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Electronic structure of Ag^{2+} impurities in halide lattices

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Abstract. The composition of electronic levels as well as optical transitions associated with AgCl_6^{4-} and AgF_6^{4-} complexes have been studied through $MS\text{-}X\alpha$ and SCCEH calculations performed as a function of equatorial (R_{eq}) and axial (R_{ax}) metal–ligand distances. The scheme and composition of levels for AgCl_6^{4-} is rather different from that for AgF_6^{4-} and other more ionic systems. The first transition for $\text{KCl}:\text{Ag}^{2+}$ (observed at $12\,500\text{ cm}^{-1}$) is assigned to a jump involving the $5a_{1g}$ orbital which is mainly built (about 70%) from 3p orbitals of axial chlorine atoms. Aside from explaining reasonably the five optical bands experimentally observed for $\text{KCl}:\text{Ag}^{2+}$, the present work indicates that the first allowed charge-transfer transition of AgF_6^{4-} would lie in the ultraviolet region and confirms that the unpaired electron in AgCl_6^{4-} spends a little more time on equatorial ligands than on the central ion. All these results are consistent with a high value ($\chi = 2.8$) for the optical electronegativity of Ag^{2+} . The dependence of electronic transitions (and also of unpaired spin densities f_σ and f_π) on R_{eq} and R_{ax} is found to be rather similar for both AgF_6^{4-} and AgCl_6^{4-} complexes. The relation between such a dependence and the band widths of optical transitions is outlined.

1. Introduction

Theoretical work devoted to Ag^{2+} complexes is rather scarce [1–3], a situation which is markedly different from that for Cu^{2+} complexes. For instance, a good number of theoretical studies on the electronic structure of *simple* Cu^{2+} complexes involving halides as ligands have been performed [4–13] while no calculations on AgX_6^{4-} ($X \equiv$ halide) complexes (displaying a D_{4h} ‘elongated’ octahedral geometry) have been reported up to now. Experimentally such complexes are formed through x-irradiation of ionic lattices (such as NaF and KCl) previously doped with the stable Ag^+ cation [14–22].

The interest in calculating the electronic structure of a complex such as AgCl_6^{4-} lies in the conclusions reached from the analysis of its optical and EPR data [23]. In fact it was pointed out that the unpaired electron of AgCl_6^{4-} , although lying in the antibonding b_{1g}^* ($\sim x^2 - y^2$) level, should spend at least *the same time on ligands* as on the silver ion. Furthermore, it was suggested [23] that the optical electronegativity would be equal to $\chi = 2.8$ for Ag^{2+} and thus it would be the same as for Br^- [24]. From this the experimental $[g]$ tensor associated with *tetragonal* AgBr_6^{4-} units exhibits a surprising almost isotropic behaviour ($g_{\parallel} = 2.072(3)$; $g_{\perp} = 2.067(3)$ for $\text{CdBr}_2:\text{Ag}^{2+}$ [25]) which has been explained on the assumption again of a high localization of the unpaired electron on the four equatorial ligands and taking into account the key role played by charge-transfer excitations in the $[g]$ tensor of non-ionic MX_n ($M \equiv$ transition-metal ion) complexes [23].

As regards optical excitations on AgX_6^{4-} complexes ($X \equiv \text{F}$ or Cl) the available experimental information is relatively scarce although data have been reported for AgBF_6

compounds (B \equiv Sn, Zr or Ti) [26, 27] as well as for KCl:Ag^{2+} [14, 16, 19]. In the latter case, five different bands peaked at 12 500, 15 900, 17 800, 21 700 and 29 600 cm^{-1} have been observed, suggesting that the gap G between the highest crystal-field-like transitions and the smallest charge-transfer transition would certainly be smaller than for CuCl_6^{4-} . In this case the highest crystal-field transitions $e_g^* \rightarrow b_{1g}^*$ between the mainly d levels $e_g^*(\sim xz, yz)$ and b_{1g}^* lies at 10 970 cm^{-1} [28, 29] while the lowest charge-transfer transition $e_u(\pi + \sigma, eq) \rightarrow b_{1g}^*$ is located at 25 510 cm^{-1} , so $G = 14 540 \text{ cm}^{-1}$ [30].

When all these facts are borne in mind, carrying out a theoretical investigation upon the electronic structure of AgX_6^{4-} complexes (X \equiv halide) becomes an attractive and necessary task. Here the results of theoretical calculations made on AgF_6^{4-} and AgCl_6^{4-} complexes are reported. Aside from exploring the charge distribution associated with the unpaired electron the present work is especially devoted to understanding the optical transitions displayed by both systems. To achieve this goal, two different methods are used throughout this work: the multiple-scattering- $X\alpha$ (MS- $X\alpha$) method together with the self-consistent charge extended Hückel (SCCEH) procedure. Both have previously led to a reasonable understanding of experimental optical transitions of transition-metal complexes and in particular of charge-transfer excitations of Cu^{2+} complexes [30].

