

A Structural Explanation for the Infrared and Carbon-13 Nmr Spectra of Triiron Dodecacarbonyl

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A complete account of the structural and dynamical properties of the $\text{Fe}_3(\text{CO})_{12}$ molecule has proved to be very difficult to obtain despite the expenditure of great effort over many years. Determination of the structure of the molecule in the crystalline solid proved surprisingly difficult due to disorder but several years ago Wei and Dahl gave the correct qualitative solution to the disorder problem.¹ More recently, their model was fully substantiated and refined using data capable of resolving nearly superposed "half atoms", and as a result, the presence of marked asymmetry in the bridges was clearly demonstrated.²

A comparative structural study of $\text{Fe}_3(\text{CO})_{12}$ and three derivatives, $\text{Fe}_3(\text{CO})_{11}\text{P}(\text{C}_6\text{H}_5)_3$, $\text{Fe}_3(\text{CO})_9(\text{PMe}_2\text{Ph})_3$ and $\text{Fe}_3(\text{CO})_8(\text{SC}_4\text{H}_8)_2$ has now shown that the $\text{Fe}(\mu\text{-CO})_2\text{Fe}$ group can vary, in the different molecules in the crystalline phase, from essentially symmetric (that is, with the two Fe-C distances of each bridge equal) to extremely unsymmetric (that is, in $\text{Fe}_3(\text{CO})_8(\text{SC}_4\text{H}_8)_2$, with distances of 1.76 Å and 2.55 Å).³ In the latter case the structure approaches a non-bridged limit and the two bridging CO groups have been described as incipient bridges. These results suggest that the energy of the molecules varies only slightly over the entire range of structural variation from non-bridged to symmetrically bridged.

It has been pointed out² that complete scrambling of all CO groups over all structural sites and over all three metal atoms can occur by repeated concerted shifts of pairs of terminal CO groups in an $\text{Ru}_3(\text{CO})_{12}$ type structure into bridging positions followed by recovery of the non-bridged structure in such a way that each bridging CO ligand passes to the metal atom adjacent to the one on which it was initially located. Conversely, starting with a bridged structure, concerted opening of the bridges followed by reestablishment of new bridges on the same or other edges will

generate the same infinite series of ligand scrambling steps. It has also been noted that since the structural evidence implies that the energy varies little for $\text{Fe}_3(\text{CO})_{12}$ over the entire range of configurations, CO scrambling should occur very rapidly in this molecule. In fact, the specific suggestion was made² that the activation energy would probably be $\leq 5 \text{ kcal mol}^{-1}$ and it was shown that this would imply that even at about -160°C , the lowest practical limit for dynamic nmr studies, only a single ^{13}C signal would be observed for all 12 CO groups.

We now report that this prediction has been verified. At -150°C in a mixture of CCl_2F_2 and CHCl_2F , using a sample prepared from $\text{Fe}(\text{CO})_5$ which had been enriched to *ca.* 40% in ^{13}C , the ^{13}C resonance is a sharp singlet. This means that even if the maximum chemical shift separation were as little as 10 ppm at 25 MHz, the activation energy must be $\leq 6 \text{ kcal mol}^{-1}$.

The existence of a relatively flat potential energy surface over all configuration space between symmetrically bridged and non-bridged structures allows some insight into the nature of the species present in solution and thus suggests at least a qualitative explanation of the puzzling infrared spectra of $\text{Fe}_3(\text{CO})_{12}$ in solution.

The work of Knight and Mays⁴ and of Poliakoff and Turner⁵, and a great deal of earlier work cited in their papers shows clearly that in solution (in a non-polar solvent such as hexane) $\text{Fe}_3(\text{CO})_{12}$ has an ir spectrum which agrees neither with that expected for a non-bridged D_{3h} molecule (for which $\text{Ru}_3(\text{CO})_{12}$ and $\text{Os}_3(\text{CO})_{12}$ provide good models) nor with that expected for a C_{2v} structure, for which $\text{Ru}_3(\text{CO})_{12}(\text{NO})_2$ provides a good model, although Poliakoff and Turner showed that in an argon matrix at 20K, $\text{Fe}_3(\text{CO})_{12}$ has a spectrum which is reasonably consistent with the C_{2v} structure on the basis of its similarity to the $\text{Ru}_3(\text{CO})_{10}(\text{NO})_2$ spectrum. In particular, there is a weak band at 2110 cm^{-1} , weak and medium intensity bands at about 1870 and about 1830 cm^{-1} and a set of six clearly resolved medium to strong bands between 2015 and 2060 cm^{-1} .

