Studies of the Electronic Structure of Copper Fluorides and Copper Chlorides

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Abstract: The electronic structure of the copper halides CuF_2 (linear), $CuCl_2$ (linear), $CuCl_4^{2-}$ (T_d, D_{2d}, D_{4h}), CuF_6^{4-} (D_{4h}), and $CuCl_6^{4-}$ (D_{4h}, O_h) is studied by means of the ab initio SCF (RHF and UHF), the MSXα, and the INDO methods. Excited states due to d-d and charge-transfer transitions are calculated. It is found that the results obtained by RHF and UHF differ insignificantly from each other. Large discrepancies between the ab initio and MSXα results, for spectra as well as charge distributions, are found particularly for the chlorides. Comparison with the available experimental information shows that the excitation energies consistently come out too low in the ab initio ΔSCF calculations. The MSXα results appear to be less consistent, often suggesting an incorrect ordering of states, but in better numerical agreement with the experimental transition energies. The INDO method appears to be capable of yielding results in reasonable agreement with experiment. An analysis of the charge distribution suggests that ab initio methods predict too little and the MSXα method predicts too large σ donation, whereas the charge distribution given by the INDO method is satisfactory. Our conclusion on the calculations is that transition-metal compounds, particularly those of copper, are particularly difficult to calculate accurately and that correlation effects ought to be included in a systematic way. For linear $CuCl_2$ we deduce that both the ligand field transitions to the $^2\Pi_g$ and $^2\Delta_g$ states lie within the band observed with maximum at ~9000 cm^{-1}. Both $^2\Pi_u$ and $^2\Sigma_u^+$ charge transfer states lie within the band with the maximum at 19 000 cm^{-1} and borrowing from the $^2\Sigma_u^+$ state is responsible for most of the d-d intensity. For $CuCl_4^{2-}$ (D_{2d}) we obtain the order of states $^2B_2 < {}^2E < {}^2B_1 < {}^2A_1$, in agreement with previous work. For $CuCl_4^{2-}$ (D_{4h}) we deduce the order $^2B_{1g} < {}^2B_{2g} < {}^3E_g < {}^2A_{1g}$; although the INDO and MSXα results are in good agreement, only the ab initio ordering seems correct. For the $CuCl_6^{4-}$ cluster the ordering of states is $^2B_{1g} < {}^2A_{1g} < {}^2B_{2g} < {}^2E_g$. The position of the $^2B_{2g}$ state seems secure from polarization information; the sequence of the $^2A_{1g}$ and ^2E_g states is less secure. A discussion of the bonding and electronic structure of these complexes is given.

I. Introduction

The electronic properties and the stereochemistry of copper complexes have been the subject of several reviews.[1-3] As a first step in an attempt to arrive at a better understanding of larger systems, we have studied the electronic structure of some copper(II) complexes, small enough to be accessible to the current quantum-chemical methods.

The study of the electronic structure of even the smallest transition-metal compounds is still a difficult task, even by present-day standards. It is less than one decade ago since ab initio calculations on such systems became feasible.[4] The use of basis sets of at least double-ζ quality for both core and valence orbitals first became possible in the mid-1970s. The ab initio method is applied to several copper halides in the present work. The basis sets used are of better than dougle-ζ quality throughout, which should guarantee a certain consistency and reliability of the results. We often applied both the spin-unrestricted Hartree-Fock[5] (UHF) and the restricted Hartree-Fock[6] (RHF) methods in order to assess the differences obtained by relaxing the equivalence and symmetry restrictions.

The multiple scattering Xα (MSXα) method[7,8] has the advantage of not using radial basis sets for the expansion of the orbitals, but involves a serious approximation, the muffin-tin form of the potentials and in addition the Xα local exchange approximation.[9] In spite of these simplifications, the MSXα method has in many cases shown a reasonable agreement with experiment, in particular in the calculation of the ligand field spectra of cubic transition-metal complexes.[10-12]

The third method used in the present study was of the semiempirical type, based on the intermediate neglect of differential overlap (INDO) approximation.[13] This is the simplest of the approximate theories in which the electrostatics of the problem is well represented; INDO includes all one-center exchange terms necessary for proper representation of spectra and has previously shown its capacity to yield reliable results in the treatment of transition-metal compounds.[14-16]

By applying all three of the above-mentioned methods to the study of, primarily, the absorption spectra of copper halides, we intended to learn not only about the systems being studied, but also about the characteristic features of these methods.

One particular feature of transition-metal compounds, namely, the importance of reorganization effects upon excitation or ionization leading to a "breakdown of Koopmans' theorem",[17] has been well known for some time.[4] The implication is that it is not possible to attach the usual physical significance to the ordering and the magnitude of the orbital energies in MO-LCAO calculations on copper complexes.

Another question we considered was the dependence of the ab initio results on variations in the basis set. In their work on the $CuCl_4^{2-}$ complex, Demuynck, Veillard, and Wahlgren[18] reported drastic changes in the outcome of the Mulliken population analysis[19] as a consequence of variations in the valence part of the atomic basis. The charge distribution is intimately connected to the degree of mixing between the copper and the ligand orbitals in the bonding orbitals whose antibonding counterparts are unoccupied. In view of the historical importance of crystal field theory and ligand field theory[20,21] for the explanation of the electronic structure of transition-metal complexes, a discussion of the degree of mixing as obtained from more refined models must certainly be of relevance. A technical problem is here posed by some basic differences between the MO-LCAO and the MSXα methods, making a direct comparison of the orbital characters a rather cumbersome task.

The next section contains a brief description of the methods and section III some computational details. Section IV contains the results, together with their discussion in connection with available experimental information. A division is made into a discussion of the copper dihalides CuF_2 and $CuCl_2$, the copper tetrahalides $CuCl_4^{2-}$ (T_d, D_{2d}, D_{4h}), and the copper hexahalides CuF_6^{4-} (D_{4h}) and $CuCl_6^{4-}$ (O_h, D_{4h}). Conclusions are drawn in section V.

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0002-7863/80/1502-1278$01.00/0

II. Theoretical Models

The unrestricted Hartree–Fock equations[5] are given by

$$H\varphi_i = \left(-\frac{1}{2}\nabla^2 - \sum_{a=1}^{M} \frac{Z_a}{|\mathbf{r} - \mathbf{R}_a|} + J(\gamma) - U\right)\varphi_i = \epsilon\varphi_i \quad (1)$$

where φ_i is a spin orbital and M is the number of nuclei (with charges Z_a). Since the Coulomb operator $J(\gamma)$ and the exchange operator $U = K(\gamma)$ depend on the density matrix

$$\gamma(1,1') = \sum_{i=1}^{N} \varphi_i(1)\varphi_i^*(1') \quad (2)$$

(where N is the number of electrons), eq 1 has to be solved iteratively. The molecular orbitals are generally expanded in a Gaussian basis set, $\boldsymbol{\chi}$, with the basis functions centered on the atomic nuclei. Equation 1 is then transformed into a matrix equation:

$$\mathcal{F}C_i = \mathcal{S}C_i\epsilon_i \quad (3)$$

where $\varphi_i = \boldsymbol{\chi}C_i$ and $\mathcal{S}$ is the basis overlap matrix, $\boldsymbol{\chi}^\dagger\boldsymbol{\chi}$.

The α spin Fock matrix $\mathcal{F}^\alpha$ is given by

$$\mathcal{F}_{\mu\nu}{}^\alpha = h_{\mu\nu} + \sum_i \{(\chi_\mu{}^\alpha\chi_\nu{}^\alpha|\varphi_i\varphi_i) - (\chi_\mu{}^\alpha\varphi_i|\chi_\nu{}^\alpha\varphi_i)\} \quad (4)$$

where

$$h_{\mu\nu} = \left(\chi_\mu\middle| -\frac{1}{2}\nabla^2 - \sum_a \frac{Z_a}{|\mathbf{r} - \mathbf{R}_a|}\middle|\chi_\nu\right) \quad (5)$$

$$(\chi_\mu\chi_\nu|\varphi_i\varphi_j) = \int d\tau(1)d\tau(2)\chi_\mu{}^*(1)\chi_\nu(1)r_{12}{}^{-1}\varphi_i(2)\varphi_j{}^*(2)$$

$$= \sum_{\sigma,\lambda} C_{i\sigma}C_{j\lambda}(\chi_\mu\chi_\nu|\chi_\sigma\chi_\lambda) \quad (6)$$

where a similar expression exists for the β spin Fock matrix, $\mathcal{F}^\beta$. In ab initio Hartree–Fock calculations, all the integrals implicit in eq 5 are evaluated. It is the evaluation of the two-electron integrals of eq 6 that is the most expensive step in the ab initio calculation of electronic structure.

The intermediate neglect of differential overlap theory (INDO)[13] also solves eq 3 using eq 4. Equation 6, however, is simplified by evaluating *all* one-center two-electron integrals, only two-center integrals of the type $(\chi_\mu\chi_\mu|\chi_\gamma\chi_\gamma)$, and no three- or four-center integrals. Because of this there is a drastic reduction of the number of integrals evaluated from N^4 to N^2, and INDO calculations are typically 100–1000 times faster than the ab initio counterparts. The INDO theory that is used here is that of Bacon and Zerner, and is described in ref 14.

