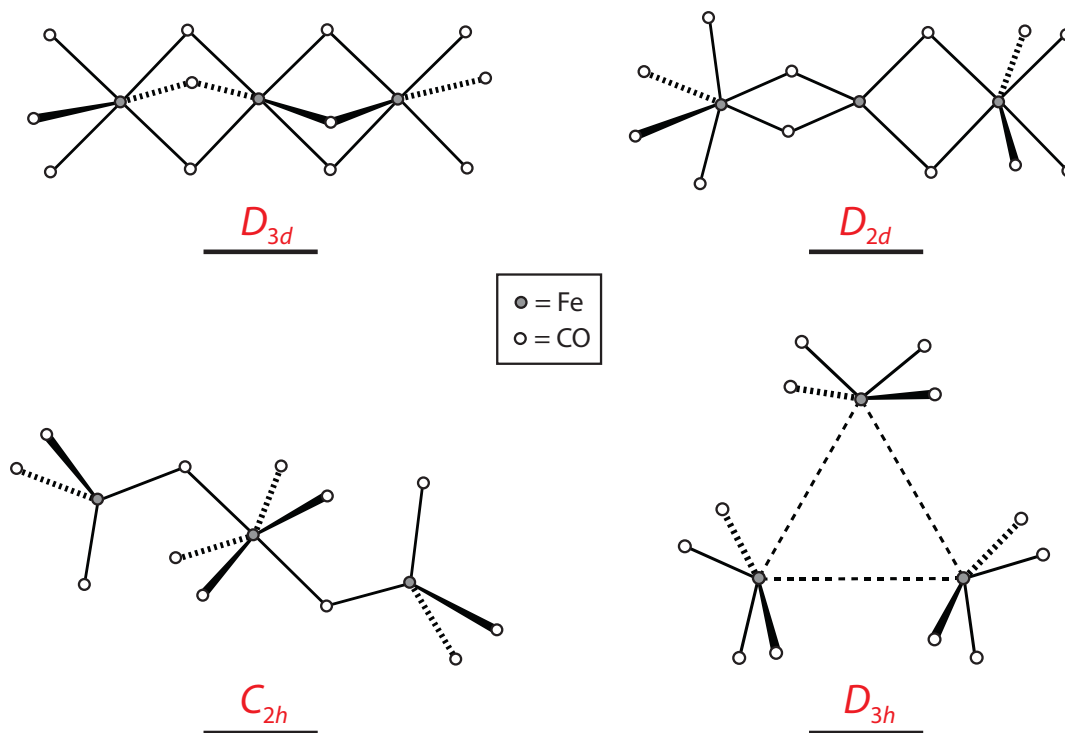


Molecular Structure: The Curious Case of Iron Tetracarbonyl

Much of the earliest organometallic chemistry concerned the synthesis and reactivity of homoleptic carbonyl compounds. Analysis of their electronic structure and geometry laid the foundation for theories of bonding in modern organotransition metal chemistry such as the effective atomic number (EAN) or 18-electron rule. One of the earliest and most intriguing examples of a metal carbonyl compound is iron tetracarbonyl, $\text{Fe}(\text{CO})_4$. The pyrophoric green compound was first prepared in 1907 by Sir James Dewar (of the eponymous flask), although it was not until over two decades later that Walter Hieber, the “father of metal carbonyl chemistry,” demonstrated through molecular weight determination measurements that the compound was trimeric. As a result, iron tetracarbonyl is more commonly referred to as triiron dodecacarbonyl in line with its molecular formula of $[\text{Fe}_3(\text{CO})_{12}]$. In this example, we will trace the history of the structural assignment of iron tetracarbonyl and consider how simple predictions from symmetry and group theory were used both correctly and incorrectly to arrive at the true solid-state structure (the molecule is fluxional in solution).

Shortly after Hieber’s determination of the aggregation state of iron tetracarbonyl, several possible structures were put forward. Most of these structures featured both terminal CO ligands, and what were believed to be “ketone-like” bridging CO ligands. The structures are displayed below in an abbreviated format.

Assign the correct point group symmetry to each structure.



Although the technique of IR spectroscopy was not prevalent at the time these structures were first proposed, its later use factors heavily into the story of iron tetracarbonyl.

Using the point symmetries from above, predict the number of IR-active CO stretches for each of the four structures. Consider bridging and terminal CO ligands separately.

