

Low Frequency Vapour Phase Infrared Spectra of Metal Carbonyls. Derivatives of the type $\text{XMn}(\text{CO})_5$, (where $\text{X}=\text{Br}, \text{Cl}, \text{H}, \text{D}, \text{CH}_3, \text{CD}_3, \text{CF}_3$)

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Summary: Many vibrations which occur in the far-infrared region of spectrum are similar to the types of vibrations found in other regions of the spectrum. They fall in the far-infrared because the atomic masses are large and/or the forces resisting the deformation are small. Most of the vibrations of metal carbonyls fall into this category and hence they give a good example of what can be expected. A number of metal carbonyls e.g. $\text{BrMn}(\text{CO})_5$, $\text{ClMn}(\text{CO})_5$, $\text{HMn}(\text{CO})_5$, $\text{DMn}(\text{CO})_5$, $\text{CH}_3\text{Mn}(\text{CO})_5$, $\text{CD}_3\text{Mn}(\text{CO})_5$ and $\text{CF}_3\text{Mn}(\text{CO})_5$, have been studied in the vapour phase for first time and it is now possible to discuss the general nature of the vibration in this region. The metal-CO stretching frequencies are found between 350 and 475 cm^{-1} . The metal-C-O bending frequencies are more scattered and fall between 275 and 650 cm^{-1} depending in part upon the phase of motion. The OC-M-CO bending modes occur between 50 and 150 cm^{-1} . Other vibrations are found in this region when one or more CO group are replaced by groups in which heavy atoms are attached to the metal. Factor which shifts the positions of the frequencies, such as mass or charge on the metal carbonyl moiety, will be discussed.

Introduction

The infrared spectra of metal carbonyl compounds below 700 cm^{-1} provides good examples of the use of this region as a supplement to higher-frequency spectra for structural studies. The spectra contains quite a few bands of reasonable intensity and the position of some of these bands may be correlated with the structural details of the molecules. This region thus serves as both a fingerprint region and as a region providing useful molecular information.

The vibrational spectra of metal carbonyls and their derivatives have been extensively studied particularly in the CO stretching region, and the frequencies of vibrations have been correlated with the acceptor abilities of the ligands and with the degree of substitution of the carbonyl complex [1, 2]. There have also been studies of lower frequency vibrations, such as the metal-carbon stretching [$\nu(\text{MC})$] and metal-carbon-oxygen bending [$\delta(\text{MCO})$] vibrations in some metal carbonyl halides and their derivatives [3].

Subsequent work on the series of $\text{XMn}(\text{CO})_5$ compounds dealt with the application of the IR spectroscopic method of assigning and analysing the

CO stretching modes to a variety of octahedral molecules derived from the group VIA carbonyls and group VIIA [4,5] metals and to $\text{M}_2(\text{CO})_{10}$ ($\text{M} = \text{Mn}, \text{Re}$) molecules [6]. Other authors [7] have used this method in varying degrees, and often in association with the kind of intensity arguments suggested by Orgel [8] in order to analyze and assign the CO stretching spectra of numerous $\text{M}(\text{CO})_x\text{L}_{6-x}$ molecules, where L_{6-x} represents a collection of donor molecules or univalent groups which are not necessarily all the same. Lewis and co-workers [9,10] made detailed studies of the spectra of $\text{M}_2(\text{CO})_{10}$ and $\text{M}_2(\text{CO})_8\text{L}_2$ molecules which lead them to comments on various features of the study by Cotton and Wings [6] on $\text{Mn}_2(\text{CO})_{10}$ and $\text{Re}_2(\text{CO})_{10}$ in particular and on the Cotton-Kraihanzel force field in general.

However, there has been no unified study in the far-infrared region and so we have performed a comparative series of far-infrared spectroscopic investigations of manganese carbonyl derivatives of the type $\text{XMn}(\text{CO})_5$, where $\text{X} = \text{CH}_3, \text{CD}_3, \text{H}, \text{D}, \text{CF}_3, \text{Cl}, \text{Br}$. Following the number of metal-carbon stretching and metal-carbon-oxygen bending

vibrations active in the far-infrared region, accurate values for the band maxima in the 700-10 cm^{-1} region have been obtained for these complexes

The far-infrared data can potentially reveal the effect of the X (ligand) in $\text{XMn}(\text{CO})_5$ on the bonding in the $\text{Mn}(\text{CO})_5$ group. No systematic study of the infrared spectra of these molecules in the region 500-10 cm^{-1} in the vapour phase has been previously reported, although some data have been reported in solution and Nujol mull [11]. Vibrational assignments have been made for all these molecules in the present work, partly by comparison with earlier condensed phase work.

This work will deal with the two related problems. First procedures for enlarging the body of experimental data pertaining to Mn-C stretching and Mn-C-O bending modes of particular molecules will be discussed. Second, using this data, the assignment will be reviewed and evaluated where possible in terms of the implication for bonding models of the compounds.

Methylmanganesepentacarbonyl

$\text{CH}_3\text{Mn}(\text{CO})_5$ is one of the best known examples of a molecule with a σ -bonding interaction between a transition metal and an organic alkyl group [12]. This compound has been the subject of a number of structural studies, involving gas-phase electron diffraction [13], X-ray diffraction, incoherent inelastic neutron scattering [14], and vibrational spectroscopy [15]. These have left uncertain two structural features associated with the methyl group, its geometry and its internal rotational motion. The disordered structure of the Mn crystal meant that no geometric information could be obtained from the X-ray study, while the hydrogen positions were not located by the electron-diffraction experiment. Vibrational data are more complete, but despite of several infrared investigations [14, 15], a number of vibrational assignments are still open to question. In particular, the attribution [16] of the Mn- CH_3 stretch to a band 100 cm^{-1} higher in energy than any of the Mn-CO stretches runs counter to expectation based on the longer Mn- CH_3 distance (2.19 Å) vs. Mn-CO distance (1.86 Å). Given the incompleteness of previous IR assignments in condensed phase work, we have carried out a study of this compound in the

gas phase in the region 500-10 cm^{-1} . $\text{CD}_3\text{Mn}(\text{CO})_5$ was also prepared and analysed in order to assist in the spectral assignment.

