Nanochemistry: Iron Cluster Reactions with Methyl Iodide

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Previous experiments have shown that the ionization/dissociation of iron pentacarbonyl clusters can lead to the formation of iron ions and iron cluster ions and that these species can further react with dopant molecules to yield chemically rearranged products. The present experiments characterize similar reactions with methyl iodide molecules and clusters. Heteroclusters of the form $[Fe(CO)_5]_m(CH_3I)_nAr_p$ are created in an expanding supersonic jet of the component molecules. Following ionization by a 30 ps, 266 nm laser pulse, extensive dissociation, aggregation, and chemical rearrangement occur leading to ionic products which are characterized by mass spectrometry. Cluster ions of the type $Fe_mI_n^+$, $Fe(CH_3I)_n^+$, and $FeI_m(CH_3I)_n^+$ are observed as products. The stability of the binary parent ion $Fe(CH_3I)^+$ is demonstrated for the first time.

I. Introduction

For several decades, a number of subdisciplines within physics, chemistry, and material sciences have focused on the properties of ever-smaller particles[1] and structures. This trend has been driven, not only by scientific curiosity or by instrumental capabilities but by the needs of modern applications in fields such as microelectronics, catalysis, aerosol science, and biotechnology. At the other end of the size scale, spectroscopic and structural understanding of aggregates of atoms and molecules has advanced to ever-larger clusters.[2] The two trends have collided in the nanoscale size regime with particles less than 50 nm in size or clusters of 10−500 atoms or molecules. Adding to the fascination with matter of this size is the appearance of quantum effects and the evolution of many size-dependent (or surface-area-dependent) properties. Although the understanding of structural and electronic properties in this size range is becoming mature, the study of nanochemistry is still in its infancy.

Clusters represent a phase of matter intermediate between a gas and a solid where chemical reactions can be probed in a nanostructurally controlled environment. Once a reactive species is formed within a van der Waals cluster, a reaction partner is typically only a few atomic units away. One reason for the strong interest in clusters is the potential for providing nanoscale size and composition control and the possibility that such control will lead to new insights into condensed phase reactions or even the discovery of new size-dependent chemistry. Ideally, one would like to produce clusters of selected size and composition; however, nozzle gas expansions typically yield a distribution of clusters established by the thermodynamics and kinetics of the expansion process. Still, cluster size and composition can be regulated in an average sense by choice of gas mixture and expansion conditions to provide control of the reaction medium.

Multiphoton ionization (MPI) mass spectrometry is a versatile method for probing cluster distributions and intracluster chemistry. Over the last several years we have utilized resonant and nonresonant MPI and time-of-flight (TOF) mass spectrometry to study homogeneous and binary molecular clusters produced in pulsed gas expansions which contain a variety of inorganic, organic, and organometallic molecules.[3−11]

Various types of reactions can be photochemically initiated in such clusters. Excitation to dissociative states can yield fragmentation of either the neutral or ion chromophore. The fragments can potentially be caged, escape the cluster, be retained as solvent-separated components, or react further if a suitable reaction partner is available. One method of controlling fragmentation is by moving the excitation wavelength in or out of dissociative regions. Another way to control fragmentation is with the laser pulse width. When a dissociative resonance lies in the neutral manifold of states, ionization and dissociation are kinetically competing processes and changing to shorter, more powerful laser pulses can favor ionization as the preferred path. Previous studies of MPI of $(NO)_2$ and $(NO)_3$ at wavelengths resonant with neutral dissociation produce only NO^+ fragment ions using nanosecond pulses, but yield large numbers of parent ions with a high peak power picosecond laser.[3−6,12] It has recently been demonstrated that even higher power femtosecond pulsed lasers can produce intact parent ions from many systems which are prone to photofragmentation.[13,14] In general, shorter and higher peak power pulses appear to be a way to achieve the soft ionization condition essential for chemical physics studies.

The possibilities for photoinduced intracluster chemistry increase dramatically when the product ion or fragment becomes a free radical. Intracluster polymerization reactions consistent with radical chain mechanisms have been demonstrated in our lab for carbon disulfide.[7] In this case, the cluster reactions appear to follow a mechanism analogous to the collisional chemistry that occurs in the gas phase from equivalent precursors.