D_{3d}

D_{3d}	E	$2C_3$	$3C_2$	i	$2S_6$	$3\sigma_d$
$\Gamma_{\text{CO(t)}}$	6	0	0	0	0	2
$\Gamma_{\text{CO(b)}}$	6	0	0	0	0	2

$$\Gamma_{\text{CO(t)}} = A_{1g} + E_g + A_{2u} + E_u$$

IR-active: $A_{2u} + E_u$ (2 modes)

$$\Gamma_{\text{CO(b)}} = A_{1g} + E_g + A_{2u} + E_u$$

IR-active: $A_{2u} + E_u$ (2 modes)

D_{2d}

D_{2d}	E	$2S_4$	C_2	$2C_2'$	$2\sigma_d$
$\Gamma_{\text{CO(t)}}$	8	0	0	0	4
$\Gamma_{\text{CO(b)}}$	4	0	0	0	2

$$\Gamma_{\text{CO(t)}} = 2A_1 + 2B_2 + 2E$$

IR-active: $2B_2 + 2E$ (4 modes)

$$\Gamma_{\text{CO(b)}} = A_1 + B_2 + E$$

IR-active: $B_2 + E$ (2 modes)

C_{2h}

C_{2h}	E	C_2	i	σ_h
$\Gamma_{\text{CO(t)}}$	10	0	0	2
$\Gamma_{\text{CO(b)}}$	2	0	0	2

$$\Gamma_{\text{CO(t)}} = 3A_g + 2B_g + 2A_u + 3B_u$$

IR-active: $2A_u + 3B_u$ (5 modes)

$$\Gamma_{\text{CO(b)}} = A_g + B_u$$

IR-active: B_u (1 modes)

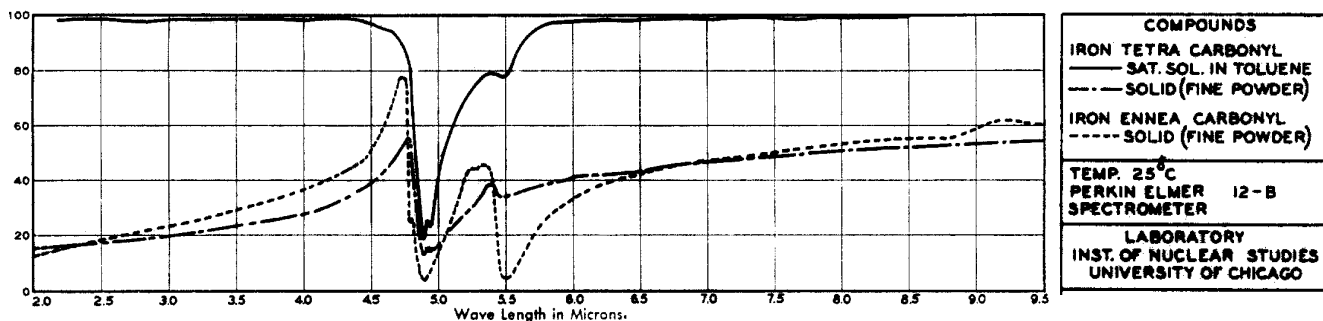
D_{3h}

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
$\Gamma_{\text{CO(t)}}$	12	0	0	6	0	2

$$\Gamma_{\text{CO(t)}} = 2A_1' + A_2' + 3E' + A_2'' + E''$$

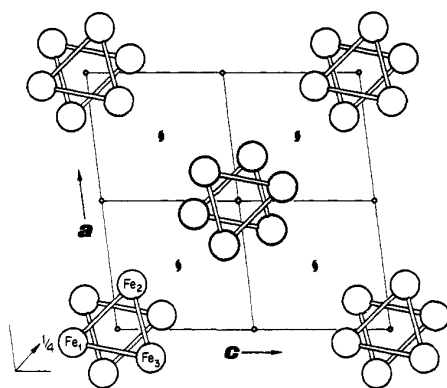
IR-active: $3E' + A_2''$ (4 modes)

This simple analysis of IR allowed CO stretches appears quite unequivocal. In no instance do any of these structures display the same number of terminal and bridging IR active CO stretches. Unfortunately, IR analyses of $[\text{Fe}_3(\text{CO})_{12}]$ were not performed until the 1950's, and even then, the data was hotly disputed (not to mention of much lower resolution than what we obtain with modern spectrometers). The first data collected on solid iron tetracarbonyl displayed two strong bands at 2020 and 2043 cm^{-1} assignable to terminal CO ligands, and one weak band at 1833 cm^{-1} assignable to bridging CO ligands (see below). Based on this preliminary data, the structure of $[\text{Fe}_3(\text{CO})_{12}]$ was assigned to that of the D_{2d} isomer.