The orbitals may also be expanded around each atomic center A as

$$\varphi(\mathbf{r}) = \sum_{l,m} C_{lm}{}^{A}R_{lm}{}^{A}(r)Y_{lm}(\theta,\phi) \quad (7)$$

where r, θ, and ϕ refer to the spherical coordinates around center A. In the multiple scattering method the functions $R_{lm}{}^{A}(r)$ are numerically integrated, which can, in practice, be done only after rather drastic approximations. A local approximation, the Xα approximation, to the exchange operator is used.[9] The potentials are approximated as "muffin-tin" potentials.[7,8] Each atomic center is surrounded by a sphere with radius b_A in which the potential is spherically symmetric:

$$U \sim V(\mathbf{r}) \sim V_0{}^{A}(r) \text{ for } r < b_A \quad (8)$$

Equation 1 is now integrated outward in each atomic sphere. The atomic spheres are normally chosen tangential to each other and are further surrounded by an outer sphere with radius b_{out}. We have

$$V(\mathbf{r}) = V_0{}^{out}(r) \text{ for } r > b_{out} \quad (9)$$

In the interstitial region, finally, the potential is approximated to be constant. The eigenvalue condition is obtained by requiring the orbitals and their derivatives to match at the sphere surfaces.

The system is stabilized by a so-called Watson sphere with a homogeneously distributed positive charge equal to the excess negative electron charge of the cluster.

In both methods the total wave function is approximated as a single Slater determinant. In the Hartree–Fock method there is no term which represents correlation in the one-particle equation.[23] The Xα exchange approximation used in the MSXα method is, in principle, an approximation to the Hartree–Fock exchange term. It has been argued that the Xα exchange has its own merits and in some sense includes a correlation contribution,[9,23] but it seems that these arguments are rather weak.

III. Computational Details

The ab initio calculations were carried out by means of the programs MOLECULE,[24] ALCHEMY-SCF[25] (open-shell restricted HF), and UHF.[26]

In using RHF for open-shell systems some care has to be taken in the calculation of degenerate states in order to avoid the symmetry breaking caused by excitation of an electron from a molecular orbital having an equivalent counterpart in another irreducible representation. In such situations, the requirement of symmetry and equivalence restrictions often necessitates the specification of noninteger occupation numbers for open-shell orbitals.

In all open-shell cases UHF yields a state which is not completely symmetry adapted.[27] Sometimes even the point-group symmetry of the state considered cannot be retained. This situation occurs quite frequently in calculations on symmetric molecules, since the highest symmetry assumed in the MOLECULE program is D_{2h}.

The ab initio calculations were done using basis sets of double-ζ quality for the core and of extended type for the valence orbitals. In order to study the influence of the basis we used several different sets in the calculation for CuF_2. As the results of this study are somewhat technical we report only the computations on three bases, and defer more detailed discussion. Bases set 2 (BS2) differs from BS1 by the inclusion of 4p-type atomic orbitals. BS3 also includes these 4p AOs, but differs from BS1 and BS2 in utilizing a basis optimized for F^- rather than F. The basis sets used in this study are summarized in Table I.

In the MSXα calculations we used the Liberman-Batra modification of Johnson's and Smith's program.[39,40] The muffin-tin spheres were tangential (Table II). For CuF_2 we used the same F radius as in earlier work.[10] For the chlorides we used the ratio 0.77 between the copper and chlorine radius for $CuCl_2$ and $CuCl_2{}^{2-}$ (D_{4h} and T_d). The copper radius then obtained was used in the remaining calculations. The α values were taken from Schwarz.[41]

For precise details of the INDO program we refer to Bacon and Zerner's recent paper.[14] No modifications were made to the method described there.

In both the ab initio and INDO calculations considered in this paper we frequently encountered serious convergence problems. In order to deal with these difficulties in an adequate way, new developments in addition to the well-known existing procedures like damping and level shifting[42] had to be carried out. Details are reported elsewhere.[43,44]

IV. Results and Discussion

A. Copper Dihalides. CuF_2 and $CuCl_2$. The copper atom has a ^2S ($d^{10}s$) ground state. Upon complexation with two halogen atoms in the formation of the linear dihalide, copper formally loses two electrons to the halogens to become d^9. Assuming the

Table I. Interatomic Distances and Basis Sets Used in the Calculations

clusters		interatomic distances, Å		basis set	
compd	symmetry	Cu-X$_1$	Cu-X$_2$ (axial)	Cu	X
CuF_2	$D_{\infty h}$	1.759[a]		14,9,5 to 8,4,3[b]	9,5 to 4,3[c]
CuF_2	$D_{\infty h}$	1.759[a]		14,11,5 to 8,7,3[b]	9,5 to 4,3[c]
CuF_2	$D_{\infty h}$	1.759[a]		14,11,5 to 8,7,3[d]	9,5 to 4,3[e]
$CuCl_2$	$D_{\infty h}$	2.020[f]		14,11,5 to 8,7,3[d]	12,9 to 6,5[g]
CuF_6^{4-}	D_{4h}	1.937[h]	2.275[i]		
$CuCl_4^{2-}$	T_d	2.265			
$CuCl_4^{2-}$	D_{2d}	2.230			
$CuCl_4^{2-}$	D_{4h}	2.265[j]		14,9,5 to 8,4,3[b]	12,9 to 6,5[g]
$CuCl_6^{4-}$	O_h	2.265			
$CuCl_6^{4-}$	D_{4h}	2.265[k]	2.950[k]		

[a] As obtained in the calculation by Basch et al., ref 29. Regarding other distances used, see text. [b] Reference 28; see text. [c] Reference 30, for fluorine. [d] See text and ref 32. [e] Reference 31, for F ion. [f] Reference 32. Regarding other distances used, see text. [g] Reference 33. [h] From CuF_2, ref 34 and 35. [i] For Cs_2CuCl_4, ref 3 and 36. [j] For $(nmpH)_2CuCl_4$, ref 3 and 37. [k] From $CuCl_2{}^2$, ref 3 and 38.

Table II. Sphere Radii Used in the MSXα Calculations

cluster	symmetry	R_{Cu}, au	R_X, au
CuF_2	$D_{\infty h}$	1.474	1.850
$CuCl_2$	$D_{\infty h}$	1.6557	2.1615
$CuCl_4^{2-}$	D_{4h}	1.8874	2.4590
$CuCl_4^{2-}$	D_{2d}	1.8874	2.3274
$CuCl_4^{2-}$	T_d	1.8874	2.4590
$CuCl_6^{4-}$	O_h	1.8874	2.4590
$CuCl_6^{4-}$	D_{4h}	1.8874	1.7726 2.4126[a]
$CuCl_6^{4-}$	D_{4h}	1.8874	2.4590 3.6873[a]

[a] Sphere radii for the axial halides.

Table III. Excitation Energies (cm^{-1}) from $^2\Sigma_g{}^+$ Ground State of CuF_2[f]

method		$^2\Pi_g$	$^2\Delta_g$	$^2\Sigma_u$	$^2\Pi_u$
RHF[a]	K	17 930	11 437		
RHF[b]	K	13 768	11 187		
RHF (BS1)[c]	Δ	4073	8749	52 323	52 784
RHF (BS2)[c]	Δ	3687	7704	60 312	60 795
RHF (BS2)[c]	K	19 194	9392	109 734	113 820
RHF (BS3)	Δ	4357	8736		
UHF (BS1)[c]	Δ	4221	8952		
UHF (BS2)[c]	Δ	3643	7857	55 001	55 480
UHF (BS3)[c]	Δ	4270	8873		
MSXα-TS[c]	Δ	8790	15 492		
INDO[d]	Δ	11 390	13 193		17 025
AOM[e]		7000	11 000		

[a] Reference 29, vertical excitation at R = 1.759 Å. [b] Reference 29, adiabatic excitation. [c] Vertical excitations at R = 1.759 Å, this work (Δ = ΔSCF). BS1, BS2, and BS3 are described in the text and in Table I. [d] Vertical excitations at optimized distance R = 1.82 Å. [e] Reference 51, angular overlap model, vertical excitations at R = 1.80 Å. [f] Δ = ΔSCF; orbitals optimized self-consistently for each state. K = frozen orbitals of the ground state.

z axis as the molecular axis, classical crystal field considerations suggest that the d_{z^2} orbital should lie highest in energy and be singly occupied. The d_{xz} and d_{yz} orbitals of π_g symmetry and the $d_{x^2-y^2}$ and d_{xy} orbitals of δ_g symmetry are all doubly occupied. Laporte forbidden transitions are $^2\Sigma_g{}^+ \rightarrow {}^2\pi_g$ and $^2\Sigma_g{}^+ \rightarrow {}^2\Delta_g$, with the former excitation lower according to classical considerations.

