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The Electronic Structure of FeO_4^{2-}, RuO_4, RuO_4^-, RuO_4^{2-} and OsO_4 by the HFS-DVM Method

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The electronic structures of FeO_4^{2-}, RuO_4, RuO_4^-, RuO_4^{2-} and OsO_4 have been investigated using the Hartree-Fock-Slater Discrete Variational Method. The calculated ordering of the valence orbitals is $2t_2$, $1e$, $2a_1$, $3t_2$ and t_1 with the t_1 orbital as the highest occupied. The first five charge transfer bands are assigned as: $t_1 \rightarrow 2e(\nu_1)$, $3t_2 \rightarrow 2e(\nu_2)$, $t_1 \rightarrow 4t_2(\nu_3)$, $3t_2 \rightarrow 4t_2(\nu_4)$ and $2a_1 \rightarrow 4t_2(\nu_5)$.

It is suggested that a *d-d* transition should be observed at 1.5 eV in RuO_4^- and RuO_4^{2-}.

Key words: Tetraoxo complexes – Group VIII oxides and oxyanions – Hartree-Fock-Slater discrete variational method (HFS-DVM)

1. Introduction

Spectral investigation of tetraoxo transition metal complexes (MO_4^{n-}) was first carried out by Teltow [1] in 1938. Since then electronic spectra have been reported for most known tetraoxo complexes [2–4] and some analogous tetrathio and tetraseleno complexes [2, 3]. Molecular orbital theory has been used extensively to interpret the *uv* spectra [5–14] after the pioneering work of Wolfsberg and Helmholz [5]. Although there is now some agreement on the ordering of the molecular orbitals of the well studied MnO_4^- [7–9, 11–14], doubt still remains as to the ordering and energies of the orbitals in most other systems and therefore in the assignments that have been made for the observed spectral transitions.

Because they are volatile and relatively stable, OsO_4 and RuO_4 have frequently been the subject of spectroscopic [2, 15–18] investigation. The corresponding oxyanions have received less attention [4, 8, 19]. The third member of the valence isoelectronic series FeO_4 is unknown, a fact which is not surprising when one considers the relative stabilities of OsO_4 whose standard free energy is −69.3 kcal/mol and RuO_4 whose standard free energy is −33.8 kcal/mol [20]. However, several oxyanions of iron are known.

In this communication we present a coherent analysis of the photoelectron and optical spectra of the known tetraoxo complexes of group VIII transition metals by means of the Hartree-Fock-Slater Discrete Variational molecular orbital method (HFS-DVM). The HFS-DVM method of Ellis and Painter [21] has been

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shown to give nearly quantitative results in the calculation of ionization potentials and transition energies [22] for $TiCl_4$ and VCl_4.

2. Method

2.1. Discrete Variational Method

Using the DVM method [21] one finds the molecular spin orbitals u_i and the orbitals energies ε_i by solving approximately the Hartree-Fock-Slater one electron equation [23]

$$\{T(1)+V_N(1)+V_C(1)+V_X(1)\}u_i(1)=\varepsilon_i u_i(1)\,, \tag{1}$$

The operators for kinetic energy (T), nuclear-electron attraction (V_N), coulomb repulsion (V_C) and the exchange potential (V_X) are defined in atomic hartree units as

$$T(1)=-\tfrac{1}{2}\nabla^2(1)\,, \tag{2}$$

$$V_N(1)=-\sum^{\text{nuclei}}\frac{Z_g}{r_{1g}}\,, \tag{3}$$

$$V_C(1)=\int\frac{\varrho(2)}{r_{12}}\,d\tau_2\,, \tag{4}$$

and

$$V_X(1)=-K(\delta_{m,\alpha}\varrho^{\alpha}(1)^{1/3}+\delta_{m,\beta}\varrho^{\beta}(1)^{1/3})\,, \tag{5}$$

where Z_g is the nuclear charge of nucleus g, $\varrho^{\alpha}(1)$ and $\varrho^{\beta}(1)$ are the electron densities with α and β spins respectively, and m represents the electron s_z spin component. In this work we have taken $K=3(3/4\pi)^{1/3}$ (full Slater exchange); however, we note that values of the exchange scaling parameter are often chosen between K and $2/3K$ to obtain improved agreement with experiment [22, 23, 29b].

