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Observation and Photoelectron Spectroscopic Study of Novel Mono- and Diiron Oxide Molecules: FeO_y^- ($y = 1-4$) and $Fe_2O_y^-$ ($y = 1-5$)

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Abstract: We study novel iron oxide molecules involving one and two iron atoms by anion photoelectron spectroscopy at 3.49 and 4.66 eV photon energies. Vibrationally resolved photoelectron spectra and low-lying excited states are obtained for FeO_y^- ($y = 1-4$) and $Fe_2O_y^-$ ($y = 1-5$). In both series, the photoelectron spectra become particularly sharp and better resolved for the higher oxides, FeO_3^-, FeO_4^-, $Fe_2O_4^-$, and $Fe_2O_5^-$. The electron affinity of the neutral oxide molecules is observed to increase with the number of oxygen atoms, suggesting a sequential oxidation behavior. For the monoiron oxide series, an oxidation saturation is observed as evidenced by the leveling-off of the electron affinity from FeO_3 to FeO_4. The structures and chemical bonding of these oxide molecules are discussed based on the sequential oxidation behavior. Isomers involving possibly O_2 or O_3 complexes are also observed for the diiron oxides above Fe_2O.

Introduction

The interaction between oxygen and iron is one of the most important chemical processes both due to the importance of iron as oxygen carriers in biological systems and due to its relevance to corrosion. Despite the wide interest in the iron−oxygen systems, few iron oxide molecules have been observed and studied. The FeO monoxide is one of the most studied and well-understood iron oxide species.[1−8] Even though many studies have been directed at the FeO_2 species[1,9−16] due to its relevance to oxygen transport in biological systems,[17] its true ground state structure and electronic structure are still not completely understood. There have been few observations of the higher monoiron oxides[10,11] and little understanding of their structure and bonding.

Diiron oxo complexes are common structural motif in a class of metalloproteins that are important as oxygen carriers and methane oxygenases.[18,19] Many inorganic complexes containing diiron oxo groups have been synthesized and characterized.[20−24] However, few diiron oxide molecules[25−27] have been studied in the isolated form even though such studies may provide essential insight into the electronic and chemical bonding properties of the molecules and the complexes containing them.

In the present contribution, we report the first systematic study of two series of iron oxide molecules (FeO_y, $y = 1-4$; Fe_2O_y, $y = 1-5$) using anion photoelectron spectroscopy at both 3.49 and 4.66 eV photon energies. Vibrationally resolved photoelectron spectra and low-lying excited states are obtained for all the species. These two series of molecules can be viewed as sequential oxidation of the iron atom and the iron dimer. A direct correlation is observed between the oxidation state of the iron atoms and the electron affinity of the oxide molecules. We find that for the monoiron series the electron affinity of the oxide molecules increases with the number of oxygen atoms and levels off from FeO_3 to FeO_4. For the diiron series, the EA increases monotonically through the full range of oxygen content studied here. Isomers with low electron affinity are also observed for the diiron series. Important bonding and structural information is obtained and discussed based on the experimental observation.

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The systematic study allows insight to be obtained into the nature of the chemical bonding of iron that possesses multiple oxidation states. Some of the diiron oxides are found to be structurally similar to those known in diiron oxo complexes.

Experimental Section

The experimental apparatus used for this study has been described in detail elsewhere.[28,29] Briefly, it couples a laser vaporization cluster source with a magnetic bottle time-of-flight photoelectron analyzer.[30] An intense pulsed laser beam is focused onto a pure iron target, producing a plasma containing iron atoms in both charged and neutral states. A helium carrier gas, seeded with 0.5% O_2 and delivered by two pulsed molecular beam valves, is mixed with the plasma. The reactions between the iron atoms and the oxygen produce the desired $Fe_xO_y^-$ clusters. The helium carrier gas and the oxide clusters undergo a supersonic expansion, forming a cold and collimated molecular beam by two skimmers. The negative clusters are extracted at 90° from the beam and subjected to a time-of-flight mass analysis. The clusters of interest are mass selected and decelerated before photodetachment by a pulsed laser beam. The detachment laser beam from a Nd:YAG laser (355 or 266 nm, 7 ns pulse width) is not focused and has a 5 mm diameter spot size in the detachment zone defined by an aperture outside the vacuum chamber. Typically, a pulse energy between 0.5−5 mJ is used, corresponding to a laser fluence of 2.5−25 mJ/cm^2. A higher laser fluence is used at 355 nm to obtain a stronger photoelectron signal. Lower fluences are used for the 266 nm to reduce low energy noises due to scattered photons interacting with surfaces near the detachment zone.

