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FeO_4: A unique example of a closed-shell cluster mimicking a superhalogen

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First-principles calculations based on the generalized gradient corrected density-functional theory reveal that iron tetraoxide (FeO_4), in spite of its closed-shell structure, has an electron affinity that is larger than that of any known halogen atom. This novel property is shown to be a manifestation of the special bonding characteristics of *d*-electron systems and can play an important role in chemical and biological processes. [S1050-2947(99)01505-X]

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That atomic clusters with specific size and composition can mimic the chemistry of atoms and thus be regarded as ''superatoms'' has opened a new line of investigation in recent years. Consider, for example, compounds such as LiF_2, $LiCl_2$, NaF_2, $NaCl_2$, BF_4, AlF_4, PF_6, AlO_2, PO_3, and ClO_4. These clusters consist of *sp* elements and have one common characteristic feature: they can all be represented by a formula unit MX_m where the coordination number *m* fulfills the requirement $mn=k+1$; *n* is the normal valence of the ligand atom, *X*, while *k* is the maximal valence of the central atom, *M*. An extra electron in the $MX_m{}^-$ anion fills in the molecular orbital (MO) which does not contain contributions from the central atom by symmetry. Thus, these compounds have very high electron affinities that can reach values as high as 9 eV [1]. While in the neutral state these compounds are weakly bound [2,3], and in some cases, like PF_6, they are even thermodynamically unstable [4,5], their negative anions are very stable. These compounds play important roles in chemical synthesis.

While studies of *sp* superhalogens have been carried out for over a decade, not much emphasis has been placed on similar investigations involving transition-metal elements. Earlier theoretical efforts were concentrated at evaluating the vertical detachment energies from the anions of transition-metal oxides and fluorides at geometries taken from x-ray-diffraction data on salts [1]. These studies were performed with the discrete-variational X_α method [6,7], which is known to bias towards underestimating binding energies of extra electrons [8,9]. In particular, no data are available on the thermodynamic stability of *d* superhalogens. This is rather surprising as transition-metal oxide clusters such as MnO_x and FeO_x play important roles not only in physical chemistry but also in biological processes. For example, manganese oxo-compounds are important in photosynthesis and iron serves as an oxygen carrier in biological systems.

An iron atom with its eight valence electrons ($3d^6 4s^2$) interacting with four divalent oxygen atoms ($2s^2 2p^4$) has to be expected to have a closed-shell ground state. Indeed, we performed optimizations for FeO_4 states with higher multiplicities ($2S+1=3,5,7$) and found them to be higher in energy at least by 0.7 eV compared to the singlet ground state. Consequently, iron tetraoxide should possess a low electron affinity ($\approx$1 eV). On the other hand, MnO_4 with a hole in the highest occupied molecular orbital (MO) (Mn has an $[\mathrm{Ar}](3d^5 4s^2)$ configuration and thus the maximal valence of seven) should have a high electron affinity. We have studied the equilibrium geometries and energetics of FeO_4 and MnO_4 in neutral and anionic forms using the generalized gradient approximation within the density-functional theory. While MnO_4 is found to be a superhalogen with an adiabatic electron affinity of 5.0 eV, which is consistent with the characteristics of *sp* superhalogens, the electron affinity of closed-shell FeO_4 is found to be 3.8 eV, which is larger than the highest electron affinity of any halogen atom, namely, of Cl (3.62 eV). This unusual behavior is shown to be due to the special bonding characteristics of *d*-electron systems and opens up new possibilities for designing superhalogens involving transition-metal elements.

Our calculations are based on the molecular orbital theory where the molecular orbitals are constructed from linear combinations of atomic orbitals centered at the individual nuclear sites. We represent the atomic orbitals by a Gaussian basis ($6\text{-}311+G^*$) which consists of $[10s7p4d1f]$ for Fe and Mn, and $[5s4p1d]$ for O. The geometries were optimized without symmetry constraints for all allowable spin multiplicities using the steepest descent method in the GAUSSIAN94 code [10]. The exchange-correlation potential was treated within the generalized gradient approximation with Becke's exchange [11] and Perdew-Wangs' correlation [12] referred as to BPW91 below.