Experimental information on the dihalides of copper is somewhat scarce and consists of electron spin resonance (ESR) studies and optical spectra in the case of CuF_2[45] and optical and vibrational spectra in the case of $CuCl_2$.[46-50]

1. CuF_2. The CuF_2 molecule is thought to be linear and with essentially ionic bonds. Ab initio calculations were carried out previously by Basch, Hollister, and Moskowitz.[29] These authors used a minimal basis set for the core and a double-ζ basis set for the valence shell. Their excited states were obtained by the frozen-orbital approximation. We have also calculated these excitations using the frozen-orbital approximation and report these values for BS2. That the ΔSCF results, marked "Δ" in Table III, are calculated below those for frozen-orbital approximation, marked "K", is expected, as the latter contain no relaxation for the excited state. Clearly the role of relaxation for the $^2\pi_g$ state is important, reversing the order of $^2\pi_g$ with $^2\Delta_g$.

From Table III we note that the calculated transition energies are affected very little in passing from BS1 to the larger basis BS2, and even to BS3 that utilizes the F$^-$ basis. This is to some extent a consequence of the local nature of the d-d excitations and the fact that these orbitals have the same representation in all three bases. We note further that the Mulliken population analysis changes only slightly for this change of basis; comparing the very different BS1 to BS3, the net charge on copper for the ground state decreases from 1.64 to 1.59, and the total overlap population increases only slightly from 0.27 to 0.33. Another ramification of the local nature of the excitations is that these populations are essentially the same for the $^2\Sigma_g{}^+$ ground state as they are for the $^2\pi_g$ and $^2\Delta_g$ states (Table IV).

In the MSXα calculations the excitation energies have been calculated using Slater's transition-state theory.[9] The results obtained are about a factor of 2 larger than those obtained from SCF ab initio calculations.

The INDO results obtained are also given in Table III. They are in reasonably good numerical agreement with the results obtained from MSXα theory. The calculated expectation values of the spin operator S^2 for the $^2\Sigma_g$, $^2\pi_g$, and $^2\Delta_g$ states are 0.7522, 0.7503, and 0.7502, respectively, which are all close to the correct value 0.75. This is consistent with the fact that UHF and RHF ab initio calculations yield nearly the same results. Also in accord with the ab initio findings is the result that the charge on copper changes only very slightly upon electronic excitation: for all three states the charge is about 1.0 (Table IV).

Table III also contains for comparison an estimate of transition energies from the "angular overlap model".[51-54] Our conclusions from Table III are that there exist two low-lying excitations in CuF_2, $^2\Sigma_g{}^+ \rightarrow {}^2\pi_g$ and $^2\Sigma_g{}^+ \rightarrow {}^2\Delta_g$, and that the transition energy of the former is smaller by 3000-5000 cm^{-1}.

Experimentally no absorption was found in the regions 11 000-30 000 or 1000-5000 cm^{-1}. The region where we might predict to see these transitions, 5000-11 000 cm^{-1}, was not experimentally accessible.[45]

The spin orbital energies by the Hartree-Fock, INDO, and MSXα methods are summarized in Tables V and VI, respectively. The HF methods give higher orbital energies for all the occupied F(2p)-type molecular orbitals than for the occupied

Table IV. Net Mulliken Populations by the UHF (BS2) and INDO Methods on Copper and Integrated Charges in the Copper MSXα Spheres for the Low-Lying States of CuF_2 and $CuCl_2$

		CuF_2			$CuCl_2$		
states		ab initio	INDO[a]	MSXα	ab initio	INDO[a]	MSXα
$^2\Sigma_g{}^+$	α	14.32	14.42	26.22	14.54	14.37	26.83
	β	13.30	13.60		13.51	13.44	
	net	1.38	0.98		0.95	1.19	
$^2\Pi_g$	α	14.31	14.46	26.23	14.52	14.38	26.84
	β	13.33	13.54		13.55	13.46	
	net	1.36	1.00		0.93	1.16	
$^2\Delta_g$	α	14.33	14.51	26.18	14.55	14.59	26.72
	β	13.32	13.49		13.54	13.41	
	net	1.35	1.00		0.91	1.17	
$^2\Sigma_u{}^+$	α	14.10	14.11		14.22	14.09	26.90
	β	14.33	14.58		14.30	14.23	
	net	0.57	0.30		0.48	0.68	
$^2\Pi_u$	α				14.23	14.10	26.90
	β				14.25	14.13	
	net				0.52	0.77	

[a] The INDO results are deorthogonalized assuming the atomic basis as a symmetrically orthogonalized basis of STOs, to which nine core electrons have been added.

Table V. Molecular Orbital Eigenvalues (au) and Characteristics of CuF_2 and $CuCl_2$ $^2\Sigma_g{}^+$ State

	$CuCl_2$				CuF_2 (BS2)			
	ab initio		INDO		ab initio		INDO	
symmetry	RHF	UHF	UHF	symmetry	RHF	UHF	UHF	character
$8\sigma_g{}^+$	−0.841	−0.882	−1.056	$6\sigma_g{}^+$	−0.795	−0.861	−0.946	$3d_{z^2}$
$3\pi_g$	−0.456	−0.455	−0.476	$2\pi_g$	−0.558	−0.559	−0.545	halide "p"
		−0.456	−0.475			−0.558	−0.542	
$4\pi_u$	−0.477	−0.477	−0.490	$3\pi_u$	−0.580	−0.580	−0.566	halide "p"
		−0.477	−0.489			−0.581	−0.563	
$7\sigma_u{}^+$	−0.500	−0.498	−0.514	$5\sigma_u{}^+$	−0.585	−0.584	−0.549	halide "p"
		−0.501	−0.498			−0.585	−0.489	
$9\sigma_g{}^+$	−0.572	−0.528	−0.493	$7\sigma_g{}^+$	−0.640	−0.581	−0.503	halide "p"
		−0.562	−0.534			−0.631	−0.552	
$1\delta_g$	−0.783	−0.806	−0.951	$1\delta_g$	−0.746	−0.771	−0.886	$3d_{x^2-y^2}$, $3d_{xy}$
		−0.757	−0.919			−0.722	−0.856	
$2\pi_g$	−0.836	−0.851	−0.976	$1\pi_g$	−0.798	−0.814	−0.912	$3d_{xz}$, $3d_{yz}$
		−0.818	−0.956			−0.782	−0.893	
$6\sigma_u{}^+$	−1.080	−1.079	−0.945	$4\sigma_u{}^+$	−1.482	−1.483	−1.390	halide "s"
		−1.081	−0.940			−1.483	−1.376	
$7\sigma_g{}^+$	−1.096	−1.109	−0.883	$5\sigma_g{}^+$	− 1.491	−1.493	−1.341	halide "s"
		−1.096	−0.923			−1.491	−1.316	

Table VI. Orbital Energies and Charge Distributions of the Spin-Polarized MSXα Calculation for the $^2\Sigma_g{}^+$ Ground State of CuF_2

			sphere charges, % of e$^-$ [a]			
orbital	spin	energies, au	Cu	F	int	out
$7\sigma_g{}^+$	α	−0.330	56.3	28.4	14.5	0.8
	β	−0.309				
$2\pi_g$	α	−0.375	66.3	25.6	7.9	0.2
	β	−0.348	73.5	18.2	8.1	0.2
$1\delta_g$	α	−0.400	89.7	0.0	10.3	0.0
	β	−0.369	89.3	0.0	10.7	0.0
$1\pi_g$	α	−0.455	24.2	61.0	14.0	0.8
	β	−0.440	17.0	68.0	14.0	1.0
$6\sigma_g{}^+$	α	−0.489	33.5	56.6	8.8	1.1
	β	−0.471	28.4	61.3	9.1	1.2

[a] int = interstitial region; out = outer-sphere region.

Cu(3d) type. The UHF and RHF results are very similar. The exception is the unoccupied $3d_{z^2}$ β spin orbital, which has a high orbital energy owing to the fact that all unoccupied orbitals in the Hartree–Fock methods are subject to an $N + 1$ particle potential. The differences noted in the UHF and RHF α spin orbital energies (occupied) of the $3d_{z^2}$ orbital are also expected, and are related to the exchange terms.

The MSXα orbital energies (Table VI) are in the same order as in the crystal field or ligand field theories. The $3d_{z^2}$ spin orbitals have the highest energies, in agreement with the "aufbau" principle. The mixing between Cu(3d) and F(2p) is surprisingly high, when compared to the result obtained by other methods examined here.

In Figure 1 we have plotted the radial functions defined in eq 8 referring to the Cu center. We notice that the 4s components are rather large fractions of the atomic 4s orbital. The 4s charge component integrated to, let us say, $r = 2.0$ au is very small, however. This must be kept in mind when the Mulliken 4s or 4p charges are interpreted. They do not have the same localization or meaning as the 3d charges.

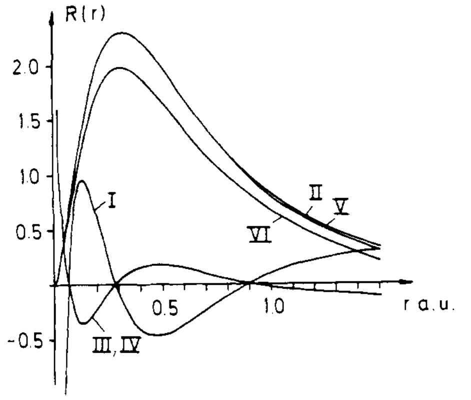

Figure 1. The copper orbitals: I and II, the atomic 4s and 3d atomic orbitals, respectively, in the configuration $3d^94s^2$; III, R_0 (Cu) by the ab initio method for the singly occupied MO in CuF_2; IV, R_0 (Cu) by the MSXα method; V, R_2 (Cu) by the ab initio method; VI, R_2 (Cu) by the MSXα method.

