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VIBRATIONAL FORCE CONSTANTS IN (TRIMETHYLENEMETHANE)-IRON TRICARBONYL

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Summary

A valence force field has been calculated for (trimethylenemethane)iron tricarbonyl, using approximations of a well-established type. The force constants are largely as expected from general considerations of bonding in this molecule; in particular the C—C stretching force constant (4.41 mdyne $Å^{-1}$) is rather low, about the usual value for a single bond. Many of the observed wavenumbers are found to involve complex mixtures of internal coordinates.

Introduction

In a previous publication [1] the vibrational spectrum of (trimethylenemethane)iron tricarbonyl, $[C(CH_2)_3]Fe(CO)_3$, was reported and assigned for the first time. In order to gain a deeper insight into the vibrational properties and bonding of this interesting species we have carried out a normal coordinate analysis using these spectroscopic data. Transition metal π-complexes have been studied in this manner rather rarely in the past. Two of us have recently reported [2] a normal coordinate analysis of (cyclobutadiene)iron tricarbonyl, $(C_4H_4)Fe(CO)_3$; a simplified version of the general valence force field was employed, and because of the low overall symmetry and low barrier to rotation about the (C_4H_4)—Fe bond the molecule was treated as two independent fragments, (C_4H_4)—Fe and R—$Fe(CO)_3$ (i.e. C_4H_4 as a point mass). An apparently reasonable, although doubtless not unique, solution was found for the problem, and these force constants were consistent with generally-held views on the bonding in this complex. Other π-complexes to be subjected to normal coordinate analyses are ferrocene [3], bis(benzene)chromium [4-6] and benzenechromium tricarbonyl [7,8], by Cyvin and his coworkers. These authors concluded that the internal force-field of the $C_5H_5^-$ or C_6H_6 ligand is not altered on complex formation, frequency shifts being due to kinematic coupling effects, although no details of the final force field were given. Some partial calculations on ferrocene have been described by Lippincott and

Nelson [9] and by Hyams [10], while for $(C_6H_6)Cr(CO)_3$ a highly-approximate force field was reported by *Cataliotti et al.* [11].

Transition metal carbonyls, on the other hand, have been subjected to a very extensive and thorough series of force constant calculations by Jones and his coworkers, viz $Ni(CO)_4$ [12], $M(CO)_6$, (M = Cr, Mo or W) [13], $Fe(CO)_5$ [14], $Co(CO)_3(NO)$ [15], and $Mn(CO)_5Br$ [16]. Considerable use was made of data referring to samples enriched in ^{13}C or ^{18}O, and with this amount of data a close approach to the general quadratic valence force field could be made. A number of interaction force constants appeared to be transferable from one carbonyl system to another, and use will be made of this observation in the present case.

Experimental

The preparation of (trimethylemethane)iron tricarbonyl, and the methods of obtaining the spectra were reported previously [1]. The assignments pro-

TABLE 1

VIBRATIONAL ASSIGNMENT FOR $(C(CH_2)_3)Fe(CO)_3$

(All figures in cm^{-1})

A_1	C—H stretch	2976
	C≡O stretch	2061
	CH_2 in-plane deformation	1474
	CH_2 wag	989
	CC_3 stretch	918
	CC_3 deformation	802
	Fe—C—O deformation	604
	Fe—(CO) stretch	440
	Fe—$[C(CH_2)_3]$ stretch	372
	OC—Fe—CO deformation	
A_2	C—H stretch	
	CH_2 twist	
	CH_2 rock	
	Fe—C—O deformation	
	Fe—$[C(CH_2)_3]$ torsion	
E	C—H stretch	3086
	C—H stretch	3019
	C≡O stretch	1994
	CH_2 in-plane deformation	1456
	CC_3 stretch	1348
	CH_2 twist	1025
	CH_2 wag	900
	CH_2 rock	815
	Fe—C—O deformation	581
	Fe—C—O deformation	510
	Fe—(CO) stretch	493
	CC_3 deformation	471
	Fe—$[C(CH_2)_3]$ tilt	351
	OC—Fe—CO deformation	
	$[C(CH_2)_3]Fe—(CO)_3$ deformation	95

posed on the basis of these data, and which will be used in this work are summarised in Table 1.

