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Ab Initio Theoretical Study on Geometries, Chemical Bonding, and Infrared and Electronic Spectra of the $M_2O_7^{2-}$ (M = Cr, Mo, W) Anions

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An *ab initio* SCF theoretical study has been carried out on the optimized geometries, atomic populations, electron densities, and infrared/electronic spectra of the $M_2O_7^{2-}$ anions (M = Cr, Mo, W) using various basis sets of different quality. The results concerning geometrical arrangements and electron densities are analyzed and rationalized, and the most important bands of infrared and electronic spectra are assigned and compared with experiment. Theoretical results are in fair agreement with experimental data, when available, and serve as predictions otherwise.

Introduction

Experimental studies of solid-state dichromate and dimolybdate salts are found abundantly in the literature, the characterization of the $M_2O_7^{2-}$ (M = Cr, Mo) unit having been carried out by means a number of methods. For dichromates, geometry elucidation studies have been performed for $(NH_4)_2Cr_2O_7$,[1] $K_2Cr_2O_7$,[2] and $Rb_2Cr_2O_7$.[3,4] Furthermore, experimental vibrational spectra are available for $(NH_4)_2Cr_2O_7$, $Na_2Cr_2O_7$, $K_2Cr_2O_7$,[5,6] and $(PyH)_2Cr_2O_7$.[7] Finally, electronic spectra are available for $K_2Cr_2O_7$ in potassium halide matrices[6] and for $(PyH)_2Cr_2O_7$.[7] As to dimolybdates, geometry and infrared spectra have been elucidated for several organic $R_2Mo_2O_7$ compounds.[8–10] For dichromates, experimental evidence dictates that the $Cr_2O_7^{2-}$ unit has a nonlinear Cr–O–Cr angle.[1–4] In contrast, at least one dimolybdate has been found featuring a linear Mo–O–Mo angle;[10] this linear structure corresponds to a $(PPN)_2Mo_2O_7$ salt (PPN: $Ph_3P{=}N^+{=}PPh_3$). However, a question is made as to whether substituting Mo by Cr would render the M–O–M angle linear. Finally, to our knowledge, no experimental data for ditungstates are available.

From a theoretical point of view, vibrational spectra and force constants calculations have been limited to several $Cr_2O_7^{2-}$ salts[11] through the analysis of the factor group and site analysis and the use of normal coordinates with different idealized symmetries. Mention must be made here of a recent review on the spectroscopy of chromium(VI) species.[12]

In contrast to the scarcity of theoretical studies on $X_2O_7^{2-}$, the last few years have seen an outgrowing number of applications of quantum-mechanical methods not only to inorganic and organometallic structure but also to the reactivity of these chemical systems.[13,14] For instance, geometries and vibrational frequencies have been recently calculated from an *ab initio* SCF study on $LiClO_4$ and Li_2SO_4,[15] on the coordination structures of $M^+XY_3^-$ and $M^+XY_4^-$ ion pairs,[16] on molecule–cluster models,[17] and on transition metal dimers.[18] Another nice example involves the full characterization of the Wilkinson catalyst mechanism, which has been elucidated through *ab initio* methods.[19] Such a methodology has been also used to study molecular hydrogen and hydride transition metal complexes,[20,21] borohydride complexes,[22] metallocycles,[23] polynuclear complexes,[24] and the vibrational frequencies of small inorganic and organometallic compounds.[25] Using the semiempirical INDO method as modified by Bacon and Zerner,[26] the force constants for several transition metal ion–ligand bonds have been calculated, a good agreement with vibrational spectroscopic data having been found.[27] Finally, density functional theory (DFT) has been used to compute vibrational frequencies of several organometallic compounds.[28] The outcome of this presently growing amount of theoretical studies is that quantum chemistry has reached a stage where at least semiquantitative structural and spectroscopic determinations can be made (for recent reviews see refs 29 and 30), in such a

