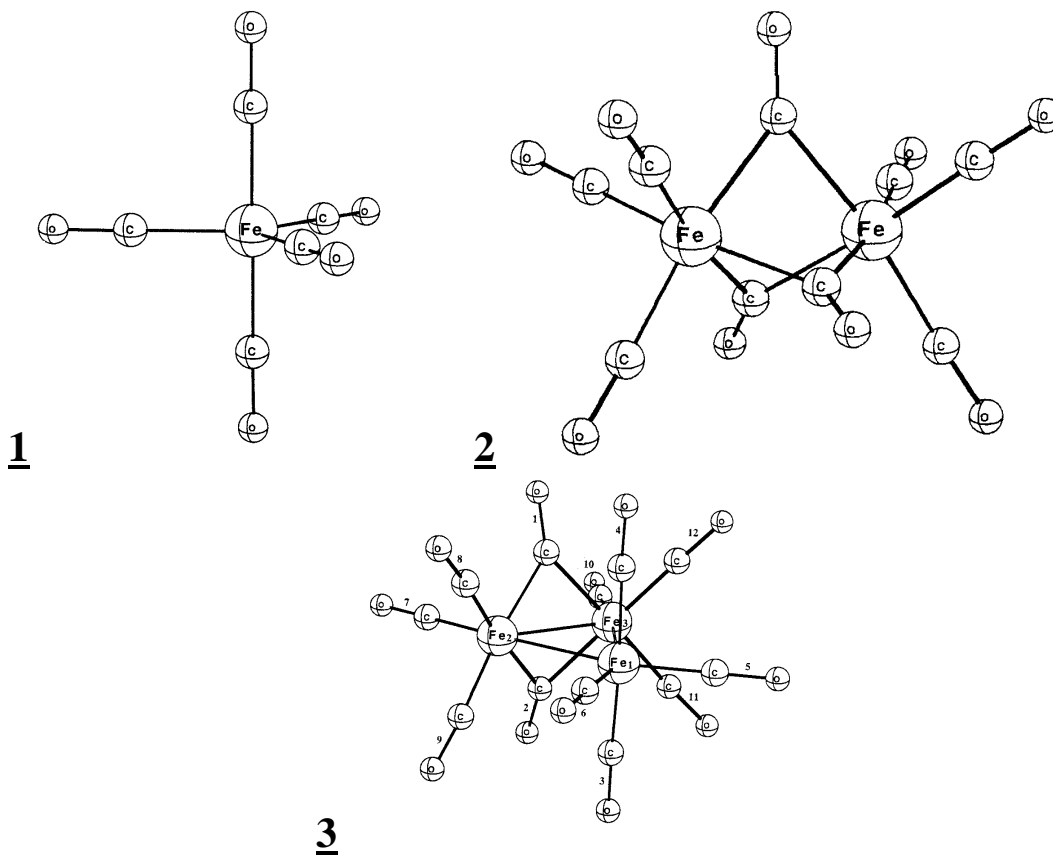


## Inelastic Neutron Scattering Studies of Iron Carbonyls

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Iron carbonyl compounds play a central role in organometallic chemistry. The best known iron carbonyls are  $\text{Fe}(\text{CO})_5$  (**1**),  $\text{Fe}_2(\text{CO})_9$  (**2**) and  $\text{Fe}_3(\text{CO})_{12}$  (**3**).



In recent years, there have been hundreds of publications per year related to these iron carbonyls. However, compared with the large quantities of experimental studies, theoretical studies with quantum mechanical methods are few, especially for the largest structure, di- $\eta$ -carbonyldecacarbonyltri-triangulo-iron,  $\text{Fe}_3(\text{CO})_{12}$ . The dearth of theoretical studies follows from the computational requirements; transition metals require much larger basis sets than the first- and second-row elements. Unfortunately, the Hartree-Fock self-consistent-field method (HF SCF) has not proven reliable for compounds containing transition metals. High-quality post-HF methods, such as the configuration interaction (CISD) or coupled cluster CCSD(T) methods, which scale according to the sixth to seventh power with respect to the size of molecule, are typically applied to molecules of more modest size.

The theoretical study of large molecules containing transition metals such as  $\text{Fe}_3(\text{CO})_{12}$  at a reliable level of theory has, therefore, been practically hampered. However, density functional theory has been shown to be able to make such large systems tractable and as a test of the theory the structures and vibrational frequencies of all three molecules were calculated using the large basis sets required for reliable results (Schaefer et al., J. Phys. Chem. A 102 (1998) 5298). The optimised structures and vibrational frequencies are generally in good agreement with the crystal structures. Even for a molecule as extensively studied as  $\text{Fe}(\text{CO})_5$ , however, there are disagreements with the literature. This degree of agreement becomes markedly worse for  $\text{Fe}_2(\text{CO})_9$  and  $\text{Fe}_3(\text{CO})_{12}$  probably because of experimental uncertainty due to the fact that many of the low frequency ( $< 800 \text{ cm}^{-1}$ ) modes are either weak or forbidden in the infrared and Raman spectra.

It is precisely in this region that inelastic neutron spectroscopy on TOSCA is at its best; the resolution is excellent ( $< 10 \text{ cm}^{-1}$ ), the low Q means that phonon wings are small and the large mass of the molecules means that the Debye-Waller factor is also small and the absence of selection rules means that all the modes are present in the spectrum. Together, these factors mean that sharp, well-resolved spectra can be anticipated. Since there are no hydrogen atoms in these samples, the scattering is dominated by the coherent contribution. The numerical methodology for the analysis of such cases is available from a previous study on TOSCA of  $\text{C}_6\text{F}_6$  (Braden et al, J. Phys. Chem. A, 104 (2000) 982). The low cross-section of the molecules means that large samples (which are readily obtainable since all three compounds are available commercially) are needed and an extended measurement time is required. We estimate that 48 hours per sample will be needed. Accordingly, we request 6 days on TOSCA.

This work will allow the characterisation of three molecules that are important, synthetically, catalytically and industrially, as well as providing a stringent test of state-of-the-art computational chemistry. These species are structurally interesting due to the presence of both terminal and bridging CO groups, the involvement of “back bonding” in the metal CO bonds and the presence of metal-metal bonds. These experiments will provide a demonstration case of the suitability of INS for studies of this large class of metal carbonyl compounds.