Photodissociation of Iron Oxide Cluster Cations[†]

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Iron oxide cluster cations, $Fe_nO_m^+$, are produced by laser vaporization in a pulsed nozzle cluster source and detected with time-of-flight mass spectrometry. The mass spectrum exhibits a limited number of stoichiometries for each value of n, where $m \geq n$. The cluster cations are mass selected and photodissociated using the second (532 nm) or third (355 nm) harmonic of a Nd:YAG laser. At either wavelength, multiple photon absorption is required to dissociate these clusters, which is consistent with their expected strong bonding. Cluster dissociation occurs via elimination of molecular oxygen, or by fission processes producing stable cation species. For clusters with $n < 6$, oxygen elimination proceeds until a terminal stoichiometry of $n = m$ is reached. Clusters with this 1:1 stoichiometry do not eliminate oxygen, but rather undergo fission, producing smaller $(FeO)_n^+$ species. The decomposition of larger clusters produces a variety of product cations, but those with the 1:1 stoichiometry are always the most prominent and these same species are produced repeatedly from different parent ions. These combined results establish that species of the form $(FeO)_n^+$ have the greatest stability throughout these small iron oxide clusters.

Introduction

Transition metal oxides are important in applications such as electronics,[1–4] catalysis,[3–8] and magnetic materials.[1–4] Numerous studies have focused on the properties of the bulk materials as well as the nanoparticle and gas phase cluster oxides. Nanoparticle oxides have applications in areas such as magnetism, catalysis, and medicine.[4,9–22] Iron oxide is particularly interesting because it consists of four major bulk phases, all of which exhibit unique properties.[1–3] FeO, wüstite, has a rock salt-type structure with defects, generally referred to as $Fe_{1-x}O$.[13e] This phase is paramagnetic at room temperature and antiferromagnetic below 183 K.[17] It is used in semiconductors[1–3] and as a nonmagnetic precursor that is easily converted into magnetite, Fe_3O_4, or maghemite, γ-Fe_2O_3.[17] Both magnetite and maghemite have a spinel structure and are ferromagnetic allowing them to be used for magnetic recording materials.[1–3] Hematite, α-Fe_2O_3, has a corundum structure with weak ferromagnetism and is used as an antiferromagnetic insulator.[1–3] These individual phases have been the subjects of many experiments involving films[12] and nanoparticles.[13,14,17,19,21] Gas phase experiments have also been performed to investigate properties such as bonding, reactivity, and structure of small cluster oxides.[23–56] Theory has provided a further understanding of the structures and stabilities of these systems.[57–66] Because the phase of iron oxide has a dramatic influence on its properties, it is important to determine the relative stability of small clusters and how this varies with stoichiometry. We address this issue here using photodissociation studies of mass-selected cations.

Cluster stoichiometries and relative abundances of various transition metal oxide clusters have been determined using mass spectrometry.[23–41] These systems exhibit several stoichiometries for each metal increment, as opposed to the "magic numbers" seen previously for transition metal carbides.[67–73] Castleman and co-workers have reported extensive studies of transition metal oxides and their reactivities with small hydrocarbons.[28–30] Additional experiments by Bernstein and co-workers investigated mass distributions using laser photoionization at vacuum ultraviolet wavelengths.[33,34] In both experiments, the intensity patterns in mass spectra were used to infer relative cluster stability. The spectroscopy of small oxides has been studied with rare gas matrix isolation[44,45] and photoelectron spectroscopy of mass selected-ions.[46–53] Our group, in collaboration with Meijer and co-workers, used IR-resonance enhanced multiphoton ionization (IR-REMPI) to obtain vibrational spectra for several metal carbide[70] and oxide[54] cluster systems. Additional infrared resonance enhanced multiphoton photodissociation (IR-REMPD) of mass-selected ions have been performed by Fielicke, Meijer, and Asmis.[55,56] Theory has also been used to determine the structures of these transition metal oxide clusters.[57–66]

A variety of experiments have attempted to determine the stability of gas phase clusters such as metal oxides.[74,75] However, as we have discussed before,[31] mass spectrometry alone is problematic in determining relative cluster stability, because unknown ionization potentials, fragmentation processes, and size-dependent cross sections may introduce strong biases in the intensities of mass peaks and the relative concentrations associated with these clusters. Additional problems arise in cation experiments using energy-variable collision induced dissociation or photodissociation to determine the thresholds for bond breaking. Photodissociation relies on the absorption of light, which may not be efficient in the threshold region, and collisional measurements may suffer from significant kinetic shift effects at the threshold, especially for strongly bound clusters. Equilibrium measurements have been performed on the small vanadium oxide clusters,[23] photoionization has been employed on the corresponding neutrals,[26,33,34] collision induced dissociation has investigated various transition metal oxides[29,30] and photodissociation studies have been applied to certain transition metal (V, Nb, Ta, Cr, Y, La) oxides.[28,31] The combined results from these experiments provide evidence for the enhanced stabilities of certain cluster stoichiometries, and the

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patterns seen so far vary considerably with the metal. Theory has been applied to small iron oxide clusters,[60,66] but there are no previous experiments on the bonding energetics or stabilities of these systems.

We have shown that photofragmentation studies of cations can be used to determine relative cluster stabilities.[31,68,76] Stable clusters are difficult to dissociate, and they are often produced as fragment ions upon the dissociation of larger clusters. Although stable neutrals are not detected, they can be inferred using mass conservation. These methods have been used previously in our laboratory to study metal carbide,[68] metal silicon[76] and metal oxide clusters.[31] Previous photodissociation studies of transition metal oxides have found unexpected evidence for stable cluster cations and neutrals with oxidation states different from those of the most common solid phases of these compounds.[31] Iron oxide has more than one common oxidation state, and its properties, e.g., magnetism, are intimately related to its stoichiometry. It is therefore interesting to examine the stability patterns in its small clusters, as we do here with photodissociation measurements.

