Inorganica Chimica Acta, 31 (1978) 217–222
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Solid State Studies.
Pt. XV. The ν(CO) Vibrational Spectra of Four Crystalline η^5-$C_5H_5Fe(CO)_2$ Species

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Received April 8, 1978

The ν(CO) infrared and Raman spectra of a series of related η^5-$C_5H_5Fe(CO)_2X$ (X = Sn or Ge species) compounds are reported. Relative band intensities give evidence of intensity stealing by an intermolecular vibrational coupling mechanism.

Introduction

Whenever significant intermolecular vibrational coupling occurs between the vibrators in a crystal lattice any analysis based on the individual vibrators is not usually adequate to interpret the infrared and Raman spectra. In such cases a factor group analysis is required. The infrared and Raman spectra from polycrystalline samples usually suffice to determine the applicability of such an approach, often by the appearance of non-coincidences between bands of which the counter-parts in solution are coincident. Relevant to the present context, studies of the vibrational spectra of metal carbonyl species – both polycrystalline and single crystal – have been made by several groups and have clearly demonstrated the need for a factor group interpretation in most cases [1].

However, several aspects of the application of factor group analyses remain unclear. For instance, does mixing occur under C_1 site symmetry between what are, in the isolated molecule, symmetry distinct modes? This is related to another pertinent question, that of the information contained in the relative band intensities of factor group components.

We have attempted to gain further insight into such problems by a study of the ν(CO) vibrations in compounds containing the η^5-$C_5H_5Fe(CO)_2$ unit, designated (Fe). This is an attractive series of compounds to study as a wide variety of species exist that are usually reasonably easy to prepare and handle; further full crystal structure data are available for many members of the series. Another important feature is the simple vibrational nature of the isolated $Fe(CO)_2$ unit, which means that the solid state spectra are not complicated by the presence of site group splittings such as may occur when degenerate vibrations are present in the isolated molecule.

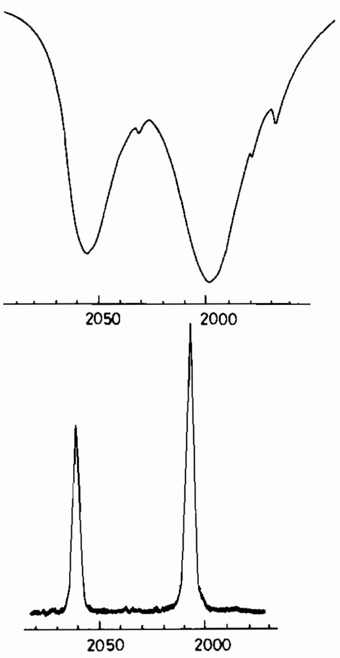


Figure 1. ν(CO) infrared (upper) and Raman (lower) spectra of crystalline η^5-$C_5H_5Fe(CO)_2SnCl_3$.

The present work is devoted to a study of four (Fe) derivatives containing $MX_n^{(4-n)-}$ groups, where M is either Sn or Ge and X is a halogen. This series was chosen because it is to be expected that the members will have electronic similarities and that any gross differences observed may well be caused by crystal structure effects such as molecular packing and orientation. Further, crystal structure data are available.

Results and Discussion

The complex (Fe)$SnCl_3$ crystallises in the triclinic $P\bar{1}(C_i^1)$ space group with Z = 2 [2, 3]. Both the solution and solid state I.R. and Raman spectra in the carbonyl stretching region are shown in Fig. 1.

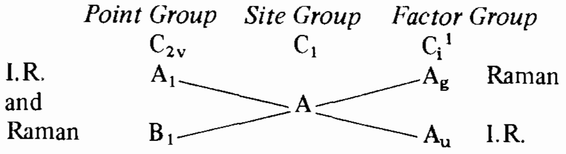
In common with most other compounds containing the (Fe) unit for which data are available,

TABLE I. ν(CO) Spectra of Crystalline η^5-$C_5H_5Fe(CO)_2$-$SnCl_3$. Relative intensities are given in brackets.

I.r.		Raman
		2060 (7.1)
2054 (8.7)	(6.5)	
2030 (1.7)		
		2007 (10)
1998 (10)	(10)	
1982 (1.7)		
1966 (4.3)		

(Fe)$SnCl_3$ shows two strong peaks in both infrared and Raman spectra of dichloromethane solutions in the 2000 cm^{-1} region. The spectra are coincident, the higher frequency (A_1) peak corresponding to the in-phase stretching vibration of the two CO groups, the lower frequency (B_1) mode being the corresponding out-of-phase vibration. In the solid state spectra there are again two peaks in both infrared and Raman.

