotential along with the small basis set (see below) should compare favorably with experimental data (when available) and with high-level calculations, such as multireference configuration interaction (MRCI), coupled-cluster (CC), or coupled-pair functional (CPF). This has already been verified for some diatomics (CuH, Cu_2, CuF, and CuCl) in our previous paper.[25] Both pseudopotentials are "large-core" (i.e. only 3d and 4s electrons are explicitly treated) and include mean relativistic effects (mass-velocity and Darwin term corrections). Spin−orbit effects were not accounted for in our calculations.

We used for copper a [2s1p2d] GTO basis set determined according to the procedure proposed by Wahlgren and Siegbahn,[41] slightly modified (see our previous paper[25] for more details). For each of the $d^{10}s^1$ (^2S) and d^9s^2 (^2D) states, a (4s7d) primitive GTO basis set was optimized and fully contracted. A (4p)/[1p] set was optimized for the low-lying $d^9s^1p^1$ (^4P) state.

For X, we selected pseudopotentials generated according to the original method of Durand and Barthelat,[42] leaving six electrons in the valence space. The pseudopotentials for oxygen and sulfur have been previously published.[43] For selenium, tellurium, and polonium, these pseudopotentials include mean relativistic effects[44] (mass-velocity and Darwin term corrections). The associated Gaussian basis sets were derived from (4s4p)/[2s2p] sets, which were optimized in a HF calculation on the ground state (^3P) of the neutral atom.[45] These basis sets were supplemented with one diffuse s and one diffuse p functions, both optimized for the anion X^- (^2P). A d polarization function, optimized for CuX, was also added, leading finally to a [3s3p1d] basis. The diffuse and polarization exponents are displayed in Table 1. The basis sets and the unpublished pseudopotentials are available from the authors upon request.

Geometry optimizations and frequency calculations for CuX and Cu_2X were performed with the Gaussian 92 program.[46] The HF pseudopotential of copper was used at the HF and MP2 levels and the correlation-corrected one only in MP2 calculations. Spin-unrestricted formalism (UHF and UMP2) was used for CuX ($^2\Pi$). In one case (CuO), the spin contamination was too high and we performed the calculations with restricted open shell formalism (ROHF and ROMP2). We did not compute the basis set superposition error (BSSE), since our correlation-corrected pseudopotential (MP2-PP) somehow compensates the inadequacy of the small basis set (see ref 25 for more details). Schwerdtfeger and Boyd,[47] as well as Li and Pyykkö[22] and Schäfer and co-workers,[21] recommend MP2 as a reliable method for the study of the weak dispersion type interactions.

III. CuX Molecules

Results for $^2\Pi$ CuX are summarized in Table 2. Several benchmark calculations on CuO and CuS are given for comparison purpose. All-electron CCSD(T) calculations were performed by Bauschlicher and Maitre,[38] correlating the valence electrons only (3d and 4s for Cu and 2s(3s) and 2p(3p) for O and S, respectively). The basis set was [8s6p4d2f], [5s4p3d1f], and [6s5p3d1f] for copper, oxygen, and sulfur, respectively. Dissociation energies (D_e) included a correction for basis set saturation, determined at the MCPF level. In a previous work, Langhoff and Bauschlicher[32] employed the CPF+RC method (coupled-pair functional with a relativistic correction determined at the first order of perturbation) in all-electron calculations. A larger basis set was used, with [9s7p4d3f1g] for copper and [6s4p3d1f] for oxygen, sulfur having an equivalent basis as in the CCSD(T) calculation mentioned before. Again, only the valence electrons were correlated. Finally, local density functional (LDF) calculations, using a double numerical basis set with polarization functions, are reported by Dixon and Gole.[36]

As mentioned by Bauschlicher and Maitre,[38] the bond in CuO and CuS is essentially a single bond. No back-donation from the $p_\pi(X)$ orbital toward the $d_\pi(Cu)$ can occur, since the d-shell of copper is complete. However, Langhoff and Bauschlicher[32] found that some back-donation occurs from $p_\pi(X)$ toward p_π(Cu), as the copper 4p orbitals are low-lying virtual orbitals.