Experimental Section

Iron oxide clusters are produced by laser vaporization in a pulsed nozzle cluster source and mass analyzed in a reflectron time-of-flight mass-spectrometer (TOF-MS), as described previously.[31,68,76] The second (532 nm) or third (355 nm) harmonic of a Nd:YAG laser (Spectra Physics GCR-11) is employed to vaporize iron from a rotating and translating metal rod. A helium mixture seeded with 20% oxygen is pulsed with a General Valve (150 psi backing pressure; 1 mm orifice) through the sample rod holder. The oxide cluster cations grow from the laser-generated plasma, producing a molecular beam of clusters. This beam is expanded into a differentially pumped source chamber and skimmed into the mass spectrometer chamber, where cluster cations are sampled with a reflectron time-of-flight instrument using pulsed acceleration plates. Pulsed deflection plates in the first flight tube section are used to size-select the ions of interest before they enter the reflectron. Photodissociation employs a Nd:YAG laser (DCR-3) at 532 or 355 nm, which is timed to intersect the clusters at the turning point in the reflectron field. Subsequently, the parent and fragment ions are mass analyzed in the second drift tube section and detected using an electron multiplier tube and a digital oscilloscope (LeCroy 9310A). Data are transferred from the digital scope to a computer via an IEEE-488 interface. Different studies were performed as a function of laser wavelength and pulse energy for each cluster size. Photodissociation used 40−50 mJ/pulse of unfocused laser beam in a spot size of roughly 1 cm^2.

Results and Discussion

The mass spectrum of the $Fe_nO_m^+$ cation clusters produced in our experiment is shown in Figure 1. Clusters containing up to 18 metal atoms and varying numbers of oxygen atoms are detected. The stoichiometries for each cluster correspond to a specific number of metal atoms, n, and oxygen atoms, m, where the most prominent mass peak within each group of clusters corresponds to $m \geq n$. For example, for $n = 3$ the mass peaks for $Fe_3O_3^+$, $Fe_3O_4^+$, $Fe_3O_5^+$ and $Fe_3O_6^+$ are observed. The mass distributions that we measure are similar to those of neutral clusters detected by VUV photoionization by the groups of Riley and co-workers[26] and Bernstein and co-workers.[34] This is the best comparison available because there are no previous mass spectra measured for cation clusters larger than $Fe_3O_3^+$.

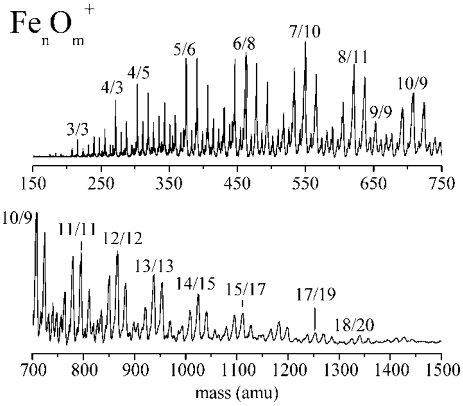

Figure 1. Time-of-flight mass spectrum for $Fe_nO_m^+$ clusters, in the lower (upper trace) and higher (lower trace) mass range using 355 nm as the vaporization laser.

To determine the relative stabilities of these various iron oxide clusters, we have mass-selected each cluster size that is present with enough intensity and photodissociated it with laser excitation at 532 and 355 nm. High laser fluences of 40−50 mJ/cm^2 pulse are necessary to achieve significant amounts of dissociation. These conditions indicate that multiple photon excitation is required to break the bonds, which is also consistent with our previous observations on other transition metal oxides.[31] Dissociation energies of the small iron oxide clusters have been measured in the range 3−5 eV/bond,[35,40,43,46] and density functional theory has been used to calculate similar bond energies for larger clusters.[60] Therefore, it is understandable that multiple photon excitation might be required for dissociation. Because the absorption spectra of these clusters are not known, it is also possible that the high fluence from the laser is required to overcome weak absorption at one or both of the wavelengths used. Though dissociation is not efficient under any conditions, 355 nm gives the best signals, perhaps because of the greater photon energy or better absorption efficiency at this wavelength. Therefore the data shown throughout this paper are those obtained at 355 nm.

Selected examples of the photofragmentation mass spectra acquired from our experiment are shown in Figures 2–10. All of the cluster ions photodissociated are listed in Table 1, along with the corresponding photofragments produced, where the most intense fragments are in bold. The photodissociation mass spectra are collected in a difference mode of operation, where spectra collected with the photodissociation laser off (only the selected parent ion present) are subtracted from the spectra collected with this laser on (which contains fragment peaks and residual parent ion). This method produces a negative parent ion peak, showing its depletion, and positive fragment ion peaks. Ideally, the combined intensities of the fragment peaks would equal the depletion of the parent ion. However, mass-discrimination effects in our instrument make it impossible to focus on both the parent and fragment ions with equal sensitivity and resolution.[77] Therefore, the parent ion peaks are presented off-scale in the negative direction to show the fragment ions with better intensity. We also use several focusing conditions to ensure that no fragment ions are missed. However, because of the mass discrimination, we do not report quantitative branching ratios for the fragment ions, but only distinguish between strong and weak intensities.

Photodissociation mass spectra for the clusters $Fe_3O_3^+$, $Fe_3O_4^+$ and $Fe_3O_6^+$, hereafter designated as the 3/3, 3/4 and

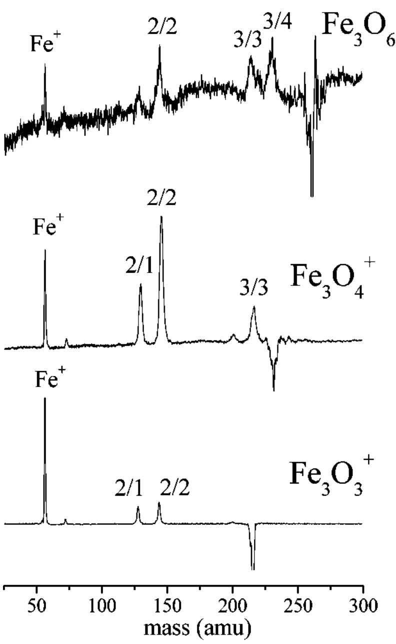

Figure 2. Photodissociation mass spectra of $Fe_3O_m^+$ clusters at 355 nm. In this figure and others shown later, the noise level reflects the combined influences of the amount of parent ion present, as well as its absorption and photodissociation efficiency.

