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## ANALYSIS OF THE VIBRATIONAL SPECTRA OF $C_6H_6CrC_6F_6$ AND $C_6D_6CrC_6F_6$ $C_{6v}$ SANDWICH COMPOUNDS

JOSEPH D. LAPOSA \*, NGUYEN HAO, BRIAN G. SAYER and MICHAEL J. McGLINCHEY \*

*Department of Chemistry, McMaster University, Hamilton, Ontario L8S 4M1 (Canada)*

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### Summary

The infrared and Raman spectra of  $C_6H_6CrC_6F_6$  and  $C_6D_6CrC_6F_6$  are analyzed, resulting in assignments for about half of the 46 normal modes in each molecule. The assignments fit well with a model of  $\pi$  electron migration from the  $C_6H_6$  ring to the  $C_6F_6$  ring.

### Introduction

The vibrational spectra of the organometallic sandwich compound dibenzenechromium,  $(C_6H_6)_2Cr$ , have been interpreted in terms of perturbation of the free benzene vibrational levels plus introduction of new ring–metal vibrations [1–5]. It is of interest to ascertain how the vibrational energy levels are further perturbed when one of the benzene rings is replaced by hexafluorobenzene, forming the mixed sandwich compound  $C_6H_6CrC_6F_6$ ; this also provides the first vibrational spectroscopic analysis of a  $\pi$ -complexed  $C_6F_6$  moiety. We have shown in earlier NMR spectroscopic studies on  $C_6H_6CrC_6F_6$  that there is considerable  $\pi$  electron migration from  $C_6H_6$  to  $C_6F_6$  in the mixed sandwich compound [6]. To aid in the vibrational assignments, the infrared and Raman spectra of  $C_6D_6CrC_6F_6$  as well as  $C_6H_6CrC_6F_6$  are reported herein.

Although the crystal structure of  $C_6H_6CrC_6F_6$  is not known at present, structural data on a related compound, viz.,  $C_6H_6CrC_6F_5P(C_6H_5)_2$  [7], indicates an eclipsed  $C_{6v}$  symmetry for  $C_6H_6CrC_6F_6$ . Even if the carbon atoms of the two rings were staggered rather than eclipsed, the  $C_{6v}$  symmetry would still be valid. In this point group, the 46 normal modes of  $C_6H_6CrC_6F_6$  can be classified as follows:  $8A_1 + 3A_2 + 8B_1 + 4B_2 + 11E_1 + 12E_2$ . The  $A_1$  and  $E_1$  modes are infrared active, while the  $A_1$ ,  $E_1$  and  $E_2$  modes are Raman active. We assume that the coupling between the two rings is small. Thus, 20 of the 46 modes will be described with Wilson's notation for benzene [8] as  $\nu_{1H}, \nu_{2H}, \dots, \nu_{20H}$ , with a similar notation for hexafluorobenzene, namely  $\nu_{1F}, \nu_{2F}, \dots, \nu_{20F}$ . These 20

TABLE 1  
DESCRIPTION, DESIGNATION, AND SYMMETRY OF THE NORMAL MODES OF  $C_6H_6CrC_6F_6$

Description	Designation	Symmetry
Ring breathing	$\nu_1$	$A_1$
C—F or C—H stretch	$\nu_2$	$A_1$
	$\nu_7$	$E_2$
	$\nu_{13}$	$B_1$
	$\nu_{20}$	$E_1$
C—C stretch	$\nu_8$	$E_2$
	$\nu_{14}$	$B_1$
	$\nu_{19}$	$E_1$
in plane C—F or C—H bend	$\nu_3$	$A_2$
	$\nu_9$	$E_2$
	$\nu_{15}$	$B_2$
	$\nu_{18}$	$E_1$
out of plane C—F or C—H bend	$\nu_5$	$B_1$
	$\nu_{10}$	$E_1$
	$\nu_{11}$	$A_1$
	$\nu_{17}$	$E_2$
in plane ring deformation	$\nu_6$	$E_2$
	$\nu_{12}$	$B_1$
out of plane ring deformation	$\nu_4$	$B_1$
	$\nu_{16}$	$E_2$
symmetric stretch of rings relative to metal atom	$\nu_{\text{SYM STR}}$	$A_1$
antisymmetric stretch of rings relative to metal atom	$\nu_{\text{ASYM STR}}$	$A_1$
symmetric tilt of rings relative to metal atom	$\nu_{\text{SYM TILT}}$	$E_1$
antisymmetric tilt of rings relative to metal atom	$\nu_{\text{ASYM TILT}}$	$E_1$
compensated in phase ring translation	$\nu_{\text{BEND}}$	$E_1$
torsion	$\nu_{\text{TOR}}$	$A_2$

schematic vibrational modes for benzene (and for hexafluorobenzene) are shown in standard texts [9]. The remaining 6 vibrations involve the metal as well as the aromatic rings; these are depicted in Nakamoto's now classic text [10]. The descriptions of all 46 modes, along with the designations used in this paper and the symmetries, are collected in Table 1.

