

## A new interpretation of the bonding and spectroscopy of the tetraoxoferrate(VI) $\text{FeO}_4^{2-}$ ion

Abdalla Al-Abdalla, Luis Seijo, and Zoila Barandiarán

Citation: *The Journal of Chemical Physics* **109**, 6396 (1998); doi: 10.1063/1.477283

View online: <http://dx.doi.org/10.1063/1.477283>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/109/15?ver=pdfcov>

Published by the [AIP Publishing](#)

---

### Articles you may be interested in

[Restricted active space calculations of L-edge X-ray absorption spectra: From molecular orbitals to multiplet states](#)

*J. Chem. Phys.* **141**, 124116 (2014); 10.1063/1.4896373

[Computational studies on the ground and excited states of  \$\text{BrOOBr}\$](#)

*J. Chem. Phys.* **124**, 204309 (2006); 10.1063/1.2197831

[Theoretical study of the photoinduced transfer among the ground state and two metastable states in  \$\[\text{Fe}\(\text{C}\_5\text{N}\_5\text{O}\)\]^{2-}\$](#)

*J. Chem. Phys.* **122**, 074314 (2005); 10.1063/1.1851975

[The nature of metal-oxide chemical bond: Electronic structure of  \$\text{PdMgO}\$  and  \$\text{PdOMg}\$  molecules](#)

*J. Chem. Phys.* **107**, 7345 (1997); 10.1063/1.474973

[A study of the structure and bonding of small aluminum oxide clusters by photoelectron spectroscopy:  \$\text{Al}\_x\text{O}\_y^-\$  \( \$x=1-2\$ ,  \$y=1-5\$ \)](#)

*J. Chem. Phys.* **106**, 1309 (1997); 10.1063/1.474085

---



# A new interpretation of the bonding and spectroscopy of the tetraoxoferrate(VI) $\text{FeO}_4^{2-}$ ion

Abdalla Al-Abdalla, Luis Seijo, and Zoila Barandiarán<sup>a)</sup>

Departamento de Química, C-14, Universidad Autónoma de Madrid, 28049 Madrid, Spain

(Received 18 March 1998; accepted 17 July 1998)

In this paper we present an *ab initio* study of the absorption spectrum of the  $\text{FeO}_4^{2-}$  ion. The wavefunctions and energies of the ground and excited states of the  $\text{FeO}_4^{2-}$  cluster are calculated by means of the Restricted Active Space self-consistent-field method (RASSCF). The molecular orbitals of the cluster with main character  $\text{Fe}(3d)$  define a complete active space; all single, double, triple, and quadruple excitations from the molecular orbitals of main character  $\text{O}(2p)$  to those of main character  $\text{Fe}(3d)$  are allowed. The multiconfigurational expansions resulting from these ligands-to-metal excitations include between 50000 to 100000 configuration state functions. The results of the calculations lead to a new interpretation of the bonding and of the absorption spectra of  $\text{FeO}_4^{2-}$  (which were observed in the solid state and in solution), both of them stem from the near degeneracy between  $\text{Fe}(3d)$  and  $\text{O}(2p)$  levels, which is ultimately due to the high and unstable oxidation state of  $\text{Fe(VI)}$  in the  $\text{FeO}_4^{2-}$  complex. The analysis of the ground and excited state wavefunctions reveals that the electronic structure of  $\text{FeO}_4^{2-}$  does not correspond to the ionic image of Ligand Field Theory [ $d^2\text{-Fe(VI)}$ +closed-shell  $\text{O}^{2-}$  ions], nor does it correspond to simple extensions of it which take into account ligands-to-metal  $2p \rightarrow 3d$  single excitations, nor to any other simple image; on the contrary, it corresponds to the superposition of a large number of configurations with a very large weight of high-order ligands-to-metal excitations, which indicates a remarkable intra-cluster inwards delocalization of electron density away from the closed-shell ligands, impelled by the unstable high formal charge of  $\text{Fe(VI)}$ . The calculated absorption spectrum allows for a thorough interpretation of the features observed in the experimental spectra measured in  $\text{Fe(VI)}$ -doped  $\text{K}_2\text{MO}_4$  ( $\text{M}=\text{S}, \text{Cr}$ ) and in 9 M  $\text{KOH}$  solution (absorption maxima, intensities, electronic origins, band shapes), which implies completely new assignments. This is particularly so for the broad intense bands observed between  $10000\text{--}25000\text{ cm}^{-1}$ , which, according to our calculations, are found to be associated to electronic transitions from the  $^3A_2$  ground state to increasingly dense sets of excited states that include not only spin singlet and triplet states (as expected for a  $d^2$  configuration from Ligand Field Theory), but also spin quintet electronic states, all of which can be understood as direct effects of the above-mentioned oxygens( $2p$ )-iron( $3d$ ) near degeneracy. © 1998 American Institute of Physics. [S0021-9606(98)30339-6]

## I. INTRODUCTION

When a transition metal ion is introduced as an impurity into an oxide or halide crystal, a new material is synthesized that exhibits new local electronic properties which are usually very interesting from fundamental and technological points of view. In particular, as the transition metal ion is embedded in a host, the set of electronic states observed in the gas phase is multiplied as a consequence of the crystal field.<sup>1</sup> These states are often involved in the potential (or actual) laser activity of the new material and their detailed understanding is a key factor in the search for new combinations of hosts and impurities with controlled laser properties. In this framework, the Ligand Field Theory, and, in particular, the Sugano–Tanabe–Kamimura diagrams,<sup>1</sup> have been a simple and usually successful tool to guide and interpret the experimental studies. However, as soon as the interactions in the local defect depart from the simple model of a perturbed

ion, more sophisticated *ab initio* quantum mechanical models become necessary for a correct interpretation of its electronic structure. This is notably so as strong metal–ligand interactions, spin–orbit coupling, and/or host effects beyond first neighbors become important.

The case addressed in this paper, the tetraoxoferrate(VI) ion  $\text{FeO}_4^{2-}$  [which is present in the solid state,  $\text{K}_2\text{MO}_4\cdot\text{Fe}^{6+}$  ( $\text{M}=\text{S}, \text{Cr}$ ), as well as in alkaline solution], is a good example where Ligand Field Theory and *ab initio* quantum chemical calculations give completely different interpretations of the bonding and spectroscopic properties, due to the existence of very strong nonionic metal–ligand interactions. As we show in this work, the  $d^2$  Ligand Field Theory model gives a very incomplete image of an actually very rich electronic structure. This has resulted in controversy in the assignments and in an oversimplified image of the excited state manifold which is actually available for study and for possible applications.

Recently, a notable amount of information on the spectroscopic and laser properties of the isoelectronic series of

<sup>a)</sup>Author to whom correspondence should be addressed; electronic mail: zoila.barandiaran@uam.es

$3d^2$  impurities Ti(II), V(III), Cr(IV), Mn(V), and Fe(VI), has been accumulated, very much related to the fact that Cr(IV) and Mn(V) have been found to lase in the near infrared (see Refs. 2–4, and references therein). According to the Ligand Field Theory, there is a crossover point in the Sugano–Tanabe–Kamimura diagrams<sup>1</sup> between triplet and singlet excited states in this series (for octahedral and tetrahedral coordinations), which should result in either broad spin-allowed or sharp spin-forbidden luminescence.<sup>1</sup> In particular, sharp-line luminescence has been detected in  $\text{TiCl}_6^{4-}$  and  $\text{VCl}_6^{3-}$  in chloride hosts, and  $\text{CrO}_4^{4-}$ ,  $\text{MnO}_4^{3-}$ , and  $\text{FeO}_4^{2-}$  in oxide hosts which has been assigned to the intraconfigurational spin-flip electronic transition:  ${}^1T_{2g} \rightarrow {}^3T_{1g}$  (in  $O_h$  coordination),  ${}^1E \rightarrow {}^3A_2$  (in  $T_d$  coordination).<sup>4–6</sup> The  $d^2$  spin-flip transition energies are expected to be slightly reduced with respect to the corresponding  ${}^1D \rightarrow {}^3F$  free ion values due to the so called nephelauxetic effect,<sup>1</sup> which has been interpreted as a consequence of the radial expansion of the  $3d$  orbitals in the crystal field; however, Brunold *et al.*<sup>4</sup> have observed a very irregular trend of this reduction at the end of the mentioned Ti(III)–Fe(VI) series, together with a very unusual, tremendous decrease observed in  $\text{K}_2\text{CrO}_4\text{:Fe}^{6+}$ , where the  ${}^1E \rightarrow {}^3A_2$  energy difference is shown to be less than 40% of the  ${}^1D \rightarrow {}^3F$  free Fe(VI) value.<sup>4</sup> These experimental results deserve some explanation.

