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Supporting Information

Reinterpretation of Dynamic Vibrational Spectroscopy to Determine the Molecular Structure and Dynamics of Ferrocene

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Table S1. Selected output from DFT calculations of Fc (SMD solvent model[1] and B3LYP/m6-31g(d)). Among a number of DFT functionals, including PBE0 and M06[2,3], the B3LYP functional gives the best reproduction of the binding energy[4], IR[5] and UV-Vis spectroscopy[6] of Fc and derivatives.

D_{5d}	Fc - CCl_4	Fc-d – CCl_4	Fc - CH_2Cl_2	Fc-d - CH_2Cl_2	Fc - gas	Fc-d - gas
ν_1/cm^{-1}	-34.2	-30.8	-43.6	-39.3	-29.9	-26.9
ν_7/cm^{-1}	459.7	434.4	461.4	435.3	461.3	435.8
$\nu_{8,9}/cm^{-1}$	458.5	448.5	457.7	447.5	459.5	449.8
D_{5h}						
ν_1/cm^{-1}	12.8	11.5	-25.0	-22.6	17.3	15.6
ν_7/cm^{-1}	466.2	439.3	465.5	438.7	471.3	443.1
$\nu_{8,9}/cm^{-1}$	485.6	473.9	484.4	472.4	488.7	477.1
$\Delta E(E(D_{5h})-E(D_{5d}))/kJ\ mol^{-1}$	-3.2	-3.2	-2.2	-2.2	-2.4	-2.4

Figure S1. Solution IR spectra in the Q_7, $Q_{8,9}$ region of Fc for samples of Fc in hexane, dilute and concentrated solutions in paraffin and as the microcrystalline solid dispersed in KBr. The band profile of the 1% Fc in paraffin is consistent with independent solute molecules in a frozen solution.