The molecular orbitals can be obtained in terms of numerical [24] or analytical (LCAO) basis functions [22]. We will expand u_i in terms of a finite set of analytical Slater orbitals (STO)

$$u_i=\sum_j C_{ij}\chi_j\,. \tag{6}$$

The linear Rayleigh-Ritz variational procedure, applied to Eq. (1) leads to the matrix form

$$\mathrm{FC}=\mathrm{SCE} \tag{7}$$

where

$$S_{ij}=\int\chi_i(1)\cdot\chi_j(1)\,d\tau_1 \tag{8}$$

and

$$F_{ij}=\int\chi_i(1)\{T_K(1)+V_N(1)\}\chi_j(1)\,d\tau_1+\int\chi_i(1)\{V_C(1)+V_X(1)\}\chi_j\,d\tau_1\,. \tag{9}$$

In the corresponding linear DVM, the overlap integral S_{ij} and the first integral in Eq. (9) are evaluated using the Diophantine numerical integration procedure developed by Haselgrove [25] and applied to molecular integrals by Conroy [26] and Ellis [27]. The last integral in Eq. (9) can be dealt with rigorously by a double numerical Diophantine integration [28] or by fitting the charge distribution $\varrho(1)$ obtained from a previous iteration [29]. The latter method corresponds to the usual SCF procedure.

In the present calculations $\varrho(1)$ is approximated by a sum of spherically symmetric charge densities around each atomic centre,

$$\varrho(1) = \sum_{g}^{\text{nuclei}} \varrho_g(1)\,, \tag{10}$$

where $\varrho_g(1)$ is obtained by Mulliken population analyses of the wavefunctions from preliminary non-empirical INDO-SCF calculations [30, 31] on the molecules concerned. The superposition of atomic charge densities in Eq. (10) have been used in previous DVM calculations [22], where the population on each centre was chosen to give a good agreement with the experimental data. A more systematic way of estimating the electronic population of each centre is to make a preliminary SCF calculation using a simple MO method, especially in the case of systems with several different atoms. In Table 3b we show the effect on the molecular orbital energy levels of RuO_4 when several different metal d orbital populations are used. From Table 3b it can be seen that the orbital energies do change as a function of the d-populations. The ordering of the levels however is the same except for $1e$ and $2t_2$. We will comment more on these two levels in connection with assignments of the photoelectron spectra.

2.2 *The Transition State Method*

The Transition State Method of Slater [23] is used to calculate excitation energies. As an example, consider the transition $t_1 \rightarrow 2e$ in RuO_4. Initially a Hyper-Hartree-Fock calculation [23] is carried out on the transition state configuration $(t_1)^{5\frac{1}{2}}(2e)^{\frac{1}{2}}$ using the non-empirical INDO-SCF method [30, 31], in order to obtain the charge distribution

$$\varrho_{av}(1) = \sum_{g} \varrho_g(1)\,. \tag{11}$$

From a spin restricted HFS-DVM calculation on $(t_1)^{5\frac{1}{2}}(2e)^{\frac{1}{2}}$ using $\varrho_{av}(1)$, one obtains, according to the transition state theory [23]

$$\varepsilon_{2e} - \varepsilon_{t1} = \tfrac{1}{8}\{3E(^3T_1) + 3E(^3T_2) + E(^1T_1) + E(^1T_2)\}\,. \tag{12}$$

The right hand side of Eq. (12) is the average energy of the configuration $(t_1)^5(2e)^1$. As the next step one constructs from $\varrho_{av}(1)$, the charge distribution

$$\varrho(1) = \sum_{g} \varrho_g^{\alpha}(1) + \sum_{g} \varrho_g^{\beta}(1)$$

corresponding to the configuration $(t_1)^{3\alpha}(t_1)^{2\frac{1}{2}\beta}(2e)^{\frac{1}{2}\alpha}$. From a spin unrestricted HFS-DVM calculation on the configuration $(t_1)^{3\alpha}(t_1)^{2\frac{1}{2}\beta}(2e)^{\frac{1}{2}\alpha}$ one derives

$$\varepsilon_{2e}^{\alpha} - \varepsilon_{t_1}^{\beta} = \tfrac{1}{2}\{E(^3T_1) + E(^3T_2)\} \tag{13}$$

where the right hand side is an average energy of triplet states due to the configuration $(t_1)^5(2e)^1$. From Eqs. (12) and (13) one finally obtains average triplet and singlet transition energies.