The calculations used the programs described by Snyder and Schachtschneider [17,18] as well as one not described hitherto. This program provided an alternative method for refining the set of force constants, using an algorithm devised by Marquardt [19]. This program will be described in detail subsequently [20].

The set of internal coordinates used for the $[C(CH_2)_3]Fe(CO)_3$ system are shown in Fig. 1, while the symmetry coordinates are listed in Table 2.

Since the number of force constants needed to define the general valence force field far exceeds the number of vibrational wavenumbers, it is necessary to fix a number of the former arbitrarily, usually at zero, although some interaction force constants could be transferred from the work of Jones et al. on $M(CO)_6$ (M = Cr, Mo or W; these species were chosen because they contain M—C—O units at 90° to each other [13]). A further necessary approximation stems from the fact that insufficient data on overtone bands were available to calculate anharmonicity corrections. The work of Jones et al. on metal carbonyls, however, suggests that only for C≡O stretching modes is this a significant factor [12-16]. Finally, the dimensions of $[C(CH_2)_3]Fe(CO)_3$ determined

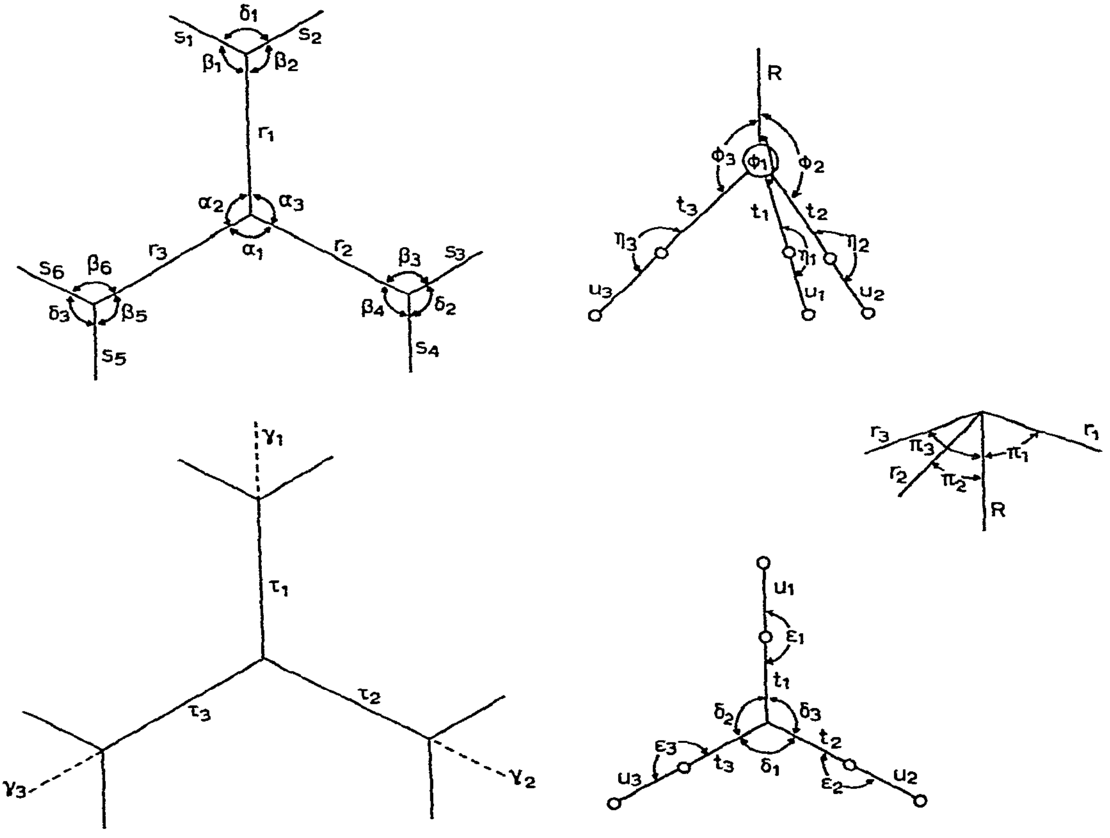

Fig. 1. The internal coordinates of $[C(CH_2)_3]Fe(CO)_3$.

