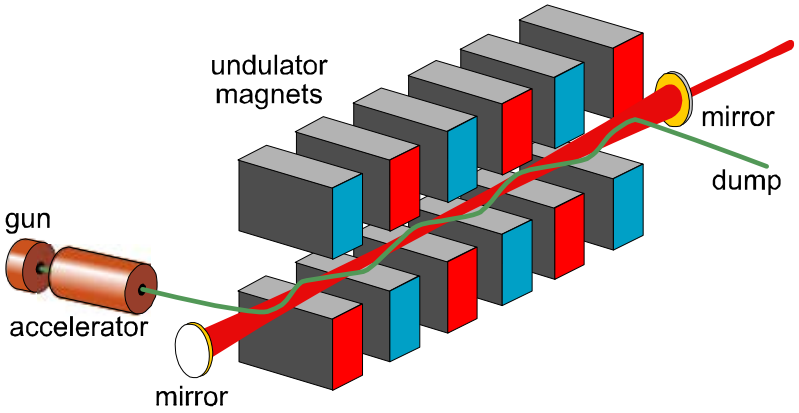
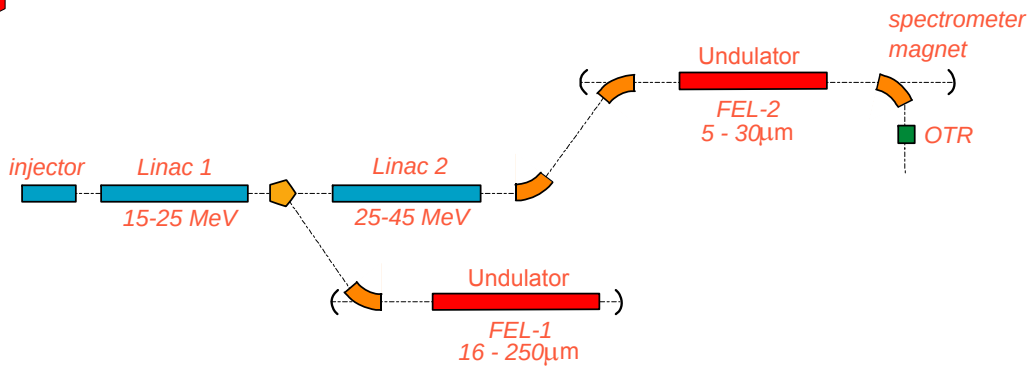
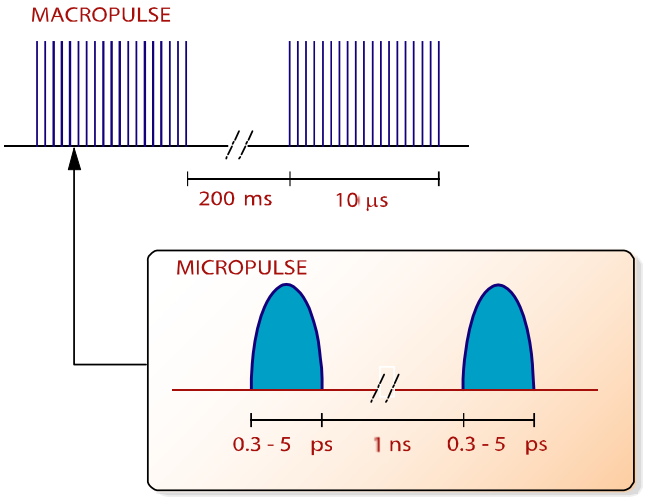
Free Electron Laser for Infrared eXperiments "FELIX"







- Continuously tuneable between 40 - 2000 cm^{-1}
- Macropulse energy: 50 - 100 mJ @ 5 or 10 Hz
- Bandwidth: Transform limited - typically 0.2-0.5% of central λ
- Tuned by varying magnet spacing - increases tuning range and stability
- User facility - excellent support & straightforward operation

Principles of FTICR-MS

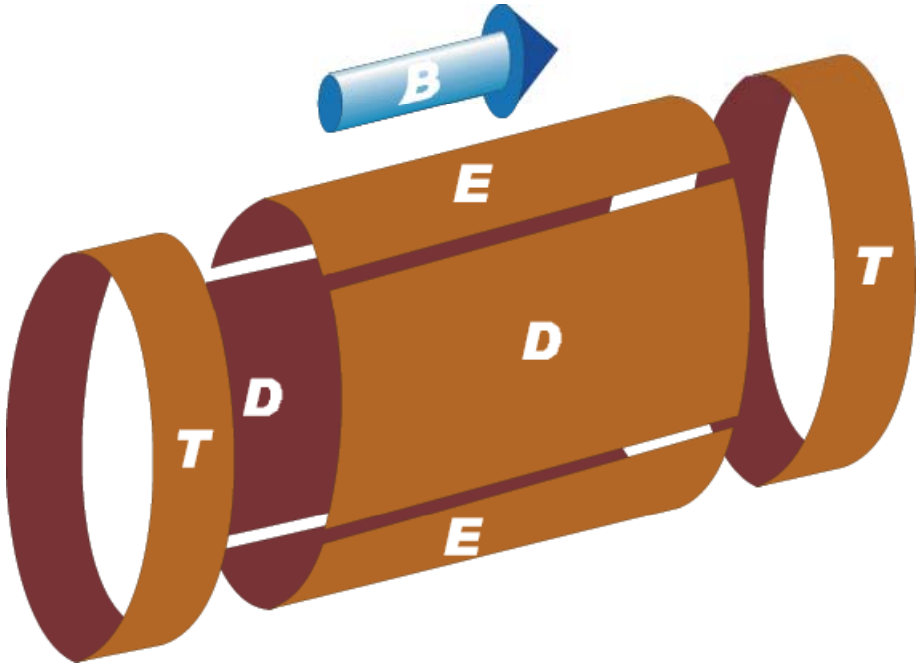
-charged particles trapped by strong, homogeneous magnetic field B (Lorentz force)

- particles orbit magnetic field with frequency dependent only on m/z (for fixed B)

- trapped particles are confined axially by small static voltage to trapping plates (T)

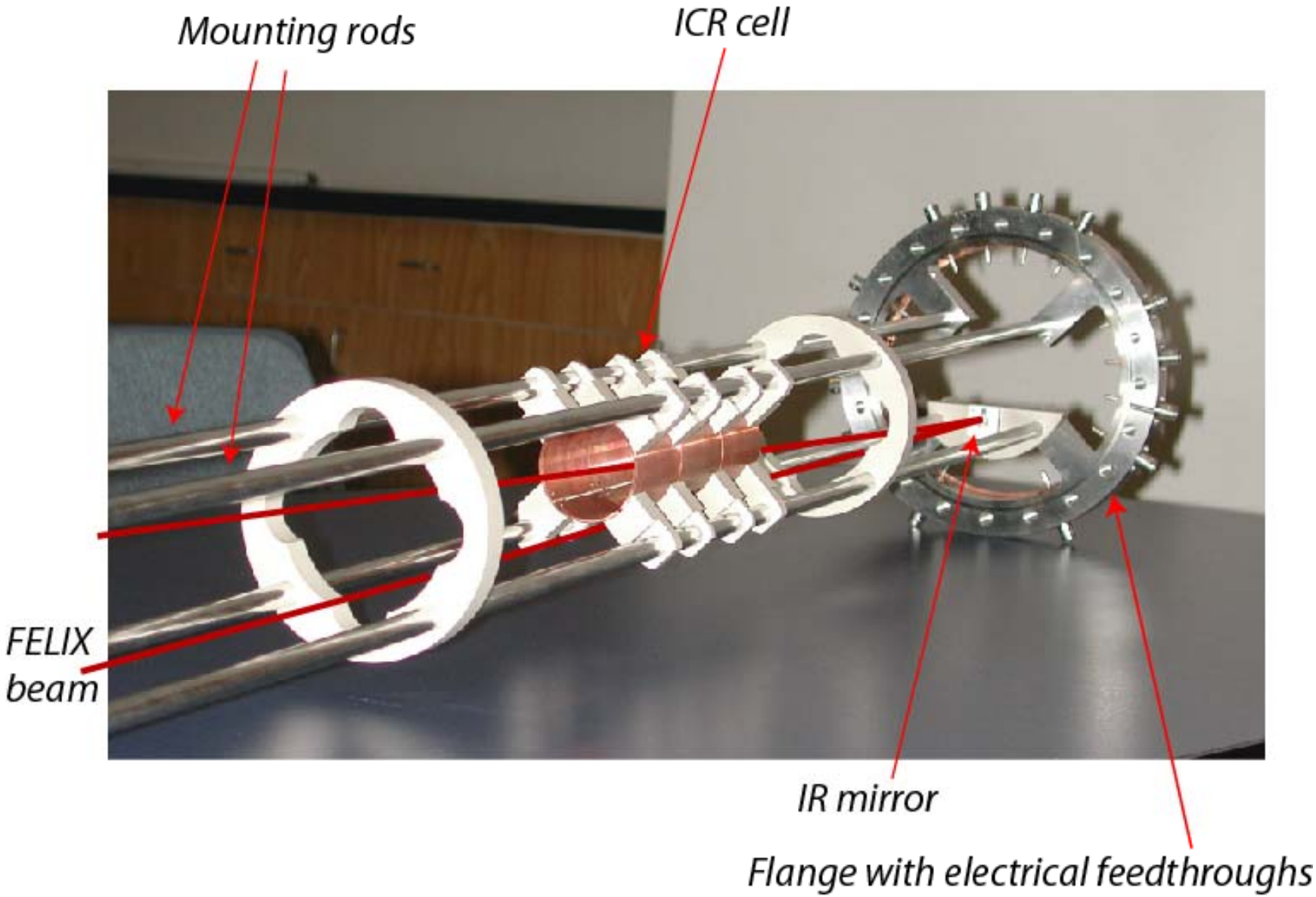
- applying RF to excite plates (E) at cyclotron frequency bunches ions and expands their orbital radii, improving dynamic range → also used to eject unwanted ions

