Metal Ion Chemistry in Clusters Initiated by Ionization/Dissociation of Organometallic Precursors

S. Bililign,[†] L. Liu, C. S. Feigerle, and John C. Miller*

Chemical and Biological Physics Section, Oak Ridge National Laboratory, PO Box 20008, Oak Ridge, Tennessee 37831, and Department of Chemistry, University of Tennessee, Knoxville, Tennessee 37996

Received: February 6, 1997; In Final Form: April 16, 1997[⊗]

A novel method is described for the initiation and observation of metal ion−molecule reactions in clusters. A heterocluster composed of organometallic molecules and reactant species is formed by coexpansion in a supersonic jet. Photoionization of the precursor molecules by a picosecond, 266 nm laser pulse efficiently strips away the ligands, leaving metal ions and metal cluster ions in close proximity to reactant molecules. Subsequent ion−molecule reactions take place which are followed by monitoring the products by time-of-flight mass spectrometry. Using iron pentacarbonyl as an example, the formation of metal ions and cluster ions is demonstrated, and their reaction with nitric oxide and nitrous oxide is described.

Introduction

The study of the reactions of metal atoms and ions is as old as the field of chemistry itself. Metals constitute one of the fundamental building materials for our society, and the properties and reactions of metals are of prime importance. Chemical reactions involving metals can both degrade the materials of interest (oxidation, corrosion) and allow the synthesis of new materials with desirable properties. Alternately, metals, in their role as catalysts, can enhance the creation of other useful substances. While a great deal has been learned about the chemistry of metals through study of their bulk reactions in solution or in the gas, liquid, or solid phase, modern molecular beam techniques, which afford a glimpse of the reaction of individual atoms and molecules under single-collision conditions, hold the best promise for detailed understanding of their chemical behavior.[1,2]

In the past decade molecular beam based studies have been extended to discrete clusters of metal atoms or ions.[3,4] Ranging in size from dimers to assemblies of thousands of atoms, metal-containing clusters can be generated and characterized using an array of modern techniques, often involving lasers and mass spectrometry. Measurement of cluster properties as a function of size has been of particular interest due to the potential for these studies to improve understanding of how physical and electronic properties evolve as particles grow from atoms through finite clusters to the bulk solid. More recently, the chemistry of clusters has become a growing area of study with the recognition that size-dependent rates may produce unique chemical pathways or products. The economic importance of transition metal catalysts makes clusters containing these metals and their chemistry a prime subject for such investigations.

Several techniques are currently in use for the study of ion−molecule reactions of metallic cluster ions. In a recent review, Parent and Anderson[5] describe three categories of such experiments: high-pressure flow techniques, Fourier transform ion cyclotron resonance mass spectrometry, and high- and low-energy ion beam methods. The most common way to create the cluster ions is by some variation of a laser ablation source popularized by the early work of Smalley and his group.[6] If a metal is ablated into a supersonic expansion of a carrier gas, the resultant cooling enhances the cluster formation and stability. Following formation (and sometimes size selection), the cluster ions may be reacted with another species in subsequent collisions on a time scale ranging up to milliseconds. Product detection almost always utilizes some form of mass spectrometry. A potpourri of recent, representative studies of iron cluster chemistry is given in ref 7.

In the present paper we describe a very general method for the production and reaction of metal ions and cluster ions within a single cluster in a collisionless environment. Beginning with a neutral heterocluster containing an organometallic precursor and the reactant molecules of interest, a high-power, picosecond laser is used to ionize the precursor molecule. In all the cases described here, the metal atom source is iron pentacarbonyl, $Fe(CO)_5$. Numerous studies have shown that multiphoton ionization (MPI) of this molecule in the ultraviolet results in partial or complete removal of the labile carbonyl ligands, leaving bare metal ions. If several precursor molecules are present in a cluster, the ionization/dissociation process can result in iron cluster ions, Fe_n^+. These ions may also be formed in electronic excited states if excess photons are absorbed. At this point, unlike other techniques, no collision is required for ion−molecule chemistry to begin. The desired reaction partners are already present in the heterocluster and available for reaction with the newborn ion. The resultant product ions are then identified by mass spectrometry. Two groups have previously reported similar studies, also using iron pentacarbonyl as a metal atom source.[8,9] Similar laser-induced chemical reactions involving nonmetallic molecules have been previously studied in our laboratory.[10,11]

Experimental Section

The experimental apparatus has been described previously,[10−12] and a schematic may be found elsewhere.[12]

Briefly, the isentropic core of a pulsed supersonic expansion is selected by a skimmer and intersected at 90° with a focused laser beam. The mass-to-charge ratios of the ions that are formed are analyzed using a linear time-of-flight mass spectrometer. The pulsed valve is commercially available (R. M. Jordon Co.). A 0.5 mm nozzle aperture diameter and backing pressures of several atmospheres were typically used in these experiments. The nozzle-to-ionization-region distance is adjust-

---

* Author for correspondence.