We further note that the 3d component of the singly occupied RHF orbital for CuF_2 (Figure 1) is almost as large as the atomic 3d orbital. The MSXα component is, however, significantly smaller. In the corresponding doubly occupied σ orbital the 3d component is very small in the RHF case but rather large in the MSXα case (essentially equal to the difference between curves II and VI in Figure 1). The σ donation is therefore much larger in the MSXα case.

The σ donation by the INDO method is about 10%. This value appears more reasonable than either the ab initio Hartree–Fock or the MSXα values. Comparison to experimental g values has indicated that the ab initio value is too small and the MSXα value too large.[55]

We have examined the geometry of CuF_2 using both the BS2 UHF and the INDO methods. The former suggests a bond length of 1.698 Å, the latter 1.820 Å. No detailed studies have been made using the INDO technique on other fluorine-containing compounds for comparison. As mentioned, there is very little experimental information available for CuF_2. We can, however, attempt to extrapolate information from $CuCl_2$. Leroi et al.[47] examined the infrared spectrum of $CuCl_2$ and observed the asymmetric stretch ν_3 496 cm^{-1} indicating a force constant of about 2.46 mdyn/Å. The force constants for the diatomics CuF and CuCl are estimated at 3.33 and 2.30 mdyn/Å, respectively.[46] Assuming a linear relationship suggests a value of K_e for CuF_2 of 3.56 mdyn/Å. Our calculated value of K_e = 5.75 mdyn/Å for CuF_2 from the UHF calculations would be increased by the inclusion of the spin-orbit interaction, perhaps by as much as 20% (see Lohr[56]), and we are led to the conclusion that configuration interaction will be important in flattening the HF potential energy curve and increasing the bond length.

Most of the calculations reported in Table III were performed at R = 1.579 Å, the bond length suggested by Basch et al.[29] In additon, the INDO calculations suggest that the linear configuration is lowest in energy, but the molecule should readily bend: a distortion of 10° costs only 0.7 kcal/mol of energy. From the INDO method, which usually overestimates bending force constants by a factor of 3, we obtained a force constant of K_θ = 1.59 mdyn/Å, suggesting a bending frequency of 338 cm^{-1}. Similar estimates made below indicate that CuF_2 is a much "stiffer" molecule than is $CuCl_2$.

A summary of all energies calculated by ab initio methods is given in Table VII. Although we are principally interested in energy differences in this work, the absolute energy values we obtained will establish the quality of our results relative to those of others. Noteworthy is the advantage of utilizing a F vs. F^- basis for these complexes.

Table VII. Total Energies (au) of CuF_2 and $CuCl_2$ from ab Initio Calculations[a]

system	method (basis)	$^2\Sigma_g{}^+$	$^2\Pi_g$	$^2\Delta_g$
CuF_2	RHF (BS1)	−1837.7771	−1837.7585	−1837.7372
	UHF (BS1)	−1837.7786	−1837.7593	−1837.7378
	RHF (BS2)	−1837.7951	−1837.7782	−1837.7599
	UHF (BS2)	−1837.7965	−1837.7799	−1837.7607
	RHF (BS3)	−1836.1284	−1836.1085	−1836.0885
	UHF (BS3)	−1836.1298	−1836.1103	−1836.0893
$CuCl_2$	RHF (BS2)	−2557.8900	−2557.8826	−2557.8736
	UHF (BS2)	−2557.8918	−2557.8846	−2557.8744
	RHF (BS2)[b]	−2557.8900	−2557.8836	−2557.8738

[a] The energies of states $^2\Sigma_u{}^+$ and $^2\Pi_u$ states can be obtained by use of Table III. [b] Broken symmetry ($D_{\infty h} \rightarrow D_{2h}$).

Table VIII. Excitation Energies (cm^{-1}) from $^2\Sigma_g{}^+$ Ground State of $CuCl_2$

method	$^2\Pi_g$	$^2\Delta_g$	$^2\Pi_u$	$^2\Sigma_u{}^+$
UHF[a]	1575	3818	39 191	39 264
RHF[a]	1616	3600		
RHF[a,b]	1400	3600		
RHF[c]	2310	4753		
RHF-CI[c]	8230	10 482	15 230	
MSXα-TS[a]	6198	23 961	16 673	
INDO[a,d]	6500	8738	26 070	29 000
EH[e]	3550	4275	22 750	22 500
EH[f]	5485	7100		
ref 46	9000[g]	18 000[g]		
ref 48	4000[h]	9000[g]	19 000[g]	50 000[g]
ref 57	9000[g]	9000–19 000	19 000[g]	44 800[g]
ref 58	4200[i]	10 800[g]		

[a] This work, $R_{Cu\text{-}Cl}$ = 2.02 Å. [b] Broken symmetry. [c] Reference 60, $R_{Cu\text{-}Cl}$ = 2.16 Å (private communication). [d] $R_{Cu\text{-}Cl}$ = 2.17 Å (geometry optimization). [e] $R_{Cu\text{-}Cl}$ = 2.37 Å. [f] $R_{Cu\text{-}Cl}$ = 2.20 Å. [g] Observed peaks. [h] Estimated from crystal field theory. [i] Estimated from angular overlap model.

2. $CuCl_2$. Unlike CuF_2, $CuCl_2$ has been obtained in the vapor phase by evaporation at 750 °C.[48] At high temperatures it dimerizes and may no longer be linear. The optical spectra of $CuCl_2$ have been the subject of extensive experimental[46-50] and theoretical[32,51,56-60] studies. So far a convincing assignment of the electronic transition of $CuCl_2$ has not been possible.

In this study we use the RHF and UHF ab initio methods with BS2 and the MSXα and INDO methods. The total energies obtained from the ab initio calculations are reported in Table VII, the transition energies are summarized in Table VIII, and the orbital characteristics of $CuCl_2$ are compared with those of CuF_2 in Table V. The trends are similar to those discussed in connection with CuF_2. The d-d transition energies are calculated too low in the Hartree–Fock method, whereas the charge-transfer excitations, of $^2\Sigma_u$ and $^2\pi_u$ symmetry for $CuCl_2$, are calculated too high in energy. In the comparison of the UHF and RHF, we notice again that the results are very close. In addition we show RHF results without keeping the $D_{\infty h}$ symmetry, Table VIII, row 3. The symmetry breaking affects the $^2\pi_g$ state much more than the $^2\Delta_g$ state since the δ_g orbital is completely localized on the central copper atom.

Garner, Hillier, and Wood[60] have carried out limited CI calculations on $CuCl_2$. Their results are also reported in Table VIII; we refer to their paper for the details of the configuration interaction.

The INDO calculations yield the two d-d transitions at 6500 and 8738 cm^{-1}. These are followed by two ligand to metal charge transfer (CT) excitations, of $^2\pi_u$ and $^2\Sigma_u^+$ symmetry, at about 26 000 and 29 000 cm^{-1}.

The MSXα results shown in Table VIII seem reasonable for the $^2\pi_g$ state, but appear much too high for the $^2\Delta_g$ state. The lowest state of $^2\pi_u$ and $^2\Sigma_u^+$ symmetry, however, seem to be in reasonable agreement with the experimental charge-transfer absorption. The qualitative description of these transitions by the MSXα model, however, is somewhat surprising. First we note that the orbitals at a higher energy have a larger Cl charge than Cu charge. In the linear geometry the δ orbital has to be almost exclusively metal 3d. The transition energy by the transition-state theory is given in first order by the orbital energy differences between the orbitals involved. For the $^2\Sigma_g^+ \rightarrow {}^2\Delta_g$ transition, the energy is given approximately as the orbital energy difference between a 3d orbital and an orbital that is more chlorine than metal (Table IX) rather than between two orbitals that are metal d. This may explain the large calculated transition energy. We note also that the lowest $^2\Sigma_g^+ \rightarrow {}^2\pi_g$ transition is described as a chlorine–chlorine transition, rather than d–d. The transition energy calculated for the latter excitation is in good agreement with the experimental one, but the qualitative description of the excitation is quite different from that expected.

Examining this difficulty further, we note again that the mixing between central atom and ligand orbitals is larger in MSXα than in either the ab initio or the INDO methods, as shown in Table IX. A possible explanation for this phenomenon may lie in the recently observed[61,62] instability of the negative ions H$^-$, Cl$^-$, O$^-$, O$^-$, and F$^-$ under the Xα approximation. Cl$^-$ is stable according to HF theory as it should be, but has a positive 3p-orbital energy in the Xα approximation. According to Schwarz[61,62] the only way of curing this problem would be to artificially increase the α value in the halide region. If F$^-$ or Cl$^-$ are brought into a molecule, their stabilization requires a flow of charge away from the halogen atom, leading to a higher mixing between 3d and ligand orbital. A somewhat too large σ donation has also been found for other transition-metal halides,[63] but in those cases the effect was less pronounced than in the copper case.

