Notes

Theoretical Support for the Latest Assignment of the Electronic Spectrum of $[CrOCl_4]^-$ *

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Optimised basis set discrete variational Xα self-consistent charge calculations of the electronic spectrum for the $[CrOCl_4]^-$ ion have been performed. The agreement between observed and calculated *d–d* and charge-transfer transition energies is excellent. The first two absorption bands are definitely calculated to be *d–d* in origin. This agrees with the latest assignment, based on a reinvestigation of the low-temperature polarised absorption spectrum, and refutes earlier suggestions based on *ab initio* configuration interaction and multiple scattering Xα computations.

The pioneering theoretical study[1] of the electronic structure of $[VO(H_2O)_5]^{2+}$ has generated considerable interest in d^1 mono-oxo species. Detailed spectroscopic and computational data have been brought together in an attempt to provide a consistent description of MO^{n+} chromophores.[2–8] Extensive low-temperature single-crystal polarised electronic spectra of several vanadyl complexes[3] has led to a general interpretation of the spectral features for VO^{2+}. For five-co-ordinate pyramidal species, three low-energy *d–d* bands are usually observed labelled, after Collison *et al.*,[3] I, II, and III referring respectively to the electronic promotions $d_{xy} \longrightarrow d_{x^2-y^2}$, $d_{xy} \longrightarrow d_{xz}, d_{yz}$, and $d_{xy} \longrightarrow d_{z^2}$. A sixth ligand *trans* to the VO^{2+} oxygen pushes band III up in energy where it is often masked by intense charge-transfer absorptions.

The CrO^{3+} unit apparently presents a very different picture. Detailed studies of the $[CrOCl_4]^-$ ion have been reported[7,8] but in contrast to $[VOCl_4]^{2-}$, where all three *d–d* absorptions have been located and assigned,[4] only two bands had, until recently, been identified for the chromyl analogue. The lowest-energy band at 13 000 cm^{-1} was assigned to the $^2B_2 \longrightarrow {}^2E$ transition (band II), corresponding to the $d_{xy} \longrightarrow d_{xz}, d_{yz}$ one-electron promotion.[7,8] This agreed with the simple model proposed by Gray and co-workers[1,2] for vanadyl complexes. However, the second band at 18 000 cm^{-1} was, on the basis of *ab initio* configuration interaction (CI) calculations,[7] assigned as a Cr–O(π) ⟶ Cr–O(σ*) transition, rather than the expected $d_{xy} \longrightarrow d_{x^2-y^2}$ absorption. Yet another assignment was proposed[8] with the aid of multiple scattering Xα (MSXα) computations. The MSXα results suggested that the band at 18 000 cm^{-1} arises from chlorine to metal charge-transfer (c.t.) transitions, which obscure the higher-energy *d–d* absorptions (bands I and III). These contradictions prompted Collison to reinvestigate the low-temperature polarised spectrum of $[AsPh_4][CrOCl_4]$.[9] The 'missing' third absorption, band III, was located around 20 000 cm^{-1} and arguments were presented favouring an assignment similar to that for $[VOCl_4]^{2-}$ and the original proposal of Gray and Hare.[2] The first three absorptions for the $[CrOCl_4]^-$ ion are assigned to *d–d* transitions with band II at 11 900, band I at 17 550, and band III at 20 270 cm^{-1}.[9]

The *ab initio* CI[7] and MSXα[8] calculations not only contradict each other but also disagree with this latest assignment of the $[CrOCl_4]^-$ spectrum. Of course the difficulties of performing *ab initio* CI calculations for large transition-metal systems are formidable, both with respect to accuracy and computer resources. On the other hand, while MSXα calculations are much faster, the 'muffin-tin' potential approximation coupled with the *ad hoc* overlapping-spheres method can lead to unreliable results. There are, however, alternative local density Xα schemes which are still very fast but suffer fewer problems than the MSXα method. In particular, the discrete variational Xα (DVXα) model has consistently provided reliable, accurate results for a variety of large, transition-metal systems.[10,11] For example, a DVXα study of the spectra of a d^9 chlorocuprate complex provided quantitative reproduction of the *d–d* and c.t. absorptions.[10] Accordingly DVXα calculations of the $[CrOCl_4]^-$ ion have been undertaken (*a*) to examine whether the model reproduces experiment and (*b*) to see whether the theoretical results shed any more light on the spectral assignment for this system. As detailed below, agreement between the observed band maxima and the DVXα calculations is excellent and certainly superior to either the *ab initio* CI or MSXα results. The present calculations are also consistent with the latest assignment of the $[CrOCl_4]^-$ absorption spectrum. In particular the band at 18 000 cm^{-1} is predicted to arise from the $d_{xy} \longrightarrow d_{x^2-y^2}$ promotion. The c.t. bands are also quantitatively reproduced, but the $d_{xy} \longrightarrow d_{z^2}$ transition appears to be overestimated by about 3 500 cm^{-1}.