- current induced by moving ions is detected (D) and amplified in time domain, then Fourier Transformed to obtain frequencies of trapped ions



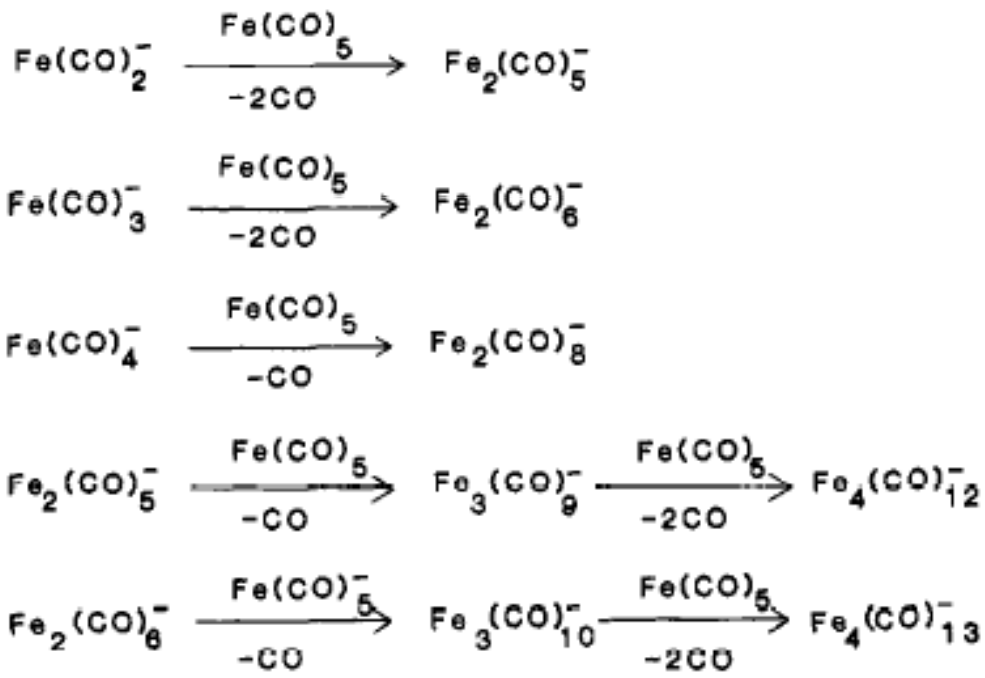
Cyclotron frequency

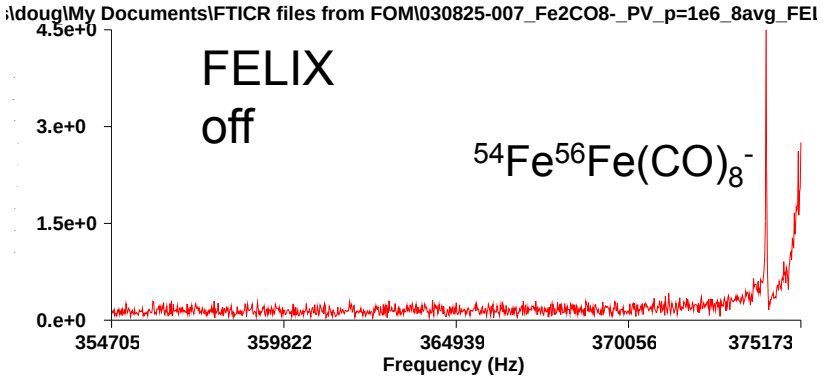
$f \sim Bz/m$

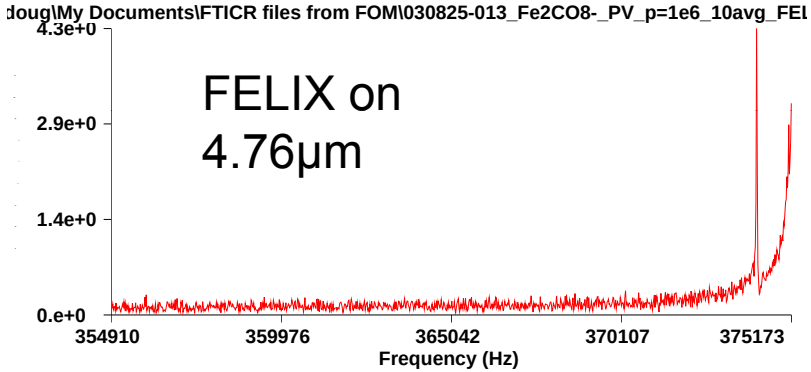

Mounting rods
ICR cell
FELIX
beam
IR mirror
Flange with electrical feedthroughs

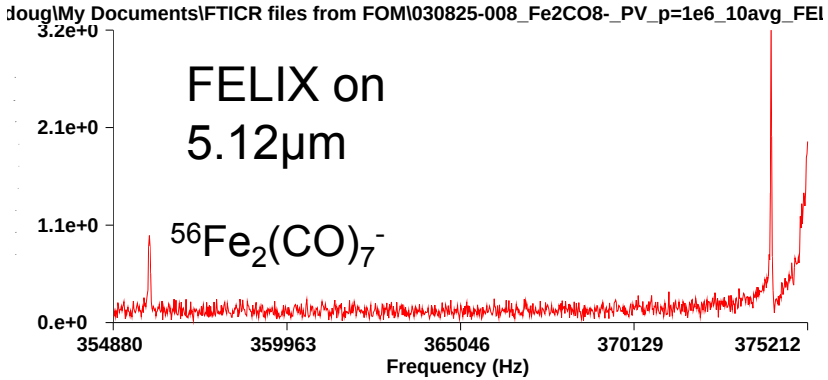
Anionic Metal Carbonyl Clustering Reactions

