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A New Proposal for the Ground State of the FeO^- Cluster in the Gas Phase and for the Assignment of Its Photoelectron Spectra

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High-level multireference CASPT2 calculations are performed to determine the electronic structures of the FeO and FeO^- clusters. Geometry optimizations of all possible low-lying states of the two unsaturated complexes are carried out at the mentioned theoretical level by calculating their potential energy curves. FeO^- is proposed to possess a $^6\Sigma^+$ ground state as opposed to the $^4\Delta$ state, which has been put forward as the ground state by previous computational studies. On this basis an alternative assignment of the photoelectron spectra of this anion is postulated. All features of these spectra are tentatively attributed to either septet or quintet states of the neutral FeO cluster. The lowest energy band in the spectra is then the result of electron detachments to the $^5\Delta$ ground state and the $^5\Sigma^+$ lowest excited state. The second lowest band might be due to the $^7\Sigma^+$. Two higher energy bands are thought to originate from two $^5\Pi$ states and a $^5\Phi$. Vibrational progressions that are observed for some bands could be explained in terms of the calculated potential energy profiles of the relevant states. Credibility for the proposed assignment is rendered by the good correspondence between experiment and our computational method concerning the bond distance and dipole moment for the ground state of FeO.

Introduction

The chemical bond between iron and oxygen is found throughout all major branches of chemistry. Oxygen carriers in biological systems rely on this bond, whereas its relevance to corrosion does not need to be stressed. It is therefore no surprise that the smallest molecule where this bond is present, namely iron monoxide, has been the subject of several experimental[1−9] as well as theoretical studies.[10−14] Transition metal monoxides in general are known to dominate the spectra of cold stars due to the high abundance of oxygen in the universe and the fact that transition metals are the final products of thermonuclear processes. Furthermore, these oxides are important entities in high-temperature terrestrial chemistry. Direct spectroscopic measurements of these species in the gas phase at room temperature is however difficult, if possible at all. Consequently, for many transition metal monoxides the main source of experimental information about their electronic structure is photoelectron spectroscopy applied to laser vaporization ion beam mass spectrometry experiments. This is also the case for FeO where the photoelectron spectra of the anionic FeO^- have been measured with the purpose to provide essential experimental data for unraveling the electronic structure of the neutral species. The information contained in these spectra is nevertheless insufficient. Assistance of theoretical considerations, in particular ab initio calculations, must be viewed as of crucial importance in assigning the nature of the observed bands.

There are several studies on the photoelectron spectra of FeO^- available in the literature. To our knowledge the earliest study was carried out by Engelking and Lineberger,[15] which dates back to 1977. Only two states were thought of being observed at the time: a vibrationally resolved ground state of FeO at about 1.50 eV and a low-lying excited state at 2.0 eV. On the basis of prior theoretical calculations[16] the ground state of the neutral was assigned as $^5\Delta$ and the excited state as $^5\Sigma^+$. Almost 20 years later a more complete picture of the electronic structure of the neutral complex was obtained by recording the photoelectron spectrum at 3.49 eV photon energy.[17] Besides the confirmation of the assignments of the low-energy part of the spectrum of reference 15, two additional features at higher energies were observed, which were both assigned as triplets. In a subsequent study from the same group[18] an additional vibrationally resolved band in the high energy part of the 4.66 eV photoelectron spectrum was observed and assigned as a photoelectron detachment to a $^3\Pi$ state. Rather surprisingly there is no complete theoretical confirmation about this interpretation of the photoelectron spectra of FeO^- available in the literature. Moreover, there are some uncertainties about the proposed assignments. In particular the strange trend of the measured intensities of the lowest energy band are not in line with a normal Franck−Condon envelope. The septet state $^7\Sigma^+$, which is thought as being situated just above the $^5\Delta$ ground state of FeO, was held responsible for this unusual vibrational progression.[17] This is quite curious since the ground state of FeO^- is believed to be quartet, which would exclude any septet state to appear with a measurable intensity in single-electron processes such the ones responsible for photoelectron spectra. Nevertheless, the same conclusion was reached a few years later by means of high resolution 532 and 690 nm photoelectron spectra and mass selected anion-zero kinetic energy photoelectron spectroscopy.[19] Additional doubt on the proposed assignments is cast by making a comparison with the photoelectron spectra of the related FeS^-.[20] The low-energy parts of the photoelectron spectra of these two anions show a striking resemblance. However, the FeS^- spectra were originally explained and later affirmed by CASPT2 calculations[21] as originating from a sextet ground state. Opposed to the interpretation for FeO^- all features in the FeS^- spectra were therefore assigned to either quintets

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or septets. In view of all these discrepancies a thorough theoretical study of the low-lying states of FeO and FeO^- by means of the multireference CASPT2 method is warranted.

Computational Details

All results presented in this contribution were obtained by carrying out CASPT2 calculations with the MOLCAS 7.0 suite of programs.[22] Although the point group of heterodiatomic molecular systems is $C_{\infty v}$, the MOLCAS software incorporates only Abelain point groups below and including D_{2h}, forcing our calculations on FeO and FeO^- to be carried out by using the C_{2v} point group and invoking the keyword LINEAR to ensure the degeneracy of the π and δ orbitals during the CASSCF part. All energies were obtained by including the scalar relativistic effects according to the so-called Douglas−Kroll transformation.

The electronic structure of low-valent unsatured complexes, such as the title compounds, can be expected to be very complex. First, for a transition metal that is situated in the second half of its series, such as iron, we can only expect a large active space to be sufficiently flexible. In particular for Fe^+, which is the formal oxidation state of iron in FeO^-, it is well-known that in an energy range of 25 000 cm^{-1} above the ground state there are no less than 12 terms present in the spectrum. Partly, this is the outcome of the near-degeneracy of the 3d and 4s levels, as is evidenced by the small splitting of 1792 cm^{-1} between the ^6D ($3d^6 4s^1$) ground state of Fe^+ and the first excited state ^4F ($3d^7$). Second, the negative charge of FeO^- causes a diffuse electronic structure with more pronounced near-degeneracy effects than in neutral systems. Third, the presence of just one ligand causes only a small splitting of the valence 3d orbitals, resulting in large interactions between the various states of the cluster. Numerous test calculations with different active spaces on all low-lying states at various internuclear distances indicated that the following active space gives the most stable results in terms of convergence of the CASSCF calculations and the consistency between the different geometries. Obviously, all the atomic orbitals of iron and oxygen that give rise to the valence molecular orbitals should be included in the active space. Our calculations indicated that this is the case for the 2p orbitals of oxygen and the 3d and 4s orbitals of iron. To guarantee sufficiently flexibility, we augmented the size of the active space by adding two empty orbitals per irreducible representation (irrep) of the C_{2v} point group. Therefore, the active space used consists of a total of 14 orbitals: six of a_1 symmetry, three of b_1 and b_2 symmetry and two orbitals of a_2 symmetry. Since these orbitals are occupied by 12 (FeO) or 13 (FeO^-) electrons, it can be denoted by generally accepted symbols as (12,14) or (13,14). By employing this active space the most promising results in connection with the interpretation of the photoelectron spectrum of FeO^- were obtained.