Our intention is not to assign all 46 fundamental modes for each of the two compounds, nor even to propose assignments for every observed band, no matter how weak. Our more modest goal is to assign all the prominent bands in the spectra and develop a picture consistent with the vibrational assignments. To our knowledge, this is the first report of vibrational assignments for molecules of  $C_{6v}$  symmetry.

### Vibrational analysis

The observed infrared and Raman band positions and intensities for  $C_6H_6CrC_6F_6$  and  $C_6D_6CrC_6F_6$  appear in Table 2. The analysis that follows (also in Table 2) is given below first for  $A_1$  modes, then  $E_1$  modes, and finally for  $E_2$  modes. A few combination bands are also assigned in Table 2, without accompanying comments.

TABLE 2

FREQUENCIES (in  $\text{cm}^{-1}$ ), INTENSITIES, AND ASSIGNMENTS FOR RAMAN AND INFRARED BANDS OF  $\text{C}_6\text{H}_6\text{CrC}_6\text{F}_6$  AND  $\text{C}_6\text{D}_6\text{CrC}_6\text{F}_6$

$\text{C}_6\text{H}_6\text{CrC}_6\text{F}_6$			$\text{C}_6\text{D}_6\text{CrC}_6\text{F}_6$		
Raman	IR	Assignment	Raman	IR	Assignment
39m			59m		
49m			108m		$\nu_{17}\text{F}$
59m			163vs	163w	$\nu_{11}\text{F}$
112m		$\nu_{17}\text{F}$	228m	226w	$\nu_{18}\text{F}$
166vs	167w	$\nu_{11}\text{F}$	261vw(br)		$\nu_9\text{F}$
237m	235w	$\nu_{18}\text{F}$	304vw		
270vw		$\nu_9\text{F}$	316m	317m	$\nu_{10}\text{F}$
310w			327 vs	327vs	$\nu_{\text{SYM STR}}$
325m	324vw	$\nu_{10}\text{F}$	425m		$\nu_6\text{F}$
340vs	340s	$\nu_{\text{SYM STR}}$		460s	$\nu_{\text{SYM TILT}}$
428m		$\nu_6\text{F}$		492s	$\nu_{\text{ASYM TILT}}$
	466s	$\nu_{\text{SYM TILT}}$	529s	535s	$\nu_{11}\text{F}$
	497s	$\nu_{\text{ASYM TILT}}$	558s	561s	$\nu_{\text{ASYM STR}}$
531s	535vs	$\nu_{11}\text{F}$	575w	576m	$\nu_{16}\text{F}$
573m	575m	$\nu_{16}\text{F}$	589vw	584w(sh)	$\nu_6\text{D}$
585s	589s	$\nu_{\text{ASYM STR}}$	638vw	637m	$\nu_{11}\text{D}$
600m(sh)	604s(sh)	$\nu_6\text{H}$	653vw	654m	$\nu_{10}\text{D}$
619w				688vw	$\nu_{18}\text{F} +$
	699w	$\nu_{18}\text{F} +$			$\nu_{\text{SYM TILT}}$
		$\nu_{\text{SYM TILT}}$		739w	$\nu_{11}\text{F} + \nu_{16}\text{F}$
	774w	$\nu_{11}\text{F} + \nu_{18}\text{F}$	803w	803m	$\nu_{18}\text{D}$
805w	800m	$\nu_{11}\text{H}$	843m	838vw(sh)	$\nu_9\text{D}$
	818vw	$\nu_{18}\text{F} +$		891m	$\nu_{\text{SYM STR}} +$
		$\nu_{\text{ASYM STR}}$			$\nu_{\text{ASYM STR}}$
883vw	882m	$\nu_{10}\text{H}$	922m	922vs(br)	$\nu_{20}\text{F}$
	893m	$\nu_6\text{F} +$	928s		$\nu_{11}\text{D}$
		$\nu_{\text{SYM TILT}}$			
923w	921vs	$\nu_{20}\text{F}$		969m	
940w	934vs	$\nu_{\text{SYM STR}} +$		1007w	
		$\nu_{\text{ASYM STR}}$			
972s	973m	$\nu_{11}\text{H}$		1035w	$\nu_{16}\text{F} +$
	984m			1060w	$\nu_{\text{SYM TILT}}$
					$\nu_{16}\text{F} +$
1006m	1006m	$\nu_{18}\text{H}$		1102vw	$\nu_{\text{ASYM TILT}}$
1040w	1034vw	$\nu_{16}\text{F} +$		1116vw	
		$\nu_{\text{SYM TILT}}$			
	1048m	$\nu_{\text{SYM TILT}} +$		1130w	
		$\nu_{\text{ASYM STR}}$			
	1072m	$\nu_{16}\text{F} +$		1137vw	$\nu_{16}\text{F} +$
		$\nu_{\text{ASYM TILT}}$			$\nu_{\text{ASYM STR}}$
	1115w			1148w	
	1139w			1162w	$\nu_{16}\text{F} + \nu_{18}\text{F} +$
					$\nu_{\text{SYM TILT}}$
1147w	1149w	$\nu_9\text{H}$	1274w	1278m	$\nu_{11}\text{F} + \nu_{11}\text{F} +$
					$\nu_{16}\text{F}$
	1161w	$\nu_{16}\text{F} +$	1283m	1287s	$\nu_{19}\text{D}$
		$\nu_{\text{ASYM STR}}$			
	1211vw			1310w	
1284vw	1285m	$\nu_{18}\text{F} +$		1333w	
		$\nu_{\text{SYM TILT}} +$			
		$\nu_{\text{ASYM STR}}$			
	1304m			1350w	
	1318m	$2\nu_6\text{F} +$	1386w(br)	1397vs	$\nu_2\text{F}$
		$\nu_{\text{SYM TILT}}$			
	1330m				