The CCSD(T) spectroscopic parameters of Bauschlicher and Maitre are quite comparable to experiment and show the reliability of this method, when employed with sufficient basis sets. Nevertheless, the authors point out that the absence of relativistic effects (which shorten the bond lengths) and the basis set limitation (note that the basis employed was already quite large) are responsible for the remaining errors. As a comparison, the CPF+RC results are in excellent agreement with experiment. The same method, applied to various copper-containing compounds by Kölmel and Ahlrichs,[20] gives accurate results for CuH, CuF, and to a lesser extent, CuCl and Cu_2. Our previous article[25] compares the results obtained with our (MP2-PP) correlation-corrected pseudopotential at the MP2 level to Kölmel and Ahlrichs' values, with a good agreement. These benchmark calculations (CCSD(T) and CPF+RC) are certainly among the most accurate[48] that can be performed for diatomics with the currently available computational resources.

On the other hand, the LDF bond lengths of Dixon and Gole[36] are too short, especially for CuO. These authors also report a slightly too short LDF Cu−Cu bond length in Cu_2 (2.196 Å, compared to 2.219 Å for the experimental value[24]). Local density functional seems therefore unsuitable for the study of these molecules, probably due to the absence of gradient correction. Note that these calculations did not take relativistic effects into account, which would have led to even shorter bond lengths.

It appears that our MP2 r_e, ω_e, and D_e values using the correlation-corrected pseudopotential (MP2-PP) are in good agreement with experiment and in any event much better than the HF-PP values, as expected. Geometries and vibrational frequencies are even more accurate than the CCSD(T) values, while dissociation energies are only slightly smaller. The MP2-PP, determined by a semiempirical scheme, gives on the whole and with low-level calculations quite accurate geometries, vibrational frequencies, and dissociation energies for CuX with

TABLE 2: Geometries, Vibrational Frequencies, and Dissociation Energies for the $^2\Pi$ CuX Molecules[a]

		MP2, this work		other calculations			
		HF-PP[c]	MP2-PP	CCSD(T)[d]	CPF + RC[e]	LDF[f]	experiment[b]
CuO[g]	r_e	1.808 (1.887)	1.752	1.771	1.721	1.688	1.724
	ω_e	567 (550)	618	572	606		640
	D_e	2.49 (0.51)	2.60	2.70	2.83		2.89[h]
CuS	r_e	2.122 (2.232)	2.071	2.107	2.045	2.029	2.051
	ω_e	386 (342)	415	385	415		415
	D_e	2.55 (1.29)	2.67	2.73	2.86		2.83
CuSe	r_e	2.229 (2.338)	2.183				2.108
	ω_e	285 (249)	305				302
	D_e	2.33 (1.17)	2.43				2.57
CuTe	r_e	2.418 (2.523)	2.380				2.349
	ω_e	2.43 (210)	258				253
	D_e	2.04 (1.06)	2.13				2.37
CuPo	r_e	2.501 (2.604)	2.465				
	ω_e	215 (185)	228				
	D_e	1.81 (0.82)	1.89				

[a] Bond lengths in Å, vibrational frequencies in cm^{-1} and dissociation energies in eV. [b] Reference 61 unless noted otherwise. [c] Parameters determined at HF level in parentheses. [d] Reference 38. [e] Reference 32. [f] Reference 36. [g] Our calculations were performed in restricted open shell formalism. See the text. [h] Reference 62. The experimental uncertainty is 0.15 eV (for D_0).