[†] Also at Physics Department, North Carolina A&T State University, 1601 East Market St., Greensboro, NC 27411.

[⊗] Abstract published in *Advance ACS Abstracts,* June 1, 1997.

S1089-5639(97)00476-3 CCC: $14.00

able from 10 to 17 cm, whereas the 1 or 2 mm diameter skimmer (Beam Dynamics) is fixed at 7.5 cm from the interaction region. Gas pulse durations range from 70 to 100 μs depending on the carrier gas.

The laser beam is focused with a 75 mm focal length lens into the jet in the region between the extraction plates of a time-of-flight (TOF) mass spectrometer. The spectrometer is of the design introduced by Wiley and McLaren and has a mass resolution ($m/\Delta m$) of about 300 in the range 1−2500 amu. A dual channel-plate electron multiplier is used to detect the photoions. The field-free region of the flight tube is approximately 0.75 m long and incorporates steering electrodes to counter the cluster kinetic energy perpendicular to the TOF axis. The nozzle, TOF assembly, and focusing lens are mounted within an 8 in. six-way cross and pumped to 10^{-7} Torr with a 6 in. liquid N_2 trapped, diffusion pump. Additionally, the TOF region is differentially pumped with a 200 L/s turbopump.

The laser system consists of an Nd:YAG laser (Quantel YG571C) which delivers 75 mJ in a 30 ps pulse (mode-locked operation) at the 1064 nm fundamental wavelength. The second, third, or fourth harmonic (532, 355, or 266 nm) of the 1064 nm output also is available. The peak power as a function of wavelength is calculated to be approximately 214, 71, and 28 TW/cm^2 for the 532, 355, and 266 nm outputs of the Nd:YAG laser in the picosecond mode. These calculations assume a Gaussian, diffraction-limited beam and perfect focusing optics. The actual peak powers are unknown, but are probably about 1 order of magnitude less.

The laser is operated at a 10 Hz repetition rate, and the opening of the nozzle aperture is triggered by a signal from the laser. The laser pulse is incident on the early edge of the gas jet in order to optimize cluster detection. After each laser pulse a distribution of masses is detected by the TOF mass spectrometer, and the mass spectrum is recorded with a digital oscilloscope (Tektronix 11402). The signal-to-noise ratio was improved by averaging spectra from about 4000 consecutive laser shots. A baseline subtraction procedure was applied in order to mitigate a sloping background due to saturation of the very large Fe^+ signal.

The initial heteroclusters are formed by mixing the iron pentacarbonyl with the intended reaction partner in an argon or methane carrier gas. Liquid $Fe(CO)_5$ is initially degassed by one or two freeze−pump−thaw cycles, and the vapor at its equilibrium vapor pressure (30 Torr) is expanded into a 1 L stainless steel mixing chamber. A nearly equal amount of reactant gas is used and sufficient carrier gas added to yield a total backing pressure of about 100 psi.

Results and Discussion

A. Generation of Iron and Iron Cluster Ions. It is well-known that multiphoton ionization of $Fe(CO)_5$ at visible and ultraviolet wavelengths results in the efficient stripping of the CO ligands and the production of bare metal ions. Since the first studies in the late 1970s,[13−15] many investigators[16] have explored the interaction of focussed lasers with metal carbonyl and other organometallic molecules to produce bare metal atoms for uses such as metal lasers[13] or metallic thin films.[17] A number of these studies have been examined by Gedanken et al.,[18] and the competition between multiphoton ionization and neutral photodissociation has been systematized. It is generally agreed that, at least at low laser power, metal carbonyl molecules undergo neutral dissociation followed by multiphoton ionization of the resulting metal atom. A few studies, however, indicate that, at the high peak powers resulting from tightly focused, high-powered or short-pulse length lasers, ionization can proceed first, either nonresonantly or via normally dissociative states of the organometallic molecule,[19−21] followed by ion fragmentation. Previous studies from this lab indicate that ionization can successfully compete with dissociation using tightly focused nanosecond[22] or picosecond lasers.[23]

