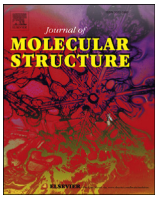
Journal of Molecular Structure xxx (2016) 1–15

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: http://www.elsevier.com/locate/molstruc



Geometrical and electronic structure of the molybdenum and tungsten halides MX_3 and MX_4 ($M = Mo, W; X = F, Cl$): Jahn-Teller effect and spin-orbit coupling[☆]

Valery V. Sliznev[*], Natalya V. Belova

Ivanovo State University of Chemistry and Technology, Research Institute for Thermodynamics and Kinetics of Chemical Processes, 153460 Ivanovo, Russia

ARTICLE INFO

Article history:
Received 22 June 2016
Received in revised form
5 August 2016
Accepted 8 August 2016
Available online xxx

Keywords:
Halide complexes
Ab initio calculation
Electronic states
Geometrical structure
Jahn-Teller effect
Spin-orbit coupling

ABSTRACT

The ground and lower-lying excited electronic states of MX_3 and MX_4 ($M = Mo, W; X = F, Cl$) molecules were systematically studied by the complete active space self-consistent field (CASSCF) and multi-configurational quasi-degenerate second-order perturbation (XMCQDPT2) methods. Scalar-relativistic effects and spin-orbit coupling were taken into account employing the third-order Douglas-Kroll-Hess (DKH) Hamiltonian and full Breit-Pauli operator. The ground orbital state of MoF_3 and $MoCl_3$ complexes is quadruplet $^4A_2'$ state in the equilibrium configuration with D_{3h} symmetry. If the spin-orbit interaction is taken into account the calculations result in two $^4E_{1/2}$ and $^4E_{3/2}$ spin-orbit states with 11–14 cm^{-1} energy differences instead of one $^4A_2'$ state. Spin-orbit interaction quenches the Jahn-Teller effect in $^2E''$ ground orbital state of WF_3 complex in D_{3h} configuration, and C_{2v} configuration with ($^4E_{1/2} + {}^4E_{3/2}$) spin-mixed state corresponds to the minimum on the PES. The WCl_3 complex reveals strong interaction of the spin-orbit states of different multiplicity. For WCl_3 complex the configuration with D_{3h} symmetry corresponds to the minimum on the PES for four lowest spin-mixed electronic states. The MoF_4, $MoCl_4$ and WCl_4 complexes possess the tetrahedral equilibrium configuration with $^3A_2$ orbital electronic state. If the spin-orbit interaction is taken into account the ground state changes to the threefold degenerated $^3T_2$ spin-orbit state with weak Jahn-Teller effect. In the case of WF_4 complex the strong Jahn-Teller effect has been discovered in the first excited ^1E singlet electronic state of the tetrahedral structure, and D_{2d} configuration with $^1A_1$ electronic state possesses the lowest energy. The comparison with available experimental data has been performed. The tendencies in molecular parameters of complexes studied were analyzed.

1. Introduction

The molybdenum and tungsten halides MX_3 and MX_4 ($M = Mo, W; X = F, Cl$) have attracted considerable interest because of their important role as the precursors and catalysts in many chemical reactions. Some of these compounds are currently used as transients in the halide method of refinement. The molybdenum and tungsten are widely used as the construction materials for different engines, which operate at high temperature and in the aggressive halogen containing medium. Consequently there has been interest in the molecular structure of the molybdenum and tungsten halides for engineering processes understanding and technologic forecasting a constructional material behavior in corresponding conditions. On the other hand, special attention has been paid to a molecular and electronic structure of the molybdenum and tungsten halides. The close energies of the electronic states with different multiplicities, the combination of strong spin-orbit coupling and Jahn-Teller effect are to be expected for these complexes. As a result, the high-symmetry structure can be distorted in an unpredictable way.

According to mass spectrometric study [1–3] the molybdenum and tungsten halides exist in the gas phase as monomeric molecules MX_n ($n = 1–6$) and their polymers. The molecular structure of free molecules of several molybdenum and tungsten halides (WCl_3[4], MoF_4[5], $MoCl_4$[6], $MoBr_4$[6,7], WCl_4[8]) has been studied by gas-phase electron diffraction (GED). The authors of [4] conclude that WCl_3 possesses T-like structure of C_{2v} symmetry. The

---

[☆] Dedicated to Prof. Georgiy V. Girichev on the Occasion of his 70th birthday.

