

## Electronic Structure and Electronic Absorption Spectra of Molybdenum and Tungsten Oxotetrachlorides

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Electronic absorption spectra of the molecules  $\text{MoOCl}_4$  and  $\text{WOCl}_4$  have been measured and their electronic structure has been calculated on the basis of the SCF- $X\alpha$ -SW theory in the overlapping atomic sphere model. Ionisation potentials and allowed optical transition energies have been found in the transition state approximation. The interpretation of the electronic absorption spectra of gaseous  $\text{MoOCl}_4$  and  $\text{WOCl}_4$  is given.

**Key words:** Molybdenum and tungsten oxotetrachlorides – Electronic structure and absorption spectra – SCF- $X\alpha$ -SW calculations.

### 1. Introduction

At present there is little information on electronic spectra and electronic structure of gaseous oxohalides of transition metals. In particular, as far as oxohalides of the metals of VI Group are concerned, a systematic study and analysis of electronic absorption, emission and fluorescence spectra were carried out only for  $\text{CrO}_2\text{F}_2$  and  $\text{CrO}_2\text{Cl}_2$ .

Electronic absorption spectra of such compounds are diffuse; it is usually difficult to resolve them properly and analyze the vibrational structure; nor can any information be obtained on the transition type. Additional complications are associated with the superposition of band systems belonging to different transitions or band subsystems resulting from the transitions between different components of upper and lower multiplets. It is evident that one must use theoretical data on electronic structure for a reliable interpretation of experimental spectra. In the case of halides and oxohalides of transition metals, the most effective calculation procedure is the SCF scattered wave approach (SCF- $X\alpha$ -SW) which has been used, in particular, for calculations of the electronic structure and interpretation of electronic absorption spectra of a series of chromium and manganese oxohalides [1-4].

We have measured visible and ultraviolet electronic absorption spectra of molybdenum and tungsten oxotetrachlorides; the electronic structure of the molecules has been calculated by the SCF- $X\alpha$ -SW method and the results have been used for interpretation of the measured spectra.

## 2. Experimental

The molybdenum oxotetrachloride was kindly supplied by V. N. Zavadovskaya who is acknowledged. The tungsten oxotetrachloride was synthesized by us in an isolated ampoule according to reaction  $WO_3 + 2WCl_6 = 3WOCl_4$  and purified by vacuum sublimation. The studied substances were charged into a quartz cuvette in a dry box. The visible and near ultraviolet absorption spectra were measured using the spectrophotometer SF-20.

## 3. Calculation Procedure

Of late, the overlapping atomic sphere model [6] is often used in the SCF- $X\alpha$ -SW calculations [5]. This model is the simplest extension of the traditional "muffin-tin" approach for the  $X\alpha$ -SW method and provides an essential improvement in the calculations of ionisation potentials, optical transition energies, and other characteristics [7, 8].

This model has been used in the present work for calculating the  $MoOCl_4$  and  $WOCl_4$  electronic structure at the equilibrium  $r(Mo-O) = 1.670 \text{ \AA}$ ,  $r(Mo-Cl) = 2.278 \text{ \AA}$ ,  $\angle OMoCl = 103.0^\circ$ ,  $r(W-O) = 1.684 \text{ \AA}$ ,  $r(W-Cl) = 2.280 \text{ \AA}$  and  $\angle OWCl = 102.6^\circ$  [9]. The overlapping sphere parameters were determined using the nonempirical Norman method [10]. The ratios of atomic sphere radii were found under the initial overlapping of atomic electron densities for a given molecular geometry on the ground of the condition of atomic sphere electroneutrality (with the account of nucleus charge) [10].

The absolute sphere radii for  $MoOCl_4$  are found from the condition of that the virial theorem is satisfied as well as possible [10, 11]. Thus, at the overlapping degree  $OD = 15\%$  for the Mo and Cl spheres (with respect to the radii of tangent atomic spheres), the virial ratio T/E was 0.99999. Further we give the OD value only for metal and chlorine atoms. The radius of the O sphere was obtained using the ratio of radii found by the Norman method.