The ionization/dissociation of clusters of iron pentacarbonyl is not as well characterized as that of the monomer. In the only previous studies, Duncan, Dietz and Smalley,[24] and later Wheeler and Duncan,[8] report the synthesis of metal nanocrystals by the MPI of $[Fe(CO)_5]_m$ clusters. In the former case, these clusters were formed by expansion of a 0.2% mixture of metal carbonyl in 15 atm of helium. In their experiments, use of an argon fluoride laser at 193 nm resulted in the generation of large numbers of Fe^+ and $Fe(CO)_2{}^+$ ions followed by a progression of peaks in the mass spectrum spaced by 56 amu, which the authors attribute to $Fe_n{}^+$ clusters. Another series of less intense peaks are found interspaced between the $Fe_n{}^+$ masses and are assigned to $Fe_m(CO)_n{}^+$ species where n is odd. Because the mass of the major isotope of iron and that of two carbon monoxide molecules is 56 amu, it is not possible by low-resolution mass spectrometry to distinguish $Fe_m(CO)_n{}^+$ molecules from $Fe_{m-1}(CO)_{n+2}{}^+$ or $Fe_{m+1}(CO)_{n-2}{}^+$, although one can specify whether the number of CO molecules is odd or even. Duncan et al.[24] argue that the odd-n clusters peaks are weak, and there is no reason to expect the corresponding even-n species to be more intense than the odd ones. They therefore conclude that the major series of intense peaks is dominated by $Fe_m{}^+$ ions rather than $Fe_m(CO)_n{}^+$ (n = even) ions. Although this argument is not ironclad, the assignment of the main series to bare iron cluster ions is further supported by the present investigations based on the chemical reaction products observed and, to a lesser extent, on isotope distributions. Using a weaker 266 nm Nd:YAG laser than is utilized in the present study, the same authors were unable to observe any cluster ion formation following MPI under otherwise similar experimental conditions. In the latter study by Wheeler and Duncan,[8] novel two-color experiments showed that aggregation and dissociation of the iron pentacarbonyl preceded ionization. To our knowledge, only one subsequent study of iron pentacarbonyl in a cluster environment has been published, and no iron cluster ions were reported in that study.[9] In both refs 8 and 9 some chemical reaction products of the iron atoms or clusters with other species in the cluster were also observed.

In the present study, MPI at 266 nm of $Fe(CO)_5$ coexpanded with methane (or with mixtures of argon and another reactant molecule of interest) produces iron ions and iron cluster ions in a distribution similar to that observed by Duncan et al.[8,24] using a 193 nm laser. Mass spectra following MPI of iron pentacarbonyl expanded in pure argon are qualitatively different ($Fe_mAr_n{}^+$ ions are observed) and will be described elsewhere.[25] Figure 1 shows a portion of the mass spectrum recorded following the 266 nm ionization of a supersonic expansion of a mixture of 30 Torr of iron pentacarbonyl with about 70 psi of methane. A series of 18 peaks spaced by 28 amu are observed (not all shown in the figure), beginning with a very large peak due to Fe^+ at 56 amu. Smaller peaks at 54, 57, and 58 amu are attributed to the other naturally occurring isotopes of iron. When care is taken to eliminate saturation, which can easily occur in signals of the major isotope of Fe^+, the intensities of the peaks are in the same ratio as the abundance of Fe isotopes in nature (91.72% ^{56}Fe, 5.8% ^{54}Fe, 2.2% ^{57}Fe, and 0.28% ^{58}Fe). In the low-mass portion of the spectrum, small peaks at 1, 2, 12, 13, 14, 15, 16, and 28 amu are easily assigned to H, H_2, C, CH, CH_2, CH_3, CH_4, and CO ions. $Fe(CH_4)^+$ is also observed as a peak at 72 amu. At higher backing pressures larger iron/methane clusters are seen and will be discussed elsewhere.[25] Like Duncan et al.,[8,24] we sort the remaining peaks

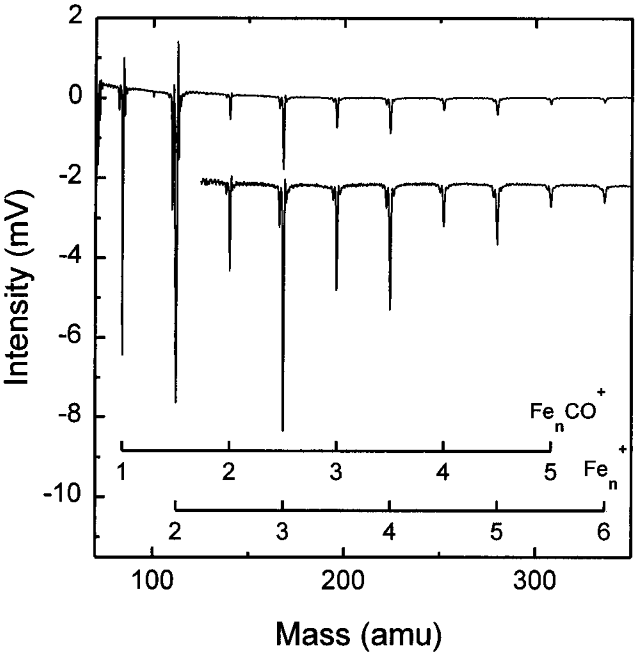

Figure 1. A portion of the laser ionization mass spectrum of an $Fe(CO)_5/CH_4$ expansion mixture. Two extended cluster series assigned as Fe_n^+ and Fe_nCO^+ are marked in the figure.

into two series identified as $Fe_m(CO)_{n,\mathrm{even}}$ and $Fe_m(CO)_{n,\mathrm{odd}}$. The former peaks are further assigned as primarily Fe_n^+ and the latter as primarily Fe_nCO^+, although each peak may also contain contributions from the other possible ions having the same mass. The major difference between the present spectrum and that of Duncan et al.[8,24] is the relative intensity of the two series. In Figure 1 they are of comparable magnitude, whereas in the previous work the "odd-n" series is considerably weaker.