Hydridemanganesepentacarbonyl

Following the initial reports of $\text{HMn}(\text{CO})_5$ preparation [17], the nature of the compound was subjected to number of studies. Investigations of the vapour phase infrared spectrum by Cotton *et al.* [18] and by Wilson *et al.* [19] led to the conclusion that the molecular symmetry is definitely lower than C_{4v} , although no complete vibrational assignments were made. Subsequently, however, La Placa, *et al.* [20] showed that $\text{HMn}(\text{CO})_5$ crystalizes such that the $\text{Mn}(\text{CO})_5$ moiety does have C_{4v} local symmetry in the solid state and suggested that it is unlikely that it would assume lower symmetry in the vapour phase. This structure determination prompted Huggins and Kaesz [21] report a prior interpretation of the C-O stretching region of the solution spectrum of $\text{HMn}(\text{CO})_5$ based upon C_{4v} symmetry. However, these studies do not solve the problem of apparent disparity between the X-ray results [20] and previous infrared data [18,19]. Since the spectra of both $\text{HMn}(\text{CO})_5$ and its deuterated analogue, $\text{DMn}(\text{CO})_5$, are identical in the 5 μm (1900-2200 cm^{-1}) region, it is only with the remainder of the spectrum that a C_{4v} assignment can be tested by the Teller-Redlich isotope product rule. In order to resolve this disparity, we have investigated the infrared spectrum of a gaseous sample of $\text{HMn}(\text{CO})_5$ which was known to be pure, so that bands due to impurities were eliminated. In this work we report the far-infrared spectrum of gaseous samples of $\text{HMn}(\text{CO})_5$ and $\text{DMn}(\text{CO})_5$ in the region 700-10 cm^{-1} and propose a vibrational assignment of the infrared active modes.

Trifluoromethylmanganesepentacarbonyl

It has been recognized from some time that, on the basis of chemical behaviour [22], where transition metal atoms are in low formal oxidation states and metal to perfluoroalkyl bonds are more stable and thus presumably thermochemically stronger than metal to alkyl bonds. It was observed, more or less simultaneously, by King and Bisnette [23] and by Cotton and McCleverty [24] that in several perfluoromethyl compounds of transition metals the C-F stretching frequencies are lower, by

the order of 100 cm^{-1} , than the frequencies found in perfluoromethyl halides. Both group of workers [25] ascribed this to π -interactions involving the filled d_{π} orbital of the metal and the empty antibonding C-F orbitals. Detailed formulation can be made either in valence bond or molecular orbital terms [23-25]. By either interpretation, it is also to be expected that the C-M bond would be strengthened in rough proportion to the weakening of the C-F bonds. Structural data showing that the bonds in perfluoroalkyl compounds are short relative to those in the normal alkyl compounds has been provided in several cases [26,27]. The purpose of the present work is an investigation of the far-infrared spectrum of $\text{CF}_3\text{Mn}(\text{CO})_5$, to characterise low frequency fundamentals and to ascertain new information on the bonding in this compound.

Halide manganesepentacarbonyl

The carbonyl halides of manganese have been of interest for some time, partly because of the metal-carbon bonds which involve d_{π} - p_{π} bonding, but also because they are quite symmetrical (C_{4v}), making a detailed discussion of their vibrational spectrum feasible. Bennett and Clark [3] have studied the infrared spectra of the series $\text{XMn}(\text{CO})_5$ where X=Cl, Br, I and assigned the metal-halogen and one of the metal-carbon stretching modes. Other low frequency data has been reported by Valenti *et al.* [28], while

Hyams [11] has made a more complete study of this series of compounds between 33 - 2200 cm^{-1} in solution and Nujol mull and based his assignment on approximate force constant calculations, while Cotton [29], and Kaesz *et al.* [30,31] have carried out a similar study for all of the halides but extended their work to intensity measurements and ^{13}C isotopic enrichment. The vibrational spectra of $\text{IRe}(\text{CO})_5$ have been reported [32] and comparison between the manganese and rhenium analogues has proved useful.

The present work is concerned with the far-infrared spectra of the manganese carbonyl halides in vapour phase. The resulting data in conjunction with infrared data reported earlier [3-30] has permitted a more complete vibrational assignment.

Results and Discussion

BrMn(CO)₅ and ClMn(CO)₅

Vapour phase IR spectra were obtained for $\text{BrMn}(\text{CO})_5$ and $\text{ClMn}(\text{CO})_5$ in the region between 500 - 10 cm^{-1} . To obtain the spectra solid deposits of the compound were condensed in the cell under vacuum. While the spectrum was being recorded the cell was maintained at ca. $40\text{ }^\circ\text{C}$ to increase the vapour pressure. The signal-to-noise ratios in both spectra shown in figures 1 and 2, are reasonable but improved spectra would have been desirable to

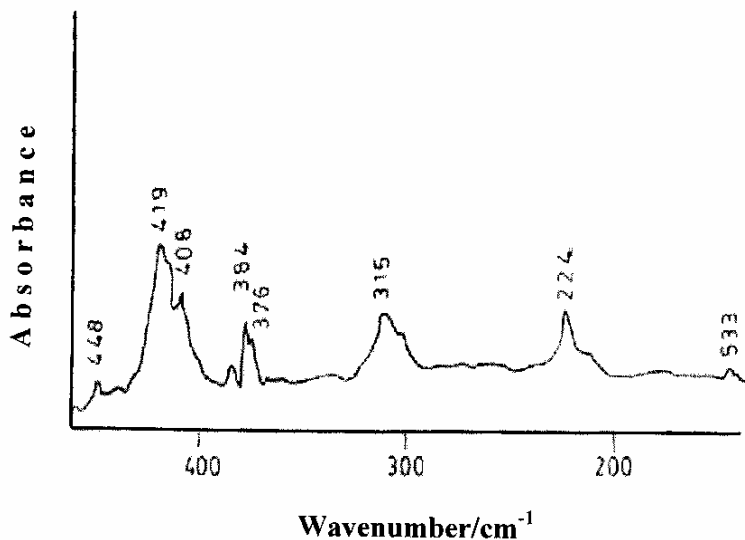


Fig. 1: Far infrared spectra of $\text{BrMn}(\text{CO})_5$.