TABLE 2

A SET OF SYMMETRY COORDINATES FOR $[C(CH_2)_3]Fe(CO)_3$

A_1	$S_1 =$	$1/\sqrt{6}(s_1 + s_2 + s_3 + s_4 + s_5 + s_6)$
	$S_2 =$	$1/\sqrt{3}(u_1 + u_2 + u_3)$
	$S_3 =$	$1/3(\delta_1 + \delta_2 + \delta_3 - \beta_1 - \beta_2 - \beta_3 - \beta_4 - \beta_5 - \beta_6)$
	$S_4 =$	$1/\sqrt{3}(\gamma_1 + \gamma_2 + \gamma_3)$
	$S_5 =$	$1/\sqrt{3}(r_1 + r_2 + r_3)$
	$S_6 =$	$1/\sqrt{6}(\alpha_1 + \alpha_2 + \alpha_3 + \pi_1 + \pi_2 + \pi_3)$
	$S_7 =$	$1/\sqrt{3}(\eta_1 + \eta_2 + \eta_3)$
	$S_8 =$	$1/\sqrt{3}(t_1 + t_2 + t_3)$
	$S_9 =$	R
	$S_{10} =$	$1/\sqrt{6}(\theta_1 + \theta_2 + \theta_3 - \phi_1 - \phi_2 - \phi_3)$
	$S_{11} =$	$1/\sqrt{6}(\theta_1 + \theta_2 + \theta_3 + \phi_1 + \phi_2 + \phi_3)$
	$S_{12} =$	$1/\sqrt{6}(\alpha_1 + \alpha_2 + \alpha_3 - \pi_1 - \pi_2 - \pi_3)$
	$S_{13} =$	$1/\sqrt{18}(2\delta_1 + 2\delta_2 + 2\delta_3 + \beta_1 + \beta_2 + \beta_3 + \beta_4 + \beta_5 + \beta_6)$
A_2	$S_{14} =$	$1/\sqrt{6}(s_1 - s_2 + s_3 - s_4 + s_5 - s_6)$
	$S_{15} =$	$1/\sqrt{3}(\tau_1 + \tau_2 + \tau_3)$
	$S_{16} =$	$1/\sqrt{6}(\beta_1 - \beta_2 + \beta_3 - \beta_4 + \beta_5 - \beta_6)$
	$S_{17} =$	$1/\sqrt{3}(\epsilon_1 + \epsilon_2 + \epsilon_3)$
	$S_{18} =$	
E_a	$S_{19a} =$	$1/\sqrt{12}(2s_1 + 2s_2 - s_3 - s_4 - s_5 - s_6)$
	$S_{20a} =$	$1/\sqrt{2}(-s_3 + s_4 + s_5 - s_6)$
	$S_{21a} =$	$1/\sqrt{6}(-u_1 + 2u_2 - u_3)$
	$S_{22a} =$	$1/\sqrt{18}(2\delta_1 - \delta_2 - \delta_3 - 2\beta_1 - 2\beta_2 + \beta_3 + \beta_4 + \beta_5 + \beta_6)$
	$S_{23a} =$	$1/\sqrt{6}(2r_1 - r_2 - r_3)$
	$S_{24a} =$	$1/\sqrt{2}(-\tau_2 + \tau_3)$
	$S_{25a} =$	$1/\sqrt{6}(2\gamma_1 - \gamma_2 - \gamma_3)$
	$S_{26a} =$	$1/2(-\beta_3 + \beta_4 + \beta_5 - \beta_6)$
	$S_{27a} =$	$1/\sqrt{6}(-\eta_1 + 2\eta_2 - \eta_3)$
	$S_{28a} =$	$1/\sqrt{2}(\epsilon_1 - \epsilon_3)$
	$S_{29a} =$	$1/\sqrt{6}(-t_1 + 2t_2 - t_3)$
	$S_{30a} =$	$1/\sqrt{6}(2\alpha_1 - \alpha_2 - \alpha_3)$
	$S_{31a} =$	$1/\sqrt{6}(2\pi_1 - \pi_2 - \pi_3)$
	$S_{32a} =$	$1/\sqrt{6}(-\theta_1 - \theta_2 + 2\theta_3)$
	$S_{33a} =$	$1/\sqrt{6}(-\phi_1 + 2\phi_2 - \phi_3)$
	$S_{34a} =$	$1/6(4\delta_1 - 2\delta_2 - 2\delta_3 + 2\beta_2 - \beta_3 - \beta_4 - \beta_5 - \beta_6)$
E_b	$S_{19b} =$	$1/2(s_3 + s_4 - s_5 - s_6)$
	$S_{20b} =$	$1/\sqrt{12}(2s_1 - 2s_2 - s_3 + s_4 - s_5 + s_6)$
	$S_{21b} =$	$1/\sqrt{2}(-u_1 + u_3)$
	$S_{22b} =$	$1/\sqrt{6}(\delta_2 - \delta_3 - \beta_3 - \beta_4 + \beta_5 + \beta_6)$
	$S_{23b} =$	$1/\sqrt{2}(r_2 - r_3)$
	$S_{24b} =$	$1/\sqrt{6}(2\tau_1 - \tau_2 - \tau_3)$
	$S_{25b} =$	$1/\sqrt{2}(\gamma_2 - \gamma_3)$
	$S_{26b} =$	$1/\sqrt{12}(2\beta_1 - 2\beta_2 - \beta_3 + \beta_4 - \beta_5 + \beta_6)$
	$S_{27b} =$	$1/\sqrt{2}(-\eta_1 + \eta_3)$
	$S_{28b} =$	$1/\sqrt{6}(-\epsilon_1 + 2\epsilon_2 - \epsilon_3)$
	$S_{29b} =$	$1/\sqrt{2}(-t_1 + t_3)$
	$S_{30b} =$	$1/\sqrt{2}(\alpha_2 - \alpha_3)$
	$S_{31b} =$	$1/\sqrt{2}(\pi_2 - \pi_3)$
	$S_{32b} =$	$1/\sqrt{2}(\theta_1 - \theta_2)$
	$S_{33b} =$	$1/\sqrt{2}(-\phi_1 + \phi_3)$
	$S_{34b} =$	$1/\sqrt{12}(2\delta_2 - 2\delta_3 + \beta_3 + \beta_4 - \beta_5 - \beta_6)$

