

Photoelectron spectroscopy of FeO^- and FeO_2^- : Observation of low-spin excited states of FeO and determination of the electron affinity of FeO_2

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The photoelectron spectra of FeO^- and FeO_2^- are obtained at 3.49 eV photon energy. Transitions to the ground state ($^5\Delta$) and three low-lying excited states ($^5\Sigma^+$, $^3\Sigma^+$, and $^3\Delta$) of FeO are observed. The two low-spin excited states found at 6770 and 8310 cm^{-1} above the ground state, respectively, have not been observed before. The two Σ states, characteristic of detachment of a nonbonding electron from the FeO^- anion, exhibit no vibrational progressions while a vibrational progression is observed for each of the two Δ states. The two high-spin states $^5\Delta$ and $^5\Sigma^+$ are in agreement with a previous photoelectron study [P.C. Engelking and W. C. Lineberger, *J. Chem. Phys.* **66**, 5054 (1977)]. The $^3\Delta$ state has a vibrational frequency of 800 (50) cm^{-1} . The spectrum of FeO_2^- only shows one major feature with little vibrational structure at this photon energy. The electron affinity of FeO_2 is determined to be 2.358 (0.030) eV. © 1995 American Institute of Physics.

I. INTRODUCTION

Study of the interaction of oxygen with iron is important to such diverse processes as corrosion of structural metals and oxygen transport in biological systems. FeO and FeO_2 are the simplest molecular iron oxide systems. However, they have not been well understood and spectroscopic data on these simple molecules are scarce, in particular, for FeO_2 , whose ground state structure and symmetry is not yet known. Several spectroscopic¹⁻⁸ and theoretical^{9,10} studies have focused on FeO, and its ground state has been established to be $^5\Delta$ ($\sigma_b^2 \pi_b^4 \pi_a^2 \delta^3 \sigma_1$). The manifold of excited states of FeO, however, are very complicated and are less well known, although several excited states of FeO have been discovered.¹⁻⁸

Gas phase FeO_2 has been observed when solid Fe_2O_3 is vaporized at high temperatures.^{11,12} Several studies have concerned FeO_2 in order to probe the interaction of oxygen with Fe atoms coordinated in biological systems.¹³⁻¹⁵ The FeO_2 molecule can be viewed as a Fe+ O_2 reaction product, although ground state Fe atom is known to be quite unreactive toward O_2 .^{16,17} It can have three possible structures, a FeO_2 side-bonded adduct (I), a linear or bent Fe-O-O (II), and a linear or bent dioxide O-Fe-O (III). The FeO_2 adduct (I) is known to form in the gas phase FeO_2 reactions and in rare-gas matrices and can be converted to the dioxide (III) upon uv irradiation in the matrices.¹⁸⁻²⁰ A recent mass spectrometry study combined with an *ab initio* calculation concluded that for the positive ion FeO_2^+ a bent dioxide (III) is the most stable structure.²¹ Previous matrix studies and semiempirical calculations suggested that the most stable form of FeO_2 is a linear OFeO .^{14,18}

There is only one previous photoelectron spectroscopy (PES) study on FeO^- by Engelking and Lineberger with a 2.54 eV detachment energy.² A vibrationally resolved ground state and one low-lying excited state ($^5\Sigma^+$) were observed.

This accounts for the only observation of this excited state. However, theoretical calculations have predicted many more low-lying excited states that have not been observed experimentally.^{9,10} To our knowledge, there has been no PES study on FeO_2^- .

By vaporizing iron into a helium atmosphere containing a small amount of oxygen, we have produced FeO^- and FeO_2^- in a laser vaporization cluster beam machine. Their PES spectra are studied at 3.49 eV photon energy with a magnetic bottle time-of-flight PES apparatus.²² Because of the higher photon energy used than the previous PES study, two more new low-lying excited states are found for FeO at 6770 and 8310 cm^{-1} above the ground state, respectively. On the basis of the spectral appearance and previous theoretical calculations, these two new states are assigned to the low-spin excited states, $B^3\Sigma^+$ and $C^3\Delta$. Due to the spin selection rules, these low-spin excited states cannot be observed in optical experiments in either excitation or emission. For the FeO_2 spectrum, only one rather sharp feature is observed with little vibrational excitation. The electron affinity of FeO_2 is determined to be 2.358 (0.030) eV. The spectrum suggests that there is little geometry change from the FeO_2^- anion to the FeO_2 neutral.

