# Inelastic Neutron Scattering Studies of Benzene-containing Organometallic Complexes. Part 2.† Complexes $[Cr(\eta^6-C_6H_6)_2]$ and $[Cr(\eta^6-C_6H_6)_2]I$ ‡

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Inelastic neutron scattering spectra (0—875 $cm^{-1}$) of $[Cr(\eta^6-C_6H_6)_2]$ and $[Cr(\eta^6-C_6H_6)_2]I$ have been measured. From the spectroscopic data it has been possible firmly to assign those low-frequency modes of both compounds which involve significant displacement of the benzene ligands. In addition, the optically inactive internal modes of the benzene ligands, $\nu_4^{ip}$, $\nu_4^{op}$, $\nu_6^{op}$, and $\nu_{16}^{ip}$, have been observed. Employing the values of 59.5 and 66.0 $cm^{-1}$ assigned to the torsional mode of the benzene ligands ($\nu_{22}$) in $[Cr(\eta^6-C_6H_6)_2]$ and $[Cr(\eta^6-C_6H_6)_2]I$, values of 12.6 and 15.5 kJ $mol^{-1}$ respectively have been calculated for the barriers to benzene-group rotation. In the case of $[Cr(\eta^6-C_6H_6)_2]$, this value has been compared with the activation energy determined from n.m.r. measurements (19.1 kJ $mol^{-1}$).

THIS study continues our investigation of the low-frequency modes of vibration in organometallic complexes containing benzene ligands. We chose to study $[Cr(\eta^6-C_6H_6)_2]$ and $[Cr(\eta^6-C_6H_6)_2]I$ using inelastic neutron scattering (i.n.s.) spectroscopy for the following reasons; (*i*) to extend our previous work on systems containing one benzene rotor, $[Cr(CO)_3(\eta^6-C_6H_6)]$ and $[Mn(CO)_3(\eta^6-C_6H_6)]Br$, to those containing two; (*ii*) to attempt a firm assignment of those low-frequency modes of both complexes which either have not been previously observed or whose assignment has proved controversial; (*iii*) to observe the torsional mode of the $C_6H_6$ ligands within $[Cr(\eta^6-C_6H_6)_2]$ about the six-fold axis and to calculate a barrier height for comparison with that determined using other techniques; (*iv*) to compare the barrier to the torsion of the benzene ligands about the six-fold axis in a neutral complex, $[Cr(\eta^6-C_6H_6)_2]$, with that for an ionic species $[Cr(\eta^6-C_6H_6)_2]I$; (*v*) to serve as model compounds for the interpretation of i.n.s. spectra of adsorbed benzene.

## BACKGROUND

(*a*) $[Cr(\eta^6-C_6H_6)_2]$.—Attempts to determine the molecular symmetry of $[Cr(\eta^6-C_6H_6)_2]$ have been made by many authors employing a wide range of techniques: *X*-ray,[1-6] electron [7] and neutron [8,9] diffraction, i.r.,[10-15] far-i.r.,[16] and Raman [12,17] spectroscopy, as well as heat-capacity [18,19] and vapour-pressure [18] measurements. Despite the extensive efforts devoted to the subject, results from the various measurements are inconclusive; in some cases even users of the same technique [2-6] disagree on the molecular symmetry to be deduced from their data. Whilst knowledge of molecular symmetry is essential to the interpretation of optical spectra, and hence the broader aims of this work, it is less crucial in the assignment of i.n.s. spectra since there are no electromagnetic selection rules to be obeyed. In view of this, and evidence from the gas-phase i.r. data,[14] we have assumed that the correct molecular symmetry of $[Cr(\eta^6-C_6H_6)_2]$ is $D_{6h}$.

The $[Cr(\eta^6-C_6H_6)_2]$ molecule has 69 normal vibrations. Of these, 60 are derived from the two coupled benzene ligands, each of whose 30 normal modes ($\nu_1$—$\nu_{20}$) may be either in-phase (ip) or out-of-phase (op) with the identical vibration of the second benzene, whilst the remaining nine ($\nu_{21}$—$\nu_{26}$) result from motion of the benzene groups relative to the chromium atom. The numbering of the normal vibrations $\nu_1$—$\nu_{20}$ within each benzene ligand follows that of Wilson [20] for free benzene and the numbering of vibrations $\nu_{21}$—$\nu_{26}$ that of Fritz *et al.*[11,12]

There have been several optical (i.r. and Raman) studies of $[Cr(\eta^6-C_6H_6)_2]$ [10-17] and the assignments suggested from these for fundamentals observed below 900 $cm^{-1}$ are given in Table 1. (Bands assigned to combination modes have been ignored.) In addition, a number of normal-co-ordinate analyses (n.c.a.s) of $[Cr(\eta^6-C_6H_6)_2]$ have been attempted.[13,17,21-24] However, we have included only the results of the three whole-molecule n.c.a.s [21,23] in Table 1. From this Table it is apparent that there is disagreement over the assignment of some modes.