Another difficulty in the MSXα calculations may lie in the assumption of the "muffin-tin" potential. We might expect that the spherical potential assumed within each sphere is most reasonable for a complex of high symmetry, i.e., O_h or T_d. A linear molecule, however, is far from spherically symmetric. Further, since the ligand field splitting arises from the boundary conditions on the atomic spheres, there should be sizable penetration of the metal 3d-like function outside the metal sphere. This is not the case for Cu, where the 3d atomic orbital lies almost entirely within the Cu sphere, and the mixing is thus a sensitive function of sphere size and boundary conditions. This may contribute to the anomalous results for the copper complexes.

The assignment of the experimental bands of CuCl$_2$(g) has been the subject of some controversy. Hougen et al. assigned the bands at 9000 and 18 000 cm^{-1} to the $^2\pi_g$ and $^2\Delta_g$ excitation energies.[46] DeKock and Gruen[48,49] disagreed with this interpretation and attributed the more intense band at 19 000 cm^{-1} to a charge-transfer (CT) transition. They assigned the band at 9000 cm^{-1} to the d–d transition $^2\Sigma_g^+ \rightarrow {}^2\Delta_g$ and arrived at a value of 4000 cm^{-1} for the $^2\Sigma_g^+ \rightarrow {}^2\pi_g$ excitation. Attempts to use the angular overlap model have not led to conclusive results since there are too few experimental parameters available.[51,58,59]

An examination of Table VIII suggests the presence of two d–d transitions split by approximately 2000 cm^{-1} with the $^2\pi_g$ state lying below the $^2\Delta_g$ (if we consider the $^2\Delta_g$ state from the MSXα calculation as anomalous). There are then two possible assignments for the band centered around 9000 cm^{-1}. The first is that this band is due to the $^2\Sigma_g^+ \rightarrow {}^2\Delta_g$ transition, and that the $^2\Sigma_g^+ \rightarrow {}^2\pi_g$ transition lies at energies lower than 4000 cm^{-1} and is not yet observed.[41,50] The alternative is that both the transitions are within the band observed with $\nu_{\max} \simeq 9000$ cm^{-1}. The band in this region is broad and asymmetric.

Table IX. MSXα Orbital Energies and Charge Distributions for CuCl$_2$, Ground State $^2\Sigma_g^+$

		MSXα intersphere charges		
orbital	energies, au	Cu	Cl	INT[a]
$9\sigma_g$	$-0.325\ \alpha$	38.95	35.64	23.66
$3\pi_g$	$-0.351\ \alpha$	24.60	56.44	17.71
	$-0.338\ \beta$	30.37	51.96	16.66
$1\delta_g$	$-0.449\ \alpha$	92.14		7.85
	$-0.389\ \beta$	91.93		8.05
$2\pi_g$	$-0.426\ \alpha$	68.30	18.06	13.37
	$-0.409\ \beta$	62.36	22.56	14.73
$8\sigma_g$	$-0.456\ \alpha$	53.76	34.56	10.27
	$-0.409\ \beta$	50.30	37.32	10.84

[a] INT = intersphere region charge.

We consider these two possible assignments further. The symmetry of the ground state is $^2\Sigma_g^+$. The asymmetric stretch (ν_3 of σ_u^+ symmetry) has been observed at 496 cm^{-1} suggesting $K_e = 2.46$ mdyn/Å. From this, the frequency of the ground-state symmetric stretch (ν_1 of σ_g^+ symmetry) can be estimated at 370 cm^{-1}. The bending frequency ν_2, of π_u symmetry, has not been observed, but is likely to be very low. The INDO method, which generally overestimates force constants, suggests a value of 0.23 mdyn/Å, corresponding to $\nu_2 \simeq 108$ cm^{-1}. This value of the bending frequency corresponds well to Lohr's[56] result $\nu_2 \simeq 93$ cm^{-1}. It is clear that at the elevated temperatures (500–1000 °C) that are required to take the spectrum all modes are active: the vibronic states associated with the lowest electronic state are thus of Σ_g^+, Σ_u^+, and π_u symmetry. Considering only dipole transitions, the $^2\pi_g$ electronic state can borrow intensity from either the $^2\pi_u$ or $^2\Sigma_u^+$ CT states that we believe are responsible for the peak observed at approximately 19 000 cm^{-1}, the former through ν_3(A) and the latter through ν_2(B). In either case, the ν_1 mode of the ground state should be apparent as hot bands. The $^2\Delta_g$ electronic state can borrow from the allowed CT $^2\pi_u$ state through ν_2(C). The situation is summarized below:

$$\text{(A)}\quad {}^2\Sigma_g^+\ (\sigma_g^+) \xrightarrow{x,y} {}^2\pi_g\ (\sigma_u^+)$$

$$\text{(B)}\quad {}^2\Sigma_g^+\ (\sigma_g^+) \xrightarrow{z} {}^2\pi_g\ (\pi_u)$$

$$\text{(C)}\quad {}^2\Sigma_g^+\ (\sigma_g^+) \xrightarrow{x,y} {}^2\Delta_g\ (\pi_u)$$

Using the orbitals of the INDO calculation on the ground state, and including only one-center terms in the expression for the transition dipole, we estimate the z-polarized $^2\Sigma_g^+ \rightarrow {}^2\Sigma_u^+$ transition to have an oscillator strength of 10^{-1} and the x,y-polarized $^2\Sigma_g^+ \rightarrow {}^2\pi_u$ transition to have an oscillator strength of 10^{-3}. These estimates are in very good accord with those made by Lohr[56] and simple considerations then suggest that (B) *might* be the most intense transition.

Experimentally, the band centered at ~9000 cm^{-1} has a complicated structure.[48] There is a pronounced 360 ± 15 cm^{-1} spacing observed from 6900 to 9500 cm^{-1} with temperature-dependent intensity suggesting an active role for ν_1 of the ground state. Assignment (C) is the one most often given. If this is the case, then the $^2\pi_g$ state is not observed above 4000 cm^{-1}, or might lie under the low-energy tail of the $^2\Delta_g$ state. This last possibility, however, is not attractive as (B) should be more, not less, intense than (C). The regular progression observed between 6900 and 9500 cm^{-1} might be associated with (A) or (B). Process (A) is far less likely, as this transition should be much less intense than (B). In addition, ν_3 for the excited state would most likely be approximately equal to 496 cm^{-1}, ν_3 for the ground state, and we might expect (A) to lead to a repeated vibrational structure every $2 \times \nu_3 \approx 1000$ cm^{-1}. This is not apparent. Finally, it is difficult to explain the *total* intensity of this band without invoking (B). If the structure between 6900 and 9500 cm^{-1} is now associated with (B), then the presence of the $^2\Delta_g$ state might be responsible for the rather more complicated structure between 9500 and 12 000 cm^{-1}.

In the above discussion we have ignored spin-orbit coupling. The inclusion of this term lowers the ground state and splits the orbital degenerate $^2\pi_g$ and $^2\Delta_g$ states. The $^2\Sigma_g{}^+ \rightarrow {}^2\Delta_g$ transition can borrow through the spin-orbit operator from the $^2\Sigma_g{}^+ \rightarrow {}^2\pi_g$ transition which, in turn, gets its intensity through (A) or (B). Even considering these effects, Lohr[56] was unable to get a sufficient intensity for the $^2\Sigma_g{}^+ \rightarrow {}^2\Delta_g$ transition to explain the first band. We conclude that it is an attractive alternative to suggest that both $^2\Sigma_g{}^+ \rightarrow {}^2\pi_g$ (B) and $^2\Sigma_g{}^+ \rightarrow {}^2\Delta_g$ (C) overlap, that the former carries most of the intensity, and that the latter lies some 2000 cm^{-1} higher in energy and derives some of its intensity through the spin-orbit interaction.

The band observed with ν_{max} at 19 000 cm^{-1} we have assigned to the two ligand to metal charge transfers $^2\Sigma_g{}^+ \rightarrow {}^2\pi_u$ and $^2\Sigma_g{}^+ \rightarrow {}^2\Sigma_u{}^+$. All the calculations carried out here suggest that these transitions are at about the same energy, in contrast to the suggestion that the $^2\Sigma_u{}^+$ state should lie considerably higher in energy than the $^2\pi_u$ state.

The transition to the $^2\Delta_g$ state might, of course, also be hidden in the stronger absorption at about 19 000 cm^{-1} which we assign to the two allowed charge-transfer transitions. In that case the splitting between the $^2\pi_g$ and $^2\Delta_g$ states must be at least 4000 cm^{-1}. Although this is consistent with the MSXα and AOM calculations, we favor the hypothesis that both transitions lie within the band at 9000 cm^{-1}.

Table IV summarizes the Mulliken populations for the five lowest doublet states as calculated by the ab initio and INDO methods. The table shows the d-d nature of the two lowest excited states. In the ground state we find the d β population to be larger than the "ionic" value 4.0. The excess charge is partly a 4s charge and partly the σ donation from ligand to 3d in the bonding σ orbital (whose antibonding counterpart is unoccupied). The σ donation calculated by the INDO method is about twice as large as that obtained by the ab initio method.

The charge-transfer excitations to $^2\Sigma_u{}^+$ and $^2\pi_u$ do not lead to a total transfer of a full electron, but only to the transfer of about one-half. This charge relaxation is caused by the σ donation in the ground state and a "σ back-donation" in the excited states.