Such transitions are difficult to calculate properly through *ab initio* methods which use a moderate quality basis. In fact they underestimate the energy of valence n_{LP} levels of free X^- ion which can give rise to *negative* values of the electronic affinity of X [31] as well as place the mainly n_{LP} ligand levels *above* the mainly d levels in the case of ionic complexes. A recent example of this problem can be found in [32]. Such an important drawback is, however, circumvented in the semiempirical SCCEH method (where the energies of free ions are taken from experiment) and also in the density functional MS- $X\alpha$ procedure when used in conjunction with the Norman [33] criterion as shown by previous results on Cu^{2+} and Ni^{2+} complexes [8, 11, 30].

As previously discussed, the optical and EPR parameters of *isolated* tetragonal d^9 complexes depend upon the equatorial (R_{eq}) and axial (R_{ax}) metal-ligand distances. The actual values of R_{eq} and R_{ax} depending on the host lattice are not easy to determine especially for the present Ag^{2+} complexes as the Ag^{2+} cation is involved in only a few inorganic compounds. Therefore, in order to overcome this significant problem, it has been necessary to perform calculations as a function of R_{eq} and R_{ax} around some initial values R_{eq}^0 and R_{ax}^0 estimated from data for AgF_2 [34] as well as for compounds involving CuCl_6^{4-} units [35, 36].

2. Theoretical details

Calculations have been performed with two methods on the basis of very different approximations but the results obtained are rather similar.

A standard version of the MS- $X\alpha$ method has been used. The exchange parameters α for the different atoms were taken from the compilation of Schwarz [37, 38]. Sphere radii were chosen according to the Norman [33] procedure, allowing the atomic spheres to overlap and determining the absolute values of the radii by the condition that the virial ratio $-2\langle T \rangle / \langle V \rangle$ is as close as possible to 1. A Watson sphere coincident with the outer-sphere radius and carrying a charge of +2 was used to simulate the crystal field. Partial waves up to $l = 3, 2$ and 1 have been included in the multiple-scattering expansion for outer-sphere, silver and halide regions, respectively. Optical transition energies were determined using the Slater transition state procedure.

The calculations were performed at a non-relativistic spin-restricted level on a VAX 8350 computer with computation times of about 30 s per iteration and about 40 iterations required for convergence. We have also performed calculations in a spin-unrestricted level, so as to include quasi-relativistic corrections [39] and to increase the number of partial waves, but we find no change in the level ordering and an almost negligible variation in the charge distributions and the energies of the optical transitions.

The charge distributions shown in this work were calculated using the method of Karplus and co-workers [40, 41] for partitioning of the inter- and outer-sphere charges. The LCAO parameters of the antibonding b_{1g}^* ($\sim x^2 - y^2$) orbital used in the calculation of the parameters of unpaired spin density on ligands f_s and f_σ were obtained from these redistributed charges with a small Mulliken-like correction.

Writing the b_{1g}^* wavefunction in LCAO form as

$$|b_{1g}^*\rangle = N[|d(x^2 - y^2)\rangle - \lambda_{p\sigma}|\chi_{p\sigma}\rangle - \lambda_s|\chi_s\rangle] \quad (1)$$

where $|\chi_{p\sigma}\rangle$ and $|\chi_s\rangle$ are suitable normalized LCAOs involving valence n_{LP} and n_{LS} orbitals of ligands, the parameters f_s and f_σ are defined for the present case as

$$\begin{aligned} f_s &= \frac{1}{4}(N\lambda_s)^2 \\ f_\sigma &= \frac{1}{4}(N\lambda_{p\sigma})^2. \end{aligned} \quad (2)$$

The SCCEH calculations have been carried out following the procedure developed by Ammeter *et al* [42]. In this model the diagonal elements of the one-electron Hamiltonian are taken from the so-called VSIES depending upon the atomic charges and derived from experimental data on different free ions [43]. The dependence of VSIES with the charge for a given atomic configuration is assumed [43] to be quadratic ($\text{VSIE}(q) = Aq^2 + Bq + C$). The three VSIE coefficients used for fluorine and chlorine in this work are the same as those used in previous calculations of optical and EPR properties of MX_n complexes ($M \equiv \text{Ni}^+$, Cu^{2+} or Mn^{2+} ; $X \equiv \text{F}$ or Cl ; $n = 4, 6, 8$) [30, 44]. As regards the corresponding parameters for the nine configurations of silver employed in this work (d^n , $d^{n-1}s$, $d^{n-1}p$ for the 4d orbital and so on), they have been taken from the work by Munita and Letelier [45].