In the next sections we report average singlet, doublet, triplet, and quartet transition energies all calculated in a manner similar to the above example.

Table 1. Metal STO-basis sets used in the INDO and HFS-DVM calculations[a]

	s exponents				*p* exponents				*d* exponents		
	Fe[c]	Ru[d]	Os[d]		Fe[c]	Ru[d]	Os[d]		Fe[c]	Ru[d]	Os[d]
1*s*	25.38	43.57	75.53	2*p*	10.60	19.96	35.79	3*d*	5.35	10.07	18.36
2*s*	9.75	16.30	29.23	3*p*	4.17	9.44	18.36	3*d*′	2.00	—	—
3*s*	4.48	8.09	15.51	4*p*	1.08[b]	4.67	10.22	4*d*	2.00[b]	5.38	10.22
4*s*	1.40[b]	4.22	8.81	5*p*	—	2.04[b]	5.33	4*d*′	—	2.30	—
5*s*	—	2.09[b]	4.80	6*p*	—	—	2.43[b]	5*d*	—	2.30[b]	5.57
6*s*	—	—	2.45[b]					5*d*′	—	—	2.42
								6*d*	—	—	2.42[b]

[a] In addition to the functions shown, a single set of 4*f* orbitals, with exponent 9.28, [37b] used in the INDO calculations on the Osmium complexes.

[b] Used only in HFS-DVM calculations.

[c] Ref. [35].

[d] Ref. [36].

Table 2. Oxygen STO-basis set used in the INDO and HFS-DVM calculations

	Exponents	
	INDO[a]	HFS-DVM
1*s*	7.66	7.66
2*s*	2.25	3.20
2*s*′	—	1.80
3*s*	—	1.80
2*p*	2.23	3.20
2*p*′	—	1.80
3*p*	—	1.80

[a] Ref. [37a].

2.3. Geometries and Basis Sets

The systems studied are all tetrahedral. The metal-oxygen bond distances are: FeO_4^{2-}, 1.72 Å [32]; RuO_4, 1.73 Å [32]; RuO_4^-, 1.79 Å [33]; RuO_4^{2-}, 1.80 Å [32]; OsO_4, 1.77 Å [34].

The basis sets used in the INDO and HFS-DVM calculations are shown in Tables 1 and 2. The *s*, *p* and core *d* orbitals of the metals are represented by single zeta STO's. The valence *d* orbitals are represented by double zeta STO's. In both the INDO and the HFS-DVM calculations on OsO_4 the 4*f* orbital was considered as core with a single exponent of 9.28 [37]. The 4*s* orbital of iron, the 5*s* orbital of ruthenium and the 6*s* orbital of osmium were excluded in the case of the INDO calculations for reasons previously cited [30, 31], but were included for additional flexibility in the basis set used for the final HFS-DVM calculations. Also for increased flexibility in the final calculations, additional *p* and *d* functions were added to the metal basis sets (Table 1) and a near triple zeta set of functions has been used to describe the valence shell of oxygen (Table 2).

3. Ground State Calculations

3.1 d^0-Systems

The only group VIII d^0 tetraoxo complexes that have been reported are RuO_4 and OsO_4. No analogous tetrathio or tetraseleno complexes have been reported. The electronic structure for the ground electronic states of RuO_4 and OsO_4 has recently been studied using photoelectron spectroscopy [15, 16]. These experimental results are recorded in Table 3a along with our calculated orbital energies.

On the basis of our calculations the first three ionizations must occur from the t_1, $3t_2$ and $2a_1$ levels, respectively. These three levels correspond to MO's constructed from various combinations of ligand non-bonded orbitals. Our assignment for the first three levels agrees with that proposed by Diemann and Müller [5] but is at variance with that of McGlynn and coworkers [16]. The present calcula-

