

THE VIBRATIONAL SPECTRUM OF (TRIMETHYLENEMETHANE)IRON TRICARBONYL

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SUMMARY

A vibrational assignment for the trimethylenemethane molecule, in $[\text{C}(\text{CH}_2)_3]\text{-Fe}(\text{CO})_3$, has been proposed for the first time. CC_3 stretches were found at 1348 (E) and 918 cm^{-1} (A_1), with skeletal deformations at 802 cm^{-1} (A_1 , out-of-plane), and 471 cm^{-1} (E , in plane). The $\text{Fe}(\text{CO})_3$ vibrations were closely similar to those in analogous complexes.

INTRODUCTION

A number of organic species which are either unknown or known only as transient intermediates can, however, be isolated in the form of transition-metal derivatives. Perhaps the best known and most fully characterised of such complexes is (cyclobutadiene) $\text{Fe}(\text{CO})_3$ ¹⁻⁴, although numerous other iron carbonyl derivatives of unstable organic molecules are also known^{5,6}. The most symmetrical of such compounds is (trimethylenemethane)iron tricarbonyl, $[\text{C}(\text{CH}_2)_3]\text{Fe}(\text{CO})_3$ ⁷, which has been studied by electron-diffraction techniques⁸, and shown to possess the structure shown in Fig. 1. The heavy-atom skeleton of the $\text{C}(\text{CH}_2)_3$ fragment is in the shape of a flattened pyramid (which does not deviate very far from planarity), with all three C-C bonds symmetrically equivalent.

We have initiated a detailed study of the vibrational spectra of transition-metal complexes of unstable organic molecules, by considering (cyclobutadiene) $\text{Fe}(\text{CO})_3$ ⁹. The C_4H_4 ligand showed some interesting differences in its vibrational spectrum from

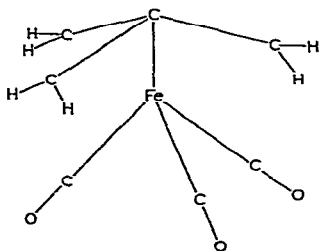


Fig. 1. Molecular structure of (trimethylenemethane) $\text{Fe}(\text{CO})_3$.

those of other cyclic ligands such as $C_5H_5^-$ and C_6H_6 . The trimethylenemethane molecule appeared to be potentially just as interesting, and we report here the first detailed vibrational assignments for that system; the only previously published vibrational data being an assignment of $C\equiv O$ stretches in $[C(CH_2)_3]Fe(CO)_3$ ¹⁰.

EXPERIMENTAL

(Trimethylenemethane)iron tricarbonyl was prepared by the reaction of an excess of 2-methylallyl chloride with $Fe_2(CO)_9$, followed by fractional distillation of the reaction mixture. This gave the desired product, as a pale yellow liquid, without isolation of the intermediate π -allyl complex, $(CH_2=CMe=CH_2)Fe(CO)_3Cl$ ¹¹.

IR spectra of the pure liquid and of solutions in cyclohexane ($C\equiv O$ stretching region only) were run on a Perkin-Elmer 521 spectrometer ($4000-300\text{ cm}^{-1}$). The instrument was calibrated using known peaks of CH_4 , HBr , CO , H_2O and NH_3 ; observed frequencies are all believed to be accurate to within $\pm 2\text{ cm}^{-1}$.

Raman spectra were obtained using a Cary Model 81 spectrometer, with a Spectra-Physics 125 He/Ne laser as excitation source (output approximately 50 mW at 632.8 nm). Samples of the pure liquid and of C_6H_{12} solutions ($C\equiv O$ stretching region only) were held in capillary tubes (internal diameter approx. 1 mm). Depolarisation ratios were obtained by rotating the plane of polarisation of the incident light by 90° and passing the scattered light through a polaroid analyser in each case (the capillary cell having been calibrated against a one-pass liquid cell, which gave accurate ρ values).

RESULTS AND DISCUSSION

The IR and Raman frequencies observed for $[C(CH_2)_3]Fe(CO)_3$ are listed in Table 1, together with the assignments of these, which will be discussed below.

Vibrational analysis

The overall symmetry of the molecule is C_{3v} , and no distinction between "local" and "overall" symmetry need be made. Nevertheless, it will be convenient to divide the analysis into two parts. For the $[C(CH_2)_3]-Fe$ unit, we expect the following numbers and types of vibration:

- (a) CH_2 stretch: $A_1 + A_2 + 2E$
- (b) CH_2 in-plane deformation (scissors): $A_1 + E$
- (c) $C-C$ stretch: $A_1 + E$
- (d) CH_2 rock (in-plane): $A_2 + E$
- (e) CH_2 twist (out-of-plane): $A_2 + E$
- (f) CH_2 wag (out-of-plane): $A_1 + E$
- (g) CC_3 deformation: $A_1 + E$
- (h) $[C(CH_2)_3]-Fe$ stretch: A_1
- (i) $[C(CH_2)_3]-Fe$ tilt: E
- (j) $[C(CH_2)_3]-Fe$ torsion: A_2

(N.B. Under C_{3v} symmetry, A_2 modes are totally inactive, A_1 and E modes are IR- and Raman-active, with the former giving rise to polarised Raman lines.)