In the MSXα method the σ donation is 0.7, which might be considered to be too large. Consequently, all low-lying excitations are predicted by the MSXα method to be of ligand to ligand type.

Table V compares the valence MOs of $CuCl_2$ with those of CuF_2 for the $^2\Sigma_g{}^+$ ground states. The ab initio and INDO results are rather similar. Qualitatively the six occupied molecular orbitals of highest eigenvalue ($3\pi_g$, $4\pi_u$, $7\sigma_u{}^+$, and $9\sigma_g{}^+$ for $CuCl_2$) are halide p, split only by 0.10 au. These are followed by the Cu 3d orbitals, then two nearly degenerate molecular orbitals ($6\sigma_u{}^+$ and $8\sigma_g{}^+$) that are mainly halides. The magnitudes of the spin polarizations for the UHF ab initio and INDO calculations upon the orbital eigenvalues are very similar with the exception of the $5\sigma_u{}^+$ molecular orbital of CuF_2.

B. $CuCl_4{}^{2-}$. Copper(II) ions show a rich variation of local geometry in the solid state. Since they are d^9 systems the first- and second-order Jahn-Teller effects are operative.[64-68] A number of other factors are also involved, however. Mutual repulsions among the ligands tend to stabilize a cubic arrangement. A number of calculations have been performed on the $CuX_4{}^{2-}$ cluster[14,18,69-70] which show that a flattened tetrahedron D_{2d} is preferred over D_{4h} and T_d. Bacon and Zerner have carried out calculations[14] on various geometries of $CuCl_4{}^{2-}$ using the INDO method also used here. They found that the optimum D_{2d} configuration is lower in energy than the D_{4h} configuration by 12.7 kcal/mol and that the D_{2d} configuration found in Cs_2CuCl_4, with a Cl-Cu-Cl angle of 130°, is stable relative to the T_d geometry by 1.4 kcal/mol. A similar result but with larger energy differences was obtained by Lohr and Lipscomb[70] using an extended Hückel method. The ab initio results by Demuynck et al.[18] are also similar suggesting that D_{2d} is lower than D_{4h} by 20 kcal/mol (Cl-Cu-Cl angle = 120°) and lower than T_d by 2 kcal/mol.

Since the Cl-Cu-Cl angle shows such variation in compounds with $CuCl_4{}^{2-}$ units, it is obvious that the geometry is determined not only by the intrinsic forces of the cluster. Sizes and chemical bonds among the counterions may be at least as important. In the extreme case the ligands may form chelates, which then, of course, have a decisive influence on the geometry.

An important factor concerning the geometry of copper tetrahalides is the temperature. It is known that some Cu^{2+} chlorides change color with temperature owing to changes in the equilibrium coordination geometry. An interesting example is the compound bis(n-methylphenethylammonium)-tetrachlorocuprate(II), $(C_6H_5CH_2NHCH_3H^+)_2CuCl_4$ ($(nmpH)_2CuCl_4$), which is square planar and green at 25 °C and distorted tetrahedral and yellow at 80 °C. We may add that this compound is the only one known to exist with a square-planar $CuCl_4{}^{2-}$ unit.

There are no cases known with well-defined $CuF_4{}^{2-}$ units. In the present work we calculate the electronic excitation energies by means of the ab initio Hartree-Fock and INDO methods (unrestricted) and the MSXα method (restricted) for $CuCl_4{}^{2-}$ clusters of D_{4h}, D_{2d}, and T_d symmetry.

1. $CuCl_4{}^{2-}$ (T_d). Although $CuCl_4{}^{2-}$ does not exist with T_d symmetry, we will mention the basic features of this limiting case. There is one d-d transition, $^2T_2 \rightarrow {}^2E$ ($e \rightarrow t_2$). The chlorine 3p orbitals form bonding combinations of σ type (a_1 and t_2) and of π type (e, t_1, and t_2). Low-lying charge-transfer excitations from all of these chlorine 3p type MOs to the Cu t_2 (3d) MO are allowed; excitations from the σ-type MOs should lie at higher energies than from those of the π type.

We have performed only MSXα calculations for this complex. The $^2T_2 \rightarrow {}^2E$ transition is calculated at 9700 cm^{-1}. The charge-transfer transitions are calculated at 7000 cm^{-1}, a value which is certainly far too low.

2. $CuCl_4{}^{2-}$ (D_{2d}). The flattening of the tetrahedron (to D_{2d}) causes a splitting of the t_2 and e orbitals. The e's go into a_1 (d_{z^2}) and b_1 ($d_{x^2-y^2}$) while the t_2's go to b_2 (d_{xy}) and e (d_{xz}, d_{yz}). The three d-d transitions are $^2B \rightarrow {}^2E$ (x,y), $^2B_2 \rightarrow B_1$ (forbidden), and $^2B_2 \rightarrow {}^3A_1$ (z).[8] The chlorine 3p-type molecular orbitals of σ type are of $a_1(a_1)$, $e(t_2)$ and $b_2(t_2)$ symmetry, while the eight of π type are $a_1(e)$, $b_1(e)$, $a_2(t_1)$, $e(t_1)$, $e(t_2)$, and $b_2(t_2)$, where the symbols in parentheses refer to their T_d parentage. There are five allowed charge-transfer excitations that should lie at low energies, one $^2B_2 \rightarrow {}^2A_1$ and two $^2B_2 \rightarrow {}^2E$ due to chlorine 3pπ to metal 3d charge transfer and lying at lower energy, and $^2B_2 \rightarrow {}^2A_1$ and $^2B_2 \rightarrow {}^2E$ due to chlorine 3pσ to metal 3d charge transfer lying at somewhat higher energy.

Experimentally, the lower energy band splits into two components at 4800 and 5500 cm^{-1} which have been assigned[73] to the $^2B_2(d) \rightarrow {}^2E_2(d)$ transition. The splitting is due in part to the lower site symmetry. A weak band in the y-polarized absorption near 8000 cm^{-1} is assigned to the for-

Table X. Excitation Energies (cm^{-1}) from $^2B_2$ Ground State of $CuCl_4^{2-}$ (D_{2d})

method	$^2B_2 \rightarrow {}^2E$	$^2B_2 \rightarrow {}^2B_1$	$^2B_2 \rightarrow {}^2A_1$
MSXα[a]	5500	11 380	10 850
INDO[a]	4622	6535	6852
AOM[b]	5550	7420	8980
AOM[b,c]	5760 5160	7620	9200
EH[d]	3880	8550	9120
exptl[e]	5500 4800	7900	9000

[a] This paper. [b] References 32 and 75. [c] Estimated with spin-orbit coupling. [d] Reference 70. [e] Reference 73.

Table XI. Excitation Energies (cm^{-1}) from $^2B_{1g}$ Ground State of $CuCl_4^{2-}$ (D_{4h})

method	$^2B_{1g} \rightarrow {}^2B_{2g}$	$^2B_{1g} \rightarrow {}^2E_g$	$^2B_{1g} \rightarrow {}^2A_{1g}$
ab initio[a] UHF	7300	8500	9500
ab initio[b] RHF	7500	9400	10 100
MSXα-TS[a]	15 839	14 000	18 472
INDO[a]	12 950	14 050	13 080
AOM[c]	11 450	15 410	12 910
exptl[d]	12 500	14 280	16 900

[a] This paper. [b] Reference 18. [c] References 75 and 81. [d] References 76 and 77.

bidden $^2B_2$(d) → $^2B_1$(d) transition, which has become partially allowed through spin-orbit coupling and through the lower site symmetry. A band at 9000 cm^{-1} is assigned to the $^2B_2 \rightarrow {}^2A_1$ transition. Five charge-transfer transitions are reported to occur at about 22 000 (shoulder), 25 000, 29 000 (shoulder), 34 000, and 43 000 cm^{-1}.[74]

Table X contains a summary of results for the d-d transitions from previous calculations,[32,70,75] from our present calculations, and from experiment.[73] For our calculations we have assumed a bond length of 2.23 Å and an angle of 129.2° as found in the structure of Cs_2CuCl_4.[36]

With the MSXα method, the transition energies were calculated by energy differences of orbitals of ground-state calculations. The calculated values are expected not to change appreciably from those calculated by the transition-state concept, because balanced relaxation is expected for these d-d transitions. The calculated $^2A_1$ and $^2B_2$ transition energies are in good agreement with the experimental spectrum, but the order between $^2A_1$ and $^2B_1$ is reversed.

A comparison of INDO results shows that the calculated excitation energies are in the same order as the experimentally observed values; the overall splittings are, however, too small.

The highest occupied orbitals are the 12 chloride 3p type as expected. The energy range covered by this "band" of 12 orbitals is about 16 000 cm^{-1}, in reasonable agreement with the range of 21 000 cm^{-1} suggested by the five peaks observed from 22 000 to 43 000 cm^{-1}.[74] The chloride 3s-type molecular orbitals are found at considerably lower energy.

We have performed no ab initio calculations on $CuCl_4^{2-}$ (D_{2d}). The lower symmetry of this complex made such calculations prohibitively expensive.