TABLE 3: Optimized Geometries[a] **for $^1A_1$ Cu_2X**

		MP2, this work		other calculations[b]		
		HF-PP[c]	MP2-PP	MP2[c]	CCSD(T)	LDF
Cu_2O	r(Cu−O)	1.788 (1.820)	1.753	1.784 (1.813)		1.749
	r(Cu−Cu)	2.622 (3.621)	2.562	2.709 (3.354)		2.406
	α(∠CuOCu)[d]	94.3 (168.3)	93.9	98.8 (135.3)		86.9
Cu_2S	r(Cu−S)	2.118 (2.203)	2.084			2.073
	r(Cu−Cu)	2.628 (3.395)	2.554			2.443
	α(∠CuSCu)	76.7 (100.8)	75.6			72.2
Cu_2Se	r(Cu−Se)	2.229 (2.313)	2.200	2.200 (2.281)	2.236	2.197
	r(Cu−Cu)	2.623 (3.394)	2.549	2.621 (3.341)	2.597	2.431
	α(∠CuSeCu)	72.1 (94.4)	70.8	73.1 (94.2)	71.0	67.2
Cu_2Te	r(Cu−Te)	2.419 (2.503)	2.395			
	r(Cu−Cu)	2.639 (3.589)	2.554			
	α(∠CuTeCu)	66.1 (91.6)	64.5			
Cu_2Po	r(Cu−Po)	2.502 (2.583)	2.480			
	r(Cu−Cu)	2.624 (3.541)	2.537			
	α(∠CuPoCu)	63.2 (86.5)	61.5			

[a] Bond lengths in Å and bond angles in degrees. [b] The calculations for Cu_2O and Cu_2S are from ref 36 and those for Cu_2Se from ref 21. [c] Geometry optimized at HF level in parentheses. [d] The experimental value is estimated at 100° ± 10° (quoted in ref 36).

respect to the known experimental values. We therefore expect that our values for CuPo are reasonable estimates, while no experimental data are known at present.

The trends in the structural and energetic properties are classical. The bond length increases and the vibrational frequency decreases as the chalcogen atom becomes heavier, due to simple size considerations. The CuX molecule becomes less and less stable when going down the group 16, as the bond looses its ionic character.

IV. Cu_2X molecules

IV.a. Geometries and Vibrational Frequencies. Geometries for the $^1A_1$ Cu_2X series are summarized in Table 3. For the sake of comparison, we also include other HF, MP2, CCSD(T), and LDF results for Cu_2O, Cu_2S, and Cu_2Se. The nonrelativistic all-electron LDF calculations from both author groups use double numerical basis sets with polarization functions.

For Cu_2O, the (apparently nonrelativistic) HF and MP2 calculations of Dixon and Gole[36] were performed with a [8s6p4d] and [5s3p2d] basis set for Cu and O, respectively. Our HF-PP results at the HF and MP2 levels are in rather good agreement with the corresponding all-electron calculations of Dixon and Gole, giving one more proof that the pseudopotential approximation is reliable, if the pseudopotential and basis set are carefully optimized. One remarkable difference is the value of the Cu−O−Cu bond angle at the HF level, but the MP2 results are in much closer agreement. The remaining errors are certainly the consequence of the differences in the basis sets and the absence of relativistic effects in Dixon and Gole's calculations.

Note that the LDF method for Cu_2O and Cu_2S yields smaller bond lengths and especially bond angles, in comparison to our MP2 results. If we consider the estimated experimental value for the Cu−O−Cu bond angle (100° ± 10°, quoted in ref 36) as reliable, then we can suppose that LDF is not appropriate. The LDF value for the Cu−O and Cu−S distances in Cu_2X is almost identical to our MP2 value with the correlation-corrected pseudopotential, but the relativistic effects were not taken into account in the former calculation, so these LDF values are again overestimated. As mentioned in section III, Dixon and Gole[36] report LDF distances for the Cu_2, CuO, and CuS molecules that are also too short in comparison to experimental data. Even if the experimental bond lengths and vibrational frequencies for Cu_2O and Cu_2S are unknown and the experimental uncertainty for the Cu−O−Cu angle is significant, our geometries are probable more accurate than the LDF results.