The parameters of overlapping spheres in  $WOCl_4$  were determined by a somewhat different method. Internuclear distances  $r(M-Cl)$  and angles  $\angle OMCl$  (M is a metal atom) are similar for both molecules, therefore the radius of the chlorine sphere in  $WOCl_4$  was assumed equal to that in  $MoOCl_4$  at  $OD = 15\%$ . The radii of W and O spheres were calculated taking into account the ratio of radii obtained by the Norman method. The corresponding OD value for W and Cl was 17.5%. Thus, at the same time, the possibility was examined for transferring the sphere parameters in molecules of the same symmetry and close geometry.

The outer sphere was tangent to chlorine spheres in all cases, its center being in the center of the square formed by the Cl atoms. Such a location of the outer sphere center in the case of MoOCl<sub>4</sub> and WOCl<sub>4</sub> corresponds to the condition of minimum volume of the intersphere region provided the outer and atomic spheres are not overlapping.

In the partial-wave expansion of the wave function, the spherical harmonics were taken into account with angular momenta  $l=0$  and 1 on the O and Cl atoms, with  $l=0, 1, 2, 3$  on the Mo and W atoms, and with  $l=0, 1, 2, 3, 4$  in the outer region of a molecule.

The exchange potential parameters  $\alpha$  for atomic spheres were taken equal to the atomic Hartree–Fock values [12]; in the outer and intersphere regions of a molecule they were determined as the average weighted values of the corresponding atomic parameters  $\alpha$ , where the number of valence electron of every atom in the molecule were the weights.

The core orbitals were not frozen during the self-consistent procedure, and they were adjusted to a new potential inside the atomic spheres at every iteration step.

#### 4. Electronic Structure of the MoOCl<sub>4</sub> and WOCl<sub>4</sub> Molecules

The energy spectrum of occupied molecular orbitals (MO) for the MoOCl<sub>4</sub> and WOCl<sub>4</sub> molecules is listed in Table 1, the MO numeration being done from the beginning of the valence MO. The ordering of occupied and free MO is practically identical for both molecules. The only exception is the inversion of 1b<sub>2</sub> and 4a<sub>1</sub> MO in MoOCl<sub>4</sub>, however the orbital energy values of these MO are close and differs less than by 0.2 eV. The eigenvalue spectrum for WOCl<sub>4</sub> is shifted by 0.2–0.3 eV towards smaller absolute values of orbital energy. Similar variations are observed also for free MO not listed in Table 1, the corresponding energy shift being 0.7–1.3 eV for lower orbitals and 0.05–0.3 eV for upper orbitals which are of the Rydberg type.

There is no unambiguous method of population analysis in the X $\alpha$ -SW procedure. While the charge fractions from specific symmetry orbitals are determined quite definitely inside each atomic sphere, the way of orbital charge distribution among atoms is rather arbitrary for the outer and intersphere molecular regions [13–15]. In the present paper, the charge fraction  $\bar{Q}$  on a molecular atom A was determined for an  $i^{\text{th}}$  MO as following:

$$\bar{Q}_i(\text{A}) = Q_i(\text{A}) + \frac{Q_i(\text{A})}{\sum_{\text{B}} Q_i(\text{B})} (Q_i^{\text{II}} + Q_i^{\text{III}}) \quad (1)$$

where  $Q_i(\text{A})$  is the charge of the  $i^{\text{th}}$  orbital in sphere A,  $Q_i^{\text{II}}$  and  $Q_i^{\text{III}}$  are the charges of the  $i^{\text{th}}$  orbital in the intersphere and outer regions of a molecule, the summation in Eq. (1) being carried out over all atomic spheres.

**Table 1.** Orbital energies and ionization potentials in MoOCl<sub>4</sub> and WOCl<sub>4</sub> (OD(Mo-Cl) = 15%, OD(W-Cl) = 17.5%)