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Table I. Optimized Geometries (in Å and deg) for the M_7^{2-} Species, Where O_C and O_T Stand for Central and Terminal Oxygens, Respectively

species	basis set	$d_{M\text{-}O_C}$	$d_{M\text{-}O_T}$	$d_{M\text{-}M}$	∠M–O–M	energy (au)
$Cr_2O_7^{2-}$	A	1.688	1.547	3.376	180.0	–2597.3389
	B	1.711	1.559	3.423	180.0	–2606.7331
	C	1.721	1.560	3.441	180.0	–2597.1898
	D	1.766	1.620	3.225	131.9	–539.8418
	E	1.819	1.513	3.409	139.2	–543.4611
	exptl	1.76–1.81	1.56–1.64	3.11–3.20	122–130	
$Mo_2O_7^{2-}$	A	1.878	1.729	3.756	180.0	–8442.4710
	B	1.892	1.734	3.783	180.0	–8467.0224
	D	1.868	1.735	3.736	180.0	–536.2005
	E	1.898	1.632	3.796	180.0	–539.8449
	exptl	1.82–1.95	1.68–1.79		153,180	
$W_2O_7^{2-}$	D	2.084	1.918	4.167	180.0	–534.9230
	E	2.112	1.905	3.995	142.1	–538.3930

way that quantum chemistry has become a valuable complementary tool in the structural characterization of inorganic compounds.

As mentioned above, the amount of experimental data on IR and UV/visible spectra of $M_2O_7^{2-}$ is scarce. Thus, the main purpose of the present paper is to carry out a preliminar theoretical study of the electronic and geometric structure of the isolated $Cr_2O_7^{2-}$, $Mo_2O_7^{2-}$, and $W_2O_7^{2-}$ dianions, along with their vibrational and electronic spectra. A secondary goal of this study is to discuss the quality of the basis sets used and the validity of the approximations introduced.

In the next section we will present the methodology used to actually carry out calculations, while in the forthcoming sections the results obtained will be discussed.

Methodology

Energy calculations have been carried out using an *ab initio* molecular orbital method at the closed-shell SCF level of theory, because the big size of the systems considered in this paper and the need to optimize geometries and compute frequencies prevents use of correlated wavefunctions.

Earlier *ab initio* studies on inorganic compounds have revealed that correct choice of the basis set is quite important.[20-24] The present study has used several basis sets that have proved to yield good geometrical results for this kind of compounds, namely Huzinaga's minimal basis sets (MINI-1 and MINI-4),[31] Hehre's extended basis set[32] (termed 3-21G), and Hay's basis set incorporating pseudopotentials[33] to account for the inner electrons. Natural population analyses (NPA) have been carried out by the method of Weinhold et al.[34] implemented as an extra link in the Gaussian 90 program.[35]

Full geometry optimizations have been always carried out, Schlegel's method requiring analytical gradients having been used.[36] Infrared spectra (frequencies and intensities) have been computed using the doubly harmonic approximation. Frequencies and normal modes have been calculated through diagonalization of the mass-weighted matrix of energy second derivatives. In turn, line intensities have been made proportional to the square of the derivative of the molecular dipole moment with respect to the respective normal mode. For all-electron calculations (involving MINI and extended basis sets), second derivatives have been calculated analytically. In contrast, second derivatives in pseudopotential calculations have been computed as finite differences of analytical first derivatives, which resulted in long computing times. Electronic spectra have been calculated through a single-excitation configuration interaction,[37] including the first 25 monoexcited configurations. Calculations mentioned in this paper have been carried out by means of differents versions of the Gaussian program.[35]

For the sake of clarity, we will label the basis sets used in this paper as follows: (A) Huzinaga's MINI-1 minimal basis set;[31] (B) Huzinaga's MINI-4 minimal basis set;[31] (C) Hehre's extended basis set;[32] (D) Hay's minimum valence basis set on the metal and effective core potential (ECP)[33] to represent its inner electrons, together with the MINI-1 basis set for the oxygens; and (E) Hay's double-ζ valence basis set and ECP on the metal, together with the 6-31G* basis set for the oxygens. Taking into account the quality of the results obtained for Cr and the increase in the number of electrons when increasing the atomic number, not all basis sets listed above have been utilized for calculations involving the Mo and W atoms.

Results and Discussion

For the three species considered in this paper, we have tried several starting points in the search procedure to locate an energetic minimum. However, only one minimum has been found for each basis set and metal. Only in the case of $Mo_2O_7^{2-}$ has a linear M–O–M angle always been found. For $Cr_2O_7^{2-}$ and $W_2O_7^{2-}$ different structures, either linear or angular, have been found depending on the particular basis set. Furthermore, it is interesting to mention that the lateral oxygens in optimized angular $Cr_2O_7^{2-}$ species, adopt a nearly eclipsed conformation, whereas $Mo_2O_7^{2-}$ and $W_2O_7^{2-}$ species show a staggered conformation.