Scheme II



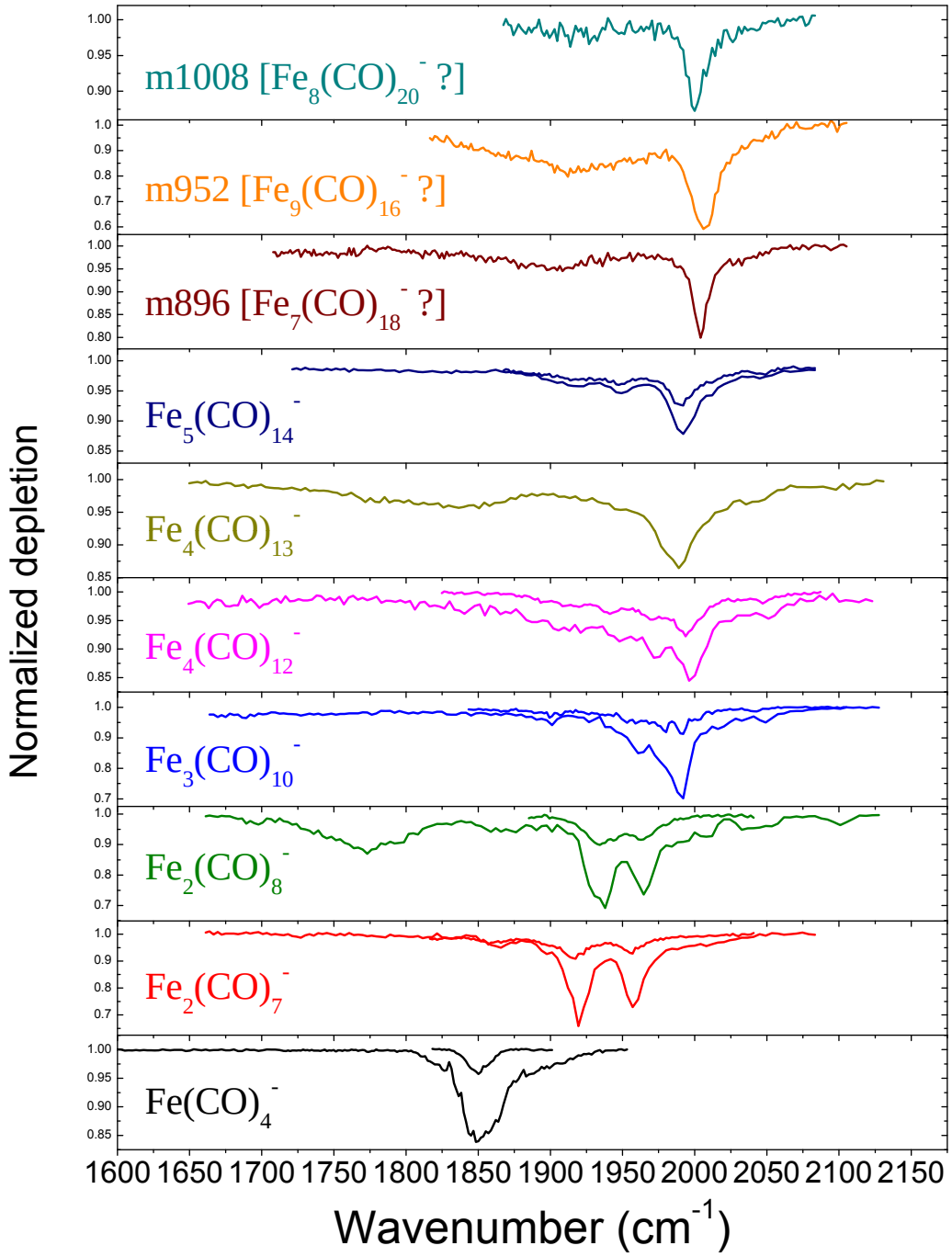

\doug\My Documents\FTICR files from FOM\030825-007_Fe2CO8-_PV_p=1e6_8avg_FEl
4.5e+0
3.e+0
1.5e+0
0.e+0
FELIX
off
$^{54}Fe^{56}Fe(CO)_8^-$
354705
359822
364939
370056
375173
Frequency (Hz)

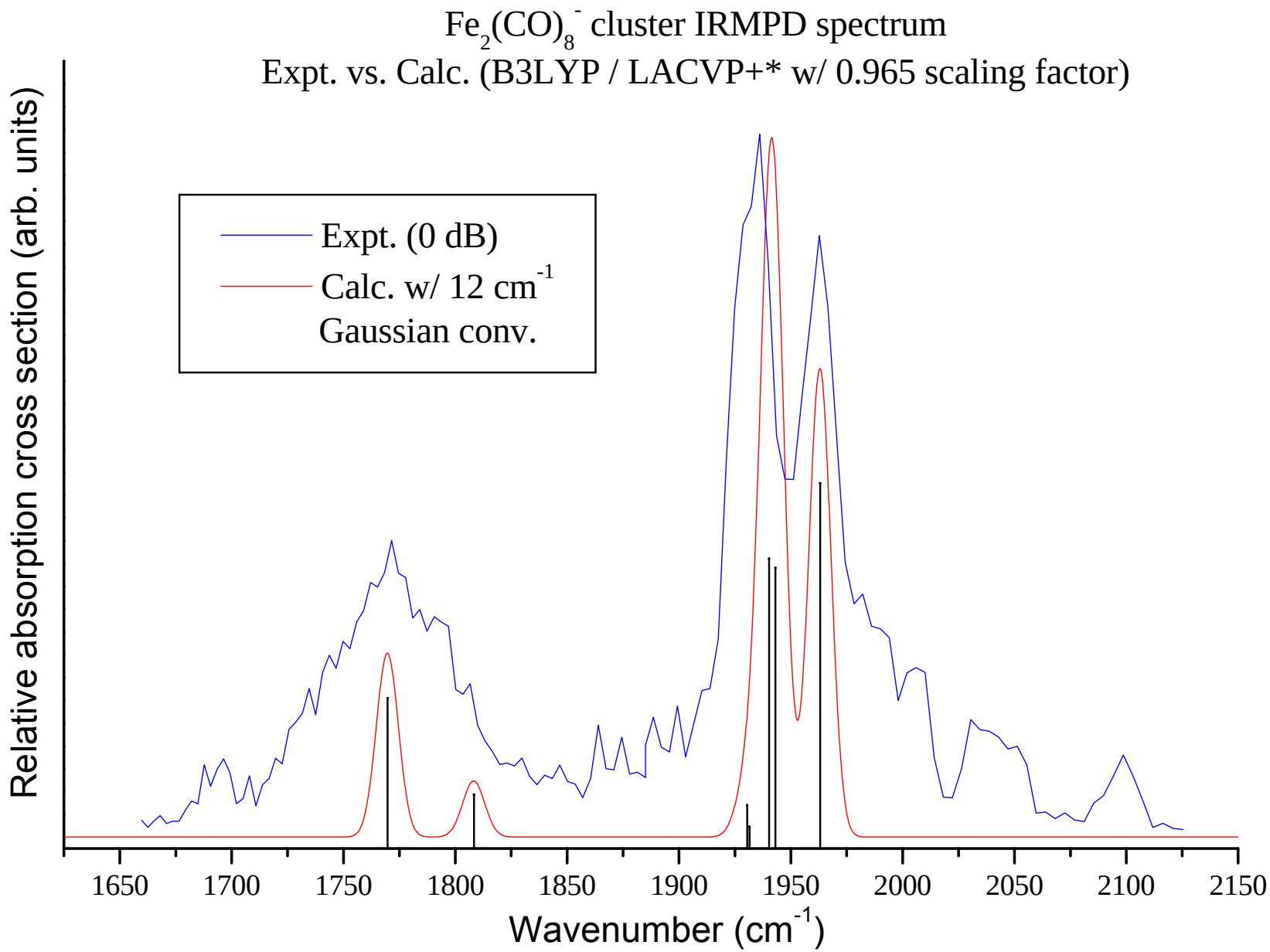

doug\My Documents\FTICR files from FOM\030825-013_Fe2CO8-_PV_p=1e6_10avg_FEl
4.3e+0
2.9e+0
1.4e+0
0.e+0
FELIX on
4.76µm
354910
359976
365042
370107
375173
Frequency (Hz)