All the 355 nm spectra are taken at 10 Hz repetition rate, while the 266 nm spectra are taken at 20 Hz with the vaporization laser off at alternating shots for background subtraction. Nearly 100% of the photoelectrons are collected by the magnetic bottle and are parallelized down to a 3.5 m long time-of-flight tube for electron kinetic energy analyses. The current version of the magnetic bottle uses a permanent magnet for the high field[29] and has an energy resolution ranging from 20 to 30 meV at 1 eV electron kinetic energy. The best resolution is often achieved right after a fresh bake of the spectrometer and deteriorates somewhat with time, mostly caused by the change of workfunction of the vacuum chambers due to the chemisorption of oxygen. The electron kinetic energy distributions are calibrated with the known spectrum of the Cu$^-$ anion and are subtracted from the photon energies to obtain the presented electron binding energy spectra.

Results

Figure 1 shows the photoelectron spectra of FeO_y^- ($y = 1-4$) at 4.66 eV photon energy. The spectra of $Fe_2O_y^-$ ($y = 1-5$) are displayed in Figure 2. Vibrational structures are resolved in most of the spectra, and they are particularly well resolved for the higher oxides, which also appear to have simpler spectra. These spectra represent transitions from the ground state of the anion to the ground and excited states of the neutrals. The broad features at the lower binding energy side in the spectra of $Fe_2O_2^-$ and $Fe_2O_3^-$ are most likely due to isomers (see below). Several electronic excited states are observed for FeO. Only one excited state is observed for most of the other species. These are labeled in the figures. The observed energies and spectroscopic constants for the FeO_y and Fe_2O_y molecules are listed in Tables 1 and 2, respectively.

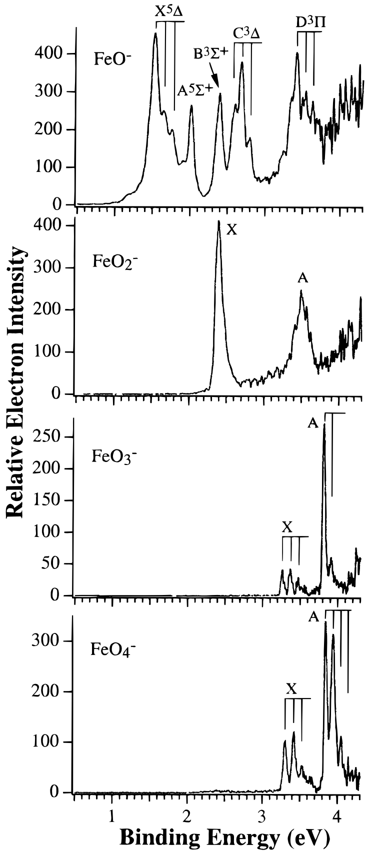

Figure 1. Photoelectron spectra of FeO_y^- ($y = 1-4$) at 4.66 eV photon energy. The vertical lines indicate the resolved vibrational structures. "X" represents the ground state of the neutrals and the other letters represent the exited states. Note the sharp, well-resolved and rather similar spectra for FeO_3^- and FeO_4^-.