Following earlier work[15−17] in other labs, we have recently demonstrated that photodissociation and ionization of clusters containing organometallics with labile ligands can lead to a rich array of intracluster chemistry. Using iron pentacarbonyl co-expanded with various possible reaction partners in argon, we

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have prepared (1) $Fe_m^+Ar_n$, where the stronger Fe−CO bonds have been photolyzed but some fraction of the argon solvent is retained,[10] (2) $Fe_m^+(NO)$, a simple substitution process,[9] (3) $FeO^+(N_2O)_n$, where FeO^+ appears as the product of the intracluster reaction of Fe^+ and N_2O, and $Fe_mO_n^+(N_2O)_p$ after additional cluster oxidation reactions,[9] and (4) $Fe^+(C_6H_6)_n$, where benzene, which usually fragments extensively under these MPI conditions, is stabilized by the presence of metal.[18] Coexpansions of precursors which can both photodissociate, such as $Fe(CO)_5$ with CS_2, provide particularly interesting systems for study.[11] This combination has been observed to readily form $Fe_mS_n^+$ cluster ions with $m = n$ as the preferred stoichiometry. Magic numbers have been observed in the cluster ion distributions from these and other precursors, with a basis that ranges from thermochemical stability for certain symmetric ionic structures to stronger chemical interactions yielding selective compound stoichiometry.

While numerous studies have been published on the preparation and physical and chemical properties of metal-containing neutral and ionic clusters, the vast majority of these involve the use of laser ablation into a supersonic expansion to incorporate metals into the cluster. Fewer investigations have involved preparing metal-containing cluster ions from neutral clusters of organometallic precursors. This approach has the advantage of allowing a nanostructurally controlled medium to be prepared **before** photochemically initiating the intracluster chemistry. In this paper we will focus on the photochemical production of metal clusters from organometallic precursors and describe the further intracluster chemical reactions of these clusters with methyl iodide molecules and clusters.

II. Experimental Section

The experimental apparatus used at the Oak Ridge National laboratory has been described previously, and a schematic may be found elsewhere.[4]

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 which 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 diameter nozzle aperture and backing pressures of several atmospheres were typically used in these experiments. The nozzle-to-ionization region distance is adjustable from 10−17 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 of 1−2500 amu. A dual channel-plate electron multiplier is used to detect the ions. 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 turbo pump.

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. Most of the present results were obtained with the 266 nm fourth harmonic at a energy of 2−4 mJ.

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 1000 consecutive laser shots.

The initial clusters are formed by mixing the iron pentacarbonyl with methyl iodide and the argon 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. Likewise, the methyl iodide is degassed and the appropriate amount expanded into a second mixing chamber. Finally, the contents of the two chambers are mixed and argon gas is added to yield a total backing pressure of about 100 psi.

III. Results and Discussion

A. Photoionization/Dissociation of Iron Pentacarbonyl Clusters. It is well-known that the multiphoton ionization (MPI) 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, many papers[19] have explored the interaction of focused lasers with metal carbonyl and other organometallic molecules to produce bare metal atoms for uses such as metal vapor lasers or metallic thin films.

Much less well studied is the ionization/dissociation of *clusters* of iron pentacarbonyl. In previous studies, Duncan, Dietz, and Smalley[15] and, later, Wheeler and Duncan[16] reported the synthesis of metal nanocrystals by the MPI of $[Fe(CO)_5]_m$ clusters. In the authors' laboratory,[9] MPI at 266 nm of $Fe(CO)_5$ coexpanded with methane produced iron ions and iron cluster ions in a distribution similar to that observed by Duncan et al.[15,16] using a 193 nm laser. A progression of peaks spaced by 56 amu was attributed to Fe_n^+ clusters (see Figure 1 of reference 9). A second, less intense series of peaks halfway between these was assigned to $Fe_m(CO)^+$ species. Similar experiments[10] expanding iron pentacarbonyl in argon expansions resulted in an interesting nonstatistical evaporation process. Extensive loss of CO molecules was observed without the concomitant loss of the more weakly bound argon components. Clusters such as $Fe_mAr_n^+$ ($m = 1,2$; $n = 1-26$) were present in the mass spectrum following the laser-induced ionization/dissociation. Of importance to the present studies, the production of metal ions and cluster ions takes place in a collisionless environment where further reaction with neighboring molecules may occur. In previous papers, the reactions of such metal clusters with NO, N_2O, and CS_2 have been described.[9,11]

