Ab initio CI Study of the Ground and Excited States of CuF_2 and $CuCl_2$

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Ab initio configuration interaction (CI) calculations of the ground, electronically excited and the ionized states (cations) are reported for CuF_2 and $CuCl_2$. The calculated results are compared with available experimental values of the UV spectrum of $CuCl_2$ and the ionization potentials obtained from the photoelectron spectrum of CuF_2.

1. Introduction

The linear copper halides, CuF_2 and $CuCl_2$ are of interest since these molecules represent the simplest copper (II) complexes whose electronic properties and stereochemistry have been reviewed extensively [1]. While it is established from various experimental and theoretical studies that the ground state of both CuF_2 and $CuCl_2$ is a ${}^2\Sigma_g^+$ state, the relative ordering of the lower lying electronically excited states and the interpretation of the UV and photoelectron spectra are of some controversy [2–5]. For CuF_2, the photoelectron spectra have recently been reported, but again the interpretation of nine peaks observed in the ionization energy region between 11.0 and 21.0 eV has not been satisfactory in a previous study [6]. In view of these discrepancies in previous experimental and also in theoretical studies which are mostly ab initio SCF calculations without or with a very limited configuration interaction (CI), we have performed an extensive CI calculation for the ground and electronically excited states of CuF_2 and $CuCl_2$ in order to clarify the existing controversy.

2. Calculation

Ab initio SCF calculations which precede the CI study employed the gaussian type orbital basis sets of Basch et al. [7], which correspond to a single zeta quality for the core orbital and to a double zeta quality for the valence shell orbitals of Cu. For fluorine we employed Huzinaga's (9s, 5p) set [8] contracted to a double zeta (4s, 2p) according to Dunning's scheme [9], and for chlorine the Dunning's (12s, 9p/6s, 5p) contraction [10] of Veillard's gaussian basis set [11] has been employed. The spin-restricted open-shell SCF calculation has first been carried out for five states of interest for CuF_2 and $CuCl_2$ [12]: ${}^2\Sigma_g^+$, ${}^2\Sigma_u^+$, ${}^2\Pi_u$, ${}^2\Pi_g$ and ${}^2\Delta_g$. The ground state (${}^2\Sigma_g^+$) of CuF_2 and $CuCl_2$ exhibited the following configurations, respectively:

$$(6\,\sigma_g)^2(1\,\delta_g)^4(7\,\sigma_g)^1(2\,\pi_g)^4(5\,\sigma_u)^2(3\,\pi_u)^4 \quad \text{for} \quad CuF_2$$

and

$$(8\,\sigma_g)^2(1\,\delta_g)^4(9\,\sigma_g)^1(7\,\sigma_u)^2(4\,\pi_u)^4(3\,\pi_g)^4 \quad \text{for} \quad CuCl_2.$$

The corresponding configurations of electronically excited states have also been generated separately by SCF calculations, and these have been employed as reference configurations for the following CI calculations of electronic states for each molecule.

The geometrical parameters of linear CuF_2 and $CuCl_2$ are $r(\mathrm{Cu-F}) = 1.759$ Å [13] and $r(\mathrm{Cu-Cl}) = 2.020$ Å [14], which are theoretically optimized values in previous studies.

In addition to the excited doublet states mentioned above, the cationic states which result from the ionization of CuF_2 and $CuCl_2$ have also been calculated by the open-shell SCF method. These ionized states are either singlet or triplet states of ${}^{1,3}\Sigma_g^+$, ${}^{1,3}\Sigma_u^+$, ${}^{1,3}\Pi_u$, ${}^{1,3}\Pi_g$ and ${}^{1,3}\Delta_g$.

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Table 1. Energies of the CI wavefunctions of the ground and excited states of CuF_2 and $CuCl_2$[a].

Electronic states and reference configurations	E(CI)[b]	ΔE(CI−SCF)	ΔE_p (kept)[c]	ΔE_p (not kept)[c].
CuF_2				
$^2\Sigma_g^+ \ldots (7\,\sigma_g)^1$	−0.63150 (1971)	−0.38694	−0.53037	−0.01446
$^2\Sigma_u^+ \ldots (5\,\sigma_u)^1$	−0.44306 (2299)	−0.43337	−0.65637	−0.01448
$^2\Pi_u \ldots (3\,\pi_u)^1$	−0.44669 (2305)	−0.43663	−0.66347	−0.01457
$^2\Pi_g \ldots (2\,\pi_g)^1$	−0.60917 (2420)	−0.38591	−0.52950	−0.01659
$^2\Delta_g \ldots (1\,\delta_g)^1$	−0.58428 (2159)	−0.38378	−0.52673	−0.01409
$CuCl_2$				
$^2\Sigma_g^+ \ldots (9\,\sigma_g)^1$	−0.48285 (1360)	−0.23801	−0.31557	−0.00751
$^2\Sigma_u^+ \ldots (7\,\sigma_u)^1$	−0.39660 (2021)	−0.28431	−0.39864	−0.00919
$^2\Pi_u \ldots (4\,\pi_u)^1$	−0.40331 (2029)	−0.28609	−0.40459	−0.00876
$^2\Pi_g \ldots (3\,\pi_g)^1$	−0.47500 (2064)	−0.23714	−0.32371	−0.00994
$^2\Delta_g \ldots (1\,\delta_g)^1$	−0.46456 (1701)	−0.23844	−0.31131	−0.00903

