Journal of Organometallic Chemistry, 76 (1974) 373—384

A NORMAL COORDINATE ANALYSIS OF (CYCLOBUTADIENE)IRON TRICARBONYL

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(Received March 14th, 1974)

Summary

By the use of judicious approximations, a valence force field has been calculated for the (cyclobutadiene)iron tricarbonyl molecule, using C_{4v} symmetry for the C_4H_4 and C_{3v} for the RFe(CO)$_3$ moiety. The data for the C_4H_4 ring represent the first attempt to obtain a reasonably complete vibrational force field for such a species. The high frequency of the "ring-breathing" mode results from the large CC stretch/stretch interaction terms. For RFe(CO)$_3$, the results were in accord with those for analogous systems; it is proposed that the assignments of one of the Fe—C—O deformations and the Fe—C stretch (both of *E* symmetry) should be changed, as should those for the *E* symmetry C—Fe—C and (C_4H_4)—Fe—(CO)$_3$ deformations.

Introduction

In a previous publication [1] the vibrational spectrum of (cyclobutadiene)-iron tricarbonyl was reported and assigned for the first time. In order to gain a deeper insight into the vibrational properties and bonding in this complex we have carried out a normal coordinate analysis using these spectroscopic data. Only a very limited number of such analyses have been performed hitherto on transition metal π-complexes. The most ambitious have been by Cyvin et al. on ferrocene [2], dibenzenechromium [3—5], and benzenechromium tricarbonyl [6,7]. These authors conclude that the internal force field of the ligand is unchanged upon complex formation, the observed frequency shifts being accounted for by kinematic coupling effects. The details of the calculations and of the resulting force field are, however, rather obscure in the published reports.

Ferrocene has also been the subject of an early calculation by Lippincott and Nelson [8] (where the normal coordinate analysis was carried out on an isolated C_5H_5 unit) and a recent one by Hyams [9] [on an Fe—(C_5H_5) unit; using the ferrocene frequencies assigned to modes of *u*-symmetry]. The latter work also considered a number of possible internal coordinates by which the iron-

(C_5H_5) stretch might be represented and the use of all five Fe—C bond vectors proved to be the most satisfactory.

The only remaining normal coordinate analysis on a π-bonded cyclic hydrocarbon was carried out on $(C_6H_6)Cr(CO)_3$ by Cataliotti et al. [10]. This well illustrates some of the problems inherent in this type of work, for in the absence of Raman data an erroneous assignment was proposed, and an approximate force field was obtained which reproduced exactly the frequencies of the incorrect assignment.

When considering the metal carbonyl moiety, however, a great number of previous calculations are available upon which to base further work. The most relevant are those carried out by Jones et al. on $Ni(CO)_4$ [11], $M(CO)_6$, (M = Cr, Mo, W) [12], $Fe(CO)_5$ [13] and $Co(CO)_3(NO)$ [14]. All of these made extensive use of isotopic substitution, and in all cases a close approach was made to the general quadratic valence force field. The results from the hexacarbonyls [12] are of particular relevance to the present work, in which the M—C—O units are at 90° to each other, as they are (approximately) in $(C_4H_4)Fe(CO)_3$, since it was shown that a number of interaction constants were transferable from one such system to another.

Experimental

The preparation of (cyclobutadiene)iron tricarbonyl and the methods of obtaining the spectra were reported previously [1]. The assignment proposed on the basis of these data, and which will be used in this work, is summarised in Table 1.

TABLE 1

VIBRATIONAL ASSIGNMENT FOR $(C_4H_4)Fe(CO)_3$
(all figures in cm^{-1})

(a) Vibrations of C_4H_4—Fe (C_{4v} symmetry)

A_1	C—H stretch	3132	B_2	Ring stretch	1327
	Ring stretch	1234		I.p. CH def.	964
	O.o.p. CH def.	824	E	C—H stretch	3132
	Fe—(C_4H_4) stretch	398		Ring stretch	1327
A_2	i.p. CH def.			I.p. CH def.	975
	Fe—(C_4H_4) torsion			O.o.p. CH def.	939
B_1	C—H stretch	3132		Fe—(C_4H_4) tilt	471
	I.p. ring def.	957			
	O.o.p. CH def.	774			
	O.o.p. ring def.	506			

(i.p. = in-plane; o.o.p. = out-of-plane)

(b) Vibrations of $Fe(CO)_3$ (C_{3v} symmetry)