Moreover, Fe(VI)-doped  $\text{K}_2\text{CrO}_4$  and Fe(VI)-doped  $\text{K}_2\text{SO}_4$  [where Fe(VI) is in the center of a slightly distorted tetrahedron] must exhibit, according to the Ligand Field Theory for  $d^2$  ions in high field materials, two narrow spin-forbidden and two broad spin-allowed bands in the low energy absorption spectrum, associated to  $d \rightarrow d$  electronic transitions from the  ${}^3A_2$  ground state to  ${}^1E$ ,  ${}^1A_1$ ,  ${}^3T_2$ , and  ${}^3T_1$  excited states, respectively, which should be seen in the polarized absorption spectra, splitted according to the actual  $T_d \rightarrow C_s$  distortion in the crystals. Their relative intensities should be very different, since only the  ${}^3A_2 \rightarrow {}^3T_1$  electronic transition is electric dipole allowed in  $T_d$  site symmetry and the observed  $T_d \rightarrow C_s$  splittings are very small. As a matter of fact, the measured polarized absorption spectra<sup>7–9</sup> have been assigned accordingly, in spite of the fact that the broad absorption bands actually observed show intensities and complex structures which are hard to understand within the framework of the Ligand Field Theory without resorting to very significant mixings enabled by  $T_d \rightarrow C_s$  distortion and spin-orbit coupling.

In this paper we have calculated the vertical absorption spectrum of the  $\text{FeO}_4^{2-}$  ion in  $T_d$  symmetry. The most notable result we have obtained in this system is the evidence of the tremendous impact that high-order  $2p \rightarrow 3d$  ligands-to-metal excitations have in the wavefunctions and energies of the  $\text{FeO}_4^{2-}$  cluster ought to ligands( $2p$ )–Fe( $3d$ ) near degeneracy. This result contrasts with those we have obtained in many other transition metal impurities in oxide and halide hosts [ $d^2$ : V(III);<sup>10</sup>  $d^3$ : V(II),<sup>11–13</sup> Cr(III);<sup>14,15</sup>  $d^4$ : Cr(II);<sup>16,17</sup>  $d^8$ : Ni(II);<sup>18</sup>  $d^9$ : Cu(II),<sup>19</sup> and Me(II), Me=Sc–Zn<sup>20</sup>], where the configurational space created by considering the metal ( $3d$ ) orbitals as a complete active space was enough to properly represent nondynamic electron correlation associated to near degeneracy. The high formal oxida-

tion state of Fe(VI) seems to stabilize the Fe( $3d$ ) orbitals and turn the usual energy gap between the metal  $3d$  and ligands  $2p$  orbitals into near degeneracy. Using a multielectronic language, this means a densely packed zeroth-order multiconfigurational space. The wavefunctions which are needed to properly account for this strong nondynamic interactions between iron and the oxygens are of the RASSCF type<sup>21,22</sup> and are expanded in a multiconfigurational space which includes not only all possible  $d^2$  configurations, but also all single- and high-order (double, triple, and quadruple)  $2p \rightarrow 3d$  ligands-to-metal excitations, which leads to very large expansions ranging between 50000 and 100000 configuration state functions. As we show in this paper, the inspection of the RASSCF wavefunctions reveals that the electronic structure of the complex is neither  $d^2$ , nor can it be represented by any simple monoconfigurational label without this choice being an oversimplification. The description of the bonding which is obtained with this type of wavefunction can be simplified as follows: The high formal charge of Fe(VI) originates a strong reorganization of the electron densities which flow inwards, away from the ligands becoming very delocalized inside the  $\text{FeO}_4^{2-}$  volume. This pronounced charge shift is clearly illustrated by the Mulliken population analysis of the RASSCF wavefunctions, which assigns atomic charges +0.87 and –0.72 to Fe and O, respectively, and total electronic population 6.21 to the Fe  $3d$  basis functions in the ground state.

The calculation of the absorption spectrum leads to a very good agreement with the features of the available experimental spectra both in the solid state and in solution,<sup>7–9</sup> but the assignments are very different from those accepted so far. This is naturally due to the different configurational bases which the Ligand Field Theory and *ab initio* quantum mechanical methods propose for modeling the bond and spectroscopy of these materials. In particular, as we show in this paper, we find that only the first two low intensity spin-forbidden bands can be described by the electronic transition to one single excited state:  ${}^1E$  and  ${}^1A_1$  (using  $T_d$  notation), respectively; they cannot, however, be described as intraconfigurational  $d \rightarrow d$  electronic transitions and this explains their unexpected low values relative to those in the free ion. The rest of the broad, structured, and increasingly intense absorption band systems are shown to be due to electronic transitions to separate sets of excited states, rather than to the Ligand Field Theory  ${}^3A_2 \rightarrow {}^3T_2$ ,  $a^3T_1$ ,  $b^3T_1$  excitations. These sets of excited states become increasingly dense as one gets to higher energy values. Furthermore, the  $d^2$  scheme leading to singlet and triplet spin couplings completely breaks down in this material, since spin quintet excited states are found to be part of the absorption bands as low as  $15000 \text{ cm}^{-1}$  and beyond.

In Secs. II and III we describe the details of the calculations and the wavefunctions. In Sec. IV the computed absorption spectrum is presented and compared with the experimental spectra of  $\text{FeO}_4^{2-}$  in  $\text{K}_2\text{CrO}_4$  and  $\text{K}_2\text{SO}_4$  crystals and in a 9 M KOH solution, the new assignments are justified, and the limitations of the present calculations are discussed. The conclusions of this work are presented in Sec. V.

TABLE I. Bond lengths of the  $\text{MO}_4$  tetrahedra from single crystal studies in  $\text{K}_2\text{MO}_4$  ( $\text{M}=\text{S}, \text{Cr}, \text{Fe}$ ). All numbers are in Å.

	$\text{K}_2\text{SO}_4$ <sup>a</sup>	$\text{K}_2\text{CrO}_4$ <sup>b</sup>	$\text{K}_2\text{FeO}_4$ <sup>c</sup>
M–O(1)	1.459(4)	1.637(1)	1.646
M–O(2)	1.473(4)	1.654(2)	1.655
M–O(3)	1.472(5)	1.648(1)	1.662
Averaged M–O	1.469	1.646(1)	1.656(6)

<sup>a</sup>Reference 25.<sup>b</sup>References 25,26.<sup>c</sup>Reference 27.

## II. THE $\text{FeO}_4^{2-}$ MODEL SYSTEM

The experience gathered in the *ab initio* model potential embedded cluster calculations in transition metal impurities in oxide and halide crystals has shown that the host effects on the electronic spectra are significant and mostly indirect, that is, through the host-dependent local geometry distortions.<sup>20</sup> Consequently, the geometry optimization of the defect cluster, embedded in *ab initio* model potentials which represent the surrounding crystal,<sup>23,24</sup> becomes, customarily, the first step of a theoretical study of the absorption spectra.

The tetraoxoferrate(VI)  $\text{FeO}_4^{2-}$  cluster appears to be a very different case. In fact, even though the environment of the  $\text{FeO}_4^{2-}$  ion is clearly different in the  $\text{K}_2\text{CrO}_4$  and  $\text{K}_2\text{SO}_4$  hosts (relevant parameters of their crystal structures are given in Table I), and in an alkaline solution, the absorption spectra of the  $\text{FeO}_4^{2-}$  ion in these materials are observed to be very similar, as we discuss in more detail in Sec. IV. This can only be an indication of very small environmental effects on the electronic structure of an essentially identical  $\text{FeO}_4^{2-}$  ion, which suggests that the intracluster interactions are very dominant. Consequently, the bared  $\text{FeO}_4^{2-}$  cluster should be a meaningful model for study and the  $\text{FeO}_4^{2-}$  geometry corresponding to the experimental perfect  $\text{K}_2\text{FeO}_4$  crystal structure data<sup>27</sup> (cf. Table I: average Fe–O distance is 1.66 Å) should be a sound alternative to the theoretical geometry optimizations. This bared tetrahedral cluster model is very convenient from the computational point of view. In fact, since the Fe(VI) site symmetry in the  $\text{K}_2\text{CrO}_4$  and  $\text{K}_2\text{SO}_4$  hosts is very low (Cs), the inclusion of the embedding potentials in the calculations would reduce the molecular point group available for the calculations from tetrahedral to Cs, which results in a significant increase in computational effort; this is more so, as it is found that the theoretical study of the  $\text{FeO}_4^{2-}$  ion demands exceptionally large multiconfigurational expansions in order to describe nondynamic correlation, as we show in the next section. In consequence with the last comments, all the calculations presented in this work have been done for the bared  $\text{FeO}_4^{2-}$  cluster at the fixed  $R(\text{Fe}–\text{O})=1.66$  Å distance in  $T_d$  symmetry. The  $\text{FeO}_4^{2-}$  wavefunctions and energies were calculated using MOLCAS, a standard quantum mechanical molecular suite of programs which allows for the use of flexible monoelectronic basis sets and multiconfigurational expansions as well as the inclusion of *ab initio* model potentials.<sup>28</sup> The following 100 contracted Gaussian basis set was used. For the all-electron iron atom the (14s11p5d) basis set of Wachters<sup>29</sup> augmented with one

