Inelastic Neutron Scattering Studies of Benzene-containing Organometallic Complexes. Part 1. Complexes [Cr(CO)$_3$(η^6-C$_6$H$_6$)] and [Mn(CO)$_3$(η^6-C$_6$H$_6$)]Br †

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Inelastic neutron scattering spectra (0—875 cm^{-1}) of [Cr(CO)$_3$(η^6-C$_6$H$_6$)] (1) and [Mn(CO)$_3$(η^6-C$_6$H$_6$)]Br (2) have been measured. In addition, low-frequency i.r. (60—600 cm^{-1}) and Raman (0—1 000 cm^{-1}) spectra of (2) are reported for the first time. Those low-frequency modes of both compounds which involve significant benzene-ligand displacement have been assigned. From the assignments of the benzene-ligand torsion (ν_{22}) in complexes (1) and (2) to bands at 88.5 and 116.5 cm^{-1} respectively, values for the activation energy for benzene-group rotation have been calculated to be 27.5 and 46.5 kJ mol^{-1} respectively. In the case of complex (1), this value has been compared with that determined from n.m.r. measurements (17.6 kJ mol^{-1}).

THE investigation of low-frequency modes of vibration in organometallic complexes is of considerable interest for the determination of force constants, molecular potentials, *etc.* Such studies are also an important aid in the interpretation of spectroscopic data on adsorbed species. However, it is in the low-frequency region that optical studies are most difficult and assignments have often proved most controversial.

Inelastic neutron scattering (i.n.s.) spectroscopy is not subject to electromagnetic selection rules, but is particularly sensitive to normal modes which involve significant proton motion.[1] This contrasts with optical experiments where some modes may be forbidden and others associated with only small dipole moment or polarisability changes. Thus the two techniques may often be complementary; *e.g.* if a complex contains both hydrogenous and non-hydrogenous ligands, those normal modes associated with the former ligand(s) will be most prominent in the i.n.s. spectrum and those with the latter, in the optical spectra.

We chose to study [Cr(CO)$_3$(η-C$_6$H$_6$)] (1) and [Mn(CO)$_3$(η-C$_6$H$_6$)]Br (2) using i.n.s. spectroscopy for the following reasons: (*i*) to attempt a firm assignment of those low-frequency modes of (1) which have either not been previously located or have been subject to controversy; (*ii*) to identify the torsional mode of the η-C$_6$H$_6$ ligand within complex (1) about its six-fold axis and to calculate a barrier height for comparison with data from other techniques; (*iii*) to compare data for the well studied neutral complex (1) with those for an ionic species [Mn(CO)$_3$(η-C$_6$H$_6$)]$^+$, for which no assignments are available; and (*iv*) to serve as model compounds for the interpretation of i.n.s. data on adsorbed benzene.

Since the completion of this work the i.n.s. spectrum (10—2 000 cm^{-1}) of [Cr(CO)$_3$(η-C$_6$H$_6$)] (1) has been reported.[2] The purpose of that study was to use the intensities of observed i.n.s. bands to test valence force fields proposed on the basis of optical studies. Our objective is quite different and the investigations complement each other. For instance, their work at low frequencies is less extensive than ours and their spectra display considerably lower resolution.

BACKGROUND

(*a*) [Cr(CO)$_3$(η-C$_6$H$_6$)] (1).—Following initial structural determinations,[3-6] a more comprehensive study of (1) by Rees and Coppens [7,8] showed that the benzene ligand essentially retains six-fold symmetry. From electron-diffraction studies (413 K), Chiu *et al.*[9] have concluded that (1) is a mixture of several conformers in the vapour phase, the benzene ligand behaving essentially as a free rotor. In agreement with this, the activation energy (17.6 ± 0.4 kJ mol^{-1}) for the rotation of the benzene group within solid phase (1),[10] calculated from measurements of the spin–lattice relaxation time, has been suggested to arise from *inter-* rather than *intra*-molecular forces.

Of the 51 normal vibrations of (1), 30 (ν_1—ν_{20}) are derived from internal modes of the benzene ligand, 15 (ν_{25}—ν_{34}) result from internal modes of the Cr(CO)$_3$ moiety, and 6 (ν_{21}—ν_{24}) represent motions of the benzene group relative to the Cr(CO)$_3$ moiety. The numbering of the benzene ligand modes follows the scheme of Wilson [11] for the free molecule whilst the numbering of the modes of the Cr(CO)$_3$ moiety follows that of Fritz and Manchot.[12] In this study we are concerned principally with ν_{21}—ν_{24} and hence consideration of the spectroscopic data available will be restricted to the region below 950 cm^{-1}. There have been many optical spectroscopic studies [12-21] and normal co-ordinate analyses (n.c.a.s) [2,15,22-26] of compound (1) which have covered this region of the spectrum. However, these have differed either in their assignments or in the assumptions made in the calculations and, as a result, there has been considerable controversy over assignments. Table 1 summarises the optical assignments in the literature and Table 2 the results of the various published n.c.a.s.

One of the principal advantages of using i.n.s. spectroscopy to study molecules arises because the intensities of the bands depend, apart from known experimental parameters, on the displacement of the scattering nucleus.[1] As these can, in principle, be calculated from

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† (η^6-Benzene)tricarbonylchromium and (η^6-benzene)tricarbonylmanganese(I) bromide respectively.