A_1	C—O stretch	2052	E	C—O stretch	1971
	Fe—C—O def.	611		Fe—C—O def.	585
	Fe—C stretch	431		Fe—C—O def.	513
	C—Fe—C def.	135		Fe—C stretch	513
A_2	Fe—C—O def.	?606		C—Fe—C def.	104
				(C_4H_4)—Fe—$(CO)_3$ def.	94

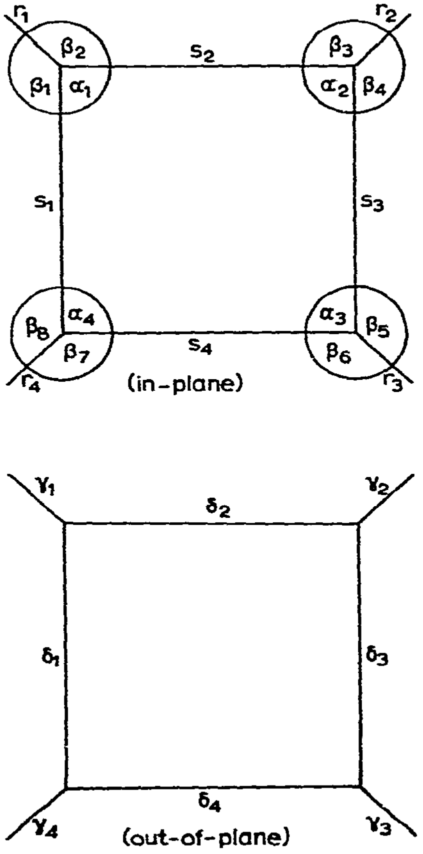
Calculation of force constants

The computer programs used for the force field calculations were those described by Snyder and Schachtschneider [15,16].

Since the vibrational assignment was achieved using the concept of "local" symmetry, as shown in Table 1, the analysis was performed in two separate sections i.e. upon an isolated C_4H_4 ring, of C_{4v} symmetry; and an $RFe(CO)_3$ system, ($R = C_4H_4$; treated as a point mass), of C_{3v} symmetry. The lack of interaction between the two parts of the complex, as indicated by the free rotation of the C_4H_4 ring with respect to the $Fe(CO)_3$ unit [17,18] may be advanced as evidence in support of this procedure.

The sets of internal coordinates used for the C_4H_4 ring and for the $RFe(CO)_3$ system are illustrated in Figs. 1 and 2 respectively.

The nature of the problem requires that certain approximations must be made in the calculations. First, the number of force constants considerably exceeds the number of observed frequencies, and thus a number of the former must be fixed arbitrarily (usually at zero). Second, since sufficient data on the fre-



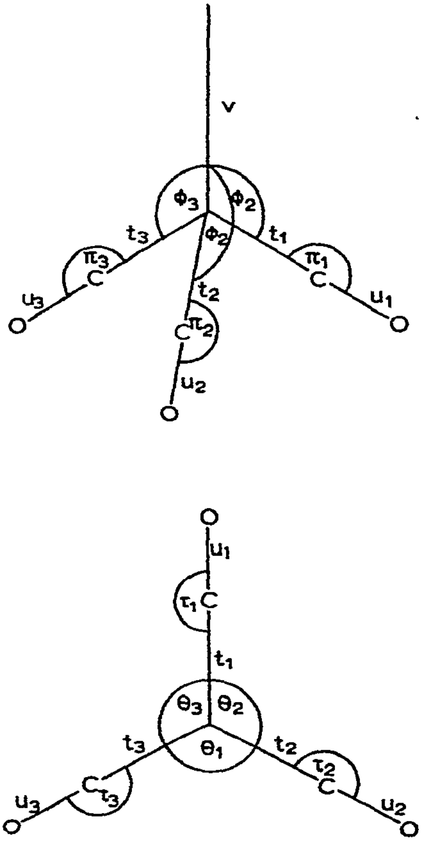


Fig. 1. The internal coordinates of cyclobutadiene.

Fig. 2. The internal coordinates of $RFe(CO)_3$ ($R = C_4H_4$).

quencies of overtone bands to determine anharmonicity corrections were not available, these corrections were assumed to be negligible. However, the work of Jones et al. [11—14] on metal carbonyls shows that only for C≡O stretching modes is this a significant factor. Third, the molecular dimensions determined for the vapour by Davis and Speed [17] were assumed to apply in the liquid phase also (Fig. 3). Finally, the approximation of "local" symmetry, as applied in this case, is such that the Fe—C_4H_4 tilting mode is not included in the problem.