First this active space was utilized to perform geometry optimizations. For each of the four irreproducible representations of the C_{2v} point group, the lowest quartet and sextet anionic (FeO^-) states and lowest triplet, quintet, and septet neutral (FeO) states were considered. The necessary energy profile diagrams for each of these states were obtained by means of single-point CASPT2 calculations, which use the CASSCF wave functions as zero-order wave functions in a second-order perturbation treatment for the dynamic correlation energy. Part of the correlation energy was retained by using the [8s,7p, 5d, 4f, 2g] and [6s, 5p, 4d, 2f] ANO-RCC basis sets for Fe and O, respectively, as implemented in the MOLCAS 7.0 package, and by correlating in addition to the valence electrons of the active space the 3p electrons of iron. A least-squares fitting of these energy profiles to a quadratic polynomial delivered equilibrium bond distances and vibrational frequencies. Throughout the text these calculations will be referred as computational level **I**.

During a second step a larger ANO-RCC basis sets [8s,7p, 6d, 4f, 2g, 1h] for iron and [7s, 6p, 4d, 3f, 1g] for oxygen were used and the 3s electrons of iron and the 2s electrons of oxygen were additionally correlated in CASPT2. By using this more elaborated computational level, which we denote as level **II**, a more reliable determination of the ground state of the anionic FeO^- cluster was undertaken. A tentative assignment of the photoelectron spectrum of the same cluster is proposed by calculating at this level **II** all possible candidate states of the neutral FeO at the equilibrium bond distance of the anionic ground state, in other words applying the Franck−Condon principle. During the CASPT2 step standard values for all keywords were used, for example, IPEA = 0.25, and no level shift was applied.

Results and Discussion

General Considerations. Experimental evidence for the existence of the FeO and FeO^- clusters in the gas phase has been available for a long time now. Already from early theoretical studies the basic aspects of their electronic structures, which are in line with the general perceptions of transition metal complexes, were obtained. In the following sections we will demonstrate that this early description is confirmed by our state-of-the-art computational model. It is therefore to some extent surprising that rather recent research described an electronic structure that somewhat deviates from this picture, in the sense that the character of some valence orbitals depart from what can logically be expected or a different ordering of the orbitals.[18,23,24] Before going into a detailed discussion we would like to draw the reader's attention to the basic principles that lie at the heart of the electronic structure of these type of unsaturated complexes The first one is the simple fact that due to its high electronegativity the oxygen atom will acquire two electrons from the more electropositive iron atom, giving rise to a closed shell O^{2-} ligand. The remaining valence electrons and resulting charge on iron depends on the total charge of the cluster, being six electrons and a formal charge +2 for the neutral complex, while the anionic cluster has seven valence electrons on iron giving the cation a formal charge of +1. Because of the electrostatic attraction between the iron cation and the oxygen anion, the valence orbitals of the two constituent parts overlap which induces some covalency to the resulting chemical bond, causing the actual charges on the constituent atoms to be lower than the formal charges.

According to a second principle which can quite generally be applied to nearly all transition metal complexes, the closed shell valence orbitals of the ligand are situated energetically below the partially occupied metal valence orbitals. For the title clusters this means that the oxygen 2p orbitals give rise to doubly occupied *bonding orbitals* with a smaller iron contribution that is proportional to the covalency of the metal−oxygen bond. The corresponding molecular orbitals are 8σ ($2p_z$) and 3π ($2p_x$ and $2p_y$). The 2s orbital of oxygen does not significantly participate in these covalency effects as is evident from our calculations. Upon bond formation the metal orbitals are transformed into two sets of molecular orbitals. Those iron orbitals that interact with the oxygen 2p shell result in *antibonding* orbitals as a consequence of the higher energy position before this interaction. At a lower energy we have the 4π level ($3d_{xz}$ and $3d_{yz}$) as mildly antibonding orbitals and at a higher energy the strongly antibonding 10σ orbital (mainly $3d_{z^2}$). The second set of iron

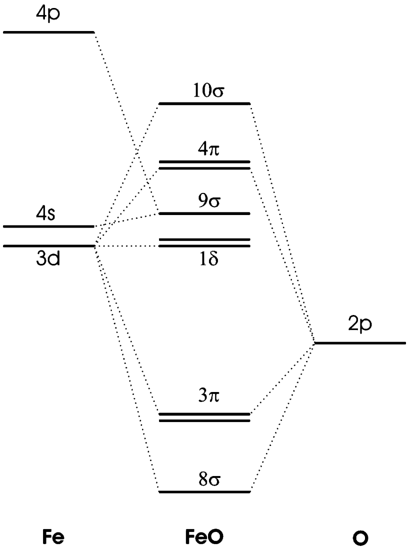

Figure 1. General schematic orbital diagram for iron−oxygen diatomics. Molecular orbitals can be divided into three groups. At lowest energies are the bonding orbitals (8σ, 3π) that have predominantly oxygen 2p character. Nearly or pure iron nonbonding orbitals (9σ, 1δ) are positioned at the middle of the diagram. At the highest energies we find the antibonding mainly iron orbitals (4π, 10σ).