[a] Atomic units. References CI energy: − 1836.0 a.u. (CuF_2) and − 2556.0 a.u. ($CuCl_2$).
[b] Values in parentheses are the dimension of the CI wavefunctions.
[c] Energy portions retained or discarded (see text for a detail).

A CI calculation has been carried out for each state of interest using the above mentioned reference configurations. As orbitals of variable occupancy in the CI calculation, we adopted 32 and 31 valence orbitals for CuF_2 and $CuCl_2$, respectively. The 7 or 16 lowest lying orbitals are assumed to form a frozen core and were kept fixed. All configurations derived from single and double excitations from each reference configuration which lie within an energy threshold of 10^{-5} a.u. were included in the CI calculation. Within the truncation of the MO bases and the perturbation threshold, the dimension of the CI wavefunction was 1971 for CuF_2 and 1360 for $CuCl_2$ in their $^2\Sigma_g^+$ ground state.

The energies of the CI wavefunction and the energy decreases with respect to the SCF energies of the reference configurations are summarized in Table 1. The ΔE_p values refer to portions of energy retained (ΔE_p(kept)) or discarded (ΔE_p(not kept)) by the second-order perturbation theory with the energy threshold of 10^{-5} a.u. It may be noted that the ΔE_p (not kept) value is only less than 3% of the ΔE_p (kept) value in all states considered in this study.

3. Results and Discussion

In Table 2 the calculated excitation energies and oscillator strengths obtained from the CI calculations are summarized. The first excited state in both molecules is shown as a $^2\Pi_g$ state which lies 0.61 eV and 0.21 eV above the $^2\Sigma_g^+$ ground state of CuF_2 and $CuCl_2$, respectively. The relative ordering of the electronic states in both molecules turned out to be the same with $^2\Sigma_g^+ < {}^2\Pi_g < {}^2\Delta_g < {}^2\Pi_u < {}^2\Sigma_u^+$. This same ordering of states has also been recently

Table 2. A summary of the calculated excited energies and oscillator strengths (f) of CuF_2 and $CuCl_2$[a].

Electronic states	ΔE(CI)		f[b]
	eV	cm^{-1}	
CuF_2			
$^2\Sigma_g^+$ (ground state)			
$^2\Sigma_u^+$	5.13	41 377	0.161 (x)
$^2\Pi_u^+$	5.03	40 571	0.038 (y, z)
$^2\Pi_g$	0.61	4 920	0.0
$^2\Delta_g$	1.28	10 324	0.0
$CuCl_2$			
$^2\Sigma_g^+$ (ground state)			
$^2\Sigma_u^+$	2.35	18 955	0.281 (x)
$^2\Pi_u$	2.16	17 422	0.001 (y, z)
$^2\Pi_g$	0.21	1 694	0.0
$^2\Delta_g$	0.50	4 033	0.0

[a] The molecule lies in the x-axis.
[b] The oscillator strengths have been calculated by $f = \frac{2}{3}|t|^2 \Delta E$, where t and ΔE are the transition moment and transition energy.

reported by de Mello et al. [15], who summarized other previous ab initio and semiempirical MO studies in addition to their own calculations. The first two transitions, $^2\Pi_g \leftarrow {}^2\Sigma_g^+$ and $^2\Delta_g \leftarrow {}^2\Sigma_g^+$ with excitation energies 4920 cm^{-1} and 10 324 cm^{-1} in CuF_2 are dipole forbidden. On the other hand, the dipole allowed transitions, $^2\Pi_u \leftarrow {}^2\Sigma_g^+$ and $^2\Sigma_u^+ \leftarrow {}^2\Sigma_g^+$ with calculated transition energies 40 571 and 41 377 cm^{-1} carry appreciable amounts of oscillator strength (f) of 0.038 (y) and 0.161 (y). Comparing these results with previous ab initio SCF and semiempirical MO studies [15], [16], the two dipole allowed transitions $^2\Pi_u \leftarrow {}^2\Sigma_g^+$ and $^2\Sigma_u^+ \leftarrow {}^2\Sigma_g^+$ have significantly higher transition energies (> 52 000 cm^{-1}) in all levels of calculations in the previous study, even though the energy differences between the $^2\Pi_u$ and $^2\Sigma_u^+$ states seem to agree with each other. The energy difference between these two states amounts to less than 1000 cm^{-1}. There are no experimental UV spectra in the gas phase available as yet to compare with these calculated values.