TABLE 1

VIBRATIONAL SPECTRA (cm^{-1}) AND ASSIGNMENTS FOR $[\text{C}(\text{CH}_2)_3]\text{Fe}(\text{CO})_3$

IR (liquid film)	Raman ^a (liquid)	Assignment
3086 m	3086 w (dp)	CH_2 stretch (<i>E</i>)
3018 m	3020 m (dp)	CH_2 stretch (<i>E</i>)
2976 w		CH_2 stretch (A_1)
2916 vw	2913 w (dp)	? 1456 + 1474
ca. 2062 s	2067 m (p)	
(2059 s ^b)	(2063 mw (p) ^b)	$\text{C}\equiv\text{O}$ stretch (A_1)
ca. 1980 vs	1989 s (dp)	
(1993 s ^b)	(1995 m (dp) ^b)	$\text{C}\equiv\text{O}$ stretch (<i>E</i>)
1474 m		CH_2 scissors
1456 m		CH_2 scissors
1387 w		915 + 471
1347 w	1349 m (dp)	$\text{C}-\text{C}$ stretch (<i>E</i>)
1262 vw		800 + 471
1157 vw		2 × 579
1103 w (br)		603 + 510
1023 w	1026 m (dp)	CH_2 twist (<i>E</i>)
	989 m (p)	CH_2 wag (A_1)
916 m	920 s (p)	$\text{C}-\text{C}$ stretch (A_1)
900 m		CH_2 wag (<i>E</i>)
814 (sh)	815 (sh) (? dp)	CH_2 rock (<i>E</i>)
800 m	803 m (p)	(out-of-plane) CC_3 deformation (A_1)
748 w		?
727 w	726 w (p)	2 × 371
603 s	605 vw ? (p)	$\text{Fe}-\text{C}-\text{O}$ deformation (A_1)
579 s	582 vw, ? (dp)	$\text{Fe}-\text{C}-\text{O}$ deformation (<i>E</i>)
510 s		$\text{Fe}-\text{C}-\text{O}$ deformation (<i>E</i>)
	493 m (dp)	$\text{Fe}-(\text{CO})$ stretch (<i>E</i>)
471 w	471 m (dp)	(in-plane) CC_3 deformation (<i>E</i>)
438 m	441 m (p)	$\text{Fe}-(\text{CO})$ stretch (A_1)
371 w	373 s (p)	$\text{Fe}-[\text{C}(\text{CH}_2)_3]$ stretch (A_1)
350 vw	352 m (dp)	$\text{Fe}-[\text{C}(\text{CH}_2)_3]$ tilt (<i>E</i>)
	95 s (br) (dp)	Skeletal deformations

^a p = Polarised, dp = depolarised.^b Solution in C_6H_{12} .

For $\text{Fe}(\text{CO})_3$, a similar calculation yields the following results:

- (a) $\text{C}\equiv\text{O}$ stretch: $A_1 + E$
- (b) $\text{Fe}-(\text{CO})$ stretch: $A_1 + E$
- (c) $\text{Fe}-\text{C}-\text{O}$ deformation: $A_1 + A_2 + 2E$
- (d) $\text{C}-\text{Fe}-\text{C}$ deformation: $A_1 + E$

and finally, involving the whole molecule:

- (e) $[\text{C}(\text{CH}_2)_3]-\text{Fe}-(\text{CO})_3$ deformation: *E*

Assignment of frequencies to the $[\text{C}(\text{CH}_2)_3]-\text{Fe}$ unit

The assignment of the internal modes of the trimethylenemethane fragment will be assisted by a comparison of the observed frequencies with those listed and

assigned for the guanidinium ion, $[\text{C}(\text{NH}_2)_3]^+$, the most closely analogous system for which data are available¹².

Three C-H stretches are expected ($A_1 + 2E$), both in the IR and Raman spectra. Only two bands which can be so assigned are seen in the latter, at 3086 and 3020 cm^{-1} . As both are clearly depolarised, they must correspond to the E modes (coincident IR bands occur at 3086 and 3018 cm^{-1}), with the A_1 mode being assigned to the IR band at 2976 cm^{-1} , which has no Raman counterpart. This weakness of the totally symmetric mode in the Raman spectrum is rather unusual.

