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Electronic Structure and One-Electron Properties of the MoO_2Cl_2 Molecule. Electronic Spectra of the MoO_2Cl_2, MoO_2Br_2 and WO_2Br_2 Molecules

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The SCF-X_α-SW method in an overlapping atomic spheres approximation has been used to calculate the electronic structure, ionization potentials, energies and oscillator strengths of the allowed optical transitions and also some of the one-electron properties of the MoO_2Cl_2 molecule. The electronic absorption spectra of vapours over molybdenum and tungsten dioxodibromides have been measured. Interpretation of the experimental electronic absorption spectra of the MoO_2Cl_2, MoO_2Br_2 and WO_2Br_2 molecules is discussed.

Key words: Molybdenum and tungsten dioxodihalides – Electronic structure and absorption spectra – SCF-X_α-SW calculations.

1. Introduction

Molybdenum and tungsten form two series of volatile oxohalides, viz., MOX_4 and MO_2X_2. The electronic structure and spectra of the $MoOCl_4$, $WOCl_4$ and $WOBr_4$ have been studied by us earlier [1, 2]. In the present work use is made of the SCF-X_α-SW approximation to calculate the energy spectrum, some of the one-electron properties and optical spectrum of the MoO_2Cl_2 molecule. The electronic spectra of molybdenum and tungsten dioxodibromides have also been measured and discussed in this paper.

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2. Calculation Procedure

The electronic structure of the MoO_2Cl_2 molecule (the C_{2v} symmetry) was calculated by the SCF-X_α-SW method in an overlapping atomic spheres approximation [3]. The ratios between the radii of the overlapping spheres were determined by the "nonempirical" Norman method [4]. As in the case of calculation of the $MOCl_4$ molecules [1], the overlapping degree (OD) of atomic spheres and, hence, the absolute values of their radii were determined from the condition of the best virial theorem fulfillment at the equilibrium geometry. The outer sphere was positioned in such a way that it was tangent to the atomic O and Cl spheres, the intersphere region volume being minimal.

The following geometric equilibrium parameters were employed for MoO_2Cl_2 [5]: $R(\text{Mo—Cl}) = 2.259$ Å, $R(\text{Mo—O}) = 1.698$ Å $\measuredangle \text{OMoO} = 104°$, $\measuredangle \text{ClMoCl} = 112°$ (the planes OMoO and ClMoCl are perpendicular to each other).

The virial ratio T/E where T = kinetic and E = total energy of the molecule, at the OD of the atomic Mo and Cl spheres equal to 18.5% (with respect to the radii of the tangent Mo and Cl spheres) was 1.00001. In what follows, in the text and tables, the OD values are connected with the overlapping of these Mo and Cl spheres, the absolute values of the radii for the O spheres being determined automatically, based on the Norman method [4]. In addition, we performed a series of calculations of the electronic structure at OD = 15%. In this case the virial ration T/E became somewhat worse, being enlarged to 1.00034. OD decreasing allowed to study the dependence of calculated values on the OD variation. On the other hand, as evidenced by calculations of the potential curves of diatomic molecules by the X_α-SW method, the OD decrease at a fixed molecule geometry corresponds to an increase of internuclear distances at a fixed OD. Within the frameworks of the X_α-SW method this enables one, to some extent, to study the dependence of the calculated values on small variations in the molecular geometry.

The partial-wave expansion of the wave functions and the exchange parameters α of the molecule space, as well as details of the calculations on the ground state wave functions, ionization potentials and optical transition energies of the MoO_2Cl_2 molecule were similar to those of the $MoOCl_4$ and $WOCl_4$ molecules [1].

The one-electron properties of MoO_2Cl_2 were calculated by an approximate method [6–8]. In analyzing the MO populations and calculating the effective atomic charges, use was made of the same method of assigning the charge of the intersphere and outer molecular regions to each of the atoms as in the case of calculations of one-electron properties [6–8].

The oscillator strengths for the one-electron transitions were obtained in a transition state approximation for the final and initial states of the one-electron optical transition by using the potential gradient as the operator of dipole transition [9].