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Concurrent with the vibrational analysis of $[\text{Fe}_3(\text{CO})_{12}]$ during the 1950s, the technique of X-ray diffraction was being employed to determine the crystalline structure. Data collected around 1957 could not be solved conclusively, but were consistent with a triangular arrangement of iron atoms (see below). In addition, the space symmetry of the crystal required an inversion center to be present in the molecule. The only triangular structure considered up until this point (D_{3h}) possessed no inversion center. Nonetheless, the presence of the apparent symmetry was ascribed (correctly) to a disorder within the crystal and some consensus was reached regarding the D_{3h} structure for $[\text{Fe}_3(\text{CO})_{12}]$. This assignment was further strengthened by data confirming an identical structure type for the osmium analog, $[\text{Os}_3(\text{CO})_{12}]$.

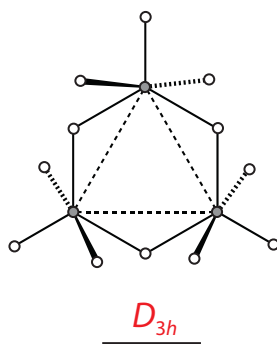


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But what about the lower energy peaks in the IR spectrum assigned to bridging CO ligands?! The original IR data had been called into question shortly after the diffraction data was published by new IR work in 1957 that sought to assign the weak absorptions in the bridging CO region to overtones

instead of fundamentals arising from bridging CO stretches. This newer work also identified an additional weak absorption in the terminal CO region at 1997 cm^{-1} and a second absorption in the bridging CO region near 1825 cm^{-1} . That same year (1957) yet another IR study was published that looked at a single crystal of $[\text{Fe}_3(\text{CO})_{12}]$. This data clearly demonstrated a polarization dependence for the unresolved bands in the bridging CO region arguing against the assignment of these bands as overtones. The band in the bridging CO region was found to show a substantial polarization with light normal to the trigonal rings (parallel to the crystallographic b axis in the figure shown above).

Consider a new hypothetical structure containing a trigonal arrangement of atoms and three-bridging CO ligands (displayed below). What is the point group of this structure? Determine the number of IR-allowed CO stretches. Is the predicted polarization for the mode(s) due to the bridging CO ligands consistent with the experiment described above?



D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
$\Gamma_{\text{CO}(t)}$	9	0	1	3	0	3
$\Gamma_{\text{CO}(b)}$	3	0	1	3	0	1

$$\Gamma_{\text{CO}(t)} = 2A_1' + 2E' + A_2'' + E''$$

$$\text{IR-active: } 2E' + A_2'' \text{ (3 modes)}$$

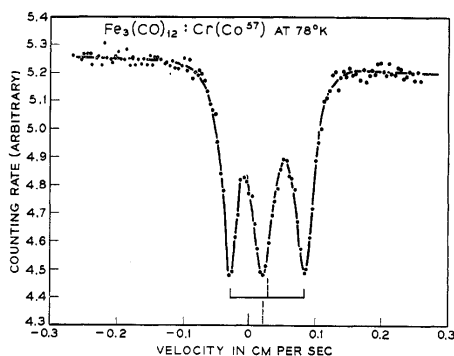
$$\Gamma_{\text{CO}(b)} = A_1' + E'$$

$$\text{IR-active: } E' \text{ (1 modes)}$$

The sole IR-active mode for the bridging CO ligands has E' symmetry and therefore should not show polarization normal to the Fe_3 plane (in the z -direction). The intensity of the E' mode should actually *decrease* with z -polarized light since it would be predicted to show an x,y -polarization. This result is inconsistent with that found in the study described above. Therefore the hypothetical D_{3h} structure displayed above is likely incorrect.

Thus, by the end of the 1950s, the solid-state structure of $[\text{Fe}_3(\text{CO})_{12}]$ was still very much a mystery. X-ray diffraction data had established a trigonal arrangement of iron atoms, with conflicting reports arguing for and against the presence of bridging carbonyl ligands. Taken together, none of the available data was consistent with any of the structures proposed above (D_{3d} , D_{2d} , C_{2h} or D_{3h}).

