Molybdenum(VI) Dioxodihalides: Agreement with Experiment and Prediction of Unknown Properties Through Density Functional Theory

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ABSTRACT

Density functional calculations are reported for the molecular structures, harmonic vibrational frequencies, UV/visible spectra, and oxo-transferability of MoO_2X_2 (X = F, Cl, Br, I). Available experimental data have been used to check the validity of the theoretical calculations. Given the good agreement between theory and gas-phase experiment, predictions have been issued for the less studied members of this family of compounds. Furthermore, electronic spectra of the full series have been computed for the first time. For all transitions studied, excitation energies decrease in the order F > Cl > Br > I. Finally, the labilization of Mo—O bonds generated by the HOMO—LUMO transition, which is related to the oxygen-atom transfer reaction in the active site of molybdenum oxidoreductases, was also investigated. For MoO_2Cl_2 and MoO_2Br_2 compounds, the HOMO−LUMO transition yields a considerable lengthening of the Mo—O bond, yet not requiring a large excitation energy.   © 1997 John Wiley & Sons, Inc.

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Introduction

At present, there is considerable interest on d^0 dioxodihalides of transition metals because of their importance in vapor transport of Mo and W as volatile metal oxyhalides in high-performance halogen lamps [1, 2]. In addition, these MO_2X_2 molybdyl compounds form a class of versatile oxidizing agents able to deliver oxygen atoms to most types of oxidizable organic groups. More specifically, oxyhalides of molybdenum are involved in catalytic olefin metathesis. Oxidation of alkanes, alcohols, and alkenes by dioxodichloride of Mo(VI) or Cr(VI) leads to a novel reactivity where pathways include metallocycle intermediates. From a theoretical point of view, an elegant study of some of the mechanistic aspects of these oxidation reactions was reported by Rappé and Goddard [3] some time ago.

Experimentally, three dioxodihalides of molybdenum are known, namely, MoO_2F_2, MoO_2Cl_2, and MoO_2Br_2. On the contrary, MoO_2I_2 has not been synthesized yet, although there was an attempt to prepare it by passing iodine vapor over hot MoO_2 [4], no reaction being observed up to 600°C. While MoO_2Cl_2 has attracted the most interest, the other molecules have received much less attention, experimental data being available only for the most stable species (X = Cl, Br). Electron diffraction measurements of MoO_2Cl_2 [5] and mass spectral studies of MoO_2Br_2 [6] showed them to be monomeric distorted tetrahedral (C_{2v}) molecules in the gas phase. Since Barraclough and Stals [6] obtained the infrared and mass spectra of MoO_2Cl_2 and MoO_2Br in the gas phase for the first time in 1965, there have been several experimental studies of this family of compounds [4–7]. Reinvestigations were necessary to check the results of earlier works in which significant differences were reported [7]. Even when the unstability of products was not a drawback, reaching an accurate resolution became not always easy. In some cases, compounds decomposed at temperatures that were too low to allow enough vapor pressure for spectral measurements. As a whole, the literature provides more than one example [8] illustrating that uncertainties found in experimental characterizations were often due to the techniques employed, which carried about difficult interpretations of data.

Computational quantum chemistry is now an established part of the chemist's armory. It can be used as an analytical tool in the same sense that an NMR spectrometer or X-ray diffractometer can be used to resolve the structure of a compound [9]. Depending on the problem under study, different methods (semiempirical, DFT, ab initio) can be considered. Not only does quantum chemistry complement experimental data when required [10], but it is useful even before the experiment. Thus, one of its most interesting appeals is as a predictive tool [11]. The continuous search for improvements in the methodology of calculation has led up to a stage where at least semiquantitative structural and spectroscopic theoretical predictions can be made to assist the synthesis and characterization of new compounds [12].

Until the last decade, the former paragraph was applicable to organic molecules [13]. However, inorganic systems require more accurate calculations to describe the large variety of chemical bonds and hybridization schemes found across the periodic table. Moreover, inorganic compounds having the largest real interest are those involving transition metals. Unfortunately, they also offer the biggest challenge to conventional ab initio methods [14]: Accounting for electron correlation effects often implies high time-consuming procedures [15–22].