The assignment of the mass spectral peaks to iron cluster ions, and to iron cluster ions with a single CO ligand, is based on several arguments. First, the similarity with the previously published spectrum of Duncan et al.[8,24] suggests starting with their assignment. Their original argument would be less convincing based on the present data as the relative intensity of the two series is so similar. However, a similar assignment can be argued based on other factors. First, several previous MPI mass spectrometric studies[15,21,24] of iron pentacarbonyl monomers also report that the major ions observed are Fe^+, $FeCO^+$, and $Fe(CO)_2^+$, which lends credence to the supposition that similar processes in clusters of iron pentacarbonyl would yield primarily iron cluster ions and ions with small numbers of CO ligands attached. Second, the ratios of the measured intensities of peaks split due to the presence of the various iron isotopes are in reasonable agreement with those predicted from the natural abundances. For example, the ratio measured for the intensity of the peaks at 138 and 140 amu is 0.13, which agrees well with that expected for Fe_2CO^+ (predicted ratio of $^{54}Fe^{56}FeCO^+$ to $^{56}Fe_2CO^+$ is 0.126) but is inconsistent with $Fe(CO)_3^+$ (predicted ratio of $^{54}Fe(CO)_3^+$ to $^{56}Fe(CO)_3^+$ is 0.063). Similarly, the measured intensity ratio between masses 166 and 168 is 0.16, which is closer to the 0.190 predicted for Fe_3^+ than the 0.126 expected for $Fe_2(CO)_2^+$. The intensity ratio between ions containing all ^{56}Fe and the chemically equivalent ion with one ^{54}Fe substituted tends to increase with n as expected for both the Fe_n^+ and Fe_nCO^+ series; however, the errors in the measured isotopic ratios increase rapidly due to the weakening intensity for the larger clusters and degrading resolution. In the next section we will offer additional arguments based on chemical reaction products which also support the assignments given above.

The mechanism for the production of Fe^+ ions in the cluster environment is presumably similar to that of the isolated monomer, as discussed above. That is, depending on the laser power, the ions could be formed by decarbonylation of the neutral followed by MPI of the bare metal atom or, at higher laser power, ionization followed by dissociation (or, of course, a mixture of the two). The cluster environment probably has little influence on the process,[9] leading to the same two possibilities for iron clusters. Decarbonylation before ionization would simply lead to a locally high concentration of iron atoms which, exceeding the equilibrium vapor pressure, would condense. Such homonuclear nucleation has been investigated in shock-heated iron pentacarbonyl by Bauer and co-workers.[26] Alternately, if ionization occurs first, then dissociation and condensation could occur via the ionized clusters. However, in a cluster environment a third possibility exists. A cycle of ion–molecule condensation within the cluster followed by further decarbonylation is plausible based on previous observations of such reactions. Ion cyclotron resonance experiments[27,28] have characterized reactions such as $Fe^+ + Fe(CO)_5 = Fe_2(CO)_4^+ + CO$ and $Fe(CO)_n^+ + Fe(CO)_5 = Fe_2(CO)_m + (5 + n - m)CO$. Repeated cycles of similar reactions produce cluster ions up to $Fe_6(CO)_{18}^+$. Analogous reactions involving negative ions have also been studied.[29] Similarly, in several MPI experiments at high source pressures similar reactions have been characterized or postulated.[21,30] In the intense laser field of the present experiments, species such as $Fe_m(CO)_n^+$ would be expected to continue to lose ligands until the bare metal cluster is formed.

On the basis of the present data, it is not possible to differentiate these mechanisms. Wheeler and Duncan[8] have shown that, at least in their experiments, a major pathway is neutral dissociation followed by ionization. In contrast, Whetten et al.[21] have shown that the ion–molecule mechanism is active in their (noncluster) experiments. For the present results, taken at the highest laser powers yet, it seems reasonable to expect some combination of all possible mechanisms. Two previous studies from this lab involving nonmetallic clusters have implicated similar ion–molecule polymerization.[10,11] However, for the purposes of cluster reaction studies of Fe^+ and Fe_n^+ ions, the details of the formation mechanism are of secondary interest.

B. Ligand-Exchange and Other Ion–Molecule Reactions Involving Nitric Oxide. With a ready source of Fe and Fe_n neutrals and ions in a cluster environment as described above, it is a straightforward to dope the cluster with a reactant molecule and observe any resulting chemical reactions by the appearance of new ions in the mass spectrum. Figure 2 shows the results of such an experiment where 30 Torr of $Fe(CO)_5$ is combined with 100 psi of a 1% NO/Ar mixture and coexpanded into the mass spectrometer source region. Chemical reactions are initiated as before by two-photon ionization/dissociation of the iron pentacarbonyl.