For Cu_2Se, we compare our results to the MP2 and CCSD(T) calculations performed by Schäfer and co-workers,[21] who used for copper the small-core relativistic pseudopotential and the [6s5p3d] basis set of Dolg et al.[49] Although we cannot directly compare our [2s1p2d] small basis to the basis used by Schäfer and co-workers, our basis set and HF pseudopotential (HF-PP) combination reproduces well the (relativistic) Hartree−Fock spectrum for copper, as does the small-core pseudopotential and [6s5p3d] basis set association (see refs 25 and 49). It is therefore expected that our large-core HF pseudopotential results are equivalent to the small-core pseudopotential values obtained by Schäfer et al. These authors described selenium by a large-core relativistic pseudopotential and a [3s3p1d] basis set. Our treatment of Se (see section II) is almost equivalent, with one additional primitive function for the s and p symmetries in our basis set.

These authors emphasize the need for two p functions in the copper basis set to describe accurately the polarization and correlation effects. In some test calculations, they used only one p function at the MP2 level, which resulted in incorrect geometries, comparable to the HF geometry displayed in Table 3. Nevertheless, with our (4p)/[1p] set, we obtain the correct geometry for Cu_2Se. One contracted function is thus certainly sufficient, at least for this particular case, if the exponents are well distributed.

Our calculations with the HF pseudopotential are in good agreement at the HF and MP2 levels with the results of Schäfer and co-workers. As was stated in section II, the MP2 level is already sufficient for an accurate description of the dispersion type interaction originating from electron correlation and its consequences on the geometries (one may here compare the MP2 and CCSD(T) results in Table 3). Indeed, the replacement of the HF-PP by the correlation-corrected pseudopotential has only a little effect on the geometries. However, it *does* have a significant effect on the dissociation and transition structure energies, as we mention further (see section IV.c). As we expected, the large-core HF-PP gives results similar to the small-core values of Schäfer et al. (as a comparison, Li and Pyykkö[22] have performed MP2 calculations for Au_2Se and $(AuPH_3)_2Se$ with a small-core and a large-core pseudopotential. The Au−Se−Au bond angle is ∼6° larger with the latter pseudopotential). This result is an additional proof that the quality of the atomic spectrum has a significant impact on the molecular results.

Although our MP2 results using the correlation-corrected pseudopotential show a similar value for the Cu−Se−Cu angle compared to the CCSD(T) treatment, they display slightly shorter Cu−Se and Cu−Cu bond lengths. In the absence of experimental data, it is not easy to conclude about that point for the geometry of Cu_2X. Compared to the CCSD(T) and our MP2-PP results, the LDF Cu−Se−Cu angle is too small. Moreover, the bond lengths are also slightly underestimated and should be even shorter, since the LDF method employed did not include relativistic effects. Our general impression about the inadequacy of LDF for these molecules is thus confirmed.

The vibrational frequencies are displayed in Table 4. The only other theoretical values available are the LDF frequencies of Dixon and Gole[36] for Cu_2O and Cu_2S. These values are quite close to our MP2 frequencies determined with the correlation-corrected pseudopotential. The differences between the two sets of values certainly come from the inadequacy of the LDF method (see above), in particular for the bending mode, since the Cu−X−Cu angles are significantly too small at the LDF level. In the absence of experimental values, it is not easy to conclude about the validity of the correlation-corrected pseudopotential for frequencies. However, considering the excellent behavior of the latter pseudopotential for CuX, we expect the MP2-PP values to be quite accurate for Cu_2X as well.