*d*-type diffuse function<sup>30</sup> and a (3*f*) polarization function<sup>31</sup> was used contracted as (62111111/4211111/3111/3). The oxygens were described using the 1*s ab initio* core model potential of Ref. 32. The corresponding (5*s*5*p*) valence basis set, augmented by one diffuse *p* function for the anion<sup>33</sup> was contracted as (41/411). The full basis set of  $\text{FeO}_4^{2-}$  was used to calculate the ground state of the 26 electron  $\text{O}_4^{2-}$  cage at the tetrahedral  $R(\text{Fe}–\text{O})=1.66$  Å structure in order to ascertain possible contributions of basis set superposition errors (BSSE) to the charge distribution in the  $\text{FeO}_4^{2-}$  complex. When the ground state of  $\text{O}_4^{2-}$  was calculated at the  $2p$   $a^2t_2^6e^4t_1^6$  closed-shell SCF level, the Mulliken total atomic electronic populations were found to be  $\text{Fe}(-0.20)$  and  $\text{O}(6.55)$ . When a RASSCF wavefunction was calculated including all single and double excitations from the  $2p$  closed-shell  $a^2t_2^6e^4t_1^6$  orbitals to the remaining  $2p$   $t_2$  set, their values changed insignificantly to  $\text{Fe}(-0.17)$  and  $\text{O}(6.54)$ . These results, together with the very small contributions of the Fe basis functions observed in the final molecular orbitals of the  $\text{O}_4^{2-}$  cage, indicate acceptable low levels of BSSE, which, in particular, can be ruled out as the origin for the observed charge shifts in the  $\text{FeO}_4^{2-}$  calculations presented in this work.

The actual multiconfigurational expansions used for the ground and excited state cluster wavefunctions are described next.

## III. THE $\text{FeO}_4^{2-}$ WAVEFUNCTIONS

In 3*d* transition metal impurities, it is quite common that the nondynamic correlation associated to the  $d^n$  manifold can be described by Complete Active Space SCF (CASSCF)<sup>34</sup> wavefunctions with an active space defined by the molecular orbitals of main character metal-3*d*, CASSCF(3*d*). These CASSCF(3*d*) wavefunctions become suitable multireferences of subsequent post-CASSCF treatments which try to include as much dynamic correlation as possible in the calculation of the electronic spectrum. In the present case, however, the demands of the  $\text{FeO}_4^{2-}$  cluster turned out to be very different. In effect, when the CASSCF(3*d*) wavefunction for  $\text{FeO}_4^{2-}$  is being calculated, the multiconfigurational space appears to be insufficient: The MCSCF procedure, if convergent at all, clearly shows that some molecular orbitals of main character ligands-2*p* appear in the final natural orbital active space. The need to enlarge the CAS to include ligand orbitals is evident and it is associated to the fact that all the Fe(3*d*) and  $\text{O}_4(2p)$  orbitals are close in energy.<sup>35</sup> This fact naturally invites us to use a CASSCF(2*p*,3*d*) wavefunction, where the whole set of five Fe(3*d*) and twelve  $\text{O}_4(2p)$  orbitals constitute the new active space; but this CASSCF(2*p*,3*d*) wavefunction increases too much the computational costs, even within the  $T_d$  symmetry. An alternative to this CASSCF(2*p*,3*d*) is the Restricted Active Space SCF (RASSCF)<sup>21</sup> wavefunction described next. The RASSCF method allows us to extend the Fe(3*d*) active space of the MCSCF procedure with all the  $\text{O}_4(2p)$  orbitals at once, ruling out in this way any possible biased choice of orbitals, at a time that it allows to keep the size of the problem manageable, through the restriction of the maximum

TABLE II. Results of RASSCF calculations of the  ${}^3A_2$  ground and  ${}^1E$ ,  ${}^1A_1$  excited states in a tetrahedral  $\text{FeO}_4^{2-}$  cluster at the Fe–O distance 1.66 Å. A maximum of four holes is allowed in the subspace of the twelve  $\text{O}_4(2p)$  orbitals and a maximum of six electrons are distributed in the five  $\text{Fe}(3d)$  orbitals.

Total No. of configuration state functions: <sup>a</sup>	${}^3A_2$	${}^1E$	${}^1A_1$
Number of configurations with $C_i \geq 0.05$ : <sup>b</sup>	101543	59987	60352
$d^2$ :	1(0.005)	1(0.005)	1(0.003)
LTM-single excitations:	7(0.075)	7(0.072)	8(0.066)
LTM-double excitations:	27(0.274)	25(0.270)	25(0.255)
LTM-triple excitations:	36(0.231)	38(0.257)	39(0.233)
LTM-quadruple excitations:	1(0.003)	2(0.013)	2(0.013)
Total:	72	73	65
Total weight:	0.588	0.617	0.570
Results of Mulliken population analysis:			
Gross atomic population of the $3d$ basis functions	6.21	6.25	6.26
Total charge on Fe	+0.87	+0.83	+0.81
Total charge on O	−0.72	−0.71	−0.70

<sup>a</sup>The calculations are done using  $C_{2v}$  symmetry.

<sup>b</sup>Weights are given in parentheses. LTM stands for Ligands-to-Metal.

number of holes that are allowed in the  $\text{O}_4(2p)$  orbital space; if it is high enough, the RASSCF and CASSCF( $2p,3d$ ) results can be expected to be sufficiently close. In this work we have allowed a maximum of four holes in the space of the twelve  $\text{O}_4(2p)$  orbitals.

In Table II we present some information extracted from the RASSCF wavefunctions of the ground state  ${}^3A_2$  and the first two excited state  ${}^1E$  and  ${}^1A_1$ . All these three electronic states belong to the  $e^2$  electron configuration, according to Ligand Field Theory.<sup>1</sup> Our calculations describe them, however, in a very different way. In Table II we analyze the most important configurations, in this case those whose CI coefficient ( $C_i$ ) is greater or equal to 0.05 in the final RASSCF wavefunction. For the three states it can be observed that (i) the weight of the  $d^2$  ( $e^2$ ) Ligand Field configuration in the RASSCF wavefunction is very small ( $\leq 0.5\%$ ); (ii) the ligands-to-metal  $2p \rightarrow 3d$  single excitations, usually called ligand-to-metal charge transfer configurations, amount to some 7%; (iii) ligands-to-metal double and triple excitations are very important, their accumulated weight being about 50%; (iv) a large number of configurations (some 70), contribute to the wavefunction with  $C_i \geq 0.05$ , however, their total weight is only about 60%. All these observations lead to the following conclusions: The electronic structure of  $\text{FeO}_4^{2-}$  does not correspond to the  $d^2$  ionic image of Ligand Field Theory,<sup>1</sup> nor it does correspond to simple extensions of it which only take into account ligands-to-metal  $2p \rightarrow 3d$  single excitations,<sup>36,37</sup> nor to any other simple image. On the contrary, it corresponds to the superposition of a large number of configurations, which represents a remarkable intra-cluster delocalization of electron density inwards, away from the closed shell ligands, impelled by the unstable high oxidation state of Fe(VI). This charge shift can be observed on the results of the Mulliken population analysis of the RASSCF  ${}^3A_2$  ground and  ${}^1E$  and  ${}^1A_1$  excited state wavefunctions in Table II. The charge on the oxygens in the ground state, −0.72, appears to be notably reduced compared to the formal closed-shell  $\text{O}^{2-}$ , which clearly reveals a notable charge flow towards the metal ion whose charge appears to be about +0.87. A further, probably not very sig-

nificant, increase of this charge shift is observed in the excited states, where the charges on the oxygens become −0.71 and −0.70.