The adiabatic electron affinity (EA) of the neutral molecules can be determined fairly accurately from the binding energy of the $\nu = 0$ vibrational feature when vibrational structure is resolved for the ground state. The EA values are represented in Tables 1 and 2 by the binding energy of the ground state. It is seen clearly that the EA increases with the number of oxygen atoms in both oxide series. The EA appears to level off from FeO_3 to FeO_4 for the monoiron series. These are plotted in Figure 3 together with the EA values of the Fe atom[31] and the Fe_2 dimer.[32]

The PES spectra usually do not depend on the detachment laser fluences. Thus a higher fluence is preferred to obtain stronger photoelectron signals. However, when photodissociation of the size-selected parent anion competes with photodetachment, the photoelectron spectra can vary with the detachment laser fluences because the negative photofragments can also be detached by the same laser pulse. Such is the case for FeO_4^-. The spectrum shown in Figure 1 is taken at a very low laser fluence of about 1.5 mJ/cm^2. At higher laser fluences, extra features at the lower binding energy side appear, as shown in Figure 4 taken at a laser fluence of 10 mJ/cm^2, while the main features remain the same.

Discussion

Sequential Oxidation: Oxidation State versus Electron Affinity. Our most interesting observation is shown in Figure 3, which displays the relationship between the electron affinity and the number of oxygen atoms in the mono- and diiron oxide molecules. The EA is a measure of the ability of the neutral molecule to stabilize a negative charge in its ground state. For

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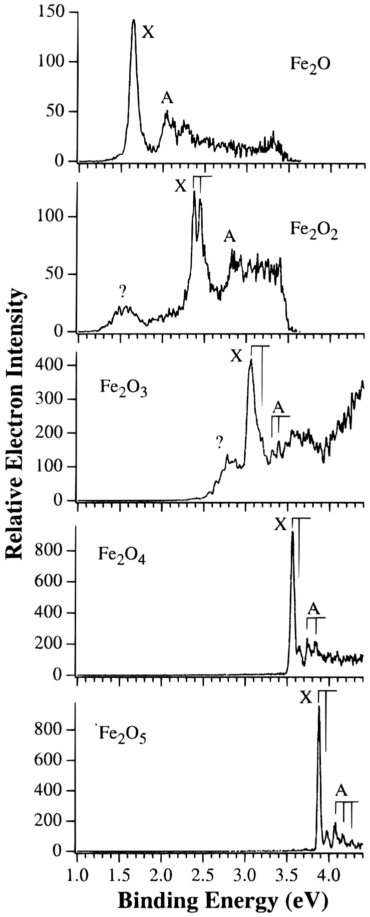

Figure 2. Photoelectron spectra of $Fe_2O_y^-$ ($y = 1-5$). The spectra of Fe_2O^- and $Fe_2O_2^-$ are taken at 3.49 eV photon energy while that of the higher oxides are taken at 4.66 eV. The vertical lines indicate the resolved vibrational structures. "X" represents the ground state of the neutrals and "A" represents the exited states. The "?" in the spectra of $Fe_2O_2^-$ and $Fe_2O_3^-$ indicates features of possible isomers, that complicate the spectra. Note the sharp and well-resolved spectra for $Fe_2O_4^-$ and $Fe_2O_5^-$.

Table 1. Observed Energies and Spectroscopic Constants for FeO_y ($y = 1-4$) from the Photoelectron Spectra of the Anions

	state	BE (eV)	term value[b] (eV)	vibrational freq[b] (cm^{-1})
FeO	X	1.50 (4)	0	950 (80)
	A	1.98 (4)	0.48 (2)	
	B	2.36 (4)	0.86 (2)	
	C	2.56 (4)	1.06 (2)	800 (60)
	D	3.39 (6)	1.89 (3)	850 (90)
FeO_2	X	2.36 (3)	0	
	A	3.31 (6)[a]	0.95 (4)	
FeO_3	X	3.26 (4)	0	850 (50)

[a] Estimated adiabatic binding energy. The vertical binding energy is 3.46 eV as determined from the band maximum. [b] Relative energies can be determined more accurately.

the iron oxide molecules, substantial ionic bonding character is expected because the O atom is much more electronegative. Therefore, the extra charge should be localized on the iron atoms because in the neutral form the Fe atoms are expected to be slightly positively charged. On the basis of this simple ionic picture, the nearly linear increase of the EA with the number of oxygen atoms suggests that the charge transfer for the subsequent oxygen addition is approximately equal. Thus, the linear relation between the EA and the number of O atoms suggests a sequential oxidation process.