TABLE 1

Comparison of the optical spectroscopic wavenumbers (cm^{-1}) and assignments of [$Cr(CO)_3(\eta^6-C_6H_6)$] (1) reported by various authors for fundamentals occurring below 950 cm^{-1} *

Raman [17–20]	I.r. [12–15,17,19]	Fritz and Manchot [12]	Adams [13]	Brown and Carroll [14]	Cataliotti *et al.*[15]	Adams and Squire [17]	Schäfer *et al.*[18]	Hyams and Lippincott [19]	Buttery *et al.*[20]
	39							Lattice modes	
47	43—49					ν_{24} and lattice mode			
68	60—87							ν_{24}	
108—114 (93)	119—121					ν_{26}	ν_{28}	ν_{28}	ν_{28}
131—148	146—153					ν_{28}	ν_{24}	ν_{26}	ν_{26}
296—298 (301, p)	296—301	ν_{21}		ν_{21}	ν_{21}	ν_{21}	ν_{21}	ν_{21}	
	306	ν_{27}	ν_{27}				ν_{27}		
328—334	326—333	ν_{23}			ν_{23}	ν_{23}	ν_{23}	ν_{23}	
(332—338, dp)									
426—427	418—424	ν_{16}			ν_{16}	ν_{16}	ν_{16}	ν_{16}	
485—487	483—487	ν_{26}	ν_{25}	ν_{25}		ν_{25}	ν_{26}	ν_{25}	ν_{25}
(480—483, p)					ν_{27}				
489—491	488—492					ν_{27}		ν_{27}	ν_{27}
534—537	533—540	ν_{25}	ν_{34}	ν_{34}	ν_{25}		ν_{25}		
(532—536, p)						ν_{34}		ν_{34}	ν_{34}
543—545							ν_{34}		
614—617	611—615	ν_6			ν_6	ν_6	ν_6	ν_6	
640—644	628—646	ν_{33}	ν_{33}	ν_{33}	ν_{34}	ν_{33}	ν_{33}	ν_{33}	ν_{33}
654								ν_{11}	
658	654—659				ν_{31}	ν_{32}		ν_{32}	ν_{32}
663—668 (657, p)	664—670	ν_{31}	ν_{31}		ν_{33}	ν_{31}	ν_{31}	ν_{31}	ν_{31}
799—800 (793, p)	784—786	ν_{11}				ν_{11}	ν_{11}	ν_{10}	
902—906	901—911	ν_{17}				ν_{10}	ν_{10}	ν_{17}	

* Solution Raman data given in parentheses; p = polarised, dp = depolarised. Vibrations have been renumbered where necessary to follow the convention of Fritz and Manchot.[12] Although some studies have taken into consideration the additional effect of site-group symmetry, only the generic vibration under C_{3v} symmetry is given in this Table. The i.r. and Raman wavenumber range stated arises from the spread quoted for the same band in the different studies. (In the case of the i.r. data only, an additional cause of the range is the slightly differing values recorded for the same band depending upon whether measurement was made at ambient or liquid N_2 temperature.)

TABLE 2

Comparison of optical spectroscopic wavenumbers (cm^{-1}) with assignments from various n.c.a.s of [$Cr(CO)_3(\eta^6-C_6H_6)$] (1) below 950 cm^{-1} [a]

	Cataliotti *et al.*[15]		Cyvin and co-workers [23,24]		Adams *et al.*[25]			Bisby *et al.*[26]		Jobic *et al.*[2]	
Observed value [12,15,17–19,26]	Calc. value	Assignment	Calc. value	Assignment	Calc. values		Assignment	Calc. value	Assignment	Calc. value	Assignment
					47 [b]	47 [c]	ν_{22}			46	ν_{22}
	74	ν_{28}						79	ν_{28}		
93	93	ν_{26}			86	86	ν_{24}	97	ν_{24}	89	ν_{28}
			100	ν_{22}							
110—121			110	ν_{28}	123	123	ν_{26}	110	ν_{26}	118	ν_{26}
131—132	140	ν_{24}	132	ν_{24}	136	136	ν_{28}			134	ν_{24}
								273	ν_4		
298—306	298	ν_{21}	298	ν_{21}	317	308	$\nu_{21} + \nu_{25}$	304	ν_{21}	304	$\nu_{21} + \nu_{25}$
306			306	ν_{27}							
330—333			332	ν_{23}	321	322	$\nu_{23} + \nu_{27}$	343	ν_{23}	335	$\nu_{23} + \nu_{27}$
424—427			426	ν_{16}	437	434	$\nu_{27} + \nu_{23}$	433	ν_{16}	424	ν_{16}
			465	ν_{32}							
478—488	488	ν_{27}	486	ν_{26}	497	505	$\nu_{25} + \nu_{21}$	483	ν_{25}	497	$\nu_{25} + \nu_{31}$
490					465	458	ν_{16}			496	$\nu_{27} + \nu_{34}$
					503	504	ν_{32}				
524—537	538	ν_{25}	535	ν_{25}				528	ν_{33}		
								538	ν_{32}	551	ν_{32}
540—543			543	ν_{34}	546	546	ν_{34}	544	ν_{34}	560	ν_{33}
614—615			614	ν_6	658	621	ν_6	611	ν_6	617	$\nu_{34} + \nu_{27}$
621—644	633	ν_{34}	644	ν_{33}	626	634	ν_{33}	625	ν_{27}	627	ν_6
										632	ν_4
659	659	ν_{31}									
659—668	667	ν_{33}	664	ν_{31}	665	671	ν_{31}	657	ν_{31}	657	$\nu_{31} + \nu_{26}$
			707	ν_4	749	710	ν_4				
783—800			800	ν_{11}	690	762	ν_{11}	785	ν_{11}	788	ν_{11}
902—904			902	ν_{10}	865	933	ν_{10}	902	ν_{10}	905	ν_{10}

[a] The range of observed wavenumbers stated arise from the spread quoted for the same band in different studies. [b] This column results from refinement (I) [25] which kept the force constants for the benzene ligand fixed at those of benzene. [c] This column results from refinement (II) [25] which produced the most general force field possible.

spectroscopic data, i.n.s. spectra provide a severe test of any assignment scheme. This is because *both* the band positions and their intensities are functions of the same parameter set, the transition frequencies and the reduced masses (or moments of inertia). It has been shown in detail recently [27,28] that the intensities of i.n.s. bands are a function of an energy-dependent Debye–Waller (DW) factor (e^{-2W}) which contains a generally unknown contribution from lattice modes. The usual assumptions are that the DW factor is isotropic and, moreover, normally has a magnitude of unity ($e^{-2W} = 1$). However, these unsophisticated approximations must remain a major criticism of many of the n.c.a.s applied to i.n.s. data to date.