TABLE 2 (continued)

$C_6H_6CrC_6F_6$			$C_6D_6CrC_6F_6$		
Raman	IR	Assignment	Raman	IR	Assignment
1387m(br)	1395vs	$\nu_{2F}$	1410vs		$\nu_{19F}$
	1406vs	$\nu_{19F}$	1457m(sh)		$\nu_{1F} + \nu_{20F}$
1439m	1440m(sh)	$\nu_{19H}$	1496vw		$\nu_{16F} + \nu_{20F}$
1485vw(br)	1494w	$\nu_{16F} + \nu_{20F}$	1514w		
	1533w		1534w		
	1601w(br)		1545w		
	1619m	$\nu_{18F} + \nu_{20F} +$ $\nu_{SYM TILT}$	1620m(br)		$\nu_{18F} + \nu_{20F} +$ $\nu_{SYM TILT}$
1649vw		$\nu_{8F}$	1700w		
	1682w		1894w		
	1726vw(br)		1915w		
	1758w		1950w		$\nu_{2F} +$ $\nu_{ASYM STR}$
	1807m		1969w		$\nu_{19F} +$ $\nu_{ASYM STR}$
	1856w		2086w(br)		
	1896m		2253w		$\nu_{20D}$
	1919vw		2265w		
	1971m	$\nu_{2F} + \nu_{16F}$	2274w		
	2265w		2296vw		
	2460w		2316w		$\nu_{2D}$
	2580vw		2335w		
	2739vw		2458w(br)		
	2927vw	$\nu_{20H}$	2749w		
	2951vw				
3092w	3090w	$\nu_{2H}$			

s = strong, m = medium, w = weak, v = very, sh = shoulder, br = broad

### $A_1$ modes

$C_6F_6$  ring. In the  $C_6F_6$  ring of  $C_6H_6CrC_6F_6$  and  $C_6D_6CrC_6F_6$ , hereafter denoted as F ring, the vibrations should not vary significantly with deuterium substitution for hydrogen. 3  $A_1$  Raman and infrared active bands are expected, namely  $\nu_{1F}$ ,  $\nu_{2F}$  and  $\nu_{11F}$ . From the positions of these bands in  $C_6F_6$  [11,12], along with their expected medium to strong intensity in the Raman, these can be unambiguously assigned.  $\nu_{1F}$ , the ring breathing mode, appears at 535  $cm^{-1}$  in the IR for both isotopes and at 531/529  $cm^{-1}$  in the Raman. In  $C_6F_6$  this band is found at 559  $cm^{-1}$ . The C—F stretch  $\nu_{2F}$  is assigned to 1395/1397  $cm^{-1}$  for the isotopic pair from the very strong infrared bands. The Raman bands for the pair are of weak to medium intensity. Since there are no other medium intensity Raman bands within  $\pm 400$   $cm^{-1}$  of this band that are isotopically invariant, this assignment seems justified. In  $C_6F_6$ , mode  $\nu_2$  occurs at 1490  $cm^{-1}$ . The umbrella mode,  $\nu_{11F}$  is assigned to the very strong Raman bands at 166/163  $cm^{-1}$ . The corresponding infrared intensities are weak. The next strong Raman band is about 180  $cm^{-1}$  distant. In  $C_6F_6$ ,  $\nu_{11}$  is assigned to 215  $cm^{-1}$ . It should be noted that all these  $A_1$  F ring fundamentals appear at a lower frequency in the sandwich compounds as compared to  $C_6F_6$  itself.