3/6 species, respectively, are shown in Figure 2. In this figure and others shown later, the noise level reflects the combined influences of the amount of parent ion present, as well as its absorption and photodissociation efficiency. This is why the signal level for the 3/6 cluster is worse than those for the 3/4 and 3/3 species. The 3/4 and 3/6 fragment to 3/3 and 3/4 respectively, via a loss of either two oxygen atoms or molecular O_2. We cannot detect neutral fragments, and therefore throughout this paper we use brackets, e.g., [O_2], to indicate our uncertainty about the neutral losses. Castleman and co-workers also reported the inferred loss of neutral molecular oxygen in the collisional dissociation of oxygen rich iron oxide clusters.[30] This same behavior is seen again in our data for the $n = 2$ group (data not shown), where the 2/1, 2/2 and 2/3 fragment ions are produced from 2/3, 2/4 and 2/5 parents, respectively. Additionally the 2/6 and 2/8 clusters produce the 2/2 fragment via the elimination of two or three units of [O_2].

In the $Fe_3O_m^+$ complexes, the loss of [O_2] is not observed at the fragment ion 3/3, which is the smallest ion produced by the cluster source in the $n = 3$ group. Instead, the 3/3 parent ion fragments by losing both iron and oxygen. This 3/3 ion is also produced prominently in the fragmentation of larger 3/m parent ions. As shown below, it is also produced repeatedly as a fragment from many larger clusters containing more iron atoms. The same kind of behavior is found for the $n = 2$ cluster group, where oxygen elimination occurs above the 2/2 cluster, and 2/2 is produced as a fragment from larger species. We therefore identify the 2/2 and 3/3 clusters as the most stable species in their respective cluster groups. As shown below, this same 1:1 stoichiometry is seen throughout these iron oxide cluster fragmentation processes.

TABLE 1: Stoichiometries of Iron Oxide Photofragments ($M_nO_m^+ = n/m$) Detected at 355 nm (Most Prominent Stoichiometries Indicated in Bold)

parent cluster	fragment ions
1/4	1/2, **Fe**$^+$
1/6	**1/2**, Fe$^+$
2/2	2/1, **Fe**$^+$
2/3	2/2, 2/1, **Fe**$^+$
2/4	**2/2**, Fe$^+$
2/5	**2/3**, 2/2, 2/1, 1/2, **Fe**$^+$
2/6	2/2, **Fe**$^+$
2/8	**2/2**, 2/1, 1/2, **Fe**$^+$
3/3	2/2, 2/1, **Fe**$^+$
3/4	3/3, **2/2**, 2/1, Fe$^+$
3/5	3/3, **2/2**, 2/1, 1/2, **Fe**$^+$
3/6	3/4, 3/3, 2/2, 2/1, Fe$^+$
4/4	3/3, **2/2**, 2/1, Fe$^+$
4/5	4/4, **3/3**, 2/2, 2/1, Fe$^+$
4/6	**4/4**, 3/3, 2/2, 2/1, Fe$^+$
5/5	**4/4**, **3/3**, 2/2, 2/1, Fe$^+$
5/7	**5/5**, 4/4, 3/3, 2/2, 2/1; Fe$^+$
5/8	5/7, **5/6**, 5/5, 4/4, 3/3, 2/2, 2/1, Fe$^+$
6/6	6/5, 5/7, 5/6, 5/5, 4/4, **3/3**, 2/2, 2/1, Fe$^+$
6/7	**4/6**, 4/5, **4/4**, 3/3, 2/2, 2/1
6/8	**4/5**, 4/4, 3/3, 2/2, 2/1
7/8	6/6, **5/7**, 5/6, 5/5, **4/4**, 3/3, 2/2, 2/1
7/9	6/5, **5/6**, **4/4**, **3/3**, 2/2, 2/1
7/10	6/5, 5/8, 5/7, 5/6, 5/5, 4/4, **3/3**, 2/2, 2/1, Fe$^+$
8/6	6/4, 5/6, 5/5, 4/4, **3/3**, 2/2, 2/1
8/7	7/7, 7/5, 6/7, 6/6, 5/5, 4/4, **3/3**, 2/2, 2/1
8/8	7/8, 7/7, 7/6, 7/5, 6/7, 6/6, 5/5, 4/4, **3/3**, 2/2, 2/1
8/9	7/7, 7/6, 6/8, 6/7, 6/6, 5/5, 4/4, **3/3**, 2/2, 2/1
9/8	9/7, 9/6, 8/8, 8/7, 8/6, 7/6, 6/6, 5/5, 4/4, **3/3**, 2/2, 2/1
9/9	8/9, 7/9, 6/6, 5/5, 4/4, **3/3**, 2/2, 2/1
9/10	8/8, 6/6, 5/5, **4/4, 3/3,** 2/2, 2/1
10/10	6/6, 5/5, **4/4**, **3/3**, 2/2, 2/1
10/11	10/10, 10/9, 10/8, 10/7, 9/9, 9/8, 9/7, 8/9, 8/8, 7/8, 7/7, 6/6, 5/5, **4/4, 3/3**
10/12	10/11, 10/10, 10/9, 10/8, 9/10, 9/9, 9/8, 9/7, 8/9, 7/7, 6/6, 5/5, **4/4, 3/3**
10/13	10/9, 9/9, 9/7, 8/8, 7/7, 6/6, 5/5, **4/4**, **3/3**, 2/2
11/11	11/9, 11/7, 10/10, 9/11, 9/8, 9/6, 8/9, 8/8, 7/10, 7/8 7/7, 6/6, 5/5, **4/4, 3/3,** 2/2, 2/1, Fe$^+$
11/13	11/11, 11/9, 10/10, 9/11, 9/10, 9/9, 9/8, 9/6, 8/8, 7/7, 6/6, 5/5, **4/4, 3/3,** 2,2, 2/1, Fe$^+$
12/12	12/10, 11/11, 10/11, 10/9, 9/11, 9/10, 9/9, 9/8, 8/9, 8/8, 7/7, 6/6, 5/5, **4/4, 3/3**, 2/2, 2/1, Fe$^+$
13/14	13/12, 11/11, 11/9, 10/11, 10/10, 9/10, 9/9, 8/8, 7/7, 6/6, 5/5, **4/4**, **3/3**, 2/2, 2/1, Fe$^+$
14/15	13/13, 12/12, 12/10, 11/11, 10/11, 10/9, 9/11, 9/10, 9/9, 9/8, 8/9, 8/8, 7/7, 6/6, 5/5, **4/4, 3/3,** 2/2, 2/1, Fe$^+$
15/17	13/13, 13/11, 12/13, 11/11, 10/10, 9/9, 8/8, 7/7, 6/6, 5/5, **4/4,** 3/3, 2/2, 2/1, Fe$^+$
16/19	15/13, 14/15, 13/13, 12/13, 11/11, 10/10, 9/9, 8/8, 7/7, 6/6, 5/5, **4/4, 3/3,** 2/2, 2/1, Fe$^+$
17/19	16/16, 15/15, 14/14, 13/13, 12/12, 11/11, 10/10, 9/9, 8/8, 7/7, 6/6, **5/5, 4/4, 3/3**, 2/2, 2/1, Fe$^+$