The intensities of the bands in each spectra are approximately equal, but the bands are now non-coincident. This non-coincidence is in accordance with predictions of a C_i factor group analysis as shown below. Spectral data are given in Table I.

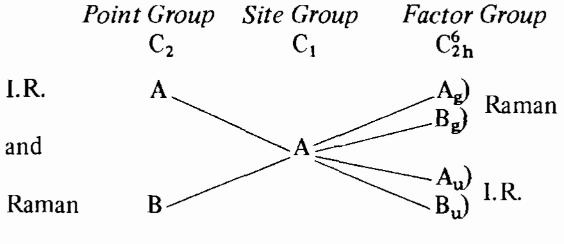


There are two points of particular interest to be noted in the spectra of tuis compound. The first is the observation of rather similar intensity patterns in the solution and solid state spectra.

This behaviour is to be expected on the simple oriented gas model because the existence of a centre of symmetry relating two vibrators forces the molecular vibrational axes to be parallel (this applies equally to the derived dipole moments in the infrared and derived tensor elements in the Raman). A simple addition of the molecular quantities is, therefore, all that is needed to explain the solid state observations.

The second point concerns the small peaks which are seen in the solid state infrared spectrum of this compound. Similar peaks occur in the spectra of all of the species reported in this paper. As is evident for the present compound, the peaks cannot have a factor group origin. Further, their reproducibility with respect to sample preparation and purification indicates that they are not caused by impurities. A common explanation for such peaks has been to ascribe them to ^{13}CO-containing molecules. This explanation assumes that the mass effect of this isotopic substitution is sufficient to effectively completely decouple the oscillators from the $\nu(^{12}CO)$ modes. Work which we have carried out on the other species suggests that such decoupling only occurs in the absence of significant factor group effects [4]; However, the absence of factor group effects is not in accord with the general observations in this paper. A further piece of evidence supporting this view is gained by a comparison with the ^{13}CO modes in the solution infrared spectra, where rather different relative intensities and positions are observed. Our current opinion is that small peaks such as these originate in multi-phonon processes, which are only spectrally apparent because of intensity stealing from a nearby strong band.

$(Fe)_2SnCl_2$ and $(Fe)_2GeCl_2$ are isomorphous, crystallising in the monoclinic space group $C_{2/c}(C_{2h}^6)$ with Z = 4 but with four independent $Fe(CO)_2$ moieties per primitive unit cell on general sites [5–7]. The close similarity between the structures of these compounds extends to relatively minor details of orientation in the unit cell. Their solid state spectra in the 2000 cm^{-1} region are shown in Fig. 2 and Table II. It is evident that an isolated-molecule approach is inadequate to describe the spectra and that a factor group interpretation is indicated. The correlation between point, site and factor groups are given below, together with the spectral activities predicted.



In solution four infrared and four coincident Raman peaks are predicted for a molecule of C_2 symmetry, assuming that all molecular CO vibrators are coupled. Alternatively, one may regard the molecular symmetry as C_{2v}, in which case only three ν(CO) features are expected in the solution infrared spectrum. Not surprisingly, the observed spectrum consists of three strong and one weak band; it is clear from their general pattern that this is yet another example in which the magnitude of the coupling between CO groups separated by three atoms is not too dissimilar from that between CO groups bonded to a common metal atom. Although we have not been able to obtain solution Raman data for a given conformation these would be expected to differ from solution infrared data only in peak intensity.

In the solid state the molecules clearly have C_2 symmetry and so the correlation table given above is appropriate. The observed spectra show four infrared bands and four Raman bands of which three are