Computational Details

The DVXα model is a numerical, local-density scheme enjoying considerable success with transition-metal systems. The method has been described elsewhere[11] and only those details relevant to the present study are included here.

Spin-restricted DVXα self-consistent charge (SCC)[12] calculations have been carried out on the C_{4v} $[CrOCl_4]^-$ ion. Geometrical data were taken from the *X*-ray structure of the tetraphenylarsonium salt: Cr–O 1.519, Cr–Cl 2.240 Å, and O–Cr–Cl 104.5°.[13] Near-minimal basis sets were employed (up to 4*p* on Cr, 2*p* on O, and 3*p* on Cl) with the core functions (up to 3*p* on Cr, 1*s* on O, and 2*p* on Cl) frozen and orthogonalised against the valence orbitals. The basis set was further constrained by applying an external potential well of depth −2 a.u., with inner and outer radii of 4 and 6 a.u. respectively for

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* *Non-S.I. units employed:* a.u. ≈ 5.29×10^{-11} m, eV ≈ 1.60×10^{-19} J.

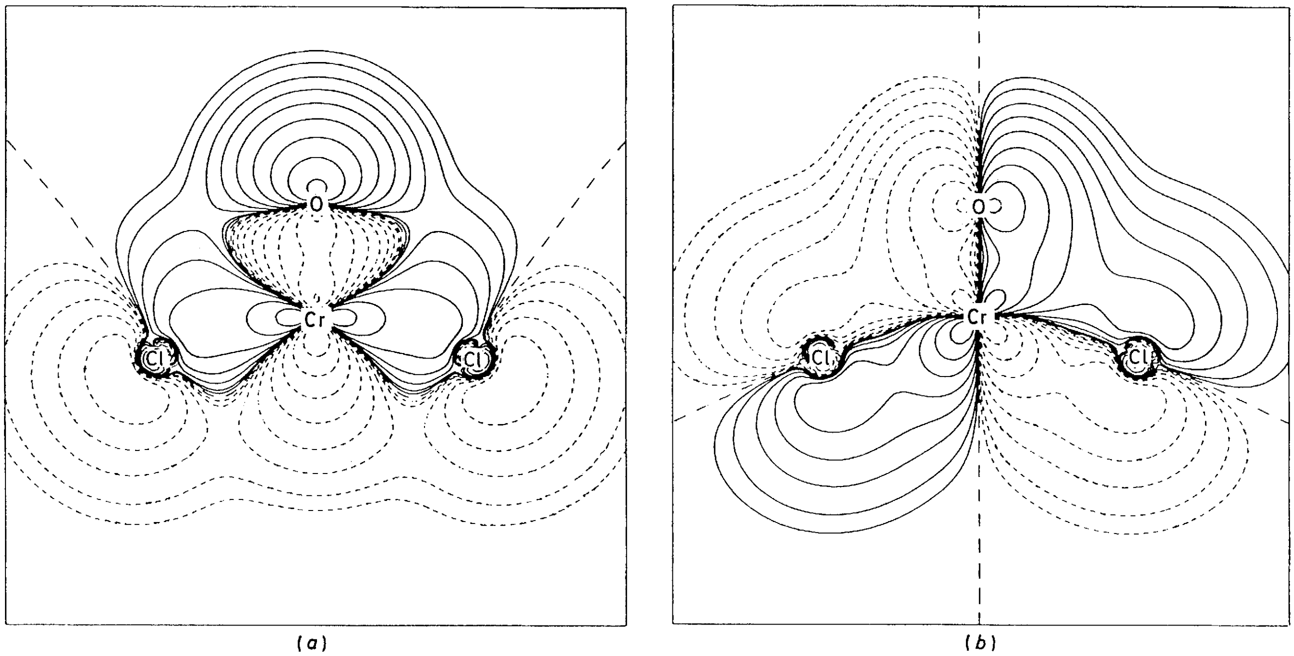

Figure. DVXα molecular orbital plots for $[CrOCl_4]^-$ in the xz plane: solid, small dashed, and long dashed lines represent respectively positive, negative, and zero contours (successive contours differ by a factor of two). (*a*) $3a_1$ σ Symmetry m.o. (*b*) $2e$ π Symmetry m.o.

