

NORMAL COORDINATE ANALYSIS OF THE TOTAL FERROCENE COMPLEX

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SUMMARY

The results of a total normal coordinate analysis of ferrocene, $\text{Fe}(\text{C}_5\text{H}_5)_2$, are reported. As in a previously published total vibrational analysis of dibenzenechromium, interesting kinematic couplings between some ligand and some framework normal modes of the complex can be observed, and these account for some frequency shifts from free (ionic) to complexed cyclopentadienide without any change in the harmonic force field of the ligand. Calculated mean amplitudes for ferrocene are compared with those determined by an electron diffraction study and with the corresponding values in the free cyclopentadienide anion.

INTRODUCTION

In view of some unusual kinematic phenomena which were discovered in the course of a total normal coordinate analysis of dibenzenechromium¹ and other π -benzene sandwich compounds², we were interested in a total vibrational analysis of ferrocene, $\text{Fe}(\text{C}_5\text{H}_5)_2$, and especially with possible couplings between some internal ligand and some framework normal modes. Such couplings exist in benzene-sandwiches^{1,2} and they cause a significant difference in the force fields calculated for benzene as an independent entity³ or as a dependent part¹ of such complexes. If $\text{Cr}(\text{C}_6\text{H}_6)_2$ is analyzed as a 25 atom molecule¹ (with C_6H_6 treated as an integral part of the structure) some of the typical frequency shifts in the vibrational spectra between free and complexed benzene can be explained (and reproduced by the identical force field) on the basis of internal coupling. If a partial vibrational analysis of $\text{Cr}(\text{C}_6\text{H}_6)_2$ is performed³ (with C_6H_6 treated as an independent ligand), these frequency shifts can only be explained by considerable changes in the force constants. Before the total normal coordinate analyses were available, these changes were sometimes attributed^{1,2} to orbital properties of the ligands.

We wanted to make a similar comparison between a total and a partial vibrational analysis for $\text{Fe}(\text{C}_5\text{H}_5)_2$ ⁴. As in the case of benzene, comparisons between the free (ionic)⁵ and complexed (covalent) cyclopentadienide anion are possible.

RESULTS AND DISCUSSION

Classification of vibrational modes

The present calculations are based on an eclipsed structure of symmetry D_{5h} for ferrocene with planar C_5H_5 ligands. Structural parameters were taken from electron diffraction results⁶. Hartley and Ware's frequency assignment was used⁷ with the Raman values replaced by the Laser results⁸ and inactive frequencies were chosen according to suggestions of Fritz⁹ (Table 2). The following types of symmetry

TABLE 1

VIBRATIONAL FREQUENCIES (cm^{-1}) FROM THE FINAL HARMONIC FORCE FIELD FOR $C_5H_5^-$

The calculated frequencies are identical to observed values¹⁰. Values in parentheses represent tentative assignments.

A'_1	3043	983		
A'_2	(1381)			
E'_1	3039	(1455)	1003	
E'_2	3096	1447	1020	565
A''_2	710			
E''_1	625			
E''_2	(890)	(663)		

TABLE 2

VIBRATIONAL FREQUENCIES (cm^{-1}) FROM THE FINAL HARMONIC FORCE FIELD FOR $Fe(C_5H_5)_2$

The calculated frequencies are identical with observed values.

$A'_1 (A_{1g})$	3100 ^a	1105 ^a	812 ^a	301 ^a		
$A'_2 (A_{2g})$	1249 ^b					
$E'_1 (E_{1u})$	3098 ^c	1414 ^c	1006 ^c	840 ^c	490 ^c	179 ^c
$E'_2 (E_{2g})$	3070 ^a	1356 ^a	1175 ^a	1059 ^a	892 ^a	600 ^a
$A''_1 (A_{1u})$	(1253) ^b	(150) ^d				
$A''_2 (A_{2u})$	3098 ^c	1107 ^c	818 ^c	477 ^c		
$E''_1 (E_{1g})$	3085 ^a	1412 ^a	999 ^a	835 ^a	390 ^a	
$E''_2 (E_{2u})$	(3035) ^b	(1351) ^b	(1188) ^b	(1054) ^b	(892) ^b	(567) ^b

^a Raman values ref. 8 with the assignment of ref. 7. ^b Approximate inactive frequencies taken from ref. 9.