As the first excitations mainly depend upon the interaction between 4d orbitals of silver and n_{LP} and n_{LS} valence orbitals of the corresponding halide, we have used Clementi-Roetti [46] wavefunctions to describe such orbitals and to calculate the overlap integrals involved. The radial part of the 5s and 5p orbitals of silver is simply described by a single exponential function with an exponent equal to 2.2775 in both cases.

3. Discussion

Tables 1 and 2 depict the highest occupied electronic levels of AgF_6^{4-} calculated for $R_{\text{eq}} = 2.10 \text{ \AA}$ and $R_{\text{ax}} = 2.50 \text{ \AA}$ using the SCCEH and MS-X α methods, respectively. The main features obtained through both calculations are similar and can be summarized as follows.

(1) The unpaired electron lies in the antibonding $3b_{1g}$ which is mainly built from the $4d(x^2 - y^2)$ wavefunction of silver. The MS-X α value $f_\sigma = 11.5\%$ is higher than those derived for the analogous CuF_6^{4-} ($f_\sigma = 5.3\%$) [47] and NiF_6^{5-} ($f_\sigma = 2.2\%$) [30] complexes involving the 3d ions Cu^{2+} and Ni^+ , respectively. A similar situation is obtained

Table 1. Relative energies and charge distributions for the highest valence orbitals of the complex AgF_6^{4-} obtained in a $\text{MS-X}\alpha$ calculation with $R_{\text{eq}} = 2.10 \text{ \AA}$ and $R_{\text{ax}} = 2.50 \text{ \AA}$.

Orbital	Energy (eV)	Charge distribution (%)						
		Ag			F_{eq}		F_{ax}	
		5s	5p	4d	2s	2p	2s	2p
3b _{1g}	0	—	—	59.8	3.2	37.0	—	—
5a _{1g}	-0.990	1.2	—	55.0	0.3	10.2	1.3	32.0
2b _{2g}	-1.853	—	—	76.4	—	23.6	—	—
3e _g	-2.034	—	—	73.3	—	16.8	—	9.9
3a _{2u}	-2.712	—	2.0	—	—	7.2	0.0	90.8
2e _g	-2.715	—	—	2.4	—	14.1	—	83.5
4e _u	-2.752	—	0.0	—	0.1	1.6	—	98.3
1a _{2g}	-3.388	—	—	—	—	100.0	—	—
4a _{1g}	-3.593	5.2	—	24.1	0.0	3.5	0.4	66.8
3e _u	-3.599	—	1.8	—	—	98.2	—	0.0
1b _{2u}	-3.670	—	—	—	—	100.0	—	—
2a _{2u}	-4.082	—	3.2	—	—	89.2	0.2	7.4
2e _u	-4.259	—	7.9	—	—	90.9	—	1.2
1e _g	-4.410	—	—	25.7	—	68.3	—	6.0
1b _{2g}	-4.877	—	—	26.2	—	73.8	—	—
3a _{1g}	-5.334	8.3	—	19.9	0.8	70.9	0.0	0.1
2b _{1g}	-5.622	—	—	39.4	0.6	60.0	—	—

Table 2. The same as for table 1 for a SCCEH calculation.

Orbital	Energy (eV)	Charge distribution (%)						
		Ag			F_{eq}		F_{ax}	
		5s	5p	4d	2s	2p	2s	2p
3b _{1g}	0	—	—	77.3	1.0	21.6	—	—
5a _{1g}	-1.061	1.0	—	74.2	0.2	7.7	0.2	16.8
2b _{2g}	-1.548	—	—	78.7	—	21.3	—	—
3e _g	-1.808	—	—	79.7	—	13.0	—	7.3
4e _u	-3.436	—	0.0	—	—	0.0	—	100.0
3a _{2u}	-3.447	—	0.5	—	—	0.1	—	99.4
2e _g	-3.522	—	—	3.9	—	5.0	—	91.1
4a _{1g}	-3.782	1.5	—	9.7	0.0	9.1	0.0	79.7
1a _{2g}	-4.365	—	—	—	—	100.0	—	—
3e _u	-4.381	—	0.2	—	—	99.8	—	0.0
1b _{2u}	-4.405	—	—	—	—	100.0	—	—
2a _{2u}	-4.429	—	0.2	—	—	99.7	0.0	0.1
2e _u	-4.479	—	1.1	—	0.0	98.9	0.0	0.0
1e _g	-4.793	—	—	16.4	—	82.0	—	1.7
3a _{1g}	-4.907	0.9	—	14.9	0.1	80.8	0.0	3.3
1b _{2g}	-5.066	—	—	21.3	—	78.7	—	—
2b _{1g}	-5.197	—	—	21.5	0.2	78.3	—	—

through SCCEH where the f_{σ} -values are 7.3%, 4.0% and 2.0% for AgF_6^{4-} , CuF_6^{4-} and NiF_6^{5-} , respectively. This already supports a higher optical electronegativity χ for Ag^{2+} than for Cu^{2+} . The analysis of the experimental EPR parameters reported for NaF:Ag^{2+} [21] within the framework given in [48] leads to a value $f_{\sigma} = 8.3\%$ and thus the present $\text{MS-X}\alpha$ and SCCEH values are close to it.