The contribution of non-bonded interactions to the total potential for re-orientation of the benzene group in $[Cr(\eta^6-C_6H_6)_2]$ about their hexad axis has been calculated by Campbell *et al.*[25] using atom–atom potentials. Intramolecular forces were found to be independent of angle whilst intermolecular forces displayed a six-fold periodicity. Reasonable agreement was obtained between the experimental value for the activation energy for benzene-group rotation derived from pulse-n.m.r. measurements (19.1 kJ $mol^{-1}$) and the calculated value ($\approx$16.7 kJ $mol^{-1}$).

(*b*) $[Cr(\eta^6-C_6H_6)_2]I$.—The *X*-ray crystal structure of $[Cr(\eta^6-C_6H_6)_2]I$ {which in contrast with $[Cr(\eta^6-C_6H_6)_2]$ has always been assumed from spectral evidence to possess $D_{6h}$ symmetry [11,12]} has been determined by Morosin.[26]

I.r. and Raman spectra of $[Cr(\eta^6-C_6H_6)_2]I$ were measured by Fritz *et al.*[11,12] Subsequently Saito *et al.*[27] re-investigated the i.r. spectrum. The assignments of the

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† For Part 1 see ref. 29.

‡ Bis($\eta^6$-benzene)chromium and bis($\eta^6$-benzene)chromium-(I) iodide.

TABLE 1

Wavenumbers (cm$^{-1}$) and assignments of [Cr($\eta^6$-$C_6H_6$)$_2$] suggested from experiment and n.c.a. for the region below 900 cm$^{-1}$ ($D_{6h}$ symmetry is assumed) [a]

| | | | | | | | Cyvin and co-workers [21–23] | |
|---|---|---|---|---|---|---|---|---|
| I.r. [11–16] [b] | Raman [12,17] | Fritz *et al.*[11,12] | Snyder [13] | Fritz and Fischer [16] | Ngai *et al.*[14] | Schäfer *et al.*[17] | Calculated value | Assignment |
| (140) | | $\nu_{26}$ | | | | | | |
| 152 | | | | $\nu_{22}$ | | | 152 | $\nu_{22}$ |
| 171/159 | 178 | | | $\nu_{26}$ | | | 170—171 | $\nu_{26}$ |
| | 270—277 | $\nu_{21}$ | | | | $\nu_{21}$ | 254—277 | $\nu_{21}$ |
| (305) | | $\nu_{22}$ | | | | | | |
| | 332—335 | $\nu_{24}$ | | | | $\nu_{24}$ | 334—335 | $\nu_{24}$ |
| | | | | | | | 399—409 | $\nu_{16}{}^{ip}$ |
| | 400 | | | | | $\nu_{16}{}^{op}$ | 399—409 | $\nu_{16}{}^{op}$ |
| 450—459 [c] | | $\nu_{23}$ | $\nu_{23}$ | $\nu_{25}$ | $\nu_{23}$ | | 459 | $\nu_{25}$ |
| 480—492 [c] | 490 | $\nu_{25}$ | $\nu_{25}$ | $\nu_{23}$ | $\nu_{25}$ | | 439—490 | $\nu_{23}$ |
| | 604 | | | | | $\nu_6{}^{ip}$ | 604—606 | $\nu_6{}^{ip}$ |
| | | | | | | | 604—606 | $\nu_6{}^{op}$ |
| | | | | | | | 709 | $\nu_4{}^{ip}$ |
| | | | | | | | 709 | $\nu_4{}^{op}$ |
| 780—796 | | $\nu_{11}{}^{ip}$ | $\nu_{11}{}^{ip}$ | | $\nu_{11}$ | | 794—916 | $\nu_{11}{}^{ip}$ |
| | 791 | | | | | $\nu_{11}{}^{op}$ | 791—880 | $\nu_{11}{}^{op}$ |
| | 811 | | | | | $\nu_{10}{}^{ip}$ | | |
| 830—836 | | $\nu_{10}{}^{op}$ | | | [2 × $\nu_{24}$ + $\nu_{26}$] or<br>[2 × $\nu_{24}$ + $\nu_{22}$] | | | |
| | | | | | | | 860—864 | $\nu_{10}{}^{ip}$ |
| 860 | | | | | $\nu_{10}{}^{op}$ | | 860—885 | $\nu_{10}{}^{op}$ |