The spectrum is qualitatively similar to that shown in Figure 1; that is, a series of about 20 peaks spaced by 28 amu (not all shown in the figure) are observed, starting from the Fe^+ mass. However, in the present spectrum every other peak is split into a doublet spaced by 2 amu. The lower mass peak of the pair is again assigned to Fe_nCO^+ clusters, whereas the new peak is easily identified as Fe_nNO^+. Peaks previously described as Fe_n^+ clusters do not show development of any new peaks 2 amu away. These observations not only demonstrate a well-known class of organometallic ligand-exchange reactions but serve to substantially bolster the assignments given in the previous section.

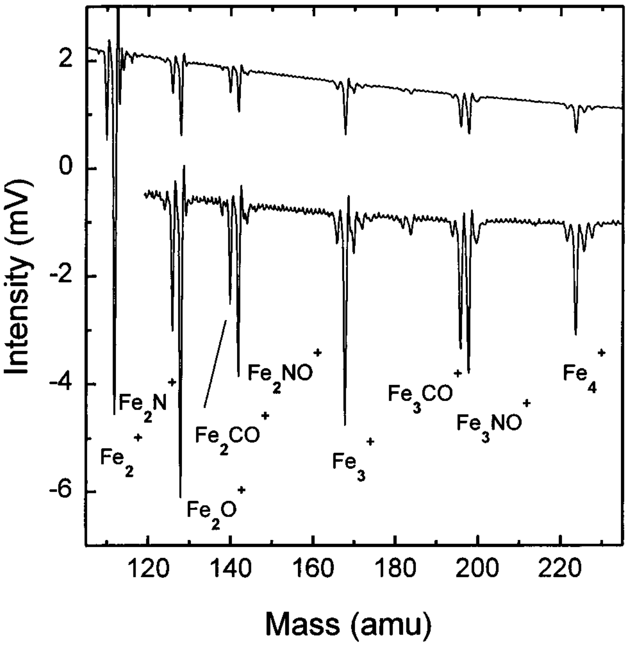

Figure 2. A portion of the laser ionization mass spectrum of a Fe(CO)$_5$/NO/Ar expansion mixture. The spectrum shows ligand exchange of NO for CO in peaks assigned as Fe$_n$CO in the spectrum of Figure 1.

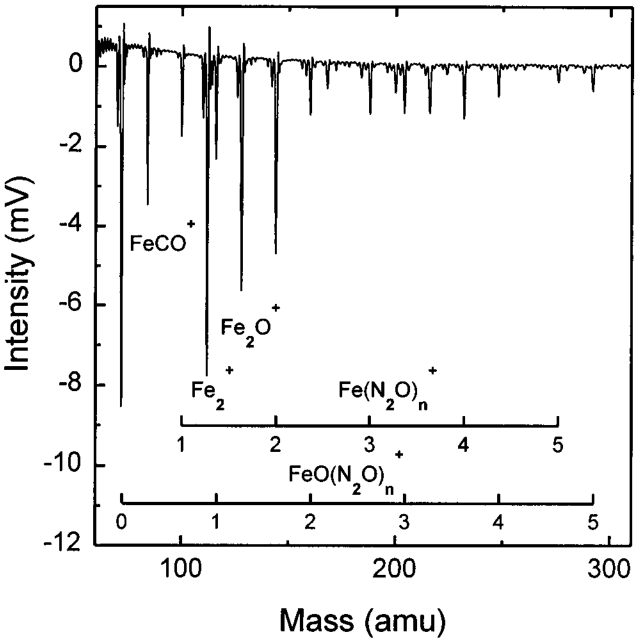

Figure 3. A portion of the laser ionization mass spectrum of an Fe(CO)$_5$/N$_2$O/CH$_4$ expansion mixture. The assignment given in the figure for some of the peaks is not unique, and further discussion of the assignments may be found in the text.

Foster and Beachamp[27] have previously studied the gas-phase ion chemistry of iron pentacarbonyl by ion cyclotron resonance spectroscopy. In particular, they studied ligand displacement reactions between Fe(CO)$_n^+$ with both σ- and π-bonding ligands. Nitric oxide was the most strongly π-accepting ligand studied, and they observed the "facile, sequential replacement of the CO groups in Fe(CO)$_n^+$" with up to three NO molecules. That is, for FeCO$^+$, Fe(CO)$_2^+$, and Fe(CO)$_3^+$ ions, one, two, or three CO ligands were replaced by NO molecules. Three, however, is the maximum number of displacements; for Fe(CO)$_4^+$ only up to three NO's react, and for Fe(CO)$_5^+$ the replacement of only one NO molecule is observed. These results, when applied to the possible peak assignment in Figure 2, substantially confirm the identifications given in the previous section. For instance, all of the peaks assigned as pure iron clusters, Fe$_n^+$, remain as single peaks after reaction with NO. If the Fe$_2^+$ peak at 112 amu contained a major contribution from Fe(CO)$_2^+$, we would expect to see new peaks at 114 and 116 amu, corresponding to FeCONO$^+$ and Fe(NO)$_2^+$. In light of the results of Foster and Beachamp,[27] the absence of extra peaks is strong evidence that those masses correspond to completely decarbonylated iron clusters. Similarly, for the peaks assigned as iron clusters with a single CO ligand, the appearance of one and only one NO substitution is strong evidence for the proposed assignment. The reaction with nitric oxide thus serves as a sort of titration, yielding an estimate of the numbers of carbon monoxide ligands in the cluster.