II. EXPERIMENT

The PES apparatus has been described in detail elsewhere.²² Only a brief account will be given here. The apparatus couples a laser vaporization cluster source²³ with a magnetic bottle time-of-flight (MTOF) photoelectron analyzer.²⁴ A Q-switched Nd:YAG laser is used as the vaporization laser, with 20 mJ of the second harmonic output (532 nm) focused to a 1 mm diameter spot onto a pure iron target. To generate FeO^- and FeO_2^- , the helium carrier gas is seeded with 0.05% O_2 (10 atm total stagnation pressure) and delivered by two pulsed molecular beam valves. The plasma

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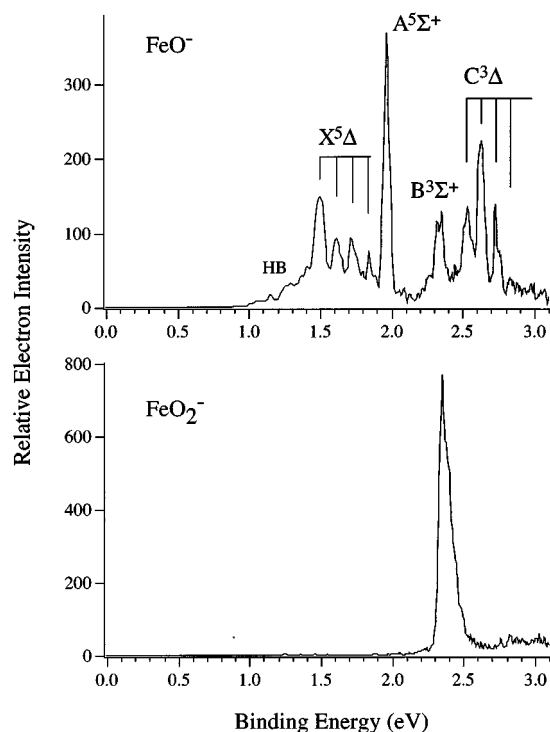


FIG. 1. The photoelectron spectra of FeO^- and FeO_2^- at 3.49 eV photon energy (355 nm).

reactions between the laser vaporized iron atoms and the O_2 produce a series of Fe_xO_y^- clusters, in which FeO^- and FeO_2^- are the smallest ones. The FeO_2^- species is present in much higher abundance than the FeO^- anion. The helium carrier gas and the oxide clusters undergo a supersonic expansion and form a cold molecular beam collimated by two skimmers. To optimize the FeO^- mass signal, the vaporization laser has to be fired at the leading edge of the carrier gas pulse when the pressure in the nozzle is lower. Consequently, the supersonic cooling effect is not the most favorable when the FeO^- signal is optimized. This effect is shown in its PES spectrum by the observation of hot band excitations.

The negative clusters are extracted perpendicularly from the beam with a 1 kV high voltage pulse and subjected to a time-of-flight mass analysis. The TOF mass spectrometer has a mass resolution ($M/\Delta M$) of about 500, which is sufficient to resolve all the isotopes for the small Fe_xO_y^- clusters. The clusters of interest are mass selected by a three-grid mass gate and subsequently decelerated by a momentum decelerator before interacting with the detachment laser. The third harmonic output (355 nm) of another Q-switched Nd:YAG laser is used for the photodetachment. More than 98% of all the photoelectrons are collected by the magnetic bottle and parallelized down to a 3.5 m long TOF tube for electron kinetic energy analysis. The electron kinetic energy distributions are calibrated with the known spectrum of the Cu^- anion. The energy resolution in a TOF PES spectrometer is dependent on the electron kinetic energy. The current spectrometer has an energy resolution of better than 30 meV at 1 eV electron kinetic energy as measured from the spectrum of Cu^- .

TABLE I. Observed peak positions, term values, and assignments for the FeO^- and FeO_2^- photoelectron spectra.