[a] The numbering of normal modes has been changed where necessary so that those resulting from internal vibrations of the benzene ligands follow the numbering convention of Wilson [20] for free benzene, whilst the remaining modes follow the numbering scheme of Fritz *et al.*[11,12] The range of values for each band results from different wavenumbers being quoted (or generated in the case of n.c.a.) for the same band in different studies. [b] Values suggested from combination-band analysis are shown in parentheses. [c] In i.r. work carried out by Nakamoto *et al.*[15] a band at 489 moved to 491 cm$^{-1}$ on the application of pressure and one at 453 to 475 cm$^{-1}$. It was believed that $\nu_{23}$ involved a volume change greater than that of $\nu_{25}$ and would therefore be more sensitive to pressure. Accordingly, the band at 453—475 cm$^{-1}$ was assigned to $\nu_{23}$ and that at 489—491 cm$^{-1}$ to $\nu_{25}$.

TABLE 2

Wavenumbers (cm$^{-1}$) and assignments of [Cr($\eta^6$-$C_6H_6$)$_2$]I suggested from experiment and n.c.a. for the region below 900 cm$^{-1}$ ($D_{6h}$ symmetry is assumed) [a]

| | | | | Schäfer *et al.*[17] and Cyvin *et al.*[24] | | |
|---|---|---|---|---|---|---|
| I.r.[11,12,27] | Raman [11,12] | Fritz *et al.*[11,12] | Saito *et al.*[27] | Calculated values [b] | | Assignment |
| (144) | | $\nu_{26}$ | | | | |
| | 279 | $\nu_{21}$ | | | | |
| (303) | | $\nu_{22}$ | | | | |
| | 333 | $\nu_{24}$ | | | | |
| 415—418 | | $\nu_{23}$ | $\nu_{23}$ | | | |
| | 420 | $\nu_{16}{}^{op}$ | | | | |
| 466—4[illegible] | | $\nu_{25}$ | $\nu_{25}$ | | 459 | $\nu_{25}$ |
| | | | | | 490 | $\nu_{23}$ |
| (543) | | $\nu_{16}{}^{ip}$ | | | | |
| 616 | | $\nu_6{}^{ip}$ | | 615.9 | | $\nu_6{}^{ip}$ |
| (630) | | $\nu_6{}^{op}$ | | | | |
| | 790 | $\nu_{11}{}^{op}$ | | | | |
| 795 | | $\nu_{11}{}^{ip}$ | $\nu_{11}{}^{ip}$ | 795 | 794 | $\nu_{11}{}^{ip}$ |
| | 805 | $\nu_{10}{}^{ip}$ | | | | |
| 857—858 | | $\nu_{10}{}^{op}$ | $\nu_{10}{}^{ip}$ | 857 | | $\nu_{10}{}^{op}$ |

[a] See footnotes *a* and *b* in Table 1. [b] Left-hand column from ref. 17, right-hand column from ref. 24.

fundamentals observed below 900 cm$^{-1}$ are displayed in Table 2. Two incomplete and approximate n.c.a.s of [Cr($\eta^6$-$C_6H_6$)$_2$]I have been published as part of studies carried out by Cyvin and co-workers.[17,24] The results of these are also included in Table 2.

To our knowledge, no investigation has been made of the barrier to the rotation of the benzene groups within [Cr($\eta^6$-$C_6H_6$)$_2$]I.