Besides the mechanistic study of [3], only a recent article by Deeth [23] analyzed optimized geometries and vibrational frequencies for MoO_2F_2 and MoO_2Cl_2, using density functional theory (DFT). However, theoretical calculations on the other two members of the family are still lacking. Furthermore, no theoretical studies on the electronic spectra of these compounds have been made yet. Thus, the main purpose of this article was to assess the geometrical, vibrational, and electronic properties of the family of species MoO_2X_2. In particular, calculations for X = Br, I and for UV/visible spectra of all members will be reported and compared with experiment when possible. The quality of predictions issued will also be assessed. As an interesting outset of the structural calculations, we also investigate the effect of halide substitution on the activation of the oxo-metal bond, in relation to the oxygen-transfer reaction which is an important process occurring in the active site of the molybdenum enzymes involved in the metabolism of small molecules and in the respiratory chain [24].

Methodological aspects about optimum theoretical conditions were discussed in a previous work [14], where we performed a systematic study on CrO_2F_2 using both conventional ab initio and density functional methodologies. Several basis sets were tested at Hartree–Fock (HF) and post-HF levels, and different functionals, auxiliary basis sets, and numerical integration schemes through various DFT-program systems were compared. That study showed that, to obtain a correct description, at least an 11-active-orbital CASSCF (Complete Active Space SCF) calculation was required. Metal–ligand distances were predicted by second-order Møller–Plesset theory (MP2) to be too long, whereas HF systematically underestimated bond lengths by 0.1 Å. On the contrary, nonlocal density functional theory revealed itself as an appropriate, cost-effective procedure to carry out the theoretical study of this kind of transition metal dioxodihalides. In view of these conclusions, the present work has been performed using DFT; a theoretical study at the CASSCF level of calculation would render the present study prohibitive. It is worth noting that the series studied in [14] (M = Cr) and in this article (M = Mo) belong to a group of very few compounds where HF systematically gives metal–ligand bonds shorter than experimentally observed, when the general trend is to overestimate them by 0.05–0.2 Å [25].

Computational Details

All calculations reported in this article were carried out by using the DFT-based package ADF (Version 1.1.3), developed by Baerends and co-workers [26]. The numerical integration scheme employed was that of te Velde and Baerends [27]. A triple-ζ STO basis set was used for the $4s$, $4p$, $4d$, $5s$, and $5p$ orbitals of molybdenum. For fluorine $(2s, 2p)$, chlorine $(3s, 3p)$, bromine $(3d, 4s, 4p)$, and oxygen $(2s, 2p)$, double-ζ basis sets augmented by an extra polarization function were employed. A similar basis set for iodine was not available, so a triple-ζ STO basis extended with a polarization function was used instead for this halogen. It is unlikely that the choice of a better basis set for iodine could affect the validity of results along the series under study. Electrons in lower shells were treated within the frozen core approximation. A set of auxiliary s, p, d, f, and g STO functions, centered on all nuclei, was introduced for the sake of fitting the one-electron molecular density and Coulomb potential accurately in each SCF cycle. All calculations were performed including gradient corrections to the local density approximation part of the density functional: Becke's nonlocal correction for exchange [28] and Perdew's nonlocal correction for correlation [29].

Singlet excitation energies for electronic spectra were evaluated according to a procedure developed by Ziegler et al. [25, 30] through Slater's sum rules. The particular form for the exchange energy (E_x) has a number of features which makes it difficult to evaluate space and spin multiplets in an unambiguous way within approximate DFT. It can be resolved by realizing that E_x only is applicable to a single-determinant wave function and that, therefore, exchange energies for multiplets represented by linear combinations of determinants must be evaluated indirectly by Slater's sum rules. A detailed discussion of such a procedure has been given elsewhere [30]. It is important to note that, from a theoretical point of view, it is hard to predict electronic spectra, errors of 0.5–1.0 eV being not unusual using the aforementioned procedure. However, it has been found [14] that in the CrO_2F_2 species results obtained by means of this methodology are much more comparable to experiment than are those obtained from HF, MP2, or the singly and doubly excited configuration interaction method (CISD).

Geometry optimizations were carried out with the method of Versluis and Ziegler [31] implemented in the ADF program, which do not contain derivatives with respect to the relativistic terms. Relativistic effects have shown to play an important role in the structural chemistry and energetics of molecules containing heavy atoms such as tungsten and $5d$ homologs [32–34]. However, the influence of relativity is less clear in the case of Mo. For instance, it was shown that in $M(CO)_6$ compounds (M = Cr, Mo, W) with W—CO bond relativistic corrections afforded a final value which was in better agreement with experiment, whereas the M—CO distance for Cr and Mo remained unaffected after relativistic effects had been included. Regarding first bond dissociation energies, a better fit was obtained by adding relativistic effects, particularly for M = W. In the present work, first-order relativistic corrections were included only for single-point calculations of the HOMO–LUMO transitions through the Pauli formalism [35–37].