The course of the calculations was as follows: an initial simple valence force field was assumed for each moiety of the molecule, i.e. no off-diagonal terms were included in the F matrix (initial values for these force constants were taken by analogy with other carbocyclic ring and metal carbonyl systems). The values of the force constants were allowed to vary in order to obtain the closest possible agreement between observed and calculated frequencies, and from the errors in the calculated frequencies of the modes an indication was given of which interaction terms should be most significant. Such terms were successively added to the initial force field, up to the limit imposed by the number of observed frequencies, discarding those which gave no significant improvement in the frequency fit. The only restriction placed upon this process is that certain force constants known to be significant had to be kept at fixed, non-zero values. The reason for this is that if some sets of related force constants (i.e. those which are strongly correlated with each other) were all allowed to vary freely while searching for a best fit, certain matrices became very nearly singular, which caused the calculation to become ill-conditioned, and hence no convergence occurred.

Two such "fixed" force constants were found to be necessary for the C_4H_4 fragment, f_s and f_γ (i.e. those associated with C—C stretching and out-of-plane C—H bending respectively). In the $RFe(CO)_3$ calculation, the interaction constants f_{tu} and f_{tv} (the Fe—C/C—O and Fe—C/Fe—R stretch/stretch interactions) had to be treated thus. The methods for obtaining optimum values for these constants will be outlined below.

Calculated force field for the C_4H_4 ring

The final force-field obtained for the complexed cyclobutadiene ring is

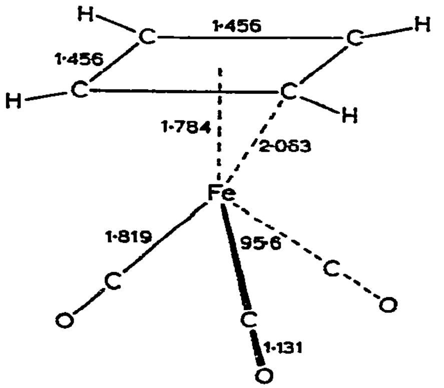


Fig. 3. The molecular dimensions of $(C_4H_4)Fe(CO)_3$.

TABLE 2

THE SYMMETRY COORDINATES FOR CYCLOBUTADIENE (C_{4v} SYMMETRY)

A_1	S_1	$= \frac{1}{2}(r_1 + r_2 + r_3 + r_4)$
	S_2	$= \frac{1}{2}(S_1 + S_2 + S_3 + S_4)$
	S_3	$= \frac{1}{2}(\gamma_1 + \gamma_2 + \gamma_3 + \gamma_4)$
	S_4	$= 1/\sqrt{12}\,(\beta_1 + \beta_2 + \beta_3 + \beta_4 + \beta_5 + \beta_6 + \beta_7 + \beta_8 + \alpha_1 + \alpha_2 + \alpha_3 + \alpha_4)$
A_2	S_5	$= 1/\sqrt{24}\,(\beta_1 + \beta_2 + \beta_3 + \beta_4 + \beta_5 + \beta_6 + \beta_7 + \beta_8 - 2\alpha_1 - 2\alpha_2 - 2\alpha_3 - 2\alpha_4)$
	S_6	$= \frac{1}{2}(\delta_1 + \delta_2 + \delta_3 + \delta_4)$
	S_7	$= 1/\sqrt{8}\,(\beta_1 - \beta_2 + \beta_3 - \beta_4 + \beta_5 - \beta_6 + \beta_7 - \beta_8)$
B_1	S_8	$= \frac{1}{2}(r_1 - r_2 + r_3 - r_4)$
	S_9	$= 1/\sqrt{12}\,(\beta_1 + \beta_2 - \beta_3 - \beta_4 + \beta_5 + \beta_6 - \beta_7 - \beta_8 - \alpha_1 + \alpha_2 - \alpha_3 + \alpha_4)$
	S_{10}	$= \frac{1}{2}(\gamma_1 - \gamma_2 + \gamma_3 - \gamma_4)$
	S_{11}	$= \frac{1}{2}(\delta_1 - \delta_2 + \delta_3 - \delta_4)$
	S_{12}	$= 1/\sqrt{24}\,(\beta_1 + \beta_2 - \beta_3 - \beta_4 + \beta_5 + \beta_6 - \beta_7 - \beta_8 + 2\alpha_1 - 2\alpha_2 + 2\alpha_3 - 2\alpha_4)$
B_2	S_{13}	$= \frac{1}{2}(S_1 - S_2 + S_3 - S_4)$
	S_{14}	$= 1/\sqrt{8}\,(\beta_1 - \beta_2 - \beta_3 + \beta_4 + \beta_5 - \beta_6 - \beta_7 + \beta_8)$
E_a	S_{15a}	$= 1/\sqrt{2}\,(r_1 - r_3)$
	S_{16a}	$= \frac{1}{2}(S_1 - S_2 - S_3 + S_4)$
	S_{17a}	$= \frac{1}{2}(\beta_3 - \beta_4 - \beta_7 + \beta_8)$
	S_{18a}	$= 1/\sqrt{2}\,(\gamma_1 - \gamma_3)$
	S_{19a}	$= \frac{1}{2}(\delta_1 - \delta_2 - \delta_3 + \delta_4)$
	S_{20a}	$= 1/\sqrt{6}\,(\beta_1 + \beta_2 - \beta_5 - \beta_6 + \alpha_1 - \alpha_3)$
	S_{21a}	$= 1/\sqrt{12}\,(\beta_1 + \beta_2 - \beta_5 - \beta_6 - 2\alpha_1 + 2\alpha_3)$
E_b	S_{15b}	$= 1/\sqrt{2}\,(r_2 - r_4)$
	S_{16b}	$= \frac{1}{2}(S_1 + S_2 - S_3 - S_4)$
	S_{17b}	$= \frac{1}{2}(\beta_1 - \beta_2 - \beta_5 + \beta_6)$
	S_{18b}	$= 1/\sqrt{2}\,(\gamma_2 - \gamma_4)$
	S_{19b}	$= \frac{1}{2}(\delta_1 + \delta_2 - \delta_3 - \delta_4)$
	S_{20b}	$= 1/\sqrt{6}\,(\beta_3 + \beta_4 - \beta_7 - \beta_8 + \alpha_2 - \alpha_4)$
	S_{21b}	$= 1/\sqrt{12}\,(\beta_3 + \beta_4 - \beta_7 - \beta_8 - 2\alpha_2 + 2\alpha_4)$