$C_6H_6$  ring. The H ring modes are expected to shift with deuteration, similar to shifts observed for the corresponding modes in the pairs  $C_6H_6/C_6D_6$  [13]

and  $(C_6H_6)_2Cr/(C_6D_6)_2Cr$  [14]. Thus, the ring breathing mode  $\nu_{1H}/\nu_{1D}$  is assigned to strong Raman bands at  $972/928\text{ cm}^{-1}$ . The corresponding modes for  $C_6H_6/C_6D_6$  are at  $993/945\text{ cm}^{-1}$  and for  $(C_6H_6)_2Cr/(C_6D_6)_2Cr$  are  $970/920\text{ cm}^{-1}$ . The C—H stretching mode  $\nu_{2H}$  is assigned to the weak Raman band at  $3092\text{ cm}^{-1}$  (also at  $3090\text{ cm}^{-1}$  as a weak IR band). Since the IR active C—H stretch  $\nu_{20H}$  ( $E_1$ ) and Raman active C—H stretch  $\nu_{7H}$  ( $E_2$ ) are also expected in the  $3000\text{ cm}^{-1}$  region, as well as combination bands involving C—C stretches, this assignment is only tentative. In any event, the  $3092\text{ cm}^{-1}$  band moves to  $2314\text{ cm}^{-1}$  on deuteration. In  $C_6H_6/C_6D_6$ ,  $\nu_2$  appears at  $3073/2303\text{ cm}^{-1}$ , and in  $(C_6H_6)_2Cr/(C_6D_6)_2Cr$  at  $3053/2267\text{ cm}^{-1}$ .

The umbrella mode  $\nu_{11H}$  proved to be somewhat elusive. It is known that  $\nu_{11}$  is at  $673\text{ cm}^{-1}$  in  $C_6H_6$  and moves up to  $791\text{ cm}^{-1}$  in  $(C_6H_6)_2Cr$ . In the  $600\text{--}800\text{ cm}^{-1}$  range for  $C_6H_6CrC_6F_6$ , only one band exhibited both IR and Raman activity ( $805\text{ cm}^{-1}$  in the Raman and  $800\text{ cm}^{-1}$  in the IR), and thus could be a suitable candidate for  $\nu_{11H}$ . However, in  $C_6D_6CrC_6F_6$ , bands at  $803\text{ cm}^{-1}$  in both the IR and Raman are present. If the bands near  $800\text{ cm}^{-1}$  in both  $C_6H_6CrC_6F_6$  and  $C_6D_6CrC_6F_6$  have a common parentage, then a  $\nu_{11H}$  attribution would not be reasonable since  $\nu_{11H}$  is isotope sensitive. However, neither F ring fundamentals, nor fundamentals involving the complex as a whole, are expected in the  $800\text{ cm}^{-1}$  region. The answer to this problem is supplied by a consideration of  $\nu_{18H}$ , an in plane C—H bending mode. This fundamental appears at  $1037/814\text{ cm}^{-1}$  in the pair  $(C_6H_6)_2Cr/(C_6D_6)_2Cr$ . In  $C_6H_6CrC_6F_6$  a medium intensity band is observed in the IR and Raman at  $1006\text{ cm}^{-1}$ . This is assigned to  $\nu_{18H}$ , and the aforementioned  $803\text{ cm}^{-1}$  band as the  $C_6D_6CrC_6F_6$  analogue, i.e.,  $\nu_{18D}$ . Thus,  $\nu_{11H}$  is assigned to the bands at  $805\text{ cm}^{-1}$  in the Raman and  $800\text{ cm}^{-1}$  in the IR. Since  $\nu_{11H}$  is expected to shift on deuteration ( $673/496\text{ cm}^{-1}$  for  $C_6H_6/C_6D_6$  and  $791/566\text{ cm}^{-1}$  for  $(C_6H_6)_2Cr/(C_6D_6)_2Cr$ ), both  $637$  and  $654\text{ cm}^{-1}$  in the infrared and Raman spectra of  $C_6D_6CrC_6F_6$  are suitable candidates. Bands of lower frequency than this are isotope invariant from partners seen in  $C_6H_6CrC_6F_6$ ;  $637\text{ cm}^{-1}$  has been chosen since its intensity best matches that seen in  $C_6H_6CrC_6F_6$ .

In summary, compared to  $C_6H_6$ ,  $\nu_{1H}$  moves down in frequency,  $\nu_{2H}$  changes only slightly, and  $\nu_{11H}$  moves up considerably.