Results and Discussion

This section is divided as follows: First, molecular structures and vibrational frequencies are computed for the best-known species to check the validity of calculations; second, attention is focused on the prediction of structures and infrared spectra for the less studied or unknown molecules; third, the UV-visible spectra of all considered MoO_2X_2 compounds are carefully examined and compared; and, finally, the influence of the ligand electronegativity on the oxo-transfer process caused by the HOMO–LUMO transition is discussed.

GEOMETRICAL PARAMETERS AND INFRARED SPECTRA: CALCULATED VS. OBSERVED VALUES

These complexes are formally d^0 or Mo(VI), so π-donor ligands such as X^- and O^{2-} having electrons in $p\pi$ orbitals can interact with appropriate empty $d\pi$ orbitals of the metal atom. Therefore, the bonding between Mo and ligand atoms can be described as a $d\pi$–$p\pi$ interaction [38].

Four independent geometrical parameters, $r(Mo{=}O)$, $r(Mo{-}X)$, $\angle OMoO$, and $\angle XMoX$, were chosen to define geometries consistent with the assumed C_{2v} molecular symmetry [5, 6]. In this section, we are centered on $X = Cl, Br$ for which calculated metal–ligand bond distances (Table I) are slightly longer than are the correspond-

ing experimental values with an average $+1.8\%$ deviation, while the calculated Mo—Br bond length is slightly shorter than experiment (-1.0% deviation). To our knowledge, the geometry of MoO_2Br_2 has never been computed before. Our results for MoO_2Cl_2 are in accord with those reported earlier by Deeth [23]. Interestingly, in a systematic study of transition-metal compounds, Sosa et al. [39] showed that the trend for local DFT methods was to underestimate bond lengths between halogen and first-row transition metals.

The observed vibrational spectra of MoO_2Cl_2 [2] and MoO_2Br_2 [40] are reported to be fully consistent with a tetrahedral C_{2v} structure. Thus, the nine fundamental modes of vibration of a pentatomic molecule having this symmetry belong to nondegenerate species [41] and are shown to be $\Gamma_{vib} = 4A_1 + A_2 + 2B_1 + 2B_2$, of which four are described as stretching modes (ν), two as bending modes (δ), two as rocking (σ), and one as torsion (τ). Table II gathers both observed and calculated frequencies. The root mean square deviations fall within 18 cm^{-1} for MoO_2Cl_2 and 20 cm^{-1} for MoO_2Br_2.

In conclusion, for MoO_2Cl_2 and MoO_2Br_2, bond lengths are reproduced with an accuracy of 0.05 Å and bond angles turn out to be within 1–3° of experimental data (Table I), whereas the average error between observed and calculated vibrational frequencies is only of 4–5% (Table II). The agreement found with experiment allows us to extend this study to the less known members of this family of compounds.

TABLE I
Calculated and observed geometrical parameters for compounds MoO_2X_2 (X = F, Cl, Br, I); bond lengths in Å and angles in degrees.

Compound	$r(Mo{-}O)$	$r(Mo{-}X)$	$\angle XMoX$	$\angle OMoO$	$\angle XMoO$	Source
MoO_2F_2	1.723	1.885	112.4	106.3	109.5	Calcd.
	(1.71)	(1.94)	—	—	—	Exp.[a]
MoO_2Cl_2	1.726	2.267	111.1	107.1	109.6	Calcd.
	1.686	2.258	113.9	106.3	109.1	Exp.[b]
MoO_2Br_2	1.729	2.380	111.1	107.5	109.5	Calcd.
	1.683	2.403	111.7	107.8	109.3	Exp.[c]
MoO_2I_2	1.731	2.601	111.3	108.4	109.3	Calcd.
	—	—	—	—	—	Exp.

[a] Estimation [42].
[b] [7].
[c] [7].

TABLE II
Vibrational frequencies (in cm^{-1}) corresponding to the nine normal modes of compounds MoO_2X_2 (X = F, Cl, Br, I).