The (in-plane) CH_2 deformations (scissors) are expected to give rise to bands at ca. 1500 cm^{-1} , e.g. in $(\text{C}_2\text{H}_4)\text{Fe}(\text{CO})_4$ they were found at 1509 and 1446 cm^{-1} ¹³ (medium to strong in the IR, weak in the Raman spectrum). In the present study, no Raman bands were seen in this region, but there were two IR absorptions of medium intensity at 1474 and 1456 cm^{-1} . These must correspond to the $A_1 + E$ CH_2 deformations, but in the absence of Raman polarisation data, no specific assignment is possible.

Angell *et al.*¹² in their study of the $[\text{C}(\text{NH}_2)_3]^+$ ion, found that the two CN_3 stretches gave rise to bands at ca. 1650 and 1006 cm^{-1} . The former was assigned to the E mode (strongly coupled with the NH_2 deformation of E symmetry), the latter to the A_1 mode. The totally symmetric CC_3 stretch in $\text{C}(\text{CH}_2)_3$ must be assigned to a very strong, and strongly polarised, Raman band at 920 cm^{-1} (916 cm^{-1} in the IR). A depolarised Raman band of medium intensity, at 1349 cm^{-1} (IR absorption at 1347 cm^{-1}) can be assigned to the degenerate stretching mode. It is very likely, however, that extensive coupling will occur between this mode and the CH_2 deformation of E symmetry (1474 or 1456 cm^{-1}), so that the descriptions of these modes must be approximate¹⁴.

The remaining CH_2 deformations may be considered next. One CH_2 twist (out-of-plane) is IR- and Raman-active (E symmetry), as are one CH_2 rock (in-plane, E) and two CH_2 wags (out-of-plane, $A_1 + E$). The twisting and wagging motions would be expected to give rise to bands in the region 900–1100 cm^{-1} , with the rocking mode at ca. 800 cm^{-1} ¹⁵. The symmetric wag (A_1) must correspond to the polarised Raman band at 989 cm^{-1} (no IR counterpart), while the most likely candidate for the wagging mode of E symmetry is an IR band at 900 cm^{-1} (no corresponding Raman feature.) Depolarised Raman bands at 1026 and 815 cm^{-1} (both with coincident IR absorptions), must be the CH_2 twist (E) and CH_2 rock (E) respectively.

The only remaining vibrations involving $\text{C}(\text{CH}_2)_3$ alone are the two skeletal CC_3 deformations. The CC_3 skeleton of the trimethylenemethane molecule does not depart too greatly from planarity, and in planar XY_3 systems the in-plane deformation mode (E) occurs at a lower frequency than the out-of-plane deformation (A_1); the latter, furthermore, gives a polarised Raman line. The A_1 mode deformation (corresponding to the out-of-plane mode) is therefore assigned to a medium-intensity Raman band (polarised) at 803 cm^{-1} {IR absorption at 800 cm^{-1} ; in $[\text{C}(\text{NH}_2)_3]^+$ the analogous mode was found¹² at 722 cm^{-1} }. The mode corresponding to the in-plane deformation is believed to occur in the same region as a number of $\text{Fe}(\text{CO})_3$ vibrations {e.g. 515 cm^{-1} in $[\text{C}(\text{NH}_2)_3]^+$ }¹². Two depolarised Raman bands, of comparable intensity are found at 493 and 471 cm^{-1} ; they must be the (E symmetry) $\text{Fe}(\text{CO})$ stretch and the remaining CC_3 deformation. As the degenerate $\text{Fe}(\text{CO})$ stretch in the closely analogous $(\text{C}_4\text{H}_4)\text{Fe}(\text{CO})_3$ is found at 513 cm^{-1} , we prefer to assign the lower-frequency band to the CC_3 skeletal deformation.

We must next consider the vibrations involving the whole $\text{Fe}-[\text{C}(\text{CH}_2)_3]$ group. The $\text{Fe}-[\text{C}(\text{CH}_2)_3]$ torsion is of A_2 symmetry and therefore totally inactive. Fe -(hydrocarbon) stretches are found generally in the $350\text{--}400\text{ cm}^{-1}$ region^{9,13,16}, e.g. for (cyclobutadiene)- Fe , the stretch gives a strong, polarised Raman line at 398 cm^{-1} . In the present study, we have observed a closely analogous feature at 373 cm^{-1} , (with a weak IR absorption at 371 cm^{-1}) which can be assigned to the (A_1) $\text{Fe}-[\text{C}(\text{CH}_2)_3]$ stretch. The tilting motion of the trimethylenemethane molecule with respect to the Fe atom is believed to give rise to the medium-intensity, depolarised Raman band at 352 cm^{-1} (very weak IR absorption at 350 cm^{-1}). It is rather unusual for this frequency to be lower than that of the (hydrocarbon)- Fe stretch, but the tilting frequency has been observed over a wide range in similar systems (from 471 cm^{-1} in (cyclobutadiene) $\text{Fe}(\text{CO})_3$ ⁹ to 363 cm^{-1} in (butadiene) $\text{Fe}(\text{CO})_3$ ¹⁶).