Again, discussion of the mechanism of the formation of Fe$_n$NO$^+$ species is clouded by the possibility that the ligand exchange reaction could occur in either the neutral iron pentacarbonyl molecule or via ion−molecule chemistry as discussed above. However, the observation of large numbers of ions in the undoped experiments lead us to prefer a sequential mechanism where ionization and ligand-stripping occur first, followed by ion−molecule reactions similar to those observed in previous ICR experiments.

Inspection of Figure 2 reveals several other peaks that must be the product of chemical reactions occurring within the cluster. In particular, the ions corresponding to Fe$_n$N$^+$ and Fe$_n$O$^+$ are observed for $n = 1$, 2 and 3. The peaks for $n = 2$ are especially prominent. Although not labeled in the figure, the $n = 3$ peaks are readily apparent at mass 182 and 184 amu. The previous ICR studies of Beachamp involving NO reactions with various Fe(CO)$_n^+$ species did not mention any other ion−molecule reaction products, and no such reactions are reported in the literature to our knowledge. Likewise, reactions that could account for these species via neutral channels are not known. It is possible that, in our rather high-peak power ionization environment, electronically excited cluster ions are produced which lead to these products. However, it seems most probable that these ions are the product of reactions with N$_2$O or NO$_2$ molecules, which are present as impurities in most nitric oxide samples. Alternately, Poth *et al.*[31] have argued that N$_2$O molecules are formed from intracluster reactions within nitric oxide clusters. The ion−molecule reactions Fe$^+$ + N$_2$O = FeO$^+$ + N$_2$ and Fe$^+$ + NO$_2$ = FeO$^+$ + NO are well-known, as will be discussed in the next section. Fe$_n$O$_x$ products from iron cluster reactions with O$_2$ are also well-documented. It also may be possible that the iron dimer reaction with NO is facilitated by the cluster environment. In similar experiments on Mo(CO)$_6$ clusters, Peifer and Garvey[32] have observed the formation of MoO$^+$ and MoO$_2^+$ species. Also, Wheeler and Duncan[8] observe Fe$_n$O$^+$ and Fe$_n$O$_2^+$ when coexpanding iron pentacarbonyl with oxygen and photoionizing the mixture.

Although species like FeN or FeO and their ions are reasonably well-studied, the Fe$_n$NO$^+$ molecules are not well-known. They have only recently been observed in matrix isolation experiments where some calculations were performed to aid in the assignments.[33,34]

C. Reactions with N$_2$O. A number of experiments were performed by mixing iron pentacarbonyl and nitrous oxide in various concentration ratios. In some cases argon or methane was additionally added as a carrier gas. Figure 3 shows the results of laser photoionization/dissociation of about 30 Torr of Fe(CO)$_5$ mixed with equal parts of N$_2$O in a methane carrier at a total backing pressure of about 110 psi. A very rich spectrum is obtained which at higher mass develops into two cluster series separated by 16 amu (not all shown in the figure). The two series each comprise about 16 peaks spaced by 44 amu, which is the mass of a nitrous oxide molecule. The two series differ by the mass of an oxygen atom. The simplest assignment for these two series is $Fe(N_2O)_n^+$ and $FeO(N_2O)_n^+$ as shown in the figure; however, these identifications are complicated by the possibility of oxidation of iron clusters to yield $Fe_xO_y(N_2O)_n^+$ species. Because the mass of FeO_2 (88 amu) is equal to that of $(N_2O)_2$, it is impossible to distinguish highly oxidized iron clusters from small iron and iron oxide molecules solvated by nitrous oxide molecules. For instance, the peak at 144 amu could be assigned as either $Fe(N_2O)_2^+$ or $Fe_2O_2^+$, and the peak at 160 amu could be either $FeO(N_2O)_2^+$ or $Fe_2O_3^+$. Most likely, each peak contains contributions from both possible species. Additional studies with differing concentrations or using different reaction partners would be necessary to resolve this ambiguity. Alternately, isotopically substituted nitrous oxide would provide mass separation of the different species. Such experiments are planned for the future. The following discussion will consider each mechanism separately.