^c IR general assignment, ref. 7. ^d Value taken tentatively from dibenzenechromium, ref. 14.

coordinates were constructed, the identity of the ligands being preserved as much as possible: (i). In-phase ligand vibrations; "symmetrical" combinations of free C_5H_5 vibrations of structure $2A'_1 + A'_2 + 3E'_1 + 4E'_2 + A'_2 + E'_1 + 2E''_2$. (ii). Out-of-phase ligand vibrations; "anti-symmetrical" combinations of free C_5H_5 vibrations with total symmetry of $2A''_2 + A''_1 + 3E''_1 + 4E''_2 + A'_1 + E'_1 + 2E'_2$. (iii). Compensated in-phase ligand translations of $E'_1 + A'_2$. (iv). Out-of-phase ligand librations of $E'_1 + A'_1$. (v). Parallel out-of-phase ligand translations of symmetry A'_1 . (vi). Deformed out-of-phase ligand translations of E'_1 . The vibrational frequencies for ionic $C_5H_5^-$ were taken from ref. 10 (Table 1).

Harmonic force field

As in the case of benzene^{1,2} some of the most characteristic differences in the

vibrational spectra of free (ionic) and complexed (covalent) C_5H_5 are found for the non-planar vibrations. Thus, following the assignment defined above, the non-planar CH-bendings A_2'' and E_1'' of the free cyclopentadienide anion are shifted from 710 cm^{-1} and 625 cm^{-1} to approximately 815 cm^{-1} (A_1' out-of-phase; A_2'' in-phase) and approximately 840 cm^{-1} (E_1' out-of-phase; E_1'' in-phase), respectively, in ferrocene. In spite of these frequency shifts, the values observed for the complex can be reproduced by a force constant which is identical with that of the free ligand [0.2156 mdyne/\AA (A_2''), but with a normalisation different from that used in ref. 10; value of the diagonal G-matrix element 1.37681 ; and 0.1384 mdyne/\AA (E_2''); value of the diagonal G-matrix element 1.66259]. This surprising result can be explained by kinematic coupling between frequencies number 2 (A_1') and 9 (A_2'') and the metal ligand stretchings number 4 and 11, respectively, and between number 14 (E_1') and 19 (E_1'') and the framework normal modes number 16 and 21, 22, respectively. Table 3 gives the values

TABLE 3

OBSERVED AND CALCULATED FREQUENCIES (cm^{-1}) OF A_{1g} , A_{2u} , E_{1g} AND E_{1u} IN $Fe(C_5H_5)_2$

Force field from free (ionic) cyclopentadienide anion was used without any modification for ligand vibrations. Free C_5H_5 frequencies are included for comparison. Force constants for framework normal modes were adjusted to give an even spread of errors for the corresponding frequency and the one coupled to it, when corresponding off-diagonal elements of the force constant matrix were zero. See Tables 2 and 3 for references concerning the observed frequencies.

$A_1' (A_{1g})$	calcd.:	3043	983	941	272	
	found:	3100	1105	812	301	
	C_5H_5 :	(3043) (A_1')	(983) (A_1')	(710) (A_2'')		
$A_2'' (A_{2u})$	calcd.:	3043	983	892	407	
	found:	3098	1107	818	477	
	C_5H_5 :	(3043) (A_1')	983 (A_1')	(710) (A_2'')		
$E_1'' (E_{1g})$	calcd.:	3040	1572	944	673	383
	found:	3085	1412	999	835	390
	C_5H_5 :	(3039) (E_1')	(1455) (E_1')	(1003) (E_1')	(625) (E_1'')	
$E_1' (E_{1u})$	calcd.:	3055	1580	973	859	482 293
	found:	3098	1414	1006	840	490 179
	C_5H_5 :	(3039) (E_1')	(1455) (E_1')	(1003) (E_1')	(625) (E_1'')	

for these species of ferrocene calculated with the unchanged free cyclopentadienide force field which reproduces exactly the observed spectra of the molecule (Table 1). It is seen that, in most cases, these approximate calculations reproduce or even exaggerate the frequency shifts observed for the mentioned non-planar CH-deformations. No off-diagonal non-zero element in the force constant matrix was used in these calculations between the ligand and the framework vibrations. The coupling is due only to non-vanishing off-diagonal elements in the corresponding G-matrix blocks. No such coupling is possible if C_5H_5 is treated in a partial vibrational analysis of ferrocene⁴ as an independent entity with symmetry D_{5h} . Then the values of the corresponding force constants¹⁰ must be increased considerably¹² to reproduce the observed frequency shifts.