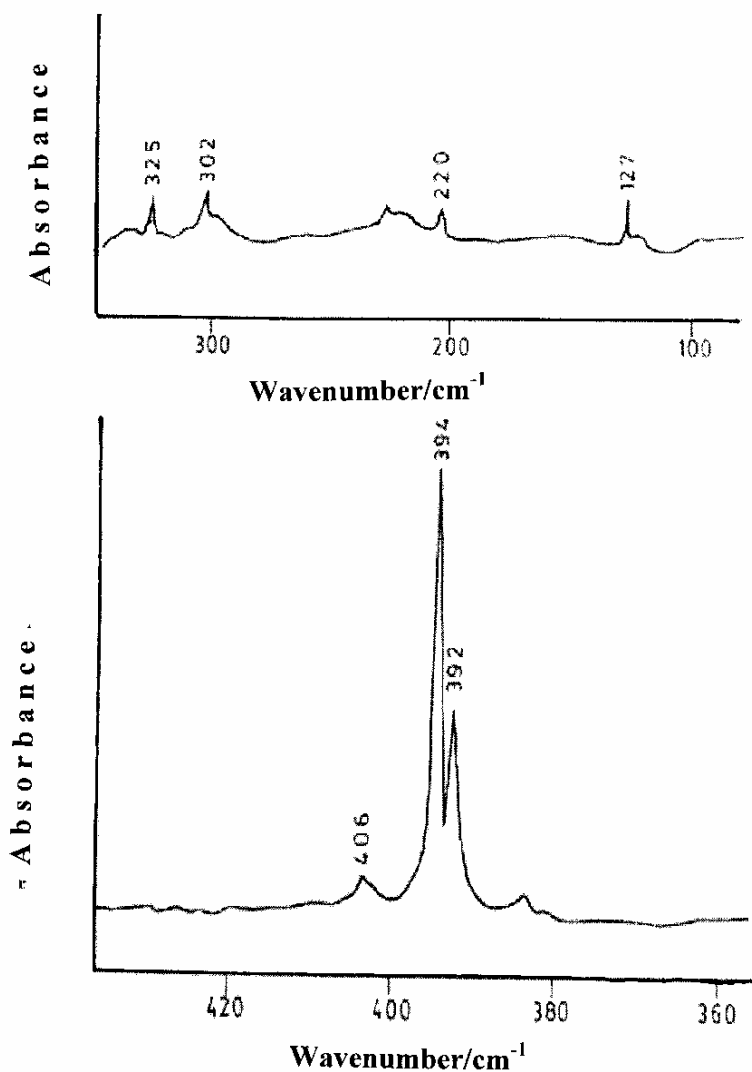


Fig. 2: Far-infrared spectra of ClMn(CO)₅.

identify weak absorption bands that may be obscured by noise. Unfortunately the cell could not be heated to temperatures above 40 °C because of compound decomposition.

Based on chemical and infrared evidence [5], the molecular structure of XMn(CO)₅ (where X = Br,Cl) is thought to be pseudo-octahedral (C_{4v} symmetry). The irreducible representations for the normal modes of vibration for this symmetry are

$$\Gamma_{\text{vib}}^{C_{4v}} = 7A_1 + A_2 + 4B_1 + 2B_2 + 8E$$

A₁ and E modes are both infrared and Raman active, B₁ and B₂ are only Raman active; and the A₂ mode is both Raman and infrared inactive.

Eight fundamentals are expected for XMn(CO)₅ molecule in the region 700-200 cm⁻¹ four E and four A₁ modes. These consist of Mn-C stretching vibrations, Mn-C-O bending vibration and a Mn-X stretching vibration. Below 200 cm⁻¹ four absorption bands are expected and they should approximately correspond to the following motions, A₁ and E out of plane CMnC deformation, E CMnC

in plane deformation and E XMnC deformation [11, 28]. Only eight bands are observed in the case of BrMn(CO)₅ and seven for ClMn(CO)₅. Because the modes of the same symmetry type are known to be extensively mixed in the low frequency region, non of the frequencies in this region will be comprised of the assigned motion alone. This caveat applies particularly to the A₁ and E modes in the Mn-C stretching and Mn-C-O bending regions.

Due to the relatively large mass of Br and the small bond strength of Mn-Br in relation to Mn-CO, it is reasonable to expect that the lowest frequency (E) mode will correspond to CMnBr bending. Thus we have tentatively assigned the band at 53 cm⁻¹ in figure 6.1 to the CMnBr bending mode, which is expected to occur below 70 cm⁻¹ [2]. This mode is almost certainly the lowest fundamental frequency of the Mn(CO)₅Br molecule and is expected to be extensively mixed with the CMnC bending modes. No clear corroboration of this assignment could be obtained by changing the halogen atom to Cl as the spectra of this compound in the region in question were markedly different from the spectrum of Mn(CO)₅Br [11, 37]. It is found that a band observed at 127 cm⁻¹ in spectrum of ClMn(CO)₅ which is below the usual Mn-C stretching region, is assigned to the ClMnC bending mode. Clearly this assignment is in line with the expected mass effect of the halides i.e the lighter chloride has a higher frequency mode than the bromide. The band observed at 302 cm⁻¹ in spectrum of ClMn(CO)₅ is assigned to Mn-Cl stretching mode and the band observed at 224 cm⁻¹ in the spectrum of BrMn(CO)₅ corresponds to the Mn-Br stretching mode. This is consistent with the assignment of several metal-halogen stretching vibrations reported earlier [3]. The stronger bands observed at 378 cm⁻¹ in BrMn(CO)₅ and 394 cm⁻¹ in ClMn(CO)₅ are assigned to the (A₁) Mn-C stretching mode; this mode has been observed at 372 cm⁻¹ in IRe(CO)₅. Similarly the bands observed at 384 cm⁻¹ in BrMn(CO)₅ and 392 cm⁻¹ in ClMn(CO)₅ have been assigned to E Mn-C-O bending modes by analogy with the assignment of Valenti et al. [28] on solid-state spectra of metal halide carbonyls. These bands were previously reported as shoulders but in our experiment they are quite well resolved, especially in the case of BrMn(CO)₅. The band observed at 448 cm⁻¹ in the spectrum of BrMn(CO)₅ corresponds to Mn-C-O bending vibration. This assignment was made by

analogy with Adams and Seure [38] solid-state work in which the corresponding band was at 470 cm⁻¹. The weak band observed at 220 cm⁻¹ in ClMn(CO)₅ is unexplained.

There were no major differences between the gas phase spectra in the current work and in previous studies on solutions and the solid-state, apart from modes frequency shifts. Other research groups have investigated the solution and solid-state spectra of ClMn(CO)₅ and BrMn(CO)₅ in the mid-infrared spectral region and found that differences only occurred in the C-O stretching region [3,37]. The present study sheds further light on how condensed phase influence the metal-carbon stretching and metal-carbon-oxygen bending frequencies. The data assembled in tables 1 and 2 (comparison between gas phase and solution and solid-state spectrum) shows that the frequency shifts for XMn(CO)₅ from solution to vapour phase are mostly upward, are all relatively small, but are not equal. If an average shift ±10 cm⁻¹ were applied to all bands no serious error between gas phase and solution would be introduced.