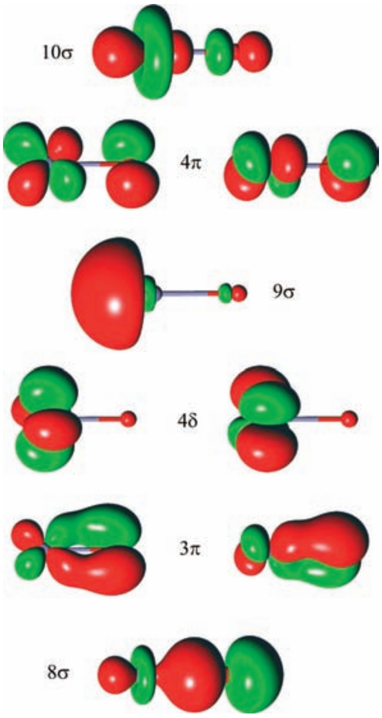

Figure 2. CASSCF natural orbitals as calculated for the $^7\Sigma^+$ high-spin state of FeO. Only those active space orbitals that are either singly or doubly occupied in the leading configuration of the CASSCF wave function of the mentioned state are depicted. The orbitals of the other states of FeO and FeO$^-$ discussed in the text have very similar shapes, except for the 9σ orbital for which the shape depends strongly on the state considered. For some states it turns out to be rather a 4s−d$_\sigma$ hybrid.

orbitals contains besides the remaining 3d$_{xy}$ and 3d$_{x^2-y^2}$ also 4s. They lie at the basis of the *nonbonding orbitals* 1δ and 9σ. The former level comprises 3d$_{xy}$ and 3d$_{x^2-y^2}$ as a consequence of their zero overlap with the 2s and 2p orbitals of oxygen. The suitable 3d orbitals of this ligand lie too high in energy to play any part in the bond formation process. Essential in the analysis of the properties of the title clusters is the nonbonding character of the 9σ orbitals, which is the outcome the hybridization of 4s with 4p (vide infra) in some states or a hybrid 4s−3d$_\sigma$ in other states. A summary of the preceding discussion is shown in the orbital correlation diagram of Figure 1. In the following paragraphs we will illustrate in detail this picture of the electronic structure by calculating the relative positions of the low-lying electronic states in their equilibrium distances at the CASPT2 level and by an analysis the molecular orbital plots as we obtained them by the CASSCF technique.

FeO. For the neutral FeO with its six valence electrons to be distributed among the six iron valence orbitals, a maximal spin multiplicity of 7 is possible. As a matter of fact just one low-lying *septet state* is possible, namely the one in which all six valence electrons occupy each just one of the dominant iron orbitals with a parallel spin. The resulting $^7\Sigma^+$ state answers therefore to the following configuration: $9\sigma^1\ 1\delta^2\ 4\pi^2\ 10\sigma^1$. This is illustrated in the CASSCF orbital plots for this state in Figure 2. Indeed, all the antibonding, that is, 4π and 10σ, as well as the nonbonding 9σ and 1δ orbitals are singly occupied and clearly possess a major metal contribution. Figure 2 shows clearly that the nonbonding nature of the 9σ orbital is indeed the outcome of a 4s−4p hybridization, which causes this orbital to have its electron density placed around the internuclear axis pointing away from the oxygen ligand. The low-lying orbitals 8σ and 3π on the contrary have predominant oxygen character, exhibiting a bonding interaction with the iron part and are double occupied in the leading configuration of the CASSCF wave function. These observations therefore constitute a first confirmation for the above proposed description of the electronic structure. Further proof can be obtained from the other septet states which were indeed calculated at much higher energies. Within the applied computational approach they can only be realized by formally transferring an electron from the bonding 3π oxygen orbital to either the nonbonding 1δ iron orbital, giving rise to nearly degenerate $^7\Pi$ or $^5\Phi$ states with their equilibrium structures at 1.29 eV above $^7\Sigma^+$, or to the antibonding 4π level, resulting in a $^7\Delta$ positioned even higher at 1.65 eV. In summary, of all these septets, $^7\Sigma^+$ has the largest number of electrons in bonding orbitals. Therefore, its energy is the lowest and its equilibrium bond distance of 1.679 Å is the shortest of all septets mentioned in Table 1. The specific value of the bond distance will be important when we analyze the photoelectron spectra of FeO$^-$. The $^7\Delta$ state has the largest bond distance of 1.953 Å of all the septets studied, simply because it has the most electrons in the antibonding oribtals 4π and 10σ, namely four, when compared to the $^7\Pi$ or $^5\Phi$ states, which have only three electrons in these orbitals. Their bond distances are indeed intermediate and equal 1.886 Å. Besides the found bond distances, also the calculated CASPT2 harmonic frequencies for these septets are fully in line with their binding characteristics. The largest frequency is found for the $^7\Sigma^+$ and amounts to 743 cm^{-1}, noticeably larger than the values of 635 and 603 cm^{-1} obtained for $^7\Pi$ or $^5\Phi$ and $^7\Delta$, respectively.

To understand the relative position of the *quintets* some refinement of the above presented electronic structure is necessary. A possible way to derive quintet states would be to start from the lowest septet state $^7\Sigma^+$ and to change the spin of one of the unpaired electrons occupying a valence iron orbital. Our CASPT2 calculations clearly show that this does not lead to one the low-lying quintet states of FeO. Indeed, changing the spin of an unpaired electron of $^7\Sigma^+$ no longer forces us, on the basis of the Pauli principle, to keep the most antibonding orbital (10σ) occupied. It becomes possible to pair this electron with an electron already present in one of the lower lying

TABLE 1: Results at the Computational Level I for the Low-Lying States of the Neutral FeO and Anionic FeO$^-$ Clusters

state (C_{2v})	state ($C_{\infty v}$)	leading configuration[a]	bond length[b] (Å)	vibrational frequency[b] (cm^{-1})	relative energy[c] (eV)
			FeO		
experiment[25]			1.616	881	
$^5A_1$, $^5A_2$	$^5\Delta$	$8\sigma^2 3\pi^4 9\sigma^1 1\delta^3 4\pi^2 10\sigma^0$	1.615	880	0.00
$^5A_1$	$^5\Sigma^+$	$8\sigma^2 3\pi^4 9\sigma^2 1\delta^2 4\pi^2 10\sigma^0$	1.622	861	0.01
2x$^5B_1$, 2x$^5B_2$	$^5\Pi_a$, $^5\Phi$	$8\sigma^2 3\pi^4 9\sigma^1 1\delta^3 4\pi^1 10\sigma^1$	1.663	859	0.74
$^5B_1$, $^5B_2$	$^5\Pi_b$	$8\sigma^2 3\pi^4 9\sigma^1 1\delta^2 4\pi^3 10\sigma^0$	1.649	707	0.97
$^7A_1$	$^7\Sigma^+$	$8\sigma^2 3\pi^4 9\sigma^1 1\delta^2 4\pi^2 10\sigma^1$	1.679	743	0.18
2x$^7B_1$, 2x$^7B_2$	$^7\Pi$, $^5\Phi$	$8\sigma^2 3\pi^3 9\sigma^1 1\delta^3 4\pi^2 10\sigma^1$	1.886	635	1.47
$^7A_1$, $^7A_2$	$^7\Delta$	$8\sigma^2 3\pi^3 9\sigma^1 1\delta^2 4\pi^3 10\sigma^1$	1.953	603	1.83
2x$^3B_{1,}$ 2x$^3B_2$	$^3\Pi_a$, $^3\Phi$	$8\sigma^2 3\pi^4 9\sigma^2 1\delta^3 4\pi^1 10\sigma^0$	1.639	685	0.95
$^3A_{1,}$ $^3A_2$	$^3\Delta$	$8\sigma^2 3\pi^4 9\sigma^1 1\delta^3 4\pi^2 10\sigma^0$	1.601	932	1.40
			FeO$^-$		
$^6A_1$	$^6\Sigma^+$	$8\sigma^2 3\pi^4 9\sigma^2 1\delta^2 4\pi^2 10\sigma^1$	1.683	805	0.00
$^6A_1$, $^6A_2$	$^6\Delta$	$8\sigma^2 3\pi^4 9\sigma^1 1\delta^3 4\pi^2 10\sigma^1$	1.688	830	0.36
$^6B_1$, $^6B_2$	$^6\Pi$	$8\sigma^2 3\pi^4 9\sigma^1 1\delta^2 4\pi^3 10\sigma^1$	1.702	971	1.08
$^4A_1$, $^4A_2$	$^4\Delta$	$8\sigma^2 3\pi^4 9\sigma^2 1\delta^3 4\pi^2 10\sigma^0$	1.635	879	0.21
$^4B_1$, $^4B_2$	$^4\Pi$	$8\sigma^2 3\pi^4 9\sigma^2 1\delta^2 4\pi^3 10\sigma^0$	1.686	794	0.67

