Molecular Orbital Calculations of Cu-Halides

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An ab initio HF MO theory is applied to CuX, CuX_2 (X = F and Cl) and $(CuCl)_3$. Although the detailed sequence of energy levels depends upon the basis set used, high-lying orbital energy levels have largely halogen p-like character, whereas low-lying orbital energy levels have largely Cu 3d-like character. This is in agreement with the chemical intuition of a highly ionic character of these compounds.

I. Introduction

Recently extensive UPS experiments on the vapor of various metal halides have been reported. These metal halides are considered to be largely ionic because of the large difference of the electronegativity of their component atoms. The interpretation of the spectra of alkali [1, 2] and alkaline earth [3] halides are relatively straight-forward. In the spectra of II_B metal halides [4–8], in which the metal atom has a closed d shell, the halogen like p levels are well separated from the metal like d levels because the metal like d levels lie very deeply. However, the situation is much more complicated for transition- [9, 10] and I_B- [11–15] metal halides, because the metal d like levels and the halogen p like levels lie at a similar energy region. Lee and Potts [11] reported UPS experiments of copper fluoride vapor and interpreted them as coexistence of CuF and CuF_2. Potts and Lyus [2] and MacNaughton et al. [13, 14] have reported UP spectra of gaseous copper- and silver-halides, where the halogen atoms are Cl, Br and I. In the CuCl vapor there is evidence [16] of the existence of trimer, $(CuCl)_3$. Due to the coexistence of several species the interpretation of the spectra is not so easy in these cases.

On the other hand, there are several theoretical reports [17–19] on transition- and I_B-metal halides. The recent ab initio Hartree-Fock (HF) MO calculations have shown that the relaxation and correlation energies associated with the open d-shell are very large [19]. This is known as a breakdown of Koopmans' theorem. It is one of difficulties in the theoretical treatment of these halides.

Recently Mello et al. [18] reported HF and MSX_α calculations of CuF_2 and $CuCl_2$. Their calculations show that although the HF method gives higher orbital energies for occupied halide p-like levels than for occupied Cu 3d-like ones, the MSX_α method gives reverse ordering to CuF_2. Berkowitz et al. [15] reported UP spectra of silver halides (AgX, X = Cl, Br and I) and X_α-DVM-SCC calculations of them. From their calculations they concluded that halide p-like levels lie at higher energies than Ag 4d-like levels. They also reported a similar calculation on $(CuCl)_3$, which shows that Cu 3d-like levels lie at higher energies than Cl 3p-like levels, although their calculation on a CuCl monomer shows that Cl 3p-like orbitals, which couple very strongly with Cu 3d, lie above and below the Cu 3d-like levels. Lee and Potts [11] have performed HF and ΔSCF calculations on CuF when they interpreted their UP spectra of copper fluoride. Their ΔSCF calculations show that F 2p- and Cu 3d-like levels lie in the similar energy range.

These metal halides should be rather ionic because of the large electronegativity difference between the component atoms. Then, it is expected that when a Cu atom interacts with a halogen atom, electrons transfer largely from the Cu to the halogen atom, reducing the Cu 3d orbital energy.

The present paper reports ab initio HF MO calculations on CuF, CuF_2, CuCl, $CuCl_2$ and $(CuCl)_3$ in order to get a qualitative picture of these systems from the ab initio MO point of view.

II. Method and Model

Ab initio restricted HF MO calculations were performed. An effective potential replacing the Ar core of Cu atom was employed [20]. Then only the

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valence 3d, 4s and 4p orbitals for Cu were taken into account. Two kinds of basis sets were used in the calculations of CuF and CuF_2. The one is relatively accurate and is composed of the [3s2p] set for F [21] and the [2s1p2d] set for Cu after Wachters [22] and Hay [23]. The 4s and 3d functions are composed of 4 and 6 primitives, respectively. The contraction coefficients were determined by an HF calculation for the Cu $3d^{10}4s^1$ state. The exponent for the p function is taken as 0.12.