The $\text{Fe}-[\text{C}(\text{CH}_2)_3]$ assignments are summarised in Table 2.

TABLE 2

ASSIGNMENT OF FREQUENCIES (cm^{-1}) FOR $[\text{C}(\text{CH}_2)_3]\text{-Fe}$ IN $[\text{C}(\text{CH}_2)_3]\text{Fe}(\text{CO})_3$

C-H stretching	A_1	2976
	A_2	Not observed
	E	3086
	E	3019
CH ₂ in-plane deformation	A_1	1474
	E	1456
CC ₃ stretches	A_1	918
	E	1348
CH ₂ rock	A_2	Not observed
	E	815
CH ₂ twist	A_2	Not observed
	E	1025
CH ₂ wag	A_1	989
	E	900
CC ₃ deformation	A_1	802
	E	471
$\text{Fe}-[\text{C}(\text{CH}_2)_3]$ stretch	A_1	372
$\text{Fe}-[\text{C}(\text{CH}_2)_3]$ tilt	E	351
$\text{Fe}-[\text{C}(\text{CH}_2)_3]$ torsion	A_2	Not observed

Assignment of frequencies to the $\text{Fe}(\text{CO})_3$ unit

These are expected to be very similar to those proposed for the complexes (cyclobutadiene)- and (butadiene)- $\text{Fe}(\text{CO})_3$ ^{9,16}.

Two $\text{C}\equiv\text{O}$ stretches should be observed, for C_{3v} symmetry $\text{Fe}(\text{CO})_3$, and two are found, at 2061 and 1994 cm^{-1} (in dilute C_6H_{12} solutions, the frequencies quoted

being the mean of the observed IR and Raman values). Polarisation data indicate that the higher frequency feature belongs to the A_1 mode. It is interesting to compare the values of the totally symmetric $C\equiv O$ stretches in (cyclobutadiene)-, (2051 cm^{-1}), (butadiene)-, (2057 cm^{-1}), and (trimethylenemethane)- $Fe(CO)_3$ (2061 cm^{-1}). Studies of (substituted arene)- $Cr(CO)_3$ complexes¹⁷ have shown that very slight changes in the electron-donating power of the hydrocarbon in (hydrocarbon)- $M(CO)_3$ complexes are accurately mirrored by the values of the symmetric $C\equiv O$ stretching frequencies (a stronger electron donor giving a stronger $M-C$, and therefore a weaker $C\equiv O$ bond). Thus we can suggest the following series for electron-donating ability [in $Fe(CO)_3$ complexes]: cyclobutadiene > butadiene > trimethylenemethane.

The assignment of most of the lower-frequency bands is quite straightforward. The $Fe-CO$ stretches are at $440 (A_1)$ and $493\text{ cm}^{-1} (E)$, while the $Fe-C-O$ deformations give almost identical frequencies to the equivalent modes in $(C_4H_4)Fe(CO)_3$, *i.e.* $604 (A_1)$, $581 (E)$ and $510\text{ cm}^{-1} (E)$, with the (inactive) A_2 mode not observed.

The skeletal deformation regions ($< 150\text{ cm}^{-1}$) in the butadiene and cyclobutadiene complexes were very similar^{9,16}. Thus weak, polarised, and strong, depolarised, Raman bands (in the range 135 to 104 cm^{-1}) were assignable to A_1 and E $C-Fe-C$ deformations, respectively, with a strong depolarised Raman band at ca. 100 cm^{-1} due to the (hydrocarbon)- $Fe-CO_3$ deformation (E symmetry). In the trimethylenemethane complex, however, only one Raman band was found below 150 cm^{-1} , a broad, strong, depolarised feature at 95 cm^{-1} . It would appear that the two E modes must be very close in frequency in this complex, with the symmetric deformation either too weak to observe or accidentally degenerate with the other two.

The $Fe(CO)_3$ assignments are summarised in Table 3.

TABLE 3

ASSIGNMENT OF FREQUENCIES (cm^{-1}) FOR $Fe-CO_3$ IN $[C(CH_2)_3]Fe(CO)_3$

C≡O stretching	A_1	2061
	E	1994
Fe-CO stretching	A_1	440
	E	493
Fe-C-O deformation	A_1	604
	A_2	Not observed
	E	581
C-Fe-C deformation	E	510
	A_1	295
	E	95
$[C(CH_2)_3]-Fe-CO_3$ deformation	E	95

CONCLUSION

A virtually complete assignment of the hitherto (vibrationally) uncharacterised trimethylenemethane molecule has been possible, together with data for the $Fe(CO)_3$ vibrations of (trimethylenemethane) $Fe(CO)_3$.

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