[a] Leading configurations of the CASSCF wave function. [b] Equilibrium bond distances and harmonic vibrational frequencies obtained by the CASPT2 technique for the various states. [c] Relative CASPT2 energies of the equilibrium conformations of each state with respect to the CASPT2 energy of the ground state structure of the relevant cluster.

nonbonding iron orbitals. There are two possibilities. A transfer from 10σ to the 1δ level gives rise to a $^5\Delta$ with a $9\sigma^1$ $1\delta^3$ $4\pi^2$ $10\sigma^0$ leading configuration in the CASSCF wave function, while a transfer $10\sigma \rightarrow 9\sigma$ results in $^5\Sigma^+$ of the $9\sigma^2$ $1\delta^2$ $4\pi^2$ $10\sigma^0$ configuration. Both these quintet states have more or less the same equilibrium distances, that is, 1.615 Å for $^5\Delta$ and 1.622 Å for $^5\Sigma^+$, which are much shorter than the bond distance of $^7\Sigma^+$ due to the increased bond order for the quintets. As shown in Table 1, the energy difference between these two quintets amounts to only 0.01 eV, illustrating that the two nonbonding levels, that is, 9σ and 1δ, are nearly degenerate. We will show below that these are very important results for the interpretation of the photoelectron spectrum of FeO$^-$. The $^5\Delta$ state has the lowest CASPT2 energy of all the states we calculated and is therefore by just 0.01 eV the *ground state* of the FeO cluster. Both these closely spaced quintet states have similar harmonic frequencies around 870 cm^{-1} which are considerably larger than the one calculated for $^7\Sigma^+$ (743 cm^{-1}), again reflecting the stronger bonding in the quintets. The experimental value[25] of 881 cm^{-1} corresponds better to the vibrational frequency of 880 cm^{-1} for $^5\Delta$, when compared to 861 cm^{-1} for $^5\Sigma^+$. As shown by Table 1 the high-spin state $^7\Sigma^+$ is situated 0.18 eV above the ground state. The energy splitting between the antibonding 10σ orbital and the nonbonding orbitals 9σ and 1δ is therefore larger than the spin pairing energy needed to couple the two electrons with opposite spin in a nonbonding orbital: a quite remarkable result for an unsaturated complex with just one ligand. The strong electrostatic interaction between the two oppositely charged ions and the high bond order of two, are likely at the origin of this unexpected large splitting of the 3d shell.

Three other low-lying quintet states were found. The two lowest of them, that is, $^5\Pi_a$ and $^5\Phi$, are nearly degenerate and have a leading configuration $9\sigma^1 1\delta^3 4\pi^1 10\sigma^1$, in which the strongly antibonding 10σ remains occupied. Their equilibrium structures at 1.663 Å resemble the one of the lowest septet state $^7\Sigma^+$ and are positioned at 0.74 eV above the ground state conformation. The third quintet state is $^5\Pi_b$ and can be seen as a transition from the $^7\Sigma^+$, in which an electron is dropped from the strongest antibonding 10σ orbital into the less antibonding 4π level, giving a $9\sigma^1 1\delta^2 4\pi^3 10\sigma^0$ configuration. When compared with the $^5\Delta$ ground state, where this electron ends up in the nonbonding iron 1δ orbital, it is quite reasonable that the equilibrium structure of $^5\Pi_b$ is located at the much higher energy of 0.97 eV and possesses a distinct larger bond distance of 1.649 Å. Because of the decreased bonding characteristics of the $^5\Pi_a$, $^5\Phi$, and $^5\Pi_b$ their harmonic frequencies, of 859 and 707 cm^{-1}, respectively, are smaller when compared to the ground state.

According to our CASPT2 results *triplet states* are all found at energies higher than about 1 eV. The lowest are the degenerate $^3\Pi$ and $^3\Phi$ states with a equilibrium bond distance of 1.639 Å at 0.95 eV above the $^5\Delta$ ground state. The rather small bond length suggests that the strongly antibonding 10σ orbital is not occupied as is indeed the case in the leading configuration of the calculated CASSCF wave function: $9\sigma^2$ $1\delta^3$ $4\pi^1$ $10\sigma^0$. Somewhat surprisingly, the second highest state in Table 1, the $^3\Delta$, at 1.40 eV has the shortest bond distance of 1.601 Å and the highest harmonic frequency of all states mentioned in Table 1. A possible explanation can be found in the fact that it has the same leading configuration as the ground state, from which it therefore derived by a simple spin flip. The rather high position of the triplet states is the outcome of the compact nature of the 3d orbitals of any transition metal compound. The resulting large 3d−3d exchange energy cannot be counterbalanced by the small energy separation between the nonbonding orbitals (9σ, 1δ) and the mildly antibonding 4π orbital. For the same reason singlet states are thought to be positioned at even higher energies.