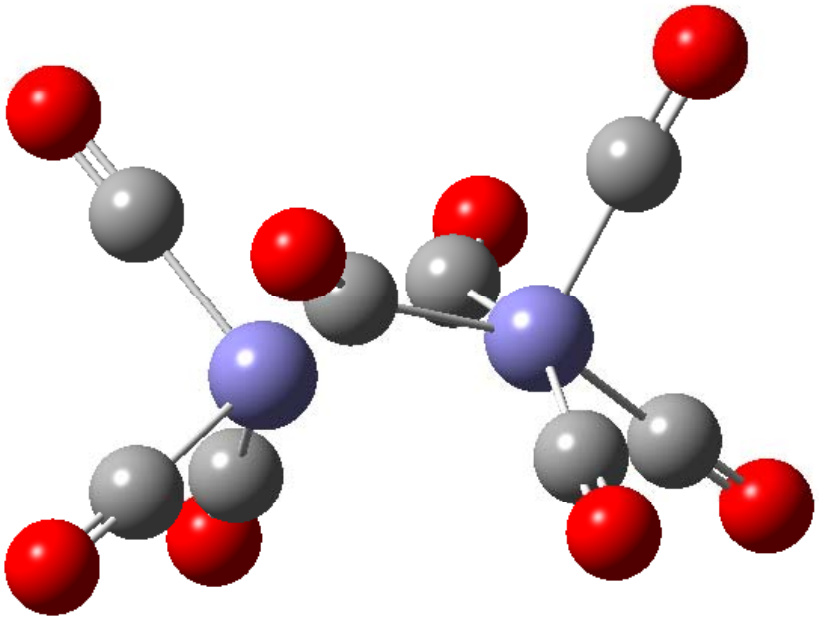

doug\My Documents\FTICR files from FOM\030825-008_Fe2CO8-_PV_p=1e6_10avg_FEl
3.2e+0
2.1e+0
1.1e+0
0.e+0
FELIX on
5.12µm
$^{56}Fe_2(CO)_7^-$
354880
359963
365046
370129
375212
Frequency (Hz)

SORI up to higher masses

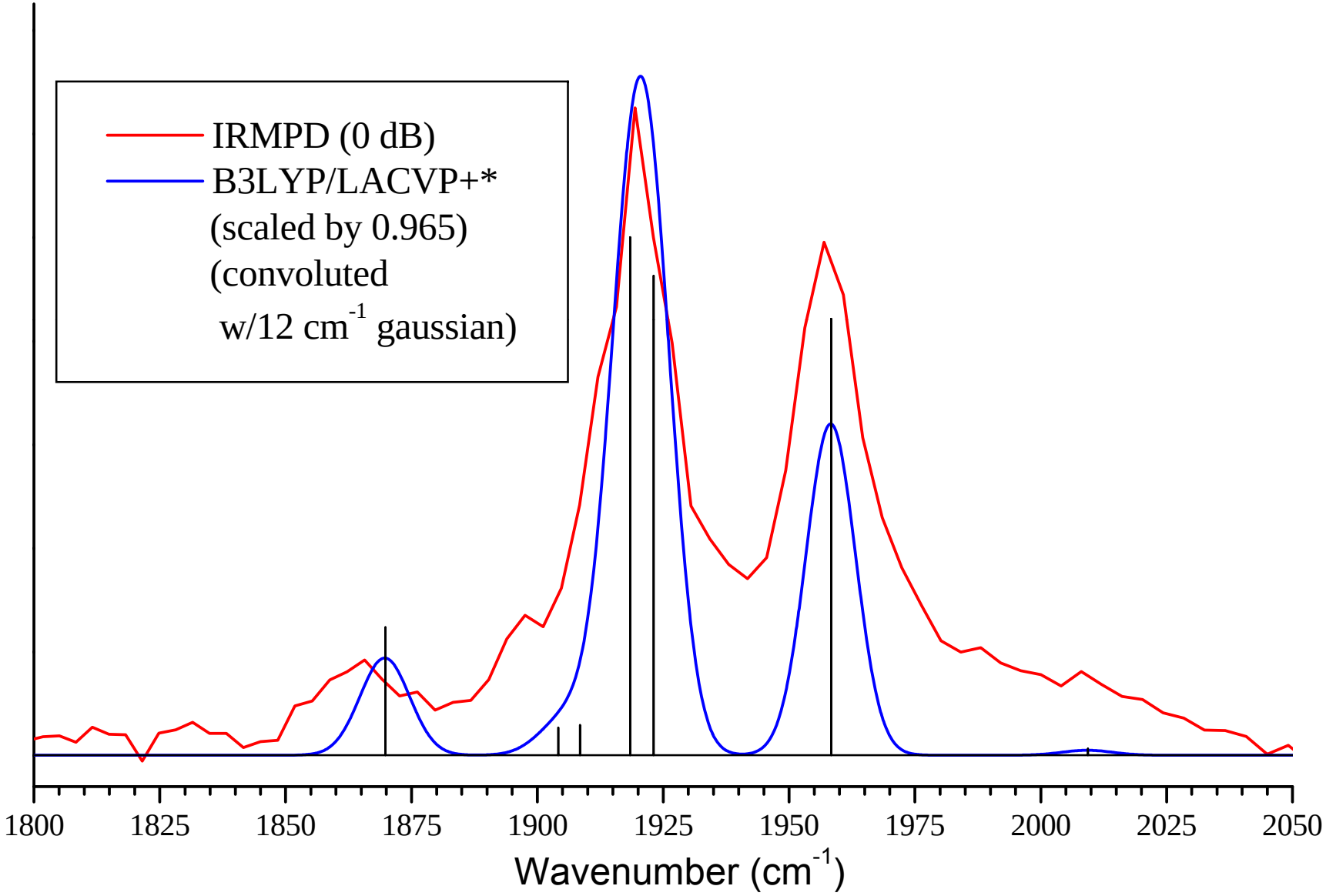
- By adding additional frequencies to the SORI excitation pulse, larger and larger cluster can be synthesized
- In each case, a large percentage (40-100%) of the ion population is transferred into the target mass channel
- Spectra show a blue shift with increasing size, converging to a value around 2000 cm^{-1}
- Structure in spectrum also disappears with increasing size -- indication of transition from organometallic complexes to metal-cluster-adsorbate systems?

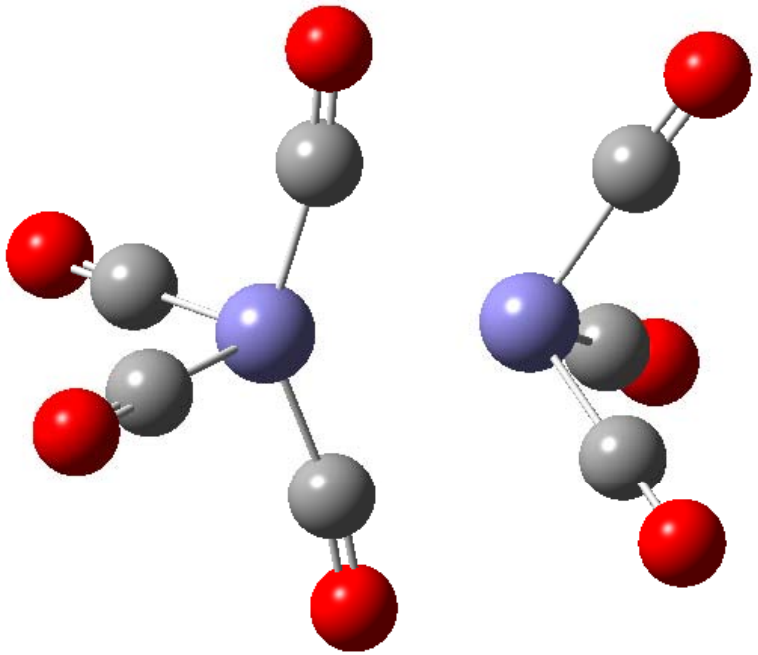



$Fe_2(CO)_8^-$ cluster IRMPD spectrum
Expt. vs. Calc. (B3LYP / LACVP+* w/ 0.965 scaling factor)
Expt. (0 dB)
Calc. w/ 12 cm-1
Gaussian conv.
Relative absorption cross section (arb. units)
1650
1700
1750
1800
1850
1900
1950
2000
2050
2100
2150
Wavenumber (cm-1)