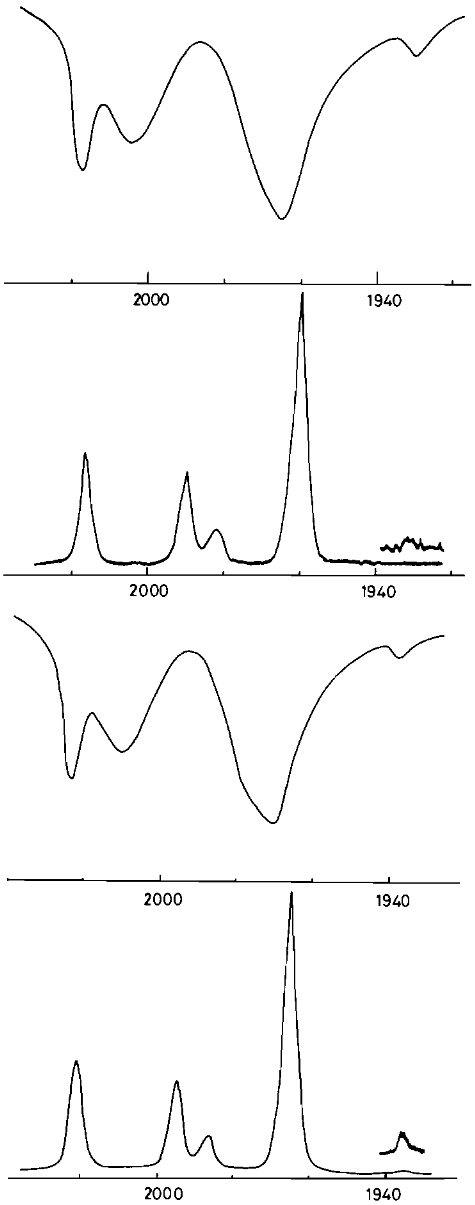


Figure 2. ν(CO) infrared (upper) and Raman (lower) spectra of crystalline a) $[\eta^5$-$C_5H_5Fe(CO)_2]_2SnCl_2$ and b) $[\eta^5$-$C_5H_5Fe(CO)_2]_2GeCl_2$.

TABLE II. ν(CO) Spectra of Crystalline $[\eta^5$-$C_5H_5Fe(CO)_2]_2SnCl_2$ (A) and $[\eta^5$-$C_5H_5Fe(CO)_2]_2GeCl_2$ (B). Relative intensities are given in brackets.

A		B	
I.r.	Raman	I.r.	Raman
2018 (8.6)		2023 (8.2)	
	2016 (3.7)		2021 (4.4)
2004 (6.4 br)		2009 (7.2 br)	
	1988 } (4.8)		1994 (3.6)
	1982 }		1985 (1.3)
1971 (8.6 sh)		1974 sh } (10)	
1966 (10)		1970 }	
	1960 (10)		1965 (10)
1930 (w)		1937 (w)	

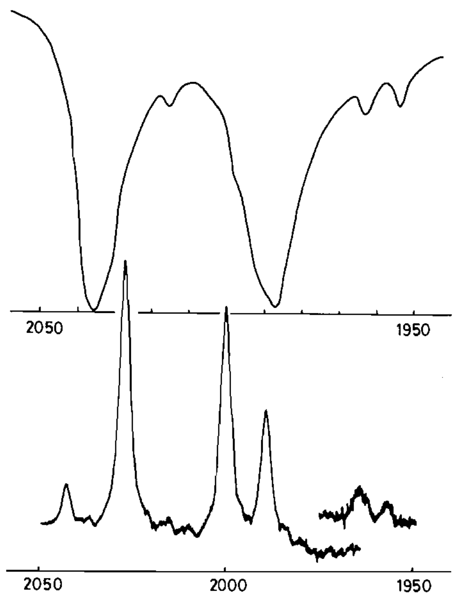


Figure 3. ν(CO) infrared (upper) and Raman (lower) spectra of crystalline η^5-$C_5H_5Fe(CO)_2SnBr_3$.

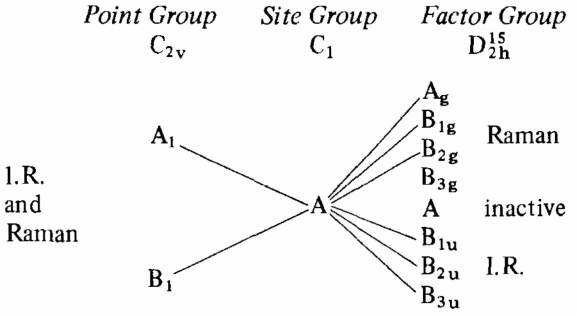
clearly non-coincident; one near coincidence is probably accidental. Either spectrum *on its own* might therefore be interpreted on an isolated molecule basis; it is the comparison between them that makes the presence of factor group splitting clear. It is pertinent to note that when Z = 2 for a centrosymmetric primitive unit cell, the factor group modes may be regarded as ++ or +– combinations of corresponding modes of the isolated molecules, one combination being infrared and the other Raman active. The relative phases in these combinations refer to behaviour under the operation of inversion in the centre of symmetry so that the arguments developed above for $(Fe)SnCl_3$ also apply to $(Fe)_2SnCl_2$ and $(Fe)_2GeCl_2$, provided that no coupling occurs between modes which, whilst of the same symmetry in the solid state, are of different molecular symmetry parentage. In this context it is relevant to comment on magnitudes. The coupling between the individual vibrators of an $Fe(CO)_2$ group produces a splitting of *ca.* 50 cm^{-1} whilst the coupling between the two $Fe(CO)_2$ units in any one molecule leads to a splitting of about half of this amount. The correlation field produces average splittings of about 8 cm^{-1}, taking the simplest interpretation of the solid state spectra (no 'crossing over' of bands).