MO <sup>a</sup>	MoOCl <sub>4</sub>		WOCl <sub>4</sub>	
	-E <sub>orb.</sub> (eV)	IP (eV)	-E <sub>orb.</sub> (eV)	IP (eV)
1a <sub>2</sub>	9.38	12.07	9.10	11.77
5e	9.92	12.57	9.69	12.33
3b <sub>1</sub>	9.97	12.63	9.71	12.34
4e	10.26	12.89	10.03	12.64
5a <sub>1</sub>	10.59	13.17	10.32	12.90
3e	10.96	13.57	10.77	13.39
1b <sub>2</sub>	12.03	14.65	11.81	14.43
4a <sub>1</sub>	11.84	14.49	11.87	14.54
2b <sub>1</sub>	13.16	15.92	13.11	15.91
2e	13.89	17.16	13.94	17.46
3a <sub>1</sub>	16.75	20.41	17.21	21.14
1e	22.18	24.93	21.93	24.68
1b <sub>1</sub>	22.32	25.09	22.17	24.94
2a <sub>1</sub>	22.60	25.34	22.41	25.15
1a <sub>1</sub>	28.87	32.74	29.64	33.75
Vacant orbital energies (-E)				
2b <sub>2</sub>	8.40		7.56	
6e	6.96		6.11	
4b <sub>1</sub>	4.73		3.49	
6a <sub>1</sub>	4.02		3.19	
7a <sub>1</sub>	1.81		1.58	
8a <sub>1</sub>	0.49		0.41	
7e	0.21		0.15	

<sup>a</sup> The MO numeration starts from the beginning of valence MO

It was shown in [15] that the atomic charges for each MO found from Eq. (1) are well agreed with the values determined by a LCAO MO method, in particular by the CNDO method.

The  $Q_i(A)$  can then be divided to fractions assigned to  $s$ -,  $p$ -,  $d$ -, etc. electrons if the fractions of  $s$ -,  $p$ -,  $d$ -electron charge, obtained for charge distribution in each atomic sphere, are used as weights. So calculated populations  $\tilde{Q}_s$ ,  $\tilde{Q}_p$ ,  $\tilde{Q}_d$ , and  $\tilde{Q}_f$  for all occupied and three lower vacant MO are given in Table 2. There is certainly some error in the population calculations because of arbitrary assignment of  $Q_i^{II}$  and  $Q_i^{III}$  to each of atoms according to Eq. ((1). However, if the  $Q_i^{II}$  and  $Q_i^{III}$  values are relatively small (it is just the case for MoOCl<sub>4</sub> and WOCl<sub>4</sub>), the errors associated with their redistribution will also be comparatively small. Most of the charge fraction in the intersphere region is located on the  $e$ -symmetry MO for the molecules studied. For these molecules, we examined different ways of assignment [13] of  $Q_i^{II}$  and  $Q_i^{III}$  to each of atoms and established that if the intersphere region contains less than 10–15% of full MO population, a way of  $Q_i^{II}$  and  $Q_i^{III}$  assignment to each of atoms is not essential.