Multiple fragment ions are already observed in these small clusters, and this tendency becomes greater in the larger clusters studied here. It therefore becomes interesting to consider the mechanism of fragmentation that might produce multiple fragments. In the dissociation of the $Fe_3O_3^+$ ion, for example, the loss of [FeO] produces 2/2 and a small amount of 1/1 fragment ions. These product ions can be formed through either two direct processes acting in parallel, as in (a) and (b), or by one sequential process, as in (c):

$$3/3^+ \rightarrow 2/2^+ + 1/1 \qquad \text{(a)}$$

$$3/3^+ \rightarrow 2/2 + 1/1^+ \qquad \text{(b)}$$

$$3/3^+ \rightarrow 2/2^+ + 1/1 \qquad 2/2^+ \rightarrow 1/1^+ + 1/1 \qquad \text{(c)}$$

However, it is unlikely that processes (a) and (b) occur simultaneously; fragmentation processes like this usually yield

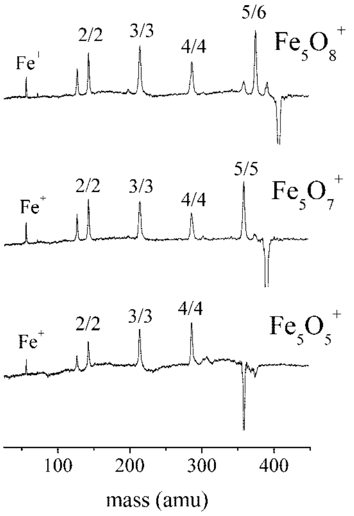

Figure 3. Photodissociation mass spectra of $Fe_5O_m^+$ clusters at 355 nm.

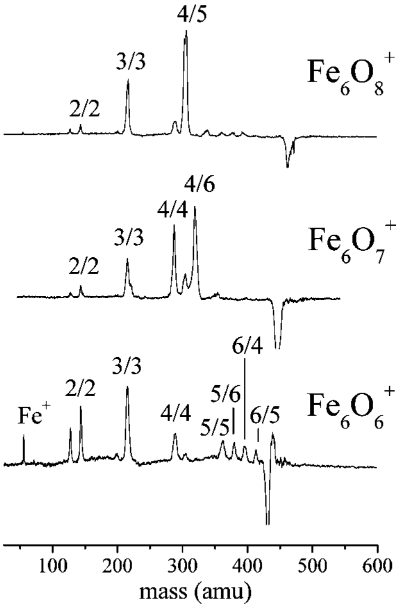

Figure 4. Photodissociation mass spectra of $Fe_6O_m^+$ clusters at 355 nm.

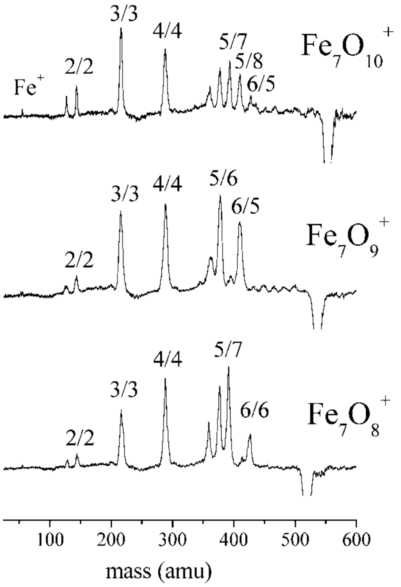

Figure 5. Photodissociation mass spectra of $Fe_7O_m^+$ clusters at 355 nm.