by electron diffraction in the gas phase (Fig. 2) [21], were assumed to apply in the liquid phase (to which the vibrational data refer) also.

Preliminary calculations were performed in which the molecule was divided into $[C(CH_2)_3]$—Fe and R—$Fe(CO)_3$ fragments. The procedure adopted

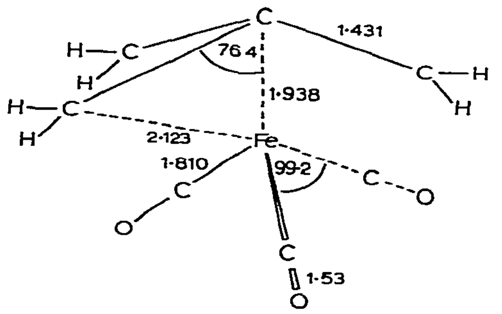

Fig. 2. The molecular structure and dimensions of $[C(CH_2)_3]Fe(CO)_3$.

was as follows: a simple valence force field was assumed initially, i.e. no off-diagonal elements were included in the F matrix, the values being chosen by analogy with those for (cyclobutadiene)iron tricarbonyl [2], and for other metal carbonyl systems. These force constants were allowed to vary freely to obtain the closest possible fit with the observed wavenumbers. The remaining errors were noted, and suitable interaction terms were added to the F matrix (only those which gave a significant improvement in the calculated wavenumbers being retained), up to the limit imposed by the number of observed wavenumbers. It was found, however, that certain force constants known to be significant had to be kept at fixed, non-zero values, since if they were allowed to vary freely no convergence could be obtained. For such force constants, optimum values were found by carrying out a series of calculations with them at differing, fixed values.