Table 3a. Molecular orbital energies for RuO_4 and OsO_4

MO	RuO_4			OsO_4		
	Calc. eV	Obs.^{a,b} eV	Obs.^{a,c} eV	Calc. eV	Obs.^{a,b} eV	Obs.^{a,c} eV
$4t_2$	-8.61^{d}	—	—	-7.62^{d}	—	—
$2e$	-10.01^{d}	—	—	-9.94^{d}	—	—
t_1	-11.32	12.09^{e}	12.16–12.46	-11.44	12.32^{e}	12.39–12.82
$3t_2$	-12.58	12.91^{e}	12.60–12.90	-12.44	13.14^{e}	13.17–13.38
$2a_1$	-13.28	13.78	13.97–14.08	-12.87	13.50^{e}	13.55–13.77
$1e$	-17.58	13.88		-18.39	14.54^{e}	14.66
$2t_2$	-17.76	16.03	15.50	-18.01	16.31	16.4 –16.8

[a] By Koopmans' theorem the ionization potential is approximately the negative of the *Hartree-Fock* orbital energy; however, binding energy corrections to HFS eigenvalues can be important. The calculated values listed are simply the HFS non-SCF orbital eigenvalues; we would in principle prefer to perform an SCF calculation of the $(MO_4)^{+\frac{1}{2}}$ transition state levels. The observed quantities are values for ionization potentials obtained by photoelectron spectroscopy.

[b] Ref. [16].

[c] Ref. [15].

[d] Virtual orbitals.

[e] These assignments differ from those of Ref. [16]. See text.

Table 3b. Molecular orbital energies for RuO_4 using different atomic populations[a]

MO	$d^{5.5}$ (eV)	$d^{6.0}$ (eV)	$d^{6.18\,b}$ (eV)	$d^{6.5}$ (eV)
$4t_2$	-9.67	-8.71	-8.61	-7.27
$2e$	-10.58	-9.89	-10.01	-8.79
t_1	-10.88	-11.24	-11.32	-11.69
$3t_2$	-12.13	-12.34	-12.58	-12.79
$2a_1$	-13.10	-13.33	-13.28	-13.41
$1e$	-19.99	-18.14	-17.58	-16.38
$2t_2$	-19.52	-18.24	-17.76	-16.88

[a] For construction of $\varrho_{Ru}(1)$ of Eq. (10).

[b] Obtained from an INDO-SCF calculation.

tions indicate that the next two levels, $1e$ and $2t_2$, correspond to MO's with large contributions from ligand $2p$ orbitals and the d orbitals of the metal. We assign to them the observed [16] ionizations at 13.88 eV and 16.03 eV, respectively, for RuO_4 and at 14.54 eV and 16.31 eV, respectively, for OsO_4.

Although satisfactory agreement between calculated and experimental ionization potentials is obtained, the data of Table 3b suggest that even better agreement could be achieved if a higher metal d orbital population were used than that suggested by the INDO SCF preliminary step. This is particularly true in the case of the $1e$ and $2t_2$ levels which are very sensitive to the d population that enters into Eq. (10).

3.2. d^1-Systems[1]

RuO_4^- and FeO_4^- are the only known d^1 tetraoxo complexes of group VIII. The results of our spin restricted calculation on RuO_4^- which are shown in Table 4, suggest that the odd electron should occupy the $2e$ level. The symmetry of the ground state is therefore ^2E. The separation of the $2e$ level from the $4t_2$ level, the $10Dq$ of crystal field theory, is calculated to be 1.38 eV for RuO_4^-. This rather low value plays a big role in the assignment of the electronic spectra in a later section.

Experimental data on FeO_4^- is scant [38]. We expect that the results obtained for RuO_4^- would also reflect the properties of FeO_4^-.

3.3. d^2-Systems[1]

FeO_4^{2-} and RuO_4^{2-} are the only known d^2 tetraoxo complexes of group VIII. The ground state configuration is supposed [4] to be $\ldots(t_1)^6(2e)^2$ with the molecular state $^3A_2$ below ^1E and $^1A_1$. Our calculations, by the procedure outlined above, give an average triplet-singlet separation of 0.60 eV and 0.63 eV for FeO_4^{2-} and RuO_4^{2-} respectively, with $^3A_2$ the symmetry of the ground state in each case. All of the energies of the higher occupied orbitals in these anions are positive (Table 4). However, in a crystalline environment the potential field of surrounding cations would be expected to stabilize the molecular orbitals of the anions.