Results of electronic structure calculations of the first two members of the isoelectronic series  $\text{CrO}_4^{4-}$ ,  $\text{MnO}_4^{3-}$ , and  $\text{FeO}_4^{2-}$ , in progress in our laboratory, indicate the dominant role of the formal oxidation state in the bonding of these complexes.<sup>38</sup> In fact, as the oxidation state grows from IV to VI in the series, the ground state wavefunctions reveal a sharply decreasing dominance of the  $d^2$  configuration and an increasing importance of high-order ligands-to-metal excitations.<sup>38</sup> This trend corresponds to a notable change in nondynamic electron correlation, which makes it necessary to adapt the level of methodology used from the CASSCF( $3d$ ) level to the RASSCF level described in this Section. In order to illustrate this trend in this work, we conducted the following numerical experiment. We calculated the  ${}^3A_2$  ground state of an isoelectronic cluster using the same basis set, tetrahedral geometry, and RASSCF space definition as in the  $\text{FeO}_4^{2-}$  complex, but different nuclear attraction on the metal:  $Z=24$ . In this way the formal oxidation state of the metal is effectively lowered to IV. The results of this computational experiment can be compared to those of the Fe(VI) complex presented in Table II: In effect, the weight of the  $d^2$  configuration in the RASSCF wavefunction of the  $Z=24$  cluster appears to be about 85% (compared to 0.5% for  $\text{FeO}_4^{2-}$ ), the ligands-to-metal single excitations with  $C_i \geq 0.05$  contribute some 10%, the doubles, 1%, and no higher-order excitations appear to have a CI coefficient  $\geq 0.05$ . The Mulliken population analysis shows a total charge on the oxygens of −1.38, much closer to the formal  $\text{O}^{2-}$  and the total occupation of the  $3d$  basis functions of the metal comes down to 3.98 (compared to 6.21 for  $\text{FeO}_4^{2-}$ ). This numerical experiment clearly shows that as the formal oxidation state of the metal is lowered from VI to IV, nondynamic electron correlation effects are much smaller and the charge shift from the oxygens to the metal is notably reduced.

The need for large multiconfigurational expansions, similar to the ones used in this work, in order to account for

nondynamic correlation effects in transition metal complexes, was concluded in a detailed theoretical study of the bonding in  $\text{MnO}_4^-$ .<sup>22</sup> Our results confirm this conclusion for transition metal complexes where the formal oxidation state of the transition metal is high, like in  $\text{MnO}_4^-$  and  $\text{FeO}_4^{2-}$ . However, extensive work in transition metal ions in the solid state (halide and oxide crystals)<sup>10–20</sup> indicates that much shorter multiconfigurational spaces are flexible enough to account for nondynamical correlation in low oxidation state transition metal clusters. Altogether, we point out in this work a correspondence between an increasing formal oxidation state and nondynamic correlation demands, which should be studied in more detail and is the subject of a forthcoming paper.<sup>38</sup>

## IV. RESULTS AND DISCUSSION

### A. Vertical absorption spectra

The results of the analysis of the  $^3A_2$ ,  $^1E$ , and  $^1A_1$  wavefunctions of the previous section question the interpretation of the ground state absorptions  $^3A_2 \rightarrow ^1E$ ,  $^1A_1$  as due to the spin-flip  $e^2$  intraconfigurational electronic transitions resulting from the crystal field reduction of their parent  $^3F \rightarrow ^1D$  and  $^3F \rightarrow ^1G$  Fe(VI) atomic excitations. Moreover, these wavefunctions strongly suggest that the  $d^2$  model must be completely abandoned if the electronic structure of even higher excited states has to be calculated in detail. In particular, spin couplings corresponding to more than two open-shell electrons and leading not only to triplets and singlets, but also to quintets and septets, should be considered, since the relevance of the ligands-to-metal high-order excitations in the electronic structure of the  $\text{FeO}_4^{2-}$  manifold is manifest.

Consequently, we have conducted our study of the absorption spectrum as a search for all the electronic states of the  $\text{FeO}_4^{2-}$  cluster with spin multiplicities  $2S+1=1,3,5$ , and 7, and with energies between 0 and 26000  $\text{cm}^{-1}$  above the  $^3A_2$  ground state approximately. The methodological level described in the previous sections has been used in all these calculations. Although we have applied only the symmetry restrictions of the  $C_{2v}$  point group, the results showed degeneracies better than 200  $\text{cm}^{-1}$  and they are good representations of the  $T_d$  point-group wavefunctions for the purpose of interpretation of the nature of the excited states of  $\text{FeO}_4^{2-}$ . The results are presented in Table III; its detailed description and the discussion follow here.

It is possible to classify the calculated vertical electronic transitions into five separate sets of electronic states, which become increasingly dense and intense for higher energies; their energies are conveniently shown together in Table III, the calculated oscillator strengths of the spin- and dipole-allowed transitions are collected in Table IV. The first two sets are formed by only one excited state:  $^1E$  and  $^1A_1$ , respectively. The third set is a superposition of two spin triplets:  $^3T_2$  and  $^3T_1$ , the latter leading to spin- and dipole-allowed transition in  $T_d$  symmetry. The fourth set is formed by the superposition of three subsets of states: singlets, triplets, and quintets. The singlets and triplets span essentially the same energy interval (16700–22400  $\text{cm}^{-1}$ ) and the subset of spin quintets spans a smaller energy interval and is

originated at slightly lower energies (around 1500  $\text{cm}^{-1}$ ). Here, three spin- and dipole-allowed excitations to  $^3T_1$  states are found. We have only reached the beginning of a fifth set which, similarly to the previous one, appears to be formed by spin singlet, triplet, and quintet excited states. The wavefunctions found for all these excited states are essentially analogous to the ones discussed above, in the sense that they are large superpositions of configuration state functions, many of which are ligands-to-metal high-order excitations.

In order to compare our results with measured absorption spectra, we have also included in Table III experimental data corresponding to the polarized absorption spectra of Fe(VI) doped in  $\text{K}_2\text{CrO}_4$ <sup>7,9</sup> and in isomorphous  $\text{K}_2\text{SO}_4$ <sup>8</sup> (see also Table IV) and to unpolarized absorption spectra of  $\text{FeO}_4^{2-}$  in 9 M KOH solution.<sup>9,39</sup> We have summarized the complex experimental data in the following way: In Table III the band maxima are tabulated and the maximum absorbance is indicated in squared parentheses, when available. Electronic origins are explicitly marked and the spacing of the progression that they initiate is given in parentheses, unless they are origins to several vibrational progressions; these data are not directly comparable with our vertical calculations, but contribute to give an idea of the whole band structure. The symbols  $\parallel$  and  $\perp$  are used to group the data obtained in  $\vec{E}\parallel b$  and  $\vec{E}\perp b$  polarizations, respectively; the only exception being the data of the solution which are arbitrarily placed in the table together with the lowest energy band maxima. The same symbols have been used in Table IV, where we present the calculated and available experimental oscillator strengths.

First of all, we would like to compare the overall structure of the measured and calculated spectra (Tables III and IV). The experimental data show the existence of four bands below 26000  $\text{cm}^{-1}$ , plus an adjacent band or shoulder in the low energy side of a fifth rising very intense band observed only in  $\text{K}_2\text{SO}_4\cdot\text{Fe}^{6+}$  and in solution. The first two bands at about 6200 and 9100  $\text{cm}^{-1}$  are narrow and of very low intensity; the three other bands, are increasingly intense, broad, and complex, and cover the following energy intervals (in  $\text{cm}^{-1}$ ): in  $\text{K}_2\text{CrO}_4$ ,<sup>7,9</sup> (III): 9500–15400, (IV): 15400–22160, in  $\text{K}_2\text{SO}_4$ :<sup>8</sup> (III): 10000–16000, oscillator strength  $f=8\times 10^{-3}$ , (IV): 16000–26000,  $f=3.6\times 10^{-2}$  (4.5 times larger than that of band III) (V): >26000. The structure of the spectrum in solution is completely analogous, except for the first band, which is not detected. If these intervals and intensity patterns are compared with those corresponding to the sets of electronic states found in the calculations, namely, (I) 6300, spin- and dipole-forbidden, (II) 9200, spin- and dipole-forbidden, (III) 11200–12100, (IV) 15200–22400, and (V) >24000  $\text{cm}^{-1}$ , it is clearly seen that their structures match. This is even more evident, if the energy intervals and oscillator strengths of the intense bands are compared with our spin-allowed, dipole-allowed  $^3T_1$  sets (III): 12100,  $f=0.46\times 10^{-3}$ , (IV): 16900–22400, total oscillator strength:  $2.98\times 10^{-3}$  (6.5 times larger than that of band III), (V):  $\geq 25500 \text{ cm}^{-1}$ .