We have chosen to apply a simple model to the calculation of the intensities of i.n.s. bands in our spectra. This model assumes that the DW factor is unity and that the mean-square amplitude of vibration of an atom (or ligand) can be calculated from the formula for the mean-square amplitude of the normal co-ordinate of a harmonic oscillator.[29] Although simple, this model is very useful for obtaining approximate relative intensities of low-frequency modes and for identifying those modes which are associated with bands of very high or very low relative intensities.[30]

Jobic *et al.*,[2] by comparing observed i.n.s. intensities with those calculated as a result of proton displacements associated with each normal vibration, have tested the force fields arising from the available n.c.a.s. These authors, in accordance with common practice, also assumed that DW was unity.

(*b*) $[Mn(CO)_3(\eta\text{-}C_6H_6)]Br$ (2).—Neither the structure of (2) nor the barrier to the rotation of the benzene ligand has been investigated. It is necessary, therefore, to assume both a molecular structure and a form for the rotational barrier related to that previously described for (1). Although the i.r. spectrum of (2) has been reported [31] above 600 cm^{-1} (bands being located at 645 and 827 cm^{-1} in the region of the spectrum in which we are interested), no attempt was made to assign any modes.

EXPERIMENTAL

The complex $[Cr(CO)_3(\eta\text{-}C_6H_6)]$ (1) was purchased from Strem Chemicals Inc., whilst $[Mn(CO)_3(\eta\text{-}C_6H_6)]Br$ (2) was prepared following a literature method.[31]

I.n.s. spectra of (1) and (2) were measured with the samples (polycrystalline powders) contained in silica cells. Time-of-flight (t.o.f.) data were obtained for both complexes using the 4H5 cold neutron spectrometer [32,33] on the Dido reactor at A.E.R.E. Harwell and the IN4 rotating crystal spectrometer [34] (10 K) on the High Flux Reactor at the I.L.L., Grenoble. While 4H5 spectra of (1) were recorded at only 233 K, those of (2) were recorded at both 233 and 88 K. The resolution of IN4 is superior to that of 4H5. Beryllium-filter detector (b.f.d.) spectra [35,36] were obtained at 10 K [(1)] and 18 K [(2)] using the instrument on the Dido reactor at A.E.R.E. Harwell.

Unlike b.f.d. spectra, which can be obtained in a form immediately comparable with optical spectra by plotting 'detected neutron counts per *n* monitor counts' *versus* energy, 'raw' t.o.f. data require several corrections to be made and formulation in terms of various useful functions before comparison. To carry out these calculations, computer programs have been developed.[37,38] For comparison of i.n.s. and optical data the function $P'(\alpha,\beta)$ was calculated and is used in this work.[1]

Transition frequencies in the b.f.d. spectra have been calculated from the observed band centres using known correction factors.[35] It is important to note that the t.o.f. and b.f.d. data presented here are proportional to the amplitude-weighted density of states multiplied by the DW factor. Provided that data, on the same sample, from these two types of instrument contain at least one common band, the relative intensities can be compared directly.

It is known that for the Dido b.f.d. spectrometer there is considerable order contamination when using the Al(111) monochromator plane (<400 cm^{-1}). Consequently, at any desired wavelength (λ), a proportion of neutrons of wavelength $\lambda/2$ will be incident on the sample. Since neutron energy is inversely proportional to λ^2, there arises the possibility of observing transitions of true energy $4E$ (wavelength $\lambda/2$) apparently at an energy E (wavelength λ). However, bands due to order contamination are necessarily of relatively low intensity. Whilst the resolution function of a b.f.d. spectrometer is not Gaussian,[35] for the purpose of this work the assumption of a Gaussian bandshape is acceptable, especially when one considers the quoted errors in the band centres, and since only approximate relative intensities are required.

Far-i.r. measurements of (1) (40—250 cm^{-1}) and (2) (60—400 cm^{-1}) were made at liquid-nitrogen temperature using a Beckmann-RIIC FS720 Fourier-transform spectrophotometer, whilst the mid-i.r. spectrum of (2) was obtained at room temperature employing a Perkin-Elmer 577 spectrophotometer. With the former instrument, samples were run as Nujol mulls supported on polyethylene discs, with the latter both as CsI discs and as Nujol mulls between CsI plates.

Raman spectra were measured in the range 0—1 000 cm^{-1} with a Cary 82 Raman spectrophotometer employing for (1) a Spectra Physics model 164 argon laser at 19 436.3 cm^{-1} (200 mW power at the sample), and for (2) a Spectra Physics model 125 helium–neon laser at 15 802 cm^{-1} (6 mW power at the sample).

RESULTS AND DISCUSSION

(*a*) $[Cr(CO)_3(\eta\text{-}C_6H_6)]$ (1).—The i.n.s. spectra of (1) are shown in Figures 1 and 2 and the transition frequencies derived are summarised in Table 3.