*Vibrations involving the chromium atom.* The symmetric stretching of the two rings relative to the chromium atom, designated as  $\nu_{SYM\ STR}$ , appears at  $277\text{ cm}^{-1}$  in  $(C_6H_6)_2Cr$ . In  $C_6H_6CrC_6F_6/C_6D_6CrC_6F_6$ , this fundamental is assigned to the strong bands at  $340/327\text{ cm}^{-1}$ . The antisymmetric stretching mode is found at higher frequencies in  $(C_6H_6)_2Cr/(C_6D_6)_2Cr$ , namely at  $490/423\text{ cm}^{-1}$ . For  $C_6H_6CrC_6F_6/C_6D_6CrC_6F_6$ ,  $\nu_{ASYM\ STR}$  is attributed to the strong band at  $587/560\text{ cm}^{-1}$ . Cyvin et al. [14] have calculated isotope shifts for all six vibrations involving the metal and the rings for  $(C_6H_6)_2Cr/(C_6D_6)_2Cr$ . Unfortunately, there are few experimental data to test their predictions. For example,  $\nu_{SYM\ STR}$  is considered by them to be isotope invariant, but no band is known to occur at  $277\text{ cm}^{-1}$  in  $(C_6D_6)_2Cr$ .

We have calculated the theoretical Teller-Redlich product ratio for the  $8A_1$  fundamentals. For  $C_6D_6CrC_6F_6/C_6H_6CrC_6F_6$ , this ratio is computed to be 0.505. Our observed values, just presented, yield a value of 0.513; the agreement is excellent.

*E<sub>1</sub> modes*

*C<sub>6</sub>F<sub>6</sub> ring.* *E<sub>1</sub>* modes are expected to exhibit both IR and Raman activity. The C—F stretching mode  $\nu_{20F}$  is found as strong Raman and IR bands at 921/922  $\text{cm}^{-1}$  in  $\text{C}_6\text{H}_6\text{CrC}_6\text{F}_6/\text{C}_6\text{D}_6\text{CrC}_6\text{F}_6$ . For  $\text{C}_6\text{F}_6$ , the assignment of  $\nu_{20}$  is complicated by Fermi resonance; 1006  $\text{cm}^{-1}$  has been proposed. The C—C stretching mode  $\nu_{19F}$  is assigned to the strong IR band at 1406/1410  $\text{cm}^{-1}$ . The in plane C—F bend,  $\nu_{18F}$ , and the out of plane C—F bend,  $\nu_{10F}$ , should both occur at low frequency, since in  $\text{C}_6\text{F}_6$   $\nu_{18}$  is at 315  $\text{cm}^{-1}$  and  $\nu_{10}$  at 370  $\text{cm}^{-1}$ . However, all the bands observed in the IR and Raman below 400  $\text{cm}^{-1}$  show a very slight isotope dependence for  $\text{C}_6\text{H}_6\text{CrC}_6\text{F}_6/\text{C}_6\text{D}_6\text{CrC}_6\text{F}_6$ , so their positions offer no help in distinguishing the F ring modes from those involving chromium and both rings. Thus,  $\nu_{18F}$  has been assigned to 237/228  $\text{cm}^{-1}$  and  $\nu_{10F}$  to 325/316  $\text{cm}^{-1}$  since these are the only two bands seen to be both IR and Raman active below 400  $\text{cm}^{-1}$  that have not yet been assigned. Both  $\nu_{10F}$  and  $\nu_{18F}$  are at lower frequencies than their  $\text{C}_6\text{F}_6$  counterparts.

*C<sub>6</sub>H<sub>6</sub> ring.* Bands in the C—H stretching region are broad and weak; the C—H stretch  $\nu_{20H}$  could possibly be 2927/2253  $\text{cm}^{-1}$ . The C—C stretch  $\nu_{19H}$  is assigned to 1439/1287  $\text{cm}^{-1}$  for  $\text{C}_6\text{H}_6\text{CrC}_6\text{F}_6/\text{C}_6\text{D}_6\text{CrC}_6\text{F}_6$ . In  $\text{C}_6\text{H}_6/\text{C}_6\text{D}_6$ , this mode is observed at 1482/1333  $\text{cm}^{-1}$  and in  $(\text{C}_6\text{H}_6)_2\text{Cr}/(\text{C}_6\text{D}_6)_2\text{Cr}$  at 1426/1271  $\text{cm}^{-1}$ . The in plane C—H bend,  $\nu_{18H}$  has already been mentioned above with the *A<sub>1</sub>* modes. The out of plane C—H bend  $\nu_{10H}$  is attributed to medium intensity IR bands at 882/654  $\text{cm}^{-1}$ . This compares favourably with 846/660  $\text{cm}^{-1}$  in  $\text{C}_6\text{H}_6/\text{C}_6\text{D}_6$  and 860/669  $\text{cm}^{-1}$  in  $(\text{C}_6\text{H}_6)_2\text{Cr}/(\text{C}_6\text{D}_6)_2\text{Cr}$ .