	Peak position ^a	Term value (cm^{-1}) ^b	Vibrational frequency (cm^{-1}) ^c
FeO^-	$X \ ^5\Delta$	1.497	0
		1.616	950(50)
		1.735	
		1.851	
	$A \ ^5\Sigma^+$	1.966	3780(120)
	$B \ ^3\Sigma^+$	2.336	6770(120)
	$C \ ^3\Delta$	2.527	8310(120)
2.626			
2.725			
2.825			
FeO_2^-	X	2.358	

^aThe uncertainty of the peak position is about 30 meV. The value for FeO_2^- represents its EA.

^bThe uncertainty of the term value is estimated to be about 15 meV.

^cThe uncertainty of the relative vibrational peak positions is about 6 meV.

III. RESULTS AND DISCUSSION

The PES spectra of FeO^- and FeO_2^- are shown in Fig. 1. A window function with 5 meV width has been used to smooth the spectra. Four bands are observed for the FeO^- with vibrational structures resolved for two of the four bands (labeled X and C). Features at the low binding energy side are assigned to be due to hot band excitations, indicating that the FeO^- is not very cold as mentioned in the experimental section above. Note that the peak labeled A in the FeO^- spectrum is quite sharp with a width of only 45 meV (FWHM), which is nearly the instrumental resolution at that energy. Only one major band is observed for FeO_2^- , with no resolved vibrational structures. The width of this band indicates that there are unresolved vibrational features in the band. At the high binding energy side, there is also some very weak and unresolved features, which are at least partially due to inelastically scattered electrons present at the high binding energy side (low energy electrons). The FeO_2^- spectrum seems to show little hot band excitations. However, the apparently predominant 0–0 transition in FeO_2^- and the limited spectral resolution prevent us from a definitive statement about the FeO_2^- vibrational temperature. The observed peak positions, assignments, and obtained spectroscopic constants are summarized in Table I. The lowest binding energy features represent the electron affinities of the corresponding neutral molecules. Due to the possible nonlinearity in the spectral calibrations, the absolute peak positions can be determined in the current study to be within 30 meV. However, the relative peak positions can be determined much more accurately.

A. FeO^-

Photodetachment involves transitions from the ground state of the FeO^- to the ground and various excited states of the neutral FeO. The electronic structure of FeO has been investigated in an extensive CI calculation by Krauss and Stevens.¹⁰ Although multiconfiguration effects are expected

to be significant for an open-shell molecule such as FeO , primary photodetachment channels can be well described by single particle transitions. Thus to understand the PES spectrum of FeO^- , it is best to consider the dominant molecular orbital configurations of FeO^- and FeO . The ground state of neutral FeO is known to be $^5\Delta$ with a $\sigma_b^2\pi_b^4\pi_a^2\delta^3\sigma_1^1$ configuration, where σ_b is a bonding orbital, π_b is a bonding orbital localized on the O atom, π_a is an antibonding orbital from the Fe $d\pi$ -O $p\pi$, and δ and σ_1 are nonbonding orbitals on the Fe atom. The ground state of the FeO^- has been established to be $^4\Delta$ with a $\sigma_b^2\pi_b^4\pi_a^2\delta^3\sigma_1^2$ configuration by adding the extra electron to the nonbonding σ_1 orbital of neutral FeO .^{8,10} Both the $^4\Delta$ and $^5\Delta$ states contain multiplet states with different Ω values. The spin-orbit splittings are 226 and 185 cm^{-1} for the $^4\Delta$ and $^5\Delta$ states, respectively.⁸

1. The $X^5\Delta$ and $A^5\Sigma^+$ states

The removal of a σ_1 electron from the FeO^- leads to the ground state of FeO while the removal of a δ electron results in the $A^5\Sigma^+$ states, as indicated in Fig. 1. The ground state exhibits a vibrational progression while only one sharp peak is observed for the $^5\Sigma^+$ state with no detectable vibrational structure. This is consistent with the *ab initio* calculation that the δ orbital is a pure nonbonding orbital localized on the Fe atom.¹⁰ These two bands are in agreement with the previous PES study by Engelking and Lineberger,² except that the current study has a slightly higher resolution. The sole peak of the $^5\Sigma^+$ state is quite sharp with only 45 meV FWHM, characteristic of the instrumental resolution at that energy (about 1.5 eV electron kinetic energy). However, the relative intensity between the $^5\Delta$ and the $^5\Sigma^+$ states are quite different from the previous study: The peak of the $^5\Sigma^+$ state is considerably higher than the peaks in the ground state in the current spectrum while the previous study shows a rather low peak intensity for the $^5\Sigma^+$ peak. This can be due to two effects: (1) dependence of detachment cross sections on photon energies, and (2) poor transmission at low electron kinetic energies in the previous study, which employed a hemispherical electrostatic energy analyzer and a lower photon energy.