The adiabatic electron affinity (A_{ad}) of a neutral system is defined as the difference in the ground-state total energies of the system and its anion. Within the Born-Oppenheimer (BO) approximation employed in the present work, one may evaluate the A_{ad} as

$$A_{\mathrm{ad}}=E_{\mathrm{tot}}(N,R_e)+Z_N-E_{\mathrm{tot}}(A,R_e^-)-Z_A=\Delta E_{\mathrm{el}}^{\mathrm{ad}}+\Delta E_{\mathrm{nuc}}, \tag{1}$$

where R_e and R_e^- denote equilibrium geometries of the neutral system (*N*) and its anion (*A*), respectively. The zero-point vibration energies (*Z*) are computed within the harmonic approximation.

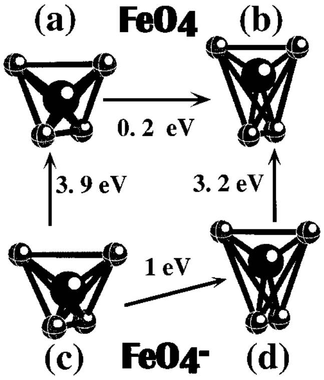

FIG. 1. Geometries of the ground states and isomers of the neutral $(a,b,2S+1=1)$ and anion $(c,d,2S+1=2)$ FeO_4 clusters.

The vertical detachment energy (E_{vd}) of an extra electron from an anion can be defined within the BO approximation as

$$E_{\mathrm{vd}}=E_{\mathrm{tot}}(N,R_e^-)+Z_N-E_{\mathrm{tot}}(A,R_e^-)-Z_A=\Delta E_{\mathrm{el}}^{\mathrm{vd}}+\Delta E_{\mathrm{nuc}}. \tag{2}$$

Since one can anticipate a rather small change in the nuclear energy due to low-amplitude displacements around the equilibrium geometry, one can use the Z_N and Z_A evaluated from harmonic frequency calculations at R_e and R_e^-, respectively. Thus, we consider ΔE_{nuc} to be the same in Eqs. (1) and (2).

First, we have optimized the ground states of FeO_4 and FeO_4^-. Iron in FeO_4 has fully saturated its formal valence $(k=8)$ and the wave function is totally symmetric: $^1A_{1g}$ within T_d symmetry of the nucleus. Since the lowest unoccupied MO in FeO_4 is degenerate and has E symmetry, a distortion of T_d symmetry is expected upon attachment of an extra electron due to the Jahn-Teller effect. Indeed, the ground state of the FeO_4^- anion has D_{2d} symmetry although the distortion from a tetrahedron is insignificant [see Figs. 1(a) and 1(c)]. Here, the O-O bonds are broken and all the four oxygens bind atomically to Fe. The distances between equivalent pairs of oxygens are 2.61 and 2.71 Å compared to 1.22 Å in the gas-phase O_2 molecule.

The bond length in FeO_4 is 1.596 Å, which is close to those in the ground states of FeO (1.608 Å), FeO_2 (1.588 Å), and FeO_3 (1.577 Å). Thus, one can surmise that the Fe-O bonds in FeO_4 may be attributed to as double bonds. According to the natural bond analysis [13] the electronic configurations of atoms in FeO_4 are $Fe(4s^{0.3}3d^{6.7})$ and $O(2s^{1.9}2p^{4.3})$, and the bonding can be considered as "ionic." In the FeO_4^- anion, the atomic configurations are $Fe(4s^{0.3}3d^{6.6})$ and $O(2s^{1.9}2p^{4.6})$, i.e., the additional electron is delocalized over four oxygen atoms.

We have also searched for other isomers of FeO_4 and FeO_4^- where the O-O distance could be shorter and closer to the O_2 bond length. Such C_{2v} configurations with a spin multiplicity of 1 and 2 for FeO_4 and FeO_4^-, respectively, have been found [see Figs. 1(b) and 1(d)]. Here, the long O-O bond lengths are 2.71 and 2.74 Å while the short bond lengths are 1.39 and 1.45 Å, in FeO_4 and FeO_4^-, respectively. Thus, while one O_2 molecule binds dissociatively, the other one binds associatively. Recently, Chertihin *et al.* [14] identified the C_{2v} structure as the ground state of FeO_4. However, since the difference in total energies of the T_d and C_{2v} configurations of FeO_4 is small, the assignment of the ground-state symmetry of FeO_4 is strongly dependent on the computational method used. The anion is more rigid, and the difference in total energies between its D_{2d} and C_{2v} configurations is about 1 eV. We will show in the following that both configurations play an important role in explaining the recent photodetachment spectra of FeO_4^-.