Let us now analyze in more detail the experimental and theoretical results. We will compare our results directly with the observed spectral features, without referring to the pres-

TABLE III. Calculated and measured absorption spectra of  $\text{FeO}_4^{2-}$  from the  $^3A_2$  ground state. All energies in  $\text{cm}^{-1}$ . BM stands for band maxima; numbers in squared brackets are maximum absorbance  $\epsilon$  in  $\text{M}^{-1}\text{cm}^{-1}$  units. EO stands for electronic origins leading to a progression whose interval is given in parentheses. Parallel and perpendicular polarizations are indicated. See the text for a detailed description and for discussion.

Calculated			Experimental			
			$\text{K}_2\text{CrO}_4\cdot\text{Fe}^{6+}$		$\text{K}_2\text{SO}_4\cdot\text{Fe}^{6+}$	Solution <sup>a</sup>
			Ref. 9	Ref. 7	Ref. 8	Refs. 9,39
$^1E$	6300	$^1E$	—	6209, 6219	6219, 6230	—
$^1A_1$	9200	$^1A_1$	9112	9119	9176	9060
$^3T_2$	11200	$^3T_2$	BM $\parallel$	12540[510]	12315[570]	
$^3T_1$	12100	BM $\perp$	13365	13280[530]	13330[580]	12670
		EO $\parallel$	10669, 10811	10650(340)	11000(800)	
		EO $\parallel$			12350(350)	
$^5E$	15200					
$^5T_1$	15300					
$^3T_2$	16700					
$^1T_1$	$^3T_1$	$a$ $^3T_1$	BM $\perp$	17930[960]	18200[1000]	17800 <sup>b</sup>
	$^5T_2$	EO $\parallel$	16292, $\perp$ 16474			
	$^3E$					
$^1T_2$	17700					
	$^5A_1$					
$^1T_1$	$^3T_1$	$b$ $^3T_1$ <sup>c</sup>	BM $\parallel$	20430[1000]		19600
	$^3T_2$	EO $\parallel$	19666, $\perp$ 19802		$\perp$ 20040(750)	
	$^3A_1$					
$^1T_2$	21500					
$^3T_1$	22400					
$^5A_2$	24000					
$^5E$	24500					
$^5A_2$	24900					
$^5T_2$	25000					
$^5T_1$	25200					
$^5T_2$	25400					
$^3T_1$	$^5A_2$	LMCT2 <sup>d</sup>	EO $\perp$		26370(780)	
$^1E$	26000				30000 <sup>b</sup>	30000 <sup>e</sup>
$^5T_2$	26300					

<sup>a</sup>Unpolarized absorption spectrum of  $\text{FeO}_4^{2-}$  in a 9 M KOH solution.

<sup>b</sup>Shoulder.

<sup>c</sup>Assignment from Ref. 9. In Refs. 7 and 8 it is assigned to a ligand-to-metal charge transfer band, LMCT1.

<sup>d</sup>Ligand-to-metal charge transfer band.

<sup>e</sup>From Fig. 1 of Ref. 9: shoulder of a very intense band peaking beyond  $35000\text{ cm}^{-1}$ .

TABLE IV. Calculated and measured oscillator strengths,  $f$ , for  $\text{FeO}_4^{2-}$ . Transition energies in  $\text{cm}^{-1}$ . BM stands for band maxima. EO stands for electronic origin. Perpendicular polarization is indicated. See the text for a detailed description and for a discussion.

Calculated				Experimental			
				$\text{K}_2\text{SO}_4\cdot\text{Fe}^{6+}$ , Ref. 8			
Band		$f$	$f_{\text{IV}}/f_{\text{III}}$			$f$	$f_{\text{IV}}/f_{\text{III}}$
I	$^1E$	6300	forbidden <sup>a</sup>	$^1E$	6219, 6230	$1.5 \times 10^{-6}$	
II	$^1A_1$	9200	forbidden <sup>a</sup>	$^1A_1$	9176	$6 \times 10^{-6}$	
III	$^3T_1$	12100	$0.46 \times 10^{-3}$	$^3T_2$	BM $\perp$ 13330	$8 \times 10^{-3}$	
IV	$^3T_1$	16900	$0.58 \times 10^{-3}$	$^3T_1$	BM $\perp$ 18200	$2.0 \times 10^{-2}$ <sup>b</sup>	(2.5)
	$^3T_1$	19300	$2.02 \times 10^{-3}$	LMCT1 <sup>c</sup>	EO $\perp$ 20040		
	$^3T_1$	22400	$0.38 \times 10^{-3}$				
	total		$2.98 \times 10^{-3}$			$3.6 \times 10^{-2}$	(4.5)

<sup>a</sup>Spin- and dipole-forbidden electronic transition in  $T_d$  symmetry.

<sup>b</sup>Estimated by assuming that the ligand field transition to  $^3T_1$  contributes substantially to the total oscillator strength  $f = 3.6 \times 10^{-2}$  of the complex band IV (Refs. 8,40).

<sup>c</sup>Ligand-to-metal charge transfer band.

ently accepted assignments, and we will discuss the latter in Sec. IV B.

The agreement in the first two narrow, low intensity bands with the spin- and dipole-forbidden  ${}^3A_2 \rightarrow {}^1E$ ,  ${}^1A_1$  calculated electronic transition energies is remarkable.

The spectral features of the third measured absorption band can be understood if it is interpreted as the superposition of the  ${}^3T_2$  and  ${}^3T_1$  excited states (the third set of states), as we discuss next. Since the ground state of  $\text{FeO}_4^{2-}$  is  ${}^3A_2$ , the only electric dipole-allowed electronic absorption transitions in  $T_d$  symmetry are those to  ${}^3T_1$  excited states. Accordingly, our  ${}^3T_1$  at  $12100\text{ cm}^{-1}$  ( $f=0.46\times 10^{-3}$ ) should give most of the intensity to the band peaking at  $12670\text{ cm}^{-1}$  in solution,<sup>9,39</sup> where the  $T_d$  symmetry is preserved. In the solid hosts  $\text{K}_2\text{CrO}_4$  and  $\text{K}_2\text{SO}_4$  the situation is more complex and rich. First of all, the site symmetry of the  $\text{FeO}_4^{2-}$  in these crystals is essentially  $T_d$  with a small  $C_s$  distortion;<sup>9</sup> this distortion produces one  ${}^3A''$  from the  ${}^3A_2$  ground state, two  ${}^3A'$  plus one  ${}^3A''$  states from the  ${}^3T_2$ , and one  ${}^3A'$  plus two  ${}^3A''$  states from the  ${}^3T_1$ . The electric dipole-allowed transitions are  ${}^3A'' \rightarrow {}^3A'$  in  $\vec{E}\parallel b$  polarization and  ${}^3A'' \rightarrow {}^3A''$  in  $\vec{E}\perp b$  polarization.<sup>9</sup> With all this in mind, we can analyze the electronic origins observed in the two crystals in  $\vec{E}\parallel b$  polarization. Two electronic origins in  $\text{K}_2\text{CrO}_4$  are reported at  $10669$  and  $10811\text{ cm}^{-1}$  by Di Sipio *et al.*,<sup>9</sup> of which only one is observed by Brunold *et al.*<sup>7,8</sup> at  $10650\text{ cm}^{-1}$ ; these authors observe this origin as well in  $\text{K}_2\text{SO}_4$  at  $11000\text{ cm}^{-1}$ , together with a third electronic origin which is  $1350\text{ cm}^{-1}$  above.<sup>7,8</sup> According to our calculations, the three observed electronic origins should be interpreted as due to the two  ${}^3A'({}^3T_2)$  and one  ${}^3A'({}^3T_1)$  components. The small energy separation between the first two  ${}^3A'({}^3T_2)$  origins,  $\sim 150\text{ cm}^{-1}$ ,<sup>9</sup> is due to the  $C_s$  distortion. [This fact is consistent with the very small splitting observed in the  ${}^1E$  in both crystals (Table III) and it indicates that the  $\text{FeO}_4^{2-}$  cluster symmetry is close to  $T_d$ .] The energy difference between the first two origins and the third one, which is approximately  $1350\text{ cm}^{-1}$  in  $\text{K}_2\text{SO}_4$ , is due to the separation between the  ${}^3T_2$  and  ${}^3T_1$  states in  $T_d$  symmetry. Our result,  $900\text{ cm}^{-1}$ , which corresponds to a Frank-Condon energy difference, is of the correct order of magnitude and seems to be a little underestimated. Regarding the observed band maxima, a consistent interpretation emerges as well. In  $\vec{E}\parallel b$  polarization, we should find an overall band which is the superposition of two almost degenerate  ${}^3A'({}^3T_2)$  bands and one  ${}^3A'({}^3T_1)$  band, the latter being more intense than each one of the two  ${}^3A'({}^3T_2)$  bands and centered at higher energy (of the order of  $1000\text{ cm}^{-1}$ ) due to its  $T_d$  parentage:  ${}^3T_1$ . In  $\vec{E}\perp b$  polarization, we should find instead the superposition of one  ${}^3A'({}^3T_2)$  and two  ${}^3A'({}^3T_1)$  bands, which should result in an overall band peaking at higher energy than in  $\vec{E}\parallel b$  polarization. According to this interpretation, the difference between the composed, observed band maxima in  $\vec{E}\parallel b$  and  $\vec{E}\perp b$  polarizations should be smaller than the energy difference between the pure  ${}^3T_1$  and  ${}^3T_2$  origins, and this is certainly so in  $\text{K}_2\text{SO}_4$ , where the band maxima in both polarizations differ by  $1015\text{ cm}^{-1}$ , whereas the  ${}^3T_1$  and  ${}^3T_2$  origins differ in  $1350\text{ cm}^{-1}$ .