A. Geometrical Analysis. In Table I we have collected the optimized geometrical parameters of the $M_2O_7^{2-}$ species together with experimental data when available. The structure of one of these compounds together with the definition of the geometrical parameters can be seen in Figure 1. At first sight, one can notice that (a) M–O distances increase along the Cr–Mo–W series and that (b) central M–O bonds (M–O_C) are fairly longer than terminal M–O bonds (M–O_T). Comparison with experiment emergers as particularly interesting because one can extract that a first meaningful parameter to test the quality of the calculation is the M–O–M angle. Thus, in a geometrical sense, the behavior of a given basis set and the quality of its results can be tested according to the value obtained for this parameter.

For $Cr_2O_7^{2-}$, different structures are found depending on the basis set: all-electron basis sets (A–C) give linear Cr–O–Cr angles, and compared with the experimental Cr–O bonds, shorter Cr–O distances are always found. The incorrect behavior of this type of basis set may be due to the fact that it is unbalanced: the metal atoms are described more poorly than the oxygens, so the valence shell of the oxygens is better described than the valence shell of chromium atoms, and hence the maximum overlap between the central oxygen and the two chromium atoms is reached when a linear structure is adopted, shorter Cr–O distances being found. The correct behavior is found for basis sets containing pseudopotentials to account for inner electrons of metal atoms (D and E): they yield angular structures, the Cr–O–Cr angle being fairly

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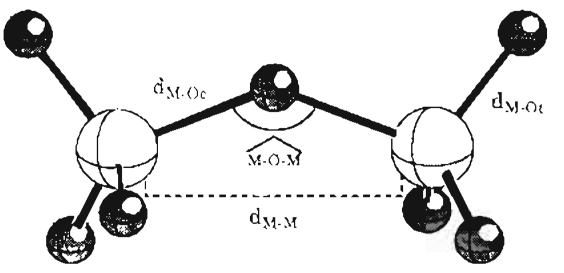

Figure 1. Adopted structure of $Cr_2O_7^{2-}$ species with basis set E and definition of the geometrical parameters used throughout the paper.

close to the experimental value. Basis set E is far larger (i.e., more expensive) than basis set D; however, if the results obtained for Cr–O distances are considered, results using basis set D lie always within the range of experimental values. This fact could be explained by the existence of a compromise in the description of both types of atoms by this basis set. Thus, although D is a modest basis set, very good geometrical results are obtained in a cheaper way. From basis set E, good results are obtained too; perhaps the most significant point, apart from a slightly open Cr–O–Cr angle, is the rather short length of the Cr–O_T bond. A nice explanation can be found in a previous work on MnO_4^-,[38] which showed that Hartree–Fock geometry optimizations can cause a source of error due to the exclusion of a nondynamical correlation correction: the fact that the 3d shell does not extend spatially beyond the 3s/3p shell is responsible for the weak metal–oxygen interaction, resulting in large M–O distances.[38,39] Basis sets D and E consider the 3d shell as the only metal valence shell, the 3s/3p shell being considered corelike in the ECP approximation; thus, here the Cr–O_T distance obtained is shorter than could be expected from a Hartree–Fock calculation with an all-electron basis set of the same quality. Furthermore, as shown in Figure 1, the $Cr_2O_7^{2-}$ structure adopts twists of about 7–9° away from an exactly eclipsed conformation, values that lie within the range of twists of 5–10° observed experimentally.[2]

For $Mo_2O_7^{2-}$, calculations have been done using all basis sets listed above except basis set C due to the fact that, from the experience acquired in the earlier $Cr_2O_7^{2-}$ calculations, the quality/cost ratio of results did not justify its use. From Table I one can see that all basis sets used yield linear Mo–O–Mo angles. Noteworthy, although experimentally some angular $Mo_2O_7^{2-}$ structures have been found, at least one work has obtained a linear structure.[10] Thus, experimental results show that the Mo–O–Mo angle is closer to linearity than the Cr–O–Cr angle; this fact is well reflected in our theoretical results. Further, all Mo–O distances agree very well within the experimental range, although again, as for Cr–O_T distances, basis set E gives shorter Mo–O_T distances.

For $W_2O_7^{2-}$ only basis sets D and E have been used, given the good results obtained in above calculations on $Cr_2O_7^{2-}$ and $Mo_2O_7^{2-}$, and the large number of electrons in this system, which makes all-electron basis sets impractical. Here, although basis set D yields a linear W–O–W angle, an angular structure is obtained with basis set E. Because no experimental data are available, no conclusive results but only predictions can be issued; according to the results obtained one would expect that $W_2O_7^{2-}$ compounds have a W–O–W angle more opened than Cr–O–Cr but less than Mo–O–Mo. In the same way, W–O distances are likely to be found within the experimental range.

