IRMPD SPECTROSCOPY OF ANIONIC IRON CARBONYL CLUSTERS

D.T. Moore, J. Oomens (FOM Institute for Plasma Physics, Nieuwegein), J.R. Eyler (U Florida, Chemistry), G. v. Helden, G. Meijer (Fritz-Haber Institute, Berlin), D.P. Ridge (U Delaware, Chemistry)

Introduction

Vibrational spectra of a series of anionic iron carbonyls have been obtained using a broad-range, wavelength-dependent IRMPD technique.[1] The evolution of the spectra as a function of size and coordinative saturation provides insight into the structures of the clusters. DFT calculations have also been carried out for the smaller clusters, providing more detailed structural information.

Experimental

The measurements were carried out using the FTICR-MS installed at the Free Electron Laser for Infrared eXperiments (FELIX) facility in Nieuwegein, the Netherlands.[2] Anionic iron carbonyl clusters ($Fe(CO)_4^-$, $Fe_2(CO)_8^-$) were formed in situ in the ICR cell by electron attachment to $Fe(CO)_5$ introduced through a pulsed valve. SORI-CID was then used to create $Fe_2(CO)_7^-$ and smaller, fragments, which reacted with background $Fe(CO)_5$ to form larger clusters (see Figure 1) during the high pressure part of the $Fe(CO)_5$ gas pulse. Ions of interest were isolated (SWIFT) and irradiated with FELIX (1-4 pulses). IRMPD spectra were recorded by monitoring the total photofragmentation yield (CO loss) as a function of the FELIX wavelength.

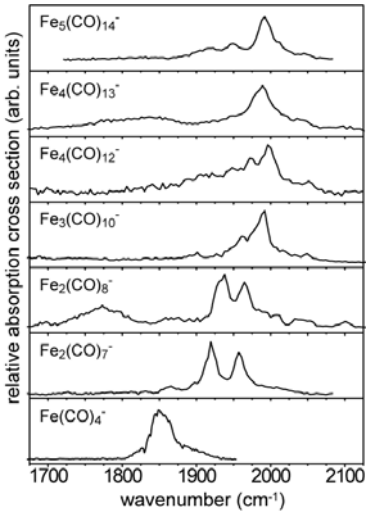

Figure 1: IRMPD spectra of anionic iron carbonyl complexes.

Results and Discussion

The experimental spectra in the CO-stretching region for clusters ranging in size from $Fe(CO)_4^-$ to $Fe_5(CO)_{14}^-$ are shown in Figure 1. One structural aspect of the clusters that can immediately be ascertained from these spectra is the presence of "bridging" carbonyls (μ^2-CO's), 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 $Fe_2(CO)_8^-$ at ~1770 cm^{-1}, and $Fe_4(CO)_{13}^-$ at ~1825 cm^{-1}. Comparing this with the known geometries of neutral iron carbonyl clusters in this size range, we find that the coordinatively saturated compounds $Fe_2(CO)_8$, $Fe_3(CO)_{12}$, and $Fe_4(CO)_{14}$ each have a structure with two μ^2-CO's. Given that $Fe_3(CO)_{10}^-$ and $Fe_4(CO)_{12}^-$ lack bridging carbonyl bands, the implication seems to be that it is the bridging carbonyls that are removed first when the degree of coordinative saturation of the clusters is reduced.

The DFT calculations for the binary clusters produced IR spectra that agreed quite well with the experimental IRMPD data, giving us confidence that the associated structures are correct. All of the clusters show evidence of increased π-back-bonding (shorter Fe-C, longer C-O bonds) when the electron is added to form the anions. In addition, the Fe-Fe bonds are lengthened upon anion formation (Table 1). Based on an earlier study of the neutral clusters, the Fe-Fe bond order decreases by 0.5 for $Fe_2(CO)_8^-$, and 1.5 for $Fe_2(CO)_7^-$.[3] Further computational work is underway to elucidate the changes in the electron density between the neutral and anionic species, and also to calculate spectra for the larger clusters.

Table 1. Fe-Fe bond lengths (Å) for binuclear iron carbonyl complexes (B3LYP/LACVP+*).

$Fe_2(CO)_7$		$Fe_2(CO)_8$	
anion	neutral	anion	neutral
2.506	2.238	2.562	2.438

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References

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