Considering first the b.f.d. spectrum (Figure 1) of (1), the internal modes of the benzene ligand may be readily identified. The i.n.s. band at 811 cm^{-1} may be assigned to ν_{11} in accordance with optical measurements and n.c.a.s. which have placed the mode in the wavenumber range 784—800 cm^{-1} (refs. 2, 12, 17, 18, 22, 24, and 26). The b.f.d. band at 665 cm^{-1} must also, in view of its relative intensity, represent an internal vibration of the benzene ligand. We assign it to ν_4 following Adams and Squire,[21] who considered that an optical transition at 654 cm^{-1} resulted from ν_4 rather than ν_{32} [17] or ν_{11} [19] as previously suggested. Additional support for this assignment may be obtained from the n.c.a. of Jobic *et al.*[2] which placed ν_4 at 632 cm^{-1}. Finally, we assign the

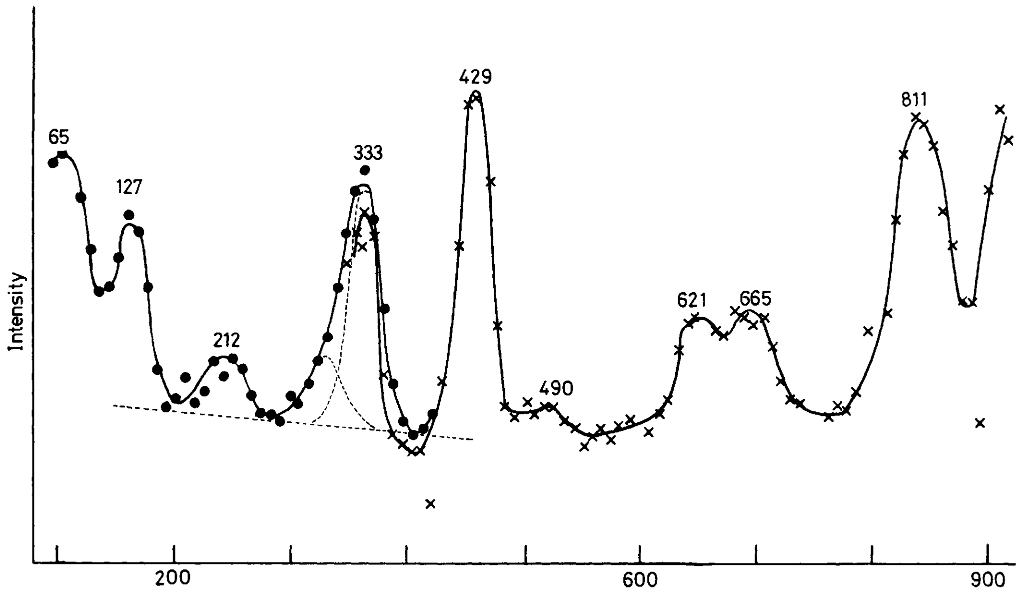

FIGURE 1 The Dido b.f.d. spectrum (10 K) of $[Cr(CO)_3(\eta^6-C_6H_6)]$ (1); (●) and (×), data obtained using the Al(111) and Al(311) monochromator planes respectively. The transition frequencies stated have been calculated from the band centres using the correction factors referred to in the text

i.n.s. bands at 621 and 429 cm^{-1}, in agreement with i.r. and Raman data[12,15,17–19] and n.c.a.s.,[2,22,24–26] to ν_6 and ν_{16} respectively.

This leaves only one unexplained feature in the b.f.d. spectrum above *ca.* 400 cm^{-1}, the weak shoulder situated at *ca.* 490 cm^{-1}. Modes ν_{25} and ν_{27} have been assigned in this region in various spectroscopic investigations[13–15,17,19,20] and by n.c.a.[2,15,25,26] Whilst carbonyl modes themselves may not involve sufficient proton motion to explain all of the observed intensities in the i.n.s. spectrum, the occurrence of mixing with modes, which are of similar frequency and which involve considerable proton motion, would enhance the intensity of the bands. Extensive mixing in this spectral region has, indeed, been noted in several of the most recent n.c.a.s carried out on (1).[2,25,26] In the particular cases of ν_{25} and ν_{27}, it has been suggested[2,25] that the former is mixed with ν_{21} and the latter with ν_{23}. Modes ν_{21} and ν_{23} represent the symmetric and antisymmetric stretches of the benzene ligand relative to the $Cr(CO)_3$ moiety respectively (see later).

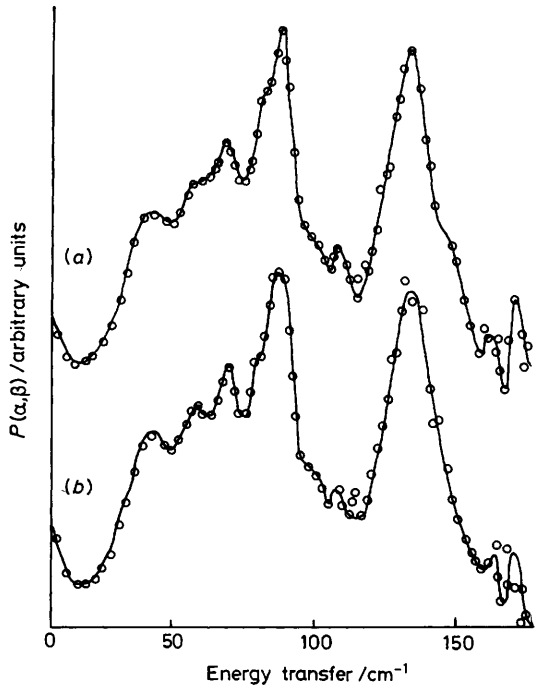

FIGURE 2 IN4 t.o.f. spectra (10 K) of $[Cr(CO)_3(\eta^6-C_6H_6)]$ (1) obtained at scattering angles of (*a*) 100 and (*b*) 91°

Below 400 cm^{-1} we do not expect to observe any vibrations derived from the internal modes of the benzene ligand. The i.n.s. bands below this value must therefore be due to metal–ligand or skeletal modes. Modes ν_{21} and ν_{23} have been generally assigned in the ranges 296—301 (refs. 12, 14, 15, and 17—19) and 328—338 cm^{-1} (refs. 12, 15, and 17—19) respectively. Whilst ν_{23} may be correlated with the intense b.f.d. band at 333 cm^{-1}, ν_{21}, in contrast, is represented only by a shoulder to the low-frequency side of this band. However, in view of the relatively small separation of these two modes and the known resolution of the b.f.d. spectrometer (35—42 cm^{-1}),[35] one would not expect them to be fully resolved. Consideration of the expected relative intensities of the two vibrations (Table 4) shows that ν_{23} (doubly degenerate rotational mode) should be $\approx$5.4 times the intensity of ν_{21} (singly degenerate translational mode). In order to test the assignments of ν_{21} and ν_{23} suggested from the optical studies, Gaussians, centred at 298 and 333 cm^{-1} respectively, were fitted to the bandshape of the b.f.d. band at 333 cm^{-1} using a Du Pont curve resolver. The