In the present work, the calculation is extended to the relatively big molecule of $(CuCl)_3$. Single zeta basis sets and effective potentials for both atoms in the calculations of copper chlorides were used to reduce computational time. The valence only single zeta basis (3 primitives for s and p orbitals) and the effective potential for Cl were taken from Refs. [24] and [25], respectively. The single zeta basis set for Cu, which was determined for the $3d^{10}4s$ state with use of 4 and 3 Gaussian primitives for the 3d and 4s orbitals, respectively, was taken from Ref. [26]. The contraction coefficient were reoptimized because of the use of an effective potential in the present calculation. In order to check the reliability of these basis sets, similar valence only calculations [24, 25] were also performed for CuF and CuF_2.

As reviewed by Pacchioni et al. [24] and Tatewaki et al. [26] the Cu 3d orbital energy is very sensitive to the basis set used, althoug the 4s orbital energy is insensitive. Table 1 shows the 3d and 4s orbital energies of the Cu $3d^{10}4s^1$ state, which were calculated with use of the present two basis sets. The table shows also the corresponding ΔSCF values and the HF limit calculation by Clementi and Roetti [27]. The 3d orbital energy given by the [2s1p2d] basis set is very near the HF limit value, whereas the one by the single zeta set is much higher. It is interesting to note that with the ΔSCF method the relaxation energy accompanied for the 3d ionization is much higher in the [2s1p2d] calculation than that in the single zeta calculation. A similar experience is also reported on calculations of $MgCl_2$ [3].

Recently several UPS experiments on gaseous atoms of IB- and transition metals have been reported [28]. Dyke et al. [28] have shown that with Cu its 4s- and 3d-levels lie at 7.7 eV and 10.5 eV, respectively, below the vacuum level. Comparison with Table 1 shows that the 3d orbital energies given by the [2s1p2d] and HF limit calculations are too deep, whereas the single zeta values and the ΔSCF value by the [2s1p2d] are in reasonable agreement with the experiment stated above.

The p orbital energies of the free halogen atoms given by the HF limit calculations [27] are −19.86 eV for F 2p and −13.78 eV for Cl 3p, whereas the experimental ionization potentials are about 17.5 eV for F 2p and about 13.0 eV for Cl 3p [29].

The models used in the present calculations are as follows. The interatomic distances between Cu and halogen atoms were taken as 1.743 Å for CuF and CuF_2 and as 2.02 Å for CuCl and $CuCl_2$. The former value is the experimental bond distance in CuF [30]. The latter value, which was used in HF calculations of $CuCl_2$ by Mello et al. [18], is the estimated value for CuCl by Stevenson [31]. Linear models for the dihalides were used. The molecular axis was taken as the z-axis. In the calculation of $(CuCl)_3$ the molecular geometry was taken as a planar structure (D_{3h}), as determined by Wong and Schomaker [16]. An experimental Cu-Cl distance of 2.16 Å was taken.

III. Results and Discussion

Tables 2 to 5 show calculated orbital energies and electron populations for CuF and CuF_2, CuCl and $CuCl_2$ and $(CuCl)_3$.

It is seen from Tables 2 to 4 that when a Cu atom interacts with a single halogen atom, the Cu 3d-like orbital energies decrease from the free Cu 3d energies shown in Table 1, whereas the halogen p like orbital energies increase. The Cu 3d energies decrease further when the Cu atom interacts with one more halogen atom to form a dihalogen compound. In this process the halogen p like energies

Basis	[2s1p2d]		single zeta		HF limit [27]	
	ε_i	ΔSCF	ε_i	ΔSCF	ε_i	ΔSCF
3d	−13.98	−10.05	−11.58	−11.43	−13.35	
4s	−6.20	−6.12	−6.01	−6.01	−6.47	−6.40

Table 1. The 3d and 4s orbital energies, ε_i, and the corresponding ΔSCF values for Cu $3d^{10}4s^1$ state (in eV unit).

Table 2. Orbital energies ε_i and the corresponding ΔSCF values and electron populations for CuF and CuF_2 in the [2s 1p 2d/3s 2p] basis calculation.

a) Orbital energies (eV).

CuF				CuF_2		
Character		ε_i	ΔSCF	Character		ε_i
F2p	σ	− 11.99	− 9.48	F2p	πg	− 15.71
	π	− 12.52	− 9.29		σu	− 15.83
Cu 3d	δ	− 15.30	− 12.04		πu	− 16.11
	π	− 15.94			σg	− 18.96
	σ	− 16.39		Cu 3d	σg^*	− 23.62
F2s	σ	− 37.61			δg	− 24.69
					πg	− 25.84
				F2s	σu	− 40.62
					σg	− 41.02

* This level is singly occupied. Other levels are doubly occupied.

b) Electron populations.