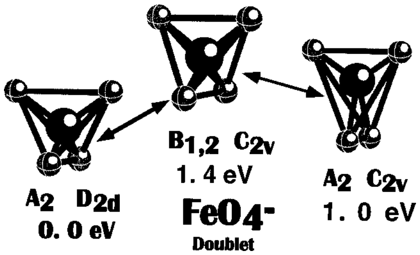

FIG. 2. Ground-state, transition states, and stable isomer geometries of FeO_4^- corresponding to a multiplicity of 2.

In order to check if there are additional anion states of C_{2v} symmetry, we have optimized the anion geometry for all four types of irreducible representations of C_{2v} point group of symmetry. The geometries and the total energies of the $^2A_1$ and $^2A_2$ states have converged to the ground-state geometry and the total energy, respectively, whereas $^2B_1$ and $^2B_2$ states were found to have the same geometrical parameters and to be energetically degenerate.

Frequency calculations have revealed an imaginary mode of a_2 symmetry for both $^2B_1$ and $^2B_2$ states, which couples these two transition states, since the direct product $B_1*a_2*B_2=A_1$ for the $\langle\Phi_{\mathrm{in}}|\nu|\Phi_{\mathrm{fin}}\rangle$ matrix element, i.e., it contains the totally symmetric representation and cannot vanish by symmetry. Coupling through a mode of a corresponding symmetry can lead to a transition into the ground or (C_{2v},A_2) states. These $^2B_1$ and $^2B_2$ states are above the anion ground state by 1.4 eV, which provides an estimate for the barrier height between two stationary anion states of A_2 symmetry (see Fig. 2).

A direct search for the barrier height between the FeO_4^- D_{2d} and C_{2v} states (both have A_2 symmetry) with the synchronous transit method stopped at the barrier height of 0.7 eV and the geometry close to that of the $^2B_1$ and $^2B_2$ states. Apparently, the nonconvergence is related to mixing of three energy-degenerate states of A_2, $^2B_1$, and $^2B_2$ symmetries at that point.

Optimized anion configurations for multiplicities $M=2S+1$ up to 8 are presented in Fig. 3. Surprisingly, the total energies of these configurations, which are stationary according to frequency calculations, are lower than the total energy of the neutral ground state by 3.15, 1.8, and 0.4 eV for $M=4$, 6, and 8, respectively. This means that all these excited states are stable against autodetachment of an extra electron.

The adiabatic electron affinity of FeO_4 computed according to Eq. (1) is 3.8 eV, which is larger than the electron affinity of any of the halogen atoms. Note that Cl has the largest EA, namely, 3.62 eV, whereas O and Fe have EA's of 1.46 and 0.16 eV, respectively [15]. The high A_{ad} of FeO_4 is rather surprising because FeO_4 is a cluster with a closed

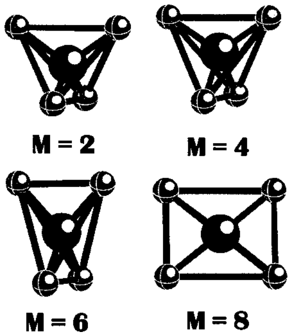

FIG. 3. Geometrical configurations of ground ($M=2$) and excited states ($M=4$, 6, and 8) of FeO_4^-.

TABLE I. Energies corresponding to vertical electron detachment from low-lying FeO_4^- states to neutral FeO_4 states with various allowable spin multiplicities. (For description, see the text.) All values are in eV.

FeO_4^-			FeO_4		
				$2S+1$	
$2S+1$	Symm.	ΔE_{tot}	1	3	5
2	D_{2d}	0.0	3.9	4.9	
	C_{2v}	0.9	3.2	4.2	
4	C_{2v}	0.7		4.9	4.9

electronic shell, and it is known from a large number of examples of *sp*-closed shell systems [16,17] that closed-shell systems possess low electron affinities (typically about 1 eV or less). The vertical detachment energies of an extra electron in FeO_4^- and MnO_4^- computed according to Eq. (2) are higher than the A_{ad}'s of FeO_4 and MnO_4 by 0.1 eV only, i.e., 3.9 and 5.1 eV in the ground state FeO_4^- and MnO_4^-, respectively. We note that a previous estimate [18] of 3.4 eV for the E_{vd} of FeO_4^-, obtained within the X_α approximation, is somewhat underestimated compared to our present result, whereas the X_α E_{vd} of 5.0 eV for MnO_4 matches the value computed in the present work.