Table 2. Observed Energies and Spectroscopic Constants for Fe_2O_y ($y = 1-5$) from the Photoelectron Spectra of the Anions

	state	BE (eV)	term value[b] (eV)	vibrational freq[b] (cm^{-1})
Fe_2O	X	1.63 (4)	0	
	A	2.02 (6)	0.39 (3)	
Fe_2O_2	X	2.36 (5)	0	670 (70)
	A	2.80 (7)[a]	0.44 (5)	
Fe_2O_3	X	3.06 (4)	0	810 (100)
	A	3.31 (7)[a]	0.25 (5)	650 (80)
Fe_2O_4	X	3.56 (4)	0	710 (60)
	A	3.74 (4)	0.18 (2)	720 (60)

[a] Estimated binding energy. The spectrum is complicated by the presence of another isomer. [b] Relative energies can be determined more accurately.

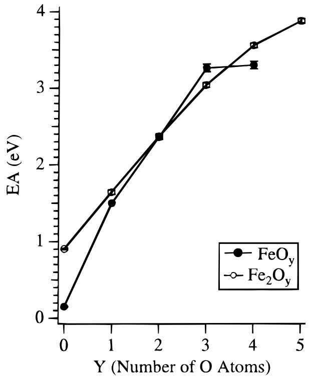

Figure 3. The electron affinity of the mono- and diiron oxide molecules versus the number of O atoms.

If we use the formal oxidation state of −2 for the O atom, then each O addition increases the oxidation state of the Fe atom by +2 in the monoiron series and by +1 in the diiron series. The maximum known oxidation state for the Fe atom is +6, which is reached in FeO_3. Thus, one more O addition will not be able to further oxidize the Fe atom, i.e., an oxidation saturation. This explains perfectly the leveling-off of the EA from FeO_3 to FeO_4, implying that there must be an O−O bond in FeO_4. For the diiron series, this maximum oxidation state is still not achieved even at Fe_2O_5 (+5). This suggests that the EA should further increase with further addition of an O atom to Fe_2O_6. Unfortunately, the signal for the $Fe_2O_6^-$ mass from our cluster source was too weak for it to be studied here.

We have found similar oxidation behavior for other metal oxide cluster series as well.[29,33] However, no such linear relation is observed for the silicon oxide cluster series,[34,35] which are covalent-bonded molecules. Therefore, the linear EA increase with O atoms is a strong indicator of ionic bonding, characteristic of metal oxides. This will be important in our later discussion of the structures of these oxide molecules.

Electronic and Geometric Structures of the Monoiron Oxides: FeO_y ($y = 1-4$). We have reported the photoelectron spectra of FeO^- and FeO_2^- recently at 3.49 eV photon energy.[1] We refer the readers to the previous work for a more extensive discussion and assignment of the lower-lying states accessed at the 3.49 eV photon energy. Only the new features observed at the present higher photon energy will be discussed here. Since the electronic structure of FeO is well understood, it also serves here as a good starting point to discuss the higher oxides. The current FeO^- and FeO_2^- spectra shown in Figure 1 are taken at 4.66 eV at a slightly reduced resolution due to higher electron

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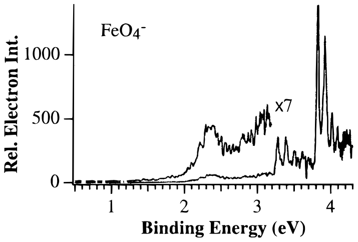

Figure 4. The photoelectron spectrum of FeO$_4^-$ taken at a higher detachment laser fluence (10 mJ/cm^2), showing lower energy features due to photodissociation of the parent FeO$_4^-$ anion (FeO$_4^-$ → FeO$_2^-$ + O$_2$).