3. $CuCl_4^{2-}$ (D_{4h}). The only compound known with a discrete $CuCl_4^{2-}$ unit with square-planar geometry is $(nmpH)_2CuCl_4$ below 25 °C. All other chlorocuprates(II) containing planar $CuCl_4^{2-}$ are known to form infinite sheets as a result of polymerization, which gives rise to tetragonally elongated $CuCl_6$ octahedra.

The solid-state electronic spectrum of $(nmpH)_2CuCl_4$[76,77] at 77 K shows three distinct peaks at 16 900, 14 300, and 12 500 cm^{-1}, shifting to 16 100, 13 600, and 11 500 cm^{-1} at 25 °C.

The compound $Pt(NH_3)_4CuCl_4$, which was assumed for a very long time to be square planar, has absorptions at 14 300, 13 100, and 10 900 cm^{-1}.[78,79] Its structure, however, has recently been determined[80] to be of distorted octahedral symmetry and its absorbtion spectrum can be much better understood as such.

The $CuCl_4^{2-}$ (D_{4h}) ground state is of $^2B_{1g}$ symmetry and three are three possible d-d transitions. The transition at 14 300 cm^{-1} is assigned[77] to d_{xz}, $d_{yz} \rightarrow d_{x^2-y^2}$ (^2E_g), the one at 12 500 cm^{-1} to $d_{xy} \rightarrow d_{x^2-y^2}$ ($^2B_{2g}$), and the one at 16 900 cm^{-1} to $d_{z^2} \rightarrow d_{x^2-y^2}$ ($^2A_{1g}$) (Table XI).

Theoretical calculations based on the RHF,[18] the extended Hückel,[81] the angular overlap,[75,82] and the INDO (only CT energies)[83] methods have been carried out prior to our own calculations. An MSXα calculation by Johnson and Wahlgren[84] is also reported in the literature, but no excitation energies were calculated. Table XI contains a comparison of all the d-d transitions.

The ab initio results using the UHF and RHF theories agree reasonably well with each other. As in the case of CuF_2 and $CuCl_2$, the excitation energies come out too low, in the case of UHF by an average factor of 1.7 for the three calculated transitions.

The MSX results are in reasonably good numerical accord with the experimental values but the $^2B_{1g}$ and ^2E_g states are reversed compared to the assignment of ref 77 (Table XI). The order obtained in MSXα calculations of Johnson and Wahlgren is similar, but it would appear from their orbital energies that the splitting between these three states is considerably greater.

The INDO results are in rather good numerical agreement with the experimental values, but the splittings calculated are two small, and the ^2E_g state is calculated as the highest of these nearly degenerate ligand field transitions. The INDO results and those obtained from AOM are reasonably similar.

Experimentally the three bands centered at 12 500, 14 300, and 16 900 cm^{-1} are well separated.[76,77] The first and last of these bands show well-defined vibrational structure with a regular spacing of 265 ± 20 cm^{-1} and possess a very similar envelope. The central band shows a poorly defined but clearly different structure, and has approximately twice the intensity of each of the other two bands.

Chlorine to metal charge transfer bands of ^2E_u and $^2B_{2u}$ symmetry are (x,y) and z polarized, respectively. From the orbital structure of the UHF ab initio or INDO calculations we estimate $^2B_{2u}$ and ^2E_u charge transfer excitations to be nearly degenerate and of near equal intensity, followed by a second ^2E_u state with ~10 times greater intensity about 10 000 cm^{-1} above the former two (from a chlorine (3pσ-type MO to metal d). The $^2A_{1g}$ and $^2B_{2g}$ crystal field excitations can borrow from the ^2E_u state through one of the two e_u in-plane modes; the ^2E_g can borrow from ^2E_u through the out-of-plane a_{2u} or b_{2u} modes. Since the b_{2u} vibration does not involve the copper, it is not a good candidate to invoke for this borrowing. The ^2E_g transition can borrow from the allowed $^2B_{2u}$ charge-transfer band through one or both of the e_u vibrations, the $^2B_{2g}$ has no first-order vibronic borrowing from the $^2B_{2u}$, and the $^2A_{1g}$ can only use the unpropitious b_{2u} vibration. It is thus most tempting to assign the first and last transitions as $^2B_{2g}$ and $^2A_{1g}$, respectively, both borrowing from ^2E_u. The vibrational structure of approximately 265 cm^{-1} seen on these bands is most likely due to the a_{1g} vibration as suggested by Cassidy and Hitchman,[76] and is in reasonably close agreement with a frequency of 276 cm^{-1} observed for the a_{1g} mode of the ground electronic state of $(nmpH)_2CuCl_4$ seen in Raman spectroscopy. We assign the lowest state as $^2B_{2g}$, as all our calculations

Table XII. Experimental Data on Excitation Energies[a] (cm^{-1}) and Structures of Copper Hexafluorides

compd	$^2B_{1g} \rightarrow$ $^2A_{1g}$	$^2B_{1g} \rightarrow$ $^2B_{2g}$	$^2B_{1g} \rightarrow$ ^2E_g	ref	structure	ref	distortion[b]
CuF_2	(7500)[c]	8825	11 375	72, 94	distorted rutile; layers of octahedra sharing edges and sharing corners with octahedra of neighboring chains	95, 96	0.850
$KCuF_3$	(7200)[c]	8975	11 575	72, 94	tetragonally distorted perovskite lattice; three-dimensional and linear linking of the CuF_6^{4-} octahedra	88, 91	0.856
$NaCuF_3$		9100	11 550	72	monoclinic; not linear three-dimensional linking of the CuF_6^{4-} octahedra	97	0.852
$CsCuF_3$			12 000	72			
K_2CuF_4	(8000)[c]	9237	11 825	72, 94 98,100	tetragonal; two-dimensional linking of the CuF_6^{4-} octahedra. The layers of CuF_6^{4-} octahedra are linked by the K^+ ions.	88, 92	0.865
Na_2CuF_4		9700	12 184	72, 94	monoclinic; CuF_6^{4-} octahedra sharing opposite edges. The octahedra layers are isolated and separated by the Na^+ ions.	99	0.806
Rb_2CuF_4		9575	12 100	72, 98 100	tetragonal		
Ba_2CuF_6		9950	12 800	98, 100	orthorhombic; layers consisting of axially elongated CuF_6^{4-} octahedra, two-dimensionally connected by corners (in an antiferrodistortive order)	90, 93	0.804

[a] Average values. [b] Ratio short/long (distance average values). [c] Observed shoulders.

Table XIII. Excitation Energies (cm^{-1}) from $^2B_{1g}$ Ground State of CuF_6^{4-} (D_{4h})

method	$^2B_{1g} \rightarrow {}^2A_{1g}$	$^2B_{1g} \rightarrow {}^2B_{2g}$	$^2B_{1g} \rightarrow {}^2E_g$
MSXα[b]	(2750)[c]	13 058	(10 600)[c]
	21 180		14 375
INDO[b]	8070	12 000	12 700
EH[a]	4600	14 000	14 000
exptl[d]	7500	8825	11 375
	8000	9237	11 825

[a] Reference 103. [b] See Table XII. The geometry for the calculation was taken from CuF_2. A better model for isolated units, however, is K_2CuF_4. [c] The numbers in parentheses represent states that are more CT type; see text. [d] For CuF_2 and K_2CuF_4, see Table XII.

suggest this order. The central band then is probably ^2E_g band (split somewhat due to the actual D_{2h} distortion observed for the crystal) borrowing from ^2E_u through a_{2u}, or from $^2B_{2u}$ through e_u. Our inferred assignment of the spectrum is that given in Table XI and is in accord with that most often given, and thus only the ab initio ordering seems correct. Another ordering, consistent with polarization information, is $^2E_g > {}^2B_{2g} > {}^2A_{1g}$.[82] Although this sequencing of states is consistent with the INDO results, we do not consider it as appealing for the reason just presented.

The ground state of $CuCl_4^{2-}$ (D_{4h}) has been studied by Demuynck, Veillard, and Wahlgren.[18] A complete description of the computational details can be found in Demuynck's thesis.[85] Demuynck et al. found extremely basis set dependent Mulliken populations.[5,18] It is uncertain whether these differences represent a real difference in the orbitals or are a consequence of the Mulliken method. The large variations in the results of Demuynck et al.[18,85] may, alternatively, be due to their poor minimal basis description of the core. Our basis set has double-ζ quality for the core which contributes to more stable Mulliken populations.

The Mulliken populations obtained here and by Demuynck et al.[18] in most of the basis sets indicate a σ donation to the 3d shell of only 0.1. The MSXα method suggests a σ donation of 0.7, almost certainly too large. Experimental σ donations, obtained by magnetic resonance,[86,87] suggest a σ donation of 0.25, which is close to the value suggested by the INDO method.

As to the inclusion of point charges around the $CuCl_4^{2-}$ cluster in order to simulate the crystal environment, our own experience coincides with the observations made by Demuynck et al.;[18] the point charges cause a stabilization of all orbital energies by ~0.3 au, without affecting the excitation energies in any significant way.