Compound MoO_2X_2	A_1 $\delta(MX_2)$	A_2 τ	B_1 $\sigma(MO_2)$	B_2 $\sigma(MX_2)$	A_1 $\delta(MO_2)$	A_1 $\nu(MX_2)$	B_2 $\nu(MX_2)$	A_1 $\nu(MO_2)$	B_1 $\nu(MO_2)$	Source
MoO_2F_2	172.8	225.1	231.4	254.8	341.6	670.3	698.4	947.8	959.5	Calcd.
	(190)	(250)	(275)	275	365	692	705	987	1012	Exp.[a]
MoO_2Cl_2	168.0	114.7	221.4	198.8	321.0	424.9	451.6	947.2	932.7	Calcd.
	167	116	202	180	338	434	450	997	971	Exp.[b]
MoO_2Br_2	147.9	80.3	196.8	181.0	358.1	261.9	353.7	938.7	924.1	Calcd.
	147	82	184	161	378	262	338	995	970	Exp.[c]
MoO_2I_2	129.7	64.6	171.6	170.4	294.0	199.4	333.2	931.0	917.4	Calcd.
	—	—	—	—	—	—	—	—	—	Exp.

[a] [47].
[b] [2].
[c] [40].

GEOMETRICAL PARAMETERS AND IR SPECTRA: PREDICTIONS

Definitive experimental data appear to be lacking for geometries of MoO_2F_2 and MoO_2I_2, although several rough estimations have been reported for the former [42]. Owing to the good accuracy obtained for MoO_2Cl_2 and MoO_2Br_2, the calculated structures shown in Table I for MoO_2F_2 and MoO_2I_2 can offer a consistent theoretical prediction, awaiting future confirmation from experimental observations. Thus, the Mo—I distance is predicted to be ca. 2.6 Å. Probably, the calculated Mo—O bond lengths for X = F, I should be about 0.04 Å shorter, given the deviation observed from X = Cl, Br. In the case of the dioxodifluoride, a similar structure was recently reported by Deeth [23].

Another interesting point concerns bond angles. First, the $\angle XMoO$ angle remains constant at approximately 109° along the series, being insensitive to the change of the halogen atom. Second, in all cases, the $\angle OMoO$ angle is predicted to be smaller than the $\angle XMoX$ angle. This is in contradiction to valence shell electron pair repulsion theory (VSEPR) [43]: The VSEPR principle states that formal double bonds require a greater proportion of the coordination sphere around a central atom than do single bonds. Thus, one would apparently expect the opposite order ($\angle OMoO > \angle XMoX$). However, our results are in excellent accordance with the experimental study of Marsden et al. [44] for CrO_2Cl_2 who also noted that VSEPR theory incorrectly predicts a larger $\angle OMO$ angle (M = transition metal). It is well known [45] that the ideas of the VSEPR model usually fail for transition metals. It seems that terminal bonds for transition metals to oxygen are less sterically demanding than are those from main-group elements, given the readily accessibility of d orbitals for transition elements. Therefore, the present results look correct and are in good agreement with those previously observed. Reasons leading to VSEPR failure have also been investigated for CrO_2F_2 [14, 46] through a topological analysis of the electronic charge distribution. In particular, values of the charge density (ρ_{BCP}) and the Laplacian of the charge density ($\nabla^2\rho_{BCP}$) at the bond critical point revealed a pronounced ionic character for the Cr—F bond, so the unexpectedly large FCrF angle is suggested to be partially caused by electrostatic repulsions between fluorine atoms.

A rigorous determination of the complete vibrational spectrum for MoO_2F_2 has not been possible yet, especially for the lowest vibrational frequencies [47]. No spectral data exist either for MoO_2I_2 since it has not yet been synthesized. According to our calculations (Table II), the two Mo—X stretching modes in MoO_2F_2 lie at 698.4 and 670.3 cm^{-1}, while in MoO_2Cl_2 (451.6 and 424.9 cm^{-1}) and in MoO_2Br_2 (353.7 and 261.9 cm^{-1}), they are found at lower and lower frequency, because of the increase in the halogen mass. Furthermore, the separation between both stretching frequencies increases within the series. In MoO_2I_2, the two Mo—I stretches are computed to be even more separated than in the former and to lie in the range 195–335 cm^{-1} as shown in Table II.