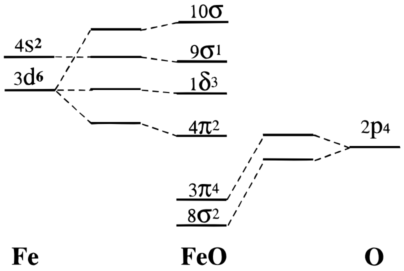

Figure 5. The schematic ordering and occupations of the molecular orbitals of the FeO molecule, showing that the O-derived orbitals lie below those of the Fe 3d-derived orbitals.

kinetic energies. One more excited state is observed for both FeO and FeO$_2$: feature D for FeO and feature A for FeO$_2$ as labeled in Figure 1. There seem to be real signals at higher binding energies in both spectra. But they do not appear to be well defined due to strong noise in this spectral range and will not be further discussed. We do not observe isomers for FeO$_2^-$ involving weakly bonded Fe/O$_2$ complexes as is observed in a recent matrix infrared experiment.[9] Such complexes should yield weak features at lower binding energies in the photoelectron spectrum because they are expected to have lower EA than the oxide.[29]

The FeO$^-$ spectrum exhibits a strong photon energy dependence. Notably, the A$^5\Sigma^+$ peak is the strongest feature in the 3.49 eV spectrum, while its intensity is substantially reduced with respect to the other features at the higher photon energy. This indicates that its total photodetachment cross section is strongly energy dependent. The molecular orbital (MO) diagram and ordering of FeO are shown schematically in Figure 5. In the anion, the extra electron enters the 9σ orbital.[4,5] The X, A, B, and C states have been assigned and discussed in detail before.[1] They result from removing an electron from the 9σ or 1δ orbitals. The newly observed state, D, is assigned to be from removing a 4π electron, resulting in a $^3\Pi$ state. The term value for this highly excited state is 1.89 eV. It has never been observed before since the transition between this state and the ground state is spin-forbidden.

It is important to note that all the spectral features observed for FeO derive from the Fe 3d orbitals (the 9σ orbital is really a *spd* hybrid).[5] The primarily O-derived orbitals (8σ and 3π) lie much deeper in energy and cannot be accessed at the photon energies used currently. This is essential to understand the spectra of the higher oxide molecules, in which more 3d electrons are transferred to the additional O atoms, resulting in simpler electronic structures for the higher oxide molecules. This is indeed the case, as evidenced in Figure 1 by the simpler spectra of the higher oxides. Only two states are observed in each case for FeO$_2$, FeO$_3$, and FeO$_4$. Compared to the FeO spectrum, all these features of the higher oxides should be derived mainly from the Fe 3d orbitals. However, more detailed electronic assignments of these features are not possible without accurate theoretical calculations because the occupation and ordering of the MOs cannot be determined *a priori*. We will focus on the structural and bonding aspect for which significant information can be derived from the observed spectra.

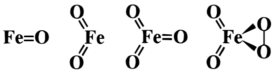

Figure 6. Schematic drawing of the structures of the monoiron oxides. Note that the FeO$_4$ molecule contains an O−O unit.

From the oxidation state concept discussed above, there should be no O−O bond in FeO$_2$ and FeO$_3$. Each O atom should form a formally Fe═O double bond with the Fe atom. This saturates the oxidation state of Fe (VI) at FeO$_3$. Therefore it is expected that there should be an O−O bond in FeO$_4$, implying that the electronic structure of FeO$_4$ should be similar to that of FeO$_3$. This is evidenced by the similarity between the photoelectron spectra of FeO$_3^-$ and FeO$_4^-$ and the fact that the EA of FeO$_4$ is also similar to that of FeO$_3$. Another piece of evidence for the existence of an O−O bond in FeO$_4$ comes from the photodissociation of the FeO$_4^-$ anion at high laser fluences, as shown in Figure 4. The broad feature near 2.3 eV is from photodissociation products that are further detached by the same laser pulse. Among the possible dissociation products, the binding energy of that feature can be due to either FeO$_2^-$ or O$_3^-$. The O$_3^-$ can be eliminated because a much stronger band near 3.5 eV would be expected for O$_3^-$ as well.[36] We conclude that this broad feature is due to detachment of a vibrationally hot FeO$_2^-$ formed by an O$_2$ loss from FeO$_4^-$ (FeO$_4^-$ → FeO$_2^-$ + O$_2$). A previous mass spectrometric study on the FeO$_4^-$ anion also suggests that it has at least one intact O−O unit.[10]