The first two excitations in $CuCl_2$ are similarly the $^2\Pi_g \leftarrow {}^2\Sigma_g^+$ and $^2\Delta_g \leftarrow {}^2\Sigma_g^+$ transitions with excitation energies of 1694 and 4033 cm^{-1}, which are dipole forbidden. The dipole allowed transitions $^2\Pi_u \leftarrow {}^2\Sigma_g^+$ and $^2\Sigma_u^+ \leftarrow {}^2\Sigma_g^+$ with transition energies of 17 422 and 18 955 cm^{-1} carry f values of 0.001 (y) and 0.281 (x), respectively. Unlike for CuF_2, the optical spectra of the gas phase $CuCl_2$ have been reported previously [3]. The UV spectrum is characterized by two absorption bands with maxima at 9000 cm^{-1} and 19 000 cm^{-1}. As to the assignments of these UV bands, there has been some controversy in the literature. Hougen et al. [2] and Smith [14] proposed that both bands are due to the $^2\Pi_g \leftarrow {}^2\Sigma_g^+$ (9000 cm^{-1}) and $^2\Delta_g \leftarrow {}^2\Sigma_g^+$ (19 000 cm^{-1}). DeKock and Gruen [3] and Lever and Hollebone [5] proposed, however, that the 9000 cm^{-1} band should be due to $^2\Delta_g \leftarrow {}^2\Sigma_g^+$ and the $^2\Pi_g \leftarrow {}^2\Sigma_g^+$ transition would lie below 5000 cm^{-1}. Garner et al. [16] proposed that the 19 000 cm^{-1} band was due to the $^2\Pi_u \leftarrow {}^2\Sigma_g^+$ transition and the 9000 cm^{-1} band corresponds to the $^2\Delta_g \leftarrow {}^2\Sigma_g^+$ transition. Finally, de Mello et al. [15] recently proposed that the band observed at 19 000 cm^{-1} may be assigned to the $^2\Pi_u \leftarrow {}^2\Sigma_g^+$ and $^2\Sigma_u^+ \leftarrow {}^2\Sigma_g^+$ transitions and that the band observed at 9000 cm^{-1} is due to a combination of $^2\Pi_g \leftarrow {}^2\Sigma_g^+$ and $^2\Delta_g \leftarrow {}^2\Sigma_g^+$ transitions.

The proposals made by Garner et al. [16] and de Mello et al. [15] as to the assignment of the 19 000 cm^{-1} band are qualitatively confirmed by the present CI calculation in that the $^2\Sigma_u^+$, $^2\Pi_u \leftarrow {}^2\Sigma_g^+$ transitions are responsible for this band.

However, as shown in Table 2, the oscillator strength of the $^2\Sigma_u^+ \leftarrow {}^2\Sigma_g^+$ transition ($f = 0.281$) is much larger than that of $^2\Pi_u \leftarrow {}^2\Sigma_g^+$ and therefore the $^2\Sigma_u^+ \leftarrow {}^2\Sigma_g^+$ transition is believed to be essentially responsible for this band. As proposed by de Mello et al. [15], the lower lying 9000 cm^{-1} band is confirmed as the combination of the two transitions, $^2\Pi_g$, $^2\Delta_g \leftarrow {}^2\Sigma_g^+$. These dipole forbidden transitions may become allowed through a slight deviation from the $D_{\infty h}$ symmetry.

The calculated ionization potentials of CuF_2 and $CuCl_2$ are summarized in Table 3. Among other things, it is shown that the energy gap of the resulting singlet and triplet cationic states of each symmetry is very small. While there is no experimental photoelectron spectrum (PES) available for

Table 3. Energies of the CI wavefunctions of the cationic states of CuF_2 and $CuCl_2$ [a].