Concerning the nature of the ground state of FeO our CASPT2 results are in line with previous computational studies. Nearly all computational techniques used so far predict the ground state as $^5\Delta$.[11−13] This a remarkable result since its the energy difference with the $^5\Sigma^+$ and $^7\Sigma^+$ states is calculated by us as being less than 0.2 eV, which can be considered as the reliability margin for present day computational approaches. It is therefore not surprising that in some instances a different ground state is found. For instance, the hybrid B3LYP method in combination with a 6-311+G* basis places the septet state 0.01 eV below the quintet state.[11,14] A result that is in clear contradiction with experiment because the calculated harmonic vibrational frequencies (808 cm^{-1}) and bond distance (1.668 Å) at this level deviate too much from their experimental values of 881 cm^{-1} and 1.616 Å.[25] However, in the same study a pure DFT treatment by using BPW91, predicts a quintet ground state possessing a bond length of 1.6082 Å and a harmonic frequency of 907 cm^{-1}, a much better match with experiment. To our knowledge the most detailed wave function calculation dates back to 1995.[12] The authors concluded that, especially for FeO, single-reference based techniques such as the CCSD(T) perform poorly, whereas the multireference CASSCF/ICACPF technique is better suited to treat this molecule. Their calculated spectroscopic parameters for the $^5\Delta$ state, $r_e = 1.609$ Å and ω=885 cm^{-1}, correspond very well with experiment. There is no mentioning about the low-lying septet or other quintet states. On the basis of these previous calculations and from our results we can conclude that the $^7\Sigma^+$ state is not the ground state of FeO. As a direct result of the occupation of the strong antibonding nature of the 10σ orbital, its larger bond length and lower vibrational frequency deviate too much from the well-known experimental values. Both $^5\Delta$ and $^5\Sigma^+$ should be considered as candidate ground states. We favor the former quintet not solely because of its slightly lower CASPT2 energy, but also on the grounds of its calculated equilibrium bond distance and vibrational frequency ($^5\Delta$: $r_e = 1.615$ Å, $\omega = 880$ cm^{-1}. $^5\Sigma^+$: $r_e = 1.622$ Å, $\omega = 861$ cm^{-1}), which both agree better with the corresponding experimental values ($r_e = 1.616$ Å, $\omega = 881$ cm^{-1}).

FeO^-. Adding an extra electron to FeO to form the singly charged anion, can most favorably be done in one of the vacant nonbonding orbitals. Starting from the $^7\Sigma^+$ state the additional electron can enter the half-filled 9σ orbital to form the $^6\Sigma^+$ state of the $9\sigma^2 1\delta^2 4\pi^2 10\sigma^1$ configuration. Alternatively, augmenting the occupation of the 1δ orbitals results in the $^6\Delta$ state with a $9\sigma^1 1\delta^3 4\pi^2 10\sigma^1$ configuration. Both states were calculated as the lowest of their symmetries and therefore are present in Table 1. The energy difference between them is surprisingly rather large and amounts to 0.36 eV in favor of the $^6\Sigma^+$. As a matter of fact this state is the lowest of all the FeO^- states and therefore is suggested by us as its *ground state*. Since both these anionic *sextet states* just differ from the neutral $^7\Sigma^+$ state by the occupancy of the nonbonding orbitals, their equilibrium bond distances are almost equal among each other: 1.679 Å for $^7\Sigma^+$, 1.683 Å for $^6\Sigma^+$, and 1.688 Å for $^6\Delta$. The vibrational frequencies of 805 and 830 cm^{-1} for $^6\Sigma^+$ and $^6\Delta$, respectively, are somewhat larger than the value of 743 cm^{-1} calculated for $^7\Sigma^+$. The application of the computational strategy as outlined in the introduction afforded one more sextet state, namely a $^6\Pi$. Here the extra electron occupies the antibonding 4π level, giving the following total occupancy of the iron valence orbitals: $9\sigma^1 1\delta^2 4\pi^3 10\sigma^1$. Consequently, its equilibrium structure is energetically positioned at a much higher energy of 1.08 eV, exhibiting a larger bond length of 1.702 Å. Rather surprisingly, the vibrational frequency of 971 cm^{-1} is particularly large, in fact it is the largest of all states calculated.

The $^6\Sigma^+$ ground state of FeO^- state has the strongly antibonding 10σ orbital occupied. As is the case for the neutral cluster we must consider low-spin states, such as *quartets,* which arise when the electron is removed for this highest orbital and coupled by means of a spin flip to an electron of the lower lying nonbonding 1δ level or mildly antibonding orbital 4π. Our computational strategy indeed yielded these quartet states as presented in Table 1. Logically, the $^4\Delta$ state ($9\sigma^2 1\delta^3 4\pi^2 10\sigma^0$) for which the transfer is to the 1δ level, represents the lowest quartet state of the anionic complex. Since this state has fewer electrons in antibonding orbitals, namely two, its equilibrium bond distance is considerably shorter (1.635 Å) and its vibrational frequencies larger (879 cm^{-1}). It is comparable to the bond length of the lowest quintets of the neutral system. Energetically the $^4\Delta$ structure is located just 0.21 eV above the equilibrium structure of the ground state, a value at the edge of the expected reliability margin of the applied computational approximation. The larger number of electrons in antibonding orbitals for the second quartet state $^4\Pi$ ($9\sigma^2 1\delta^2 4\pi^3 10\sigma^0$) results in a larger bond length of 1.686 Å. Energetically, it is estimated by our CASPT2 calculations at 0.67 eV above the $^6\Delta$ ground state.

Surprisingly, there is to date just one ab initio study[11] published for the anionic FeO^- complex. By using pseudopotentials, the CI (SD) + Q calculations presented in this study proposed the $^4\Delta$ state as the ground state, possessing a bond length of 1.652 Å, an ionization potential around 0.95 eV, and a vibrational frequency of 846 cm^{-1}. No reference to a low-lying sextet state was made. More recently, three references to DFT or hybrid calculations can be found in the literature. The oldest is a pure DFT study by using the BPW91 functional, in which spin multiplicities ranging from 2 to 10 were considered as candidate ground states.[26] Without specifying the actual state, a quartet was found to possess the lowest energy: 0.20 eV below a sextet state. One year later this state was characterized as $^4\Delta$ at the same computational level and confirmed as the ground state of FeO^- by BLYP and B3LYP, pure DFT and hybrid techniques, respectively.[27] The energy difference with the excited $^6\Delta$ state ranges from 0.21 to 0.45 eV. In all circumstances the quartet state has a shorter equilibrium bond distance of around 1.64 Å compared to 1.69 Å for $^6\Delta$. In the most recent publication the BPW91 results were discussed in connection with the FeC^- cluster.[14] When compared to our ab initio results, we conclude that the DFT and hybrid methods confirm the stronger chemical bond in the $^4\Delta$ state with respect to $^6\Delta$. An excellent agreement is found between the BPW91 and CASPT2 calculated bond lengths and vibrational frequencies. However, of the utmost importance for the assignment of the photoelectron spectra of FeO^-, our CASPT2 study differs from the DFT-based methods concerning the nature of the ground state.