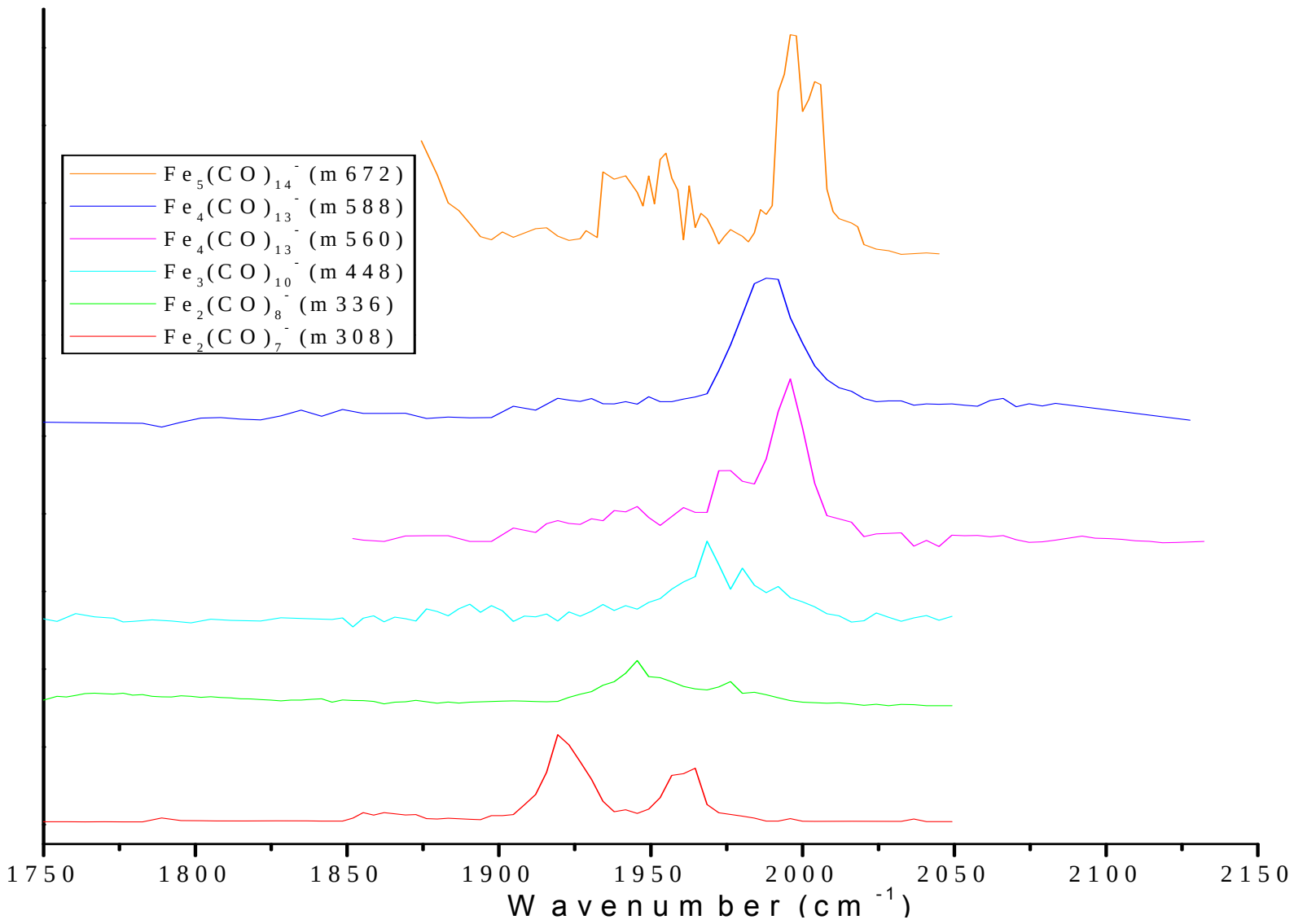


IR spectrum of anionic $Fe_2(CO)_7$ cluster

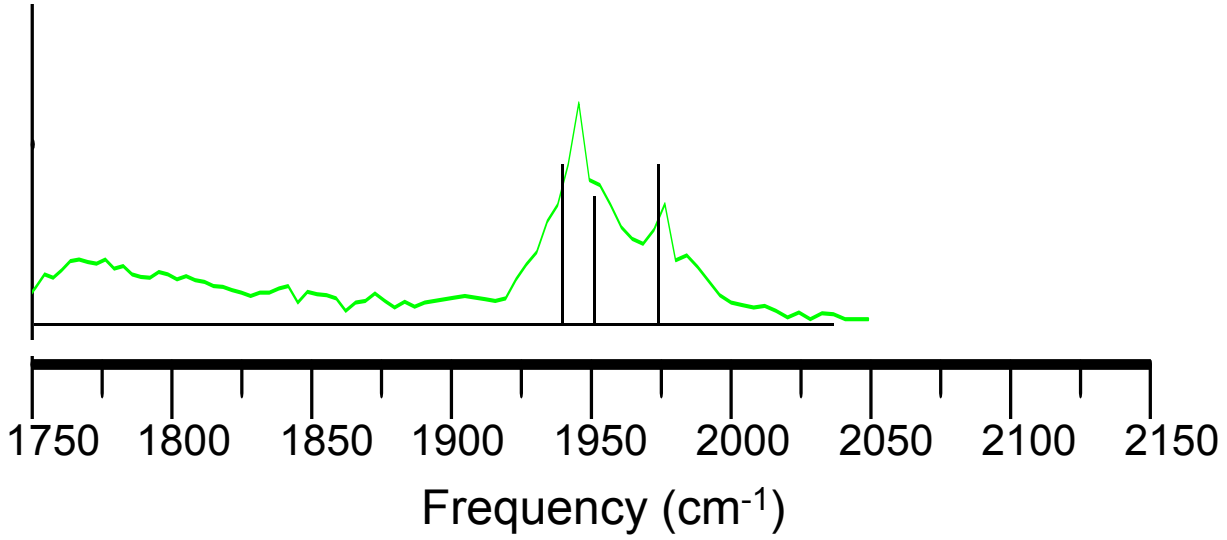


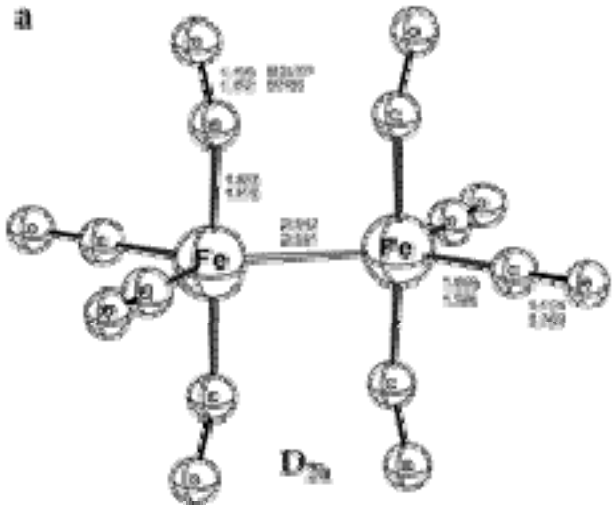


IR MPD spectra of anionic iron carbonyl clusters

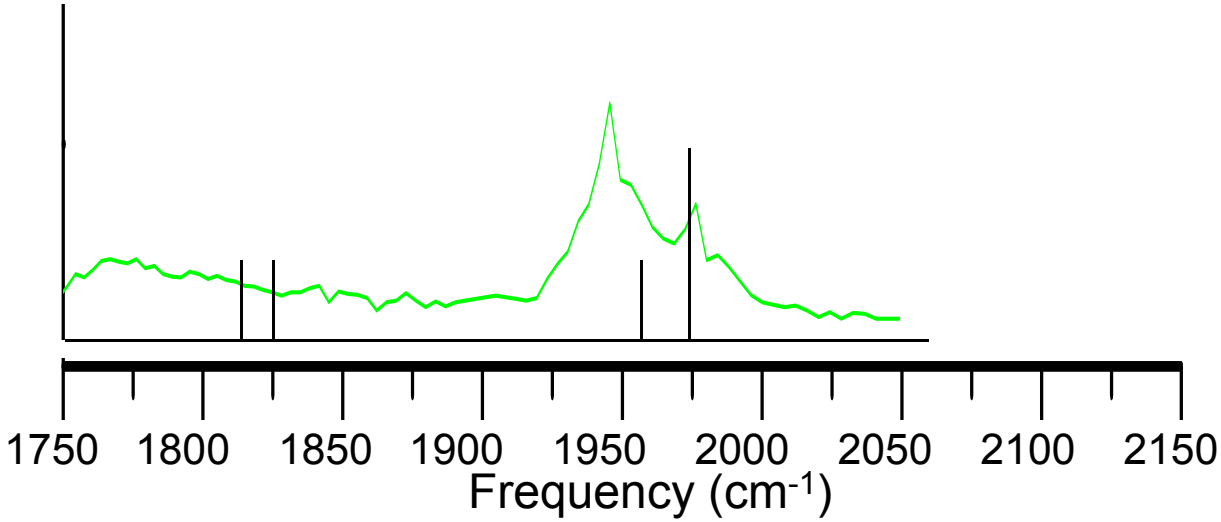


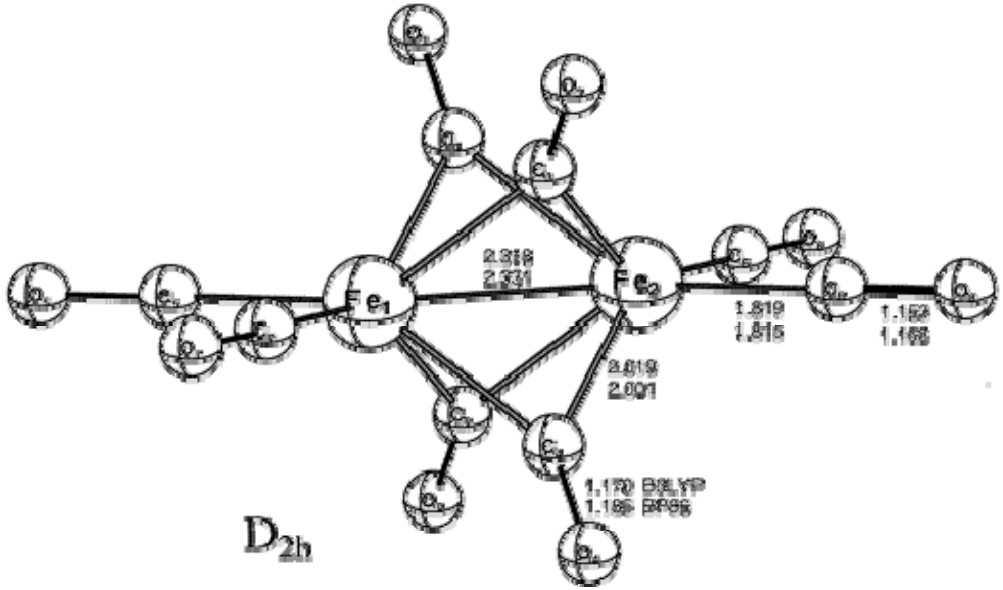
Theoretical spectrum from Schaefer's calculations for D2h unbridged structure. Frequencies lowered by 46 cm-1.