*Vibrations involving the chromium atom.* The strong IR bands at 466/460  $\text{cm}^{-1}$  are assigned to  $\nu_{\text{SYM TILT}}$ , while the strong pair at 497/492  $\text{cm}^{-1}$  are attributed to  $\nu_{\text{ASYM TILT}}$ . In  $(\text{C}_6\text{H}_6)_2\text{Cr}$  these occur at 335 and 459  $\text{cm}^{-1}$ , respectively. The remaining mode,  $\nu_{\text{BEND}}$ , otherwise referred to as a compensated in phase ligand translation, has not been assigned. In  $(\text{C}_6\text{H}_6)_2\text{Cr}$  this mode is at 171  $\text{cm}^{-1}$ . In the  $\text{C}_6\text{H}_6\text{CrC}_6\text{F}_6$  and  $\text{C}_6\text{D}_6\text{CrC}_6\text{F}_6$  Raman spectra there are some low frequency bands, but no corresponding IR activity. These have been assigned to *E<sub>2</sub>* modes.

*E<sub>2</sub> modes*

*C<sub>6</sub>F<sub>6</sub> ring.* The C—C stretching mode  $\nu_{8F}$  in  $\text{C}_6\text{H}_6\text{CrC}_6\text{F}_6$  is assigned to the weak Raman band at 1649  $\text{cm}^{-1}$ ; the corresponding mode in the deuterated compound is not observed. In  $\text{C}_6\text{F}_6$  this band is at 1655  $\text{cm}^{-1}$ . The C—F stretching mode  $\nu_7$  is at 1157  $\text{cm}^{-1}$  in  $\text{C}_6\text{F}_6$ , but the only Raman band in  $\text{C}_6\text{H}_6\text{CrC}_6\text{F}_6$  close to this frequency, 1147  $\text{cm}^{-1}$ , is assigned to  $\nu_{9H}$  (see below). The out of plane ring deformation  $\nu_{16F}$  is tentatively assigned to 574/576  $\text{cm}^{-1}$  (595  $\text{cm}^{-1}$  in  $\text{C}_6\text{F}_6$ ). The problem with this assignment is that the 573  $\text{cm}^{-1}$  Raman band is also an IR active band at 575  $\text{cm}^{-1}$ . Various alternatives have been considered, such as 575  $\text{cm}^{-1}$  being  $\nu_{\text{ASYM TILT}}$ , and the two bands 497/492  $\text{cm}^{-1}$  and 466/460  $\text{cm}^{-1}$  resulting from Fermi resonance between *E<sub>1</sub>*  $\nu_{\text{SYM TILT}}$  and the *E<sub>1</sub>* combination band  $\nu_{10F}$  and  $\nu_{11F}$ . For this alternative assignment, the fit is excellent for  $\text{C}_6\text{D}_6\text{CrC}_6\text{F}_6$ , but only marginally acceptable for  $\text{C}_6\text{H}_6\text{CrC}_6\text{F}_6$ . The in plane ring deformation  $\nu_{6F}$  is suggested to lie at 428/425  $\text{cm}^{-1}$ , close to 443  $\text{cm}^{-1}$  for  $\text{C}_6\text{F}_6$ . The weak Raman bands at 270/261  $\text{cm}^{-1}$  are attributed to the in plane C—F bend  $\nu_{9F}$  (264  $\text{cm}^{-1}$  in  $\text{C}_6\text{F}_6$ ). The 112/108

$\text{cm}^{-1}$  band could perhaps be  $\nu_{17\text{F}}$ , the out of plane C—F bend, although this frequency is quite a bit lower than the  $175 \text{ cm}^{-1}$  value in  $\text{C}_6\text{F}_6$ .

**$\text{C}_6\text{H}_6$  ring:** The only two H ring  $E_2$  modes identified are  $\nu_{9\text{H}}$  and  $\nu_{6\text{H}}$ . The Raman bands at  $1147/838 \text{ cm}^{-1}$  are assigned to the in plane C—H bend  $\nu_{9\text{H}}$ . This fundamental occurs at  $1178/869 \text{ cm}^{-1}$  in  $\text{C}_6\text{H}_6/\text{C}_6\text{D}_6$  and at  $1143/868 \text{ cm}^{-1}$  in  $(\text{C}_6\text{H}_6)_2\text{Cr}/(\text{C}_6\text{D}_6)_2\text{Cr}$ . The in plane ring deformation  $\nu_{6\text{H}}$  is attributed to Raman bands at  $600/589 \text{ cm}^{-1}$ , although, in the IR, shoulders near these frequencies are also seen. In  $\text{C}_6\text{H}_6/\text{C}_6\text{D}_6$ ,  $\nu_{6\text{H}}$  occurs at  $606/579 \text{ cm}^{-1}$ , and at  $604/566 \text{ cm}^{-1}$  in  $(\text{C}_6\text{H}_6)_2\text{Cr}/(\text{C}_6\text{D}_6)_2\text{Cr}$ .

