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Gas-Phase IR Spectroscopy of Anionic Iron Carbonyl Clusters

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Understanding the structure and bonding of transition metal carbonyls as a function of size and degree of coordinative saturation has provided a key stimulus in the development of modern inorganic chemistry.^{1a,b} Iron carbonyls have received particular attention due to their utility as catalysts.^{1c} Small, coordinatively saturated iron carbonyls ($\text{Fe}(\text{CO})_5$, $\text{Fe}_2(\text{CO})_9$, $\text{Fe}_3(\text{CO})_{12}$) are quite stable and were structurally characterized long ago.² Computational work has been done on the stable clusters,^{3a} and on the unsaturated series $\text{Fe}_2(\text{CO})_n$ ($n = 6-8$), where characterizing the metal-metal bonding was of central importance.^{3b} Currently, the experimental data that could provide support for the latter theoretical findings are incomplete; only vibrational spectroscopy of neutral $\text{Fe}_2(\text{CO})_8$ obtained by matrix isolation (MI) methods^{4a,b} and mass spectrometric (MS) studies of anionic clusters^{4c-f} have been done. Recently, MI data for neutral iron carbonyls with four Fe atoms have also been reported.^{4g} There are inherent difficulties with both techniques, in that identification of the absorbing species in MI spectroscopy can be difficult, and it can be hard to obtain direct structural information using conventional MS techniques. Recent advances in laser technology have facilitated infrared multiple-photon dissociation^{5a} (IRMPD) spectroscopy of gas-phase ions over a wide wavelength range;^{5b} an early application has been elucidation of transition metal complex structures.⁶ Here we report the first gas-phase infrared spectra of several anionic iron carbonyl clusters recorded using the FTICR apparatus^{7a} installed at the free electron laser for infrared experiments (FELIX) in The Netherlands.^{7b}

$\text{Fe}(\text{CO})_4^-$ ions were produced in situ in the ICR cell from $\text{Fe}(\text{CO})_5$ vapor by electron attachment, and $\text{Fe}_2(\text{CO})_8^-$ was formed by ion-molecule reactions at higher $\text{Fe}(\text{CO})_5$ pressures.^{4c} $\text{Fe}_2(\text{CO})_7^-$ was made using sustained off-resonance irradiation (SORI) to induce collision-activated dissociation of $\text{Fe}_2(\text{CO})_8^-$.^{8a} Double-resonance ICR experiments have shown that reactive fragments of smaller clusters can stimulate production of larger ones via ion-molecule reactions.^{4f} In the present work, clusters up to $\text{Fe}_5(\text{CO})_{14}^-$ were formed in this way, using SORI pulses to drive the reactive process. Undesired species were ejected from the ICR cell, and the ion of interest was irradiated with several pulses from FELIX. The photodissociation products and any remaining parent ion were then measured using a standard FTICR excite/detect sequence;^{8b} loss of one or more CO ligands was observed. IRMPD spectra were generated by plotting the total fragmentation yield as a function of the wavelength of FELIX.

The experimental spectra in the CO-stretching region for clusters ranging in size from $\text{Fe}(\text{CO})_4^-$ to $\text{Fe}_5(\text{CO})_{14}^-$ are shown in Figure 1. One structural aspect of the clusters that can immediately be ascertained from these spectra is the presence of "bridging"

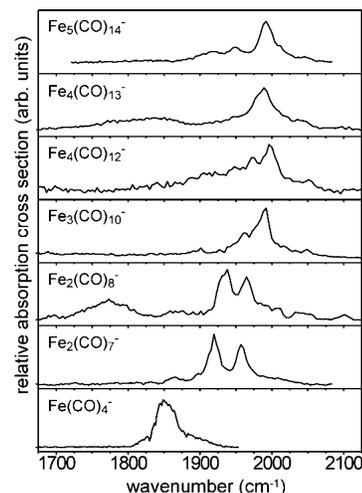


Figure 1. IRMPD spectra of anionic iron carbonyl complexes.

carbonyls (μ^2 -COs), where the C atom is coordinated to two Fe atoms, since they produce bands appearing 150–200 cm^{-1} lower than terminal carbonyls. Such features are present only for $\text{Fe}_2(\text{CO})_8^-$ at $\sim 1770 \text{ cm}^{-1}$ and $\text{Fe}_4(\text{CO})_{13}^-$ at $\sim 1825 \text{ cm}^{-1}$. It is instructive to compare these findings with results for related neutral clusters; for example, $\text{Fe}_2(\text{CO})_8$ is known to have an isomer with 2 μ^2 -COs.^{4a,b} $\text{Fe}_3(\text{CO})_{12}$ has two μ^2 -COs,^{2a,4c} which seems consistent with our observation that $\text{Fe}_3(\text{CO})_{10}^-$ lacks them. Finally, the neutral $\text{Fe}_4(\text{CO})_x$ species observed by MI spectroscopy is postulated to have $x = 14$, with two μ^2 -CO ligands.^{4g} This is again consistent with our observations of no μ^2 -COs for $\text{Fe}_4(\text{CO})_{12}^-$ and (at least) one for $\text{Fe}_4(\text{CO})_{13}^-$, and so our data tend to support the conclusions of the earlier MI work. Of course, the anionic clusters could have different preferences for terminal/bridging sites; unfortunately, there is no MI data on larger anionic clusters available for direct comparison. Another interesting feature of the spectra is the progressive blue shift of the CO-stretching modes with increasing size, reaching saturation at around the $\text{Fe}_3(\text{CO})_{10}^-$ cluster. It is well-known that adding electron density to a metal carbonyl system tends to increase the amount of π back-bonding, causing a red shift.^{6b} So, as the cluster size increases, the effect of the attached electron is distributed over a larger number of CO ligands, producing the observed shift. Finally, we find it intriguing that the general complexity of these spectra remains fairly constant as the cluster size increases, although we do not yet have an explanation for this phenomenon.