	CuF	CuF_2
F	9.699	9.621
Cu	10.301	9.757

Table 3. Orbital energies ε_i and the corresponding ΔSCF values and electron populations of CuF and CuF_2 in the single zeta calculation.

a) Orbital energies (eV).

CuF				CuF_2		
Character		ε_i	ΔSCF	Character		ε_i
F2p	σ	− 8.35	− 6.26	F2p	σu	− 10.28
	π	− 10.35	− 6.23		πg	− 12.04
Cu 3d	δ	− 13.99	− 12.48		πu	− 12.48
	σ	− 14.12			σg^*	− 12.77
	π	− 14.61		Cu 3d	σg	− 17.47
F2s		− 32.40			δg	− 19.17
					πg	− 19.83
				F2s	σu	− 33.98
					σg	− 34.52

* This level is singly occupied. This level and the Cu 3dσg level at − 17.47 eV are composed of very strong antibonding and bonding interactions between F 2p_z and Cu 3d_z2 orbitals, respectively.

b) Electron populations.

	CuF	CuF_2
F	7.584	7.591
Cu	10.416	9.818

Table 4. Orbital energies ε_i and the corresponding ΔSCF values and electron populations of CuCl and $CuCl_2$ in the single zeta calculation.

a) Orbital energies (eV)

CuCl				$CuCl_2$		
Character		ε_i	ΔSCF	Character		ε_i
Cl 3p	σ	− 9.49	− 8.92	Cl 3p	σu	− 11.74
	π	− 9.68	− 8.75		πg	− 12.18
Cu 3d	δ	− 14.33	− 13.40		πu	− 12.57
	σ	− 14.70			σg^*	− 14.26
	π	− 14.85		Cu 3d	σg	− 18.76
Cl 3s	σ	− 26.22			δg	− 20.80
					πg	− 21.63
				Cl 3s	σu	− 28.86
					σg	− 29.40

* This level is singly occupied. This level and the Cu 3d-σg level at − 18.76 eV are composed of very strong antibonding and bonding interactions between Cl 3p_z and Cu 3d_z2 orbitals, respectively.

b) Electron populations

	CuCl	$CuCl_2$
Cl	7.755	7.601
Cu	10.245	9.799

Table 5. Orbital energies and electron populations of $(CuCl)_3$ in the single zeta calculation.

a) Orbital energies (eV).

Symmetry	$-\varepsilon_i$	Character	Assignment (average energy)
e'	11.13	Cl 3p	Peak 1 (11.32)
e''	11.41		
e'	11.42		
a_2''	12.02		Peak 2 (12.16)
a_2'	12.15		
a_1'	12.32		
e'	14.65	Cu 3d	Peak 3 (14.80)
e''	14.70		
a_2''	14.82		
a_1'	14.82		
a_1'	14.93		
a_1''	14.95		
a_2'	14.97		
e''	15.42		Peak 4 (15.63)
e'	15.64		
e'	15.83		
e'	28.48	Cl 3s	
a_1'	28.68		

b) Electron populations.

Cl	7.791	Cu	10.209

decrease. These results are consistent with the electron population results shown in those tables, which indicate a large electron transfer from Cu to the halogen atom. Thus, the halogen p-like levels lie at higher energies than the Cu 3d like levels. This ionic character of these compounds differs from the metallic (or covalent) character of Cu_n ($n=1$ to 13) clusters, for which HF MO calculations [32] show that the Cu 3d energy remains roughly constant with increase of the number of atoms in the cluster.

Comparison between Tables 2 and 3 reveals a basis set dependence of the calculated results. It is natural that the orbital energies given by the [2s1p2d] basis are deeper than those by the single zeta basis. The order of the orbital energies depends upon the basis set used. These tables show also the ΔSCF values for CuF. The present calculations show that even if the ΔSCF method is used to estimate the orbital energies, the F 2p like orbitals remain at higher energies than the Cu 3d like orbitals for both basis sets. The present results are at variance with those of Lee and Potts [11]. In their calculations the F 2p like and Cu 3d like orbitals lie in a similar energy range. The valence only single zeta calculations of mono- and di-halides shown in Tables 3 and 4 show that if similar basis sets are used for F and Cl atoms, the calculated results are closely similar, independent of species of halogens.