## Discussion

$\pi$ -Complexes of hexafluorobenzene are extremely rare. To our knowledge, the only other well-characterised molecule containing a hexahapto- $\text{C}_6\text{F}_6$  ring is  $\text{C}_6\text{F}_6\text{Cr}(\text{PF}_3)_3$  [15] which was the subject of a  $^{19}\text{F}$  NMR spectroscopic study [16]. Thus, these vibrational spectroscopic data provide useful insight into the mode of bonding of a metal to such an unlikely  $\pi$ -bonding arene. The conventional wisdom would suggest that, in the continuum of bonding types inherent in the Dewar-Chatto-Duncanson model, fluoro-substituted unsaturated moieties tend to exhibit weak  $\sigma$ -donating and good  $\pi$ -accepting properties. In an extreme viewpoint, metal- $\text{C}_2\text{F}_4$  complexes may be regarded as metallocyclopropanes in which the metal has been oxidised by two units [17]. It is thus apparent that hexafluorobenzene  $\pi$ -complexes can only be stabilized when the electron deficiency imposed on the central chromium atom by the  $\text{C}_6\text{F}_6$  unit is compensated for by the other ligands. Indeed, the chemistry of  $\text{C}_6\text{H}_6\text{CrC}_6\text{F}_6$  has been interpreted in terms of an "internal oxidation" in which electron transfer has occurred from chromium to  $\text{C}_6\text{F}_6$  [18]; it is clear that the  $\text{C}_6\text{H}_6$  ring is able to compensate for the incipient build-up of positive charge at chromium since in the molecules  $\text{C}_6\text{H}_6\text{CrC}_6\text{F}_n\text{H}_{6-n}$  the  $^1\text{H}$  and  $^{13}\text{C}$  NMR chemical shifts of the  $\text{C}_6\text{H}_6$  ring correlate beautifully with the number of fluorines in the fluorinated ring [6].

The basic picture of  $\text{C}_6\text{H}_6\text{CrC}_6\text{F}_6$  which emerges from these vibrational spectroscopic assignments is one in which — with the single exception discussed below — the vibrations of the  $\text{C}_6\text{H}_6$  ring move to lower frequencies than in benzene itself and indeed show only small perturbations from the corresponding modes in  $(\text{C}_6\text{H}_6)_2\text{Cr}$  (See Table 3). Again we have to conclude, as have others before us, that the symmetric out of plane bend (or umbrella mode),  $\nu_{11}$ , is much more difficult for benzene  $\pi$ -complexes than for benzene itself. This result has been attributed to a number of causes, such as the difficulty of orbital following [1] or to kinematic effects [14], that is, to the non-vanishing of offdiagonal elements in the G sub-matrix of the appropriate symmetry species of internal symmetry coordinates in the framework of the Wilson FG matrix formulation.

We see that the vibrations of the  $\pi$ -complexed  $\text{C}_6\text{F}_6$  ring, like those of the  $\text{C}_6\text{H}_6$  ring, occur at lower frequencies than in  $\text{C}_6\text{F}_6$  itself. Archetypical of these are the ring breathing modes  $\nu_{1\text{H}}$  and  $\nu_{1\text{F}}$  which occur at  $993$  and  $559 \text{ cm}^{-1}$ , respectively, in the free arenes, and at  $972$  and  $535 \text{ cm}^{-1}$  in the complex. In a simple view where we look at potential energy effects, the weakening of the

TABLE 3

FREQUENCIES ( $\text{cm}^{-1}$ ) OF SOME IR AND RAMAN ACTIVE RING FUNDAMENTALS IN  $\text{C}_6\text{H}_6\text{CrC}_6\text{F}_6$  AND  $\text{C}_6\text{D}_6\text{CrC}_6\text{F}_6$  RELATED MOLECULES

	$\nu_1$	$\nu_2$	$\nu_{10}$	$\nu_{11}$	$\nu_{18}$	$\nu_{19}$	$\nu_{20}$
$\text{C}_6\text{H}_6$	993	3073	846	673	1037	1482	3064
$(\text{C}_6\text{H}_6)_2\text{Cr}$	970	3053	860	791	999	1430	2904
$\text{C}_6\text{H}_6$   Cr	972	3091	882	800	1006	1439	2927
$\text{C}_6\text{F}_6$	533	1395	325	166	237	1406	921
$\text{C}_6\text{F}_6$   Cr	559	1490	370	215	315	1530	1006
$\text{C}_6\text{F}_6$	532	1397	316	163	228	1410	922
$\text{C}_6\text{D}_6$	928	2314	654	637	803	1287	2253
$(\text{C}_6\text{D}_6)_2\text{Cr}$	920	2267	669	566	802	1271	2212
$\text{C}_6\text{D}_6$	945	2303	660	496	814	1333	2288

C—C framework in both rings is entirely consistent with our picture of transfer of electron density from the  $\text{C}_6\text{H}_6$  ring via the chromium to the  $\text{C}_6\text{F}_6$  ring. Thus, donation of the  $\pi$ -electrons of  $\text{C}_6\text{H}_6$  to the chromium lowers the effective bond order of the carbons in the  $\text{C}_6\text{H}_6$  ring and loosens up the vibrations resulting in lower frequencies. Concomitantly, electron density is accepted by the  $\text{C}_6\text{F}_6$  ring into its vacant  $\pi^*$  manifold hence weakening the carbon—carbon framework and lowering all the frequencies.