The vibrational spacing observed in the ground state, as shown in Table I, agrees well with the previous study, which obtained a value of 970 (60) cm^{-1} .² However, the ground state vibrational frequency for FeO has been established to be 871 cm^{-1} ,³ much smaller than the PES derived values. This is probably due to the fact that each vibrational peak in the PES spectrum contains a set of spin-orbit components, which are spaced too close to be resolved in the PES studies. This is evident from the peak widths in the $X^5\Delta$ state. Thus, the vibrational spacing obtained in the PES studies is an averaged value among all the spin-orbit components. Additionally, the intensities of the vibrational progression in the ground state are quite abnormal—the higher vibrational levels ($v=2,3$) show unusually high intensities compared to a normal Franck-Condon envelope. This effect has been attributed to a possible perturbation from another state, $^7\Sigma^+$, which the CI calculation predicted to exist about 2000 cm^{-1} above the $^5\Delta$ state.^{5,10} This is highly possible because multi-

configuration effects are expected to be important for this molecule.

2. The $B^3\Sigma^+$ and $C^3\Delta$ low-lying low-spin states

Above the $A^5\Sigma^+$ state, four more features are observed. The last three features labeled C have a constant spacing of about 800 cm^{-1} , and most likely belong to members of a vibrational progression. In fact, a fourth member can be identified for this progression. The feature labeled as B seems to be a lone feature with no higher vibrational levels, similar to the $A^5\Sigma^+$ state, and is about 6770 cm^{-1} above the ground state. The first component of the C state is about 8310 cm^{-1} above the ground state. These two low-lying excited states have never been observed previously. We will assign them based on the CI calculation and considerations of the FeO^- molecular orbital configurations.¹⁰

The σ_1 orbital of the FeO^- ground state ($^4\Delta$) is occupied with two electrons, one spin up and one spin down. The $^5\Delta$ ground state of FeO is produced by removal of the spin down electron. The removal of the spin up electron will lead to a $^3\Delta$ excited state, which is equally allowed in the photodetachment process. However, such a low-spin excited state is prohibited in optical excitations by the spin selection rules. The low-spin $^3\Delta$ excited state corresponding to the $^5\Delta$ ground state is predicted to be about 1 eV above the ground state.¹⁰ This is almost in exact agreement with the energy difference between the C state and the X ground state observed in the current PES spectrum. Thus it is natural to assign the C state to the low-spin $^3\Delta$ state with a vibrational progression. Our instrumental resolution at the C state to the low-spin $^3\Delta$ state with a vibrational progression. Our instrumental resolution at the C state should be slightly higher than at the $A^5\Sigma^+$ state due to the dependence of resolution on the electron kinetic energies. However, the vibrational peak widths in the C state are all broader than the 45 meV peak width observed for the $A^5\Sigma^+$ peak. This is consistent with the assignment to a $^3\Delta$ state, since it can result in a spin-orbit broadening similar to the $X^5\Delta$ ground state. The $^3\Delta$ state seems to have a slightly lower vibrational frequency than the $^5\Delta$ ground state.

The B state at 2.336 eV binding energy consists of only a single peak, similar to the low-lying $A^5\Sigma^+$ state, which is resulted from the removal of a spin down δ electron from FeO^- . Similarly the removal of a spin up δ electron will result in a $^3\Sigma^+$ state, which should be similar to the $^5\Sigma^+$ state. However, the previous CI calculation did not predict such a low-spin state.¹⁰ The predicted $^3\Sigma^+$ state has a configuration of $\sigma_{Op}^2\sigma_{s-d}^2\pi_b^3\pi_a^3\delta^2$, which is quite different from the currently assigned one and cannot be accessed through a one-electron transition. Nevertheless, based on the lack of vibrational structure in the B state (which is similar to the $A^5\Sigma^+$ peak), we assign it to the $^3\Sigma^+$ state with the removal of a spin up δ electron from FeO^- although its intensity seems to be much lower than the $A^5\Sigma^+$ peak. The lower intensity is probably an indication of strong mixing with other configurations. Additionally, a close examination of the B peak indicates that it also has a width that appears bigger than that of the A peak and it seems to be a doublet. However, the limited statistics and instrumental resolution pre-

vent us from making a definitive statement about the spectral width here. In any case, it seems that the $^3\Sigma^+$ state involves strong multiconfiguration effects.