Table 4. Calculated MO energy levels of RuO_4^-, RuO_4^{2-} and FeO_4^{2-}

	RuO_4^- (eV)	RuO_4^{2-} (eV)	FeO_4^{2-} (eV)
$4t_2$	0.95	10.84	11.30
$2e$	-0.45	9.42	9.59
$1t_1$	-2.75	5.68	6.32
$3t_2$	-4.02	4.36	4.56
$3a_1$	-4.82	3.86	3.77
$1e$	-7.28	2.28	3.76
$2t_2$	-8.15	1.44	3.55

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[1] Our main interest in the open shell system RuO_4^-, RuO_4^{2-} and FeO_4^{2-} has been the calculation of excitation energies. For this reason, the effect of spin polarization (Unrestricted Hartree-Fock) on ground state orbital energies has not been considered. Spin polarization was however considered in the calculations of excitation energies, as mentioned in the Method section.

4. Excited States

In 1966, Gray presented a review of the status of spectral assignments for a variety of metal oxyanions including FeO_4^{2-}, RuO_4^- and RuO_4^{2-}, as well as the tetroxides RuO_4 and OsO_4 [8]. The assignments were based on the assumption that the separation of the $2e$ and $4t_2$ levels of MnO_4^{2-} is approximately 2.05 eV [9]. As a consequence, one was led to attribute bands observed at 3.22 eV, 1.57 eV, and 3.05 eV in the spectra of RuO_4^-, FeO_4^{2-} and RuO_4^{2-}, respectively, to the excitation of an electron from the $2e$ level to the $4t_2$ level, i.e. a "*d–d*" transition. Based on our calculations, we reassign the band at 3.22 eV in the RuO_4^- spectrum as arising from a charge transfer transition, $t_1 \rightarrow 2e$ and expect that the crystal field transition, $2e \rightarrow 4t_2$, of RuO_4^- must occur at the much lower energy, 1.38 eV. The recent discoveries of weak band systems starting at 1.24 eV in the spectra of MnO_4^{2-} and some related anions [39, 40] support the reassignments discussed in detail below.

4.1. Electronic Spectrum *of* RuO_4^-

In systems with closely spaced "*d–d*"and charge transfer transitions, the former may be hard to detect due to its much smaller oscillator strength. It is only recently that the "*d–d*" transitions in MnO_4^{2-} [39] and CrO_4^{3-} [40] have been detected at energies much lower than the bands that had previously been assigned to the *d–d* transitions in these species. Spectra of RuO_4^- [19] obtained by a somewhat less sophisticated technique revealed the first observable bands to be at 3.22 eV and 3.99 eV. It is noted that these bands match closely in position and oscillator strength the two charge transfer bands in the spectrum of RuO_4 which occur at 3.22 eV and 4.09 eV [17, 18]. Barring an improbable coincidence, the assignments of these bands for both species ought to be the same (Table 5 and Table 6). Our calculations imply that the *d–d* transition, $2e \rightarrow 4t_2$ occurs at 1.38 eV. The calculated energy 3.33 eV for the $t_1 \rightarrow 2e$ transition and 4.52 eV for the $3t_2 \rightarrow 2e$ transition are in good agreement with the observed bands at 3.22 eV and 3.99 eV, respectively [19]. In Table 5 we present calculated average doublet and quartet excited state energies due to the first six orbital transitions. In Table A1 of the Appendix are shown the number of different molecular states that can arise from the transitions considered in Table 5. The only transitions from the ^2E ground state that are electric dipole allowed are to the $^2T_1$ and $^2T_2$ molecular states.

Table 5. Excited states of RuO_4^-

	Calculated (eV)		Experimental[b]
Spin multiplicity	4	2	(eV)
$2e \rightarrow 4t_2$	—	1.38	—
$t_1 \rightarrow 2e$	2.65	3.33	3.22 (*f*: 0.027)
$3t_2 \rightarrow 2e$	3.86	4.52	3.92 (*f*: 0.037)
$t_1 \rightarrow 4t_2$	4.43	4.56	—
$2a_2 \rightarrow 2e$	4.52	5.20[a]	—
$3t_2 \rightarrow 4t_2$	5.64	5.73	—
$2a_1 \rightarrow 4t_2$	6.29	6.42	—

[a] Dipole forbidden.

[b] Ref. [19].