To determine structures for the smaller clusters, we carried out DFT geometry optimizations and frequency calculations;⁹ the resulting structures and calculated spectra are shown with the IRMPD spectra in Figure 2. For $\text{Fe}(\text{CO})_4^-$ [Figure 2A], the optimized structure has C_{3v} symmetry, with a calculated vibrational spectrum consisting of a doublet, split by $\sim 12 \text{ cm}^{-1}$ and centered around 1862 cm^{-1} . Only one line is observed experimentally,

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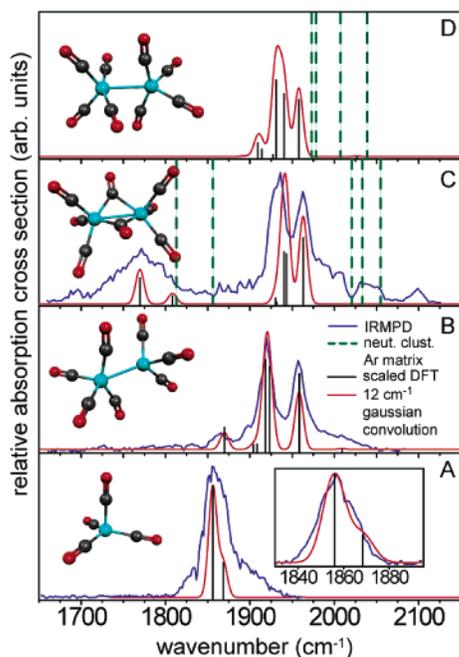


Figure 2. IRMPD and calculated B3LYP spectra (scaled by 0.965) of anionic iron carbonyl complexes (A) $\text{Fe}(\text{CO})_4^-$ (inset shows spectrum taken with 30 times lower laser power), (B) $\text{Fe}_2(\text{CO})_7^-$, (C) $\text{Fe}_2(\text{CO})_8^-$ bridged, and (D) $\text{Fe}_2(\text{CO})_8^-$ unbridged (calcd only). Band positions for neutral clusters (ref 4a) are indicated by dashed lines.

Table 1. Fe–Fe Bond Lengths (Å) for Binuclear Iron Carbonyl Complexes (B3LYP/LACVP+*)

$\text{Fe}_2(\text{CO})_7$		$\text{Fe}_2(\text{CO})_8$ (doubly-bridged)		
anion ^a	neutral ^a	dianion ^b	anion ^a	neutral ^a
2.506	2.238	2.629	2.562	2.438

^a From this work. ^b From ref 11.

presumably because the line width is too broad to resolve the underlying structure. Lowering the laser power by up to a factor of 30 to remove the effects of power broadening did not resolve the splitting, although the line did narrow significantly and began to show some asymmetry [Figure 2A, inset]. This spectrum also supports the band assignments from earlier MI work to the $\text{Fe}(\text{CO})_4^-$ complex.¹⁰ The optimized structure for $\text{Fe}_2(\text{CO})_7^-$ has C_s symmetry, with no μ^2 -CO ligands, and the calculated and experimental spectra agree very well [Figure 2B]. For $\text{Fe}_2(\text{CO})_8^-$, two structural minima were located, a C_s structure with two μ^2 -CO ligands [Figure 2C] and an unbridged, distorted D_{2d} structure [Figure 2D]. The calculation for the bridged structure agrees well with the experiment, reproducing the aforementioned 1770 cm^{-1} band. However, the unbridged structure (which is 2.86 kcal/mol more stable) also agrees well in the terminal CO region, and thus the coexistence of both species cannot be excluded. Indeed, vibrational bands for both bridged and unbridged neutral $\text{Fe}_2(\text{CO})_8$ structures (dashed lines in Figure 2C,D) were observed in argon matrixes.^{4a} Our calculations indicate that the Fe–C vibrational bands (300–700 cm^{-1}) are quite different for the two cases and thus could more conclusively resolve this issue.

The Fe–Fe distances in these systems provide a measure of the metal–metal bonding and thus are of particular interest. Calculated values (B3LYP/LACVP+*) are collected in Table 1 for neutral and ionic forms of $\text{Fe}_2(\text{CO})_7$ and $\text{Fe}_2(\text{CO})_8$. Although the CO-stretching modes probed here are not directly sensitive to the Fe–Fe bonding, the good agreement with experiment gives us some confidence in the computed structures. For the $\text{Fe}_2(\text{CO})_8$ systems,

there is an incremental increase in the bond length as the electron density increases from the neutral to the dianionic cluster.¹¹ According to the “rule of thumb” proposed by Xie et al. for the neutral clusters, the overall increase of ~ 0.2 Å should correspond to a decrease of 1 in the Fe–Fe bond order.^{3b} This is in qualitative agreement with expectations based on elementary MO level diagrams, which predict that the additional electrons would occupy an Fe–Fe antibonding orbital, reducing the bond order in steps of 1/2. The $\text{Fe}_2(\text{CO})_7$ case is more problematic, because the DFT calculations for the anion exhibit a large degree of spin contamination ($\langle S^2 \rangle \sim 1.6$), indicating significant quadruplet character in the nominally doublet state. While this might partially explain the large jump of ~ 0.3 Å in the Fe–Fe bond length, the physical relevance of highly spin-contaminated DFT results remains an open question.¹² A more thorough investigation, also including the larger clusters (more than two Fe atoms), is in progress.

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Supporting Information Available: Larger images of the cluster structures, tables of calculated and experimental frequencies, and calculated structures and frequencies for the neutral clusters (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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