TABLE 4: Vibrational Frequencies (cm^{-1}) for $^1A_1$ Cu_2X

		MP2, this work		
		HF-PP[b]	MP2-PP	LDF[a]
Cu_2O	Cu−O sym stretching (a_1)	578 (293)	636	679
	Cu−O antisym stretching (b_2)	538 (822)	581	583
	∠CuOCu bending (a_1)	129 (20)	142	163
Cu_2S	Cu−S sym stretching (a_1)	432 (341)	461	465
	Cu−S antisym stretching (b_2)	343 (377)	356	353
	∠CuSCu bending (a_1)	125 (59)	138	143
Cu_2Se	Cu−Se sym stretching (a_1)	315 (258)	335	
	Cu−Se antisym stretching (b_2)	253 (260)	260	
	∠CuSeCu bending (a_1)	120 (53)	132	
Cu_2Te	Cu−Te sym stretching (a_1)	267 (218)	283	
	Cu−Te antisym stretching (b_2)	216 (216)	221	
	∠CuTeCu bending (a_1)	113 (45)	127	
Cu_2Po	Cu−Po sym stretching (a_1)	235 (195)	250	
	Cu−Po antisym stretching (b_2)	192 (188)	196	
	∠CuPoCu bending (a_1)	114 (42)	127	

[a] Reference 36. [b] HF frequencies in parentheses.

IV.b. The Metallophilic Cu−Cu Interaction. The unusual values of the Cu−X−Cu bond angle, which can be viewed as an estimation of the Cu−Cu interaction, ask the question of the bonding in Cu_2X. As a comparison, the H−X−H bond angles in H_2X, optimized at the CI level by Sumathi and Balasubramanian,[50] are the following: 105.5°, 94.4°, 91.5°, 91.2°, and 90.9° for X = O, S, Se, Te, and Po, respectively. These values are easily interpreted in terms of sp^3 hybridization for oxygen and of an increasing tendency to form pure p bonds for the heavier elements. No interaction occurs between the hydrogens, while, for Cu_2X, the smaller value for the angle strongly suggests that an interaction exists between the two copper atoms.

There are several possible interpretations for the bonding behavior in Cu_2X. Mann and co-workers,[51] Hoffmann et al.[52] (the latter on the basis of extended Hückel calculations), and Schmidbaur et al.[6,9] suggested that the weak metal−metal interactions (in a general sense) are due to $nd(n+1)s(n+1)p$ hybridization. If this scheme were correct, this effect should already appear at the HF level, but this not the case, as can be seen for example, in Table 3 and in the following references. On the contrary, Kölmel and Ahlrichs[20] and Pyykkö and co-workers[22,53,54] have showed that this attraction is in fact a dispersion type interaction (simultaneous excitations of the d electrons on both Cu atoms), due to correlation effects and enhanced by relativistic effects. Following the latter explanation, Schäfer et al.[21] described the Cu−Cu bond in Cu_2Se as an attractive $d^{10}-d^{10}$ interaction. Finally, one can also note the ionic description ($Cu_2^+ + O^-$ or S^-) proposed by Dixon and Gole[36] for Cu_2O and Cu_2S.

In order to confirm the dispersion mechanism induced by correlation, we have performed several tests for Cu_2Se, since this molecule is located in the middle of the Cu_2X series.

We first analyzed the HF molecular orbitals for Cu_2Se. The three highest occupied orbitals are $(19a_1)^2$ $(14b_2)^2$ $(8b_1)^2$. These notations refer to the C_{2v} point group (the yz plane being the molecular plane) and count all the electrons. Figure 1 gives a qualitative representation of these orbitals. The $19a_1$ is mainly a σ_{Cu-Se} orbital, since it is a bonding combination of the Se $4p_z$ orbital and the Cu 4s orbitals. But the two 4s atomic orbitals of the copper atoms are also in a Cu−Cu bonding configuration, with admixture of the Cu $4p_y$ orbitals. The other σ_{Cu-Se} bond orbital is the $14b_2$. Finally, the $8b_1$ orbital represents essentially the nonbonding p_x electron pair on X, while showing also a nonnegligible contribution from the Cu $4p_x$ orbitals. This can be interpreted in terms of delocalization (back-donation) of the $p_\pi(X)$ electron pair into the $p_\pi(Cu)$ orbitals, as was already mentioned for CuO and CuS by Langhoff and Bauschlicher.[32]