Photoelectron Spectra of FeO^-. As mentioned in the introduction, the originally proposed assignment of the photoelectron spectra of FeO^- is still accepted in the literature.[18] The spectrum as measured at 4.66 eV photon energy is presented in Figure 3a. The lowest band around 1.50 eV, referred to as feature X in the original study, shows an unusual vibrational progression. It was assigned to an electron detachment to the $^5\Delta$ ground state of FeO. The second lowest quintet, namely $^5\Sigma^+$, is thought to be responsible for the band A at 1.98 eV. At higher energies around 2.5 eV, two more features appear. A band B at 2.36 eV above the anionic ground state and a vibrationally resolved band called C of which the lowest peak is positioned at 2.56 eV. By comparing with earlier computational results[10] the lower feature B was assigned by the authors as $^3\Sigma^+$ and the higher band C as $^3\Delta$. The high energy band labeled D at 3.39 eV was ascribed to a $^3\Pi$. As a consequence of assigning all features to either triplets or quintets, it was assumed that the ground state of FeO^- is a quartet state. This is in sharp contrast with our CASPT2 calculations that predict a sextet ground state.

To date these assignments are still accepted, although two remarks can be made that raise some doubt. A first remark is already present in the 1995 paper of Wang et al.[17] It concerns the intensities of the peaks that make up band A. The lowest energy peak of this band has the highest intensity, the intensity decreasing with increasing energy for the remaining two peaks of this band. Compared to a normal Franck−Condon envelope this is considered as unusual. The same conclusion was reached in a later study by the high resolution 532 and 690 nm photoelectron spectra and mass selected anion-zero kinetic

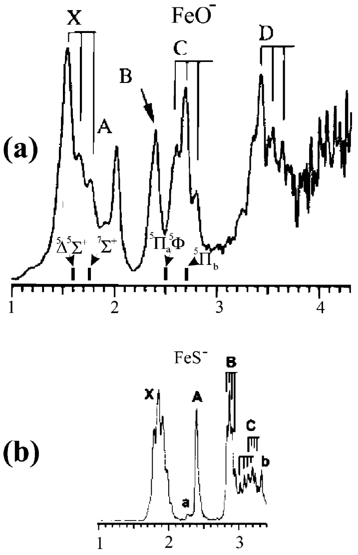

Figure 3. Vibrational resolved photoelectron spectra of FeO$^-$ (a)[18] and FeS$^-$ (b),[20] showing in the low energy part the qualitative resemblance between them. For the FeO$^-$ spectrum (a) the CASPT2 calculated electron detachment energies of the present work were included, showing the fairly good correspondence between theory and experiment.

energy photoelectron spectroscopy.[19] Spin−orbit coupling was ruled out as being at the origin of the double headed peak structures in these spectra. Quite strangely the possible interference of the assumed nearly degenerate $^7\Sigma^+$ state was proposed by both studies as an explanation. Indeed, septet states are not likely to give intense peaks in a single electron detachment photoelectron spectrum if the ground state of FeO$^-$ possesses a quartet spin multiplicity.

A second remark about the proposed assignment of the FeO$^-$ can be made from a comparison with the photoelectron spectra of the related FeS$^-$ by Wang et al.[20] In particular their 3.49 eV spectrum represented in Figure 3b shows a striking resemblance with the 4.66 eV spectrum of FeO$^-$, as recorded by the same group. Indeed, at 1.85 eV a vibrationally resolved band (denoted as X) is observed, followed at 2.40 eV by a sharp band (A). At higher energies a narrow band (B) at 1.87 eV showing some vibrational progression is flanked by a broadband (C) center around 3.15 eV. All these bands were assigned as corresponding to either quintet or septet states of FeS, with increasing energy: $^5\Delta$ (X), $^7\Sigma^+$ (A), $^5\Delta$ (B), and $^5\Pi{-}^5\Phi$ (C). The ground state of the FeS$^-$ anion is therefore assumed to be a sextet rather than a quartet, as proposed for the related FeO$^-$. This tentative assignment was later only partly confirmed by CASPT2 calculations,[21] in the sense that the ground state of the anion is indeed a sextet (rather $^6\Delta$ than $^6\Sigma^+$ for FeO$^-$) and that the two lowest bands can be ascribed to $^5\Delta$ and $^7\Sigma^+$. Bands B and C were, however, differently assigned as electron detachments to $^5\Pi{-}^5\Phi$ (B) and $^7\Pi{-}^7\Phi$ (C). A very good agreement between the computational results and experimental detachment energies was obtained.

With the purpose to raise the reliability of our recent results we performed a second set of CASPT2 calculations. As detailed in the section computational details we enlarged the basis set and increased the number of electrons correlated in the CASPT2 step (level **II**). The relative energies of the low-lying states are collected in Table 2 and their potential energy plots are depicted in Figure 4. For the purpose of gaining an idea of the reliability of this computational level on the basis of a comparison with a previous advanced computational study[28] and an accurate spectroscopic study,[24] we included the calculated dipole moments for the lowest states of the two cluster systems in Table 2. For the $^5\Delta$ ground state of FeO our CASPT2 approach predicts a dipole moment of 4.69 D. This value is significantly lower than the CISD value of 5.25 D, the averaged quadratic couple-cluster value of 5.06 D and the values of different kinds ACPF methods which range from 5.06 to 5.16 D.[28] A part of these differences is the result of the larger bond length of 1.64 Å that was used to obtain the latter results. As shown in Table 2 our CASPT2 geometry optimization yielded an equilibrium bond distance of 1.612 Å for the ground state that is considerably shorter, but agrees well with the experimental value of 1.616 Å.[6,7] At 1.64 Å we found a dipole moment of 4.87 D which compares better with the previous computational study, but is still significantly smaller. Our dipole moment of 4.69 D compares reasonably well with the spectroscopic Stark effect measurements. Depending on the specific spin−orbit coupling state of the $^5\Delta$ ground state, dipole moments in the range of 4.29 to 4.7 D were put forward.[24]

By comparing Table 1 and Table 2 for the low-lying FeO states we conclude that they agree on the energetic sequence. Further in accordance with our previous results the $^6\Sigma^+$ is confirmed as the ground state of FeO$^-$. At their equilibrium geometries the difference between the excited $^4\Delta$ state and the

TABLE 2: CASPT2 Results at the Computational Level II for the Low-Lying States of the Neutral FeO and Anionic FeO$^-$ Clusters[a]

state(C_{2v})	state ($C_{\infty v}$)	bond length (Å)	vibrational frequency (cm^{-1})	relative energy[b] (eV)	dipole moment (D)
			FeO		
$^5A_1$, $^5A_2$	$^5\Delta$	1.612	887	1.51	4.69
$^5A_1$	$^5\Sigma^+$	1.626	868	1.55	3.61
$^7A_1$	$^7\Sigma^+$	1.677	756	1.75	2.78
			FeO$^-$		
$^6A_1$	$^6\Sigma^+$	1.683	807	0.00	2.60
$^4A_1$, $^4A_2$	$^4\Delta$	1.634	878	0.13	1.77

[a] Leading configurations are the same as mentioned in Table 1. [b] Energy difference between the equilibrium conformations of the specific states and the energy of the ground state structure of the FeO$^-$ cluster.