given in Table 4, all other force constants being fixed at zero. The units in which the force constants are expressed are 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 frequencies and those calculated using this force-field are compared in Table 5. All of these agree to within the experimental error of ± 2 cm^{-1}. The forbidden (A_2) in-plane C—H deformation has a calculated frequency of 1140 cm^{-1}, which is in the region expected for such a vibration.

TABLE 3

THE SYMMETRY COORDINATES FOR $RFe(CO)_3$ (C_{3v} SYMMETRY)

A_1	S_1	$= 1/\sqrt{3}\,(u_1 + u_2 + u_3)$
	S_2	$= 1/\sqrt{3}\,(\pi_1 + \pi_2 + \pi_3)$
	S_3	$= 1/\sqrt{3}\,(t_1 + t_2 + t_3)$
	S_4	$= v$
	S_5	$= 1/\sqrt{6}\,(\theta_1 + \theta_2 + \theta_3 - \phi_1 - \phi_2 - \phi_3)$
	S_6	$= 1/\sqrt{6}\,(\theta_1 + \theta_2 + \theta_3 + \phi_1 + \phi_2 + \phi_3)$
A_2	S_7	$= 1/\sqrt{3}\,(\tau_1 + \tau_2 + \tau_3)$
E_a	S_{8a}	$= 1/\sqrt{6}\,(2u_1 - u_2 - u_3)$
	S_{9a}	$= 1/\sqrt{6}\,(2\pi_1 - \pi_2 - \pi_3)$
	S_{10a}	$= 1/\sqrt{2}\,(\tau_2 - \tau_3)$
	S_{11a}	$= 1/\sqrt{6}\,(2t_1 - t_2 - t_3)$
	S_{12a}	$= 1/\sqrt{6}\,(2\theta_1 - \theta_2 - \theta_3)$
	S_{13a}	$= 1/\sqrt{6}\,(2\phi_1 - \phi_2 - \phi_3)$
E_b	S_{8b}	$= 1/\sqrt{2}\,(u_2 - u_3)$
	S_{9b}	$= 1/\sqrt{2}\,(\pi_2 - \pi_3)$
	S_{10b}	$= 1/\sqrt{6}\,(2\tau_1 - \tau_2 - \tau_3)$
	S_{11b}	$= 1/\sqrt{2}\,(t_2 - t_3)$
	S_{12b}	$= 1/\sqrt{2}\,(\theta_2 - \theta_3)$
	S_{13b}	$= 1/\sqrt{2}\,(\phi_2 - \phi_3)$