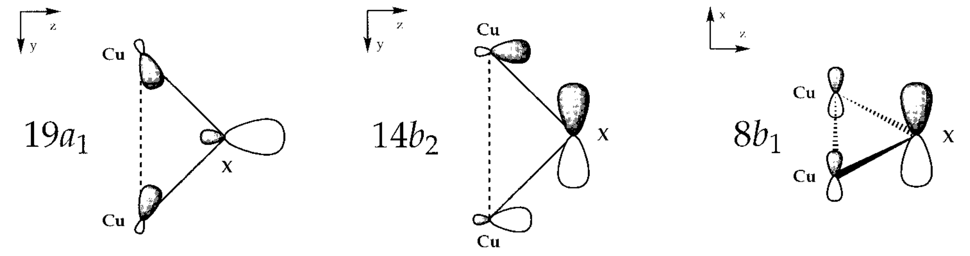

Figure 1. Highest occupied orbitals of ${}^1A_1$ Cu_2X.

TABLE 5: Pseudopotential, Basis Set, and Correlation Effects for ${}^1A_1$ Cu_2Se[a]

method	Cu basis set	r(Cu−Se)	r(Cu−Cu)	α(∠CuSeCu)
		1-Electron Pseudopotential		
RHF	sd	2.212	3.635	110.5
	spd	2.195	3.298	97.4
MP2	sd	2.229	3.603	107.8
	spd	2.208	3.161	91.4
		11-Electron Pseudopotential (HF-PP)		
RHF	sd	2.360	3.728	104.3
	spd	2.313	3.394	94.4
MP2[b]	sd	2.416	3.711	100.3
	spd	2.363	3.302	88.6
MP2	sd	2.284	3.189	88.5
	spd	2.229	2.623	72.1

[a] Bond lengths in Å and bond angles in deg. [b] d electrons not correlated.

This participation of the formally empty Cu 4p orbitals in $19a_1$ and $8b_1$ is made possible by their low energy. As a comparison, the 2p of hydrogen do not contribute to the equivalent orbitals in H_2X. This arrangement of the orbitals in Cu_2Se, which is identical in the other Cu_2X molecules (although the order of the orbitals may be different), is a first indication of the direct Cu−Cu interaction. However, there is no occupied orbital corresponding strictly to a covalent copper−copper bond at the HF level. Related to this fact, Pyykkö and co-workers[53,55,56] found insignificant Mulliken overlap populations for Au−Au interactions, suggesting therefore the lack of covalent bonds.

In order to investigate more thoroughly the effects that produce the copper−copper interaction and the bond angle shortening, we performed additional tests for Cu_2Se. First, the geometry was optimized at the MP2 level, keeping frozen the occupied d orbitals on each copper atom. This removes all d electron correlation effects, in particular the attractive $d^{10}-d^{10}$ dispersion type interaction. Moreover, we also optimized Cu_2Se (correlating all electrons) after deleting the Cu p basis set, to check the influence of these polarization functions. As we mentioned above, Schäfer et al. noticed a significant effect of the copper p functions on the geometry. Finally, HF and MP2 optimizations were performed with the copper 1-electron pseudopotential of ref 57, associated with the basis set from ref 58. The latter test studies the effect of the physical absence of the d electrons, which are treated as core electrons. The results of these tests are summarized in Table 5.