TABLE 3

The i.n.s. and optical spectroscopic wavenumbers (cm^{-1})[a] and assignments of [Cr(CO)$_3$(η^6-C$_6$H$_6$)] (1) and [Mn(CO)$_3$(η^6-C$_6$H$_6$)]Br (2)

[Cr(CO)$_3$(η^6-C$_6$H$_6$)]						[Mn(CO)$_3$(η^6-C$_6$H$_6$)]Br						
		I.n.s. value						I.n.s. value				
I.r.	Raman	B.f.d. [b]	T.o.f. [c]	T.o.f. [d]	Assignment	I.r.	Raman [e]	B.f.d. [f]	T.o.f. [c]	T.o.f. [g]	T.o.f. [d]	Assignment
									26.5 ±1.5	27.5 ±1.5	29.0 ±3.0	Lattice mode
	30m		38.5 ±2.0	44.0 ±3.0	Lattice mode							
							47m		45.5 ±2.0	45.5 ±2.0	48.5 ±2.5	Lattice mode
48m	50m		57.0 ±2.5	60.5 ±2.5	Lattice mode							
							61m			59.0 ±3.0	63.5 ±2.5	Lattice mode
	65m			70.0 ±2.5	Lattice mode							
86s		65 ± 8	68.5 ±3.0	82.0 ±2.0	Lattice mode							
						82(sh) [h]	78m	83 ± 8	79.0 ±3.5	84.0 ±3.5	86.0 ±2.0	Lattice mode
				88.5 ±2.0	ν_{22}							
121s	111vs			101.0 ±1.5 109.0 ±1.5	ν_{28}	118s	124m				102.5 ±1.5	ν_{28}
								113 ± 8	105.0 ±5.0	114.0 ±5.0	116.5 ±1.5	ν_{22}
											134.5 ±1.0	ν_{26}
	132vs			134.5 ±1.0	ν_{24}	154(sh)					145.0 ±1.0	
							163vs	136 ± 8	143.5 ±7.0	147.0 ±6.5		ν_{24}
		127 ± 8	128.5 ±6.0			162vw					153.0 ±0.5	
151m				148.5 ±1.0	ν_{26}							
				163.5 ±0.5 171.5 ±0.5	Overtones or combination bands							
		212 ± 8			Combination band	203s		223 ± 8				Overtone or combination band
						285(sh)	270w	264 ± 8				Combination band
	298vs				ν_{21}	295m						ν_{21}
		333 ± 8				310w	317w	334 ± 8				
	333w				ν_{23}	334w	334w					ν_{23}
						372w						
		429 ± 8			ν_{16}	418vw		424 ± 8				ν_{16}
		490 ± 8			ν_{25}, ν_{27}	456w	461w					ν_{25}, ν_{27}
						519vs						ν_{34}
						595vs						ν_{33}
		621 ± 8			ν_6	613(sh)		610 ± 8				ν_6
						638vs						ν_{31}
		665 ± 8			ν_4			660 ± 8				ν_4
		811 ± 8			ν_{11}	819w		842 ± 8				ν_{11}
						845vvw						
						981vvw	984w					ν_1

[a] vs = Very strong; s = strong; m = medium; w = weak; vw = very weak. [b] Data recorded using Dido b.f.d. spectrometer at 10 K. [c] Data recorded using 4H5 t.o.f. spectrometer at 233 K. [d] Data recorded using IN4 t.o.f. spectrometer at 10 K. [e] This compound gave poor Raman spectra. [f] Data recorded using Dido b.f.d. spectrometer at 18 K. [g] Data recorded using 4H5 t.o.f. spectrometer at 88 K. [h] Shoulder on Polythene peak.

results showed the high-frequency band to be 4.3 times the intensity of that of the lower frequency, in fair agreement with the prediction given that these modes are believed[2,25] to be extensively mixed with the carbonyl modes ν_{25} and ν_{27}.

The 212 cm^{-1} transition in the b.f.d. spectrum of (1) (which is not observed in the t.o.f. spectra) has not been located by either i.r. or Raman spectroscopy,[17-19] nor has its frequency been predicted from n.c.a.[2,15,24-26] The only inactive (A_2) vibration of (1), predicted to occur below 1 000 cm^{-1}, which has not been firmly assigned is ν_{22}. However, the intensity displayed by the band at

212 cm^{-1} is considerably less than that which would be predicted for ν_{22} (Table 4). Furthermore, the height of the barrier to rotation of the benzene ligand relative to the $Cr(CO)_3$ moiety calculated using this frequency would be unreasonably high. Hence the band at 212 cm^{-1} may represent a combination band, possibly resulting from the bands resolved in the IN4 t.o.f. spectra (see later) at 88.5 and 134.5 cm^{-1} (= 223.0 cm^{-1}). Alternatively it could be due to the band at 811 cm^{-1} appearing at 212 cm^{-1} as a result of order contamination.

TABLE 4

Predicted relative intensities for internal vibrations of $[Cr(CO)_3(\eta^6\text{-}C_6H_6)]$ or $[Mn(CO)_3(\eta^6\text{-}C_6H_6)]^+$ involving motion of the benzene ligand relative to the chromium atom

Mode *	Predicted relative intensity
Torsion $[C_6H_6\text{–}Cr(CO)_3]$ (ν_{22})	2.7
Ring tilt (ν_{23})	5.4
$\delta[C_6H_6\text{–}Cr\text{–}(CO)_3]$ (ν_{24})	2.0
$\nu_{sym}(Cr\text{–}C_6H_6)$ (ν_{21})	1.0

* ν_{22} and ν_{23} may be considered to represent singly and doubly degenerate rotational modes respectively and ν_{21} and ν_{24} singly and doubly degenerate translational modes respectively.