It was noted above that f_s and f_γ could not be allowed to vary during the calculations. The values quoted were obtained by taking a series of fixed values for them, and choosing those which gave the closest frequency-fit. For f_s this procedure yielded an unambiguous result, but for f_γ the calculation was insensitive to its variation within the range 0.41—0.47 mdyne Å rad^{-2}. The value quoted (0.43 mdyne Å rad^{-2}) was that which gave what was thought to be the most

TABLE 4

THE FORCE FIELD OBTAINED FOR CYCLOBUTADIENE[a]

f_r	5.76	f_{ss}	−0.19
f_s	5.37	f'_{ss}	0.94
f_α	1.71	f_{rs}	0.08
f_β	0.35		
f_γ	0.43	$f_{s\beta}$	0.31
f_δ	0.47	$f_{\gamma\delta}$	0.08
		$f_{\gamma\gamma}$	0.05
		$f'_{\gamma\gamma}$	−0.05

[a] The units are as given in the text. f_i is an internal valence force constant related to the internal coordinate of type i — see Fig. 1; f_{ij} and f'_{ij} are interaction terms relating the internal coordinates of types i and j. The constants f_{ij} refer to interactions between adjacent coordinates, while f'_{ij} refer to interactions between non-adjacent coordinates.

TABLE 5

OBSERVED AND CALCULATED FREQUENCIES FOR CYCLOBUTADIENE

Symmetry	Observed (cm^{-1})	Calcd. (cm^{-1})	Symmetry	Observed (cm^{-1})	Calcd. (cm^{-1})
A_1	3132	3134	B_2	1327	1326
	1234	1233		964	963
	824	824			
			E	3132	3128
A_2		1140		1327	1329
				975	976
B_1	3132	3134		939	939
	957	956			
	774	774			
	506	506			

realistic potential energy distribution (see below), but this value is clearly not so well-defined as those for the other force constants.

It may be instructive to compare the results for the C_4H_4 ring with those obtained for the analogous carbocyclic systems C_6H_6 [19—21] and $C_5H_5^-$ [22, 23] (Table 6), noting that data on valence force constants for these species π-bonded to a transition metal are not available. The comparison will be not exact, therefore, but preliminary calculations on the complexed benzene ring in $(C_6H_6)Cr(CO)_3$, using the same approximations as here, suggest [24] that changes in the force constants on going from free to complexed benzene are quite small.

The trends in CH and CC stretching force constants are consistent with the changes in hybridisation at the carbon atoms in the three rings. Thus, the in-

TABLE 6

COMPARISON OF THE FORCE FIELD OF C_4H_4 WITH THOSE OF FREE C_6H_6 AND $C_5H_5^-$ [a]

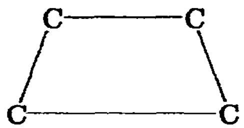
	C_6H_6	$C_5H_5^-$	C_4H_4
f_{CH}	5.06	5.10	5.76
f_{CC}	6.24	5.57	5.37
f_{CCH}	0.51		0.35
f_{CCC}	1.04		1.71
$f_{\gamma CH}$	0.45	0.28	0.43
$f_{\delta CC}$	0.26		0.47
$f_{CC/CC}$ (*o*)	0.76	0.29	—0.19
(*m*)	—0.23		
(*p*)	0.35	—0.37	0.94
$f_{CC/CH}$			0.08
$f_{CC/CCH}$	0.18		0.31
$f_{\gamma CH/\delta CC}$	—0.15		0.08
$f_{\gamma CH/\gamma CH}$ (*o*)	—0.07		0.05
(*m*)	0.00		
(*p*)	0.01		—0.05

[a] All units as in Table 4.

creased p-character in the C—C bond as the ring size decreases is in line with the decreasing C—C stretching force constant, since the overlap of pure p-orbitals would be expected to give weaker bonding than overlap between two sp^2 hybrids. Similarly, increasing s-character in the C—H bond explains the increases in C—H stretching force constant. The latter argument may be supported by data on free ethylene [25,26], in which the hybridisation at the C is sp^2, and on complexed ethylene in $(C_2H_4)Fe(CO)_4$ [27], where it is much closer to sp^3. In the former, f_{CH} is 5.59 mdyne Å^{-1}, and in the latter 5.22 mdyne Å^{-1}.

When we consider the bending force constants, we see only a very slight change in $f_{\gamma CH}$ (the out-of-plane CH deformation), while the change in f_{CCH} (the in-plane CH deformation) is not easy to rationalise. The force constants relating to deformation of the ring, however (f_{CCC} and $f_{\delta CC}$) are both much larger for C_4H_4 than for C_6H_6, clearly reflecting the greater rigidity expected for the smaller ring.