Table-1: Frequencies and assignment of vapour phase spectrum of BrMn(CO)₅.

Gas Phase	Wavenumbers/cm ⁻¹		Assignment ^A
	Solution	Solid	
53	50	50	(E) CMn Br bending
224	219	222	(A ₁) Mn-Br stretching
315			(A ₁) Mn-C stretching
378			(A ₁) Mn-C stretching
384	384		(E) Mn-C-O bending
408	405	405	(E) Mn-C stretching
419	415	415	(E) Mn-C stretching
448	472	471	(E) Mn-C-O bending

A- Assignments made mainly by comparison with work reported in references [11] and [28].

Table-2: Frequencies and assignment of the vapour phase spectrum of ClMn(CO)₅.

Gas phase	Wavenumbers/cm ⁻¹		Assignment ^A
	Solution	Solid	
127	126	126	(E)ClMn-C bending
220			
302	292	295	(A ₁) Mn-Cl stretching
325			(A ₁) Mn-C stretching
392	384	382	(E) Mn-C-O bending
394	390		(A ₁) Mn-C stretching
403	406	409	(E) Mn-C stretching

A- Assignments made mainly by comparison with work reported in references [11] and [28].

It is difficult to make an unequivocal assignment without observing every possible band. There is no doubt that substantial mode mixing occurs in the fundamental modes in the low frequency region. Thus the Mn-C stretching motion and the Mn-

C-O bending motion have a pronounced tendency to mix and one can expect some mixing of the axial and planar stretching motion in the A_1 vibrations. While a detailed discussion of the bonding in the $XMn(CO)_5$ compounds requires a force field calculation, it is possible to make some qualitative comments concerning the observed frequencies. It is interesting to note what happens to the metal carbon stretching and metal-carbon-oxygen bending frequencies if the halides are substituted in the order Cl and Br. The bromide, being less electronegative, should leave the most negative charge on the metal atom. The carbon-oxygen force constant should change in order $Mn(CO)_5Cl > Mn(CO)_5Br$. This change would be reflected in the correspondingly increasing frequencies to higher modes in $ClMn(CO)_5$ spectrum than $BrMn(CO)_5$. However, since these frequencies change very little from halide to halide.

HMn(CO)₅ and DMn(CO)₅

Manganese pentacarbonyl hydride in C_{4v} symmetry would be an approximately octahedral molecule with the hydrogen located on C_4 axis [18,19]. The irreducible representation of the vibration in this molecule are the same as in $BrMn(CO)_5$ and $ClMn(CO)_5$ and are:

$$\Gamma_{\text{vib}}^{C_{4v}} = 7A_1 + A_2 + 4B_1 + 2B_2 + 8E$$

Of the modes, only A_1 and E modes are infrared active. Seven modes involving Mn-CO stretching and Mn-C-O bending motions are expected in the region $800-300\text{ cm}^{-1}$, four E and three A_1 modes [7]. Two E modes and one A_1 mode are expected in the very low frequency region (below 300 cm^{-1}) consisting of O-C-Mn-C-O deformations [7, 39].

We have recorded IR spectra of a pure gaseous sample of $HMn(CO)_5$ in the region between $800-10\text{ cm}^{-1}$ for the first time in an attempt to characterise low frequency vibrations of this molecule. In making the vibrational assignment for $HMn(CO)_5$, reference is made to the work of Hyams and Lippincott [11] on $XMn(CO)_5$ ($X=Cl, Br$) and Wilson on $HMn(CO)_5$ [19]. Figures 3 and 4 show the low frequency spectra of $HMn(CO)_5$ and $DMn(CO)_5$.

There are six bands observed in the spectrum of $HMn(CO)_5$ in the region $800-300\text{ cm}^{-1}$, which are clearly fundamentals and not structural components of other bands while below 300 cm^{-1} three bands are observed. In case of $DMn(CO)_5$ we observe seven bands in the region $800-300\text{ cm}^{-1}$, Due

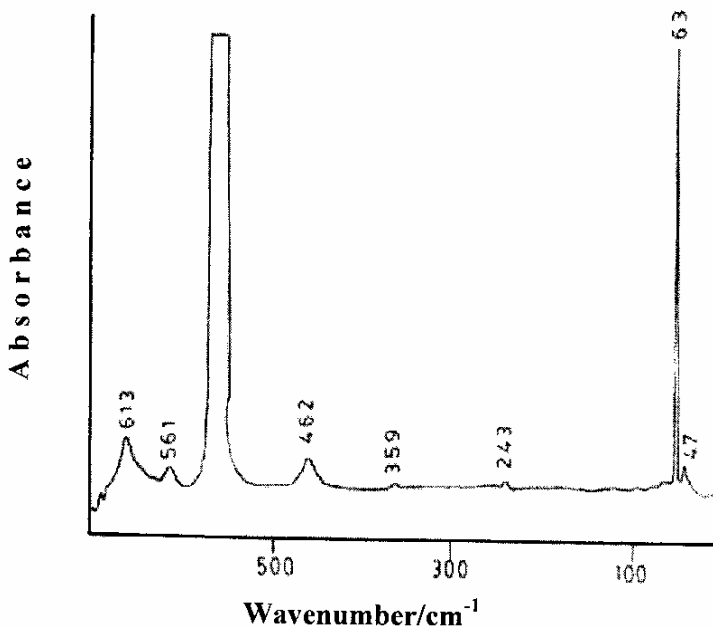


Fig. 3: Far-infrared spectra of $HMn(CO)_5$.