The FeO$_2$ molecule has been more extensively studied.[9−16] The most stable form has been concluded to be a bent O═Fe═O structure with a bond angle of about 141 degree.[9] Our FeO$_2^-$ spectrum consists of two broad features without vibrational structure, suggesting excitation of the low frequency bending mode. This is consistent with a bent structure for FeO$_2$, that has a rather low bending frequency. There have been few studies on the FeO$_3$ and FeO$_4$ molecules before. A previous matrix study suggested that a D_{3h} FeO$_3$ was observed.[11] The calculated symmetric stretching frequency for the D_{3h} FeO$_3$ is 792 cm^{-1}. Our photoelectron spectrum for FeO$_3^-$ is surprisingly simple with well-resolved vibrational structures for both the observed states (X and A). The observed vibrational frequency is about 850 cm^{-1} for both states, in reasonable agreement with the previous calculated symmetric stretching frequency for the D_{3h} FeO$_3$. The simple photoelectron spectrum also agrees with a highly symmetric FeO$_3$ and that there is only very slight geometry change along the Fe−O stretching coordinate. The rather high Fe−O stretching frequency in FeO$_3$ suggests that the Fe−O bonds are quite strong, comparable to that in the FeO monoxide. Therefore, we conclude that our observed FeO$_3$ is due to the D_{3h} FeO$_3$ with three Fe═O bonds.

The photoelectron spectra of FeO$_4^-$ and FeO$_3^-$ are surprisingly similar except that there is more extensive vibrational excitation in the FeO$_4^-$ spectra. The vibrational frequency in the ground state of FeO$_4$ is even higher than that in FeO$_3$. The fact that FeO$_4$ has a similar EA suggests that the Fe atom in FeO$_4$ has a similar oxidation state as in FeO$_3$, as mentioned above. The similar photoelectron spectra imply they both have similar electronic structure. All these indicate that FeO$_4$ is formed simply by replacing an O atom in FeO$_3$ with an O−O unit while maintaining a similar bonding character. It follows

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that the FeO_4 molecule should contain two Fe═O bonds and an O−O unit bonded to the Fe atom. The O−O bond is most likely perpendicular to the FeO_2 plane, resulting in a C_{2v} FeO_4. The structures of the FeO_y ($y = 1-4$) molecules are summarized in Figure 6, which shows clearly in the formal sense the increase of the oxidation state of Fe from +2 in FeO to +6 in FeO_3 as well as in FeO_4.

Electronic and Geometric Structures of the Diiron Oxides: Fe_2O_y ($y = 1-5$). The most striking feature of the diiron oxide series is the observation of the prominent ground state peak in all the molecules except $Fe_2O_2^-$ and $Fe_2O_3^-$, where broader features are observed at lower binding energies along with the prominent features. Similar to the monoiron series, the spectra become quite sharp and simple for the higher oxides with well-resolved vibrational structures. The broad features at the lower binding energy side in the spectra of $Fe_2O_2^-$ and $Fe_2O_3^-$ are assigned to other isomers, possibly involving intact O−O unit. This will be discussed later. The reasons for this assignment are as follows: (1) They are not due to photodissociation because their intensities do not depend on the laser fluences or wavelengths (355 and 266 nm). (2) The systematic sharp and prominent peaks observed in all the spectra are quite similar. The increase of EA with the number of O atoms has now been observed in several transition metal oxide cluster systems and seems to be general in metal oxide clusters. The broad low energy feature in the $Fe_2O_2^-$ spectrum clearly does not fit with this general trend. (3) Similar broad features at the lower binding energy side can also be discerned for the $Fe_2O_4^-$ and $Fe_2O_5^-$ spectra but at a much lower signal level (Figure 2). These broad features can be clearly observed at 3.49 eV photon energy, suggesting that similar isomers also exist for $Fe_2O_4^-$ and $Fe_2O_5^-$ at a much lower abundance. In the following we discuss the main oxide series first, then the possible isomers.