In summary, we have computed geometries that agree fairly well with experimental data. Errors can still be present due to basis set incompleteness and to the neglect of electron correlation; this notwithstanding, it has been noted that the errors in Hartree–Fock calculations owing to the lack of nondynamical correlation are generally smaller for second and third row metals.[40,41] This could explain the fact that all basis sets used for $Mo_2O_7^{2-}$ give Mo–O distances within the experimental range, so the results obtained for $W_2O_7^{2-}$, except perhaps for the W–O–W angle, are correct enough to be predictive.

Table II. Atomic Charges Calculated through a Mulliken Population Analysis (MPA) and a Natural Population Analysis (NPA) for the Three $M_2O_7^{2-}$ Species Where M Stands for the Metal Atom and O_C, O_T, and $O_{T'}$ Stand for Central and Terminal Oxygens, Respectively

		$Cr_2O_7^{2-}$		$Mo_2O_7^{2-}$		$W_2O_7^{2-}$	
basis set	atom	MPA	NPA	MPA	NPA	MPA	NPA
A	M	+1.573		+1.563			
	O_C	−0.914		−0.834			
	O_T	−0.705		−0.728			
B	M	+1.427		+1.580			
	O_C	−0.852		−0.842			
	O_T	−0.667		−0.731			
C	M	+1.433					
	O_C	−0.934					
	O_T	−0.660					
D	M	+0.736	+1.484	+0.962	+1.752	+0.699	+1.687
	O_C	−0.656	−0.933	−0.693	−1.001	−0.596	−1.004
	$O_{T'}$	−0.480	−0.690	−0.538	−0.750	−0.467	−0.728
	O_T	−0.464	−0.664	−0.538	−0.750	−0.467	−0.728
E	M	+1.455		+1.876		+1.729	
	O_C	−1.043		−1.142		−0.969	
	$O_{T'}$	−0.660		−0.768		−0.739	
	O_T	−0.637		−0.768		−0.753	

B. Population and Density Analyses. Atomic charges Q_α can be computed by the widely used Mulliken population analysis (MPA) as an outcome of the SCF wave function through the formula $Q_\alpha = Z_\alpha - \sum_{\mu\in\alpha}(PS)_{\mu\mu}$. However, a recent refinement has emerged as a powerful alternative, namely the so-called natural population analysis (NPA),[34] which shares with the Mulliken method its low computer cost and seems to overcome the basis set dependence, one of the most serious limitations of the MPA.

In Table II we have gathered the results of the MPA for the three species studied and for the various basis sets utilized. However, NPA has been performed for basis set D because no meaningful results were obtained from the MPA with this basis set. At first glance, the most significant points that one can notice are that (a) either MPA (excluding the results obtained with basis set D) or NPA charges seem to leave the metal atoms with a formal charge of ca. +2 au, the central oxygens with ca. −1 au, and the terminal oxygens with ca. −0.7 au, the central oxygens being always more negative than the terminal ones, since they withdraw electronic charge simultaneously from two metal atoms, (b) the charges obtained from NPA with basis set D and from MPA with basis set E are almost the same, and (c) if one takes these last two analyses as the most correct results, one can obtain an ordering of the tendency of the metal atom to accept electrons from the ligand. As it stands, the ordering established has been Mo < W < Cr. A qualitative interpretation of this ordering can be made according to well-known classical inorganic considerations:[42] Mo should accept less electron density from oxygen than Cr because the tendency to accept electrons decreases with the increase in atomic weight. However, going further to W involves apparition of the inner *f* electrons, which implies more ability to accept electrons from oxygen than could be expected. Thus, the ordering obtained theoretically seems to be correct.

When the ordering arising from population analyses (Mo < W < Cr) is compared with the ordering obtained above for the M–O–M angle from the geometrical analysis (M = Mo > W > Cr), it is clear that a relationship between both can be

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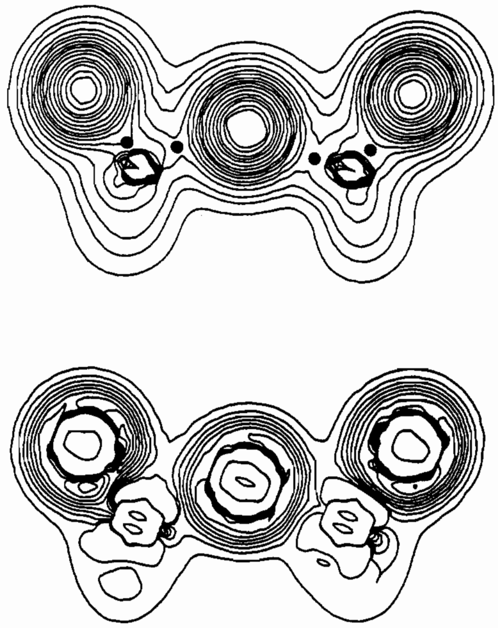