Of the interaction terms, the most significant are those involving the stretching of two C—C bonds. For C_4H_4, the "*para*" interaction, f'_{ss}, is large and positive. In order to explain this let us see what happens when one C—C bond is stretched:



The tendency will be for the opposite C—C bond to contract, and hence be strengthened, and the increased CCC angles at this bond also indicate that the C—C bond between them will involve overlap between orbitals of greater s-character. By the argument above, this will strengthen the bond. Both of these effects are in agreement with the sign of the calculated interaction constant.

The symmetric, "ring-breathing" mode of C_4H_4 was found to occur at a much higher frequency than the analogous modes in C_6H_6 or $C_5H_5^-$. This cannot be explained in terms of the diagonal stretching force constant, which decreases with ring size. The magnitude and sign of the f'_{ss} interaction term, however, would clearly lead to a high frequency for this vibration, which requires simultaneous increases or decreases in the lengths of all four C—C bonds.

Potential energy distribution for the vibrations of C_4H_4

Calculation of the vibrational eigenvectors for the C_4H_4 system shows that many of the normal modes involve more than one type of internal coordinate. Hence we must recognise that the association (e.g. in Table 1) of one frequency with one specific symmetry coordinate (virtually all of which are constructed as linear combinations of one type of internal coordinate) is an approximation. In many respects a more realistic and useful description of the normal modes is given by the diagonal elements of the potential energy distribution (each element calculated as $L_{ji}^2 F_{jj}/\lambda_i$ where F_{jj} is a valence force constant and L_{ji} is the associated eigenvector for any normal mode of frequency $\nu_i = \lambda_i^{1/2} N^{1/2}/2\pi C$, where ν_i is in cm^{-1}, N is Avogadro's number and all masses are expressed in atomic units) rather than by association with specific symmetry coordinates.

TABLE 7

DIAGONAL ELEMENTS OF THE POTENTIAL ENERGY DISTRIBUTION FOR C_4H_4[a]

	ν (cm^{-1})	f_r	f_s	f_α	f_β	f_γ	f_δ
A_1	3132	0.99					
	1234		0.89				
	824					0.92	
B_1	3132	0.99					
	957			0.90	0.09		
	774					1.74	0.52
	506					0.11	0.73
B_2	1327		0.85				
	964				1.07		
E	3132	0.99					
	1327		0.78	0.24	0.23		
	975		0.05		0.84		
	939					0.90	

[a] All elements < 0.05 are not included.

These diagonal elements are listed for each of the normal modes of C_4H_4 in Table 7 (elements less than 0.05 are omitted), and they show that for the A_1 block no significant mixing actually occurs. In the B_1 block however, the modes giving bands at 774 and 506 cm^{-1} are associated with both f_γ and f_δ, and hence mixing of out-of-plane C—H and ring deformations is occurring, as might be expected from the similarity of the frequencies and the natures of the modes. In the B_2 block there is no appreciable mixing, while in the E block the band at 1327 cm^{-1} represents a mode having relatively large contributions from in-plane C—H and ring deformations, as well as C—C stretching. To sum up, therefore, the normal modes of the C_4H_4 ring show relatively little mixing of motions of internal coordinates, and thus the assignments quoted in Table 1 may stand as reasonable approximations.

Calculated force field for $RFe(CO)_3$ ($R = C_4H_4$)

The final force field obtained is given in Table 8. The f_{tu} and f_{tv} interaction constants had to be constrained (see above), and all force constants not listed were set at zero. The units are the same as those in Table 4. The observed fre-

TABLE 8

THE FORCE FIELD OBTAINED FOR $RFe(CO)_3$ ($R = C_4H_4$)[a]

f_t	2.98	f_{uu}	0.39
f_u	16.01	f_{tu}	0.70
f_v	3.24	$f_{t\pi}$	−0.21
f_θ	0.55	f_{tv}	0.57
f_ϕ	0.27	$f_{\theta\theta}$	0.12
f_τ	0.75		
f_π	0.57		

[a] Force constant definitions analogous to those in Table 4; units as given in the text.