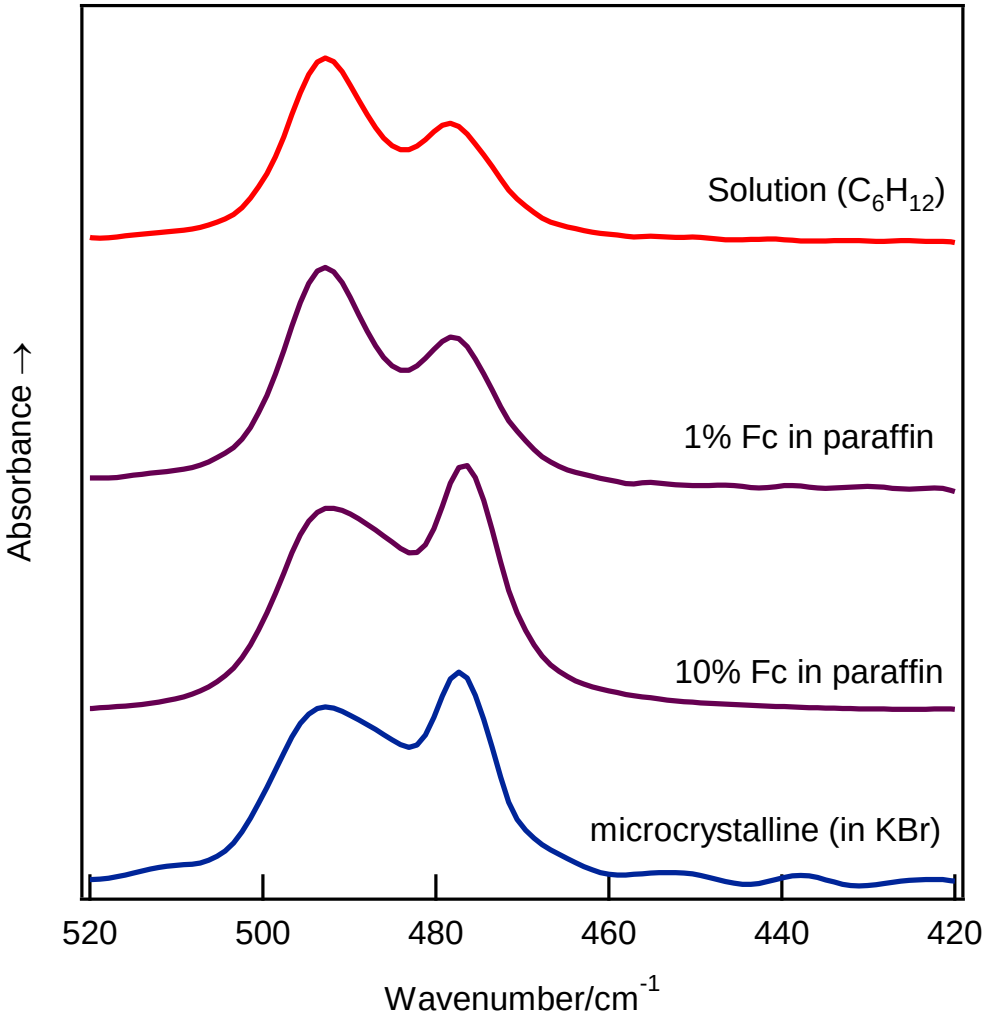
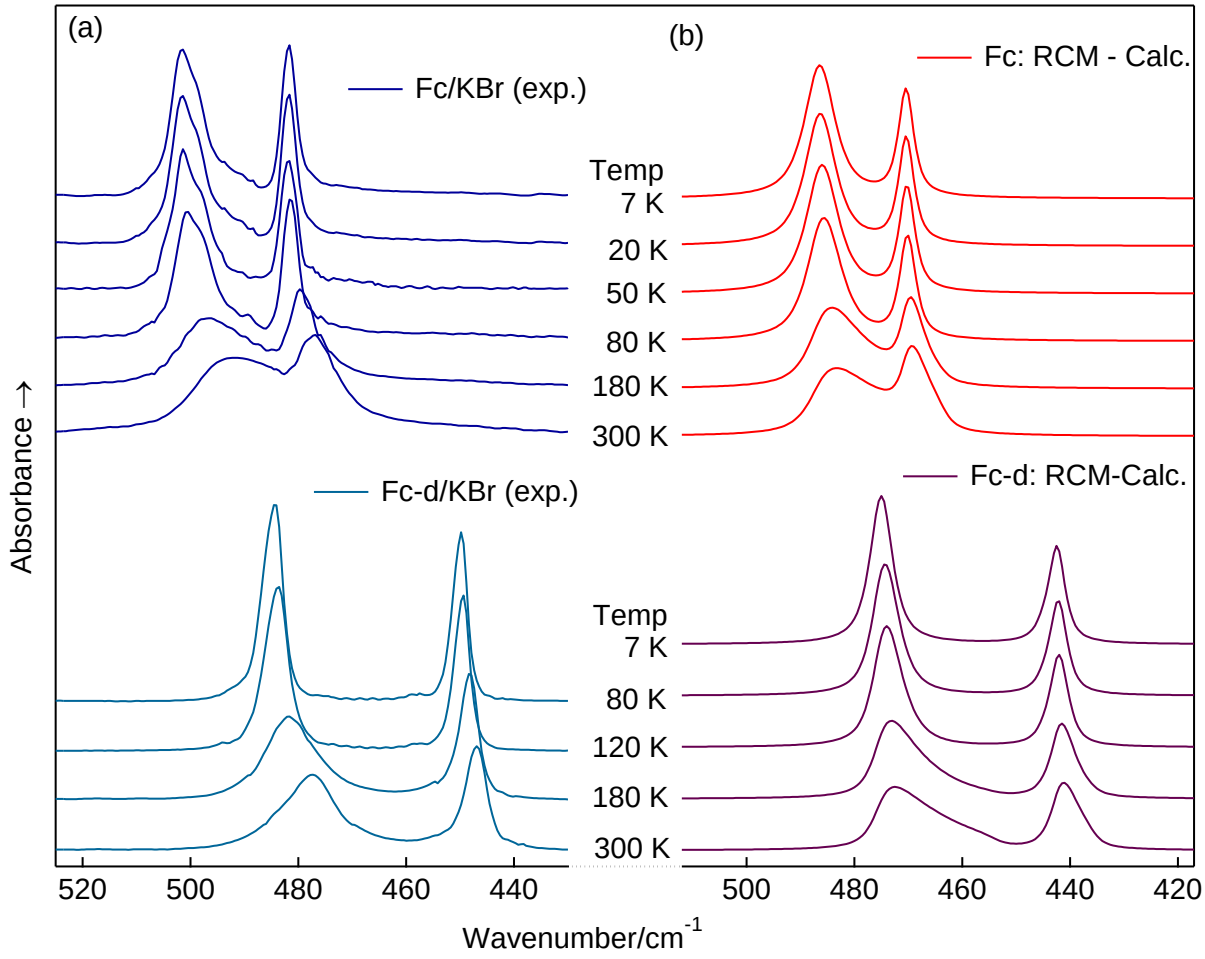