In the limit of small amounts of iron pentacarbonyl where the formation of iron clusters would be inhibited, the observed reaction products can again be rationalized by considering a two-step process. In the first, the iron pentacarbonyl (which is "solvated" by the surrounding nitrous oxide molecules) is photoionized and stripped of the CO ligands. The resulting Fe^+ ion is then available for facile ion−molecule reaction with the neighboring N_2O molecules. The reaction $Fe^+ + N_2O = FeO^+ + N_2$ was first characterized by Kappes and Staley[35] by ICR spectroscopy and more recently by Bohme and co-workers[36,37] using the selected ion flow tube (SIFT) technique. In the latter studies, species like $FeO(N_2O)_n^+$ with n up to 3 were observed. In their experiments, sequential ion−molecule reactions occurred in subsequent collisional encounters. In the present experiments, the cluster environment allows such reactions to occur within a single cluster in a collisionless regime. An interesting difference between the two sets of results is the observation in the SIFT results of an upper limit of $n = 3$. Those authors postulated that the three nitrous oxide molecules were arranged in a C_{3v} symmetry which would saturate the bonding capability of the iron and prevent further reaction. In the present results, no magic number is observed for $n = 3$, and clusters are observed with monotonically decreasing intensity up to $n = 20$.

When extensive clustering of the iron is present, oxidation of Fe neutral or ion clusters by N_2O would appear to be a reasonable alternative. The oxidized iron cluster ions could then undergo condensation reactions with nitrous oxide in the cluster to form $Fe_xO_y(N_2O)_n^+$, in much the same way as $FeO(N_2O)_n^+$ are formed from reaction of FeO^+ and N_2O in the SIFT experiments. Unfortunately, there is little guidance for this in the literature. Although a number of studies[38−42] have mapped the reactions of both neutral and ionized iron clusters with oxygen, no one, to our knowledge, has observed similar reactions involving N_2O. Our molecular beam is known to include large iron clusters as was shown in Figure 1, and the studies of others[38−42] indicate that extensive oxidation from even trace amounts of oxygen is to be expected. It is certainly reasonable to anticipate similar oxidation reactions involving N_2O. Large amounts of Fe_2O^+ are observed in our mass spectrum, which suggests that this pathway may be of importance. Future experiments are planned to further elucidate the details of the $Fe(CO)_5/N_2O$ reactions.

Acknowledgment. Research is sponsored by the office of Health and Environmental Research, U.S. Department of Energy, under Contract DE-AC05-96OR22464 with Lockheed Martin Energy Research Corp. J.C.M. acknowledges the use of a NATO International Collaboration Grant (CRG 950660) during the course of this work and helpful discussions with M. Velegrakis and S. Georgiou. S.B. acknowledges support, in part, by an appointment to the Nuclear Regulatory Commission's Historically Black Colleges and Universities Faculty Research Participation Program administered by the Oak Ridge Institute of Science and Education through a cooperative agreement between the U.S. Department of Energy and the U.S. Nuclear Regulatory Commission. Exploratory experiments by M. Z. Martin are also acknowledged.

References and Notes

(1) Eller, K.; Schwarz, H. *Chem. Rev.* **1991**, *91*, 1121.

(2) Freiser, B. *J. Mass Spectrom.* **1996**, *31*, 703.

(3) Castleman, Jr., A. W.; Keese, R. G. *Chem. Rev.* **1986**, *86*, 589.

(4) Märk, T. D. *Int. J. Mass Spectrom. Ion Processes* **1987**, *79*, 1.

(5) Parent, D. C.; Anderson, S. L. *Chem. Rev.* **1992**, *92*, 1541.

(6) Dietz, T. G.; Duncan, M. A.; Powers, D. E.; Smalley, R. E. *J. Chem. Phys.* **1981**, *74*, 6511.

(7) Andersson, M.; Persson, J. L.; Rosén, A. *J. Phys. Chem.* **1996**, *100*, 12222. Wang, L.-S.; Wu, H.; Desai, S. *Phys. Rev. Lett.* **1996**, *76*, 4853. Gehret, O.; Irion, M. P. *Chem. Phys. Lett.* **1996**, *254*, 379. Conceição, J.; Loh, S. K.; Lian, L.; Armentrout, P. B. *J. Chem. Phys.* **1996**, *104*, 3976.

(8) Wheeler, R. J.; Duncan, M. A. *J. Phys. Chem.* **1986**, *90*, 3876.

(9) Lyktey, M. Y. M.; Xia, P.; Garvey, J. F. *Chem. Phys. Lett.* **1995**, *238*, 54.

(10) Desai, S. R.; Feigerle, C. S.; Miller, J. C. *J. Phys. Chem.* **1995**, *99*, 1786.

(11) Martin, M. Z.; Desai, S. R.; Feigerle, C. S.; Miller, J. C. *J. Phys. Chem.* **1996**, *100*, 8170.