There are two principal difficulties with the spectrum of $\text{Fe}_3(\text{CO})_{12}$ in nonpolar solvents. First, the absorption in the region of bridging CO groups is of very low relative intensity and inconsistent with the presence of 1/6 of all CO groups as bridges. Second,

the absorption in the terminal CO region is very broad and lacks resolution into the four peaks expected for a D_{3h} structure let alone the seven or more peaks expected for any one less symmetrical structure. The appearance of the solution spectrum can be explained when the evidence cited above as to the nearly equi-energetic character of a whole range of structures, varying from D_{3h} (non-bridged) to C_{2v} (symmetrically bridged on one edge) is taken into account.

The weakness of the absorption in the bridging region indicates that only a very small fraction (perhaps 5 - 10%) of the molecules is present with structures at or near the limiting, symmetrically bridged (C_{2v}) structure. Moreover, the fact that there is a range of structures capable of absorbing in the bridging region can account for the fact that what little absorption does occur there is broad. The absence of a weak peak at *ca.* 2110 cm^{-1} is also easily explained because there are relatively few molecules having structures close to the C_{2v} limit which would give rise to such a band and because, again, these molecules exist over a continuous range of such structures, each absorbing at a slightly different frequency.

The remaining 90 - 95% of the molecules probably have structures lying in a continuum toward the D_{3h} limit, but with varying degrees of incipient bridging pairs. The spectrum of terminal CO absorptions will vary continuously as the structure varies through the continuum. The band energy for a CO group is a fairly sensitive function of the degree to which that group has moved from a strictly terminal role into an incipient bridging role. This is shown³ by the fact that in $\text{Fe}_3(\text{CO})_8(\text{C}_4\text{H}_8\text{S})_2$, where two CO groups have moved only a little way toward bridging positions, they give rise to absorption as low as about 1900 cm^{-1} . Moreover, as any two CO groups change their degree of bridging character all of the CO modes due mainly to the remaining ten CO groups will change somewhat in frequency.

The broad, unresolved terminal CO absorption of $\text{Fe}_3(\text{CO})_{12}$ in solution can thus be understood as the convolution of many spectra due to a whole range of structures with varying degrees of establishment of bridging.

A further observation which is consistent with the above considerations is that the spectrum varies with solvent polarity as expected, since the C_{2v} (bridged) structure is the most polar while the D_{3h} structure is non-polar. As solvent polarity increases, increased

absorption in the bridging region due to tilting of the potential energy surface in favor of the bridged structure should be observed, and as Fig. 1 shows, it is.

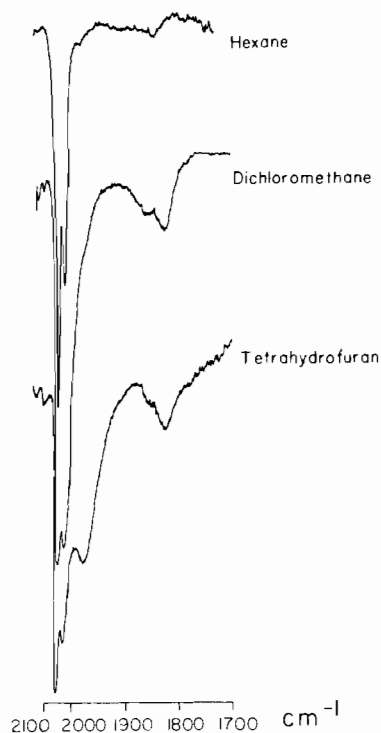


Fig. 1. Infrared spectra of $\text{Fe}_3(\text{CO})_{12}$ in the CO stretching region showing the effect of solvent polarity upon the relative intensity of the bands due to symmetrical, or nearly symmetrical, bridging CO groups.

While we believe that the proposals made here regarding the infrared spectra are qualitatively correct we are cognizant of the need for more detailed and quantitative experimental study and analysis before this problem can be regarded as fully resolved.

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