The mechanism for the production of Fe^+ ions in the cluster environment is presumably similar to that of MPI of the isolated monomer.[19] 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. The same two possibilities exist for the formation of the iron clusters. In that case, following the decarbonylation to form iron neutrals or ions, the metal atoms may react with other

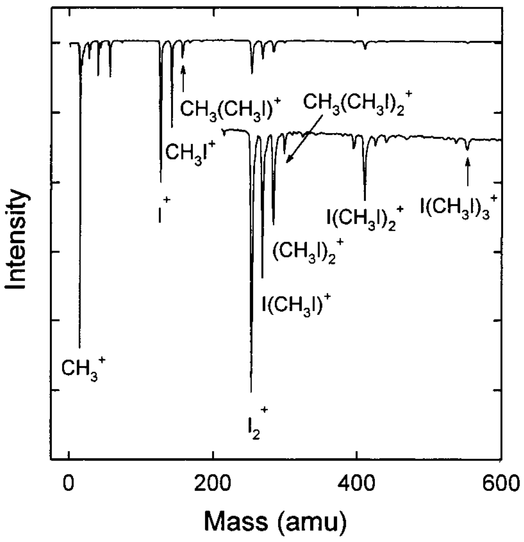

Figure 1. A portion of the laser ionization mass spectrum of a neat methyl iodide/argon expansion mixture. The 250 Torr of methyl iodide was diluted in the argon carrier gas and expanded at a pressure of about 100 psi.

iron pentacarbonyl molecules or other atoms to coalesce into dimers, trimers, etc. Their internal energy content is then reduced by the loss of argon atoms from the cluster. Again, the dissociation/coalescence could precede ionization or follow it. However, for the purposes of the study of subsequent cluster reactions of Fe^+ and Fe_n^+ ions, the details of the formation mechanism are of secondary interest.

B. Photoionization/Dissociation of Methyl Iodide Clusters. Like iron pentacarbonyl, methyl iodide readily photodissociates upon ultraviolet irradiation and has been a model compound for studies of the photophysics and spectroscopy of unimolecular decay processes.[20] Again, in the past decade, the advent of supersonic expansions has allowed extension of these studies to clusters of methyl iodide. Successive generations of lasers have enabled the photodissociation dynamics of these clusters to be probed on nanosecond,[21−23] picosecond,[24] and, finally, femtosecond[25,26] time scales. Following dissociation, intracluster chemistry results in a range of final cluster products. Both neutral and ion−molecule chemistry has been observed.[21−26] In the latter case, comparisons may be made with electron impact induced reactions in cluster beams[27,28] and in older collisional association studies.[29,30] Finally, laser ablation mass spectrometry of cryogenic, condensed phase, methyl iodide films yields chemical products similar to those observed in the cluster studies and illustrates the utility of comparing the gas-phase cluster environment to that of the condensed phase.[31−33] Some negative ion studies of methyl iodide clusters have also appeared.[34,35]

Figure 1 shows the mass spectrum recorded following the ionization/dissociation of a methyl iodide/argon expansion by picosecond pulses of 266 nm light. Typically, the expansion mixture is made by mixing 300 Torr of methyl iodide with argon to yield a total backing pressure of 90−100 psi. The spectrum contains a series of “groups of peaks” spaced by approximately 142 amu, which represents the mass of $\mathrm{CH_3I}$. Each group is comprised of 3−5 peaks which differ from each other by 15 amu, the mass of a methyl group, but contain the same number of iodine atoms. Typically, the first peak in the group (although not always the most intense) is identified as I_n^+ and the last peak (again, usually small) is $\mathrm{CH_3(CH_3I)}_n^+$. The intermediate peaks represent successive loss of $\mathrm{CH_3}$ groups. For instance, the peaks between about 250 and 300 amu are $\mathrm{I_2}^+$, $\mathrm{I(CH_3I)}^+$, $\mathrm{(CH_3I)_2}^+$, and $\mathrm{CH_3(CH_3I)_2}^+$ with masses of 254, 269, 284, and 299 amu, respectively. The next group of peaks is $\mathrm{I_3}^+$, $\mathrm{I_2(CH_3I)}^+$, $\mathrm{I(CH_3I)_2}^+$, $\mathrm{(CH_3I)_3}^+$, and $\mathrm{CH_3(CH_3I)_3}^+$. These assignments are confirmed by comparison with a corresponding spectrum obtained by starting with deuterated methyl iodide. Clearly, the highest mass peak in each group, $\mathrm{CH_3(CH_3I)}_n^+$, must arise from a cluster of at least $n + 1$ methyl iodide molecules, and the preceding peaks may arise from any sized cluster greater than or equal to n. In general, each peak may have contributions from ions from several different precursors. In the most extensive spectra, the series may be followed out to peaks which must arise from at least the methyl iodide eight-mer.