**Table 2.** The MO populations (%) in MoOCl<sub>4</sub> and WOCl<sub>4</sub>

MO	MOCl <sub>4</sub>	M(Mo/W)				O		Cl	
		$\bar{Q}_s$	$\bar{Q}_p$	$\bar{Q}_d$	$\bar{Q}_f$	$\bar{Q}_s$	$\bar{Q}_p$	$\bar{Q}_s$	$\bar{Q}_p$
4b <sup>†</sup>	Mo	0	0	54.5	0.4	0	0	3.6	41.5
	W	0	0	50.2	0.5	0	0	15.7	33.6
6e <sup>x</sup>	Mo	0	0.2	63.0	0.8	0	17.1	0.3	18.6
	W	0	0.3	65.5	1.0	0	15.8	0.3	17.1
2b <sub>2</sub> <sup>x</sup>	Mo	0	0	68.8	0	0	0	0	31.2
	W	0	0	71.2	0	0	0	0	28.8
1a <sub>2</sub>	Mo	0	0	0	0	0	0	0	100.0
	W	0	0	0	0	0	0	0	100.0
5e	Mo	0	0.7	2.0	0.8	0	2.3	0.1	94.1
	W	0	0.7	1.4	1.1	0	1.6	0.1	95.1
3b <sub>1</sub>	Mo	0	0	0.1	0.4	0	0	0	99.5
	W	0	0	0	0.5	0	0	0	99.5
4e	Mo	0	0.5	0.3	0.8	0	4.6	0	93.8
	W	0	0.7	0.6	1.0	0	4.4	0	93.3
5a <sub>1</sub>	Mo	0	1.2	0.2	0	0	1.0	0	97.6
	W	0	1.6	0.2	0	0	0.9	0	97.3
3e	Mo	0	3.9	4.1	0.2	0	11.7	0.3	79.8
	W	0	5.0	4.3	0.2	0	10.6	0.4	79.5
4a <sub>1</sub>	Mo	9.5	0	3.9	0.8	0	3.8	1.4	80.6
	W	11.2	0	4.5	0.8	0	3.1	1.9	78.5
1b <sub>2</sub>	Mo	0	0	34.2	0	0	0	0	65.8
	W	0	0	31.4	0.2	0	0	0	68.4
2b <sub>1</sub>	Mo	0	0	42.1	0.1	0	0	2.2	55.6
	W	0	0	38.7	0.2	0	0	2.8	58.3
2e	Mo	0	0.2	32.3	1.1	0	59.7	0.2	6.5
	W	0	0.2	29.1	1.5	0	62.8	0.2	6.2
3a <sub>1</sub>	Mo	1.2	2.2	25.4	2.1	6.3	61.2	0.4	1.2
	W	1.5	2.4	21.9	2.5	8.1	62.2	0.4	1.0
1e	Mo	0	1.2	0.5	0.2	0	0	98.0	0.1
	W	0	1.5	0.6	0.4	0	0	97.4	0.1
1b <sub>1</sub>	Mo	0	0	4.1	0.1	0	0	95.5	0.3
	W	0	0	5.5	0.2	0	0	93.8	0.5
2a <sub>1</sub>	Mo	1.6	0.1	1.2	0.1	0	0	96.6	0.4
	W	2.1	0.2	1.5	0.1	0	0.1	95.4	0.6
1a <sub>1</sub>	Mo	2.6	8.0	11.1	3.0	72.2	3.1	0	0
	W	3.2	9.8	13.2	4.4	64.6	4.8	0	0

It is seen from Table 2 that all occupied MO in both molecules can be attributed to five groups. The lowest MO 1a<sub>1</sub> is formed mainly by the oxygen *s*-orbitals with some admixture of metal *p*- and *d*-functions. The second group is formed by MO 2a<sub>1</sub>, 1b<sub>1</sub>, and 1e, determined exclusively by the chlorine *s*(3*s*) orbitals. The third group contains orbitals 3a<sub>1</sub> and 2e which are linear combinations of oxygen *p*-functions and metal *d*-functions. The fourth group includes 2b<sub>1</sub>, 1b<sub>2</sub>, 4a<sub>1</sub>, and 3e MO formed by chlorine *p*-orbitals with a considerable admixture of metal *d*-orbitals (2b<sub>1</sub>, 1b<sub>2</sub>) and oxygen *p*-orbitals. At last, the fifth group is constituted from 5a<sub>1</sub>, 4e, 3b<sub>2</sub>, 5e, 1a<sub>2</sub> MO formed by

**Table 3.** Atomic effective charges in molecules MoOCl<sub>4</sub> and WOCl<sub>4</sub>

	MoOCl <sub>4</sub>			WOCl <sub>4</sub>		
	method 1	method 2	method 3	method 1	method 2	method 3
Q <sub>M</sub> <sup>x</sup>	+0.461	+1.218	+1.286	-0.100	+1.159	+1.222
Q <sub>O</sub> <sup>x</sup>	+0.011	-0.394	-0.326	+0.080	-0.359	-0.294
Q <sub>Cl</sub> <sup>x</sup>	-0.118	-0.206	-0.240	+0.005	-0.200	-0.232

chlorine orbitals mainly of the *p*-type. Most of occupied MO in both molecules are strongly localized. The populations of upper MO in both molecules differ by no more than 1–2%. For the lower MO, which are more delocalized, this difference is of 1–8%.

Three lowest vacant MO important for optical spectrum interpretation are formed mainly by the metal *d*-orbitals with the admixture of chlorine and oxygen *p*-functions.