[*] Corresponding author.

E-mail address: sliznev@mail.ru (V.V. Sliznev).

http://dx.doi.org/10.1016/j.molstruc.2016.08.017

Please cite this article in press as: V.V. Sliznev, N.V. Belova, Geometrical and electronic structure of the molybdenum and tungsten halides MX_3 and MX_4 ($M = Mo, W; X = F, Cl$): Jahn-Teller effect and spin-orbit coupling, Journal of Molecular Structure (2016), http://dx.doi.org/10.1016/j.molstruc.2016.08.017

tetrafluoride and tetrachloride of molybdenum were found to be tetrahedral [5,6], whereas equilibrium structure of WCl_4 corresponds to C_{2v} symmetry [8]. Two different GED studies of molybdenum tetrabromide have been reported with rather conflicting conclusions about the structure of $MoBr_4$: either with tetrahedral T_d[6] or C_{2v}[8] symmetry. Vibrational IR spectra were recorded for the products of MoF_6 photolysis in argon matrix [9], and for the species obtained by transmission of F_2 gas-phase over the molybdenum and tungsten heated at 100–1100 °C and isolated in argon matrix [10]. According to the spectral data in case of molybdenum the gas phase consists of MoF_n ($n = 3,4,5,6$) [9,10] molecules, trimers $(MoF_5)_3$[10] and $MoOF_4$[10]. In case of tungsten only WF_6 and WOF_4 are present in the gas phase [10]. The bands observed in IR spectra were assigned in terms of tetrahedral T_d configuration for MoF_4[9,10] and symmetric D_{3h} configuration for MoF_3[10].

The first quantum chemical (QC) studies (ROHF, MP2, CASSCF + SOCI) of MoF_3, WF_3, MoF_4 and WF_4 were performed in 2000 [11,12]. One year later the results of DFT/B3LYP study of WF_3[13], WCl_3[14], WF_4[13], WCl_4[14] were published. According to QC data [11,13,14] high-spin electronic state $^4A_2'$ with D_{3h} geometric configuration is the ground state of MoF_3, WF_3 and WCl_3 complexes. The first excited electronic state for these molecules was predicted to be Jahn-Teller $^2E''$ term [11,13,14]. The ground and first excited electronic states of WF_4 were found to be $^1A_1$ (D_{2d}) and $^3A_2$ (T_d), respectively [12,13]. On the contrary, in case of MoF_4 and WCl_4 triplet $^3A_2$ with tetrahedral T_d configuration corresponds to the ground state, whereas singlet $^1A_1$ (D_{2d}) is the first excited state [12,14].

Thus, the available up to date information about geometrical and electronic structure of the molybdenum and tungsten halides is poor and imperfect. The effects of spin-orbit coupling (SOC) have not been studied yet. The aim of the present work is a systematic study of the geometrical and electronic structure of MX_3 and MX_4 molecules ($M = Mo, W$; $X = F, Cl$) in ground and low-lying excited electronic states by quantum-chemical methods. The influence of spin-orbit coupling (SOC) on the molecular parameters will be analyzed.

2. Preliminary consideration

According to the authors of [11,12] the molybdenum and tungsten tri- and tetrahalides are the complexes of strong ligand field, and the low-spin states are stabilized. Furthermore, in this case the low-spin and high-spin states can possess close energies. The ground and lower-lying excited electronic states of MX_3 and MX_4 molecules, which can be considered as ionic systems $[M^{n+}][X^-]_n$, arise from the states of free cations with open valence *d*-shells, d^3 and d^2 for M^{3+} and M^{4+}, respectively. Table 1 contains electronic states of M^{3+} and M^{4+} cations along with the corresponding states of MX_3 and MX_4 complexes. The correlations of the orbital and spin-orbit electronic states are shown in Table 2. Possible electronic states for cations and complexes (Tables 1 and 2) have been determined using group theory and the character tables [15].