Cr and Cl and 2 and 4 a.u. respectively for O. The basis was optimised as previously described.[10] A total of 3 504 sampling points were used distributed such that *ca.* 1 100, 400, and 500 points were associated respectively with Cr, O, and Cl. This distribution scheme ensures a numerical error of approximately ± 0.02 eV in molecular orbital (m.o.) energies and ± 0.002 in atomic orbital populations, relative to the limit of a very large number of sampling points. All charge densities and orbital populations are based on Mulliken analyses.[14] Estimates of the transition energies were computed using Slater's transition-state formalism.[15] In this procedure, a calculation is performed using m.o. occupations corresponding to the halfway point in the transition. Transition-state data are generally in better agreement with experiment than Xα m.o. energy differences.

Results and Discussion

All three theoretical methods, *ab initio* CI, MSXα, and DVXα, give closely comparable descriptions of the (ground state) bonding in $[CrOCl_4]^-$. The metal–ligand interactions are relatively covalent as indicated by the (DVXα) computed atomic charge distribution of $Cr^{1.11}O^{-0.24}Cl^{-0.47}$ compared to the notional ionic charges of $Cr^{5.0}O^{-2.0}Cl^{-1.0}$. A more quantitative picture emerges from a detailed Mulliken population analysis of the DVXα wavefunction (Table 1).

The singly occupied m.o. is the $2b_2(d_{xy})$ orbital leading to the expected $^2B_2$ ground state. Below this is a set of levels ($3e \longrightarrow 1a_2$) which are largely Cl $3p$ non-bonding functions followed by three Cr–Cl bonding orbitals ($4a_1 \longrightarrow 2b_1$). The next level down ($3a_1$) is the main Cr–O σ-bonding m.o. while below that is the Cr–O π-bonding orbital ($2e$). Lower still are the non-bonding Cl $3s$ m.o.s ($2a_1 \longrightarrow 1b_1$) with the oxygen $2s$ orbital ($1a_1$) the lowest valence function. Above the singly occupied $2b_2$ orbital come the remaining d functions. The $6e$, $4b_1$, and $6a_1$ orbitals can be identified as Cr–O π^*, Cr–Cl antibonding, and Cr–O σ^* functions respectively. The predicted d-orbital energy sequence is $2b_2(d_{xy}) < 6e(d_{xy},d_{yz}) < 4b_1(d_{x^2-y^2}), < 6a_1(d_{z^2})$, in agreement with the original semi-empirical predictions of Gray and co-workers[1,2] as well as the MSXα results.[8] The d-orbital sequence derived from the DVXα (and MSXα) ground-state m.o. energies is also the same as the relative excited-state energies (see below), in contrast with the *ab initio* CI calculations[7] where this is not the case. The remaining virtual m.o.s are the Cr $4s$ ($7a_1$) and Cr $4p$ ($7e$ and $8a_1$) functions.

The nature of the Cr–O and Cr–Cl bonds is shown in the Figure. Plots were generated in the xz molecular plane which contains the chromium and oxygen atoms plus two chlorine ligands. The $3a_1$ orbital [Figure (*a*)] shows the Cr–O σ bond while the $2e$ orbital [Figure (*b*)] shows the Cr–O π bond. Strong overlap between the metal and oxygen functions is apparent with somewhat smaller Cr–Cl features, consistent with the relatively weaker Cr–Cl interaction. These differences are reflected by the magnitudes of the metal–ligand overlap charges. The total Cr–O overlap amounts to 0.974 e, comprising 0.382 σ and 0.612 π. The total overlap per Cr–Cl bond is only 0.429 e. The importance of π bonding in M–O linkages has been emphasised before[1] and the present results confirm the strength of this interaction.

All three theoretical models give similar descriptions of the metal–ligand bonding but the DVXα results are much more successful at reproducing the electronic spectrum. Transition-state calculations for *d–d* and allowed c.t. absorptions are presented in Table 2. The band located at *ca.* 17 600 cm^{-1} is calculated to be a *d–d* transition, in agreement with the most recent experimental assignment.[9] *Ab initio* CI and MSXα treatments assigned this band to Cr–O(π) $\longrightarrow$ Cr–O(σ^*)[7] and Cl $\longrightarrow$ Cr[8] charge transfer respectively. Collison[9] also found a third, previously unreported band with an origin at 20 270 cm^{-1}. He assigns this to the $^2B_2 \longrightarrow {}^2A_1$ ($d_{xy} \longrightarrow d_{z^2}$) transition leading to a close parallel between the spectral assignment of $[CrOCl_4]^-$ and $[VOCl_4]^{2-}$. The present DVXα calculations place this band some 3 500 cm^{-1} too high although the numerical agreement for the *d–d* transitions is still superior to the *ab initio* CI and MSXα treatments (see the first three entries in Table 2).