In the final harmonic force field which reproduces exactly the observed vibrational spectrum of ferrocene (Table 2) off-diagonal force constants had to be introduced. The non-planar CH-deformations were reproduced without any change in the corresponding diagonal force constants.

Mean amplitudes of vibration

With the final harmonic force field which gave an exact reproduction of the observed vibrational spectra of $C_5H_5^-$ and $Fe(C_5H_5)_2$ the mean amplitudes of vibration for these molecules were calculated (Table 4). As in the case of free and com-

TABLE 4

OBSERVED AND CALCULATED MEAN AMPLITUDES FOR FERROCENE YND CALCULATED MEAN AMPLITUDES FOR THE CYCLOPENTADIENIDE ANION

Numbering of atoms as in ref. 13. All values in Å

Distance type	Equil. dist.	Electron diffraction [$Fe(C_5H_5)_2$]	Vibrational analysis			
			C_5H_5		$Fe(C_5H_5)_2$	
			0° K	298° K	0° K	298° K
C_1-C_2	1.429	$0.047 \pm 0.003^{a,b}$	0.0464	0.0466	0.0465	0.0466
Fe-C	2.056	$0.062 \pm 0.003^{a,b}$			0.0588	0.0738
C_1-H_1	1.116	0.084 ± 0.012^a $(0.092 \pm 0.006)^b$	0.0770	0.0770	0.0769	0.0769
Fe-H	2.805	0.157 ± 0.027^a $(0.124 \pm 0.009)^b$			0.1125	0.1179
C_1-C_3	2.312	0.058 ± 0.007^a $(0.054 \pm 0.002)^b$	0.0597	0.0625	0.0583	0.0608
C_1-H_2	2.270	0.063 ± 0.016^a $(0.145 \pm 0.015)^b$	0.0995	0.1000	0.0985	0.0989
C_1-H_3	3.388	0.121 ± 0.039^a $(0.158 \pm 0.017)^b$	0.0953	0.0971	0.0944	0.0960
C_1-C_6	3.316	0.097 ± 0.022^a $(0.101 \pm 0.008)^b$			0.0954	0.1384
C_1-C_7	3.611	0.150 ± 0.024^a $(0.193 \pm 0.019)^b$			0.0853	0.1182
C_1-C_8	4.042	0.119 ± 0.014^a $(0.117 \pm 0.020)^b$			0.0700	0.0830
H_1-H_2	2.741		0.1588	0.1598	0.1536	0.1544
H_1-H_3	4.435		0.1248	0.1262	0.1240	0.1253
C_1-H_6	3.500				0.1553	0.1758

^a Electron diffraction; ref. 6. ^b Electron diffraction; ref. 13.

plexed benzene¹ the calculated values for free (ionic) and complexed (covalent) cyclopentadienide are very similar. The agreement between the observed^{6,13} and calculated values for ferrocene is good for all values which are not affected by internal rotation. Deviations in the other cases may be due to several factors. There is still some uncertainty about the exact assignment of all frequencies in the vibrational spectra of ferrocene. A change in the assignment, of course, could change the calculated mean amplitudes. On the other hand some of the observed (electron diffraction)

vibrational amplitudes may be somewhat uncertain, since in general it is difficult to refine vibrational amplitudes for unresolved (close neighbour) distances from the electron diffraction pattern. A special additional difficulty arises in this study from internal rotation of the ligands. This difficulty is reflected in the different sets of amplitudes given in the different electron diffraction studies^{6,13}. It shows that calculations of mean amplitudes of vibration can be expected to be of help in decisively determining structural details of this kind which are difficult to be resolved on the basis of electron diffraction alone. In a similar way the transfer of vibrational amplitudes from vibrational to electron diffraction studies may help to distinguish between different sets of possible bond distances in a molecule, as reported for dibenzenechromium¹¹.

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