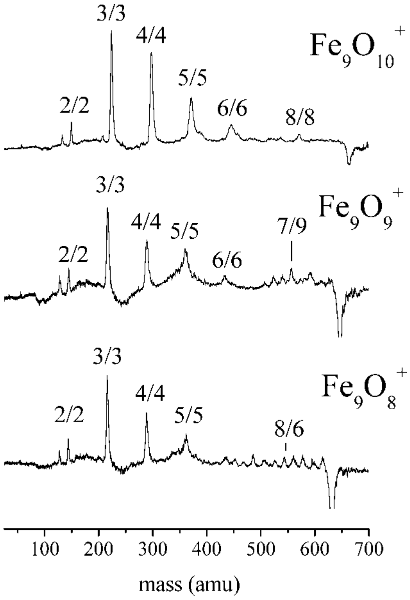

Figure 6. Photodissociation mass spectra of $Fe_9O_m^+$ clusters at 355 nm.

a charge on the species with the lower ionization potential. It is conceivable that both 2/2 and 1/1 have the same ionization potential, so that both are equally probable, but it is more likely that 2/2 has the lower IP and that a sequential process like (c) occurs. Variation of the laser power might be able to distinguish between these two processes. To test this, we performed laser power studies on selected cluster sizes (over the range of 5−50 mJ/cm^2 pulse at 355 nm and 15−125 mJ/cm^2 pulse at 532 nm). In essentially every case, reduction in the laser power caused fragment ions closest to the mass of the parent ion to remain intense, whereas the lower mass fragments were reduced in relative intensity. This behavior is consistent with sequential fragmentation. Additionally, it is usually true that larger clusters have lower ionization potentials, and so we do not expect the elimination of large neutral photofragments. Smaller ions throughout these studies therefore most likely come from sequential fragmentation processes, in which multiple small neutral species, e.g., [FeO], are eliminated. We cannot prove this mechanism, but it does seem to be consistent with all of the available data.

The same kind of dissociation seen for the $n = 3$ clusters is found again for the $Fe_4O_m^+$ ($m = 4−6$; data not shown) and $Fe_5O_m^+$ ($m = 5−8$) species (shown in Figure 3). In both of these groups, power dependence seems to indicate a sequential dissociation mechanism. In both cases, the first step in the decay of oxygen-rich clusters is the elimination of [O_2], producing the 4/4, 5/5 and 5/6 fragments from the 4/6, 5/7 and 5/8 parent clusters, respectively. Again, clusters with the 1:1 ratio of iron and oxygen (e.g., $Fe_4O_4^+$ and $Fe_5O_5^+$) fragment by an initial loss of [FeO]. After this, a sequence of smaller $(FeO)_n^+$ ions are produced, presumably by the loss of additional [FeO] units. The only other kind of fragment ion seen here is the Fe_2O^+ species, which was also seen in the $n = 3$ fragmentation data. This overall behavior establishes that the 4/4 and 5/5 species

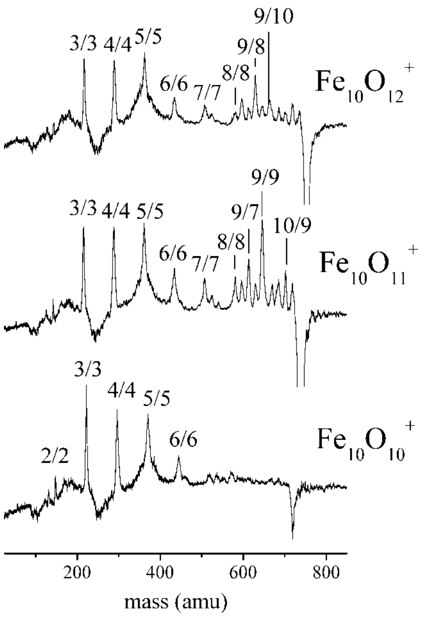

Figure 7. Photodissociation mass spectra of $Fe_{10}O_m^+$ clusters at 355 nm.

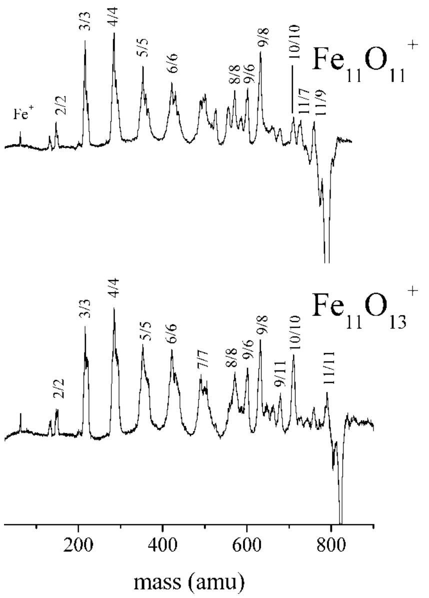

Figure 8. Photodissociation mass spectra of $Fe_{11}O_m^+$ clusters at 355 nm.

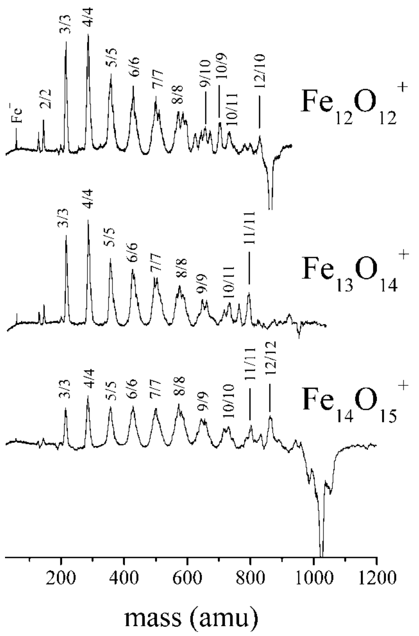

Figure 9. Photodissociation mass spectra of $Fe_{12}O_{12}^+$ (top), $Fe_{13}O_{14}^+$ (middle) and $Fe_{14}O_{15}^+$ (bottom) clusters at 355 nm.