Within each group of peaks, the relative intensity pattern changes with cluster size. For instance, in the first two multiplets, the I^+ and $\mathrm{I_2}^+$ peaks, respectively, are dominant. However, for $n = 3$ and larger, the $\mathrm{I(CH_3I)}_n^+$ ion is the most abundant species; after about $n = 5$ it is the only peak observed. The changing trend in intensities reflects fragmentation branching ratios that differ depending on the degree of solvation of the cluster. The excitation/ionization event is considered to be localized on a single molecule within the cluster and assumed to take place on a faster time scale than fragment escape from the cluster. That is, following multiphoton absorption, the initial excited cluster is a solvated methyl iodide molecule, $\mathrm{CH_3I}^{*/+}\mathrm{(CH_3I)}_n$, where the */+ symbol denotes an excited or ionized molecule. The fragmentation steps may subsequently proceed by loss of an iodine or methyl fragment as follows:

$$\mathrm{CH_3I}^{*/+}(\mathrm{CH_3I})_n \rightarrow \mathrm{I}^{*/+}(\mathrm{CH_3I})_n + \mathrm{CH_3}$$

or

$$\mathrm{CH_3I}^{*/+}(\mathrm{CH_3I})_n \rightarrow \mathrm{CH_3}^{*/+}(\mathrm{CH_3I})_n + \mathrm{I}$$

The branching ratio for such reactions will depend on several factors including the ionization potential of the clustered fragment, the kinetic energy of the escaping $\mathrm{CH_3}$ or I groups, and the solvation energy of the remaining fragment. Because of the large mass difference between the methyl group and the iodine atom, the methyl fragment will retain more kinetic energy and thus can more easily escape the solvent cage. Furthermore, the solvation energy of the iodine atom or ion is expected to be the larger, thus also hindering its escape. Such caging effects should vary with the cluster size, leading, in the limit of large n, to the observed dominance of the $\mathrm{I(CH_3I)}_n^+$ peaks relative to those of $\mathrm{CH_3(CH_3I)}_n^+$ in the spectrum.

These spectra may be compared with similar mass spectra in the literature obtained by electron impact[24,27,28] or by nanosecond,[24] picosecond,[24] or femtosecond[25,26] laser ionization. In general, similar peaks may be identified in each case, but with dramatically different relative intensities. Electron impact at low energy[24] (20 eV) yields cluster mass spectra with the parent ions as the most intense peaks, while higher energy[24,28] (35−60 eV) results in a range of fragment ions similar to those of Figure 1. In contrast, laser ionization with nanosecond pulses[24] yields $\mathrm{CH_3}^+$, I^+, and $\mathrm{CH_3I}^+$ ions from monomer beams, but $\mathrm{I_2}^+$ ions provide the only hint that dimer and higher clusters are present in cluster beams. Femtosecond laser ionization[26] favors the parent cluster ion for the first two groups of peaks, but higher clusters yield a distribution similar to those in the present study employing picosecond pulses. We note that, unlike the case of iron pentacarbonyl discussed in section III.A and ref 10, no clusters with argon are seen in any similar methyl iodide studies, presumably because of faster energy randomization compared to the rate of photofragmentation.