Figure 2. Electron isodensity contour map (top) and Laplacian of the charge density (bottom) in an for the $Cr_2O_7^{2-}$ species in the Cr–O–Cr plane, computed using basis set E. Values of $\rho(\vec{r})$ at the bond critical points are shown in Table V.

Table III. Density Values (in $Å^{-3}$) at the Bond Critical Points Found between the Metal and the Central Oxygen (M–O_C) and between the Metal and Terminal Oxygens (M–O_T) from the Isodensity Contour Maps

	M–O_C		M–O_T	
species	D	E	D	E
$Cr_2O_7^{2-}$	0.83	0.36	1.28	0.51
$Mo_2O_7^{2-}$	0.70	0.27	1.00	0.59
$W_2O_7^{2-}$	0.50	0.32	0.76	0.40

established: the more tendency to accept electrons the metal has, the more angular the structure is. Thus, accumulation of electron density along the M–O_C bonds could be an important factor to take into account when searching for an explanation of the particular structure adopted by a given species.

Although information furnished by population analyses is highly valuable, a deeper study is needed to fully understand the electronic details. For this purpose electron density $\rho(\vec{r})$ contour maps are presented in Figure 2. One must realize that while $\rho(\vec{r})$ is a physical observable, atomic charges are not. For instance, electron densities can be obtained from X-ray diffraction patterns or by Fourier projections.[1] Furthermore, the electron density can be used to carry out a variety of analyses, of which the most interesting one is due to Bader, who has exploited the topological properties of the electron density.[43] Figure 2 depicts, in a plane containing the maximum possible number of atoms, the isodensity contour (top) and the Laplacian of the charge density (bottom) for the $Cr_2O_7^{2-}$ species using basis set E. The isodensity map shows clearly nuclei (with concentric lines around them), and bond critical points (BCP, marked with a dot). These last points have a minimum value of the density along a line connecting two nuclei, but exhibit a density maximum in a direction orthogonal to that line (i.e., they are saddle points in a two-dimensional density surface). The BCP obtained using basis sets D and E are collected in Table III, and show that these two basis sets share the fact that the outer BCP value is always larger than the inner BCP value. However, whereas for basis set D both types of metal–oxygen bonds become weaker when the atomic number of the metal is increased, for basis set E the larger the BCP value for M–O_C, the more angular is the species, thus agreeing very well with the population results reported above. In fact, the different ordering in the BCP values is consistent with the population analysis performed for each basis set.

Table IV. Main Two Vibrational Frequencies (in cm^{-1}) for the Three $M_2O_7^{2-}$ Species Studied

		basis set					
species	description	A	B	C	D	E	exptl
$Cr_2O_7^{2-}$	ν_{as}(Cr–O–Cr)	1119	1025	1019	922	732	737–796
	ν_{as}(Cr–O_3)	1262	1200	1174	1113	837	924–966
					1120	859	
					1133	869	
$Mo_2O_7^{2-}$	ν_{as}(Mo–O–Mo)	998	942		1030	781	783–795
	ν_{as}(Mo–O_3)	1095	1054		1145	831	880–885
$W_2O_7^{2-}$	ν_{as}(W–O–W)				900	774	
	ν_{as}(W–O_3)				921	804	
						807	
						811	
						814	

Another remark on the density analysis concerns the characteristics of the metal–oxygen bond. Given the differences in the electronegativities between the two atoms, one might think that the M–O bond has mainly an ionic character. To check this idea, we have computed the Laplacian of the charge density $\nabla^2\rho(\vec{r})$ (Figure 2, bottom). For the sake of simplicity, only positive values have been depicted; however, they suffice to see that, according to the interpretation provided by Bader,[43] our theoretical results indicate that all metal–oxygen bonds have mainly an ionic character because no negative values of the Laplacian are found between the bonded atoms.

It is possible to compare these theoretical results with experimental densities of the $Cr_2O_7^{2-}$ unit arising from a Fourier projection.[1] Although the experimental data are not very explicit, qualitative agreement with our results is apparent.