The fourth observed absorption band is more intense and much more complex than the previous one (see Fig. 1 of Ref. 8, for instance): It is actually formed by the superposition of two intense bands which we describe and analyze next. In solution it is seen as a large asymmetric peak with a shoulder at about  $17800\text{ cm}^{-1}$ , before it reaches its maximum at  $19600\text{ cm}^{-1}$ .<sup>9,39</sup> In  $\text{K}_2\text{CrO}_4$  Di Sipio *et al.*<sup>9</sup> have detected two almost equally intense bands with electronic origins at about  $16400$  and  $19700\text{ cm}^{-1}$  in parallel and perpendicular polarizations which exhibit the vibrational structure; the authors comment that the structure is not sufficiently sharp to reveal the crystal-site splitting due to the  $T_d \rightarrow C_s$  distortion. In the same crystal with  $\vec{E}\perp b$  polarization, Brunold *et al.*<sup>7</sup> observed a weakly structured band peaking at  $17930\text{ cm}^{-1}$ , followed by a structured band showing a progression of  $750\text{ cm}^{-1}$ . With  $\vec{E}\parallel b$  polarization the structure of the latter band is more pronounced and its maximum absorbance is observed at  $20430\text{ cm}^{-1}$ . These authors observe similar features in  $\text{K}_2\text{SO}_4$ : A broad band with little structure peaks at  $18200\text{ cm}^{-1}$ . The adjacent band shows nine members of a progression of  $750\text{ cm}^{-1}$  built on the electronic origin at  $20040\text{ cm}^{-1}$ . The results that we obtained in the fourth set of states are consistent with all these spectral features. We will focus in the spin triplet states, since the intensity of the band should be essentially driven from them. It is observed that they describe two separate subsets, following closely the two experimental bands. The first subset is formed by three very close triplets (surrounded by two singlets and one quintet):  ${}^3T_2(16700)$ ,  ${}^3T_1(16900)$ , and  ${}^3E(17400)$  and correspond to the first experimental band whose maximum intensity should be mainly due to the  ${}^3T_1$  state ( $f=0.58\times 10^{-3}$ ). Our calculated  ${}^3T_1(16900)$  compares very well with the first maximum observed in solution at  $17800\text{ cm}^{-1}$ , and the band maxima observed with  $\vec{E}\perp b$  polarization in the crystals at  $17930\text{ cm}^{-1}$  and  $18200\text{ cm}^{-1}$  can be interpreted as the superposition of all the  $A''$  components of the three triplets: one  $A''({}^3T_2)$ , two  $A''({}^3T_1)$ , and one  $A''({}^3E)$ , of which  ${}^3T_1$  should give most of the intensity of the weakly structured band observed. In addition, these triplets should lead to four electronic origins in each polarization, associated to the 2, 1, 1  $A'$  components of  ${}^3T_2$ ,  ${}^3T_1$ , and  ${}^3E$ , respectively, with  $\vec{E}\parallel b$  polarization and 1, 2, 1  $A''$  with  $\vec{E}\perp b$  polarization, which in the experiment are not discerned, due to the lack of a sharp structure.<sup>9</sup> Instead, only one origin is detected in each polarization, which we interpret as the superposition of the components of the essentially degenerate  ${}^3T_2$  and  ${}^3T_1$ . In effect, the origin observed with  $\vec{E}\parallel b$  polarization can be interpreted as resulting from the 2, 1  $A'$  components of  ${}^3T_2$  and  ${}^3T_1$ , respectively, and that observed with  $\vec{E}\perp b$  polarization, from their 1, 2  $A''$  components; their observed shift by  $182\text{ cm}^{-1}$ , correlates very well with the energy difference which we find between  ${}^3T_2$  and  ${}^3T_1$ : some  $200\text{ cm}^{-1}$ . The second subset of spin triplets is formed by four electronic states separated by intervals of some  $1000\text{ cm}^{-1}$  (surrounded by two singlets and preceded by one quintet):  ${}^3T_1(19300)$ ,  ${}^3T_2(20400)$ ,  ${}^3A_1(21300)$ ,  ${}^3T_1(22400)$ . Two of them are  ${}^3T_1$ . The calculated energy transition to  ${}^3T_1(19300)$  ( $f=2.02\times 10^{-3}$ ) appears to be very close to the maximum observed



in solution and in the  $\text{K}_2\text{CrO}_4$  crystal with  $\vec{E}\parallel b$  polarization. Also, the only electronic origins actually observed in the crystals, in both polarizations, can be associated to the first possible components of the calculated triplets, namely, those of the  ${}^3T_1(19300)$ : the  $\vec{E}\parallel b$  origin at  $19666\text{ cm}^{-1}$  to the  $A''$  component and the more intense  $\vec{E}\perp b$  at  $19802\text{ cm}^{-1}$  origin to the superposition of the remaining two  $A'$  components; their difference giving an idea, again, of the small  $T_d\rightarrow C_s$  splitting of  ${}^3T_1$ . However, the most striking feature of this high energy side of the fourth band is the contour of the progression starting at  $20040\text{ cm}^{-1}$  in  $\text{K}_2\text{SO}_4$  which cannot be completely observed in  $\text{K}_2\text{CrO}_4$  due to the intense absorption of the  $\text{K}_2\text{CrO}_4$  host. In effect, the nine peaks which form the  $750\text{ cm}^{-1}$  progression built on the  $20040\text{ cm}^{-1}$  origin, are very broad to be associated simply to the vibrational structure of  ${}^3T_1$  alone. If we take into account the electronic states which we find from  ${}^5A_1(18500)$  to the higher  ${}^3T_1(22400)$  ( $f=0.38\times 10^{-3}$ ), the complex structure of the band could be interpreted as the superposition of a complex manifold of electronic states which can mix due to the small  $C_s$  distortion and by spin orbit coupling, driving intensity mainly from the two  ${}^3T_1$  states located at  $19300$  ( $f=2.02\times 10^{-3}$ ) and  $22400\text{ cm}^{-1}$  ( $f=0.38\times 10^{-3}$ ).

Finally, of the fifth set of states, we have only calculated the first singlet and triplet roots and all quintets which appear up to the same energy limit. The only purpose of these calculations is to show the beginning of a new presumably more dense set of electronic states.

## B. Comparison with previous assignments

We discuss now the assignments given so far to all spectral features observed experimentally and their comparison with the assignments suggested by our calculations, which we have just discussed above.