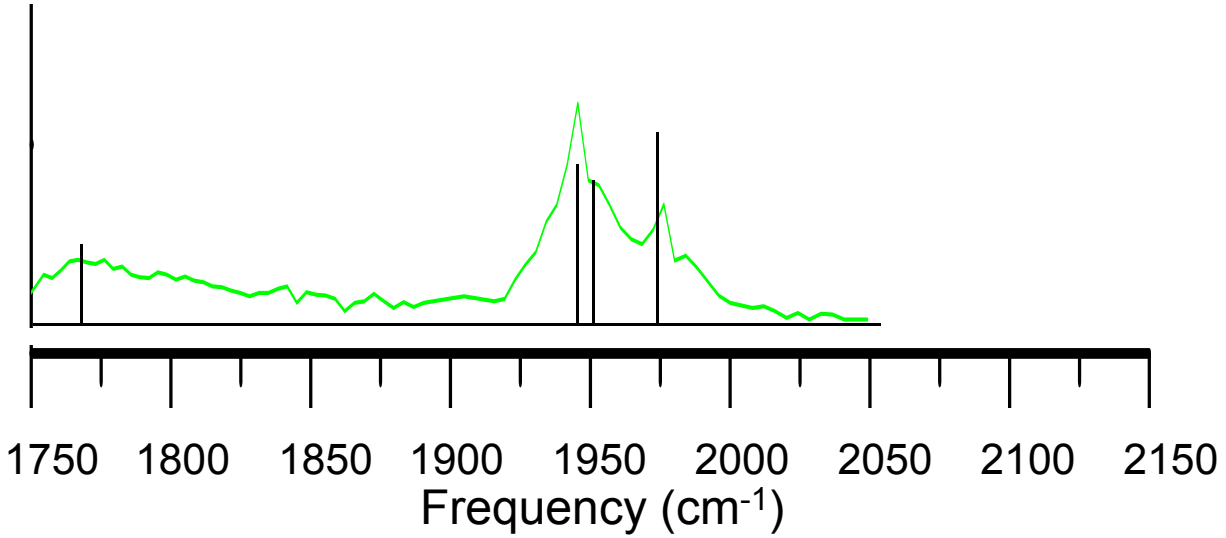


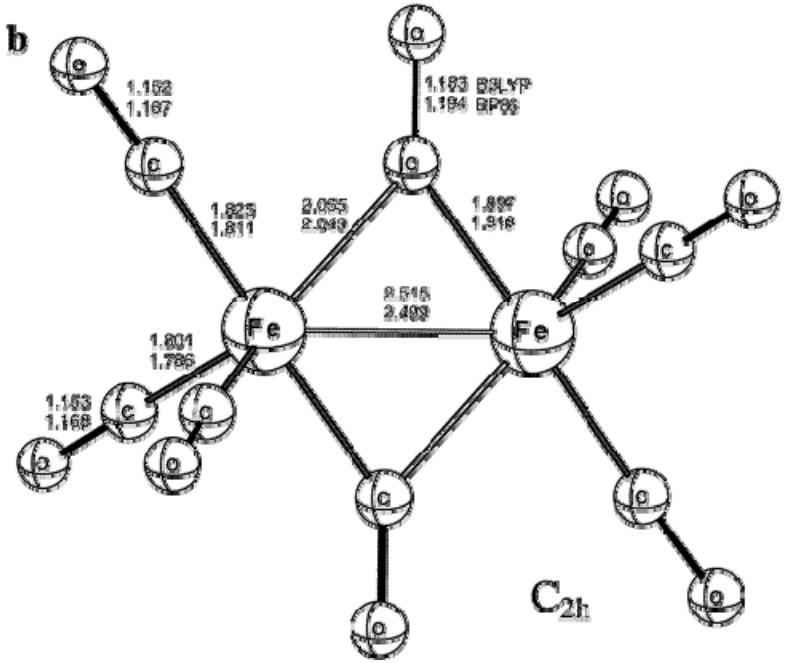
Theoretical spectrum from Schaefer's calculations for tetrabridged structure. Average lowered by 40 cm-1and range expanded 10% about average. Imported from Excel plot



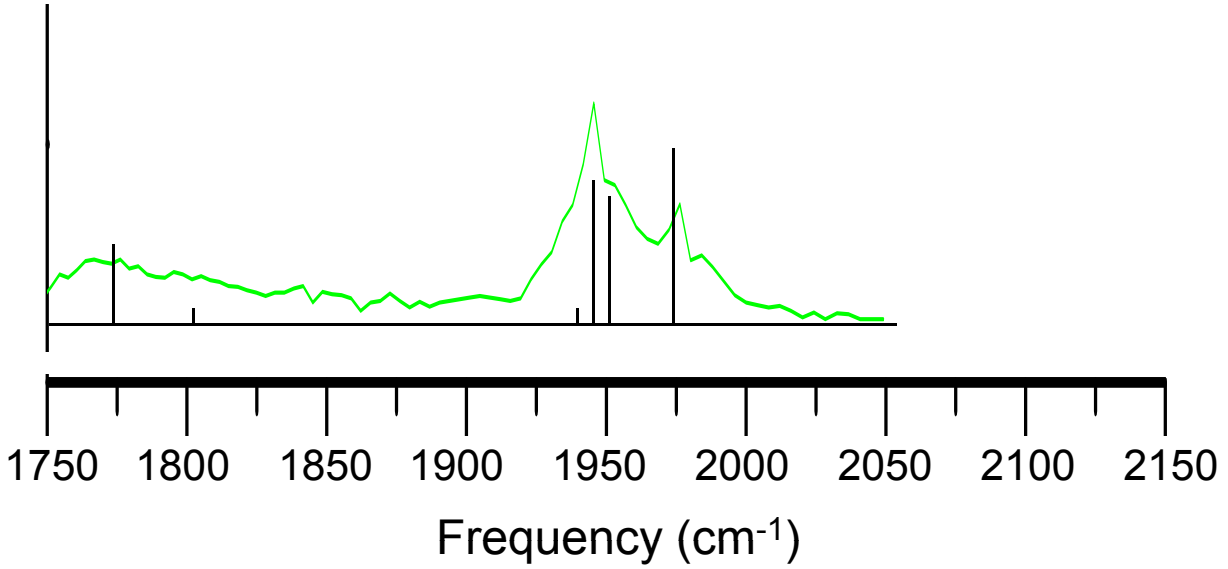


Theoretical spectrum from Schaefer's calculations for a dibridged C2h structure. Average lowered by 57 cm-1. Imported from Excel plot