## EXPERIMENTAL

The [Cr($\eta^6$-$C_6H_6$)$_2$] was purchased from Strem Chemicals Inc. and [Cr($\eta^6$-$C_6H_6$)$_2$]I prepared from the neutral species following a standard literature method.[28]

I.n.s. spectra of both complexes (polycrystalline powders) were measured in silica cells. Neutron energy gain time-of-flight (t.o.f.) data for both complexes were obtained at 233 K using the 4H5 cold-neutron spectrometer on the Dido reactor at A.E.R.E. Harwell, whilst neutron energy loss t.o.f. data for [Cr($\eta^6$-$C_6H_6$)$_2$]I only were measured at 10 K employing the IN4 rotating-crystal spectrometer at the Institut Laue-Langevin (I.L.L.), Grenoble. Further details of these spectrometers may be found elsewhere.[29]

Neutron energy loss spectra of [Cr($\eta^6$-$C_6H_6$)$_2$] (18 K) and [Cr($\eta^6$-$C_6H_6$)$_2$]I (12 K) were measured at higher energy transfers using the beryllium-filter detector (b.f.d.) spectrometer on the Dido reactor at A.E.R.E. Harwell. An account of the b.f.d. spectrometer has been given previously.[29]

Further details of data analysis and the significance of the functions used in the graphical representation of the data are given in an earlier paper.[29]

Far-i.r. measurements (40—250 cm$^{-1}$) were made at liquid-nitrogen temperature using a Beckman-RIIC Fourier-transform spectrophotometer, whilst the mid-i.r. region was scanned 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 of [Cr($\eta^6$-$C_6H_6$)$_2$]I only were measured in the range 0—900 cm$^{-1}$ with a Cary 82 Raman spectrophotometer employing a Spectra Physics model 125 helium–neon laser at 15 802 cm$^{-1}$ (6 mW power at the sample).

## DISCUSSION

(*a*) [Cr($\eta^6$-$C_6H_6$)$_2$].—I.n.s. spectra of [Cr($\eta^6$-$C_6H_6$)$_2$] are shown in Figures 1 and 2 while the transition frequencies derived are summarised in Table 3.

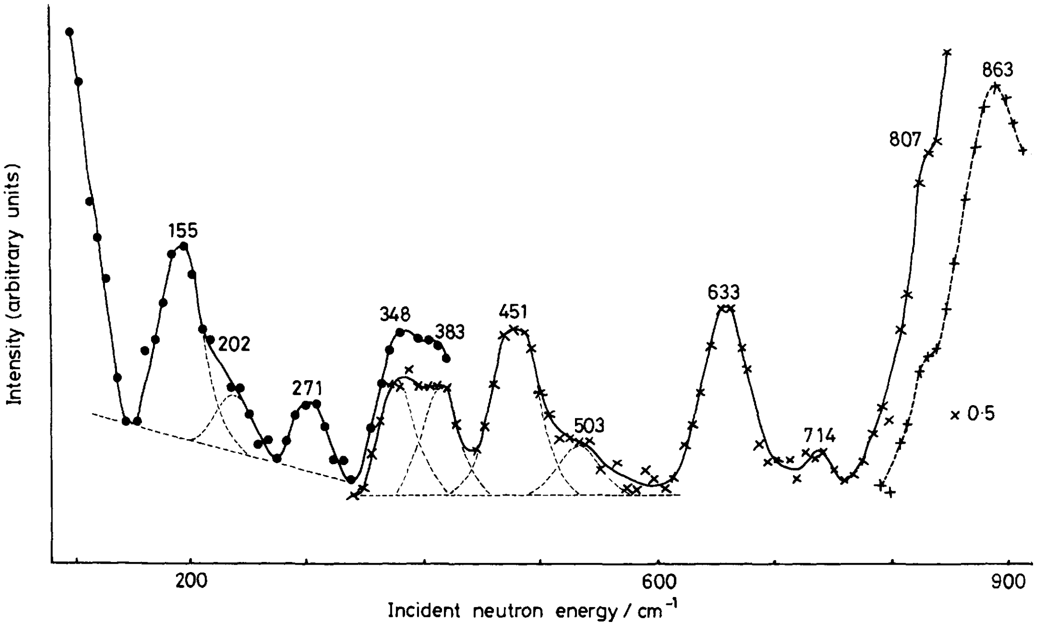

FIGURE 1 The Dido b.f.d. spectrum (18 K) of [Cr($\eta^6$-$C_6H_6$)$_2$]; (●) and (×) data collected using the Al(111) and Al(311) monochromator planes respectively. The transition frequencies stated have been calculated from the band maxima using known correction factors [29]