The EA vs O atom trend for the diiron series is similar to the monoiron series, suggesting that this series can be viewed as a sequential oxidation of the Fe_2 dimer—each O atom is individually bonded to the two Fe atoms with a similar amount of charge transfer. Our previous study of single O atom adsorption on small iron clusters predicted that Fe_2O has a C_{2v} triangle structure with a bridging O atom.[27] There have been few other studies on any of these diiron oxide molecules[25,26] except that a rhombus Fe_2O_2 unit has been seen in a number of organometallic complexes.[20−24] Therefore, detailed assignments of the observed electronic states will not be attempted at the present time and only qualitative structure and bonding aspects of these molecules are discussed. The best way to understand the electronic structure of these oxides is to start from the Fe_2 dimer and to compare with the monoiron oxides discussed above.

The Fe_2 ground state configuration may be described as $(3d^{14})\sigma_{4s}^2$, where $3d^{14}$ represents collectively the MOs formed from the 3d atomic orbitals and σ_{4s}^2 represents the σ bonding orbital between the Fe atoms.[37] Analogous to the monoiron oxide series, when Fe_2 is oxidized the O-derived orbitals lie below the Fe 3d-derived orbitals (see Figure 5), formally resulting in a charge transfer of two electrons from Fe_2 to the O atom. Subsequent oxidation will result in more charge transfer from the Fe_2 to the O atoms; each O addition increases formally the oxidation state of the Fe atoms by +1. The observed spectral features should all be derived from the orbitals involving the Fe atoms. Similar to the monoiron series, the increased charge transfer from the Fe atoms to the O atoms explains the fact that the electronic structure of the higher oxides appears to be simplified, as evidenced by the seemingly simpler photoelectron spectra. From the rather high observed vibrational frequencies, the interactions between the Fe and O atoms are strengthened at the higher oxides. The rather sharp spectral features suggest that the detached electrons are from non-bonding or weakly bonding orbitals, which are consistent with the nature of the Fe 3d-derived orbitals.

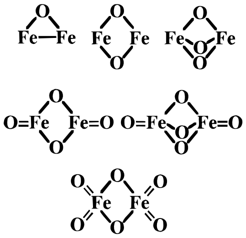

Figure 7. Schematic drawing of possible structures for the diiron oxide molecules, consistent with the sequential oxidation concept. For the hypothetical structure of Fe_2O_6, the four terminal O atoms and the two bridging O atoms are on perpendicular planes.

The spectra of the diiron oxide species are quite similar, each with a prominent ground state peak and a lower intensity excited state peak. There is also a second exited state peak for Fe_2O at about 2.8 eV that is partially overlapped with the A state. The spectra of $Fe_2O_2^-$ and $Fe_2O_3^-$ are obviously complicated by the existence of isomers that have substantial abundance. The spectra of $Fe_2O_4^-$ and $Fe_2O_5^-$ are best resolved, each with one excited state. These two spectra are also very similar, except that Fe_2O_5 has a higher EA and higher vibrational frequencies in both the ground and excited states.

On the basis of the above discussions, it is interesting to speculate about the possible structures of these diiron oxides. These are shown in Figure 7. All the structures are consistent with the sequential oxidation concept, and the oxidation states of the Fe atoms can be counted by the bonds they form with O atoms, and they increase sequentially from +1 in Fe_2O to +5 in Fe_2O_5. The oxidation state of Fe is still not saturated at Fe_2O_5. This is also obvious from the EA vs O atom curve shown in Figure 3. We predict that there should be a stable Fe_2O_6 molecule, whose possible structure is also included in Figure 7.