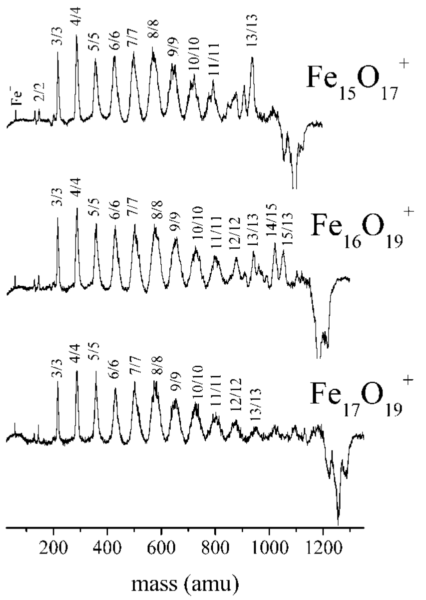

Figure 10. Photodissociation mass spectra of $Fe_{15}O_{17}^+$ (top), $Fe_{16}O_{19}^+$ (middle) and $Fe_{17}O_{19}^+$ (bottom) clusters at 355 nm.

are the most stable cations in the $n = 4$ and $n = 5$ groups, and reinforces our earlier conclusions about the 2/2 and 3/3 species.

The fragmentation spectra of the $Fe_6O_m^+$ ($m = 6-8$) and $Fe_7O_m^+$ clusters ($m = 8-10$) are shown in Figures 4 and 5, respectively. One noticeable difference in the dissociation patterns for both groups is that the tendency to lose [O_2] is no longer observed. Instead, for the 6/7, 6/8 and all three $n = 7$ parents, we see the immediate loss of both metal and oxygen. The fragmentation of 6/7 and 6/8 ions essentially jumps over the possible $n = 5$ fragments, and produces instead $n = 4$ species. In addition to the (now) expected 4/4 species, the most intense fragments are 4/5 from 6/8 and 4/6 from 6/7. The inferred neutrals in these cases are [2/3] and [2/1]. The 2/3 stoichiometry is of course the same as that of the common bulk phase. The 4/4 fragment is more intense from 6/7, where again the neutral loss could be [2/3]. The $n = 7$ group also shows this tendency to lose [2/3] or [2/1] neutrals, as demonstrated by 7/10 → 5/7, 7/9 → 5/6 and 7/8 → 5/7. After these initial losses of metal oxide neutrals, all of these systems continue to fragment producing predominantly the 1:1 stoichiometries seen already, presumably by losses of [FeO]. The 6/6 is anomalous here as the only ion so far that loses oxygen to produce stoichiometries less than the 1:1 ratio. On the basis of the patterns seen so far, we might have expected clusters such as 5/5 and 6/6 to be produced prominently in these dissociation events, but these ions are not observed. Either these 1:1 species are not as stable as some of the smaller ones, or there is some change in structures or stabilities in the $n = 6$ and 7 size range that either dynamically or energetically does not favor these fragments.

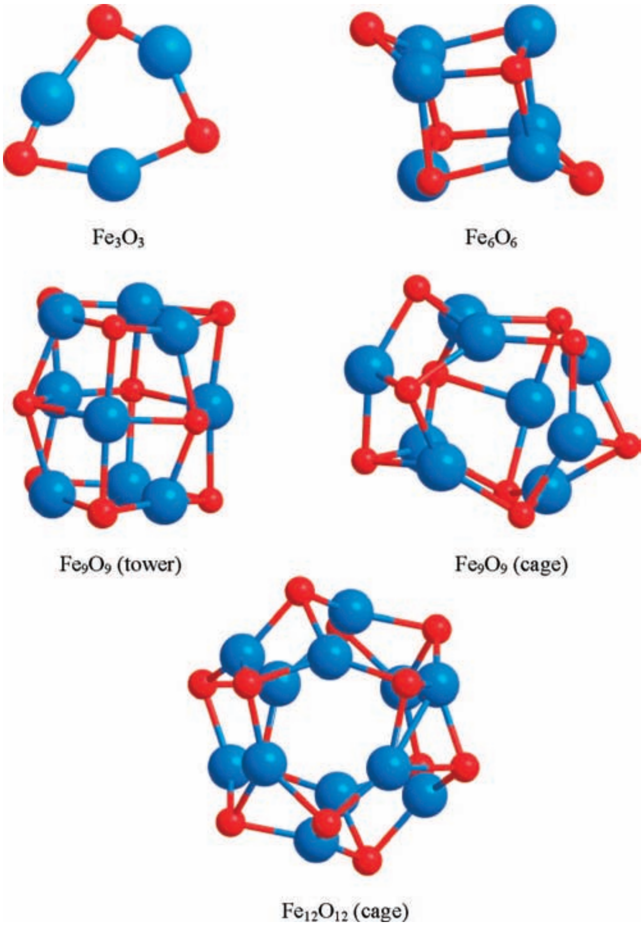

Figure 11. Structures of neutral Fe_nO_m clusters computed by Khanna and co-workers.[60]

Figures 6 and 7 show the fragmentation data for the $Fe_{9-10}O_m^+$ clusters. The $n = 9$ ions all prefer to fragment by losing 3−4 metal atoms and various numbers of oxygens. There are hardly any fragment masses close to the parent ions, but instead we find the $(FeO)_n^+$ fragments seen before, for n smaller than about 5−6. In the $n = 10$ group, the 10/11 and 10/12 species both produce many fragments close to the parent mass, with losses of both oxygen only and metal oxide neutrals. The 10/10 ion, however, behaves more like the $n = 9$ group, with no loss of small units. In the lower mass range, the smaller fragments for all the $n = 9$ and 10 species are again the $(FeO)_n^+$ species.