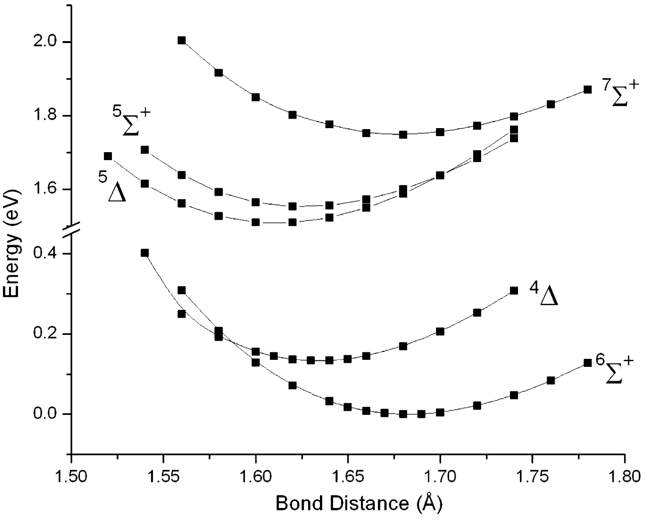

Figure 4. CASPT2 potential energy profiles as obtained at the computational level **II** for the $^6\Sigma^+$ and $^4\Delta$ ground state candidates of FeO$^-$. The former state has the lowest energy conformation at larger bond distances. It is therefore responsible for the observed photoelectron spectra of this anionic cluster. Also included are the states ($^7\Sigma^+$, $^5\Sigma^+$, and $^5\Delta$) of the neutral FeO that are responsible for the two lowest bands in the spectra.

TABLE 3: CASPT2 Energies of FeO Low-Lying States Calculated at the Equilibrium Bond Distance of the FeO^- ${}^6\Sigma^+$ Ground State (1.683 Å), Employing the Computational Level II, and Comparison with the Experimental Photoelectron Spectral Data

state (C_{2v})	state ($C_{\infty v}$)	relative CASPT2 energies (eV)	observed energies[18](eV)
		FeO^-	
${}^6A_1$[a]	${}^6\Sigma^+$	0.00	0.00
${}^4A_1$, ${}^4A_2$[a]	${}^4\Delta$	0.17	
		FeO	
${}^5A_1$, ${}^5A_2$[a]	${}^5\Delta$	1.59	1.50
${}^5A_1$[a]	${}^5\Sigma^+$	1.61	1.50
${}^7A_1$[a]	${}^7\Sigma^+$	1.75	1.98
${}^7B_1$[a]		3.53	
${}^7A_2$[a]		4.3	
${}^5A_1$[b]		3.14	
		3.35	
		3.50	
		4.40	
		4.49	
${}^5A_2$[c]		3.28	
		3.60	
		3.43	
		4.06	
		4.68	
${}^5B_1$[c]		2.52	2.36
		2.54	2.36
		2.73	2.56
		3.44	
		3.54	
		3.59	

[a] States calculated as single roots. [b] CASPT2 calculation on individuals states with the orbitals of an average CASSCF calculation over seven roots of the indicated symmetry. The two lowest states are not included since they were calculated as individual roots at CASSCF. [c] CASPT2 calculation on individuals states with the orbitals of an average CASSCF calculation over six roots of the indicated symmetry.

ground state is 0.13 eV, a value somewhat smaller than obtained with the smaller basis set. For all states mentioned in Table 2 the spectroscopic parameters, that is, bond distances and vibrational frequencies are to a high degree reproduced. With this firm establishment of the low-lying states of both systems we can start to assign the photoelectron spectra of FeO^-. The ground state of this cluster is ${}^6\Sigma^+$ with a bond distance of 1.683 Å. For this bond distance and on the more elaborated computational level **II** we calculated the energetic positions of all possible low-lying quintets and septets of FeO. The ${}^5\Delta$, ${}^5\Sigma^+$, and ${}^7\Sigma^+$ states were calculated as single roots, while the higher states were, per irrep of the C_{2v} subgroups, approximated with the orbitals of an average CASSCF state, which included seven roots for a_1 and six roots for the other irreps. The results and a confrontation with the experimental band positions of the photoelectron spectra can be found in Table 3. According to this table the lowest peak in the photoelectron spectra of FeO^- at 1.50 eV is the outcome of electron detachments to two states of the neutral system: to the ground state ${}^5\Delta$ and the first excited state ${}^5\Sigma^+$. Figure 4 shows that at the equilibrium distance of ${}^6\Sigma^+$, these two systems are by coincidence nearly degenerate. Their equilibrium bond distance of around 1.62 Å is much shorter (0.06 Å) than the one of ${}^6\Sigma^+$, as a consequence of the removal of an electron from the strongly antibonding 10σ orbital. All these facts could explain why they are observed as the single band X in the spectra with a pronounced but abnormal Franck−Condon vibrational progression[17] and the double-headed structures mentioned for this band.[19] The second observed feature at 1.98 eV corresponds to a removal of an electron from the nonbonding 9σ orbital. Therefore, as can been seen in Figure 4, the resulting neutral ${}^7\Sigma^+$ has a similar bond distance as the anionic ${}^6\Sigma^+$ ground state and accordingly no vibrational progression is observed for that transition. In the region around 2.5 eV two features are present. In Table 3 the only states calculated in this region are ${}^5\Pi_a$, ${}^5\Phi$, and ${}^5\Pi_b$, all ${}^5B_1$ or ${}^5B_2$ (C_{2v}). Several attempts to perform a geometry optimization of these three states at level **II**, failed. Since for the other states, the differences between Table 1 and 2 are not large, we can safely carry out the analysis of this part of the experimental spectrum by using the bond distances obtained at level **I**. However, a single point calculation (at 1.683 Å) of the three ${}^5B_1$ states as an average root at computational level **II** were possible and are presented in Table 3. The degenerate ${}^5\Pi_a$ and ${}^5\Phi$ are positioned at an average energy of 2.55 eV by CASPT2. According to Table 1, they have the 10σ orbital occupied and a relatively large bond distance of 1.663 Å. The narrow band at 2.36 eV of the spectrum is assigned to these states, which indeed have similar bonding characteristics as ${}^6\Sigma^+$. The underlying state for the vibrational resolved band centered around 2.56 eV needs to have a significant different bond distance as the anionic ground state. This is the case for the ${}^5\Pi_b$ state, for which Table 1 shows a shorter bond distance of 1.649 Å as the outcome of the depopulation of the 10σ orbital. At the high energy side, Table 3 contains a large number of states in the region around 3.5 eV. We find that this is responsible for the rather unstructured appearance of peaks in the experimental photoelectron spectrum in this region.