B. FeO_2^-

The sharp feature of the FeO_2^- spectrum indicates that there is little geometry change between the anion and the neutral and that the photodetachment removes a nonbonding electron from FeO_2^- . The width of this feature is slightly higher than the instrumental resolution, suggesting a low frequency bending vibration is weakly excited since the stretching frequencies observed for the various isomers of FeO_2 in matrices are all quite large,^{18–20} well within our experimental resolution. On the basis of our instrumental resolution, the FeO_2 bending frequency is probably no larger than about 350 cm^{-1} . The EA of FeO_2 is determined to be $2.358(0.030)\text{ eV}$, which is quite high compared to that of FeO . The nonbonding nature of the detached electron suggests that it is probably from a nonbonding $3d$ type of orbital on the Fe atom, similar to the δ orbital in FeO .

Both Fe and O_2 have every low EAs.^{25,26} Therefore, the high EA observed for the FeO_2 in the current work seems inconsistent with a side bonded FeO_2 (I) adduct or a linear or bent Fe–O–O (II) type of structure. On the other hand, from simple chemical considerations it is well known that the most stable oxidation states of Fe and O atoms are +3 and –2, respectively. Thus a FeO_2^- molecule in the form of $\text{O}^{2-}\text{Fe}^{3+}\text{O}^{2-}$ is expected to be quite stable (this is a formal chemical consideration and does not mean that FeO_2^- is a pure ionic molecule). In this formal oxidation state, the Fe atom has a rather stable d^5 configuration. Thus the removal of such a nonbonding d electron is expected to yield a high EA for FeO_2 . These formal considerations are consistent with the current PES spectrum.

The ground state symmetry of FeO_2 is not known. At least a FeO_2 adduct (I) is known to exist, which can be converted to an OFeO structure upon uv irradiation in rare gas matrices.^{18–20} Previous semiempirical calculations suggested that a linear OFeO is the most stable.¹⁴ A recent mass spectrometry and *ab initio* study concluded that the FeO_2^+ cation has a bent structure in which the Fe atom has a formal oxidation state of +5, and that a side-bonded FeO_2^+ adduct is metastable and can be easily converted to the more stable bent OFeO^+ dioxide form.²¹ The same study also suggested that FeO_2^- has an OFeO^- type of structure. This is consistent with the current experiment. However, it is still not known if the OFeO^- species is bent or linear. Regardless, the current study suggests that the neutral has a similar structure as the anion and that there is a very small bond angle change from the anion to the neutral OFeO .

IV. SUMMARY

We have produced FeO^- and FeO_2^- in a laser vaporization cluster source and obtained their PES spectra with vibrational resolution (for FeO^-) at 3.49 eV photon energy. Two new low-lying low-spin excited states are discovered for the FeO molecule at 6770 and 8310 cm^{-1} above the ground state. These two states are assigned to the $B\ ^3\Sigma^+$ and

$C\ ^3\Delta$ states, respectively. The $^3\Sigma^+$ state shows little vibrational structure, similar to the previously known $A\ ^5\Sigma^+$ state, which is due to the removal of a nonbonding and spin down δ electron from the FeO^- . The $C\ ^3\Delta$ state displays a well-resolved vibrational structure with an average frequency of $800(50)\text{ cm}^{-1}$.

The FeO_2^- spectrum represents the first PES study on this molecule and yields an electron affinity of $2.358(0.030)\text{ eV}$ for FeO_2 . The spectrum shows very little stretching vibrational structure and only very weak and unresolved bending vibrations with a frequency no larger than about 350 cm^{-1} . The PES spectrum suggests that the detachment removes a nonbonding d electron from FeO_2^- and that the FeO_2 neutral is quite similar to the anion. The current PES result is consistent with a linear or bent OFeO structure.

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