(2) As the occupied $5a_{1g}$, $2b_{2g}$ and $3e_g$ levels are the closest to $3b_{1g}$, they are also mainly built from the 4d level of Ag^{2+} . Thus the picture of *first* excitations is qualitatively similar to that of a crystal-field description.

(3) Below the preceding levels, those labelled as $4e_u$, $3a_{2u}$, $2e_g$ and $4a_{1g}$ mainly built from $2p(F_{ax}^-)$ levels of axial ligands are located. A gap appears between both sets of levels. The value of such a gap is smaller in the MS-X α calculation (equal to about 0.7 eV) than in the SCCEH calculation (equal to about 1.5 eV).

(4) The electronic levels mainly made from equatorial $2p(F_{eq}^-)$ wavefunctions are separated by about 1.6 eV from the mainly axial levels in both calculations. Qualitatively this separation follows from the different electrostatic potential seen by an electron located in equatorial or axial ligands [30]. As in the present case the axial ligands lie farther from silver than do the equatorial ligands, the $2p(F_{ax}^-)$ levels are *raised* with respect to $2p(F_{eq}^-)$ levels.

The information given in tables 1 and 2 is thus basically similar to that for elongated complexes such as NiF_6^{5-} and CuF_6^{4-} although the covalence is higher for AgF_6^{4-} .

Table 3. Relative energies and charge distributions for the highest valence orbitals of the complex AgCl_6^{4-} obtained in a MS-X α calculation with $R_{eq} = 2.45 \text{ \AA}$ and $R_{ax} = 3.10 \text{ \AA}$.

Orbital	Energy (eV)	Charge distribution (%)						
		Ag			Cl _{eq}		Cl _{ax}	
		5s	5p	4d	3s	3p	3s	3p
$3b_{1g}$	0	—	—	44.5	3.1	52.4	—	—
$5a_{1g}$	-0.999	0.80	—	21.9	0.2	9.4	0.6	67.1
$3a_{2u}$	-1.503	—	1.0	—	—	11.0	0.1	87.9
$3e_g$	-1.519	—	—	0.1	—	11.6	—	88.3
$4e_u$	-1.622	—	0.1	—	0.1	1.5	—	98.3
$1a_{2g}$	-1.909	—	—	—	—	100.0	—	—
$2e_g$	-2.062	—	—	33.8	—	57.5	—	8.7
$2b_{2g}$	-2.074	—	—	48.4	—	51.6	—	—
$3e_u$	-2.240	—	2.2	—	0.2	97.6	—	0.0
$1b_{2u}$	-2.360	—	—	—	—	100.0	—	—
$2a_{2u}$	-2.958	8.8	3.0	—	—	84.3	0.7	12.0
$4a_{1g}$	-2.958	—	—	44.0	0.1	13.0	0.8	33.5
$2e_u$	-3.250	—	9.0	—	0.3	89.5	—	1.2
$1e_g$	-3.743	—	—	65.2	—	31.9	—	2.9
$1b_{2g}$	-4.155	—	—	51.3	—	48.7	—	—
$3a_{1g}$	-4.705	8.7	—	31.0	1.8	58.5	—	—
$2b_{1g}$	-4.923	—	—	54.2	1.1	44.7	—	—

Nevertheless the preceding disposal and composition of levels is significantly changed when we look at the corresponding results for AgCl_6^{4-} collected in tables 3 and 4 and whose more conspicuous features are the following.

(1) Although the unpaired electron also lies on the antibonding $3b_{1g}$ orbital, this orbital cannot be considered a mainly 4d orbital as the electronic population lying on equatorial ligands is a little higher than that on silver ion. The f_σ values derived from MS-X α and SCCEH calculations are 15.5% and 15.3%, respectively, to be compared with the value $f_\sigma = 17.7\%$ obtained from the analysis of experimental EPR data [23].

Table 4. The same as table 3, in a SCCEH calculation.