The effective charge of atoms in molecules can be found in a similar way using formulae of the type (1) or other ones describing intersphere and outer charge [13] (Table 3). We have used the following approaches: 1 – the effective charge was calculated in accordance with Eq. (1), 2 – the full charges in the intersphere and outer molecular regions were attributed to all atoms, 3 – the full charges of intersphere and outer regions were attributed to atoms with weights equal to the number of valence electrons of the corresponding atoms.

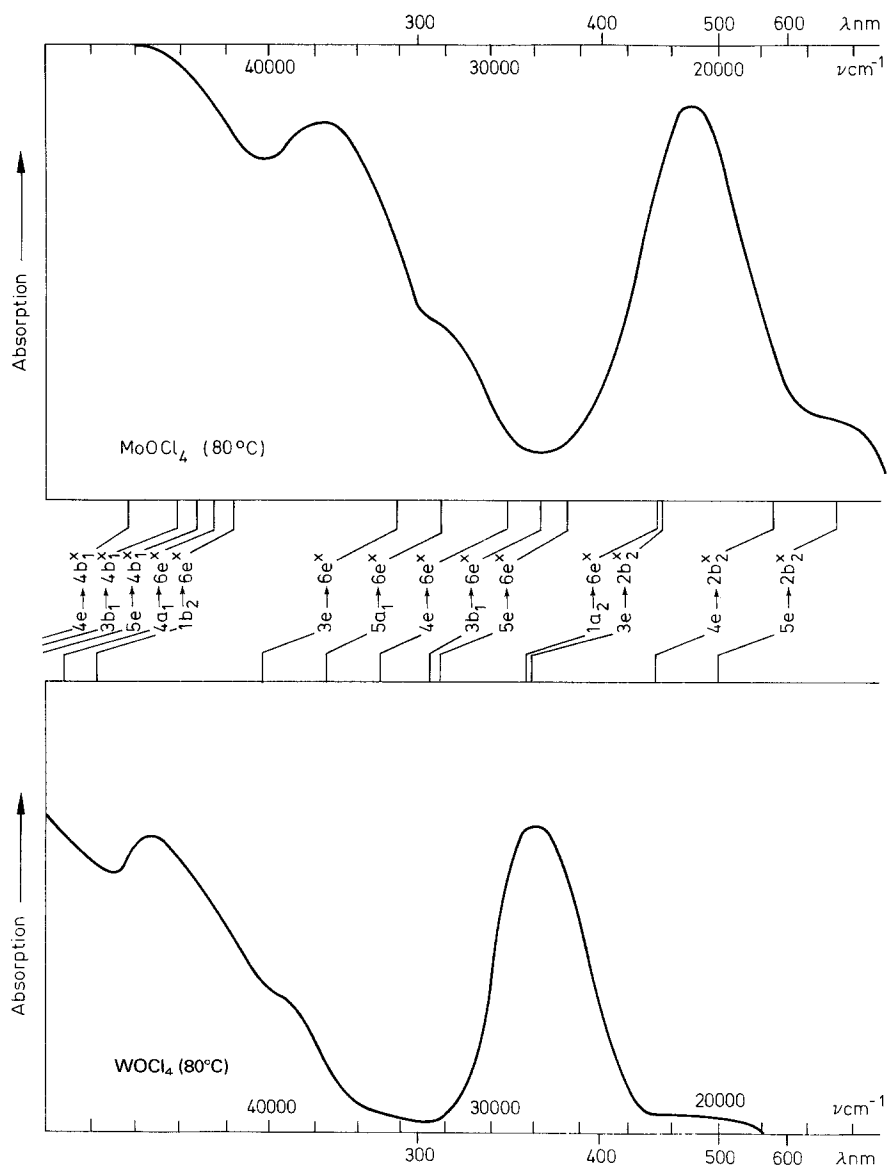
It is seen from Table 3 that the first approach results in a rather improbable charge distribution, especially in the case of WOCl<sub>4</sub>. The effective charges calculated by procedures 2 and 3 have similar values. Consider now the obtained results in more detail. The charges of Cl atoms do not change practically when going from MoOCl<sub>4</sub> to WOCl<sub>4</sub>; such behaviour could be expected due to similarity in geometry. The effective charges on metal and oxygen atoms in WOCl<sub>4</sub> are smaller a little than the corresponding charges in MoOCl<sub>4</sub> (by ≈ 0.04–0.06).