The remaining low-frequency b.f.d. bands are best discussed in conjunction with the t.o.f. spectra, particularly the IN4 spectra (Figure 2), in which they are better resolved. Assignment of these is anticipated to be somewhat complicated because the $Cr(CO)_3$ skeletal modes, ν_{26} and ν_{28}, as well as the $C_6H_6\text{–}Cr(CO)_3$ vibrations, ν_{22} and ν_{24}, have been assigned in this region of the spectrum.[2,15,16,17-20,24-26] Furthermore, the two former modes need not be of zero intensity, because with ν_{26} the vibration can be envisaged as causing a large displacement of the chromium atom (and hence the protons of the benzene group riding on it), and with ν_{28} its symmetry is identical to that of ν_{24} (thus allowing the possibility of mixing). Indeed, if the influence of site-group symmetry is taken into account, it is possible for mixing to occur between components of ν_{26} and ν_{24} and between components of ν_{28} and ν_{22}.

Bands at 146—153 (i.r.)[17,19] and 131—148 cm^{-1} (Raman)[17-20] have been variously assigned to ν_{28},[17] ν_{24},[18] and ν_{26}.[19,20] An i.n.s. band is found at 134.5 cm^{-1} (IN4 t.o.f. spectra). Its intensity is such that it may only be reasonably assigned to either ν_{22} or ν_{24}. Comparison of the IN4 t.o.f. spectra of (1) with those of (2) (see later) shows that there is a band analogous to the 134.5 cm^{-1} transition in the spectrum of the latter complex, but which is split into components at 145.0 and 153.0 cm^{-1}. In the case of (2) this vibration may be firmly assigned to ν_{24} and we will therefore follow this assignment for (1).

The remaining very intense band in the IN4 t.o.f. spectra of (1) located at 88.5 cm^{-1} must represent the only mode involving considerable motion of the benzene ligand which has yet to be assigned, ν_{22}. Further evidence for this assignment may be seen from the marked change in frequency with temperature displayed by this band in moving from within the contour of the 57.0—68.5 cm^{-1} band in the 4H5 spectra (233 K) to a position at 88.5 cm^{-1} in the IN4 spectra (10 K). Similar findings have been observed in the i.r. spectrum of (1) in which a band located at 60 cm^{-1} (ambient temperature) was found to move to 87 cm^{-1} (77 K).[17] Whilst this vibration was assigned by Adams and Squire [17] to a lattice mode, it is now apparent that it must represent ν_{22}. The frequency for ν_{22} (10 K) indicated in this work (88.5 cm^{-1}) is in poor agreement with that suggested for the mode from the n.c.a.s of Adams *et al.* (47 cm^{-1}) [25] and Jobic *et al.* (46 cm^{-1}),[2] but in better agreement with that of Cyvin and co-workers (100 cm^{-1}).[23,24]

There are weak features at 101.0, 109.0, and 148.5 cm^{-1} (IN4 t.o.f. spectra). The first two bands are situated at frequencies close to those assigned to ν_{28} in some of the more recent optical studies carried out on (1) [110—114 (Raman), 121 cm^{-1} (i.r.)].[18-20] Similarly, the latter transition (148.5 cm^{-1}) occurs close to those assigned to ν_{26} [134—148 (Raman), 146 cm^{-1} (i.r.)] in the two latest spectroscopic studies.[19,20]

Of the remaining unassigned bands, those at 163.5 and 171.5 cm^{-1} have no analogues in either i.r. or Raman spectra and must therefore be assigned to overtones or combination bands, since all of the normal modes involving significant hydrogen motion have been assigned (*viz.* $2 \times 82.0 = 164.0$ cm^{-1}, $2 \times 88.5 = 177.0$ cm^{-1}, or $88.5 + 82.0 = 170.5$ cm^{-1}).

The bands at 44.0, 60.5, 70.0, and 82.0 cm^{-1} undoubtedly represent external modes in view of the fact that all intramolecular vibrations expected in the t.o.f. spectra of (1) have been located.

(*b*) $[Mn(CO)_3(\eta\text{-}C_6H_6)]Br$ (2).—I.n.s. spectra of (2) are shown in Figures 3 and 4 and the transition frequencies derived are summarised in Table 3. The results of optical measurements are also presented in this Table, together with previously unreported i.r. data for the region below 600 cm^{-1} and Raman data below 1 000 cm^{-1}. We will review initially the assignment of bands present in the i.n.s. spectra, but include, wherever possible, discussion of optical bands analogous to them.

Following the i.n.s. spectroscopic assignments for complex (1) (Table 3), the internal benzene-ligand modes of (2) may be identified within the b.f.d. spectrum (Figure 3). Thus ν_{11} may be assigned at 842 cm^{-1} (819 cm^{-1}, i.r.), a slightly higher frequency in (2) than that recorded for the equivalent vibration in (1) (811 cm^{-1}). In contrast with ν_{11}, both ν_4 and ν_{16} appear at frequencies in (2) [660 and 424 (418 cm^{-1}, i.r.) respectively] which are comparable with those established for complex (1) (665 and 429 cm^{-1} respectively). The ν_{16} band of (2) displays asymmetry in its band profile to higher energy. This presumably results, in the case of the cationic species, from the same cause as that suggested for (1) (see earlier).

The only intramolecular benzene vibration of (2) remaining unassigned in the b.f.d. spectrum, ν_6, is represented by a band at 610 (613 cm^{-1} i.r.). This frequency is similar to that suggested for ν_6 in (1) (621 cm^{-1}).