Although, the above proposed assignment of the photoelectron spectra of FeO^- explains rather nicely the observed presence or absence of a vibrational progression of the experimental bands, some uncertainties remain unsolved for the moment which make it unquestionably tentative. Indeed, Table 1 shows that the detachments ${}^6\Sigma^+ \rightarrow {}^5\Delta$, ${}^6\Sigma^+ \rightarrow ({}^5\Pi_a, {}^5\Phi)$ and ${}^6\Sigma^+ \rightarrow {}^5\Pi_b$ are not one-electron processes and therefore should occur only with low intensities. A possible explanation for this discrepancy might be the breakdown of this selection rule as a consequence of the calculated orbital relaxations upon ionization, which are calculated to be extremely pronounced for the 9σ orbital. For instance, the nature of this orbital was found to vary from a 4s−4p hybrid for ${}^6\Sigma^+$ to a mainly 4s−$3d_\sigma$ hybrid orbital for ${}^5\Delta$. Also spin−orbit coupling might mix certain configurations giving rise to increased transition probabilities. Although preliminary calculations indicate that this is not the case for the ${}^6\Sigma^+ \rightarrow {}^5\Delta$ transition, it might be important for the higher quintet states. Additionally, the multiconfigurational nature of the states will contribute to the cross sections of the proposed transitions. Finally, a shift of the CASPT2 energies of the three lowest FeO^- states (${}^6\Sigma^+$, ${}^4\Delta$, and ${}^6\Delta$) within the error bars of the computational method, can make the energy differences quite small. As a result a possible coexistence of multiple states in the experiment should be considered as well. In conclusion for the discussion of the photoelectron spectra of FeO^-, we would like however to point out that there is firm experimental evidence[19] that three states of FeO are needed to account for the low-energy part (<2 eV) of the spectra. On the basis of the reliability of the CASPT2 method as obtained from our previous CASPT2 studies on unsaturated transition metal complexes,[29−37] we strongly believe that these states are ${}^7\Sigma^+$, ${}^5\Sigma^+$, and ${}^5\Delta$. They are separated from higher lying states by at least 0.75 eV, an energy gap that is much larger than the expected computational error. This implies a sextet ground state for FeO^- which is most likely $^6\Sigma^+$. A qualitative vibrational analysis and the calculated CASPT2 relative energies result in the proposed assignation of the experimental bands in the photoelectron spectra. Orbital relaxations, multiconfiguration effects, spin−orbit coupling, or the population of the low-energy states of FeO$^-$ could be responsible for their intensities. However, since we are unable to calculate these transition probabilities our assignment should be regarded as tentative for the time being.

Conclusion

At both CASPT2 computational levels used in this contribution the ground state conformation of the anionic FeO$^-$ cluster is proposed to be the $^6\Sigma^+$ state of the $9\sigma^2 1\delta^2 4\pi^2 10\sigma^1$ configuration. As the consequence of the occupation of the strongly antibonding 10σ orbital the calculated equilibrium structure possesses a rather large bond distance of 1.683 Å. This finding opposes the results of previous DFT or hybrid DFT studies which consistently predict the $^4\Delta$ state as the ground state of FeO$^-$. For the neutral cluster FeO our CASPT2 calculations concur with previous work in predicting a $^5\Delta$ ground state of the configuration $9\sigma^1 1\delta^3 4\pi^2 10\sigma^0$. As 10σ is not occupied its bond length is considerably shorter calculated at 1.612 Å, which compares excellent with the experimental value of 1.616 Å. Also a good agreement between experiment and theory is found for the vibrational frequency and the dipole moment. Indeed, a second-order polynomial fit to the CASPT2 potential energy curve gave a harmonic vibrational frequency of 887 cm^{-1}, to be compared with the experimental frequency[25] of 881 cm^{-1}. Nearly a perfect match is also found for the adiabatic electron affinity of FeO. The CASPT2 energy difference between the two equilibrium structures after correcting for zero-point vibration energies, amounts to 1.52 eV, while from photoelectron spectra[17] a value of 1.497 eV is proposed. By applying the Franck−Condon principle the photoelectron detachment energies to all relevant low-lying quintet and septet states of neutral FeO cluster were calculated and compared to the observed bands in the spectra. The lowest energy vibrational resolved band around 1.50 eV is attributed to detachments to two states of FeO, namely $^5\Delta$ and $^5\Sigma^+$. Both these states have the 10σ orbital not occupied and have therefore distinctly shorter bond distance (around 1.62 Å) than the $^6\Sigma^+$ ground state of FeO$^-$, which indeed implies a vibrational resolved band in the spectrum. Both quintet states in question are as good as degenerate and could explain the unusual observed Franck−Condon envelope of this band. The $^7\Sigma^+$ state is energetically positioned slightly higher and has the 10σ orbital occupied. Its bond distance (1.677 Å) compares to the one of the anionic ground state, which explains the rather narrow band at 1.98 eV in the spectra. The remaining two distinct observed features around 2.5 eV are to be ascribed to quintet states of FeO. The lower sharper band at 2.36 eV is predicted by CASPT2 to be the result of the $^5\Pi_a$ and $^5\Phi$ states ($9\sigma^1 1\delta^3 4\pi^2 10\sigma^1$). The vibrational resolved band at 2.56 eV corresponds to $^5\Pi_b$ ($9\sigma^1 1\delta^2 4\pi^3 10\sigma^0$). The fact that the 10σ orbital is not occupied for this state induces a shortening of the bond distance and a broad resolved band. We concluded that based on the calculated CASPT2 energies and bond distances, a complete new assignment of the experimental photoelectron spectra of FeO$^-$ could be proposed. Since no firm evidence about the band intensities could be given, further computational study is needed to solve this remaining outstanding issue.

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