TABLE III. ν(CO) Spectra of Crystalline η^5-$C_5H_5Fe(CO)_2$-$SnBr_3$. Relative intensities are given in brackets.

I.r.	Raman
	2043 (1.4)
2036 (10)	
	2027 (10)
2016 (0.5)	
	2000 (8.2)
	1989 (5.0)
1987 (9.8)	

The third case which we consider is that of (Fe)-$SnBr_3$. This compound crystallises in the orthorhombic space group P_{bca} (D_{2h}^{15}) with 8 molecules in the unit cell [8]. It is evident that the increased number of molecules in a unit cell will give rise to more complicated spectra.

The observed solid state spectra, Fig. 3, clearly demonstrate the need for a factor group approach. The analysis and predictions for this complex are given below. The data are detailed in Table III.



Eight Raman and six infrared bands, with no conicidences, are predicted. The spectra, neglecting small satellite bands, are obviously much simpler than this showing two strong infrared and four Raman bands; and an explanation must be sought.

A comparison with the three species already discussed in this paper makes it clear that the spectra are to be interpreted on a molecular basis together with a small correlation field effect. This latter perturbation is evidently smaller than the coupling between the $Fe(CO)_2$ units in $(Fe)_2SnCl_2$ and $(Fe)_2$-$GeCl_2$. Indeed, the average correlation field effect seems fairly constant for all of the compounds reported in this paper (*ca.* 8 cm^{-1} splittings), a finding which is perhaps not unexpected.

Two reasons have previously been advanced when unexpected spectral simplicity has been found for species clearly showing factor group splittings. Firstly, there may be a fortuitous molecular orientation within the unit cell leading to low resultant intensities for some bands [9]. Secondly and not necessarily distinct, the effective vibrational unit cell may differ from the crystallographic [10].

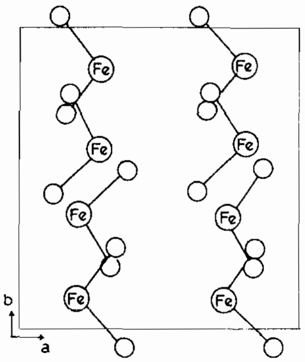


Figure 4. The unit cell of η^5-$C_5H_5Fe(CO)_2SnBr_3$ viewed down the *c* axis. Each CO group is represented by a circle.

A diagram of the crystallographic unit cell of $(Fe)SnBr_3$ is shown in Fig. 4. From this it is apparent that the dipole moment change associated with the A_1 mode of the isolated molecule is constrained largely to a direction parallel to the crystallographic a-axis with only small contributions parallel to the b- and c-axes.

The dipole change associated with the B_1 mode, however, has only small components parallel to the a- and c-axes and is predominantly directed parallel to the b-axis. If these restrictions are made absolute the modified prediction is that the infrared and Raman spectra should each consist of two strong bands, in good apparent agreement with the observed infrared spectrum. The Raman spectrum shows two strong bands, one of medium intensity and one rather weaker.

It is evident that whilst the simple analysis given above gives a reasonable qualitative account of the two spectra, the molecular "misalignment" is such that more quantitative calculations are needed before it can be concluded that molecular alignment is the correct explanation of the spectra. We have therefore performed quantitative calculations using the orientated gas model. In view of the apparent similarity of factor group effects for all the species considered in this paper we have carried out similar analyses for all of them. This comparison will, hopefully, provide some test of the applicability of the oriented gas model to $(Fe)SnBr_3$; in particular, deviations caused by mixing between modes of different molecular parentage should be indicated.

The C–O bond axes were taken to define both vector and a tensor axis (effectively, therefore, we assumed colinear M–C–O bonds). The derived bond polarizability tensors were assumed to be ellipsoids of revolution so that only two (*a*, the transverse component and *b* the longitudinal) quantities were needed to define them. The ratio of the two principal derived polarizability tensor elements was varied. Of

TABLE IV. Predicted ν(CO) Intensity Ratios.