One has to be cautious in the analysis of these results, since simultaneous effects occur when deleting the Cu p basis set or freezing the d electrons. It appears that both the p functions and the correlation of the d electrons play a significant role for the copper−copper distance and thus for the bond angle. In terms of bond angle reduction and using the spd basis set, the correlation of the d electrons has a more significant effect than their mere HF physical presence (16.5° vs 3°). This indicates that replacing the d-shell of copper by a pseudopotential is not a dramatic approximation *at the HF level*. The presence of the Cu p basis set reduces the angle by ∼10° at the HF level, giving the order to magnitude for the p polarization effect and the back-donation described above. At the MP2 level, there is a marked d(Cu)−p(Cu) correlation effect (∼4.5°) (Pyykkö et al.[8,53] obtained a similar result for $(ClAuPH_3)_2$, when deleting the Au p basis set). Correlating all but the d electrons reduces the bond angle by only ∼6° with the 11-electron pseudopotential (and the spd basis set). It is coherent to find almost the same value with the 1-electron pseudopotential. Pyykkö and co-workers[8] also showed the crucial role of correlating the d electrons in order to describe the metallophilic interaction.

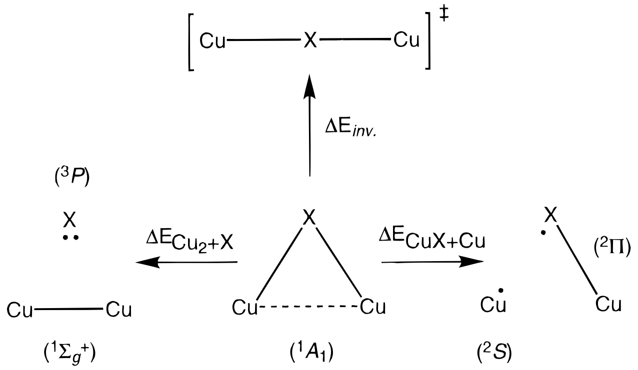

Figure 2. Dissociation modes and transition state for ${}^1A_1$ Cu_2X.

Considering these results, we conclude that the dominant effect explaining the short copper−copper bond distance and the small bond angle is the attractive $d^{10}-d^{10}$ dispersion, as was mentioned by Schäfer et al.[21] The copper 4p orbitals play an important role, both at the HF level (polarization and back-donation) and through d(Cu)−p(Cu) correlation.

Since the Cu−Cu interaction is mainly due to the attractive $d^{10}-d^{10}$ dispersion, the Cu−Cu distance is almost constant through the whole series, as can be seen in Table 3. As the Cu−X bond length increases with the size of X, the Cu−X−Cu bond angle naturally decreases throughout the series. Theoretical[22] and experimental[59,60] results (the latter with ligand-covered molecules) for Au_2S, Au_2Se, and Au_2Te indicate a similar trend for the Au_2X series.

In our previous work,[25] we computed the Cu−Cu bond length in the Cu_2^+ molecule (for which no experimental data exist). The MP2 value using the correlation−corrected pseudopotential is 2.459 Å (as a comparison, the all-electron CPF+RC value, calculated by Kölmel and Ahlrichs,[20] is 2.466 Å). The average Cu−Cu distance for Cu_2X is thus 0.092 Å (or 3.7%) longer than the bond length in Cu_2^+. This result is not in favor of a strictly ionic model. The fact that Cu_2X has a significant ionic character, as was stated by Dixon and Gole,[36] is correct, but seems to be only a straightforward consequence of the differences in electronegativity of Cu and X.

IV.c. Energetics. The dissociation of Cu_2X can follow two directions, which are presented in Figure 2. Table 6 gives the corresponding dissociation energies. The correlation effects are quite significant, as the HF D_e's are much smaller than the MP2

TABLE 6: MP2 Dissociation Energies[a] (kJ/mol) for $^1A_1$ Cu_2X

	HF-PP[b]		MP2-PP	
	ΔE_{CuX+Cu}	ΔE_{Cu_2+X}	ΔE_{CuX+Cu}	ΔE_{Cu_2+X}
Cu_2O	376 (50)	455 (66)	398	459
Cu_2S	321 (124)	407 (218)	339	407
Cu_2Se	298 (118)	362 (200)	314	360
Cu_2Te	267 (111)	303 (183)	281	298
Cu_2Po	249 (93)	263 (142)	263	257

[a] The dissociation modes are described in Figure 2. [b] HF dissociation energies in parentheses.