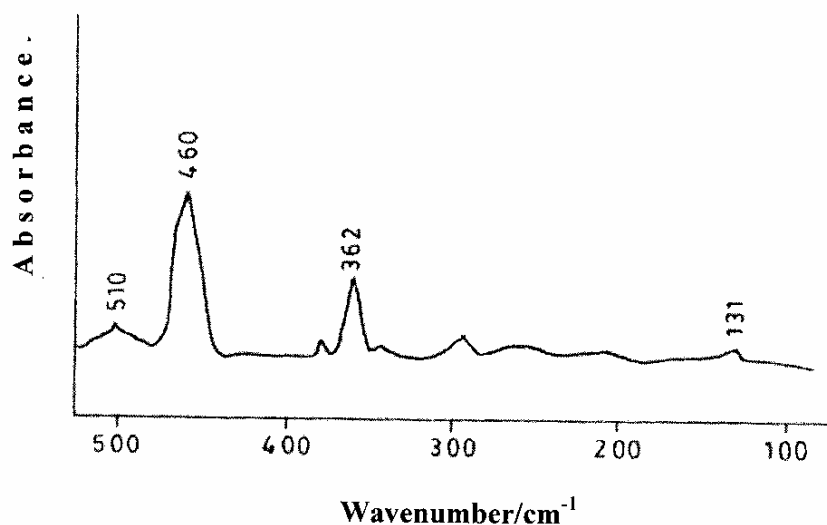


Fig. 4: Far-infrared spectra of DMn(CO)₅.

to the difficulty in preparing DMn(CO)₅ free of the hydride isotopomer, there has been disagreement among several investigators [18,19] as to just which maxima observed belong to DMn(CO)₅ itself and which belong to traces of HMn(CO)₅ impurity. There are considerable number of bands in this region (Below) which apparently shifted are disappeared upon deuteration and also there is sufficient disagreement in the literature about the existence and position of bands in this region. In this portion (between 800-300 cm⁻¹) of the hydride spectrum there are four strong bands at 731, 663, 613 and 462 cm⁻¹ while strong DMn(CO)₅ bands occur at 729, 661, 606 and 456 cm⁻¹. It is helpful in assigning these bands to refer to the work on the XMn(CO)₅ compounds by Edgell and Cengel [39], who have made middle frequency assignments for these compounds.

The strong band in the spectrum of HMn(CO)₅ at 462 cm⁻¹ is assigned to an A₁ mode of Mn-CO stretching vibration, this is consistent with the same vibration at 460 cm⁻¹ in DMn(CO)₅ and also accord with the XMn(CO)₅ (X=Br, Cl, I) assignment, this band observe at 471 cm⁻¹ in this series, non of the A₁ modes can shift very much upon deuteration.

Several strong bands still remain to be assigned in these spectra, namely the HMn(CO)₅ bands at 731, 663, and 613 cm⁻¹. The XMn(CO)₅ correlation indicates that the 663 cm⁻¹ hydride band is

an A₁ mode involving Mn-C-O bending motion. The key to understanding the other two hydride bands is provided by the discussion of Edgell *et al.* [39]. These 731 and 613 cm⁻¹ bands are E modes and also correspond to Mn-C-O bending vibrations. The analogous bands are found at 729 and 608 cm⁻¹ in the DMn(CO)₅ spectrum. The band observed at 561 cm⁻¹ in the hydride spectrum is due to an E mode analogous to the 542 cm⁻¹ deuteride mode and which consists largely of Mn-C-O bending motion. There is a band of DMn(CO)₅ at 510 cm⁻¹, which is absent in the hydride spectrum, that is assigned to an E mode of Mn-CO stretching motion. Cotton *et al.* [18] assigned this band at 511 cm⁻¹ in the spectrum of DMn(CO)₅. The bands observed at 359 cm⁻¹ for the hydride and 362 cm⁻¹ for the deuteride are assigned to an E mode correspond to Mn-C-O bending motion; this proposal is based on analogy with the result of Edgell *et al.* on HMn(CO)₅.

The assignment for all the modes observed in the spectra of HMn(CO)₅ and DMn(CO)₅ is given in the table 3. In the very low frequency region, weak bands observed at 243 and 47 cm⁻¹ and a strong band at 63 cm⁻¹ in the spectrum of HMn(CO)₅. We refer to the work of Edgell and Hyams [4, 5] on the XMn(CO)₅ (X = Br, Cl, I) compounds. They observed that there are two far-infrared bands characteristic of the Mn(CO)₅ moiety in these compounds at 64 and 88 cm⁻¹ in the solution spectra

Table-3: Frequencies and assignment of vapour phase spectra of $\text{HMn}(\text{CO})_5$ and $\text{DMn}(\text{CO})_5$.

Wavenumber/cm ⁻¹			Assignment
$\text{HMn}(\text{CO})_5$ Wilson [Ref 1]	$\text{DMn}(\text{CO})_5$ (observed)	$\text{HMn}(\text{CO})_5$ (observed)	
731	729	731	(E) Mn-C-O bending
663	661	663	(A ₁) Mn-C-O bending
612	608	613	(E) Mn-C-O bending
562	542	561	(E) Mn-C-O bending
	510		(E) Mn-CO stretching
462	460	462	(A ₁) Mn-CO stretching
362	362	359	(E) Mn-C-O bending
	131	243	(E) C-Mn-C bending
		63	(A ₁) C-Mn-C bending
		47	(E) C-Mn-C bending

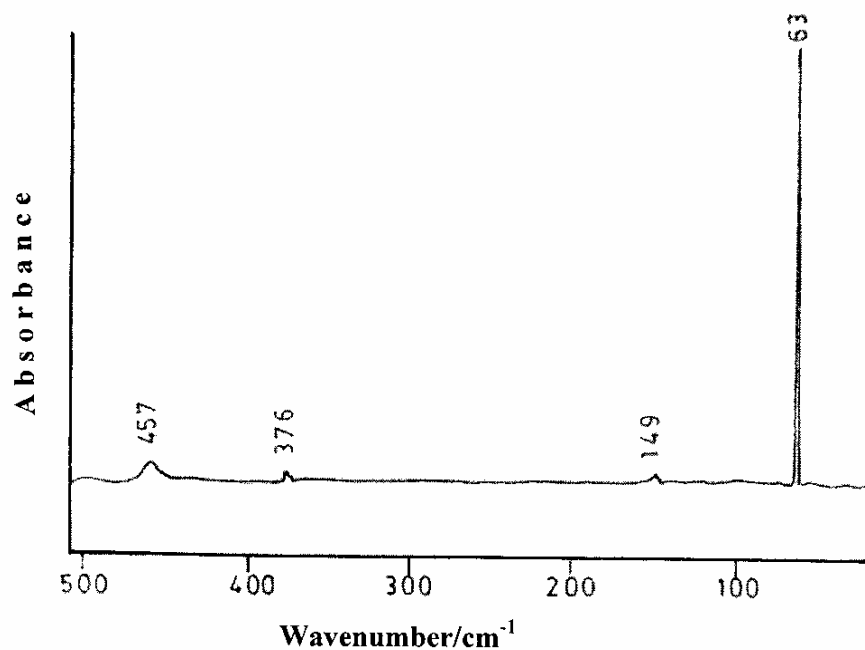
Assignments made mainly by comparison with work reported in references [18] and [19].