Force fields were thereby obtained for the separated fragments $[C(CH_2)_3]$-Fe and R—Fe$(CO)_3$, and these were used to find an acceptable force field for the molecule treated as a whole. It was necessary at this stage to introduce a few terms involving interaction between internal coordinates in the two fragments, of which $f_{\pi\eta}$ and $f_{\tau\epsilon}$ were found to be significant, and also a force constant corresponding to the "whole molecule" torsion, f_μ.

Results and discussion

Calculated force field for $[C(CH_2)_3]Fe(CO)_3$

The final force field obtained is summarised in Table 3, all other force constants being fixed at zero. The units in which the force constants are expressed as as follows: *(a)* stretching and stretch/stretch interactions, mdyne $Å^{-1}$, *(b)* bending and bend/bend interactions, mdyne Å rad^{-2}, and *(c)* stretch/bend interactions, mdyne rad^{-1}. The observed and calculated wavenumbers are listed in Table 4, the greatest error being 3 cm^{-1} for the C—H stretch of E symmetry. The values for the inactive A_2 modes are all reasonable (C—H stretch, 3080; CH_2 twist, 1117; CH_2 rock, 864; Fe—C—O deformation, 483; torsion, 237 cm^{-1}). The last value is highly artificial, however, as it did not prove possible to obtain a well-defined value for the force constant associated with it, f_μ.

We will first discuss the diagonal force constants associated solely with

TABLE 3

FINAL FORCE FIELD FOR $[C(CH_2)_3]Fe(CO)_3$[a]

Stretching force constants:	f_R	2.83
	f_r	4.41
	f_s	5.36
	f_t	3.04
	f_u	16.18
Bending force constants:	f_α	1.41
	f_β	0.77
	f_γ	0.29
	f_δ	0.36
	f_τ	0.16
	f_θ	0.98
	f_ϕ	0.31
	f_ϵ	0.82
	f_η	0.62
	f_π	3.27
	f_μ	not clearly defined
Stretch—stretch interactions	f_{Rt}	0.57
	f_{rR}	0.75^b
	f_{rs}	-0.75^b
	f_{rs}'	0.39
	f_{tu}	0.70^b
	f_{uu}	0.36
Stretch—bend interactions:	$f_{R\pi}$	0.97
	$f_{r\pi}$	0.90^b
	$f_{r\beta}$	0.10
	$f_{t\eta}$	-0.09
Bend—bend interactions.	$f_{\alpha\pi}$	0.31^b
	$f_{\gamma\pi}$	0.22
	$f_{\gamma\pi}'$	0.15
	$f_{\pi\pi}$	0.44^b
	$f_{\pi\eta}$	0.22
	$f_{\tau\epsilon}$	-0.18

[a] Units as given in the text. f_i is an internal valence force constant related to the internal coordinate of the type *i* see Fig. 1. *f_{ij}, are interaction terms relating to internal coordinates of types of i and j.* The constants f_{ij} refer to interactions between adjacent, f_{ij}' those between non-adjacent coordinates.
[b] Constrained values.

the $C(CH_2)_3$ ligand. The C—C stretching force constant (f_r) is 4.41 mdyne Å^{-1}, which is comparable with that for a single C—C bond (ca. 4.5 mdyne Å^{-1}). A simple view of the bonding in the free ligand would indicate a C—C bond order of 1.33, and so the result for the complex indicates a substantial interaction of the π-electrons of the CC_3 skeleton with the Fe atom. This is consistent with the qualitative bonding scheme suggested by Churchill and Gold [22]. The value of f_s, the C—H stretching force constant (5.36 mdyne Å^{-1}) is reasonable for approximately sp^2 hybridised carbon (5.598 mdyne Å^{-1} in ethylene [23]).

There is rather little to say about the force constants associated with the deformations of the CH_2 group (in-plane deformation or "scissors", rock, wag and twist), all being quite similar to those found generally for CH_2 units, with sp^2 hybridised carbon; any differences from e.g. ethylene [23] are insignificant at this level of approximation.