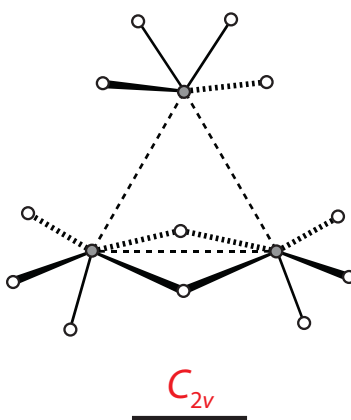
Now enter the 1960's and a new technique, that of Mössbauer spectroscopy. The Mössbauer effect was discovered in 1957 and consists of the resonant absorption of gamma rays by solids. This absorption results from high-energy transitions of nuclei within atoms (NOT spin transitions – they are of much lower energy). The usefulness of this technique is that for certain atoms such as ^{57}Fe , detailed information about the environment of the nucleus in question (geometry, oxidation state, etc.) can be ascertained. Mössbauer spectroscopy was applied to $[\text{Fe}_3(\text{CO})_{12}]$ in 1963, and yielded the following spectrum:



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What the Mössbauer spectrum of solid $[\text{Fe}_3(\text{CO})_{12}]$ showed was that there were in fact *two* distinct iron sites in the molecule (one doublet and one singlet), comprising 3 iron atoms in a ratio of 2:1. This meant that the D_{3h} structure could not be correct, as it should possess three equivalent iron atoms and therefore one distinct site. As of yet, no structure had been put forth that was consistent with the previously determined diffraction data, IR data, and also with the new Mössbauer data. It was not until shortly after the first reports of the Mössbauer spectrum of iron tetracarbonyl were published, that a graduate student, Nils Erickson, put forth the correct structure. Erickson was working with a related compound, $[\text{Fe}_3(\text{CO})_{11}\text{H}]^-$, and proposed the following structure to account for both iron tetracarbonyl, and the hydride derivative he was examining.

What is the point group of this molecule?



As is clear from the diagram, the correct structure for iron tetracarbonyl contains two different iron sites. The first site has a single iron atom with 4 terminal CO ligands and *no* bridging CO ligands, and the other site comprises two iron atoms, each having 3 terminal CO ligands and 2 bridging CO ligands. This structure type was later confirmed by improved X-ray diffraction data that clearly resolved the crystallographic disorder and later determined that in the crystal there is a slight asymmetry of the bridging carbonyl ligands. Mystery solved.

Let us now check and make sure that the true solid-state structure of iron tetracarbonyl is consistent with the obtained data (all of it!). Clearly, the structure is consistent with the Mössbauer data – two iron sites in a 2:1 ratio. Furthermore, the structure is also consistent with the early X-ray diffraction data. The iron atoms are arranged in a trigonal fashion, with a crystallographic disorder responsible for the observed inversion symmetry. What about the IR data?

Determine the IR-active CO stretching modes for the correct structure of $[\text{Fe}_3(\text{CO})_{12}]$.

C_{2v}	E	C_2	$\sigma(xz)$	$\sigma(yz)$
$\Gamma_{\text{CO(t)}}$	10	0	4	2
$\Gamma_{\text{CO(b)}}$	2	0	0	2

$$\Gamma_{\text{CO(t)}} = 4A_1 + A_2 + 3B_1 + 2B_2$$

$$\text{IR-active: } 4A_1 + 3B_1 + 2B_2 \text{ (7 modes)}$$

$$\Gamma_{\text{CO(b)}} = A_1 + B_2$$

$$\text{IR-active: } A_1 + B_2 \text{ (2 modes)}$$

Our analysis gives the following results: 7 IR active modes for the terminal CO ligands and 2 IR active modes for the bridging CO ligands. In the original IR data, all 7 modes for the terminal CO ligands were not resolvable, appearing as a broad band or as 2-3 sharper bands (see above). The 2 modes for the bridging CO ligands were observed in the early work as discussed above.

Should the IR-active modes for the bridging CO ligands show a polarization dependence?

Yes, since the bridging CO ligands are directed almost normal to the trigonal Fe_3 plane, we expect a substantial polarization for the B_2 mode with light perpendicular to the Fe_3 plane (electric dipole vector transforms as B_2 in C_{2v} symmetry). The polarization of the terminal CO ligands will be masked by the multitude of absorptions all occurring within a relatively narrow frequency window.

Subsequent work has identified all 9 CO stretching modes of the molecule using more advanced techniques and quantum chemical calculations. Thus, the message resulting from the case study of $[\text{Fe}_3(\text{CO})_{12}]$ is that one technique (even crystallography) may not be sufficient to correctly determine the structure of some molecules. Additional support obtained through complimentary analytical techniques is always a good idea!!

Further Reading

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