The photodissociation spectra of selected $n = 11-17$ clusters are shown in Figures 8–10. In some of these fragmentation spectra, particularly those in Figure 10, there are additional peaks to the side of the main parent ion depletion peaks. This is the result of a small amount of leakage by the mass gate of clusters with one more or less oxygen atoms than the desired cluster ion, because the gate cannot achieve perfect mass selection at these high masses. However, although the experiment is not perfect here, the fragments that result are primarily those from the desired parent ion because it is present in larger amounts than the adjacent masses. As shown, these systems exhibit extensive fragmentation with product ions at virtually every smaller n value. The masses near the 1:1 stoichiometries are seen throughout, but there is no other obvious pattern. There is an occasional example of elimination of the $[Fe_2O_3]$ species, as in the 11/11 → 9/8, 13/14 → 11/11 and 14/15 → 12/12 processes, but these are not extremely prominent. Beyond the extensive number of fragments, the most obvious aspect of these spectra is the increased width of the mass peaks, particularly in the $n = 6-10$ mass range. Because of this width, we cannot make definitive mass assignments in this region, but the masses are so close to the 1:1 stoichiometries that we have labeled them this way. It is tempting to conclude that these broad peaks are the result of the poorer mass resolution of our time-of-flight instrument at higher masses. However, this cannot be the case because we see sharper mass peaks for even higher mass ions, e.g., the 11/11 fragment from 13/14 or the 13/13 fragment from 15/17. The widths of the masses in the middle of the spectrum must therefore come from the dynamics of fragmentation. It is well-known in mass spectrometry, and especially in time-of-flight mass spectrometry, that the *rate* of fragment ion production is connected intimately with the acceleration rate out of the ion source. When these two rates are comparable, broadened or so-called "metastable" ion peaks can be observed.[78] Prompt fragmentation (faster than the acceleration time scale) leads to sharp peaks, whereas delayed fragmentation (slower than the acceleration) goes undetected. The behavior here is completely consistent with metastable ion fragmentation as the source of the broadened mass peaks.

The fragmentation behavior of these larger clusters is quite remarkable and warrants further discussion. First of all, the observation of so many photofragments here indicates either that there are many dissociation channels taking place in parallel or that there is a sequence of elimination steps proceeding all the way down to the small clusters. As discussed earlier, our power dependence studies suggest the latter sequential mechanism. The extent of fragmentation then suggests that many cluster bonds have been broken by photoexcitation. Khanna and co-workers have computed that the per atom binding energy of iron oxide neutral clusters is about 4−5 eV.[60] If we allow for molecular elimination of FeO (dissociation energy 4.18 eV),[42] as suggested by our data, then the energy per fragmentation event will be somewhat less than this. However, our laser photon energy at 355 nm is 3.49 eV. Therefore, production of small fragments like the 2/2, 3/3 and 4/4 from parent ions such as the $n = 17$ species here, must require the absorption of perhaps 10−15 photons. If we further consider that significant excess energy might be required to cause a dissociation rate within the 2−4 μs time period of the acceleration out of the reflectron region, then more energy and more photons would be required. Although multiple photon absorption is certainly possible in a system like this, the absorption of such an extreme number of photons seems unlikely. It is more likely that these clusters already contain a large amount of internal energy before they are excited, and that the photon energy adds to this to accomplish dissociation. Such internal energy is not unexpected from the growth of cluster oxides. Because the bond energies are high, the condensation processes in the cluster source heat the clusters internally, and this internal energy cannot be relaxed completely in the finite time available for collisions to occur with the rare gas atoms in the expansion out of the source.

These considerations can also provide some insight into the metastable peaks seen in the middle of the mass spectrum, as discussed above. It is tempting to conclude that those peaks where broadening occurs represent clusters that are more difficult to dissociate, and hence they fragment at a slower rate. However, if we consider that all the clusters have considerable internal energy, it is easy to see how dissociation would be fast initially, and then slow as the sequence of neutral elimination steps eventually cools the cluster by evaporation. The broadened mass peaks therefore most likely result at the cluster sizes when the combined influences of the internal energy present from cluster growth, the energy deposited by photoexcitation and the rate of cooling caused by fragmentation/evaporation bring the rate of fragmentation into the right time frame. The broadening here is then likely an accident of the energies and rates of dissociation rather than a result of special cluster stability at these intermediate sizes. Consistent with this, the per-atom binding energies calculated for the corresponding neutral iron oxide clusters are all about 4.5 eV, independent of cluster size in the range from $n = 2$ through $n = 12$.[60]

These data show conclusively that the most stable cation clusters throughout these measurements all have a 1:1 stoichiometry. This is true up to the cluster sizes with $n = 12-13$, which are the largest cluster masses observed as photofragments. We have also shown that the inferred neutral stoichiometry FeO occurs repeatedly, whereas Fe_2O_3 elimination is seen only occasionally. As in our previous work, we interpret the production of the stable species from a variety of parent ions and under different dissociation laser conditions (wavelength, power) to indicate the intrinsic relative stability of these clusters. Also consistent with this, some of these same stoichiometries are apparent as abundant species in the distribution of clusters which grew initially from the cluster source (e.g., 3,3; 11,11; 12,12; 13,13).