TABLE 7: Inversion Barrier ΔE_{inv} (kJ/mol) for $^1A_1$ Cu_2X

	MP2, this work			
	HF-PP[b]	MP2-PP	MP2[a,b]	LDF[a]
Cu_2O	34 (~0)	52	41 (3)	76
Cu_2S	82 (33)	110		
Cu_2Se	104 (49)	135		
Cu_2Te	119 (61)	150		
Cu_2Po	142 (78)	178		

[a] Reference 36. See also text. [b] HF barriers in parentheses.

values. The MP2-PP results should be more accurate than the HF-PP values (both obtained at the MP2 level), considering the effect obtained for the diatomics (see Table 2). The stability of Cu_2X decreases when going down the group 16, as it does in CuX. The dissociation toward CuX + Cu is more favorable than toward Cu_2 + X, but the difference between the two modes decreases and the order is even reversed for X = Po (with the correlation-corrected pseudopotential). One can note that the dissociation energy of the Cu−X bond is quite larger in Cu_2X than in CuX, since the copper−copper interaction is also broken in the dissociation process. The difference between these two values can be understood as an estimation of the Cu−Cu interaction energy. The computed values are around 80 kJ/mol, excepted for Cu_2O, with 147 kJ/mol. As a comparison, we computed the bond energy in Cu_2 and obtained 189 kJ/mol (using MP2-PP, see ref 25). This confirms that the copper−copper interaction is a weak bond and also reveals a particular behavior for oxygen, compared to the heavier atoms.

We also computed the barrier corresponding to the transition structure with linear geometry (which was optimized at the same levels as the minimum). This structure exhibits two degenerate imaginary frequencies. The results are displayed in Table 7. As expected, the barrier increases as X becomes heavier, reflecting the reluctance of heavy atoms to maintain sp hybridization. The trend is similar for the two pseudopotentials, but the MP2-PP values should be more reliable, considering the previous results for the geometries. Note the almost nonexistent barrier for Cu_2O at the HF level, which is coherent with the large value of the Cu−O−Cu angle (168.3°) and the very weak bending frequency for the minimum (20 cm^{-1}). Dixon and Gole[36] also obtained a very small HF barrier for Cu_2O. These authors also performed MP2 and LDF calculations for the linear structure, but it is not clear whether their MP2 and LDF barriers were computed after optimization of the linear geometry at these levels of calculation or using the HF structure, the latter possibility then overestimating the barrier. Their MP2 result is close to our values using HF-PP and MP2-PP, but the LDF barrier is significantly higher. The LDF result should again be considered with caution, as mentioned before.

V. Conclusion

The CuX and Cu_2X series have been investigated using low-cost calculations. The accurate results obtained for CuX permited us to enforce the validity of our correlation-corrected pseudopotential for copper, which performs at the MP2 level at least as good as large CCSD(T) or CPF+RC calculations. Moreover, one can hope that the good behavior of our method for the diatomics indicates that the results for Cu_2X are of comparable quality. We now have an insight into the structure and energetics of the heavier analogues of Cu_2Se, the latter molecule being the smallest unit of recently synthesized copper−selenium clusters. The structural and energetic properties show a classical behavior throughout the series. One constant feature is the weak copper−copper interaction, originating from a $d^{10}-d^{10}$ dispersion type interaction.

This work could certainly be carried on with the study of the other XY_2 and XYZ compounds, with X = O, S, Se, Te, or Po and Y,Z = Cu, Ag, or Au. The heaviest molecules can probably present some interest, due to very strong relativistic effects. Likewise, larger (and ligand-covered) $(Cu_2X)_n$ clusters could be investigated, as Schäfer and Ahlrichs did for X = Se.

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