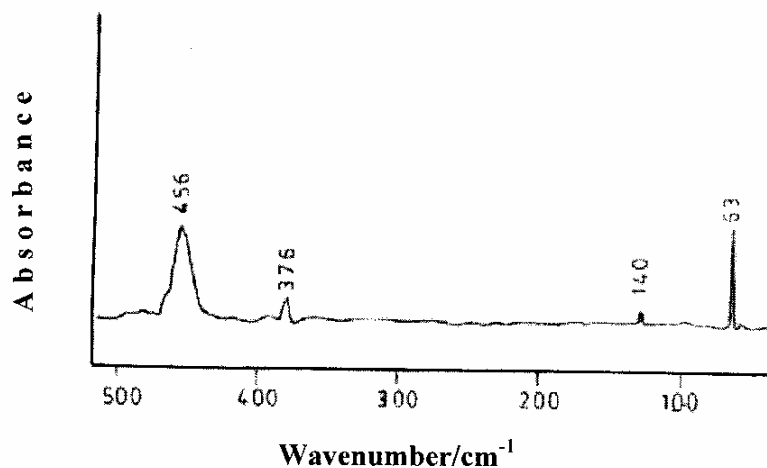
of the series. These modes are C-Mn-C deformation modes. Considering $\text{HMn}(\text{CO})_5$ and $\text{DMn}(\text{CO})_5$, we may compare their band positions to those in molecules in which the coupling between modes involving the X- and $-\text{Mn}(\text{CO})_5$ moieties is small. The band observed at 63 cm^{-1} in the vapour phase spectrum of $\text{HMn}(\text{CO})_5$ correspond to an A₁ C-Mn-C bending vibration by analogy with band at 88 cm^{-1} in $\text{BrMn}(\text{CO})_5$ and in the same way the band at 47 cm^{-1} correspond to C-Mn-C bending vibration of E symmetry by analogy with the $\text{BrMn}(\text{CO})_5$ spectrum.

$\text{CH}_3\text{Mn}(\text{CO})_5$ and $\text{CD}_3\text{Mn}(\text{CO})_5$

The vapour phase far-infrared spectra of $\text{CH}_3\text{Mn}(\text{CO})_5$ and its deuterated analogue $\text{CD}_3\text{Mn}(\text{CO})_5$ at room temperature are shown in figures 5 and 6. The $\delta(\text{MCO})$ and $\nu(\text{M-C})$ region of $\text{CH}_3\text{Mn}(\text{CO})_5$ has been partially assigned by other workers in the condensed phase studies [11, 40]. Our present analysis in the low frequency region aims to enlarge on these data to find more fundamental vibrations in this region for a vapour phase sample. We observe bands at 657, 610, 559, 457, 376, 149 and 63 cm^{-1} in the $\text{CH}_3\text{Mn}(\text{CO})_5$ spectrum and 665, 594, 456, 376, and 63 cm^{-1} in $\text{CD}_3\text{Mn}(\text{CO})_5$. Considering previous work on $\text{CH}_3\text{Mn}(\text{CO})_5$ and similar studies of $\text{BrMn}(\text{CO})_5$, we report assignments of the infrared data for $\text{CH}_3\text{Mn}(\text{CO})_5$ and $\text{CD}_3\text{Mn}(\text{CO})_5$ by drawing direct analogies [41,42]. Our assignment for this region is also based in part on correlations of the vapour phase and solid-state spectra of $\text{CH}_3\text{Mn}(\text{CO})_5$ and $\text{CH}_3\text{Re}(\text{CO})_5$ [14,15]. The assignment are summarised in table 4.

The irreducible representations for the normal modes of the vibration for $\text{CH}_3\text{Mn}(\text{CO})_5$ (if

Fig. 5: Far-infrared spectra of $\text{CH}_3\text{Mn}(\text{CO})_5$.

Fig. 6: Far-infrared spectra of $\text{CD}_3\text{Mn}(\text{CO})_5$.Table-4: Frequencies and assignment of vapour phase spectra of $\text{CH}_3\text{Mn}(\text{CO})_5$ and $\text{CD}_3\text{Mn}(\text{CO})_5$.

$\text{CH}_3\text{Mn}(\text{CO})_5$	$\text{CD}_3\text{Mn}(\text{CO})_5$	Assignment
657	665	(E) Mn-C-O bending
610	594	(A ₁) Mn-C-O bending
559		(E) Mn-C-O bending
457	456	(A ₁) Mn-CO stretching
376	376	(E) Mn-CO stretching
149		(E) C-Mn-C bending
63	63	(A ₁) C-Mn-C bending

Assignments made mainly by comparison with work reported in ref [14] and [15].

the vibration of CH_3 is not considered) are the same (C_{4v} symmetry) as in $\text{BrMn}(\text{CO})_5$ and $\text{HMn}(\text{CO})_5$. Eight modes ($4\text{A}_1+4\text{E}$) consisting of Mn-C-O bending and Mn-CO stretching vibrations are expected in the region $700\text{-}300\text{ cm}^{-1}$ and four modes (A_1+3E) are expected below 300 cm^{-1} [7]. In the case of $\text{CH}_3\text{Mn}(\text{CO})_5$ seven bands are actually observed in the vapour phase spectrum and five bands are observed in the $\text{CD}_3\text{Mn}(\text{CO})_5$ spectrum. We assign the bands observed at 657 and 559 cm^{-1} for $\text{CH}_3\text{Mn}(\text{CO})_5$ as due to E modes corresponding Mn-C-O bending vibrations. Our identification is confirmed as corrected by the polarization of the A_1 solution Raman band at 664 cm^{-1} and by the shift to higher energy of the E mode on deuteration, (in the solution infrared spectra of $\text{CD}_3\text{Mn}(\text{CO})_5$, this shift result in a single, symmetric band due to coincidental overlap of the A_1 and E modes) [41]. In the gas phase spectrum of $\text{CD}_3\text{Mn}(\text{CO})_5$ this shift results in a symmetric band at 665 cm^{-1} . The band observed at 594 cm^{-1} in $\text{CD}_3\text{Mn}(\text{CO})_5$ is also tentatively assigned to an E mode involving Mn-C-O bending motion, and

the very weak shoulder at 610 cm^{-1} in $\text{CH}_3\text{Mn}(\text{CO})_5$ is tentatively assigned to an A_1 mode correspond to Mn-C-O bending motion by analogy with the solid state spectrum of $\text{CH}_3\text{Mn}(\text{CO})_5$.