The C_{2v} triangle structure for the Fe_2O is known from our previous work.[27] The only reasonable structure for Fe_2O_2 is the rhombus structure, which is known to occur in several organometallic compounds.[20−24] Several other M_2O_2 oxides are known to possess the rhombus structure, including Cu_2O_2,[33] Si_2O_2,[38] and Ge_2O_2.[39] The Fe_2O_3 molecule may have several possible structures. The one shown in Figure 7 with three bridging O atoms is the only one with three equivalent O atoms. Cu_2O_3 is also found to have a similar structure.[33] The structures of Fe_2O_4 and Fe_2O_5 can be viewed to be built upon the structures of Fe_2O_2 and Fe_2O_3, respectively, each with two more Fe═O double bonds. The valence of the Fe atoms is better satisfied in the higher oxides, strengthening the overall Fe−O bonding as evidenced by their higher vibrational frequencies. Accurate theoretical calculations are required to definitely solve the structures of the higher oxide molecules. The present experiments provide some stringent parameters to compare with theoretical calculations that can also undoubtedly yield more insight into the nature of the chemical bonding in these unusual oxide molecules.

Finally, it is interesting to discuss the possible isomers observed for the Fe_2O_2 and Fe_2O_3 molecules. Since the EA of the Fe_2O_2 isomer is not increased compared to Fe_2O, it must involve an O−O bond. Most likely, it consists of a Fe_2-O_2

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complex. The Fe_2O_3 isomer may consist of a Fe_2O-O_2 complex or Fe_2-O_3 complex. Similarly, the Fe_2O_4 and Fe_2O_5 isomers may also consist of O_2 or O_3 units. All these isomers seem to yield rather broad features in the photoelectron spectra, consistent with their weakly bound nature. In some sense, these O_2 complexes may be more interesting because they may mimic the properties of those O_2 complexes formed in oxygen transport systems or organometallic$-O_2$ complexes, that are precursors for the cleaving of the O$-$O bond.[17]

Summary

We study two series of novel iron oxide molecules, FeO_y ($y = 1-4$) and Fe_2O_y ($y = 1-5$), using anion photoelectron spectroscopy. Important electronic and vibrational structures are obtained, providing unique information about the structures and bonding of these molecules. For both series, sequential oxidation behaviors are observed, as inferred from the near linear increase of the electron affinity versus the number of O atoms. An oxidation saturation is observed at FeO_3, consistent with the known maximum oxidation state of the Fe atom. In both series, the photoelectron spectra are observed to become simpler as the number of O atoms increases. This is consistent with a charge transfer picture where the electrons are sequentially transferred from the Fe atoms to the increasing O atoms, yielding a simpler electronic structure for the higher oxides because the O-derived orbitals all lie deeper in energy and cannot be accessed by the photon energies used. The structures of the monoiron series are found to change from a C_{2v} FeO_2 to a D_{3h} FeO_3, and finally to a C_{2v} FeO_4 that contains an O$-$O bond since the oxidation state of Fe is already saturated at FeO_3. That FeO_4 must contain an O$-$O unit is also evidenced by observation of photodissociation of the parent FeO_4^- anion, which can lose an O_2 under high laser fluences to give rise to a broad FeO_2^- feature. For the diiron series, all the spectra are observed to be quite similar, each containing a rather prominent ground state peak, followed by one or two excited state features. Isomers are also observed for the $Fe_2O_y^-$ series when $y > 1$. These isomers are particularly abundant for $Fe_2O_2^-$ and $Fe_2O_3^-$ and complicate the observed spectra. These isomers are proposed to be complexes involving O_2 or O_3 units. For the main oxide sequence, the electron affinity is observed to increase with the number of O atoms. The oxidation is observed not to be saturated at Fe_2O_5, agreeing with the maximum known oxidation state of the Fe atom. Possible structures are proposed for these oxide molecules, consistent with the experimental observations, which provide stringent tests for any theoretical calculations that can more completely elucidate the structure and bonding of these novel oxide molecules.

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