	$(Fe)SnCl_3$		$(Fe)_2SnCl_2$		$(Fe)SnBr_3$	
	I.r.	Raman*	I.r.	Raman**	I.r.	Raman***
					B_{3u} 7.5	A_g 10
Molecular A-mode region	8.7	8.7	B_u 6.4	A_g (3.7)	B_{2u} 0.8	B_{3g} 0.5
			A_u 5.6		B_{1u} 0.0	B_{2g} 0.1
						B_{1g} 0.5
				B_g + B_g (3.7)		
			A_u 5.8		B_{1u} 10	B_{1g} 0.3
Molecular B-mode region	10	10	B_u (10)	A_g (10)	B_{2u} 0.5	B_{2g} 8.2
					B_{3u} 0.0	B_{3g} 0.8
	$^*\frac{b}{a} = -1.1$		$^{**}\frac{b}{a} = -1.1$		$^{***}\frac{b}{a} = -0.8$	

particular note is the observation that even for a general derived polarizability tensor (and so intensity terms which are functions of *a*, *b* and *c*, a second transverse component) the predictions of relative intensity for the B-derived modes are independent of the ratios of these quantities. Results are given in Table III.

In the case of $(Fe)SnCl_3$ the agreement between the calculated and observed spectra is inevitably good since the data serve to uniquely define the parameters of the theory.

For both $(Fe)_2SnCl_2$ and $(Fe)_2GeCl_2$ the predictions are again in good accord with the observations, with one exception. This exception concerns the two medium intensity bands close together at 1980 and 1988 (Sn) and 1985 and 1994 (Ga) cm^{-1} in the Raman spectra. A preliminary single cyrstal Raman study of the tin compound indicated that these peaks are associated with vibrations of the same symmetry species (the two outer, stronger, bands being similarly related to each other). When the intensity of the inner pair was aggregated in the calculations, good agreement was found with the experimental observations. However, when considered separately there was no agreement. Note that this result is independent of *b/a*. We therefore conclude that there is appreciable intensity re-distribution between these two modes.

The above results provided a firm basis against which to assess the results of the calculations on $(Fe)SnBr_3$ for which, again, with one exception the quantitative predictions are in reasonable accord with experiment. The exception again concerns the Raman spectrum where no low frequency band is predicted to have more than one tenth of the intensity of the strong peak at 2000 cm^{-1}. However, it is expected that in this region there will be a mode which is of the same symmetry species as the most intense band in the Raman spectrum. If intensity transfer occurs to the low frequency mode it will involve two bands separated by less than 38 cm^{-1}. Our tentative conclusion, therefore, is that the molecular orientation explanation for the simple vibrational spectra shown by this compound is correct, but that some mixing also occurs. In measurements on $Mn(CO)_5Br$, to be reported elsewhere, we have been able to establish the presence of such mixing [11].

As part of the Raman intensity calculations the values of *b/a* were varied. Because of the similar nature of the compound studied it would be reasonable to expect some consistency between acceptable values for the various compounds. The quadratic nature of the equations leads to two roots in every case, but for all a solution was found for *b/a* ~ −0.9 ± 0.4 (Table IV); the other roots are all much larger and negative. Negative values are commonly found for *b/a* values for metal carbonyls.

Conclusion

The present study demonstrates the applicability of the factor group method to iron dicarbonyl species but strongly suggests that the apparent simplicity of the spectra obtained may be somewhat deceptive. Intensity calculations, particularly of the Raman spectra, strongly indicate that vibrations which are of common symmetry in the crystal but of different molecular parentage, may be coupled together.

Experimental

Starting from $(\eta^5\text{-}C_5H_5Fe(CO)_2)_2$ the tin [12–14] and germanium [14] compounds were prepared by literature methods and separated by repeated recrystallisation after separation using methylene chloride in a Sohxlet extraction.

Very similar infrared spectra were obtained using Nujol mulls or the corresponding potassium halide discs (anion exchange was commonly found) on PE325 and 125 spectrometers at *ca.* 1 cm^{-1} resolution. Raman spectra were difficult to obtain as the compounds only withstood about 5 mw of red laser radiation. A Spex 1401 with HeNe or Kr^+ laser was used at resolutions between 2 and 4 cm^{-1}. Intensities were generally measured by peak height, or peak height X half height width when the achieved resolution was less than the true bandwidth. No corrections for spectrometer response were made.

The calculations of infrared and Raman relative intensities followed a standard oriented gas model approach with a cylindrical bond tensor and taking relevant data for the transformation matrices from the published crystal structure determinations. The depolarisation of the incident laser light by successive reflection off the randomly distributed crystallites is assumed complete [15, 16].

Acknowledgement

One of us, SLB, is indebted to the Science Research Council for financial support.

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