The vapour phase far-infrared spectrum of $\text{CH}_3\text{Mn}(\text{CO})_5$ is dominated by a peak at 457 cm^{-1} , which can be readily assigned to an A_1 Mn-CO stretching vibration by comparison with the solid-state spectra of $\text{CH}_3\text{Mn}(\text{CO})_5$ and $\text{CH}_3\text{Re}(\text{CO})_5$. We note that the same vibration in $\text{CD}_3\text{Mn}(\text{CO})_5$ is at 456 cm^{-1} . We also observe a very weak band at 376 cm^{-1} in both $\text{CH}_3\text{Mn}(\text{CO})_5$ and its deuterated analogue; an obvious assignment for this vibration is the E mode corresponding to a M-CO stretching vibration, since it is close to the frequency observed at 375 cm^{-1} in the solid-state spectrum of $\text{CH}_3\text{Re}(\text{CO})_5$ [15].

It is generally difficult to make definitive assignments in the very low frequency region (below 300 cm^{-1}) for $\delta(\text{CMC})$ modes of metal carbonyl complexes. In the present case we find two bands in $\text{CH}_3\text{Mn}(\text{CO})_5$, a weak band at 149 cm^{-1} in $\text{CH}_3\text{Mn}(\text{CO})_5$ and a very strong band at 63 cm^{-1} in both $\text{CH}_3\text{Mn}(\text{CO})_5$ and its deuterated analogue. The vibration at 149 cm^{-1} can probably be assigned to a C-M-C bending vibration of E symmetry, and that at 63 cm^{-1} corresponds to an A_1 mode C-M-C bending vibration. The analogous bands in the solid-state spectrum of $\text{BrMn}(\text{CO})_5$ occurs at similar positions [28] i.e. 143 and 64 cm^{-1} respectively, and also in the present work these bands observed at similar position in the vapour phase spectrum of $\text{HMn}(\text{CO})_5$.

CF₃Mn(CO)₅

The IR spectrum of $\text{CF}_3\text{Mn(CO)}_5$ has been measured and interpreted in the CO stretching region in considerable detail previously [24,29]. The previous studies have all involved solution work. In the present work the infrared spectrum of $\text{CF}_3\text{Mn(CO)}_5$, has been recorded in the gas phase in the region $700\text{--}10\text{ cm}^{-1}$ for the first time.

The irreducible representations for the normal modes of vibration in $\text{CF}_3\text{Mn(CO)}_5$ (if the CF_3 vibration is not seriously considered) are the same as in BrMn(CO)_5 , HMn(CO)_5 and $\text{CH}_3\text{Mn(CO)}_5$ (assuming C_{4v} symmetry). Eight infrared active bands ($4E+4A_1$) are expected in the region below 700 cm^{-1} . These consist of M-C-O bending, Mn-CO stretching and C-F stretching vibrations. Only four bands are observed at 296 , 362 , 373 and 422 cm^{-1} ; the band at 362 cm^{-1} is strong while the other three bands are very weak. The signal-to-noise ratio in the spectrum shown in figure 7 is not very good; improved spectra would have been desirable to identify weak absorption bands that may be obscured by noise.

The spectrum of the $\text{CF}_3\text{Mn(CO)}_5$ is similar to that of BrMn(CO)_5 , HMn(CO)_5 and $\text{CH}_3\text{Mn(CO)}_5$ in the CO stretching region [44]. The correlation between $\text{CF}_3\text{Mn(CO)}_5$ and these homologous molecules in the carbon-oxygen stretching region can be easily extended to low frequency region. With

reference to the previous work [24,44] on $\text{CF}_3\text{Mn(CO)}_5$ we assume that the bands observed in the vapour phase spectrum of $\text{CF}_3\text{Mn(CO)}_5$ in the present work are due to the Mn(CO)_5 group. We can compare BrMn(CO)_5 with $\text{CF}_3\text{Mn(CO)}_5$, which is reasonable based on the similarity of Br and CF_3 in electronegativity and mass. On this basis and comparison with the vapor phase spectra of XMn(CO)_5 ($X = \text{Br, H, CH}_3$) molecules we assign the band (see table 5) observed at 296 cm^{-1} to an E Mn-C-O bending vibration, the analogous band being observed at 243 cm^{-1} in the spectrum of HMn(CO)_5 . The band observed at 362 cm^{-1} is assigned to a degenerate Mn-CO stretching vibration, with the corresponding band observed at 359 cm^{-1} in the hydride spectrum. The band observed at 373 cm^{-1} in the gas phase spectrum of $\text{CF}_3\text{Mn(CO)}_5$ most likely arises from a degenerate Mn-C-O bending vibration. The analogous band observed at 384 cm^{-1} in BrMn(CO)_5 . The band observed at 442 cm^{-1} is assigned to an A_1 Mn-CO stretching vibration by analogy with the assignments for BrMn(CO)_5 and $\text{CH}_3\text{Mn(CO)}_5$.

Table-5: Frequencies and assignments of far-IR spectrum of vapour phase $\text{CF}_3\text{Mn(CO)}_5$.

$\text{CF}_3\text{Mn(CO)}_5$	Assignment	
296	(E) Mn-C-O	bending
362	(E) Mn-CO	stretching
373	(E) Mn-C-O	bending
442	(A ₁) Mn-CO	stretching

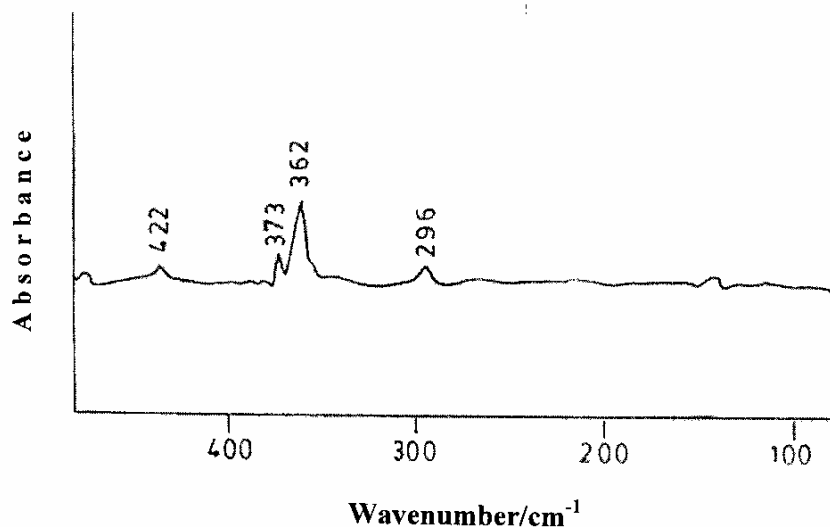


Fig. 7: Far-infrared spectra of $\text{CF}_3\text{Mn(CO)}_5$.