C. Infrared Spectra. The infrared spectra of the three species studied in this paper have been calculated for the various basis sets described above. These theoretical results are compared with experimental data, if available ($Cr_2O_7^{2-}$ and $Mo_2O_7^{2-}$), and serve as predictions otherwise ($W_2O_7^{2-}$).

In Table IV we gather the values for the two main frequencies of the three species, depending on the basis set employed. For $Cr_2O_7^{2-}$, one observes a decrease in the line frequencies when improving the quality of the basis set. This trend has already been systematically studied for a series of small molecules.[44] However, for $Mo_2O_7^{2-}$ this is not true due to the erratic values of Mo–O distances optimized with each basis set. Comparing our results with experimental data,[8-10] Huzinaga's basis sets (A and B) always give frequencies that are too large; in $Cr_2O_7^{2-}$, the slight improvement in the results obtained with the all-electron extended basis set C does not, in our opinion, compensate for the longer computing time. Finally, the quality of the results obtained with the Cr valence-electron ECP basis sets (D and E) differs substantially: while results using D do not improve significantly the results obtained with all-electron basis sets, basis set E gives values for the frequencies that are extremely close to the experimental data, so we will focus our attention in these last results. Thus, in Figure 3 we have depicted the vibrational spectra of the three species using basis set E. One can always see two intense lines corresponding to the M–O–M stretching (the most intense line) and to the terminal M–O stretching, whose values have been shown in Table IV. Although our theoretical results are in very good agreement with the experimental data available for $M_2O_7^{2-}$, one can think that the $M_2O_7^{2-}$ ion consists of two slightly distorted tetrahedra sharing one corner. Thus, in a first approximation it is possible to compare the M–O stretching of the MO_4^{2-} species with the terminal M–O stretching of the $M_2O_7^{2-}$ system. Experimental data are indeed available for the MO_4^{2-}

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(44) Yamaguchi, Y.; Frisch, M. J.; Gaw, J.; Schaefer, H. F.; Binkley, J. S. *J. Chem. Phys.* **1991**, *84*, 2262.

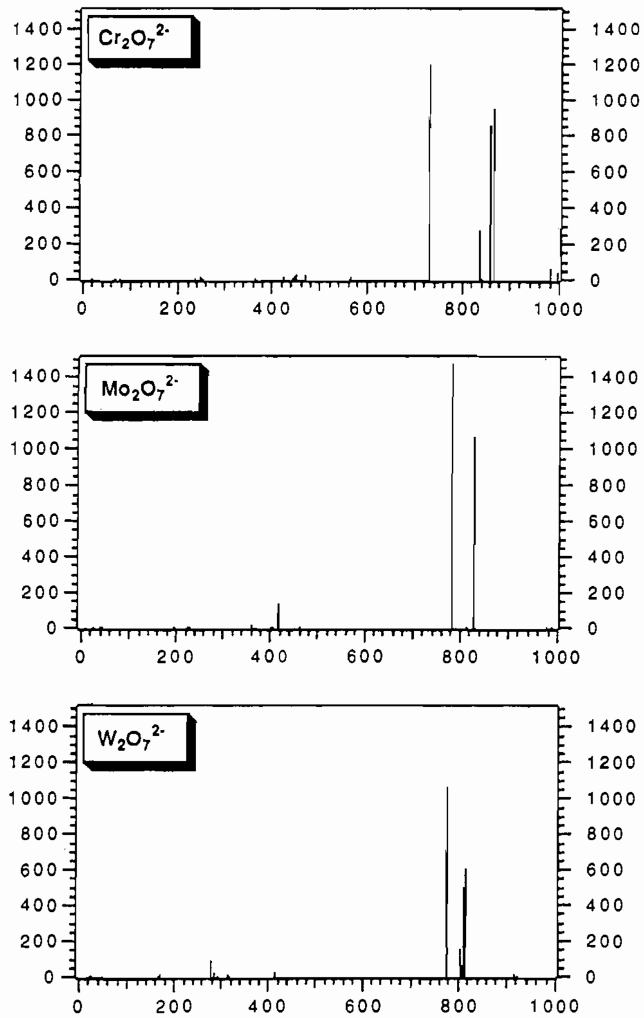

Figure 3. Vibrational spectra (ν in cm^{-1} and I in km/mol) of the three $M_2O_7^{2-}$ species, computed by means of basis set E.

species:[45,46] for CrO_4^{2-}, the Cr–O asymmetric stretching (876–896 cm^{-1}) correlates well with the data in Table IV (837–869 cm^{-1}); for MoO_4^{2-}, the Mo–O stretching (830–844 cm^{-1}) correlates well, too, with the data in table IV (831 cm^{-1}); finally, for WO_4^{2-} the W–O stretching (830–841 cm^{-1}) is in good agreement with the terminal W–O asymmetric stretching for $W_2O_7^{2-}$ (804–814 cm^{-1}). Due to the lack of experimental data for $W_2O_7^{2-}$, this last result is quite important because it gives a first estimation of the terminal W–O stretching.