The first discrepancy between our interpretation of the spectral features and the one accepted so far corresponds to the first low intensity sharp bands assigned as the intraconfigurational  $e^2$  spin flip transitions  ${}^3A_2\rightarrow {}^1E$ ,  ${}^1A_1$ . As we have discussed above, neither the ground state  ${}^3A_2$  nor the  ${}^1E$ ,  ${}^1A_1$  excited states can be described as  $e^2$ , on the contrary, these excitations and their unexpected low energy values, should be understood as excitations to the first two singlet excited states of a very rich and dense manifold. Their unexpected low energy transitions are a consequence of the above mentioned near degeneracy which results in very close lying excited states. The fact that the electronic structure of  ${}^3A_2$  and  ${}^1E$ , as indicated by their wavefunctions, is very different from the one corresponding to the  $e^2$  Ligand Field Theory description, rules out the parentage of this  ${}^3A_2\rightarrow {}^1E$  electronic transition to the  $\text{Fe(VI)}$   $d^2$  intraconfigurational  ${}^3F\rightarrow {}^1D$ ; in consequence, its relative very low value cannot be ascribed to the nephelauxetic effect.<sup>1</sup>

Our assignment is even more divergent in the third band, since, as we have shown, all spectral features are interpreted as due to the superposition of  ${}^3T_2+{}^3T_1$  in set III, instead of being assigned as the transition to the  $e^1t^1-{}^3T_2$  Ligand Field term. The assignment of this band as the electric dipole forbidden  ${}^3A_2\rightarrow {}^3T_2$  in  $T_d$  faced the problem of explaining

the observed high intensities (maximum intensities are indicated in square parentheses accompanying the band maxima in Table III; oscillator strengths are presented in Table IV, when available, but they are also apparent in the absorption spectra referred to in the tables). Di Sipio *et al.*<sup>9</sup> suggested that the intensity should be driven from the mixing of  $e^1t^1-{}^3T_2$  with the higher  $e^1t^1-{}^3T_1$  through spin-orbit coupling and  $T_d\rightarrow C_s$  distortion, in spite of the fact that the Ligand Field Theory<sup>1</sup> places this  $e^1t^1-{}^3T_1$  state at energies significantly higher than  $e^1t^1-{}^3T_2$ , since  ${}^3T_2$  is related to  $\text{Fe(VI)}({}^3F)$  and  ${}^3T_1$  is related to  $\text{Fe(VI)}({}^3P)$ , and that the authors indicated that the  $C_s$  splitting is “relatively small,  $\sim 150\text{ cm}^{-1}$ ,” so that the defect has almost  $T_d$  symmetry. As a matter of fact, they interpreted the two electronic origins they observed in  $\text{K}_2\text{CrO}_4$  (at  $10669$  and  $10811\text{ cm}^{-1}$  with  $\vec{E}\parallel b$  polarization), as the two  $A'$  components of  ${}^3T_2$ , which shows the small  $T_d\rightarrow C_s$  splitting of these two components: some  $142\text{ cm}^{-1}$ . Brunold *et al.*<sup>8</sup> justified the high intensity of the band differently: as due to mixing of  ${}^3T_2$  with ligands-to-metal charge transfer states. They observed only one electronic origin in  $\text{K}_2\text{CrO}_4$  and two in  $\text{K}_2\text{SO}_4$  with  $\vec{E}\parallel b$  polarization (Table III) and they assigned the latter two to the two  $A'$  components of  ${}^3T_2$  which, therefore, would indicate a  $T_d\rightarrow C_s$  splitting of some  $1350\text{ cm}^{-1}$ , very much in contrast with the small splitting observed by Di Sipio in  $\text{K}_2\text{CrO}_4$  and by all of them in  ${}^1E$ . As it can be seen in Table III, the electronic origins observed with  $\vec{E}\parallel b$  polarization in the three spectra indicate the existence of three, instead of two, origins. Whereas these three electronic origins cannot be explained if the band is only formed by  ${}^3T_2$ , they are naturally interpreted as corresponding to the two  $A'$  components of  ${}^3T_2$  (thus, showing its  $T_d\rightarrow C_s$  splitting), plus the  $A'$  component of  ${}^3T_1$ , which lies some  $1300\text{ cm}^{-1}$  higher in energy, as discussed above. Finally, it should be noticed that the intensity of this band is even more difficult to explain in solution, where  $T_d$  symmetry is preserved, if it were due to the  ${}^3T_2$ . As a matter of fact there has been some controversy about its assignment as the symmetry allowed  ${}^3T_1$  or as the symmetry forbidden  ${}^3T_2$ , a problem which Di Sipio *et al.* were trying to settle in their work of Ref. 9.

Finally, in the fourth band, the assignments of Di Sipio *et al.*<sup>9</sup> and of Brunold *et al.*<sup>7,8</sup> are not coincident; furthermore, none of them agrees with our interpretation of this band, which has been detailed above. In fact, the two subbands were described by Di Sipio *et al.*<sup>9</sup> as due to a strong mixture of  $e^1t^1-{}^3T_1+e^0t^2-{}^3T_1$ ; in this way their comparable high intensity could be better explained than with a sequential assignment to  $e^1t^1-{}^3T_1$  for the first subband and  $e^0t^2-{}^3T_1$  for the second which should lead to a very low intensity ought to the double  $e^2\rightarrow t^2$  excitation. On the other hand, Brunold *et al.*<sup>7,8</sup> interpreted the first subband as the excitation to  $e^1t^1-{}^3T_1$  and the second as the first ligands-to-metal charge transfer band, in order to explain its very complex contour and structure. This latter assignment faced the difficulty that its intensity, being high, is not as high as expected from a charge transfer transition.

### C. Limitations of the calculations

Before we go onto the conclusions of this paper, we would like to comment on the main limitations of the calculations, which are associated to the fact that we have not included embedding effects, nor dynamic correlation.

As we explained in Sec. II, we have calculated the absorption spectrum of  $\text{FeO}_4^{2-}$  without including embedding potentials to represent the  $\text{K}_2\text{CrO}_4$  and  $\text{K}_2\text{SO}_4$  host crystals. We have used, instead, the average of the experimental Fe–O distances in perfect  $\text{K}_2\text{FeO}_4$  to define the  $\text{FeO}_4^{2-}$  structure. Consequently, embedding effects on the electronic transitions have not been considered in this work. However, we have just seen (Table III) that the absorption spectra of Fe(VI) in the two isomorphous but considerably different  $\text{K}_2\text{CrO}_4$  and  $\text{K}_2\text{SO}_4$  hosts are extremely similar; they are also very similar to the spectrum observed in 9 M KOH solution, all of which indicates an unusual insensitivity to interactions beyond first neighbors which makes it possible that the results of the isolated  $\text{FeO}_4^{2-}$  cluster model used here compare equally well with the experimental features observed in the solids and those observed in solution.

An adequate method to include dynamic correlation in transition metal doped materials is the multireference configuration interaction method. However, in this work we have faced an unusual situation in which the references that are necessary to represent near degeneracy and which should be the bases for the multireference CI treatment, are very large expansions ranging between some 50000 to 100000 configuration state functions, which precludes the possibility of going beyond, into a multireference CI calculation. It is our opinion that there is no other justification for this approximation than the *a posteriori* observation of the systematic and overall agreement of the calculated and experimentally observed absorption spectra; this cannot be expected to be fortuitous and it can rather be understood as a cancellation of dynamic correlation effects in the energy differences. The results indicate that the dynamic correlation effects could essentially shift the whole manifold of states studied here down in the energy scale, while leaving essentially unaffected their energy differences. But, more important, it should not be expected that the inclusion of dynamic correlation would destroy the observed structure of excited states in increasingly dense sets, nor it could be expected that it would restore the simple  $d^2$  Ligand Field Theory description of the excited state manifold of  $\text{FeO}_4^{2-}$ .