TABLE 9

OBSERVED AND CALCULATED FREQUENCIES FOR $RFe(CO)_3$ ($R = C_4H_4$)

Symmetry	Observed (cm^{-1})	Calcd. (cm^{-1})	Symmetry	Observed (cm^{-1})	Calcd. (cm^{-1})
A_1	2051	2051	E	1979	1979
	611	613		585	587
	431	433		513	509
	398	397		471	470
	135	131		104	104
				94	93
A_2		531			

quencies, and those calculated using this force field are compared in Table 9. All of these agree to within ± 2 cm^{-1}, but it will be noticed that the mode described as the E symmetry Fe—C—O bend has been reassigned to 471 instead of 513 cm^{-1} The original assignment [1] was an arbitrary choice between these two figures, as there was no experimental criterion for a decision between them. The refinement proceeded much more satisfactorily with the revised assignment, however, and hence it has been adopted, since all of the other modes gave a good frequency-fit.

The forbidden (A_2) Fe—C—O deformation has a calculated frequency of 531 cm^{-1}, which is acceptable, but does not support the tentative assignment [1] of a weak Raman band at 606 cm^{-1} to this mode.

The quoted value for f_{tv} was obtained by taking a series of fixed values, that of 0.57 mdyne $Å^{-1}$ giving the closest frequency-fit. With respect to f_{tu}, on the other hand, the situation was not so straightforward. The problem converged satisfactorily for any value of f_{tu} between —0.1 and 1.1 mdyne $Å^{-1}$, the values of f_t and f_u adjusting to give a very similar set of calculated frequencies each time. In order to narrow the acceptable range, the calculations of Jones et al. on $Fe(CO)_5$ [13] and $M(CO)_6$, (M = Cr, Mo, W) [12], were taken as analogies. In all of these examples, the MC/CO stretch/stretch interaction could be unconstrained, and values close to 0.70 mdyne $Å^{-1}$ were always found. This value has been assumed here also, and we feel that this is unlikely to be significantly in error.

The values for f_t and f_u are respectively higher and lower than the equivalent values for $Fe(CO)_5$ [13], in which $f_{Fe-C,eq}$ and $f_{Fe-C,ax}$ are 2.64, 2.57 mdyne $Å^{-1}$ and $f_{CO,eq}$ and $f_{CO,ax}$ are 16.47 and 17.43 mdyne $Å^{-1}$. Thus there is greater transfer of electron density from the iron atom to the π^* C—O orbital in the case of $(C_4H_4)Fe(CO)_3$ than in the parent $Fe(CO)_5$, in agreement with the generally-held view that such π-bonded organic ligands are stronger donors and/or weaker acceptors than CO.

The value of the metal—ring stretching force constant, f_v, is 3.24 mdyne $Å^{-1}$, indicative of quite strong bonding between the iron and the C_4H_4 ligand.

All of the bending force constants are in the expected regions, although those associated with Fe—C—O bending, f_τ and f_π (0.75 and 0.57 mdyne Å rad^{-2} respectively) are significantly larger than those in $Fe(CO)_5$ (0.4 to 0.5 mdyne Å rad^{-2}) [13]. This may be related to the greater Fe—C back-π-bonding in the $(C_4H_4)Fe(CO)_3$ giving a greater overall rigidity to the Fe—C—O unit.

TABLE 10

DIAGONAL ELEMENTS OF THE POTENTIAL ENERGY DISTRIBUTION FOR RFe(CO)$_3$ (R = C$_4$H$_4$)[a]

	ν (cm^{-1})	f_t	f_u	f_v	f_θ	f_ϕ	f_τ	f_π
A_1	2051	0.06	0.94					
	611	0.21		0.13	0.13			0.43
	431	0.64		0.10				0.10
	398	0.24		0.86				0.26
	135				0.42	0.12		0.24
E	1979	0.07	1.01					
	585	0.23			0.11		0.64	
	513	0.51					0.27	0.11
	471	0.21				0.06		0.83
	104				0.15	0.83		
	94				1.00	0.11	0.07	0.05

[a] All elements < 0.05 are not included.

Of the interaction constants, the FeC/CO stretch/stretch interaction has already been discussed. The CO/CO stretch/stretch interaction term (f_{uu}) is much larger than in Fe(CO)$_5$, 0.39 mdyne Å^{-1} as against ca. 0.13 mdyne Å^{-1} [13]. Such interactions have been discussed by Jones et al. [12] in terms of dipole—dipole interactions — which must therefore be rather large in this case.

Potential energy distribution for the vibrations of RFe(CO)$_3$ (R = C$_4$H$_4$)

The diagonal elements of the potential energy distribution for the RFe(CO)$_3$ fragment are listed in Table 10.