Power-dependent fragmentation is found in the MPI of many rapidly dissociating molecules. The higher peak powers available from shorter pulsed lasers favor the formation of parent ions, while nanosecond MPI yields spectra with more extensive fragmentation. These results reflect the different ionization/dissociation mechanisms which determine the details of fragmentation for different power regimes in MPI. For rapidly dissociating molecules, nanosecond laser ionization proceeds via a mechanism where dissociation in neutral states precedes ionization (the so-called ladder switching mechanism). The neutral fragments are subsequently ionized by absorption of additional photons. More intense, shorter laser pulses provide power densities where ionization of even rapidly dissociating neutral molecules may effectively compete with the dissociation (the ion ladder mechanism). Fragmentation then proceeds from the parent ion rather than the neutral species. For clusters, where many weak bonds provide multiple dissociation pathways, these considerations are especially important. In principle, measurement of the laser power dependence of the appearance of fragment ions can shed light on these mechanisms. In the present case, however, the nonresonant ionization and the multiple dissociation pathways preclude meaningful measurements. The methyl iodide system has been studied over a wide range of laser powers and time frames and provides a rather complete set of data for illustration of these effects for monomers[36,37] and clusters.[24−26]

As discussed above, cluster fragmentation and subsequent chemistry following picosecond MPI may contain contributions from both ladder-switching (favored using nanosecond pulses) and ion-ladder (favored using femtosecond pulses) mechanisms. That is, fragmentation and chemical rearrangement may involve neutral molecules, ions, or both. In some cases,[24−26] elegant pump−probe experiments have shed light on the order of various processes. These rationales have been discussed previously[24,26−28] and will not be repeated here.

C. Chemical Reactions within Mixed Clusters of Iron Pentacarbonyl and Methyl Iodide. The ionization/dissociation of heterogeneous clusters containing both iron pentacarbonyl and methyl iodide might be expected to yield spectra that look like the sum of the two independent ion patterns (Figure 1 of ref 9 and Figure 1 of the present paper) with additional peaks that represent intracluster chemical reactions between reactive centers originating from the two parent species. Figures 2 and 3 show mass spectra of mixed clusters in two different regimes of relative concentration. The mixture used to produce Figure 2 was approximately a 1:4 ratio of $Fe(CO)_5$ to CH_3I (27 Torr/100 Torr), while that for Figure 3 was about 3 times as concentrated with a ratio of 1:13.3 (30 Torr/400 Torr). In both cases, the argon carrier gas was added to yield a total backing pressure of about 100 psi. Lower and higher concentration ratios did not yield substantially different spectra and were of overall poorer quality.

It is interesting to note in Figures 2 and 3 that, although the initial concentrations of methyl iodide exceed that of iron pentacarbonyl by factors of 4 and 13, respectively, the intensities of daughter ions from the two species are more nearly equal. This is a reflection of the lower ionization potentials of iron pentacarbonyl molecules (7.897 eV) and iron atoms (7.870 eV) relative to those of methyl iodide molecules (9.538 eV) and iodine atoms (10.451 eV). Since the ionization/dissociation laser wavelength is 266 nm (4.66 eV), two-photon processes will result in ionization of iron-containing species while species containing only methyl iodide molecules or iodine atoms require three photons to ionize. Of course species containing iron bound to methyl iodide or iodine in a cluster will also ionize with only two photons. It is generally assumed that the positive charge in such mixed clusters will reside on the iron atom since it has the lowest ionization potential. For consistency, however, we have always placed the plus sign in the representation of such a species at the end of the chemical species. That is, a mixed cluster with a iron and a methyl iodide species is labeled $FeCH_3I^+$ rather than Fe^+CH_3I.

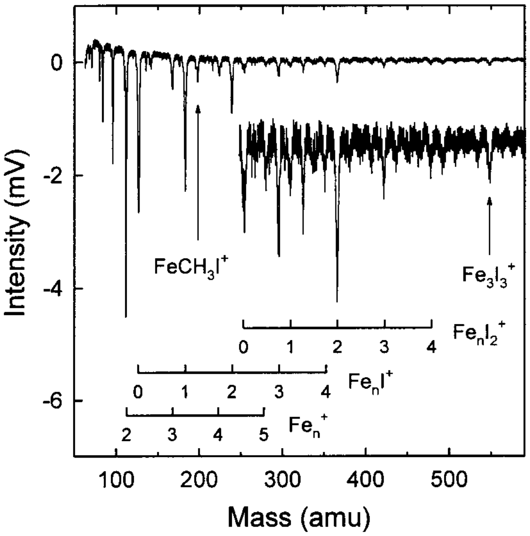

Figure 2. A portion of a laser ionization mass spectrum of an iron pentacarbonyl (27 Torr)/methyl iodide (100 Torr) mixture. The mixture was expanded in an argon carrier gas at about 100 psi.