### V. CONCLUSIONS

The bonding and spectroscopic properties of the tetraoxoferrate(VI) ion,  $\text{FeO}_4^{2-}$ , have been studied in this work by means of Restricted Active Space Self-Consistent-Field (RASSCF) calculations. The five molecular orbitals of main character Fe(3*d*) constitute a complete active space and the twelve orbitals of main character  $\text{O}_4(2p)$  constitute a restricted active space from which all single, double, triple, and quadruple  $\text{O}_4(2p) \rightarrow \text{Fe}(3d)$  excitations are allowed. The analysis of the RASSCF wavefunctions of the lowest lying excited states has shown that the electronic structure of  $\text{FeO}_4^{2-}$  does not correspond to the  $d^2$  ionic image of Ligand

Field Theory. The breakdown of the Ligand Field Theory model has been interpreted as due to the near degeneracy of the Fe(3*d*) and  $\text{O}_4(2p)$  orbitals which is found to originate a very rich excited state manifold. The calculations show that the electronic excited states lying below  $24000\text{ cm}^{-1}$  from the ground state, are grouped in four separate sets of states which are increasingly dense at higher energies and which include not only a spin singlet and triplet, but also spin quintet excited states, which are absolutely incompatible with the  $d^2$  Ligand Field Theory image. The calculated vertical absorption spectrum has been shown to reproduce the observed features of the experimental absorption spectra of  $\text{FeO}_4^{2-}$  in the solid state ( $\text{K}_2\text{CrO}_4$  and  $\text{K}_2\text{SO}_4$  hosts) and in solution. Its interpretation and the corresponding assignments have been found to be very different from those accepted so far, which are based in the  $d^2$  Ligand Field Theory. Satisfactory explanations have been given to the puzzling low energy value observed for the first electronic transition,  ${}^3A_2 \rightarrow {}^1E$ . The unexpected high intensity and shapes of the broad bands lying beyond  $10000\text{ cm}^{-1}$  (according to Ligand Field Theory predictions), have also been explained without resorting to large  $T_d \rightarrow C_s$  splittings and spin–orbit couplings; they are due to the superposition of the electronic states included in the third and fourth sets, both of which include spin and symmetry allowed  ${}^3T_1$  excited states. The large number of configuration state functions included in the RASSCF wavefunctions, precludes us from performing multireference CI calculations oriented to account for dynamic correlation. However, the overall agreement of the calculated and experimental spectra has been interpreted as a result of the cancellation of these effects in the computed energy differences.

### ACKNOWLEDGMENTS

We appreciate the contribution of Professor E. R. Davidson to this work through fruitful comments and suggestions. This work was partly supported by a grant from MEC (DGI-CYT PB95-0201) Spain. A.A.-A. gratefully acknowledges a fellowship from the Spanish Ministerio de Educación y Cultura (Beca FPI).

<sup>1</sup>S. Sugano, Y. Tanabe, and H. Kamimura, *Multiplets of Transition-Metal Ions in Crystal* (Academic, New York, 1970).

<sup>2</sup>*Tunable Solid-State Lasers*, Vol. 5 of the OSA Proceedings Series, edited by M. L. Shand and H. P. Jenssen (Optical Society of America, Washington, DC, 1989).

<sup>3</sup>*OSA Proceedings of Advanced Solid-State Lasers*, edited by G. Dubé and L. Chase (Optical Society of America, Washington, DC, 1991).

<sup>4</sup>T. Brunold, M. Herren, H. U. Güdel, U. Kesper, C. Albrecht, and D. Reinen, *J. Lumin.* **60&61**, 138 (1994).

<sup>5</sup>S. M. Jacobsen, H. U. Güdel, and C. A. Daul, *J. Am. Chem. Soc.* **110**, 7610 (1988).

<sup>6</sup>C. Reber, H. U. Güdel, G. Meyer, T. Schleid, and C. A. Daul, *Inorg. Chem.* **18**, 3249 (1989).

<sup>7</sup>T. C. Brunold, A. Hauser, and H. U. Güdel, *J. Lumin.* **59**, 321 (1994).

<sup>8</sup>T. C. Brunold, H. U. Güdel, S. Kück, and G. Huber, *J. Lumin.* **65**, 293 (1996).

<sup>9</sup>L. Di Sipio, G. De Michelis, E. Baiocchi, and G. Ingletto, *Transition Met. Chem.* **5**, 164 (1980).

<sup>10</sup>A. Al-Abdalla, L. Seijo, and Z. Barandiarán, *J. Mol. Struct.: THEOCHEM* (in press).

<sup>11</sup>S. López-Moraza, J. L. Pascual, and Z. Barandiarán, *J. Chem. Phys.* **103**, 2117 (1995).

<sup>12</sup>S. López-Moraza and Z. Barandiarán, *J. Chem. Phys.* **105**, 50 (1996).

- <sup>13</sup>S. López-Moraza, L. Seijo, and Z. Barandiarán, Phys. Rev. B **57**, 11974 (1998).
- <sup>14</sup>L. Seijo, Z. Barandiarán, and L. G. M. Pettersson, J. Chem. Phys. **98**, 4041 (1993).
- <sup>15</sup>A. Al-Abdalla, Z. Barandiarán, L. Seijo, and R. Lindh, J. Chem. Phys. **108**, 2005 (1998).
- <sup>16</sup>J. L. Pascual and L. Seijo, J. Chem. Phys. **102**, 5368 (1995).
- <sup>17</sup>J. L. Pascual, L. Seijo, and Z. Barandiarán, J. Chem. Phys. **103**, 4841 (1995).
- <sup>18</sup>R. Llusar, M. Casarrubios, Z. Barandiarán, and L. Seijo, J. Chem. Phys. **105**, 5321 (1996).
- <sup>19</sup>J. L. Pascual, L. Seijo, and Z. Barandiarán, J. Chem. Phys. **98**, 9715 (1993).
- <sup>20</sup>L. Seijo and Z. Barandiarán, Int. J. Quantum Chem. **60**, 617 (1996), and references therein.
- <sup>21</sup>P.-A. Malmqvist, A. Rendell, and B. O. Roos, J. Phys. Chem. **94**, 5477 (1990).
- <sup>22</sup>M. A. Buijse and E. J. Baerends, J. Chem. Phys. **93**, 4129 (1990).
- <sup>23</sup>Z. Barandiarán and L. Seijo, J. Chem. Phys. **89**, 5739 (1988).
- <sup>24</sup>Z. Barandiarán and L. Seijo, in *Computational Chemistry: Structure, Interactions and Reactivity*, Vol. 77B of *Studies in Physical and Theoretical Chemistry*, edited by S. Fraga (Elsevier, Amsterdam, 1992), pp. 435–461.
- <sup>25</sup>J. A. McGinety, Acta Crystallogr. B **28**, 2845 (1972).
- <sup>26</sup>K. Toriumi and Y. Saito, Acta Crystallogr. B **34**, 3149 (1978).
- <sup>27</sup>R. J. Audette, J. W. Quail, W. H. Black, and B. E. Robertson, J. Solid State Chem. **8**, 43 (1973).
- <sup>28</sup>MOLCAS version 4, K. Andersson, M. R. A. Blomberg, M. P. Fülscher, G. Karlström, R. Lindh, P.-Å. Malmqvist, P. Neogrády, J. Olsen, B. O. Roos, A. J. Sadlej, M. Schütz, L. Seijo, L. Serrano-Andrés, P. E. M. Siegbahn, and P.-O. Widmark, Lund University, Sweden, 1997.
- <sup>29</sup>A. J. H. Wachters, J. Chem. Phys. **52**, 1033 (1970).
- <sup>30</sup>P. J. Hay, J. Chem. Phys. **66**, 4377 (1977).
- <sup>31</sup>L. G. M. Pettersson (private communication).
- <sup>32</sup>S. Huzinaga, Z. Barandiarán, L. Seijo, and M. Klobukowski, J. Chem. Phys. **86**, 2132 (1987).
- <sup>33</sup>T. H. Dunning and P. J. Hay, in *Modern Theoretical Chemistry*, edited by H. F. Schaefer, III (Plenum, New York, 1977).
- <sup>34</sup>B. O. Roos, P. R. Taylor, and P. E. M. Siegbahn, Chem. Phys. **48**, 157 (1980); P. E. M. Siegbahn, A. Heiberg, J. Almlöf, and B. O. Roos, J. Chem. Phys. **74**, 2384 (1981); P. Siegbahn, A. Heiberg, B. Roos, and B. Levy, Phys. Scr. **21**, 323 (1980).
- <sup>35</sup>Note that by Fe(3d) and O<sub>4</sub>(2p) orbitals we actually mean molecular orbitals whose main contributions come from symmetry adapted Fe(3d) or O<sub>4</sub>(2p) basis functions, respectively.
- <sup>36</sup>M. Atanasov, Chem. Phys. **195**, 49 (1995).
- <sup>37</sup>M. Atanasov, H. Adamsky, and K. Eifert, J. Solid State Chem. **128**, 1 (1997).
- <sup>38</sup>A. Al-Abdalla, L. Seijo, and Z. Barandiarán, in progress.
- <sup>39</sup>A. Carrington, D. Schonland, and M. C. R. Symons, J. Chem. Soc. 659 (1957).
- <sup>40</sup>M. F. Hazenkamp, H. U. Güdel, M. Atanasov, U. Kesper, and D. Reinen, Phys. Rev. B **53**, 2367 (1996).