3. Energy Spectrum, MO Populations and One-Electron Properties of the MoO_2Cl_2 Molecule

The calculated energy spectrum of the valence occupied and lower unoccupied MO's of the MoO_2Cl_2 molecule is shown in Table 1 where the MO numeration starts with the lowest valence MO. When the OD increases, the entire MO spectrum (except for the two valence MO's) shifts towards higher absolute values of orbital energies, while retaining the MO ordering, however, this increase does not exceed 0.3–0.4 eV for unoccupied MO's and 0.1–0.2 eV for occupied MO's, the differences of the MO energies changing insignificantly. Correlation of the MO spectra in MoO_2Cl_2 and CrO_2Cl_2 [10] indicates that the lower unoccupied and upper occupied MO's in the two molecules have practically the same ordering. The largest distinction consists in the low orbital energy values for the occupied MO's in CrO_2Cl_2 (by about 3–3.5 eV lower than those in MoO_2Cl_2), which can be partially explained by a tangent atomic spheres model applied to the calculation of CrO_2Cl_2 [10]. There also occurs a substantial increase in the energy differences between the upper occupied and lower unoccupied MO's. The first ionization potential (IP) of the MoO_2Cl_2 molecule, as might be expected, is close to those of molybdenum and tungsten oxotetrachlorides [1, 2] (the IP of the MO $4b_1$ in MoO_2Cl_2 is 0.2 eV lower than that of the MO $1a_2$ in $MoOCl_4$ [1], and the experimental value of the appearance potential for the $MoO_2Cl_2^+$ ion in the mass spectrum is 12.2 ± 0.5 eV [11]).

Table 1. Orbital energies and ionization potentials in MoO_2Cl_2

MO	$-E_{orb.}$ (eV) OD = 15%	$-E_{orb.}$ (eV) OD = 18.5%	IP (eV) OD = 18.5%
$8a_1^*$	2.85	2.52	
$5b_1^*$	3.93	3.51	
$7a_1^*$	4.90	4.50	
$3a_2^*$	4.97	4.56	
$4b_1$	9.04	8.80	11.87
$2a_2$	9.16	8.94	11.94
$4b_2$	9.20	8.97	11.99
$6a_1$	9.37	9.16	12.13
$3b_1$	9.64	9.57	13.50
$3b_2$	9.87	9.91	12.54
$5a_1$	10.17	10.12	13.19
$2b_1$	11.60	11.56	14.76
$1a_2$	11.58	11.56	14.91
$4a_1$	11.80	11.82	15.20
$3a_1$	13.32	13.62	17.32
$2b_2$	14.12	14.40	18.11
$1b_1$	21.04	20.82	24.15
$2a_1$	21.11	20.89	24.22
$1a_1$	25.74	26.08	29.92
$1b_2$	25.81	26.14	29.96

Table 2. The MO populations (%) in MoO_2Cl_2 (OD = 18.5%)

	Mo				O		Cl	
MO	Q_s	Q_p	Q_d	Q_f	Q_s	Q_p	Q_s	Q_p
$5b_1^*$	—	2.11	64.02	2.15	—	10.00	4.33	17.39
$7a_1^*$	0.52	3.20	71.63	0.15	0.05	16.16	0.13	8.16
$3a_2^*$	—	—	73.42	1.27	—	20.04	—	5.27
$4b_1$	—	0.07	0.09	0.90	—	2.37	—	96.57
$2a_2$	—	—	0.74	1.38	—	9.72	—	88.16
$4b_2$	—	1.01	0.06	0.63	—	3.03	—	95.26
$6a_1$	0.04	2.83	1.01	0.01	—	6.28	0.03	89.78
$3b_1$	—	5.65	4.13	0.40	—	33.86	0.17	55.79
$3b_2$	—	2.36	0.01	3.43	0.02	93.08	—	1.10
$5a_1$	7.06	0.26	8.24	1.46	0.04	3.90	0.59	78.45
$2b_1$	—	0.03	28.68	1.00	—	44.99	0.64	24.66
$1a_2$	--	—	26.86	1.51	—	66.89	—	4.74
$4a_1$	1.41	1.80	25.13	0.62	0.16	67.51	0.03	3.34
$3a_1$	3.16	1.55	21.55	2.97	3.25	66.23	0.11	1.18
$2b_2$	—	2.38	27.28	1.37	5.28	63.21	—	0.48
$1b_1$	—	1.16	2.16	0.15	—	0.06	96.37	0.11
$2a_1$	1.00	0.60	1.31	0.35	0.02	0.02	96.52	0.17
$1a_1$	4.97	5.33	5.46	3.57	78.49	2.08	0.06	0.03
$1b_2$	—	8.73	12.91	1.75	74.23	2.35	—	0.02