The SCC approximation[11] appears to work best for relatively heteropolar bonding. For the covalent Cr–O linkage some error may therefore result. Significantly, both transition-state calculations involving orbitals with some Cr–O character

Table 1. DVXα m.o. energies (eV) and atomic orbital compositions (%) for $[CrOCl_4]^-$

		Cr				O			Cl	
Symmetry	E/eV	$3d$	$4s$	$4p_\sigma$	$4p_\pi$	$2s$	$2p_\sigma$	$2p_\pi$	$3s$	$3p$
$8a_1$	14.3320	10.7	20.6	57.0		4.8	5.6		0.0	1.4
$7e$	13.6484	0.0			89.1			3.7	1.0	6.2
$7a_1$	9.4929	0.3	62.8	22.3		0.0	0.3		1.3	12.9
$6a_1$	3.1366	52.8	0.9	12.9		0.0	21.4		0.2	11.8
$4b_1$	2.3221	63.5							0.8	35.7
$6e$	1.8671	66.4			0.0			24.2	0.1	9.4
$2b_2$*	0.2711	81.7								18.3
$1a_2$	−1.0260									100
$5e$	−1.7203	0.5			0.1			2.5	0.0	96.9
$3b_1$	−1.8245	0.3							0.0	99.7
$4e$	−2.1246	0.4			0.0			8.4	0.0	91.3
$5a_1$	−2.9203	0.3	0.1	4.4		0.5	6.3		0.0	88.4
$3e$	−3.5519	2.9			6.4			2.0	1.9	86.8
$2b_1$	−3.8238	33.6							2.0	64.4
$1b_2$	−3.8624	18.3								81.7
$4a_1$	−4.3372	0.0	9.9	1.0		1.3	13.5		3.5	70.9
$3a_1$	−4.8605	30.2	0.7	0.7		3.6	51.3		1.0	12.6
$2e$	−4.9119	29.4			2.8			59.3	0.0	8.5
$1b_1$	−13.9062	2.6							97.2	0.2
$1e$	−14.1800	0.3			1.8			0.0	97.0	0.9
$2a_1$	−14.7393	1.0	2.8	0.2		0.3	0.0		93.8	2.0
$1a_1$	−18.4099	4.9	2.3	1.5		89.4	1.6		0.3	0.1

* Singly occupied m.o.

Table 2. Comparison of DVXα transition-state calculations of the *d–d* and allowed c.t. bands with MSXα, *ab initio* CI, and experimental data (all energies in cm^{-1})