An interesting point which immediately arises is the question of  $\nu_{11}$ , the umbrella mode, in the  $\text{C}_6\text{F}_6$  ring which drops from  $215 \text{ cm}^{-1}$  in  $\text{C}_6\text{F}_6$  to  $166 \text{ cm}^{-1}$  in  $\text{C}_6\text{H}_6\text{CrC}_6\text{F}_6$ . In fluoro-arenes, one can envisage considerable overlap of non-bonding fluorine electrons with the  $\pi$  system of the arene leading to some degree of C—F multiple bonding. (Such  $2p-2p$   $\pi$  type overlap is presumed to account for the great stability of  $\text{BF}_3$  relative to  $\text{BH}_3$ .) However, in  $\text{C}_6\text{F}_6\pi$ -complexes, the fluorine non-bonded electrons must compete with the chromium  $d$  orbitals for occupancy of the  $\pi^*$ -manifold of the arene. Thus, the rigidity of the hexagon of fluorines relative to the hexagon of carbons may be considerably reduced leading to a decrease in  $\nu_{11}$ . However, for the  $\text{C}_6\text{H}_6$  ring there are no low-lying hydrogen orbitals for C—H  $\pi$ -bonding. In any event, the observed umbrella frequency for the  $\text{C}_6\text{H}_6$  ring increases on complexation.

A further point of difference between  $\text{C}_6\text{H}_6\text{CrC}_6\text{F}_6$  and  $(\text{C}_6\text{H}_6)_2\text{Cr}$  is an increase in the frequencies for the vibrations involving both rings and the metal in the asymmetric sandwich. The crystal structure of  $\text{C}_6\text{H}_6\text{CrC}_6\text{F}_5\text{PPh}_2$  [7], which presumably is prototypical of such complexes, reveals that the chromium is significantly closer to the fluorinated ring than to the benzene ring. This, of course, implies a stronger interaction of the chromium with the  $\text{C}_6\text{F}_6$  ring than with the  $\text{C}_6\text{H}_6$  ring thus accounting for the increased frequencies of the skeletal modes involving motions of the arenes with respect to the metal.



## Experimental

$C_6H_6CrC_6F_6$  was prepared and purified as described previously [18].  $C_6D_6CrC_6F_6$ , m.p.  $135^\circ C$ , was obtained by co-condensing chromium vapor with a 1 : 1 mixture of  $C_6D_6$  and  $C_6F_6$  in the metal vaporisation apparatus described elsewhere [19]. The mass spectrum shows,  $m/e$  (%), 322,  $C_{12}D_6CrF_6^+$  (65); 316,  $C_{12}D_3CrF_6^+$ ,  $C_{12}H_6CrF_6^+$  (4); 219,  $C_6F_5Cr^+$  (17); 186,  $C_6F_6^+$  (55); 136,  $C_6D_6Cr^+$  (75); 98,  $C_7D_7^+$  (45); 84,  $C_6D_6^+$  (100); 82,  $C_6D_5^+$  (60); 52,  $Cr^+$  (80).

Room temperature infrared spectra were obtained with a Nicolet model 7199 Fourier Transform Infrared Spectrometer. For the region below  $500\text{ cm}^{-1}$ , samples of  $C_6H_6CrC_6F_6$  and  $C_6D_6CrC_6F_6$  in liquid  $C_6H_6$  were placed in a 1 mm polyethylene cell. Spectra for this region were obtained after subtracting those bands due to the polyethylene cell containing benzene alone. For the region above  $450\text{ cm}^{-1}$ , KBr pellets containing the appropriate sandwich compound were used. The accuracy of the band positions is considered to be  $\pm 1\text{ cm}^{-1}$ .

Raman spectra of spinning room temperature powder samples in Pyrex capillary tubes were obtained with excitation from the green  $5145\text{ \AA}$  line of a Spectra Physics model 164 argon ion laser. The scattered radiation was detected by a photomultiplier tube after passing through a Spex model 1400 Czerny-Turner monochromator, then amplified and recorded. Estimated accuracy of the Raman bands is  $\pm 3\text{ cm}^{-1}$ .

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