The atomic MO populations of the MoO_2Cl_2 molecule are listed in Table 2. The quantities Q_s, Q_p, Q_d and Q_f are charge fractions (in %) of each MO total population juxtaposed to the *s*-, *p*-, *d*-, *f*-electrons. As can be seen from Table 2, in MoO_2Cl_2, as well as in the molybdenum and tungsten oxotetrachlorides, the upper occupied MO's are mainly formed by the Cl *p*-orbitals, whereas the three lower unoccupied MO (essential to the interpretation of the optical absorption spectra) are formed by the Mo *d*-orbitals with an admixture of the O and Cl *p*-orbitals. However, the charge distribution in MoO_2Cl_2 and $MoOCl_4$ demonstrates some substantial differences consisting, primarily, in a strong mixing of the O and Cl orbitals in the upper occupied and lower unoccupied MO's of MoO_2Cl_2. Among the upper occupied MO's there occurs an orbital ($3b_2$) formed, largely, by the O *p*-orbitals. No MO with a similar composition was observed for $MoOCl_4$. Table 2 lists populations calculated at OD = 18.5%. Decreasing OD to 15% changes the populations by no more than 1–2%.

The effective atomic charges in MoO_2Cl_2, obtained by summation of the atomic populations, are given in Table 3. This Table also presents a number of calculated one-electron properties of this molecule. As shown by a comparison of the MoO_2Cl_2 effective atomic charges with those in molybdenum and tungsten oxotetrachlorides, calculated by various methods [1, 2], the MoO_2Cl_2 molecule exhibits increased negative charge of the O and Cl atoms and, thereby, a larger ionic character as compared with $MoOCl_4$, $WOCl_4$ and CrO_2Cl_2. Increasing the bond ionicity produces, on the one hand, a strong mixing of the O and Cl

Table 3. Atomic effective charges and one-electron properties in MoO_2Cl_2. μ is the total dipole moment, 1 a.u. = 2.54177 Debye units (D), θ_{xx}, θ_{yy}, θ_{zz} are the components of the quadrupole moment tensor, 1 a.u. = 1.345046 buckinghams (B), χ is the mean value of diamagnetic susceptibility in units of 10^{-6} erg/G^2 mole. All the values were calculated in the centre-of-mass coordinate system

	OD = 15%	OD = 18.5%
q_{Mo}	1.34	1.23
q_{O}	−0.31	−0.27
q_{Cl}	−0.36	−0.34
μ	−0.60	−0.71
$\theta_{xx}(B)$	5.36	5.24
$\theta_{yy}(B)$	−5.27	−5.29
$\theta_{zz}(B)$	−0.09	−0.06
χ	−698.63	−698.22

p-orbitals and, on the other hand, a larger difference between the orbital energies of the occupied and unoccupied MO's, which is reflected by a shift of the MoO_2Cl_2 absorption spectrum towards the higher energies as compared with the above molecules. It can be seen from Table 3 that the effective atomic charges and one-electron properties do not show a great dependence on the OD of the atomic spheres. Nevertheless one should note a change of the dipole moment sign in the MoO_2Cl_2 molecule with respect to that in the molybdenum and tungsten oxotetrachlorides [1, 2]. This change is primarily governed by an increased negative charge of the O atoms. The relationship obtained between the effective atomic charges evidently reflects a real charge distribution in the molecule. This fact results from the following simple consideration. If we use the experimental geometric parameters of the MoO_2Cl_2, $MoOCl_4$ and $WOCl_4$ molecules and calculate the dipole moments of the effective atomic charge systems [1, 2] in the corresponding molecules, then the change in values and sign of the dipole moments calculated for such a system of point charges seemingly would reflect a change in values and sign of the dipole moments obtained by more accurate calculations (Table 3 and Refs. [1, 2]).

4. The Electronic Absorption Spectrum of the MoO_2Cl_2 Molecule

Table 4 lists energies of the symmetry-allowed dipole transitions calculated in a transition state approximation at OD = 15 and 18.5%. These energies are multiplicity averaged. The energies of "multiplicity-pure" transitions can differ from the presented average values by a few decimals of eV. Table 4 also gives the absolute oscillator strengths for the corresponding electronic transitions calculated similarly in a transition state approximation [9].