A comment can be made about two other IR bands. (a) For the M–O–M symmetric stretching calculated, with basis set E, we obtain for $Cr_2O_7^{2-}$ a line at 566 cm^{-1}, which agrees with the experimental range (550–567 cm^{-1}); for $Mo_2O_7^{2-}$, we obtain a line at 417 cm^{-1}, which correlates well with the experimental range (450–460 cm^{-1}); for $W_2O_7^{2-}$, one can expect that the line at 412 cm^{-1} is a good result. (b) A good agreement is found for the bridge bending line: experimental data are only available for $Cr_2O_7^{2-}$ (218–255 cm^{-1}) and are in very good agreement with our theoretical results (247 cm^{-1}); for $Mo_2O_7^{2-}$ and $W_2O_7^{2-}$ lines at 360 and 283 cm^{-1} are predicted, respectively.

It must be stressed that more correct results should be obtained through use of more extended basis sets, anharmonicity corrections, and introduction of correlation energy. These three aspects are unaddressable for this kind of inorganic compounds with our current computing power. In addition, condensed phase effects could be important in comparing experimental results with theoretical calculations.

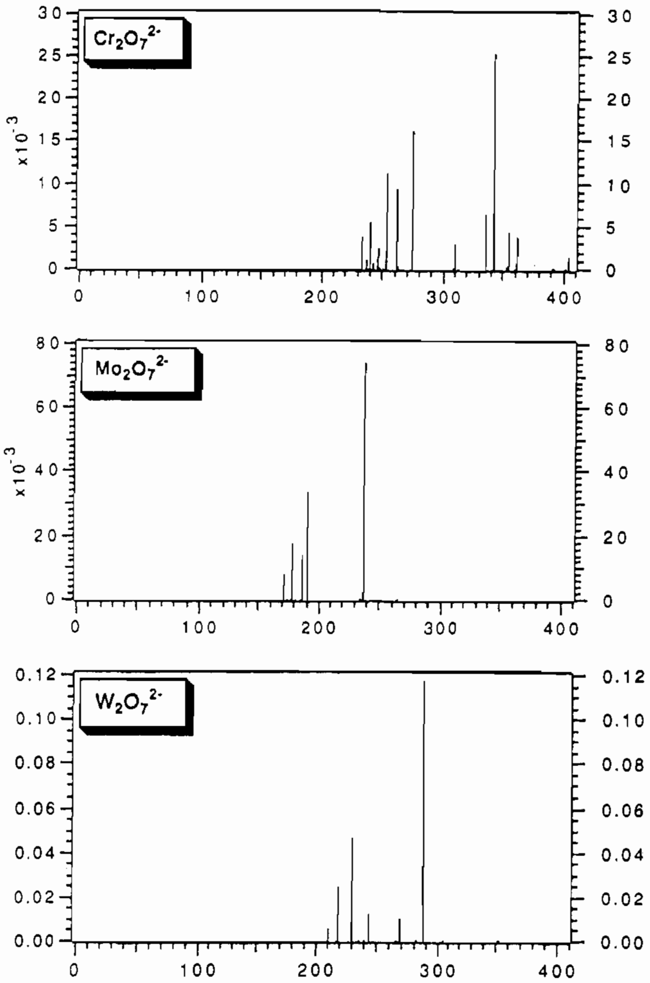

Figure 4. Electronic spectra (λ in nm together with oscillator strength) of the three $M_2O_7^{2-}$ species, computed by means of basis set D.