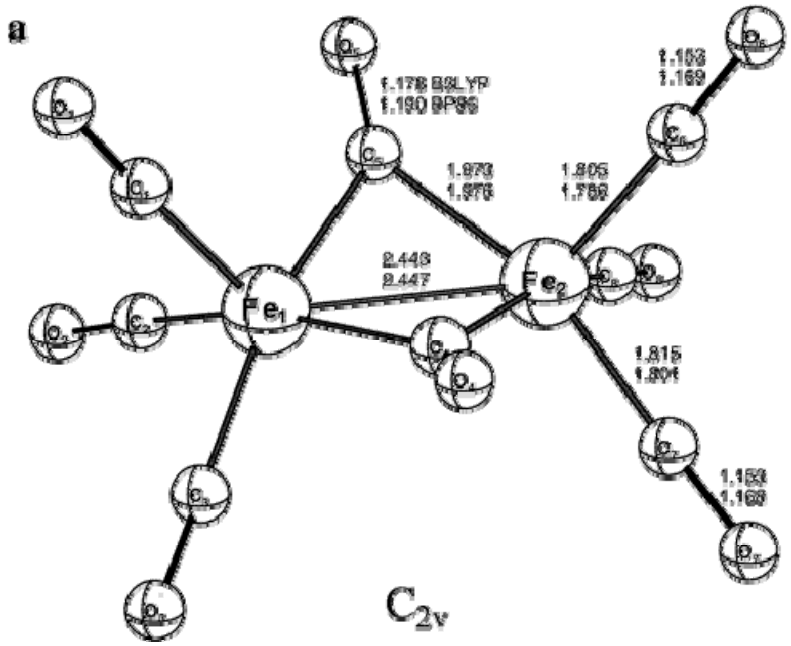




$Fe_2(CO)_8^-$ anion spectrum

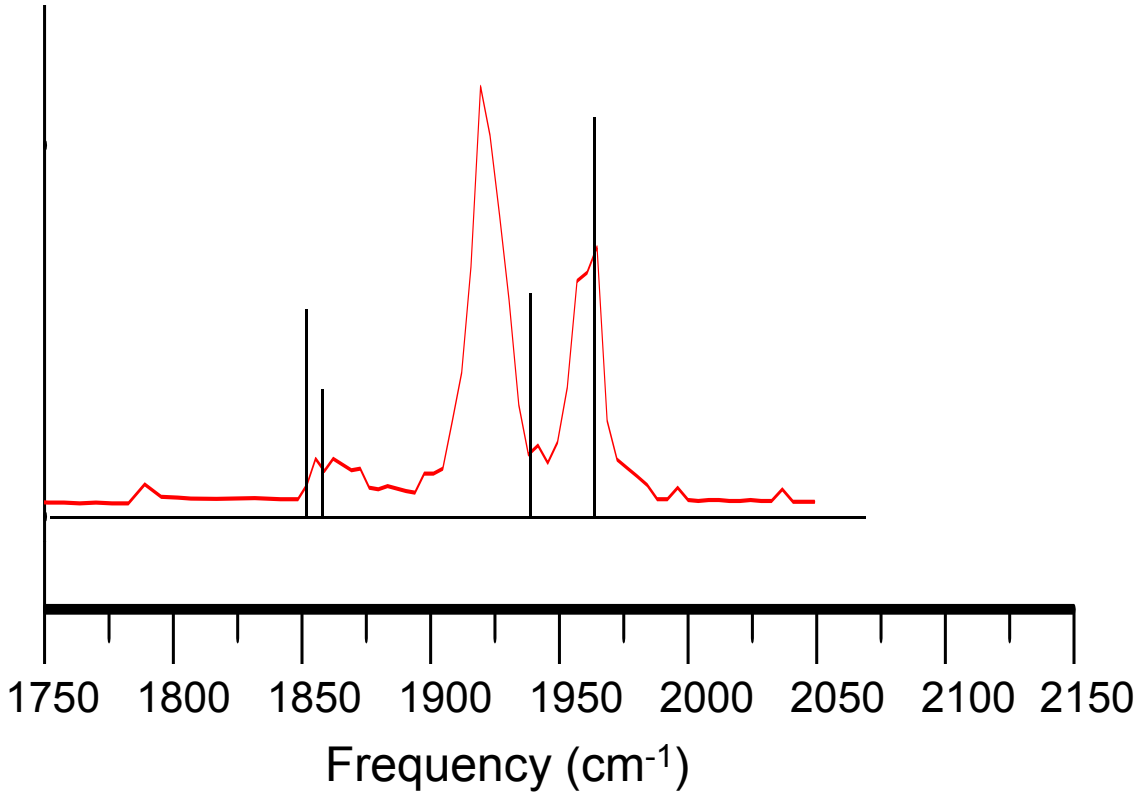


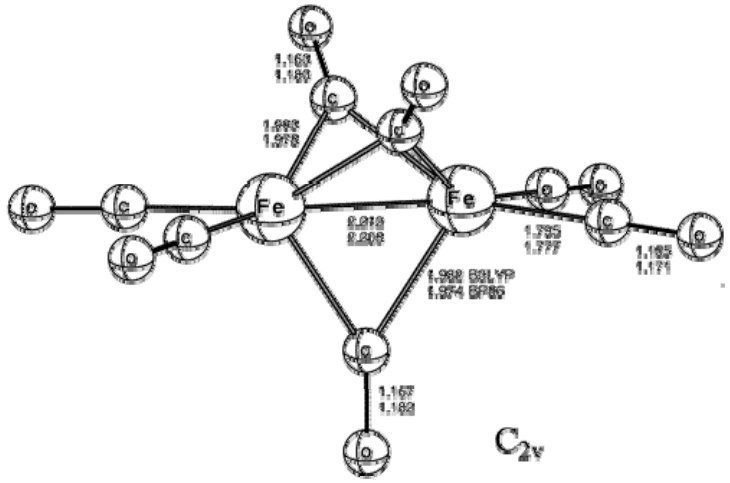
Theoretical spectrum from Schaefer's calculations for dibridged C2v structure. Average lowered by 60 cm-1 and range expanded by 10%. Imported from Excel plot



$Fe_2(CO)_7^-$ anion spectrum

$Fe_2(CO)_7$ neutral harmonic frequencies (lowered by 52 cm^{-1} and expanded by 10% about the average) and intensities from DFT calculations for triply bridged structure in ref. 1.