These patterns of cluster stability can be compared to previous experiments determining dissociation patterns,[35] reactivity studies[30] and neutral cluster distributions.[26,34] Schwarz and co-workers used collisional activated mass spectrometry to investigate the dissociation patterns of the small cation clusters where $m \leq 4$.[35] Their results showed inferred losses of FeO from the 1:1 clusters and losses of O_2 from the more oxygen rich clusters, consistent with the photodissociation patterns seen here for many different cluster sizes. The thermochemical data presented by Schwarz and co-workers for the smaller clusters suggest that the loss of FeO from Fe_3O_3 is ~20 kcal/mol lower in energy than the competitive channels of O_2 and FeO_2 elimination, and ~30 kcal/mol lower energy than the loss of atomic oxygen.[35] Castleman and co-workers have studied the reactivity of the small anion clusters (where $n = 1-2$) with CO,[30] where the most reactive clusters were determined to be the oxygen rich species. The small stable cluster 2/2 (identified here) was found to be less reactive than its oxygen rich counterparts. Additionally, Castleman reported the inferred loss of molecular oxygen from $Fe_2O_6^-$ producing $Fe_2O_4^-$, which subsequently lost FeO or FeO_2. We also see the loss of [O_2] from the corresponding cation, but we do not observe the loss of [FeO] until after two units of [O_2] are eliminated, leaving the 2/2 terminal ion. Lastly, we can compare our results with those of the photoionized neutral clusters reported by Bernstein and co-workers, where clusters were studied using the three different wavelengths, 355, 193, and 118 nm.[34] All three wavelengths show distributions where 1:1 species are the most intense features within the mass spectra. Although cross sections are not known for these species, the ionization potential has been determined using vacuum ultraviolet photoionization studies, by Leone and co-workers, to be approximately 8.56 eV for FeO.[43] Additionally Khanna and co-workers calculated the ionization potentials to be approximately 7.5 eV for each $n = m$ cluster, where $n = 2-6$.[60] These IPs indicate that multiphoton conditions are required to detect the neutral clusters using 193 and 355 nm photoionization. However, VUV photoionization at 118 nm has the best chance to ionize clusters without fragmentation, and thus may be able to detect the most abundant neutral species formed. These studies also showed that the most abundant clusters detected were those with the 1:1 stoichiometry.[34] However, photoionization with VUV could also be detecting those clusters that are easier to ionize as opposed to those that are the most stable. This possible bias in the photoionization measurements makes it impossible at present to resolve the issue of cation versus neutral stabilities.

Several groups have performed theoretical calculations on the anion and neutral iron–oxide species to determine the most stable geometries for the clusters where $n = 1-6$.[30,35,44,46,60,66] Castleman and co-workers have also performed DFT calculations on the smallest cation clusters, FeO_m^+ (where $m = 1-3$).[30] Khanna and co-workers have predicted structures for the neutral clusters that are shown in Figure 11.[60] Khanna's results also showed that clusters with the 1:1 stoichiometry were more stable than their more oxygen rich counterparts. Ring structures were found to be the most stable for clusters in the size range of $n = 2-5$. A further result of this work was the prediction that the $n = m$ species for 6/6–12/12 clusters are combinations of smaller rings in cages and tower structures, with weaker ring–ring bonding, such as those shown in Figure 11. Although our data support the stability of the 1:1 stoichiometries, we do not find any evidence suggesting that the larger clusters are formed from aggregated small cluster rings. For example, Khanna reported that the binding energy between the rings in the 9/9 cluster (3.45 eV) is less than the bond energy per atom (4.49 eV). If 9/9 were composed of three stacked rings of 3/3, we would expect to see the bonds between the rings breaking first, leaving the 6/6 and 3/3 as prominent fragments. The 3/3 is the most abundant peak in the dissociation spectrum of 9/9, but 6/6 is hardly seen at all. Instead, we see other more intense fragments (5/5, 4/4 and 2/2) with the 1:1 stoichiometry, leading to the conclusion that it is unlikely that the 9/9 is composed of stacked 3/3 rings.

It is also instructive to consider the predicted magnetism of those clusters which are found to be the most stable throughout our data. The theoretical magnetism of neutral Fe_nO_m clusters has been investigated using DFT.[66] The alignment of the magnetic moments on iron, for the $n = m$ clusters (where $n = 2-4$), changed from a ferromagnetic to antiferromagnetic arrangement with an increasing number of oxygen atoms.[66] This suggests that these small 1:1 clusters are antiferromagnetic like the bulk solid.

The stoichiometries and structures seen here for the clusters suggest what the likely oxidation states of the metal atoms are. Theoretical structures have only been calculated for the cations containing a single metal.[30] However, it is safe to assume that the structures for the cations are the same as those for the neutrals, because all small anions, neutral and cations that have been studied have the same qualitative structures.[29,33,40,41,53,59] The $Fe_2O_2^+$ cation would then have a ring structure with equivalent iron atoms, and an effective +2.5 oxidation state. This trend can be carried through all of the 1:1 clusters, where the overall oxidation state becomes closer to +2 as the cluster size increases. For example, the 7/7 cluster would have an effective oxidation state of +2.14 and that for 12/12 would be +2.08. This trend was also noted by Schwarz and co-workers in the small cation clusters,[35] and by Wang and co-workers for the small neutral clusters.[46] This +2 oxidation state for these small clusters is then the same as in bulk FeO (wüstite), but in contrast to the more common +3 oxidation state for hematite, Fe_2O_3, and the mixture of +2 and +3 in magnetite, Fe_3O_4.[1–3] As we have shown in our recent study of yttrium and lanthanum oxide clusters, clusters of the form $MO^+(M_2O_3)_n$ are the most likely cations that form for metals in the +3 oxidation state.[31d] However, there is no evidence at all for this stoichiometry here.

Conclusions

Iron oxide cluster cations produced by laser vaporization have been investigated with time-of-flight mass spectrometry and mass-selected photodissociation. A limited number of oxide stoichiometries are observed at each cluster size with a specific number of metal atoms. Photodissociation of these clusters is only possible via multiple photon excitation, consistent with strong metal oxide bonding. Dissociation produces the $(FeO)_n^+$ cation clusters repeatedly from many different parent ions. The dissociation mechanism seems to involve the loss of excess oxygen from any clusters having more than the 1:1 metal:oxygen ratio and then proceeds by successive elimination of FeO. Multiple steps of FeO elimination occur, producing small fragments even from large cluster ions. This is possible because these clusters contain significant internal energy from their condensation that adds to the photoexcitation. The oxidation state implied by these data is +2, as in FeO, with little evidence for the +3 state. Further theoretical investigations of the cation cluster structures and their magnetic properties would be useful.

The wüstite bulk FeO phase has applications for semiconductor materials. However, this phase is usually only stable at temperatures above 560 °C. If the stable 1:1 clusters found here could be isolated, perhaps via ligand coating methods,[15] it is conceivable that low temperature semiconductor phases could be produced. Likewise, $(FeO)_n^+$ particles have unfulfilled bonding capacity, and these systems may have interesting chemical and/or catalytic properties.

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