3. Calculation details

All calculations were performed using the complete active space (CASSCF) method by GAMESS US program set [16]. The active space included all d-electrons of M^{3+} or M^{4+} cation (see Table 1) on five molecular orbitals consisting mainly of valence d-metal atom orbitals. A dynamic correlation was taken into account at the level of XMCQDPT2 multiconfiguration quasi-degenerate second-order perturbation theory [17]. The doubly occupied orbitals corresponding to 1s- orbitals of F, Cl, Mo, W; 2s- and 2p- orbitals of Cl, Mo, W; and 3s-, 3p- and 3d-orbitals of Mo, W were frozen in XMCQDPT2 calculations. Scalar-relativistic effects were taken into account employing the third-order Douglas-Kroll-Hess (DKH) Hamiltonian [18,19]. The largest relativistic effects can be expected for the electronic shells of d-metal atoms. Therefore, these effects were considered only for Mo and W. Spin-orbit coupling (SOC) was taken into account using wave function from XMCQDPT2 calculations (SO-XMCQDPT2). The contribution of SOC to the Hamiltonian was described by full Breit-Pauli operator [20,21]. The problem of small-energy denominators that may appear in a perturbative expansion was solved by the intruder state avoidance (ISA) method [22]. The optimal value of *b* parameter defining the energy-denominator shifts was chosen to be 0.02 and 0.1 [22] for XMCQDPT2 and SO-XMCQDPT2 calculations, respectively. All CASSCF and XMCQDPT2 calculations have been carried out using state-average wave functions. For each multiplicity the averaging was performed over all electronic states (see Table 1) with equal weight coefficients. SPKrATZP basis sets [23–28] were used for molecular properties calculations. The geometry optimization, the calculations of force constants and harmonic vibrational frequencies were performed by the method of numerical differentiation of energies in the symmetry coordinates using ANOCOR program [29]. The vibrational symmetry coordinates of MX_3 and MX_4 molecules with different configurations (Fig. 1) are listed in Table S1.

The energy levels of free cations M^{3+} were calculated and compared with available experimental data [30] (see Table 3). The calculations with SOC taken into account were performed both for every multiplicity separately (spin-orbit state) and with consideration of interaction of spin-orbit states with different multiplicity (spin-mixed states). For Mo^{3+} cation the states with different multiplicity take part only in wave functions of four electronic states (see Table 3). In these cases the differences between calculated energies of spin-orbit and spin-mixed states are not greater than 740 cm^{-1}. For W^{3+} cation practically all states possesses spin-mixed wave functions. Furthermore, the differences in calculated energies of W^{3+} for spin-orbit and spin-mixed states reach several thousand cm^{-1} (Table 3). The average deviations of the calculated

Table 1
Electronic states of free M^{3+} and M^{4+}cations, degree of degeneracy (n) and orbital electronic states of MX_3 and MX_4 molecules.

M^{3+} (d^3)		MX_3	M^{4+} (d^2)		MX_4	
Term	n	D_{3h} structure	Term	n	T_d structure	D_{4h} structure
^4F	7	$^4A_2' + {}^4E' + {}^4A_1'' + {}^4A_2'' + {}^4E''$	^3F	7	$^3A_2 + {}^3T_1 + {}^3T_2$	$^3A_{2g} + {}^3B_{1g} + {}^3B_{2g} + 2^3E_g$
^4P	3	$^4A_2' + {}^4E''$				
^2P	3	$^2A_2' + {}^2E''$	^3P	3	$^3T_1$	$^3A_{2g} + {}^3E_g$
^2D	5	$^2A_1' + {}^2E' + {}^2E''$	^1S	1	$^1A_1$	$^1A_{1g}$
^2D	5	$^2A_1' + {}^2E' + {}^2E''$	^1D	5	$^1E + {}^1T_2$	$^1A_{1g} + {}^1B_{1g} + {}^1B_{2g} + {}^1E_g$
^2F	7	$^2A_2' + {}^2E' + {}^2A_1'' + {}^2A_2'' + {}^2E''$				
^2G	9	$^2A_1' + 2^2E' + {}^2A_1'' + {}^2A_2'' + {}^2E''$	^1G	9	$^1A_1 + {}^1E + {}^1T_1 + {}^1T_2$	$2^1A_{1g} + {}^1A_{2g} + {}^1B_{1g} + {}^1B_{2g} + 2^1E_g$
^2H	11	$^2A_2' + 2^2E' + {}^2A_1'' + {}^2A_2'' + 2^2E''$				

Please cite this article in press as: V.V. Sliznev, N.V. Belova, Geometrical and electronic structure of the molybdenum and tungsten halides MX_3 and MX_4 ($M = Mo, W$; $X = F, Cl$): Jahn-Teller effect and spin-orbit coupling, Journal of Molecular Structure (2016), http://dx.doi.org/10.1016/j.molstruc.2016.08.017