Electronic states	E(CI)	E(CI−SCF)	IP (CI) [b]	
CuF_2^+				
$^1\Sigma_g^+$	−0.10097	−0.46688	14.44	(14.32)
$^3\Sigma_u^+$	−0.07497	−0.39218	15.02	(14.74)
$^1\Sigma_u^+$	−0.07854	−0.39091	15.05	
$^3\Pi_u$	−0.12782	−0.39959	13.71	(13.86)
$^1\Pi_u$	−0.12324	−0.39840	13.83	
$^3\Pi_g$	−0.14067	−0.40126	13.36	(13.18)
$^1\Pi_g$	−0.13792	−0.40066	13.43	
$^3\Delta_g$	−0.06975	−0.39282	15.29	(15.36)
$^1\Delta_g$	−0.05885	−0.39049	15.58	
$CuCl_2^+$				
$^3\Sigma_u^+$	−1.03413	−0.23662	12.48	
$^1\Sigma_u^+$	−1.03176	−0.23553	12.55	
$^3\Pi_u$	−1.05616	−0.25868	11.88	
$^1\Pi_u$	−1.05328	−0.25817	11.96	
$^3\Pi_g$	−1.07003	−0.26078	11.50	
$^1\Pi_g$	−1.06622	−0.26001	11.61	
$^3\Delta_g$	−0.96893	−0.24775	14.26	

[a] Atomic units. References CI energy: − 1836.0 a.u. (CuF_2) and − 2555.0 a.u. ($CuCl_2$).

[b] Ionization potential obtained from the CI energies of the ground state ($^2\Sigma_g^+$) and the cationic states of CuF_2 and $CuCl_2$ in eV. Values in parentheses are the experimental values of [6].

$CuCl_2$, the experimental PES values of Dyke et al. [6] for CuF_2 may be compared with our CI results. Experimentally, nine bands were observed in the I.P. range from 11.0 to 21.0 eV. The lowest IP of CuF_2 is calculated to be 13.36 and 13.43 eV for the ${}^{3,1}\Pi_g \leftarrow {}^2\Sigma_g^+$ ionization, which is in excellent agreement with the experimental value of 13.18 eV. The first five bands observed in the experiment may be assigned as ${}^{3,1}\Pi_g$, ${}^{3,1}\Pi_u$, ${}^1\Sigma_g^+$, ${}^{3,1}\Sigma_u^+$ and ${}^{3,1}\Delta_g$. The calculated and experimental values are compared with each other in Table 3. Since the calculated singlet and triplet energy separations are too small, it is not possible to say whether the resulting cationic states are due to singlet or triplet states. As shown in Table 3, the ordering of the IP's for $CuCl_2$ turned out to be similar to that of CuF_2, the lowest PES band also being the ${}^{3,1}\Pi_g \leftarrow {}^2\Sigma_g^+$ ionization with 11.50 eV.

Table 4. Molecular properties for the ground state (${}^2\Sigma_g^+$) of CuF_2 and $CuCl_2$.

	CuF_2	$CuCl_2$
$\langle x^2\rangle$ [a]	−44.0791	−54.9992
$\langle y^2\rangle$	−19.6403	−37.3038
$\langle r^2\rangle$	−83.3596	−139.5463
$\langle 1/r\rangle$ (Cu) [b]	−134.6673	−134.6374
$\langle 1/r\rangle$ (F, Cl)	−26.6262	−64.4176
$q_{3z^2-r^2}$ (Cu) [c]	−1.4816	−1.0724
$q_{3z^2-r^2}$ (F, Cl)	−0.6064	−0.8704
ϱ (Cu) [d]	0.8704	0.9402
ϱ (F, Cl)	0.0198	0.0060

[a] Second moment in Buckingham units.
[b] Electric potential at nucleus in a.u.
[c] Electric field gradient in a.u.
[d] Spin density in a.u.

Some molecular properties for the ground state (${}^2\Sigma_g^+$) of CuF_2 and $CuCl_2$ obtained from the CI wavefunctions are listed in Table 4. They include the second moment, the electric potential, electric field gradient and the spin densities for Cu, F and Cl. Of interest is the nuclear quadrupole coupling constant of ${}^{63}Cu$ in both molecules, since there are experimental values available [17]. The NQR frequencies of CuF_2 and $CuCl_2$ are reported to be 58.34 and 37.78 MHz, respectively. The calculated electric field gradients (q) at ${}^{63}Cu$ of −1.4816 and −1.0724 a.u. for CuF_2 and $CuCl_2$ are in good agreement with the NQR values. Also, the calculated eQq value for ${}^9F$ in CuF_2 of 20.3 MHz may be compared with a recent NQR value of 19.9 MHz [18]. The calculated spin density of Cu in $CuCl_2$ is slightly larger (0.9402 a.u.) than in CuF_2 (0.9704 a.u.), while the spin density of Cl in $CuCl_2$ (0.006 a.u.) is much smaller than that of F in CuF_2. It may thus be concluded that the unpaired electron in CuF_2 and $CuCl_2$ is localized almost totally in the copper atom, which is in agreement with previous EPR study of Kasai et al. [9].

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