Transition	Nature	Excited state	DVXα	MSXα[a]	CI[b]	Observed[c]
$2b_2 \longrightarrow 6e$	$d_{xy} \longrightarrow d_{xz},d_{yz}$	^2E	13 565	8 300	9 900	11 900
$2b_2 \longrightarrow 4b_1$(F)[d]	$d_{xy} \longrightarrow d_{x^2-y^2}$	$^2B_1$	16 724	19 400		17 550
$2b_2 \longrightarrow 6a_1$(F)[d]	$d_{xy} \longrightarrow d_{z^2}$	$^2A_1$	23 757	26 600		20 270
$5e \longrightarrow 2b_2$	c.t.(Cl $\longrightarrow$ Cr)	^2E	22 671	10 700		23 000
$4e \longrightarrow 2b_2$	c.t.(Cl $\longrightarrow$ Cr)	^2E	25 077	12 900		25 000
$1a_2 \longrightarrow 6e$	c.t.(Cl $\longrightarrow$ Cr)	^2E	31 417	17 800		
$5e \longrightarrow 6e$	c.t.(Cl $\longrightarrow$ Cr)	$^2B_2$	36 199	19 200		
$3e \longrightarrow 2b_2$	c.t.(Cl $\longrightarrow$ Cr)	^2E	36 832	18 400		
$5e \longrightarrow 4b_1$	c.t.(Cl $\longrightarrow$ Cr)	^2E	36 910	28 200		36 800
$3b_1 \longrightarrow 6e$	c.t.(Cl $\longrightarrow$ Cr)	^2E	37 728	21 600		
$3b_1 \longrightarrow 4b_1$	c.t.(Cl $\longrightarrow$ Cr)	$^2B_2$	38 034	30 500		
$4e \longrightarrow 6e$	c.t.(Cl $\longrightarrow$ Cr)	$^2B_2$	38 191	20 900		
$1b_2 \longrightarrow 2b_2$	c.t.(Cl $\longrightarrow$ Cr)	$^2B_2$	38 193	23 700		
$4e \longrightarrow 4b_1$	c.t.(Cl $\longrightarrow$ Cr)	^2E	39 560	30 600		
$5e \longrightarrow 6a_1$	c.t.(Cl $\longrightarrow$ Cr)	^2E	44 431	36 500	46 000	
$5a_1 \longrightarrow 6e$	c.t.(Cl $\longrightarrow$ Cr)	^2E	44 485	26 200		
$4e \longrightarrow 6a_1$	c.t.(Cl $\longrightarrow$ Cr)	^2E	46 654	38 400		
$2e \longrightarrow 2b_2$	c.t.(O $\longrightarrow$ Cr)	^2E	46 924	34 500		
$2b_1 \longrightarrow 6e$	c.t.(Cl $\longrightarrow$ Cr)	^2E	49 613	32 300	33 500	
$3e \longrightarrow 6e$	c.t.(Cl $\longrightarrow$ Cr)	$^2B_2$	50 500	26 900		
$3e \longrightarrow 4b_1$	c.t.(Cl $\longrightarrow$ Cr)	^2E	51 171	36 000		
$1b_2 \longrightarrow 6e$	c.t.(Cl $\longrightarrow$ Cr)	^2E	51 969	32 000		
$4a_1 \longrightarrow 6e$	c.t.(Cl $\longrightarrow$ Cr)	^2E	53 441	32 000		
$3a_1 \longrightarrow 6e$	c.t.(O $\longrightarrow$ Cr)	^2E	56 482			
$2e \longrightarrow 6e$	c.t.(O $\longrightarrow$ Cr)	$^2B_2$	56 810	40 600		

[a] Ref. 8. [b] Ref. 7 (only c.t. bands which generate a single excited state included). [c] Ref. 9 for *d–d* bands, ref. 7 for c.t. bands. [d] F = Electric-dipole forbidden transition.

($2b_2 \longrightarrow 6e$ and $2b_2 \longrightarrow 6a_1$) are overestimated while that involving Cr–Cl character ($2b_2 \longrightarrow 4b_1$) is underestimated. The error is relatively small, however, with the DVXα calculation agreeing with experiment to about 10% on average.

Charge-transfer bands for $[CrOCl_4]^-$ have been reported[7] at 23 000, 25 000, and 36 800 cm^{-1}. The former two absorptions were only observable in z polarisation, the xy polarisation spectrum being too intense. Selection rules for C_{4v} therefore suggest these bands to be $^2B_2 \longrightarrow {}^2E$ transitions, which correspond to the computed $5e \longrightarrow 2b_2$ (22 671 cm^{-1}) and $4e \longrightarrow 2b_2$ (25 077 cm^{-1}) transition states. Agreement between theory and experiment is remarkable and somewhat better than that obtained for the c.t. spectrum of chlorocuprate complexes.[10] Both transitions are essentially chlorine to chromium c.t. bands. The MSXα treatment[8] gave a similar result while the *ab initio* CI calculation[7] predicted these bands to be localised within the Cr–O unit. The DVXα results also suggest that the intense absorption at about 36 800 cm^{-1} arises from chlorine to chromium c.t. transitions. A range of calculated transition-state energies from 31 417 to 39 560 cm^{-1} are all of this type and presumably contribute to the overall absorption. Oxygen to chromium c.t. bands are predicted to lie above 45 000 cm^{-1}.

Conclusions

DVXα SCC calculations of the electronic absorption spectrum of $[CrOCl_4]^-$ are in near-quantitative agreement with the experimental band maxima. There is also substantial support for the latest assignment proposed by Collison[9] who has suggested a scheme closely parallel to that for the vanadyl analogue. The first two bands are predicted to be *d–d* transitions, in contrast to previous assignments based on *ab initio* CI[7] and MSXα[8] results, which suggested the higher-energy transition of the two to be charge transfer in origin. The third *d–d* band, observed at around 20 270 cm^{-1}, is calculated some 3 500 cm^{-1} above this value but the c.t. transitions are in excellent agreement with experiment. The DVXα SCC method appears to be superior to either *ab initio* CI or MSXα schemes for predicting accurately the spectroscopic properties of transition-metal systems.

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