At longer wavelength, the ring-tilt mode, ν_{23}, may be assigned to the very intense b.f.d. band at 334 cm^{-1}, in close agreement with that measured for ν_{23} in (1) (333 cm^{-1} i.n.s.). In common with findings for (1), optical spectroscopic evidence shows that ν_{21} [predicted to be considerably less intense than ν_{23} in the i.n.s. spectrum (Table 4)] must be present within the profile of the 334 cm^{-1} b.f.d. band (at 295 cm^{-1}). However, for (2) the band profile of ν_{23} in the b.f.d. spectrum is not obviously asymmetrical and, consequently, no accurate determination of the relative intensities of the two vibrations is possible.

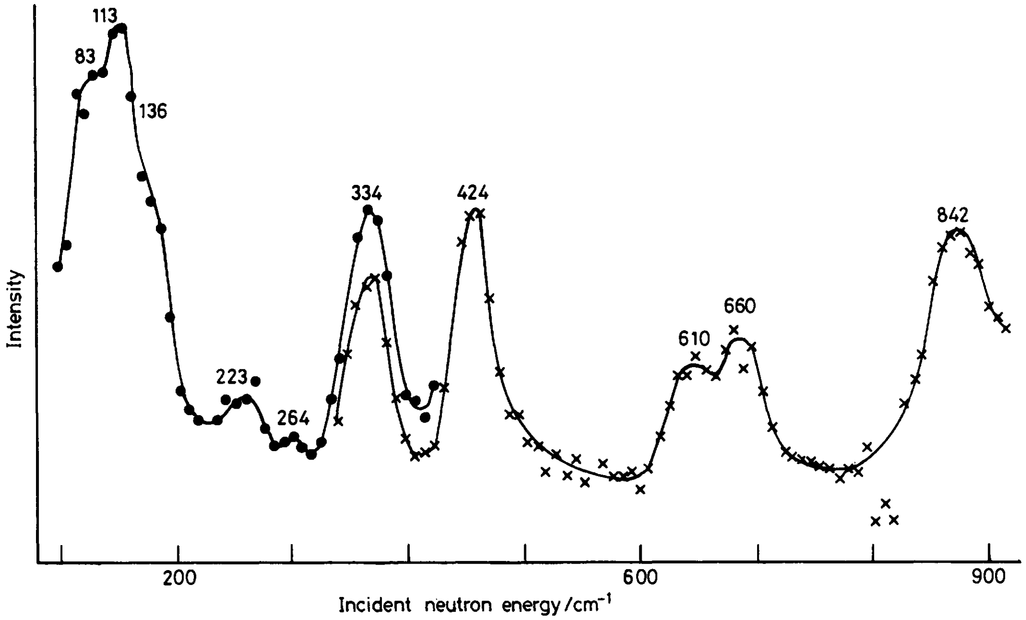

FIGURE 3 The Dido b.f.d. spectrum (18 K) of [Mn(CO)$_3$(η^6-C$_6$H$_6$)]Br (2); details as in Figure 1

Of the weak features located at lower energy (223 and 264 cm^{-1}) in the b.f.d. spectrum of (2), the former is apparently represented by a strong band in the i.r. at 203 cm^{-1}, the latter by a weak band in the Raman at 270 cm^{-1} and a shoulder in the i.r. at 285 cm^{-1}. Considering the band at 223 cm^{-1} first, no optically active fundamental vibration of (1) has been identified between *ca.* 160 and 290 cm^{-1}, whilst the only normal mode of A_2 symmetry expected below *ca.* 450 cm^{-1} is ν_{22}. For the reasons stated earlier regarding the 212 cm^{-1} transition of (1), this band cannot reasonably be assigned to ν_{22} and, consequently, must be attributed to either (*i*) a combination band ($86.0 + 116.5 = 202.5$ cm^{-1}), (*ii*) an overtone ($2 \times 116.5 = 233.0$ cm^{-1}) of bands resolved in the IN4 t.o.f. spectra (see later), or (*iii*) to the effect of order contamination (0.25×842 cm^{-1}). Likewise, the still less intense b.f.d. band at 264 cm^{-1} must be a combination band ($116.5 + 145.0 = 261.5$ cm^{-1} or $116.5 + 153.0 = 269.5$ cm^{-1}).

The lowest-frequency vibrations in the b.f.d. spectrum of (2) are again best considered together with the t.o.f. spectra in which they are better resolved. The doublet at 145.0 and 153.0 cm^{-1} [IN4 t.o.f. spectra (Figure 4)] correlates with a weak doublet at 154 and 162 cm^{-1} (i.r.) and an intense band at 163 cm^{-1} (Raman). On the grounds of both the intensity displayed by the doublet in the t.o.f. spectra (it constitutes the second most intense feature) and the splitting observed in i.r. and t.o.f. spectra, this feature must represent the only remaining unassigned mode of E symmetry which involves considerable proton motion, ν_{24}. The frequency thus assigned to ν_{24} in the t.o.f. spectra of (2) (145.0 and 153.0 cm^{-1}) compares well with that found for (1) (134.5 cm^{-1}).

As a corollary of the previous assignment, it follows that the most intense band in the IN4 t.o.f. spectra, that located at 116.5 cm^{-1}, must be assigned to the only remaining intramolecular vibration of (2), of great predicted intensity (Table 4), which has yet to be assigned, ν_{22}. Confirmation of this assignment is obtained, as in the case of the equivalent mode of (1), by the observed frequency change with temperature. [The wavenumber of ν_{22} in the t.o.f. spectra changes from 105.0 (233 K) to 114.0 (88 K) and to 116.5 cm^{-1} (10 K).]

The weak shoulder at 102.5 cm^{-1} (IN4 t.o.f. spectra) in (2) is probably represented in the optical spectra by bands at 118 (i.r.) and 124 cm^{-1} (Raman). In the i.r. and Raman spectra of (1) bands in the region 110—121 cm^{-1} have been assigned to ν_{28}.[18-20] Similarly, in the t.o.f. spectra of the same complex, we have correlated bands at 101.0 and 109.0 cm^{-1} with this vibration. We will therefore follow the conclusions reached for complex (1) and assign the 102.5 cm^{-1} t.o.f. transition of (2) to ν_{28}.