The frequency shifts resulting from halide substitution are influenced both by force constants and by atomic weights of halogens. Both the sym-

metric and asymmetric Mo—X stretching modes decrease in the order F > Cl > Br > I for two reasons: First, the atomic weight of the halogen increases, and second, the tendency to accept electrons decreases with the increase in atomic weight of halogen ligands. Thus, the p orbitals accepting electrons from the metal have the most negative energy in the case of F and become less stable from Cl to I. Mulliken population analysis confirms these results. According to information furnished by this analysis, the occupation of p orbitals in the ligand is 5.48 for F, 5.34 for Cl, 5.26 for Br, and 4.99 for I, which is in good agreement with Pauli electronegativities for this series (4.0, 3.0, 2.8, and 2.5, respectively). Therefore, the more electronegative the halogen, the more population it bears and, then, the larger the Mo—X stretching frequency. With regards to the Mo—O stretching vibration frequencies, their values decrease slightly with the increase of atomic number of the halogen, as a consequence of the corresponding slight lengthening of the Mo—O bonds. It must be noted here that geometrical and vibrational calculations for X = F, Cl agree with the results reported earlier by Deeth [23] using nonlocal gradient-corrected DFT methodology.

ELECTRONIC SPECTRA

Matrix isolation experiments obtaining the electronic spectra of MoO_2Cl_2 and MoO_2Br_2 species were reported by Levason et al. [1]. Band maxima positions for MoO_2Cl_2 were observed at 5.5 and 4.8 eV and assigned to the O → Mo and Cl → Mo electronic charge transfer excitations, respectively. For MoO_2Br_2, the position of these bands were estimated to be at 5.3 (O → Mo) and 4.9 (Br → Mo) eV.

From a theoretical point of view, the UV-visible spectra of MoO_2X_2 have not been studied yet. Much of the work about the electronic structures of tetraoxo complexes of closed-shell transition metals has focused on CrO_4^{2-} and MnO_4^-, as archetypical complexes, other systems having received less attention. Recently, Miller et al. [48] compared the lower excited states of CrO_4^{2-}, CrO_3X^-, and CrO_2X_2 (X = F, Cl) through perturbation of the electronic structure caused by changing one or more of the oxygen ligands. In the present article, trends in MoO_4^{2-} can serve as a model for the MoO_2X_2 compounds, taking also into account the effect of symmetry reduction via halide substitution $(T_d \to C_{3v} \to C_{2v})$. Thus, the

lowest energy excitations in MoO_2X_2 derive from the parent $t_1 \to e$ excitation, as shown in Figure 1.

The three highest occupied orbitals arise from the correlation $t_1(T_d) \to a_1 + b_1 + b_2(C_{2v})$ and have only slight contributions of the Mo atom. Their relative energy ordering is $b_2 > b_1 > a_1$ for X = F, $b_2 > a_2 > b_1$ for X = Cl, Br, and $b_1 > a_2 > b_2$ for X = I (Table III). Among these three orbitals, the b_2 (b_1 in the case of MoO_2I_2) is the HOMO, having the greatest oxygen amplitude and the least halogen amplitude in MoO_2F_2, where the HOMO is mainly an oxygen lone-pair MO. This is because p orbitals of oxygen are higher in energy than are p orbitals of fluorine because of the major electronegativity of F with respect to an O atom. The halogen character becomes gradually larger in the order F(0.01) < Cl(0.13) < Br(0.39) < I(0.94), while the oxygen character decreases (0.99, 0.90, 0.66, and 0.07, respectively) in the same direction. In the remaining b_1 and a_2 orbitals (b_2 and a_2 in MoO_2I_2), the halogen character is four times as much as the oxygen character (ca. 0.80 : 0.20). The only exception is found in MoO_2F_2, where the ratio is reversed (ca. 0.20 : 0.80).

FIGURE 1. Schematic energy level diagram for the highest occupied and lowest unoccupied orbitals for the ground state of MoO_4^{2-} (T_d), MoO_3X^- (C_{3v}), and MoO_2X_2 (C_{2v}). Orbitals below the dashed line are occupied in the ground state. The three highest occupied orbitals in MoO_2X_2 have the ordering and symmetry b_2, b_1, a_1 (as shown) for X = F, b_2, a_2, b_1 for X = Cl, Br, and b_1, a_2, b_2 for X = I (see text).

TABLE III

Energies and population contributions (both in au) for the orbitals derived from the parent $t_1 \to e$ in the ground state for compounds MoO_2X_2 (X = F, Cl, Br, I); the first orbitals below and above the dashed line are HOMO and LUMO, respectively.