C. CuX_6^{4-}. 1. CuF_6^{4-} (O_h and D_{4h}). The precise structure of CuF_6^{4-} has been a controversial subject. Whereas earlier X-ray crystallographic studies indicated compressed octahedral geometries for $KCuF_3$,[88] K_2CuF_4,[89] and Ba_2CuF_6,[90] more precise recent determinations suggested instead elongated structures.[91-93] For more detailed information see Table XII. Previous theoretical studies have been concerned with questions of geometry and electronic spectra.[101-106]

We have performed MSXα and INDO calculations on CuF_6^{4-} (D_{4h}). The calculated MSXα excitation energies were obtained from energy differences between the respective orbitals, since relaxation can be considered to be small for d-d transitions. Our results are displayed in Table XIII. Since we assume an isolated CuF_6^{4-} complex in our calculations, the compound best suited for comparison is K_2CuF_4. However, the transition $^2B_{1g} \rightarrow {}^1B_{2g}$ might not be expected to agree, since K_2CuF_4 shows a two-dimensional linking of the CuF_6^{4-} octahedra (sharing edges). The INDO calculations show a good agreement with the observed values and predict the correct ordering $^2A_{1g} < {}^2B_{2g} < {}^2E_g$. The greatest discrepancy, as expected, is in the $^2B_{2g}$ transition energy. The MSXα results are again characterized by valence levels at too high energy and too much metal halide mixing. Excitations that are principally charge transfer, and that have the same symmetry as d-d transitions, are thus calculated at 2750 and 10 600 cm^{-1}, making the experiment difficult to interpret.

2. $CuCl_6^{4-}$ (O_h and D_{4h}). The $CuCl_6^{4-}$ clusters are formed by $CuCl_4^{2-}$ ions linked together and forming infinite sheets. The chlorines are attached to copper in two different ways, four at shorter ("equatorial Cl's") and two longer ("axial Cl's") distance. The Cu-Cl distances of the equatorial chlorines vary from 2.274 to 2.316 Å, and the axial distances vary from 2.876 to 3.257 Å. Cl atoms as far as ~3 Å away from Cu can still be considered to be quite strongly bonded to Cu, which can be concluded from significant differences between the absorption spectra of $Pt(NH_3)_4CuCl_4$ and $(nmpH)_2CuCl_4$. The former has axial chlorines at 3.257 Å, whereas the latter has no axial Cl at all.

The absorption spectrum of, e.g., $(CH_3NH_3)_2CuCl_4$[105] consists at room temperature of a broad band centered at approximately 12 000 cm^{-1}. At −196 °C the spectrum exhibits three peaks at 11 130, 12 390, and 13 300 cm^{-1}. The position of the d_{z^2} level is expected to be sensitive to the degree of tetragonal distortion, but the ionic and similar models based on crystal field theory are incapable of predicting its actual position to any reasonable degree of accuracy. Only a full MO treatment might be expected to do justice to the effects of σ and π bonds on the d orbitals.

The three possible d–d transitions from the $^2B_{1g}$ ground state to $^2A_{1g}$ ($d_{z^2} \rightarrow d_{x^2-y^2}$), to $^2B_{2g}$ ($d_{xy} \rightarrow d_{x^2-y^2}$), and to ^2E_g (d_{xz}, $d_{yz} \rightarrow d_{x^2-y^2}$) are difficult to assign experimentally. The central peak, however, is nearly absent in the z-polarized spectrum and is assigned as $^2B_{1g} \rightarrow {}^2B_{2g}$ by Hitchman and Cassidy.[82] Repeating their argument, only this transition has no first-order vibronic coupling to the $^2B_{2u}$ z allowed charge-transfer band. Unlike the spectrum for D_{4h} $CuCl_4,^{2-}$ the first and third bands are quite different in appearance, suggesting a greater use of the $^2B_{2u}$ charge transfer state in $CuCl_6^{4-}$. We assign the first transition as $^2B_{1g} \rightarrow {}^2A_{1g}$ as suggested by the INDO and AOM[75] results, and the third transition as $^2B_{1g} \rightarrow {}^2E_g$. The INDO and AOM methods then yield good results when compared with experiment.

The MSXα results are again anomalous. The Cl 3p levels based on the axial ligands have a higher energy than the singly occupied b_{1g} level. We have constrained the calculation to the $^2B_{1g}$ state. We do this because both the INDO calculations and experimental ESR studies[86,87] confirm that the ground state is of $^2B_{1g}$ symmetry. The transitions to the $^2A_{1g}$ and to the ^2E_g states in Table XIV therefore correspond to the second states of these symmetries.

All simpler models applied to this problem suggest a considerably greater splitting between these crystal field states, with the $^2A_{1g}$ state lying much lower, at 4700–8500 cm^{-1}.[106,107] This state, however, was searched for and not found below 10 300 cm^{-1}; the state observed at 11 130 cm^{-1} we assign to $^2A_{1g}$. Finally, we note that this state does not experimentally show the great degree of sensitivity to axial distortion which we might have anticipated. We have not yet examined the sensitivity of this transition by calculation.

There are 18 molecular orbitals of chlorine 3p type. Three allowed low-lying charge-transfer excitations of $^2B_{1g} \rightarrow {}^2E_u$ and one of $^2B_{1g} \rightarrow {}^2B_{2u}$ are suggested. From the orbital eigenvalues these four transitions might be expected to span an energy range of 17 000 cm^{-1}. Experimentally, four peaks are noted at 24 000, 33 300 (broad), 38 500 (broad shoulder), and 49 000 cm^{-1}.[80] The position and appearance of those peaks seem to be nearly independent of the details of the particular structures of the $CuCl_6^{4-}$ complex examined, as might be expected for chlorines weakly coupled to each other.

IV. Conclusions

We have found that two of the three methods used in this work will yield useful information about copper halides if viewed together with the experiments. The MSXα results for the $^2\Delta_g$ state of $CuCl_2$ and the $^2A_{1g}$ state of CuF_6^{4-} are anomalous. In addition we were unable to obtain satisfactory results on $CuCl_6^{4-}$ using this method. Although yielding strikingly close numerical agreement with experiment in some cases, the MSXα method seems to be the least consistent of the methods used in studying the halides of copper. This shortcoming may well be due to the muffin-tin approximation for the often highly distorted geometries which are found experimentally for copper halides. Another source of error in our calculations may lie in the inability of Xα to give binding for Cl$^-$. This inherent difficulty of the Xα approximation may also be responsible for the highly exaggerated α donation.

A principal difference in the results between MSXα and MO-LCAO methods lies in the fact that MSXα orbitals usually obey the "aufbau" principle, whereas for transition-metal complexes the MOs do not.

Our comparisons between RHF and UHF suggest that UHF can be used with little hesitation for copper halides, since the differences due to the breaking of both spin and point-group symmetry are seen to be of minor importance.

Table XIV. Excitation Energies (cm^{-1}) from the $^2B_{1g}$ Ground State of $CuCl_6^{4-}$ (D_{4h})[e]

method	$^2B_{1g} \rightarrow {}^2A_{1g}$	$^2B_{1g} \rightarrow {}^2B_{2g}$	$^2B_{1g} \rightarrow {}^2E_g$
MSXα[a]	(−14 892)	(12 148)	(−14 112)
	(18 074)		(8033)
INDO	6600	8811	9362
AOM[b]	7480	10 900	12 930
exptl	8300[c]	10 000[c]	12 130[c]
	11 130[d]	12 390[d]	13 300[d]

[a] The numbers in parentheses are CT transitions; see text. [b] Reference 82. [c] Reference 105. [d] Reference 108. [e] The MSX d–d transition energy for $CuCl_6^{4-}$ (O_h) is 16 174 cm^{-1}.

Ab initio calculations on d–d transitions based on the SCF technique consistently yield too low values by an average factor of 1.7. The deeper reasons for this general behavior can hardly be found without a closer study of the correlation effects. Unfortunately, CI calculations on a 99-electron system like $CuCl_4^{2-}$ are, for us, prohibitively expensive. However, limited CI studies of the linear dihalides are feasible and are being planned.

The INDO results show that a well-parameterized semiempirical method may yield very reasonable results for both excitation spectrum and charge and spin distributions. Only in the $CuCl_4^{2-}$ (D_{4h}) case did the INDO method fail to yield the same order of d–d transitions as did the ab initio calculations. For this case the order suggested by INDO is the same as that suggested by AOM, but we have argued from experimental information that only the ab initio HF results seem correct.

A detailed discussion of each of the various complexes is given in the Results section. We conclude, however, with a comparison of computational time, and use for an example the ground state of the $CuCl_4^{2-}$ (D_{4h}) complex.

The ab initio UHF calculation required 565 min of computational time on the IBM 370/155. About 420 min of this time was required for the evaluation of the integrals. Full use was made of the three symmetry planes. The loss of molecular symmetry prevented us from calculating the D_{2d} complex using ab initio techniques. The MSXα calculations required about 33 min; roughly 30 min is required for the SCF. The INDO-UHF calculation required 50 s, and made no use of molecular symmetry.

Acknowledgment. We wish to thank Dr. Werner Schneider and Professor Bror Strandberg for helping us to obtain the necessary computer funds. This work was supported in part by CAPES, Brazil (P.C.M.), by NFR, the Swedish Natural Science Research Council (S.L., M.Z.), and through a grant from the National Research Council of Canada.

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