In order to find a reason for the high A_{ad} of FeO_4, we have examined the nature of the highest occupied molecular orbital (HOMO) in the FeO_4^- anion which accommodates the extra electron. This MO has a_2 symmetry and stems from the E irreducible representation of T_d point-group symmetry upon reduction to D_{2d} symmetry. The MO is a linear combination of $d_{xy}(\mathrm{Fe})+p_x(\mathrm{O}_1,\mathrm{O}_3)-p_x(\mathrm{O}_2,\mathrm{O}_4)$ and is of a bonding type with respect to oxygen-oxygen interaction and is slightly antibonding with respect to Fe-O interactions because the contribution of Fe $3d$ orbitals is about 10% only. Note that the HOMO of MnO_4^- has a pure ligand character and does not contain any Mn $3d$ orbitals by symmetry. Therefore, the difference between *sp* and *d* superhalogens could be related to a larger number and different types of molecular orbitals which can be formed from the atomic *d* manifold with respect to the *p* manifold. In particular, even closed-shell neutral clusters can have bonding HOMO's and provide rather high binding energies for an extra electron upon its filling into such a HOMO. The FeO_4 appears to present the first example of such a cluster.

We now compare our results with available experiments. Recently, Wang and co-workers [19] have obtained laser photodetachment spectra of FeO_n^- ($n\leqslant 4$). They found the A_{ad} to increase almost linearly with oxygen content and saturate at $n=4$. In the spectra of FeO_4^- obtained with photons of different energies, they have observed a weak-intensity feature beginning at $\approx$3.2 eV and a high-intensity peak beginning at 3.9 eV. In order to compare our results with the experiment, we have computed vertical detachment energies from the anion states into neutral states of permitted multiplicities according to Eq. (2). The results are given in Table I. As seen, detachment energies of an extra electron from both doublet and quartet anion states resulting in the formation of triplet neutral states are larger than 4 eV and cannot be responsible for the low-energy features in experimental spectra. Detachment of an extra electron from the anion states with $M=6$ and 8 provides energies higher than 5 eV. The detachment energy of 3.9 eV for the anion ground state fits the origin of the second high-intensity feature in the experimental spectra. Therefore, one can conclude that the value of 3.3 eV attributed to the EA of FeO_4 according to experimental measurements corresponds to an electron detachment from the ($M=2$, C_{2v}) state of FeO_4^-, while the A_{ad} defined by Eq. (1) corresponds to detachment from the ground ($M=2$, D_{2d}) state.

Because the A_{ad} of FeO_4 exceeds the EA of the most electronegative atom Cl, iron tetraoxide should be attributed to the class of superhalogens [1], in spite of its closed-shell structure. This is in sharp contrast with *sp* compounds, where MO_n superhalogens fulfill the requirement $n=(k+1)/2$, where k is the maximal formal valence of the central atom, and the extra electron fills in the MO which does not contain contributions from the central atom by symmetry.

The second important characteristic of superhalogens is related to their thermodynamic stability. In the case of *sp* superhalogens, the neutral MX_m systems are either weakly bound [2,3] or even thermodynamically unstable (e.g., PF_6 [4,5] or SiF_5 [20]) but their anions are very stable. According to our computations, the first fragmentation channel in both FeO_4 and FeO_4^- corresponds to emission of O_2. The fragmentation energy $FeO_4\rightarrow FeO_2+O_2$ is 1.74 eV, versus 3.34 eV for the $FeO_4^-\rightarrow FeO_2^-+O_2$ channel. A more stable character of the FeO_4^- anion is consistent with a higher stability of anions formed by *sp* superhalogens.

In conclusion, we have shown that the electron affinity of transition-metal oxide clusters may not follow the same trends as observed earlier for *sp*-bonded systems. The unique spatial distribution of *d* electrons renders novel electronic properties to transition-metal oxides. It is argued that even a closed-shell cluster could exhibit a superhalogen behavior. In addition, we have shown that, contrary to earlier speculations, the low-energy peak in the photodetachment spectra of FeO_4^- does not arise from detachment of an extra electron from the ground state of the anion, but from a higher-energy isomer. The adiabatic electron affinity of FeO_4, therefore, is associated with the higher-energy peak, namely 3.9 eV. Thus, the statement of Wang *et al.* [19] that the electron affinity of FeO_n clusters saturates at $n=4$ needs to be modified.

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