MoO_2F_2					MoO_2Cl_2				
Orbital	Energy	Mo	F	O	Orbital	Energy	Mo	Cl	O
$3a_2$	-0.1783	0.77	0.10	0.45	$3a_2$	-0.1795	0.73	0.11	0.46
$9a_1$	-0.1883	0.78	0.21	0.29	$9a_1$	-0.1963	0.71	0.29	0.26
$5b_2$	-0.3237	0.02	0.01	0.99	$5b_2$	-0.3172	0.01	0.13	0.90
$5b_1$	-0.3594	0.06	0.19	0.73	$2a_2$	-0.3281	0.00	0.80	0.23
$8a_1$	-0.3669	0.14	0.20	0.74	$5b_1$	-0.3298	0.00	0.83	0.20

MoO_2Br_2					MoO_2I_2				
Orbital	Energy	Mo	Br	O	Orbital	Energy	Mo	I	O
$5a_2$	-0.1709	0.72	0.11	0.46	$5a_2$	-0.1647	0.80	0.12	0.49
$12a_1$	-0.1892	0.70	0.33	0.25	$12a_1$	-0.1877	0.75	0.44	0.24
$7b_2$	-0.3041	0.00	0.39	0.66	$8b_1$	-0.2762	0.00	0.94	0.07
$4a_2$	-0.3050	0.00	0.84	0.19	$4a_2$	-0.2767	0.01	0.86	0.14
$8b_1$	-0.3055	0.00	0.91	0.12	$7b_2$	-0.2815	0.01	0.79	0.18

The two lowest unoccupied orbitals have symmetries a_1 and a_2 (the latter being higher in energy than the former) and have mainly Mo $4d$ character. This follows from the correlation $e(T_d) \to a_1 + a_2(C_{2v})$. For each compound, the a_2 orbital has a larger oxygen character and smaller halogen character than those of a_1 orbital (LUMO).

As seen in Table IV, the smallest excitation energy corresponds to the HOMO–LUMO transition only in the case X = Cl and X = Br. For MoO_2F_2 and MoO_2I_2, the excitation of minimum energy is due to $5b_2 \to 3a_2$ and $4a_2 \to 12a_1$ transitions, respectively. To analyze how relativistic effects may change values in Table IV, we recomputed the HOMO–LUMO transitions using a first-order scalar relativistic Pauli Hamiltonian. In

this case, only a slight increase of the energy gaps up to 0.1 eV was observed. Therefore, the introduction of relativistic effects, despite yielding a (qualitative) improvement in the correct direction, is not quantitatively crucial for the electronic description of MoO_2X_2 species.

Noteworthy, calculated energies decrease systematically in the order F > Cl > Br > I for any given excitation. Although this tendency seems perfectly correct for such a series, our results have to be taken cautiously because they do not agree with the only experimental study reported so far [1]. In particular, the observed fact that the lowest energy X → Mo charge transfer band in MoO_2Cl_2 should lie below the same band in MoO_2Br_2 by 0.1 eV [1] is not borne out in practice by our calcula-

TABLE IV

Transition energies (in eV) for the lowest excitations of compounds MoO_2X_2 (X = F, Cl, Br, I).

MoO_2F_2		MoO_2Cl_2		MoO_2Br_2		MoO_2I_2	
Excitation	ΔE	Excitation	ΔE	Excitation	ΔE	Excitation	ΔE
$5b_2 \to 9a_1$	4.19	$5b_2 \to 9a_1$	3.58	$7b_2 \to 12a_1$	3.32	$8b_1 \to 12a_1$	2.73
$5b_2 \to 3a_2$	4.17	$5b_2 \to 3a_2$	3.93	$7b_2 \to 5a_2$	3.78	$8b_1 \to 5a_2$	3.72
$5b_1 \to 9a_1$	4.79	$2a_2 \to 9a_1$	3.85	$4a_2 \to 12a_1$	3.43	$4a_2 \to 12a_1$	2.71
$5b_1 \to 3a_2$	5.31	$2a_2 \to 3a_2$	4.69	$4a_2 \to 5a_2$	4.29	$4a_2 \to 5a_2$	3.69
$8a_1 \to 9a_1$	5.13	$5b_1 \to 9a_1$	3.89	$8b_1 \to 12a_1$	3.48	$7b_2 \to 12a_1$	2.78
$8a_1 \to 3a_2$	5.25	$5b_1 \to 3a_2$	4.66	$8b_1 \to 5a_2$	4.31	$7b_2 \to 5a_2$	3.50

tions, which yield a Cl → Mo energy transfer larger by 0.26 eV. These differences lie within the possible errors of the method used. However, from the experimental point of view, a possibility remains that the long tails on the high-wavelength side of these bands contain unresolved charge-transfer maxima, as admitted by Levason et al. [1], whose theoretical predictions based on optical electronegativities coincide with the results obtained here. Indeed, so far only a limited number of theoretical studies have been carried out with the procedure used in this article [25], so a further discussion on the relative ordering of the positions of charge-transfer bands must await the availability of further experimental data.