Table V. Peak Positions (in nm) for the Electronic Transitions of the Three $M_2O_7^{2-}$ Species

		transition		
species	basis set	$t_1^6 \rightarrow t_1^5 e^1$	$t_1^6 \rightarrow t_1^5 t_2^1$	$t_1^6 \rightarrow t_1^5 t_2^1$
$Cr_2O_7^{2-}$	A	263	228	209
	B	287	244	220
	D	343	275	262,253
	exptl	365–375	268–275	248–260
$Mo_2O_7^{2-}$	A	263	202	
	B	269	206	
	D	237	190,187	178
$W_2O_7^{2-}$	D	287	230	219

D. Electronic Spectra. The electronic spectra for the $Cr_2O_7^{2-}$ has been already resolved experimentally [6,7,12,47]. Formally, we can consider the $M_2O_7^{2-}$ complexes as d^0, in which the metal and oxygen atoms are charged as $(M_2)^{12+}(O_7)^{14-}$, which implies O^{2-} ligands. However, as can be deduced from the previous population analyses, the charge distribution in $M_2O_7^{2-}$ is not so extreme as suggested by the formal charges but is closer to $(M_2)^{4+}(O_7)^{6-}$. Thus, if we consider that the formal electronic configuration of the metal atoms is d^0, no d–d transitions can take place, and the color of these species cannot originate this way. On the contrary, the intense colors of these kind of complexes are attributed to a charge-transfer transition in which an electron is transferred from orbitals that have a predominant ligand character to orbitals that have a predominant metal character. Thus, the transition is classified as a ligand-to-metal charge-transfer (LMCT) transition. In fact, charge-transfer bands in

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(47) Miskowski, V.; Gray, H. B.; Ballhausen, C. J. *Mol. Phys.* **1974**, *28*, 729.

the visible region of the spectrum may occur if the ligands have lone pairs of relatively high energy (as in oxygen) or if the metal has low-lying empty orbitals; a lone pair electron of oxygen (a nonbonding oxygen-localized 2p π level) is promoted to the antibonding low-lying empty d metal orbital, i.e., $M(nd\ e^*) \leftarrow O(\pi t_1)$.

In Table V we have collected the most important transitions obtained from a configuration interaction singles (CIS) calculation. From this table, comparison of theoretical and experimental electronic spectra of the $Cr_2O_7^{2-}$ merits special mention, because it is the only system for which experimental data are available. As one can see, theoretical electronic transitions obtained from basis set D agree fairly with the experimental spectrum and, as occurs with geometrical parameters, basis set D seems to be well compensated. Thus, although basis set D is a modest basis set and the geometrical structure obtained for $W_2O_7^{2-}$ does not agree with that obtained using the larger basis set E, the quality of the results obtained for the $Cr_2O_7^{2-}$ species with this basis set allows us to omit the calculation of the electronic spectra with basis set E; such a calculation would require a huge amount of computing time and memory usage. Thus, if the transitions obtained for $Mo_2O_7^{2-}$ and $W_2O_7^{2-}$ species are considered, predictions can be issued to compensate the lack of experimental data.

To give an idea of the appearance of the electronic spectra of the studied species, we have depicted in Figure 4 their calculated spectra with basis set D. One must look these pictures carefully, taking into account that the heights of the peaks do not represent the absorbance intensity of the transition but the oscillator strength, which is a parameter that is proportional to the area below the UV–visible band.

Focusing our attention on this figure gives rise to interesting qualitative conclusions. The bigger band of the $Cr_2O_7^{2-}$ electronic spectrum at 343 nm (in very good agreement with the 365–375-nm experimental band) suggests that the color of dichromate salts will be yellow–light red, as is well known experimentally; from the $Mo_2O_7^{2-}$ spectrum, the stronger band at 237 nm suggests that dimolybdate salts will be uncolored; finally, and maybe most important, the band at 287 nm from the $W_2O_7^{2-}$ spectrum permit us to predict that ditungstate salts will be uncolored–light yellow. In fact, these color considerations are consistent with the trend in LMCT explained above, that the energies of the transitions ($Cr < W < Mo$) correlate with the order of the electrochemical series, with the lowest energy transitions taking place to the most easily reduced ions ($Cr > W > Mo$); this result was already observed when population analyses were presented. This correlation is consistent with the transition being the transfer of an electron from the ligands to the metal, which corresponds, in fact, to the reduction of the metal ion by the ligands.

In conclusion, we have shown in the present paper that geometrical data, infrared spectra, and electronic spectra can be predicted and rationalized from *ab initio* MO calculations if a basis set of good enough quality is employed. As to geometrical results, we have shown that the extended basis set does not improve the results of the MINI-4 basis set, yet is considerably more expensive. With a similar expenditure of computing time, central memory usage and disk input/output, pseudopotential basis sets clearly outperform minimal and split-valence all-electron basis sets. Extended all-electron basis sets could indeed be used, but would become prohibitive given the large number of electrons. For W, the requirement of f functions further increases computing time of all-electron basis sets. Finally, one should bear in mind that these calculations correspond to gas-phase results; comparisons with condensed-phase experiments must be done with some care.

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