Experimental

Sample Preparations

Derivatives were prepared according to methods described in the literature. This is briefly summarised below;

(a) $CH_3Mn(CO)_5$

This was prepared in nitrogen atmosphere by treating $Mn_2(CO)_{10}$ with methanolic NaOH solution followed by CH_3I addition and subsequent purification by vacuum sublimation [33]. Purity was checked using low resolution Fourier transform mid-infrared (FTIR) spectroscopy and 1H NMR spectroscopy. The spectra showed no evidence of any impurities.

(b) $CD_3Mn(CO)_5$

This was prepared as above but substituting CD_3I in place of CH_3I . IR and 1H NMR spectra showed no evidence of any impurities.

(c) $HMn(CO)_5$

Under an inert gas atmosphere 0.500 g of freshly sublimed $Mn_2(CO)_{10}$ was dissolved in 25 ml of freshly distilled tetrahydrofuran (THF) and stirred over a Na/Hg amalgam (0.062 g in 50 ml Hg) for 3 hours. The solution was then filtered and solvent distilled off leaving a greyish residue. After admitting nitrogen to the flask, which now contained $NaMn(CO)_5$, 30 ml of aqueous phosphoric acid was added over a period of one hour. During the addition of phosphoric acid, the $HMn(CO)_5$ and water from the acid were distilled into an external trap containing phosphorus pentoxide where water was removed. The $HMn(CO)_5$ was identified by its infrared spectrum. The infrared spectrum showed no indication of THF and CO_2 and the purity of the sample was verified by recording a mass spectrum [34].

(d) $DMn(CO)_5$

This was prepared as in (c) above except D_3PO_4 was used in place of H_3PO_4 . However, care was taken with the vacuum line as deuterium will exchange rapidly with any protonic sites on the

glassware. Care was taken to dry all apparatus with which manganese pentacarbonyl deuteride came into contact. Because of the difficulty in preparing $DMn(CO)_5$, there has been disagreement among several researchers [18,19] as to just which maxima observed in IR spectra belong to $DMn(CO)_5$ itself and which belong to small amounts of $HMn(CO)_5$ impurity.

(e) $CF_3Mn(CO)_5$

Trifluoromethylmanganese pentacarbonyl was prepared by a method described by McClellan [35] in which $CF_3COMn(CO)_5$ was heated at $110^\circ C$ for one hour under a nitrogen atmosphere. The rate of carbon monoxide evolution was monitored by the flow through a gas bubbler. Initially, the carbon monoxide evolution should be very vigorous, but toward the end of reaction no gas evolution should occur. After the reaction period was completed the solid residue was transferred to a sublimator and trifluoromethylmanganese pentacarbonyl was isolated by sublimation. The product is a white air stable and an extremely volatile solid and its infrared spectrum exhibited strong metal carbonyl bands at 2155, 2055, and 2015 cm^{-1} . The ^{19}F NMR spectrum exhibited a single sharp resonance at -9.3ϕ due to the CF_3 group. The spectroscopic data indicated formation of a high purity $CF_3Mn(CO)_5$ sample.

(f) $BrMn(CO)_5$ and $ClMn(CO)_5$

These compounds were prepared by methods described in the literature [36]. The CO stretching region in the products were compared with earlier work [28,30] to check the purity.

Infrared Spectroscopy

Gaseous samples were examined in a 10 cm long cell equipped with polyethylene windows. The sample pressure was generally of the order of 1-5 Torr except when the intense carbonyl peaks were examined, for which it was considerably reduced. Far IR spectra of each compound were recorded using a digilab FTS 40 V far-infrared spectrometer in the region $500-10\text{ cm}^{-1}$. In the case of the manganese carbonyl halide samples, these were heated in the gas cell to increase the vapour pressure and therefore enhance weak absorption bands. Several

scans of each spectrum were taken, so that the frequencies quoted should be accurate to $\pm 2 \text{ cm}^{-1}$.

Conclusion

There were no major differences between the gas phase spectra in the current work and in previous studies on solutions and the solid-state, apart from frequency shifts. There was no evidence of gas phase splitting. It is difficult to make an unequivocal assignment without observing every possible band. There is no doubt that substantial mode mixing occurs in the fundamental modes in the low frequency region. Thus the Mn-C stretching motion and the Mn-C-O bending motion have a pronounced tendency to mix and one can expect some mixing of the axial and planar stretching motion in the A_1 vibrations. While a detailed discussion of the bonding in the $\text{XMn}(\text{CO})_5$ compounds requires a force field calculation, it is possible to make some qualitative comments concerning the observed frequencies.

That It is interesting to note in the present study how the condensed phase influences the metal-carbon stretching and metal-carbon-oxygen bending frequencies if the X (Br, Cl, H, CH_3 , CF_3) is substituted on $\text{Mn}(\text{CO})_5$. The data given in this paper shows that the frequency shifts for $\text{XMn}(\text{CO})_5$ from solution to vapour phase are mostly upward, are all relatively small, but are not equal. The only frequency observed involving the Mn-C bonds arises from a mixture of stretching and bending motions. Consequently, it is difficult to draw firm conclusions about the changes in the Mn-C bonding. However, since the normal mode frequencies change very little from one molecule to another, it can be concluded that there is little change in the Mn-C bond strength. The Mn-X bond was found to be progressively weaker in both the stretching and bending modes as the X was changed. On the basis of the above discussion it is acceptable to assume that the Mn-C bonding in the $\text{XMn}(\text{CO})_5$ compounds are similar and since the same general vibrational pattern is found in the vapour and condensed phase work there is no substantial change in in moving from one phase to other. Since the $\text{XMn}(\text{CO})_5$ molecules are known to have C_{4v} symmetry [11,28] in the solution and solid-state, then it is reasonable to conclude that this symmetry is maintained in the gas phase.

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