Orbital	Energy (eV)	Charge distribution (%)						
		Ag			Cl _{eq}		Cl _{ax}	
		5s	5p	4d	3s	3p	3s	3p
3b _{1g}	0	—	—	49.2	1.7	49.2	—	—
5a _{1g}	-1.165	0.4	—	23.2	0.1	4.8	0.1	71.6
3e _g	-1.716	—	—	3.5	—	0.1	—	96.5
3a _{2u}	-1.739	—	0.8	—	—	4.1	—	95.1
4e _u	-1.765	—	0.0	—	0.0	0.5	—	99.5
2b _{2g}	-2.160	—	—	65.0	—	35.0	—	—
2e _g	-2.285	—	—	51.1	—	47.4	—	1.5
1a _{2g}	-2.623	—	—	—	—	100.0	—	—
3e _u	-2.830	—	1.7	—	0.1	98.0	—	0.3
4a _{1g}	-3.021	3.9	—	52.2	0.0	15.7	0.2	28.1
1b _{2u}	-3.120	—	—	—	—	100.0	—	—
2a _{2u}	-3.466	—	1.0	—	—	95.2	0.1	3.7
2e _u	-3.733	—	2.6	—	0.2	96.9	—	0.2
1e _g	-4.038	—	—	45.4	—	52.6	—	2.0
3a _{1g}	-4.343	2.5	—	23.5	0.7	73.2	0.0	0.2
2b _{1g}	-4.418	—	—	49.1	0.3	50.6	—	—
1b _{2g}	-4.598	—	—	35.0	—	65.0	—	—

(2) At variance with what is found for AgF₆⁴⁻ the four levels 5a_{1g}, 3a_{2u}, 3e_g and 4e_u lying immediately below 3b_{1g} are mainly built from 3p(Cl_{ax}⁻) wavefunctions. Only in the case of 5a_{1g} is there an important amount (about 25%) of the 4d(3z² - r²) wavefunction. Thus the present picture for the first excited states of AgCl₆⁴⁻ cannot be accounted for even qualitatively on the grounds of a crystal-field description.

(3) The 2b_{2g} (2e_g) and 1b_{2g} (1e_g) levels exhibit strong hybridization between 4d and 3p(Cl_{eq}⁻) wavefunctions. MS-X α calculations give a little more of the 3p(Cl_{eq}⁻) character to 2b_{2g} and 2e_g than reached through SCCEH calculations.

(4) Both types of calculation indicate that 4a_{1g} is now mainly a 4d level, although lying about 3 eV below 3b_{1g}. Such a level is located between levels such as 3e_u and 2e_u formed essentially from 3p(Cl_{eq}⁻) atomic orbitals.

We have verified that neither the order of levels nor their composition is altered by changing R_{eq} and R_{ax} in our calculations. An increase in R_{eq} or R_{ax} tends, however, to decrease the separation between every one-electron level and 3b_{1g}.

Bearing in mind the results displayed in tables 3 and 4, let us discuss the microscopic origin of the five optical absorption bands found in KCl:Ag²⁺ [14, 16, 19]. The most intense bands have their maxima at 21 700 cm⁻¹ (here called δ_1) and 29 600 cm⁻¹ (called δ_2), respectively, while those peaked at 12 500 cm⁻¹ (Δ_1), 15 900 cm⁻¹ (Δ_2) and 17 800 cm⁻¹ (Δ_3) have oscillator strengths f_{os} lying between 1/200 and 1/30 of the value corresponding to δ_1 . As regards the ratio $f_{os}(\delta_2)/f_{os}(\delta_1)$, it has been reported to be equal to 1.9 [14].

The present calculations of electronic transitions (table 5) support the fact that δ_1 and δ_2 can be assigned to charge-transfer transitions arising from 3e_u($\pi + \sigma$) and 2e_u($\sigma + \pi$) equatorial levels. Aside from reasonable agreement between the experimental and calculated transition energies such an assignment is supported by the following facts.

(a) Experimentally [14, 16, 19] the polarization of the two transitions δ_1 and δ_2 corresponds to the electric vector lying in the equatorial plane of the D_{4h} AgCl₆⁴⁻ unit.

Table 5. Energies of the five optical transitions studied in this work for $AgCl_6^{4-}$, obtained in the SCCEH and MS-X α calculations for $R_{eq} = 2.45 \text{ \AA}$ and $R_{ax} = 3.10 \text{ \AA}$. The experimental values correspond to the KCl:Ag $^{2+}$ system.

Transition	Symbol	Energy (cm $^{-1}$)		
		SCCEH	MS-X α	Experimental
$5a_{1g} \rightarrow 3b_{1g}$	Δ_3	9 404	10 600	12 500
$2b_{2g} \rightarrow 3b_{1g}$	Δ_1	17 425	16 780	15 900
$2e_g \rightarrow 3b_{1g}$	Δ_2	18 430	16 700	17 800
$3e_u(\pi + \sigma) \rightarrow 3b_{1g}$	δ_1	22 827	22 370	21 700
$2e_u(\sigma + \pi) \rightarrow 3b_{1g}$	δ_2	30 111	29 800	29 600

(b) In other D_{4h} systems involving d^9 ions (such as $CdCl_2 \cdot Cu^{2+}$ or $(N-mph)_2CuCl_4$) the charge-transfer spectrum is essentially composed of two bands assigned to electron jumps from $3e_u(\pi + \sigma)$ and $2e_u(\sigma + \pi)$ levels made from equatorial $3p(Cl^-)$ levels [7, 11, 30].