(12) Desai, S. R.; Feigerle, C. S.; Miller, J. C. *J. Chem. Phys.* **1992**, *97*, 1793; **1994**, *101*, 4526.

(13) Trainor, D. W.; Mani, S. A. *J. Chem. Phys.* **1978**, *68*, 5481.

(14) Karney, Z.; Naaman, R.; Zare, R. N. *Chem. Phys. Lett.* **1978**, *59*, 33.

(15) Duncan, M. A.; Dietz, T. G.; Smalley, R. E. *Chem. Phys. Lett.* **1979**, *44*, 415.

(16) For more recent studies see: Lee, K.; Goo, J. S.; Ku, J. K. *Chem. Phys. Lett.* **1995**, *244*, 213 and references therein.

(17) Xu, X.; Steinfeld, J. I. *Appl. Surf. Sci.* **1990**, *45*, 281.

(18) Gedanken, A.; Robin, M. B.; Keubler, N. A. *J. Phys. Chem.* **1982**, *86*, 4096.

(19) Leutwyler, S.; Even, U.; Jortner, J. *Chem. Phys.* **1981**, *58*, 409.

(20) Fisanick, G. J.; Gedanken, A.; Eichelberger IV, T. S.; Keubler, N. A.; Robin, M. B. *J. Chem. Phys.* **1981**, *75*, 5215.

(21) Whetten, R. L.; Fu, K.-J.; Grant, E. R. *J. Chem. Phys.* **1983**, *79*, 4899.

(22) Miller, J. C.; Cheng, W.-C. *J. Phys. Chem.* **1985**, *89*, 1647.

(23) Smith, D. B.; Miller, J. C. *J. Chem. Phys.* **1989**, *90*, 5203; *J. Chem. Soc., Faraday Trans.* **1990**, *86*, 2441.

(24) Duncan, M. A.; Dietz, T. G.; Smalley, R. E. *J. Am. Chem. Soc.* **1981**, *103*, 5245.

(25) Bililign, S.; Feigerle, C. S.; Miller, J. C. To be published.

(26) Freund, H. J.; Bauer, S. H. *J. Phys. Chem.* **1977**, *81*, 994. Frurip, D. J.; Bauer, S. H. *J. Phys. Chem.* **1977**, *81*, 1001.

(27) Foster, M. S.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1975**, *97*, 4808.

(28) Fredeen, D. J. A.; Russell, D. H. *J. Am. Chem. Soc.* **1985**, *107*, 3762.

(29) Wronka, J.; Ridge, D. P. *J. Am. Chem. Soc.* **1984**, *106*, 67.

(30) Lichtin, D. A.; Bernstein, R. B.; Vaida, V. *J. Am. Chem. Soc.* **1981**, *104*, 1831.

(31) Poth, L.; Shi, Z.; Zhong, Q.; Castleman, Jr., A. W. *J. Phys. Chem. A* **1997**, *101*, 1099.

(32) Peifer, W. R.; Garvey, J. F. *J. Phys. Chem.* **1989**, *93*, 5906.

(33) Ball, D. W.; Chiarelli, J. A. *J. Mol. Struct.* **1995**, *372*, 113.

(34) Andrews, L.; Chertihin, G. V.; Citra, A.; Neurock, M. *J. Phys. Chem.* **1996**, *100*, 11235. Cheretihin, G. V.; Saffel, W.; Yustein, J. T.; Andrews, L.; Neurock, M.; Ricca, A.; Bauschlicker, C. W. *J. Phys. Chem.* **1996**, *100*, 5261. Cherihin, G.; Andrews, L.; Neurock, M. *J. Phys. Chem.* **1996**, *100*, 14609.

(35) Kappes, M. M.; Staley, R. H. *J. Am. Chem. Soc.* **1981**, *103*, 1286.

(36) Baranov, V.; Javahery, G.; Hopkinson, A. C.; Bohme, D. K. *J. Am. Chem. Soc.* **1995**, *117*, 12801.

(37) Baranov, V.; Bohme, D. K. *Int J. Mass Spectrom. Ion Processes* **1996**, *154*, 71.

(38) Rohlfing, E. A.; Cox, D. M.; Kaldor, A. *Chem. Phys. Lett.* **1983**, *99*, 161.

(39) Riley, S. J.; Parks, E. K.; Nieman, G. C.; Pobo, L. G.; Wexler, S. *J. Chem. Phys.* **1984**, *80*, 1360.

(40) Whetten, R. L.; Cox, D. M.; Trevor, D. J.; Kaldor, A. *J. Phys. Chem.* **1985**, *89*, 566.

(41) Wang, L.-S.; Wu, H.; Desai, S. R. *Phys. Rev. Lett.* **1996**, *76*, 4853.

(42) Andersson, M.; Persson, J. L.; Rosen, A. *J. Phys. Chem.* **1996**, *100*, 12222.