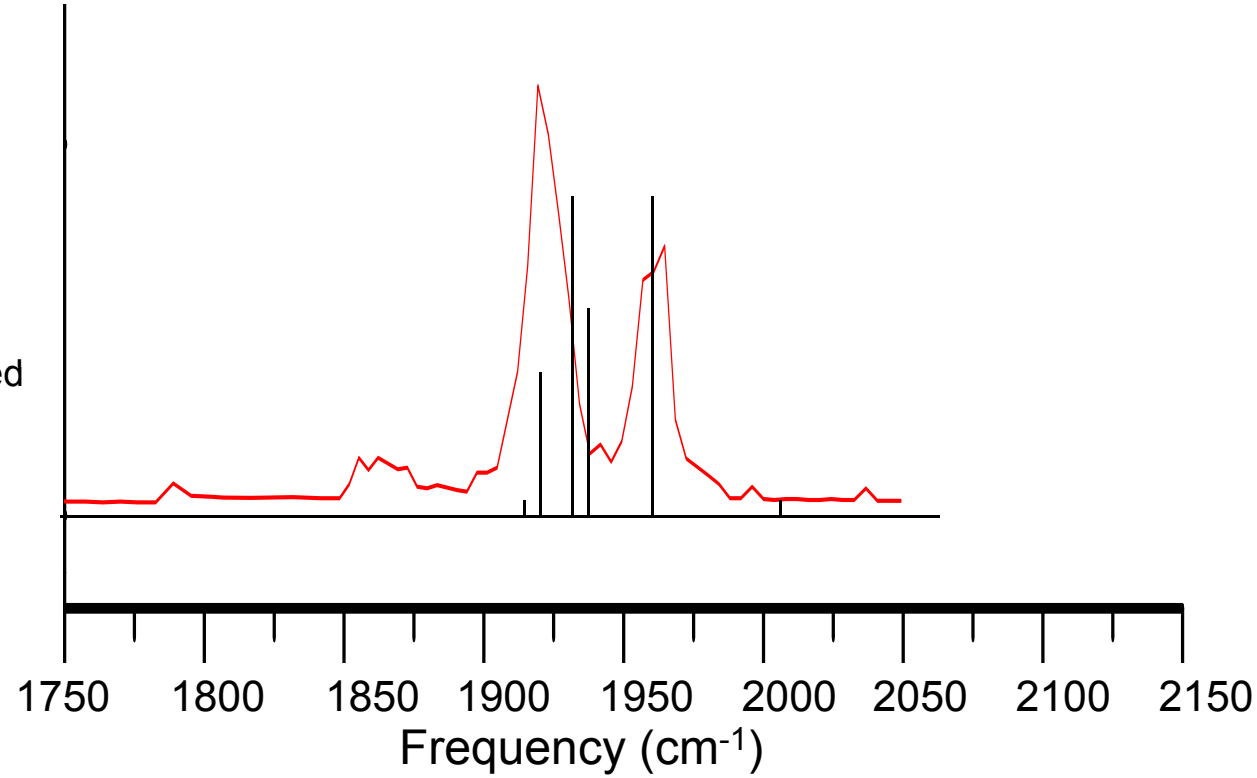


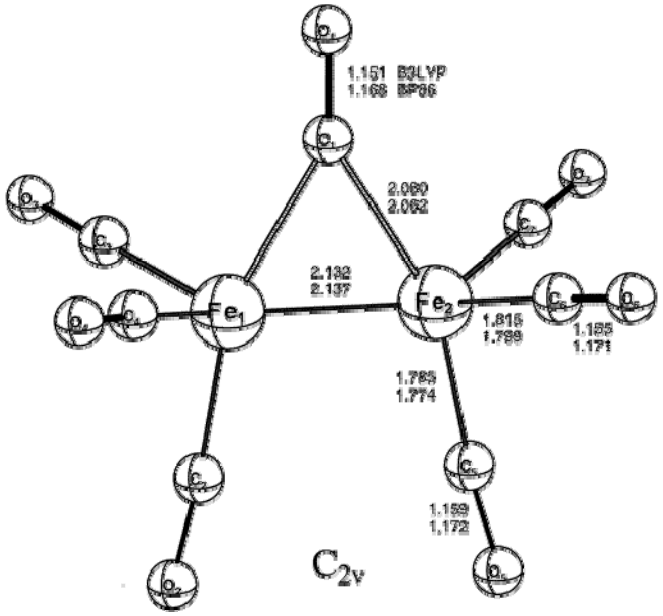
$Fe_2(CO)_7$ neutral tribridged C_{2v} structure optimized using DFT from ref. 1.

1. Xie, Schaefer and King, JACS, 122, 8746(2000)

$Fe_2(CO)_7^-$ anion spectrum

$Fe_2(CO)_7$ neutral harmonic frequencies (lowered by 52 cm^{-1} and expanded by 10% about the average) and intensities from DFT calculations for singly bridged structure in ref. 1.



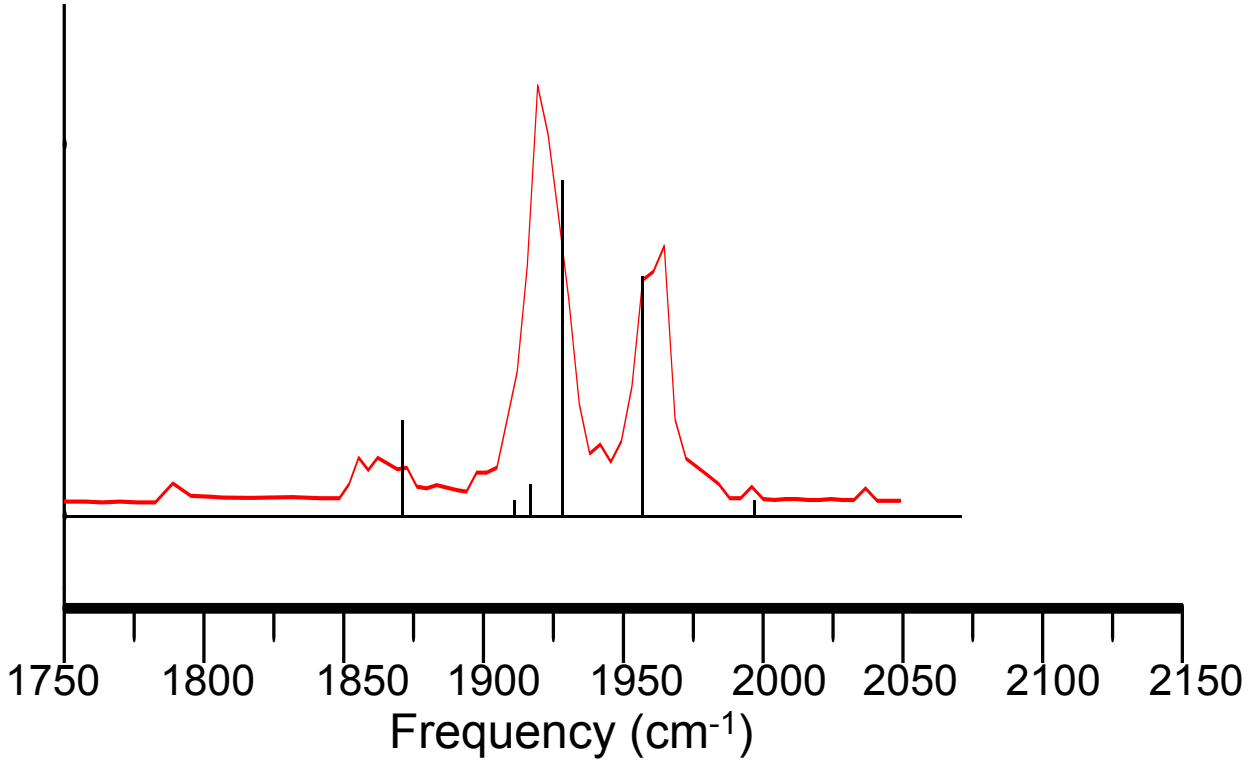


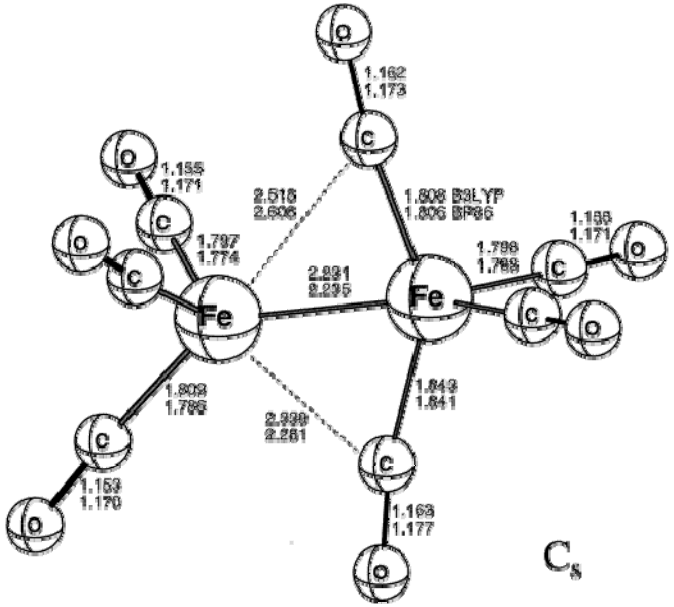
$Fe_2(CO)_7$ neutral monobridged C_{2v} structure optimized using DFT from ref. 1.

1. Xie, Schaefer and King, JACS, 122, 8746(2000)

$Fe_2(CO)_7^-$ anion spectrum

$Fe_2(CO)_7$ neutral harmonic frequencies (lowered by 62 cm^{-1} and expanded by 10% about the average) and intensities from DFT calculations for unsymmetrically doubly bridged structure in ref. 1.





$Fe_2(CO)_7$ neutral asymmetrically dibridged C_s structure optimized using DFT from ref. 1.

1. Xie, Schaefer and King, JACS, 122, 8746(2000)