Besides, for both molecules the dipole moment was calculated using the technique proposed in [16]. The dipole moment values obtained are similar for MoOCl<sub>4</sub> and WOCl<sub>4</sub> and are of  $+1.5 \pm 0.4 D$  (the *z* axis is directed along the M–O bond). The value and sign of dipole moment indicate the “reality” of effective charge values calculated by the procedure 2 and 3.

## 5. Spectra, Optical Transition Energies and Ionization Potentials

The vapor spectra of molybdenum and tungsten oxotetrachlorides are shown in Fig. 1.

According to mass spectrometric data, both compounds vaporize as monomeric molecules without decomposition [17, 18]. Shchukarev [19–21] and Oppermann [22] indicate that molybdenum oxotetrachloride dissociates as



**Fig. 1.** Theoretical and experimental spectra of  $\text{MoOCl}_4$  and  $\text{WOCl}_4$ .

$2\text{MoOCl}_4 = 2\text{MoOCl}_3 + \text{Cl}_2$  [19, 20], and tungsten oxotetrachloride disproportionates in the unsaturated vapor above  $200^\circ\text{C}$  with formation of  $\text{WO}_2\text{Cl}_2$  and  $\text{WCl}_6$  [21, 22]. The disproportionation of tungsten oxotetrachloride is also supported by the IR absorption spectra of overheated vapors [23].

In the vapor  $\text{MoOCl}_4$  spectrum ( $80^\circ\text{C}$ ) the bands 270 nm, 310 nm (shoulder), 470 nm, and a broad shoulder in range 600–700 nm have been observed. The spectrum of gaseous chlorine has one absorption band in this range with

maximum at about 325 nm. The location and relative intensity of three other bands correlate with the spectrum of solution of  $\text{MoOCl}_4$  in  $\text{CCl}_4$  [24] (265, 480 and 695 nm).

At 80° C in the  $\text{WOCl}_4$  spectrum the bands 225 nm, 255 nm (shoulder), 360 nm, 480 nm (shoulder) have been observed. Takuma and Kavakubo [25] found 255, 325, 370 and 430 nm bands in the gaseous  $\text{WCl}_6$  spectrum (the latter three are overlapped by the intense absorption band of  $\text{WOCl}_4$ ).

Thus, from the bands observed in spectra, three bands can be reliably assigned to the  $\text{MoOCl}_4$  molecules (270, 470 and 650 nm) and three to the  $\text{WOCl}_4$  molecules (225, 360 and 480 nm). The 310 nm shoulder in the  $\text{MoOCl}_4$  spectrum and the 255 nm shoulder in the  $\text{WOCl}_4$  spectrum can be associated respectively with decomposition and disproportionation of the studied compounds and with formation respectively of chlorine and tungsten hexachloride.

Ionization and optical transition energies for  $\text{MoOCl}_4$  and  $\text{WOCl}_4$  molecules calculated in the transition-state approximation [26] are given in Tables 1 and 4. The ionization potential spectrum is shifted toward larger values with respect to the orbital energy spectrum. The relaxation shift is identical for both molecules and constitutes 2.6–3.0 eV in most cases. The shift is increased up to 3.5–4.0 eV for  $3a_1$  and  $1a_1$  MO's.

The energies of optical transitions indicated in Table 4 are symmetry allowed. The corresponding energy values are obtained by averaging over multiplet transitions.

The data given in Table 4 shows that, in the range of experimental absorption

**Table 4.** Allowed optical transition energies in  $\text{MoOCl}_4$  and  $\text{WOCl}_4$  (OD(Mo–Cl) = 15%, OD(W–Cl) = 17.5%)