Figure S2 Temperature dependence of (a) crystalline Fc and Fc-d dispersed in KBr and (b) calculated band profiles using DFT-calculated spectra of the D_{5h} and D_{5d} forms of Fc and Fc-d and values of ΔE obtained from NMR measurements of Fc.[7]



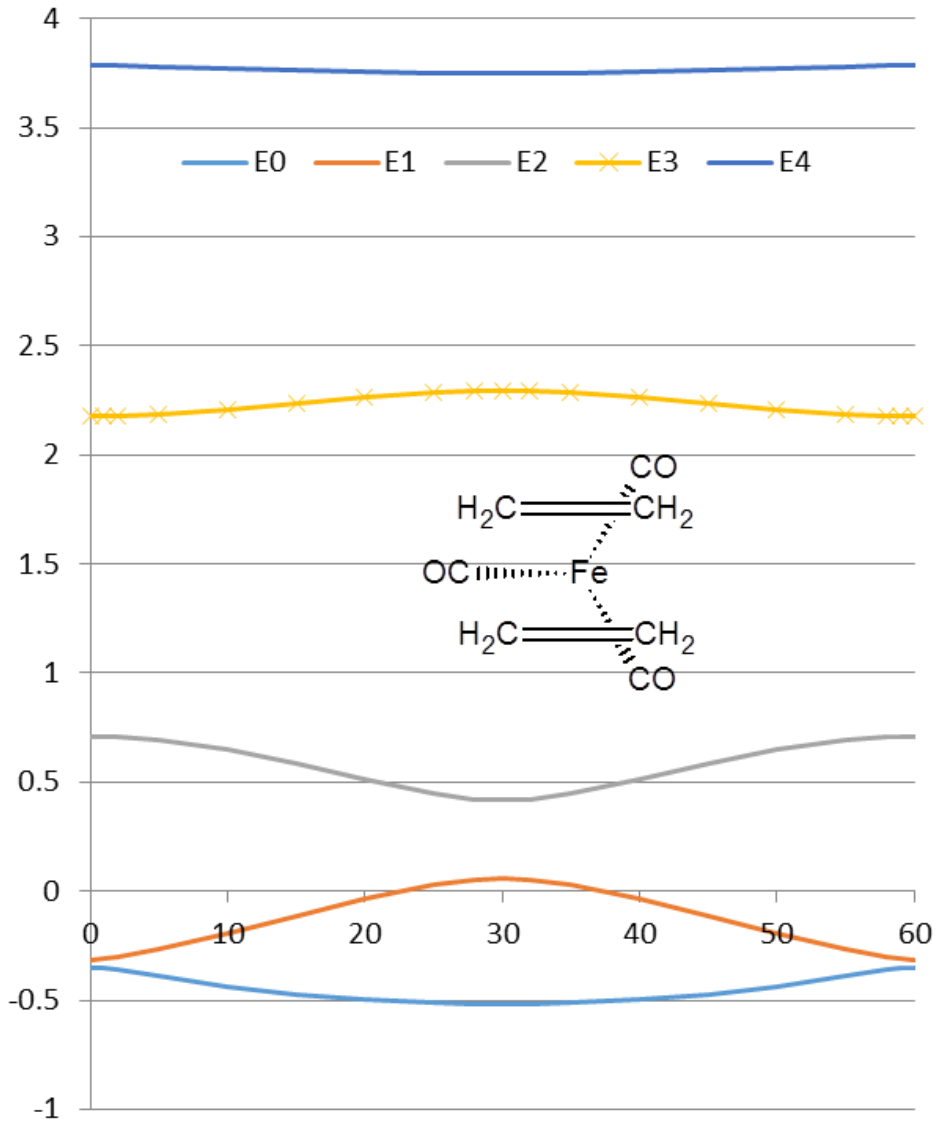


Figure S3. Ligand field calculations (conducted with an AOM approach[8]) showing the effect on the energies of the Fe d orbitals of a relative rotation of the $Fe(CO)_3$ fragment relative to the NBD ligand.

AOM parameters: (based on Hoggard[9])

e_σ (CO) = 14500 cm^{-1} e_π (CO) = -1750 cm^{-1}

e_σ (NBD) = 15000 cm^{-1} $e_{\pi\parallel}$ (NBD) = 0 cm^{-1} $e_{\pi\perp}$ (NBD) = -1500 cm^{-1}

The systematic difference in CO bond lengths in calculated Fe-C and C-O distances may be understood in terms of ligand field theory where the π anisotropy of the Fe-NBD bonding will lead to different Fe-CO π backbonding according to the orientation of the ligand.

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