(c) Preliminary calculations of oscillator strengths following the procedure by [49] give $f_{os}(\delta_2)/f_{os}(\delta_1)$ close to the experimental value [14]. On the other hand, to support the present assignment, we have also calculated the oscillator strength of the $4e_u \rightarrow 3b_{1g}$ transition (simply called δ_3) which involves the highest e_u -type orbital. The results give $f_{os}(\delta_3)/f_{os}(\delta_2) \leq 10^{-3}$. It has been pointed out [7] that, among the allowed $c \rightarrow 3b_{1g}$ charge-transfer transitions of d^9 complexes, those where the c level involves σ wavefunctions of equatorial ligands are much more intense than the others. This idea can explain the very small value of $f_{os}(\delta_3)$ as $4e_u$ is built almost only from $3p(Cl_{ax}^-)$ atomic levels. Furthermore up to now no experimental evidence of charge-transfer transitions involving jumps from $3p(Cl_{ax}^-)$ levels has been reported for $CuCl_6^{4-}$ and $CuCl_4^{2-}$ complexes.

As regards the weak optical absorption bands they are assigned to electronic jumps from the even levels $5a_{1g}$, $2b_{2g}$ and $2e_g$ to $3b_{1g}$ (table 5). Although the agreement between experimental and calculated transitions is reasonable, additional experiments would be necessary to confirm that all the three weak bands observed for KCl:Ag $^{2+}$ exhibit an oscillator strength which is temperature dependent. Because of this the assignment of one of these transitions to $4e_u \rightarrow 3b_{1g}$ cannot be fully ruled out although it seems less probable.

Therefore, from the present analysis, Δ_3 should be ascribed to an electron jump from the $5a_{1g}$ level which, although mainly only made from the axial $3p(Cl^-)$ level, involves a significant amount (about 25%) of the $4d(3z^2 - r^2)$ wavefunction, however. By contrast the transition from the mainly $4d$ level $4a_{1g}$ could be masked by the two intense charge-transfer transitions δ_1 and δ_2 as $4a_{1g}$ lies between $3e_u$ and $2e_u$ in both types of calculation (tables 3 and 4).

Table 6. Energies of the five optical transitions studied in this work for AgF_6^{4-} , obtained in the SCCEH and MS-X α calculations for $R_{eq} = 2.10 \text{ \AA}$ and $R_{ax} = 2.50 \text{ \AA}$.

Transition	Symbol	Energy (cm $^{-1}$)	
		SCCEH	MS-X α
$5a_{1g} \rightarrow 3b_{1g}$	Δ_3	8 555	9 100
$2b_{2g} \rightarrow 3b_{1g}$	Δ_1	12 486	15 220
$3e_g \rightarrow 3b_{1g}$	Δ_2	14 579	16 730
$3e_u(\pi + \sigma) \rightarrow 3b_{1g}$	δ_1	35 334	36 310
$2e_u(\sigma + \pi) \rightarrow 3b_{1g}$	δ_2	36 127	40 990

Let us briefly comment on the results for the optical transitions of AgF_6^{4-} which are collected in table 6. The calculated crystal-field-like transitions Δ_3 , Δ_1 and Δ_2 can explain reasonably well the optical spectrum displayed by AgBF_6 ($B \equiv \text{Sn, Ti or Zr}$) compounds [26, 27]. Taking AgSnF_6 as a guide, three bands peaked at 8300, 11 900 and 15 400 cm^{-1} have been found experimentally. From our calculations, such transitions can reasonably be assigned to jumps arising from the mainly 4d levels $5a_{1g}$, $2b_{2g}$ and $3e_g$.