It follows from Table 4 that in the region of the experimental absorption spectrum the observed transitions correspond to excitations from the upper occupied MO's

Table 4. Allowed optical transition energies (ΔE) and oscillator strengths (f) in MoO_2Cl_2

	OD = 18.5%		OD = 15%	
Transition	ΔE (eV)	f	ΔE (eV)	f
$4b_1-7a_1^*$	5.21	0.565	4.95	0.490
$4b_1-3a_2^*$	5.22	0.101	4.93	0.120
$2a_2-3a_2^*$	5.27	0.556	5.02	0.609
$4b_2-3a_2^*$	5.30	0.089	4.97	0.166
$4b_2-7a_1^*$	5.30	0.178	5.00	0.326
$6a_1-7a_1^*$	5.49	0.014	5.25	0.025
$3b_1-3a_2^*$	5.50	0.000	5.14	0.001
$3b_1-7a_1^*$	5.52	0.431	5.17	0.389
$4b_1-5b_1^*$	6.02	0.451	5.72	0.475
$2a_2-5b_1^*$	6.06	0.664	5.81	0.671
$3b_2-3a_2^*$	6.10	0.323	5.53	0.395
$3b_2-7a_1^*$	6.18	0.389	5.63	0.497
$5a_1-7a_1^*$	6.29	0.108	5.93	0.086
$6a_1-5b_1^*$	6.30	0.174	6.04	0.217

to the first three unoccupied MO's $3a_2^*$, $7a_1^*$ and $5b_1^*$. Analysis of the MO populations (Table 2) indicates that all the transitions presented in Table 4 are charge transfer ones. Among all the calculated properties characterizing the electronic structure of MoO_2Cl_2 the energies of the optical transitions show the greatest dependence on OD. The absolute oscillator strengths are equally sensitive to OD variations although a qualitative picture of the intensities of individual transitions remains valid.

Shown in Fig. 1 is a calculated absorption spectrum of the MoO_2Cl_2 molecule. The spectrum in this case is a superposition of the Gaussian curves 0.4 eV wide with a peak height of each of the normal distributions equal to an oscillator strength at the corresponding energy.

It can be seen even from Table 4 that the absorption spectrum consists of a large number of closely spaced overlapping bands, and two pairs of transition regions can be singled out, viz., 5.2–5.8 eV and 6.0–6.3 eV at OD = 18.5%, and 4.9–5.0 and 5.7–6.0 eV at OD = 15%. The theoretical absorption spectrum is shifted relative to the experimental one towards the short wavelength region by 0.2–0.5 eV depending on the parameters used for the overlapping spheres (Fig. 1). In the experimental absorption spectrum of MoO_2Cl_2 [12] one can observe two bands with maxima at 4.8 and 5.4 eV. The theoretical spectrum also represents two bands with maxima at 5.3 and 6.1 eV (OD = 18.5%) or 5.3 and 5.7 eV (OD = 15%). On changing OD the ratio between the peak intensities changes too, which is attributed to a larger contribution of the transitions $4b_2-3a_2^*$ and $4b_2-7a_1^*$ to the intensity of the first band with decreasing OD. The maxima of the bands are spaced by 0.8 eV (OD = 18.5%) and 0.7 eV (OD = 15%), which is close to the experimental value of 0.6 eV.

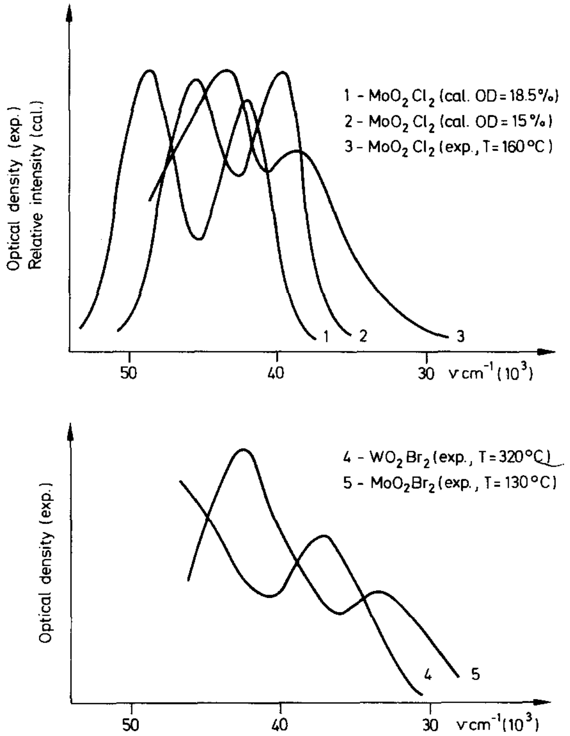

Fig. 1. Theoretical and experimental spectra of MoO_2Cl_2, MoO_2Br_2 and WO_2Br_2 molecules