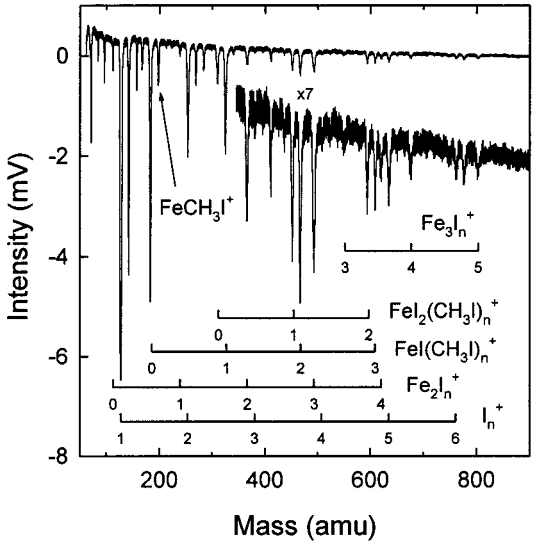

Figure 3. A portion of a laser ionization mass spectrum of an iron pentacarbonyl (30 Torr)/methyl iodide (400 Torr) mixture. The mixture was expanded in an argon carrier gas at about 100 psi.

The "methyl iodide poor" and "methyl iodide rich" spectra of Figures 2 and 3, respectively, are dramatically different. In the former case, the spectrum is dominated by ions of the type $Fe_mI_n^+$. This is reminiscent of the $Fe(CO)_5/CS_2$ heteroclusters studied previously where the $Fe_mS_n^+$ ions were prominent in the high mass portion of the spectrum.[11] In the present case, the ions series Fe_n^+ ($n = 1−5$), Fe_nI^+ ($n = 0−4$), $Fe_nI_2^+$ ($n = 0−4$), and $Fe_nI_3^+$ ($n = 3$) are identified in Figure 2. Of course, the observed clusters could also be "sorted" as FeI_n^+ ($n = 1,2$), $Fe_2I_n^+$ ($n = 1,2$), $Fe_3I_n^+$ ($n = 1−3$), and $Fe_4I_n^+$ ($n = 0−2$). In contrast, the methyl iodide rich spectrum of Figure 3 has several additional ion series as a result of the higher availability of

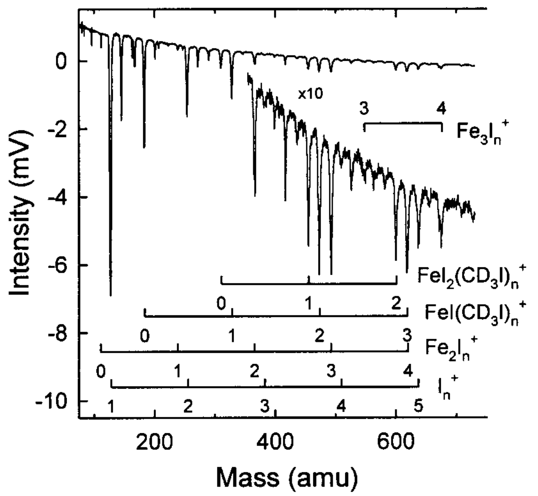

Figure 4. A portion of a laser ionization mass spectrum of an iron pentacarbonyl (30 Torr)/deuterated methyl iodide (260 Torr) mixture. The mixture was expanded in an argon carrier gas at about 100 psi.