An interesting result gathered in table 6 concerns the position of charge-transfer transitions δ_1 and δ_2 . As fluorine exhibits the highest optical electronegativity of the halides, MF_6 complexes ($M \equiv 3d$ ion) have their allowed charge-transfer transitions in the vacuum-ultraviolet region. As an example the first charge-transfer band of CrF_6^{3-} has been observed to lie at around 65 000 cm^{-1} in the excitation spectrum of $\text{Na}_3\text{In}_2\text{Li}_3\text{F}_{12}:\text{Cr}^{3+}$ [50] measured using synchrotron radiation. For AgF_6^{4-} both types of calculation indicate, however, that the first charge-transfer transition $3e_u(\pi + \sigma) \rightarrow 3b_{1g}$ would lie in the visible-ultraviolet region. This conclusion although a little surprising is not incompatible with the empirical equation obtained by Jørgensen [24] for the frequency ν_1 of the first charge-transfer transition and the value $\chi(\text{Ag}^{2+}) = 2.8$ proposed for Ag^{2+} [24]. In fact writing for AgF_6^{4-}

$$\nu_1 = K[\chi(\text{F}^-) - \chi(\text{Ag}^{2+})] + 10Dq \quad (3)$$

where $K = 30\,000 \text{ cm}^{-1}$, $\chi(\text{F}^-) = 3.9$ and taking $10Dq = 12\,000 \text{ cm}^{-1}$ it is found that $\nu_1 = 45\,000 \text{ cm}^{-1}$. So, this value, although being 25% higher than those reported in table 6, places again the first charge-transfer transition of AgF_6^{4-} in the visible-ultraviolet range. It is worth noting that charge-transfer transitions are rather sensitive to changes in R_{eq} and R_{ax} as has been demonstrated experimentally [51] and theoretically [11, 30, 52] for several Cu^{2+} complexes. Despite this, even if calculations are performed for $R_{\text{eq}} = 2.0 \text{ \AA}$ the first charge-transfer transition is found to lie at about 44 000 cm^{-1} . More details on the dependence of the optical transitions on R_{eq} and R_{ax} are given later. Recently EPR and optical data on $\text{NaF}:\text{Ag}^{2+}$ [21] have been reported. Unfortunately, in the ultraviolet region of the optical spectrum the presence of bands due to Ag^+ as well as to other colour centres formed under x-irradiation have prevented clear identification of optical bands due to AgF_6^{4-} .

A study of the dependence of optical and EPR parameters on metal-ligand distances has been shown to be of great interest as the variations in such distances (of the order of 10^{-3} \AA) can be detected through the corresponding changes in spectroscopic parameters [30]. Furthermore in the case of optical spectra such a dependence determines the Huang-Rhys factors associated with the A_{1g} vibration modes of the complex [44].

Writing the R -dependence of a given quantity Q in the vicinity of R_{eq}^0 and R_{ax}^0 as

$$Q = Q_0 R_{\text{eq}}^{-n_{\text{eq}}} \quad (4)$$

the exponents n_{eq} can be derived from molecular orbital calculations performed at different R_{eq} -values. A similar law to (4) but replacing R_{eq} and n_{eq} by R_{ax} and n_{ax} is used to describe the changes induced by variations in R_{ax} in the neighbourhood of R_{ax}^0 .

The n_{eq} and n_{ax} -values corresponding to optical transitions and also to f_σ and f_s parameters for AgF_6^{4-} and AgCl_6^{4-} complexes are collected in table 7. Let us firstly discuss the most relevant results obtained on the more ionic AgF_6^{4-} complex which are the following.

(1) The two crystal-field transitions Δ_1 and Δ_2 as well as the two charge-transfer transitions δ_1 and δ_2 are much more sensitive to changes in R_{eq} than to changes in R_{ax}

Table 7. Exponents n_{eq} and n_{ax} corresponding to optical transitions and f_s and f_σ parameters of AgF_6^{4-} and $AgCl_6^{4-}$ complexes obtained by MS-X α and SCCEH calculations.

System	Calculation method	Value of exponent n for the following						
		Δ_3	Δ_1	Δ_2	δ_1	δ_2	f_s	f_σ
AgF_6^{4-}	n_{eq} MS-X α	8.29	4.22	4.60	3.05	3.25	7.99	0.18
	n_{eq} SCCEH	10.0	4.5	5.1	4.97	4.96	8.4	-2.6
	n_{ax} MS-X α	-3.60	-0.13	-0.28	1.78	0.49	0.64	-0.41
	n_{ax} SCCEH	-3.4	0.5	0.02	1.4	1.4	0.4	-1.0
$AgCl_6^{4-}$	n_{eq} MS-X α	9.94	4.43	4.88	4.96	4.79	7.01	-1.85
	n_{eq} SCCEH	18.0	5.0	5.1	5.3	5.3	10.7	-0.4
	n_{ax} MS-X α	-3.25	0.05	0.20	0.35	0.32	0.38	-0.30
	n_{ax} SCCEH	-2.9	0.5	1.0	1.5	1.4	0.7	-0.7

in accordance with the 'planar character' of orbitals such as $3b_{1g}$, $2b_{2g}$, $3e_g$, $3e_u$ and $2e_u$. The n_{eq} values found for Δ_1 and Δ_2 lie between 4 and 5.5 as was previously found for complexes such as NiF_6^{5-} , CuF_6^{4-} , MnF_6^{4-} or CrF_6^{3-} [44]. For MnF_6^{4-} a value $n_{eq} = 4.7$ has been measured experimentally [53, 54].