The basis set dependence of the calculated results occurs also in the dihalogen compounds, CuF_2 and $CuCl_2$, for which several ab initio MO calculations [17, 18] have been reported. In these compounds the halogen $p_z\,\sigma_g$-like and Cu $3d_{z^2}\,\sigma_g$-like levels are composed of antibonding and bonding interactions between the halogen p_z and Cu $3d_{z^2}$ atomic orbitals, respectively. These interactions are very weak in the [2s1p2d] basis calculations of CuF_2 (Table 2). That is, the halogen p like orbitals and Cu 3d like orbitals are well localized on the respective atom. In the single zeta calculations of CuF_2 and $CuCl_2$ (Table 3 and 4), however, these interactions are too strong to tell which level is localized on the respective atom.

Lee and Potts [11] have reported UPS experiments on copper fluoride vapor and attempted peak assignments in terms of the coexistence of CuF and CuF_2. The present calculations, using two kinds of the basis sets (Tables 2 and 3), do not support their assignments nor propose new assignments.

The UP spectra [12 – 14] of the trimer, $(CuCl)_3$, show four main peaks at 10.0, 10.8, 12.6 and 14.0 eV below the vacuum level. Roughly speaking, they are closely similar to the UP spectra observed for other IB metal halide trimers [12 – 14]. Table 5 shows orbital energies of $(CuCl)_3$ and their main atomic character in the valence only single zeta basis calculation. As discussed in the cases of CuCl and $CuCl_2$, the high lying energy levels have largely Cl 3p-like character, whereas the low-lying levels have largely Cu 3d-like character, although there exists considerable mixing between Cl 3p and Cu 3d in the several levels. These results are consistent with the ionic character of this molecule as seen from the results of electron population. In the same table, an attempt to assign the four main peaks observed in the UPS experiments is also shown. Recently Berkowitz et al. [15] have reported X_α calculations on $(CuCl)_3$, which suggest that the high lying two peaks have mainly Cu 3d like character, whereas the low-lying two peaks have mainly Cl 3p-like character. Their results do not agree with the present HF MO calculations.

IV. Conclusion

RHF calculations of CuX, CuX_2 (X = F and Cl) and trimer $(CuCl)_3$ molecules are reported. It is shown that the detailed orbital ordering depends upon the basis set used, therefore the results should be regarded as being qualitative. The high lying orbital energy level of these molecules have largely halogen p-like character, whereas the low lying orbitals have largely Cu 3d like character. The fact that the halogen p-like levels lie at higher energies than the Cu 3d like levels is consistent with the usual chemical intuition the highly ionic character of these compounds. In fact the electron populations show large electron transfers from the Cu to the halogen atoms.

The present calculations on CuF and CuF_2 do not explain the UP spectra of copper fluoride vapour reported by Lee and Potts [11]. The present CuF calculation does not agree with the ab initio calculations reported by them because of the different basis sets used. It seems to be necessary to separate single species from a mixture in order to interprete UP spectra in detail, although it may be a very difficult task.

An attempt to assign four main peaks observed in the UPS experiment on gaseous trimer, $(CuCl)_3$ is put forth. The present calculation suggests that the high lying two main peaks are derived mainly from Cl 3p levels, whereas the low lying two peaks are derived mainly from Cu 3d levels. These results are consistent with the other results on mono- and di-halides reported in this paper. However, they do not agree with the X_α calculation.

Even within the framework of X_α theory, there seems to exist some discrepancy. For example, the X_α reports by Berkowitz et al. [15] show that with Ag monohalide (Cl, B and I), the halogen p-like orbital energies lie at higher energies than the Ag 4d-like levels, while with CuCl the situation is reversed. From a chemical point of view all I_B metal halides should have similar properties.

Recent UPS experiments [33] on Cl, Br and I adsorption on Ag surfaces have shown that the adsorbate-induced levels appear above and below the Ag 4d band. From the present calculations it is suggested that the induced levels above and below the Ag 4d band belong to the halogen p-like and the Ag 4d-like orbitals, respectively. These adsorbate induced levels arise due to the large electron transfer from Ag to the halogen atom. A similar decrease of the metal d levels is experienced in the HF calculations of Ni- and Cu-PF$_3$-clusters [34].

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