TABLE 4

OBSERVED AND CALCULATED WAVENUMBERS FOR $[C(CH_2)_3]Fe(CO)_3$

Symmetry	Observed (cm^{-1})	Calculated (cm^{-1})
A_1	2976	2975
	2061	2059
	1474	1474
	989	989
	918	918
	802	802
	604	603
	440	441
	372	373
		128
A_2		3080
		1117
		864
		483
		237
E	3086	3086
	3019	3022
	1994	1993
	1456	1456
	1348	1348
	1025	1025
	900	900
E	815	815
	581	580
	510	510
	493	493
	471	471
	351	351
		119
	95	95

The CCC deformation force constant (f_α), with a value of 1.27 mdyne Å rad^{-2}, is quite large, and indicative of a fairly rigid CC_3 skeleton in the complexed ligand.

In the absence of a quantitative description of the bonding in this complex, it is difficult to comment on the precise significance of the interaction terms involving the $C(CH_2)_3$ unit. None have values which are obviously unreasonable.

Dealing now with the other $Fe—[C(CH_2)_3]$ force constants, the value of f_R, the metal—ligand (defined as Fe—central carbon atom) stretching force constant, is 2.83 mdyne Å^{-1}, compared with 3.24 mdyne Å^{-1} in $(C_4H_4)Fe(CO)_3$ [2]. The latter, however, was obtained by considering the C_4H_4 as a point mass i.e. interactions involving internal ligand modes were ignored. The value for the present species is nevertheless consistent with a reasonably strong $Fe—[C(CH_2)_3]$ bond. A significant interaction between Fe and the terminal C atoms of the ligand is also believed to occur. Such an interaction would contribute to f_π, the Fe—C—C bending force constant, as this motion involves changing the $Fe—C_{terminal}$ distances. The calculated value of f_π is 3.27 mdyne Å rad^{-2}, which, when reduced to the dimensions of a stretching force constant, corresponds to 1.16 mdyne Å^{-1}.

A number of interaction terms involving R and/or π were found to be significant, especially $f_{R\pi}$, $f_{r\pi}$, $f_{\pi\pi}$ and $f_{\alpha\pi}$. Clearly the bonding in the Fe—[C(CH$_2$)$_3$] unit must be considered as a whole, and alteration in any part of the unit produces marked changes in the bonding of the remainder. The exact values of a number of these interaction terms may not be very significant, however, as they had to be held fixed, and optimum values were found for them by trying series of different fixed values — a less efficient procedure.

Of the force constants more closely associated with the Fe(CO)$_3$ fragment, f_t and f_u (the Fe—CO and C—O stretching force constants) are rather close to the values found for (C$_4$H$_4$)Fe(CO)$_3$ [2] [in which (C$_4$H$_4$) was treated as a point mass]. Both, however, are slightly higher than in the latter case (3.04, 16.18, as against 2.98, 16.01 mdyne Å^{-1}), which is inconsistent with the bonding model for the Fe—C—O unit, and is presumably related to the inadequacy of the (C$_4$H$_4$)Fe(CO)$_3$ calculation. By comparison with Fe(CO)$_5$ [14], however, the values all indicate a greater amount of Fe → CO back-bonding for the organo-derivatives as opposed to the carbonyl itself.

The calculated Fe—C—O bending force constants (0.82, 0.65 mdyne Å rad^{-2} for f_ϵ, f_η respectively) are substantially greater than those for Fe(CO)$_5$ (0.4-0.5 mdyne Å rad^{-2}). This suggests a greater rigidity for the Fe—C—O units, consistent with the increased Fe → CO back donation indicated by the stretching force constants.

The interaction terms involving the Fe(CO)$_3$ unit alone are quite similar to those found for (C$_4$H$_4$)Fe(CO)$_3$ [2]. However, in order to obtain a satisfactory refinement, addition of two terms corresponding to interactions between the C(CH$_2$)$_3$ and carbonyl fragments was necessary, i.e. $f_{\pi\eta}$ and $f_{\tau\epsilon}$. Both involved the Fe—C—O deformations, and were quite substantial (0.22, —0.18 mdyne Å rad^{-2} respectively).