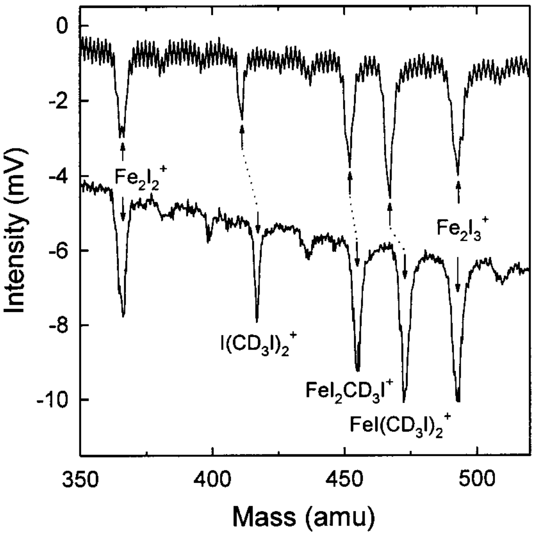

Figure 5. A comparison between corresponding portions of Figures 3 and 4 showing the isotope shifts between the protonated and deuterated species.

methyl iodide molecules and clusters. For instance, the series $FeI(CH_3I)_n^+$, $FeI_2(CH_3I)_n^+$, and I_n^+ are identified in the figure. The previously observed $Fe_3I_n^+$ series of Figure 2 is seen extended by the $n = 4, 5$ members.

For the case of mixed cluster ions containing both iron and methyl iodide species, the problem of accidental mass coincidences must be addressed. That is, the mass of an iodine atom (127 amu) is equal to that of the species Fe_2CH_3. Consequently, peaks appearing at mass 127, 183, 254, 310, etc. may be identified as I^+, FeI^+, I_2^+, FeI_2^+, etc. or, alternately, as $Fe_2(CH_3)^+$, $Fe_3(CH_3)^+$, $Fe_2(CH_3I)^+$, $Fe_3(CH_3I)^+$, etc. Although in some cases the correct identification may be made by "chemical intuition" or by analyzing the intensity distribution within a given cluster series, the most definitive solution is to use isotopic substitution to remove the mass ambiguity. Figure 4 shows a spectrum of an iron pentacarbonyl/**deuterated** methyl iodide mixture (ratio 1:9.3). The CD_3I was obtained from Cambridge Isotope laboratories and was stated to be of 99.5% isotopic purity. A peak-by-peak comparison between Figures 1−3 and Figure 4 allows the correct identification to be ascertained. As an example, Figure 5 shows a detailed comparison of a small region of the mass spectra of Figures 3 and 4 between 350 and 500 amu. Five peaks are labeled which exhibit isotope shifts of 0 amu ($Fe_2I_2^+$ and $Fe_2I_3^+$), 3 amu ($FeI_2CH_3I^+$), and 6 amu [$I(CH_3I)_2^+$ and $FeI(CH_3I)_2^+$]. These species, of course, have 0, 3, or 6 hydrogen atoms, respectively, replaced by an equal number of deuterium atoms.

The ions observed in the present study may be compared with product ions observed in noncluster, ion−molecule studies of Fe^+ with CH_3I performed by ICR[38] or guided ion beam[39] methods. In those studies, the parent ion of the simple addition process, $FeCH_3I^+$, was not observed but the $FeCH_3^+$ and FeI^+ fragment ions from oxidative reduction were observed. The reactions to form both fragment ions were found to be exothermic.[38] In the present study, in contrast, the parent $FeCH_3I^+$ ion, although small, is clearly observed in Figures 2 and 3. The parent ion stems from the cluster environment's ability to dissipate excess internal energy by evaporation of solvent molecules rather than by dissociation.

Another point of comparison between the cluster chemistry observed here and the previous ion−molecule studies concerns the product branching ratios. Allison and Ridge[38] report $FeCH_3^+$/FeI^+ ion ratios of about 50/50. Fischer et al.,[39] who can distinguish between ground-state $Fe^+(^6D)$ and excited-state $Fe^+(^4F)$ reactions, find that the excited state reaction heavily favors formation of the FeI^+ product (10/90) compared to the ground-state reaction (40/60). In the present studies, the $Fe_mI_n^+$ products are readily apparent in Figures 2−4, while the $Fe_m(CH_3)_n^+$ or $Fe_mCH_3(CH_3I)_n^+$ peaks are very small or nonexistent. Two possible conclusions arise from these comparisons. First, the present results may imply that excited state processes are more important than ground state reactions. This is certainly plausible as the method of forming the iron and iron cluster ions is energetically capable of creating many excited state species. The second possible conclusion is that large clusters are more effective at caging the massive iodine fragment (as compared to the smaller methyl portion) and incorporating it into the cluster ion fragment.

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