transition	$\text{MoOCl}_4$		$\text{WOCl}_4$	
	$\Delta E(\text{eV})$	$\Delta E(\text{nm})$	$\Delta E(\text{eV})$	$\Delta E(\text{nm})$
$5e \rightarrow 2b_2^x$	1.80	688.4	2.48	500.1
$4e \rightarrow 2b_2^x$	2.16	575.3	2.82	439.3
$3e \rightarrow 2b_2^x$	2.78	445.3	3.48	356.0
$2e \rightarrow 2b_2^x$	6.27	197.9	7.43	166.8
$1a_2 \rightarrow 6e^x$	2.79	444.4	3.50	353.8
$5e \rightarrow 6e^x$	3.31	375.1	4.03	307.6
$3b_1 \rightarrow 6e^x$	3.46	358.6	4.08	303.9
$4e \rightarrow 6e^x$	3.64	341.0	4.35	284.9
$5a_1 \rightarrow 6e^x$	4.00	309.6	4.66	266.3
$3e \rightarrow 6e^x$	4.25	291.9	4.99	248.4
$1b_2 \rightarrow 6e^x$	5.15	240.8	5.93	209.0
$4a_1 \rightarrow 6e^x$	5.25	236.1	6.10	203.2
$2b_1 \rightarrow 6e^x$	6.31	196.6	7.15	173.3
$5e \rightarrow 4b_1^x$	5.35	231.7	6.43	192.7
$3b_1 \rightarrow 4b_1^x$	5.46	227.0	6.48	191.2
$4e \rightarrow 4b_1^x$	5.72	216.8	6.78	182.8



spectrum, transitions mainly correspond to the excitations from the upper occupied MO to the first three vacant MO ( $2b_2^x$ ,  $6e^x$  and  $4b_1^x$ ). The analysis of populations listed in Table 2 shows that all calculated optical excitation energies correspond to charge transfer transitions. The  $\text{MoOCl}_4$  and  $\text{WOCl}_4$  optical spectra should have similar structures, as it follows from calculations; however the  $\text{WOCl}_4$  absorption spectrum should be shifted toward the short-wave range with respect to the  $\text{MoOCl}_4$  spectrum.

Table 4 shows that the number of transitions in the range of 200–700 nm is greater than the number of the observed bands. The reason is probably that not all the symmetry allowed transitions are intense enough to be observable in the present experiment conditions. If one takes into account that the oxygen and chlorine orbitals overlap only slightly and neglects for a moment the facts that Mo (or W) lays out of the Cl atoms plane and that the O atom is present in the molecule the system gains a symmetry of the  $D_{4h}$  point group and additional selection rules characteristic for this symmetry. When the metal atom leaves the chlorine atoms plane and the O atom is introduced, the symmetry is reduced and the indicated selection rules get become invalid; however, at small perturbations they keep their sense as approximate rules.

Instead of using this qualitative approach one can directly estimate the matrix elements for the transition dipole moments. Both approaches show that among the transitions, listed in Table 4, those of remarkable intensity must be transitions from the upper occupied  $5e$  orbital to the vacant  $2b_2^x$ ,  $4b_1^x$  orbitals and from the  $3e$  orbital to the  $2b_2^x$  orbital (the respective E values are 688.4, 231.7, 445.3 nm for  $\text{MoOCl}_4$  and 500.1, 192.7, 356.0 nm for  $\text{WOCl}_4$ ). This is in agreement with the experimental values for band maxima (650, 270, 470 nm for  $\text{MoOCl}_4$  and 480, 225, 360 nm for  $\text{WOCl}_4$ ). The transition  $5e \rightarrow 4b_1^x$  must be the most intense one from the above indicated.

Thus, the performed calculations give spectra which are in general in good agreement with the experiment, and allow a sufficiently reliable band assignment.

The lowest of the calculated ionization potentials for  $\text{MoOCl}_4$  and  $\text{WOCl}_4$  – 12.07 and 11.77 eV ( $1a_2$  orbital) are close to the values of corresponding molecular ion appearance potentials in mass spectra  $-10.6 \pm 1.0$  and  $10.8 \pm 0.5$  eV [18].

In conclusion we would like to mention that we used the non-relativistic approach throughout of the calculations represented above. The relativistic approach applied by [27] to hexafluorides of  $5d$ -metals demonstrated that relativistic effects were mainly manifested in splitting those molecular orbitals the main constituents of which were metal  $d$ -orbitals. They also led to the total rising in energies of valence and core MO's. At the same time the important point was the absence of any qualitative changes in general features of chemical bonding for these compounds as well as in appearance of their optical and photoelectron spectra. The similar behaviour one has presumably to expect in a case of the Mo and W oxochlorides.

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