5. The Electronic Absorption Spectra of MoO_2Br_2 and WO_2Br_2

Results of numerous mass spectrometric, tensimetric and spectral studies indicate that evaporation of molybdenum dioxodichloride and dioxodibromide occurs in the form of monomeric molecules [11, 13–16]. According to the mass spectrometric data, tungsten dioxodibromide also evaporates in such a form [17–19], although tensimetric results [20, 21] suggest that at temperatures over 300–320°C other processes are possible, first of all disproportionation by the following scheme:

$$2WO_2Br_2(sol) \rightleftarrows WO_3(sol) + WOBr_4(gas) \qquad (1)$$

Molybdenum and tungsten dioxodibromides were synthesized by us with the aid of the reaction:

$$MO_2 + Br_2 = MO_2Br_2 \qquad (2)$$

Spectra in the visible and UV regions were measured with an SF-20 spectrophotometer.

The electronic spectrum of vapours over molybdenum dioxodibromide consists of two bands with maxima at 235 and 300 nm, belonging to the MoO_2Br_2 molecule. In the visible region of the spectrum no absorption bands were observed. The spectrum of vapours over tungsten dioxodibromide at 300–330°C consists of only only one band at 265 nm assigned to the WO_2Br_2 molecule. At temperatures over 350°C the band intensity increased, its maximum shifted to the red side and in the visible spectral region there appeared bands at 465, 550 and 700 nm belonging to the $WOBr_4$ molecule [2]. After lowering the temperature to 300–330°C, the original shape of the spectrum was reestablished, which points to reversible nature of the process (1). A shift of the absorption maximum in the UV region is due to the superposition of the bands of WO_2Br_2 (at 265 nm) and $WOBr_4$ (at 285 nm).

A similarity between the spectra of MoO_2Cl_2 and MoO_2Br_2 together with a change in the spectral positions of the bands when passing from MoO_2Cl_2 to MoO_2Br_2 and WO_2Br_2 allows certain assumptions on the electronic structure and types of electronic transitions of molybdenum and tungsten dioxodibromides. It can be assumed that for MoO_2Br_2 and WO_2Br_2 as in the case of the $MoOCl_4$, $WOCl_4$ and MoO_2Cl_2 molecules in which spectra one can observe transitions from the upper occupied MO's formed, primarily, by the chlorine *p*-AO, to the first unoccupied MO's with a preponderating contribution of the metal *d*-AO, we also observe transitions associated with the charge transfer. If the structure of the above mentioned MO's is such as this, then, on passing from MoO_2Cl_2 to MoO_2Br_2, one can expect the spectrum being shifted to the red side, and conversely, on passing from MoO_2Br_2 to WO_2Br_2 – to the blue side. Such a change in the band maximum positions is observed experimentally (Fig. 1). The energies of the 4*p*- and 3*p*-orbitals in the neutral Br and Cl atoms differ by about 1.35 eV, and in the Br^- and Cl^- ions – by about 0.3 eV [22]. It was noted above that in MoO_2Cl_2 the effective negative charges on the O and Cl atoms are larger than those in oxotetrachlorides. This is likely to lead to the smaller band shift for the MO_2X_2 molecules than for oxotetrahalides MOX_4 when the chlorine atom is replaced by the bromine atom. Such a trend is actually observed in the measured spectra: if, on passing from $WOCl_4$ to $WOBr_4$, the maximum of the most intensive band in the visible region shifts to the red side by about 1 eV [2], then in passing from MoO_2Cl_2 to MoO_2Br_2 the shift gets smaller: 0.2–0.7 eV. As shown in Ref. [1], the MO energy spectrum of the $WOCl_4$ is shifted towards the smaller absolute values, as compared with that for $MoOCl_4$, by 0.2–0.3 eV, and for the unoccupied MO's – by 0.7–1.3 eV. This explains the total shift of the observed optical $WOCl_4$ spectrum with respect to the $MoOCl_4$ spectrum to the region of higher frequencies by 0.8–0.9 eV. A similar picture is also observed in the case of molybdenum and tungsten dioxodibromides, where the first, low-frequency band, shifts by about 0.5 eV (4.2 eV for MoO_2Br_2 and 4.7 eV for WO_2Br_2). The same order of change is valid for the appearance potentials of the corresponding molecular ions in the mass spectra: 12.2 eV for MoO_2Cl_2, 10.9 eV for MoO_2Br_2 and 11.4 eV for WO_2Br_2 [11].

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