Potential energy distribution for the vibrations of [C(CH$_2$)$_3$]Fe(CO)$_3$

The diagonal elements of the potential energy distribution matrix for any molecule (i.e. $L_{ji}^2F_{jj}/\lambda_i$, where F_{jj} is a valence force constant and L_{ji} is the associated eigenvector for any normal mode of wavenumber $\nu_i = \lambda_i^{1/2}N^{1/2}/2\pi C$, where ν_i is in cm^{-1} and N is Avogadro's number) often reveal that the association of any one observed wavenumber with one symmetry coordinate (and hence, usually, one type of internal coordinate) is an oversimplification. These diagonal elements for the normal modes of [C(CH$_2$)$_3$]Fe(CO)$_3$ are listed in Table 5 (elements < 0.05 are omitted.) They reveal that many of the wavenumbers below 1500 cm^{-1} are indeed associated with a number of different valence force constants.

Considering first the A_1 block: the bands at 2976, 2061 cm^{-1} are virtually "pure" CH, CO stretching respectively. The feature at 1474 cm^{-1} involves f_β, f_δ only, consistent with its assignment as the CH$_2$ in-plane (scissors) deformation — both β and δ are altered in this mode. The bands at 989 and 802 cm^{-1} contain contributions from CC$_3$ stretching and bending, while that at 918 cm^{-1} is due almost entirely to CH$_2$ wagging — thus the original assignment needs extensive modification.

TABLE 5

POTENTIAL ENERGY DISTRIBUTION FOR $[C(CH_2)_3]Fe(CO)_3$[a]

		f_R	f_r	f_s	f_t	f_u	f_α	f_β	f_γ	f_δ	f_τ	f_D	f_ϕ	f_c	f_η	f_π	f_μ
A_1	2976			0.97													
	2061				0.06	0.94											
	1474		0.06					0.49		0.46							
	989	0.26	0.25				0.14									0.60	
	918						0.05		1.22							0.19	
	802		0.48													0.11	
	604	0.19			0.09							0.24	0.05		0.56	0.08	
	440				0.94										0.07		
	372	0.94			0.07										0.12		
	(128)	0.08										0.58	0.11		0.25		
E	3086			0.98													
	3019			0.93													
	1994				0.07	1.00											
	1456		0.09					0.50		0.45							
	1348		0.26				0.17	0.58									
	1025							0.05	0.82		0.06					0.06	
	900		0.70	0.09			0.05	0.32	0.10								
	815		0.13						0.05		0.41			0.14			
	581				0.49						0.17	0.07		0.07	0.05	0.14	
	510				0.21							0.06	0.06		0.72		
	493		0.06				0.45				0.16	0.06		0.21		0.22	
	471		0.05		0.11		0.14				0.33			0.54	0.13		
	351		0.10		0.08		0.14									0.78	
	(119)										0.09	0.71		0.32			
	95												0.91		0.07		

[a] All elements less than 0.05 not entered.

The assignments of the 440 (Fe—CO stretch) and 372 cm^{-1} (Fe—[$C(CH_2)_3$] stretch) are both consistent with the potential energy data, but the 604 cm^{-1} band, and that calculated to be ca. 128 cm^{-1} both comprise Fe—C—O and OC—Fe—CO bending.

Similar pictures emerge from the *E* block. The CH and CO stretches involve very little mixing of internal coordinates, as does the CH_2 in-plane deformation. All the remaining features down to 400 cm^{-1}, however, show substantial contributions from several internal coordinates, and the association of, for example the band at 1348 cm^{-1} with the CC_3 stretch is highly arbitrary. For this, the potential energy distribution shows the major contribution to be from the CH_2 rock, with smaller and roughly equal contributions from the CC_3 stretch and CCC deformation. Of the low wavenumber features, that at 351 cm^{-1} is, as assigned, chiefly due to the Fe—[$C(CH_2)_3$] tilt, with the band at 95 cm^{-1} almost exclusively [$C(CH_2)_3$]Fe—$(CO)_3$ deformation. A calculated wavenumber of 119 cm^{-1} is derived from a mixture of OC—Fe—CO and Fe—C—O deformations.

Conclusion

An approximate valence force field has been calculated for [$C(CH_2)_3$]-$Fe(CO)_3$ which reproduces the observed wavenumbers very well, and is in accord with the expected bonding scheme for the molecule. Many of the wavenumbers were shown to be due to very complex normal modes, which involved several different types of internal coordinate.

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