From an analysis of the orbitals (Table III) and the energy gaps listed in Table IV, interesting qualitative predictions can be issued. Thus, the intense color of these MoO_2X_2 systems is attributed to a charge-transfer transition where an electron is transferred from orbitals having a predominant ligand character to orbitals having a predominant Mo character. The transition in MoO_2X_2 is classified thus as a ligand-to-metal charge-transfer (LMCT) transition. Charge-transfer bands in the visible region of these spectra occur because the ligands have lone pairs of relatively high energy and the metal has low-lying empty orbitals. A lone-pair electron of ligand (a nonbonding halogen-localized $5p$ π level in MoO_2I_2 or a nonbonding oxygen-localized $2p$ π level in the others) is expected to be promoted to the antibonding low-lying empty d molybdenum orbital. For instance, the energy gaps in MoO_2I_2 (Table IV) suggest a band in the electronic spectrum at approximately 400−440 nm, thus predicting that this compound will be light yellowish in color.

PREDICTIONS ABOUT REACTIVITY: OXO-TRANSFERABILITY

In the last section, we showed that the HOMO−LUMO transition energies decrease when going from fluorine to iodine. Here, we want to study the changes caused by this transition in the geometry of the MoO_2X_2 species. The variations of nuclei positions corresponding to the distortions experienced by the molecule when excited electronically will provide a hint of how labile the Mo—O bond is. Thinking in terms of oxo-transferability, the most suitable ligand will be that yielding the smallest HOMO−LUMO transition energy and largest Mo—O bond lengthening. Although

the MoO_2X_2 species are not directly related to the active site of molybdenum oxidoreductases, it is well established [49] that a $(Mo^{VI}O_2)^{2+}$ group is a structural fragment of these active sites, so results obtained here may be relevant to understand the changes suffered by these enzymes when a HOMO−LUMO transition takes place.

Table V collects the optimized structural parameters obtained when an electron is promoted from the HOMO to the LUMO. Relative changes (elongations and shrinkages) with respect to optimized geometrical parameters in the ground state are indicated in parentheses. Along the series, the changes in Mo—O and Mo—X bond distances follow opposite directions. Thus, the less the Mo—O bond length increases, the more the Mo—X distance extends. This trend is due to the nature of HOMO and LUMO, which also varies according to the electronegativity of the halogen. For instance, in MoO_2F_2, the HOMO has an important bonding contribution to Mo—O bonds, whereas the LUMO is mainly antibonding to Mo—O. The oxygen character gradually decreases in the direction F > Cl > Br. In the case of MoO_2I_2, the situation reverses, so the main contributions correspond predominantly to the p orbital of iodine (both in HOMO and LUMO). Hence, the Mo—O distances are expected to lengthen increasingly from I to F during this LMCT transition, while the Mo—X bonds are perturbed in the opposite way, reaching the maximum for MoO_2I_2, where the LUMO becomes mainly antibonding to Mo—I.

Bond angles seem especially sensitive to the variations of bond lengths, being rearranged to minimize electrostatic repulsions. Noteworthy, ∠XMoX and ∠OMoO angles compensate each other in such a way that the ∠XMoO angle remains almost constant along the series as in the ground state (Table I), ∠IMoO being the exception. On the whole, all structural changes caused by this HOMO−LUMO transition are important enough to predict the appearance of broad bands in the spectra of these compounds. In fact, it is established [25] that a large distortion of the molecular structure during a transition yields wide bands.

From the point of view of reactivity, the most important feature of these complexes is the labilization of the Mo—O bond, so attention must be focused on Mo—O bond elongations. If molybdenum−oxygen distances from Tables I and V are compared, a different trend is observed regarding the order of variation (F < Cl < Br < I for the ground state, but F > Cl > Br > I for the excited

TABLE V

Calculated geometrical parameters for MoO_2X_2 compounds (X = F, Cl, Br, I) in the excited state resulting from the HOMO – LUMO transition; values in parentheses indicate the relative change with respect to ground-state geometries; bond lengths in Å and angles in degrees.