Table 6. Excited states of RuO_4 and OsO_4

	RuO_4			OsO_4		
	Calculated (eV)		Experimental[b]	Calculated (eV)		Experimental[b]
Spin multiplicity	3	1	(eV)	3	1	(eV)
$t_1 \rightarrow 2e$	1.36	3.38	3.22 (f: 0.020)	1.37	3.34	4.34
$3t_2 \rightarrow 2e$	2.58	4.50	4.09 (f: 0.044)	2.32	4.27	5.21
$2a_1 \rightarrow 2e$	3.33	5.27[a]	—	2.80	5.13[a]	—
$t_1 \rightarrow 4t_2$	2.64	4.65	5.02	3.92	5.85	5.95
$3t_2 \rightarrow 4t_2$	3.84	5.77	5.57	4.87	6.74	6.94
$2a_1 \rightarrow 4t_2$	4.59	6.55	6.43	5.30	7.22	7.93
$1e \rightarrow 2e$	6.60	7.85[a]	—	8.20	10.31[a]	—
$2t_2 \rightarrow 2e$	7.38	8.80	—	7.30	9.40	—
$1e \rightarrow 4t_2$	7.87	9.13	—	10.83	13.31	—
$2t_2 \rightarrow 4t_2$	8.64	10.08	—	9.85	12.05	—

[a] Dipole forbidden. [b] Ref. [18].

Table 7. Excited triplet states of RuO_4^{2-} and FeO_4^{2-}

	FeO_4^{2-}		RuO_4^{2-}	
	Calculated (eV)	Experimental[a] (eV)	Calculated (eV)	Experimental[b] (eV)
$2e \rightarrow 4t_2$	1.70	1.59 (f: 0.009)	1.49	—
$t_1 \rightarrow 2e$	3.06	2.43 (f: 0.035)	3.08	3.05 (f: 0.031)
$3t_2 \rightarrow 2e$	4.89	—	4.47	—

[a] Ref. [12]. [b] Ref. [4].

Table A1. Molecular states due to excited configurations in d^1-complexes

	A_1		A_2		E		T_1		T_2	
Spin multiplicity	2	4	2	4	2	4	2	4	2	4
$(2e)^1$	—	—	—	—	1	—	—	—	—	—
$(4t_2)^1$	—	—	—	—	—	—	—	—	1	—
$(t_1)^5(2e)^2$	—	—	—	—	—	—	2	—	2	1
$(3t_2)^5(2e)^2$	—	—	—	—	—	—	2	1	1	—
$(t_1)^5(2e)^1(4t_2)^1$	2	1	2	1	4	2	4	2	4	2
$(3t_2)^5(2e)^1(4t_2)^1$	2	1	2	1	4	2	4	2	4	2
$(2a_1)^1(2e)^1(4t_2)^1$	—	—	—	—	—	—	2	1	2	1
$(2a_1)^1(2e)^2$	1	—	1	1	—	—	—	—	—	—
$(1e)^3(2e)^2$	1	—	1	—	3	1	—	—	—	—
$(1e)^3(2e)^1(4t_2)^1$	—	—	—	—	—	—	4	2	4	2

4.2. Electronic Spectra of RuO_4 *and* OsO_4

The electronic spectra of RuO_4 and OsO_4 have been extensively investigated in recent years [2, 17, 18] but there is virtually no agreement on the assignments of the observed transitions. In the most recent report, McGlynn and coworkers [18] found five charge transfer bands, in addition to some higher energy Rydberg transitions among oxygen orbitals, for both RuO_4 and OsO_4. It was assumed that the separation of the $2e$ and $4t_2$ levels is greater than 3.5 eV. As a consequence all five transitions were assigned as transitions to the $2e$ level. Our calculations suggest

Table A2. Molecular states due to excited configurations in d^0-complexes

Spin multiplicity[a]	A_1		A_2		E		T_1		T_2	
	1	3	1	3	1	3	1	3	1	3
$(t_1)^5(2e)^1$	—	—	—	—	—	—	1	1	1	1
$(3t_2)^5(2e)^1$	—	—	—	—	—	—	1	1	1	1
$(t_1)^5(4t_2)^1$	—	—	1	1	1	1	1	1	1	1
$(3t_2)^5(4t_2)^1$	1	1	—	—	1	1	1	1	1	1
$(2a_1)^1(2e)^1$	—	—	—	—	1	1	—	—	—	—
$(2a_1)^1(4t_2)^1$	—	—	—	—	—	—	—	—	1	1
$(1e)^3(2e)^1$	1	1	1	1	1	1	—	—	—	—
$(1e)^3(4t_2)^1$	—	—	—	—	—	—	1	1	1	1