Another extremely weak feature in the IN4 t.o.f. spectra of (2), at 134.5 cm^{-1}, appears to have no analogue in either i.r. or Raman spectra. However, it occurs within the range of frequencies (134—148 cm^{-1}) to which ν_{26} has been assigned in (1),[19,20] and consequently we will adopt this assignment.

In view of the preceding assignments, all the intramolecular vibrations of (2) predicted to occur in the t.o.f. spectra have been identified. The remaining unassigned IN4 t.o.f. bands at 86.0, 63.5, 48.5, and 29.0 cm^{-1} (of which the first three bands have analogues in the Raman spectrum at 78, 61, and 47 cm^{-1} respectively) must therefore represent external modes.

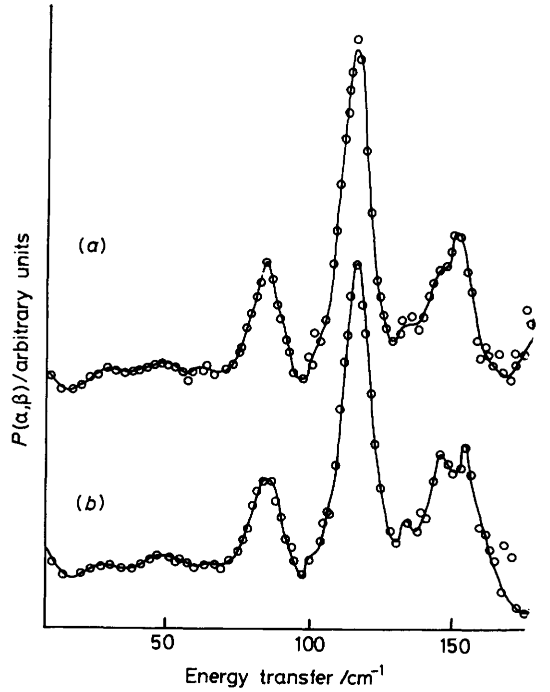

FIGURE 4 The IN4 t.o.f. spectra (10 K) of [Mn(CO)$_3$(η^6-C$_6$H$_6$)]Br (2) obtained at scattering angles of (a) 109 and (b) 91°

We will now consider the bands in the optical spectra of (2) which have not been assigned previously (Table 3). First, the band at 981 cm^{-1} in the i.r. (984 cm^{-1} in the Raman) may be assigned to the internal benzene-ligand mode $\nu_1(A_1)$ identified at 978—981 cm^{-1} in (1).[12,17-19]

Between 500 and 700 cm^{-1} in the i.r. spectrum of (2), three very intense vibrations are observed, at 638, 595, and 519 cm^{-1}. Likewise, for (1), three very intense bands have been reported in this region, which have been assigned to ν_{31} (*ca.* 667 cm^{-1}),[12,13,17-20] ν_{33} (*ca.* 635 cm^{-1}),[12-14,17-20] and ν_{34} (*ca.* 533 cm^{-1}).[13,14,17,19,20] It is reasonable to assign the three frequencies of (2) following the guidance afforded by the chromium complex, and thus the bands at 638, 595, and 519 cm^{-1} have been assigned to ν_{31}, ν_{33}, and ν_{34} respectively.

Finally the band at 456 cm^{-1} (i.r.) [461 cm^{-1} (Raman)] in (2) may be assigned to the remaining modes of the Mn(CO)$_3$ moiety expected, by analogy with (1), to occur in this area of the spectrum, ν_{25} and ν_{27}. In common with the δ(Mn–C–O) vibrations ν_{31}, ν_{33}, and ν_{34} discussed above, it is noticeable that these vibrations are located at slightly lower frequency in (2) than in (1) (483—487 cm^{-1}, ν_{25};[13,14,17,19,20] and 487—492 cm^{-1}, ν_{27} [15,17,19,20]).

(*c*) *Barrier Calculations*.—From the results of n.m.r. work [10] it has been established that the barrier to benzene-ligand rotation, about the three-fold axis of (1), arises from inter- rather than intra-molecular forces. In view of this we will make the assumption that the barrier to this rotation is six-fold. Expressing the potential function $V(\theta)$ as a Fourier cosine series we obtain equation (1), where θ is the angle of rotation of the C$_6$H$_6$ ligand,

$$V(\theta) = \sum_{n=1}^{\infty} V_{6n}/2 \,.\, (1 - \cos 6n\theta) \qquad (1)$$

about its six-fold axis, from the equilibrium position. It is believed to be a good approximation in many cases to ignore all but the first term in the series and this we shall do, thus giving equation (2). Within the harmonic oscillator approximation the second derivative of $V(\theta)$, with respect to θ, is equal to the force constant.

$$V(\theta) = V_6/2 \,.\, (1 - \cos 6\theta) \qquad (2)$$

Therefore if the torsional frequency is known V_6 may be calculated. Using the frequency assigned earlier for (1) (88.5 cm^{-1}) we calculate V_6 to be 28 ± 1 kJ mol^{-1}. Subtracting the zero-point energy ($\frac{1}{2}h\nu$) from our calculated value for V_6 yields an activation energy of 27.5 ± 1 kJ mol^{-1}, which may be directly compared with that derived from n.m.r. data (17.6 ± 0.4 kJ mol^{-1}). Similarly, using the observed torsional frequencies for (2), V_6 = 39 ± 4 (233 K), 46 ± 4 (88 K), and 48 ± 1 kJ mol^{-1} (10 K).

As expected the barrier height of the ionic species is significantly greater than that found for the neutral species. We consider that the poor agreement between the barriers determined from i.n.s. and n.m.r. data for [Cr(CO)$_3$(η^6-C$_6$H$_6$)] (1) is a consequence of our assumption of a simple six-fold cosine function for the potential.

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