Compound	$r(Mo-O)$		$r(Mo-X)$		$\angle XMoX$		$\angle OMoO$		$\angle XMoO$	
MoO_2F_2	1.807	(+4.9%)	1.905	(+1.1%)	94.7	(−15.7%)	116.9	(+10.0%)	110.7	(+1.1%)
MoO_2Cl_2	1.794	(+3.9%)	2.299	(+1.4%)	99.9	(−10.1%)	121.0	(+13.0%)	108.5	(−1.0%)
MoO_2Br_2	1.784	(+3.2%)	2.438	(+2.4%)	101.2	(−8.9%)	121.0	(+12.6%)	108.2	(−1.2%)
MoO_2I_2	1.742	(+0.6%)	2.776	(+6.7%)	75.2	(−32.4%)	115.7	(+6.7%)	114.9	(+5.1%)

state). According to Table V, the largest lengthening is found for the difluoride (+4.9%) and then it gradually decreases with the reduction of electronegativity. This notwithstanding, the excitation energy required for this change is also much larger in MoO_2F_2 than in the other dihalides (Table IV). Therefore, if an agreement between energetical considerations and donor ability must be reached, the most convenient ligands for transferring an oxygen atom turn out to be X = Cl, Br. Interestingly, it is also in MoO_2Cl_2 and in MoO_2Br_2 where the $\angle OMoO$ bond angles suffer the biggest change. A suitable application can be found, for instance, in the theoretical modelization of bulky dithiolate groups present in real molybdenum oxidoreductases: It can be computationally useful to substitute the sulfur ligands surrounding the active site by chlorine atoms, which exhibit a similar oxo-donor behavior.

Conclusions

An investigation of the full series of dioxodihalides of molybdenum(VI) (MoO_2X_2; X = F, Cl, Br, I) is reported. The present article shows that geometrical data, infrared spectra, and electronic spectra of second-row transition-metal compounds can be satisfactorily interpreted and predicted from nonrelativistic density functional calculations. As shown in a previous work [14], the nonlocal DFT approach employed here incorporates the dominant correlation effects required for these molybdenum systems of catalytic importance.

In particular, we computed molecular structures that not only agree fairly well with experiment (MoO_2Cl_2 and MoO_2Br_2), but are useful for predicting other dihalides (MoO_2F_2 and MoO_2I_2). For the former pair, results yield bond lengths and

angles which reproduce observed data within about 0.05 Å and 3°, respectively. This allows us to estimate with confidence a Mo—I bond length of 2.6 Å. In the case of X = F, Cl, our geometries are in accord with those calculated by Deeth [23]. As far as IR spectra are concerned, the most important bands were examined. In particular, frequency shifts along the series were rationalized in terms of population analysis and atomic weights. Vibrational predictions for MoO_2I_2 also seem consistent. Furthermore, we covered the lack of theoretical data regarding electronic spectra of these four dioxodihalides, for which the lowest virtual and highest occupied orbitals are described as having largely molybdenum $4d$ and ligand lone-pair character, respectively. Significant halogen contribution in the higher occupied orbitals occurs increasingly in MoO_2Cl_2, MoO_2Br_2, and MoO_2I_2. The lowest excited singlet states of MoO_2X_2 compounds are predicted to be $^1B_1$ for X = F (from the $b_2 \rightarrow a_2$ transition), $^1B_2$ for X = Cl, Br (from the $b_2 \rightarrow a_1$ or HOMO−LUMO transition), and $^1A_2$ for X = I (from $a_2 \rightarrow a_1$). The color of MoO_2I_2 has also been predicted. Finally, the structural changes produced during the charge-transfer electronic transition corresponding to the half-occupation of LUMO were investigated. We conclude that the strongest oxo-donating efficiency is expected to occur in MoO_2Cl_2 and MoO_2Br_2 species.

In summary, theoretical results agree with observed data and allow one to make valuable predictions for the less studied compounds of the MoO_2X_2 series. This last conclusion is quite important because it suggests that, by analogy, the synthesis and characterization of similar molybdenum systems is able to be assisted computationally once the optimum theoretical conditions have been found. This notwithstanding, one should bear in mind that the calculations reported here correspond to the gas phase; comparison with future

condensed-phase experiments must be done with some care. Work is in progress to extend these studies to the dimeric species $(MoO_2X_2)_2$, which are thought to be unstable in the vapors [6], but present in inert solvents.

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