(2) Δ_3 exhibits a greater dependence on R_{eq} than Δ_1 and Δ_2 do. As the Huang-Rhys factor $S(A_{1g}; eq)$ associated with the A_{1g} vibration mode of equatorial ligands is proportional to n_{eq}^2 [44], this factor alone would give rise to a band width for the Δ_3 transition which is about twice that corresponding to Δ_1 and Δ_2 . Although experimental band widths for Δ_1 , Δ_2 and Δ_3 transitions of $AgCl_6^{4-}$ have not been reported, they have been measured, however, for $CuCl_6^{4-}$ where the band width associated with Δ_3 is reported to be about 1.8 of that corresponding to Δ_2 [28, 29].

(3) Also Δ_3 is more sensitive to R_{ax} variations than Δ_1 and Δ_2 are. The negative value of n_{ax} is in accord with the increase in the separation between $5a_{1g}(\sim 3z^2 - r^2)$ and $3b_{1g}(\sim x^2 - y^2)$ levels upon the removal of the axial ligands.

(4) Although f_σ is much higher than f_s the latter parameter is, however, much more strongly dependent upon R_{eq} than the former. The microscopic origin of this situation already found in D_{4h} systems such as NiF_6^{5-} , NiF_4^{3-} and CuF_6^{4-} and also in O_h complexes such as MnF_6^{4-} is discussed in [30]. It allows one to detect R_{eq} changes through the corresponding variations in the isotropic superhyperfine constant A_s . For $AgCl_6^{4-}$, taking as a first approximation $A_s \propto f_s$, a ΔA_s of about 0.5 G is expected if $\Delta R_{eq} = 1$ pm provided that $f_s \propto R_{eq}^{-7}$ and A_s is about 15 G as derived from the analysis of experimental data. When it is borne in mind that the differences between the experimental superhyperfine tensors of $LiCl:Ag^{2+}$ and $RbCl:Ag^{2+}$ determined through EPR [15] involve errors of ± 4 G, the detection of variations $\Delta R_{eq} \simeq 1$ pm for $AgCl_6^{4-}$ would require the use of the ENDOR technique.

When comparing exponents n_{ax} and n_{eq} for AgF_6^{4-} and $AgCl_6^{4-}$ complexes, table 7 reveals that they are very similar for both complexes in spite of the different compositions of their electronic levels. Therefore, in the case of $AgCl_6^{4-}$ a change of 1 pm in R_{eq} would produce variations in δ_1 , Δ_1 and Δ_3 all of which are close to 400 cm^{-1} . This situation would be different from that existing for other more ionic systems such as AgF_6^{4-} , NiF_6^{5-} or MnF_6^{4-} . In these cases if we designate by E the energy of a given transition, $\partial E / \partial R_{eq}$ is clearly higher for charge-transfer transitions δ_1 or δ_2 than for the crystal-field transitions Δ_1 or Δ_2 . Taking as a guide the case of AgF_6^{4-} , table 7 indicates that, if R_{eq} is changed by 1 pm, the corresponding changes for Δ_1 and δ_1 would be equal to about 250 cm^{-1} and

600 cm^{-1} , respectively, because δ_1/Δ_1 is about 3. Experimental evidence for the different sensitivities of charge-transfer and crystal-field transitions to R_{eq} changes in the case of complexes with low or moderate covalences has recently been reported [51].

4. Conclusions

In conclusion we believe that the present calculations help in a better understanding of optical transitions displayed by KCl:Ag^{2+} as well as the crystal-field transitions of compounds involving AgF_6^{4-} units.

In particular the position of charge-transfer transitions for KCl:Ag^{2+} is reasonably accounted for through both types of calculation such as was found previously for other d^9 systems [7, 8, 11, 30]. The present work stresses the strong hybridization existing between 4d levels of Ag^{2+} and 3p levels of axial and equatorial chlorine atoms in the case of the very covalent AgCl_6^{4-} unit. Because of this a description in terms of antibonding (bonding) levels as being mainly d (mainly p ligand) appears to meaningless for AgCl_6^{4-} .

In the case of AgBr_6^{4-} it is expected that an unpaired electron still more delocalized appears on ligands ($4f_\sigma > 70\%$) in view of the smaller electronegativity of bromine. Calculations for this system are planned in the near future.

Because of the scarcity of optical data for system involving AgX_6^{4-} units ($X \equiv \text{F}$ or Cl), more experimental data in different host lattices are required to check the conclusions reached in this work. In particular we think that the possible existence of intense charge-transfer transitions in the UV region for systems containing AgF_6^{4-} units certainly deserves further investigation.

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