[a] Singlets and Triplets

Table A3. Molecular states due to excited configurations in d^2-complexes

Spin multiplicity	A_1			A_2			E			T_1			T_2		
	1	3	5	1	3	5	1	3	5	1	3	5	1	3	5
$(2e)^2$	1	—	—	—	1	—	1	—	—	—	—	—	—	—	—
$(2e)^1(4t_2)^1$	—	—	—	—	—	—	—	—	—	1	1	—	1	1	—
$(t_1)^5(2e)^3$	—	—	—	—	—	—	—	—	—	1	1	—	1	1	—
$(3t_2)^5(2e)^3$	—	—	—	—	—	—	—	—	—	1	1	—	1	1	—
$(t_1)^5(2e)^2(4t_2)^1$	2	3	—	2	2	1	4	5	1	4	5	1	4	5	1
$(3t_2)^5(2e)^2(4t_2)^1$	2	2	1	2	3	—	4	5	1	4	5	1	4	5	1
$(2a_1)^1(2e)^2(4t_2)^1$	—	—	—	—	—	—	—	—	—	2	3	1	2	2	—
$(2a_1)^1(2e)^3$	—	—	—	—	—	—	1	1	—	—	—	—	—	—	—
$(1e)^3(2e)^3$	1	1	—	1	1	—	1	1	—	—	—	—	—	—	—
$(1e)^3(2e)^1(4t_2)^1$	—	—	—	—	—	—	—	—	—	4	5	1	4	5	1

a reassignment in which transitions to both $2e$ and $4t_2$ levels take place. The calculated average energies for triplet and singlet excited states for RuO_4 and OsO_4 are presented in Table 6. The number of different molecular states that can arise from transitions considered in Table 6 are shown in Table A2 of the Appendix. Except for the first two transitions of OsO_4 where a deviation of about 1 eV is experienced, the agreement between calculated and experimental transition energies is quite good. The only electric dipole allowed transitions from the $^1A_1$, ground state are to the $^1T_2$ excited states.

4.3. *Electronic Spectra of* FeO_4^{2-} *and* RuO_4^{2-}

The electronic spectrum of FeO_4^{2-} [12] shows two bands; a weak band (f: 0.009) at 1.59 eV and a stronger band (f: 0.035) at 2.43 eV. Our calculations support the assignments [12] of these bands to the orbital transitions, $2e \rightarrow 4t_2$ ($^3A_2 \rightarrow {}^3T_1$) and $t_1 \rightarrow 2e$($^3A_2 \rightarrow {}^3T_1$), respectively. The energies of the corresponding transitions of RuO_4^{2-} are calculated to be 1.49 eV ($2e \rightarrow 4t_2$) and 3.08 eV ($t_1 \rightarrow 2e$). Although the former band has not been observed, the latter value is in excellent agreement with the position of the single observed band of the RuO_4^{2-} spectrum which is 3.05 eV (f: 0.031) [4].

The calculated excited state energies are given in Table 7. In Table A3 of the Appendix are shown the number of different low lying molecular states that can arise for d^2 complexes.

5. Conclusions

By use of the HFS-DVM method we have been able to correlate in a consistent manner most of the observed features of the photoelectron and optical spectra of the known tetraoxo complexes of the group VIII transition metals. For all systems the order of the higher valence orbitals is $2t_2 < 1e < 2a_1 < 3t_2 < t_1 < 2e < 4t_2$. The results of the calculations lend support to the assignment of a rather low value (1.59 eV) for the separation of the $2e$ and $4t_2$ levels in FeO_4^{2-} and lead one to predict similar values for RuO_4^{2-} (1.49 eV) and RuO_4^- (1.38 eV).

The HFS-DVM method appears to be well suited for nearly quantitative calculations on transition metal complexes. The origin of some deficiencies, for example, the poor calculated ionization potentials for the $1e$ level of RuO_4 and OsO_4 (Table 3), may be attributed to the use of the INDO method and Mulliken population analysis to construct the initial charge densities, $\varrho_g(1)$. This will be investigated by performing a complete SCF calculation.

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