We see that in this case there is often considerable mixing of the different sets of internal coordinates. The "C—O stretches" in fact only contain a very small contribution from the Fe—C stretching coordinate, but all of the bands in the 350—650 cm^{-1} region are due to extensively mixed modes. Thus descriptions of modes in this region must be very approximate, even though the major contribution in each case comes from the appropriate internal coordinate, except for the bonds at 513 and 471 cm^{-1}. These were initially assigned as an Fe—C—O deformation and an Fe—(C$_4$H$_4$) tilt respectively, but the major contributions to the modes giving these bands are from Fe—C stretching and Fe—C—O bending respectively.

The modes giving bands below 150 cm^{-1} exhibit less mixing of coordinates, although the A_1 mode at 135 cm^{-1} does contain a significant amount of Fe—C—O bending. A reversal of the original assignments of the two modes of E symmetry appears to be necessary, however, since the band at 104 cm^{-1} is largely due to (C$_4$H$_4$)—Fe—C bending, while that at 94 cm^{-1} is almost exclusively due to C—Fe—C bending.

Conclusion

Using what appear to be reasonable approximations valence force fields have been calculated for the C$_4$H$_4$ and RFe(CO)$_3$ moieties of (C$_4$H$_4$)Fe(CO)$_3$ which reproduce the observed vibrational frequencies very closely, and are consistent with those known for related systems. This is the first time that the C_4H_4 ring has been investigated in this way. Two reassignments were suggested for the vibrations of the $RFe(CO)_3$ fragment.

Acknowledgements

We are very grateful to the Science Research Council for the award of a research studentship (to D.C.A.).

References

1 D.C. Andrews and G. Davidson, J. Organometal. Chem., 36 (1972) 349.
2 J. Brunvoll, S.J. Cyvin and L. Schäfer, J. Organometal. Chem., 27 (1971) 107.
3 J. Brunvoll, S.J. Cyvin and L. Schäfer, J. Organometal. Chem., 27 (1971) 69.
4 L. Schäfer, J. Southern and S.J. Cyvin, Spectrochim. Acta, Part A, 27 (1971) 1083.
5 S.J. Cyvin, J. Brunvoll and L. Schäfer, J. Chem. Phys., 54 (1971) 1517.
6 S. Kjelstrup, S.J. Cyvin, J. Brunvoll and L. Schäfer, J. Organometal. Chem., 36 (1972) 137.
7 J. Brunvoll, S.J. Cyvin and L. Schäfer, J. Organometal. Chem., 36 (1972) 143.
8 E.R. Lippincott and R.D. Nelson, Spectrochim. Acta, 10 (1957) 30.
9 I.J. Hyams, Chem. Phys. Lett., 15 (1972) 88.
10 R. Cataliotti, A. Poletti and A. Santucci, J. Mol. Struct., 5 (1970) 215.
11 L.H. Jones, R.S. McDowell and M. Goldblatt, J. Chem. Phys., 48 (1968) 2663.
12 L.H. Jones, R.S. McDowell and M. Goldblatt, Inorg. Chem., 8 (1969) 2349.
13 L.H. Jones, R.S. McDowell, M. Goldblatt and B.I. Swanson, J. Chem. Phys., 57 (1972) 2050.
14 L.H. Jones, R.S. McDowell and B.I. Swanson, J. Chem. Phys., 58 (1973) 3757.
15 J.H. Schachtschneider and R.G. Snyder, Spectrochim. Acta, 19 (1963) 117.
16 J.H. Schachtschneider, Shell Development Co. Tech. Repts., (1964) 231/64 and (1965) 57/65.
17 M.I. Davis and C.S. Speed, J. Organometal. Chem., 21 (1970) 401.
18 D. Bailey, A.D. Buckingham, A.J. Rest and J.P. Yesinowski, Abstr. Papers, 6th Int. Conf. on Organometal. Chem., Amherst, U.S.A., 1973, Abstr. No. 246.
19 J.R. Scherer, Spectrochim. Acta, 20 (1964) 345.
20 J.R. Scherer, Spectrochim. Acta, Part A, 23 (1967) 1489.
21 N. Neto, M. Scrocco and S. Califano, Spectrochim. Acta, 22 (1966) 1981.
22 A. Sadô, R. West, H.P. Fritz and L. Schäfer, Spectrochim. Acta, 22 (1966) 509.
23 H.P. Fritz and L. Schäfer, Chem. Ber., 97 (1964) 1829.
24 G. Davidson and D.A. Duce, unpublished observations.
25 J.L. Duncan, D.C. McKean and P.B. Mallinson, J. Mol. Spectrosc., 45 (1973) 221.
26 P. Pulay and W. Meyer, J. Mol. Spectrosc., 40 (1971) 59.
27 D.C. Andrews and G. Davidson, unpublished observations.