Considering first the higher frequency (>250 cm$^{-1}$) b.f.d. spectrum of [Cr($\eta^6$-$C_6H_6$)$_2$] (Figure 1), several of the observed transitions may readily be assigned to internal modes of the benzene ligands by comparison with the results of previous i.r. and Raman studies. Hence the b.f.d. band at 863 cm$^{-1}$ may be assigned to both $\nu_{10}{}^{op}$ and $\nu_{10}{}^{ip}$ following the assignment of $\nu_{10}{}^{op}$ at 860 cm$^{-1}$ in the gas-phase i.r. spectrum [14] and the frequency of 860—864 cm$^{-1}$ calculated for $\nu_{10}{}^{ip}$ from n.c.a.[21-23] Similarly, the shoulder in the i.n.s. spectrum at $\approx$807 cm$^{-1}$ undoubtedly arises from $\nu_{11}{}^{ip}$, observed in the i.r. at 794—796 cm$^{-1}$ (refs. 11—13), and $\nu_{11}{}^{op}$, found in the Raman spectrum at 791 cm$^{-1}$ (ref. 17). It may be inferred that the i.r. and Raman-inactive modes $\nu_4{}^{ip}$ and $\nu_4{}^{op}$ are represented by the b.f.d. transition at 714 cm$^{-1}$, support being yielded both by the frequency calculated for these modes from n.c.a.s (709 cm$^{-1}$) [21-23] and by the frequency assigned to the equivalent mode in solid benzene ($\nu_4$, 703 cm$^{-1}$).[30]

The modes $\nu_6{}^{ip}$ and $\nu_6{}^{op}$ can only be reasonably assigned to the band at 633 cm$^{-1}$ (i.n.s.), although this is not particularly close to either the frequency at which the former mode was observed in the Raman spectrum (604 cm$^{-1}$),[17] or that calculated for both modes (604 or 606 cm$^{-1}$).[21-23] In view of the lack of significant intensity in our b.f.d. spectrum around 604 cm$^{-1}$, however, the optical assignments appear to be in error. Finally, the band at 383 cm$^{-1}$ (b.f.d.) may be identified as $\nu_{16}{}^{ip}$ and $\nu_{16}{}^{op}$ in agreement with Raman data,[17] in which $\nu_{16}{}^{op}$ was located at 400 cm$^{-1}$, and n.c.a.[21-23] which suggested the two vibrations to be of equal frequency and to occur at 399—409 cm$^{-1}$. It should be noted that the assignment of $\nu_{16}{}^{ip}$ to a frequency equivalent to that of $\nu_{16}{}^{op}$ runs counter to the findings of Fritz *et al.*[11,12] for [Cr($\eta^6$-$C_6H_6$)$_2$]I where $\nu_{16}{}^{op}$ was observed at 420 cm$^{-1}$ (Raman), but $\nu_{16}{}^{ip}$ was placed, from combination-band analysis, at 543 cm$^{-1}$ (a splitting between the two modes of 123 cm$^{-1}$). However, in the case of [Cr($\eta^6$-$C_6H_6$)$_2$], the absence of a transition in the b.f.d. spectrum in the region of 543 cm$^{-1}$ would seem to refute this possibility. It will be noted that in all the above cases the splittings between $\nu_n{}^{ip}$ and $\nu_n{}^{op}$ are smaller than the resolution of the b.f.d. spectrometer.

Of those modes of [Cr($\eta^6$-$C_6H_6$)$_2$] which involve motion of the ligands relative to the chromium atom ($\nu_{21}$—$\nu_{26}$), $\nu_{21}$ and $\nu_{24}$ may be assigned to the b.f.d. bands at 271 and 348 cm$^{-1}$ respectively, comparing reasonably with those reported from Raman spectra (270—277 and 332—335 cm$^{-1}$ respectively).[12,17] Additionally, it is evident that the two i.n.s. bands at 451 and 503 cm$^{-1}$ correspond to those found from the i.r. of the solid at ≈459 and ≈490 cm$^{-1}$ (refs. 11—16). Assignment of these transitions has, however, proved controversial, some authors identifying them as $\nu_{25}$ and $\nu_{23}$ respectively,[16] others adopting the reverse assignment.[11-15] It might be expected that the i.n.s. intensities of the two ring tilts ($\nu_{24}$ and $\nu_{25}$) relative to the intensities of the two stretches ($\nu_{21}$ and $\nu_{23}$) will be approximately equal (both sets of vibrations representing merely the ip and op components of the same mode). Thus, given our assignment of $\nu_{21}$ and $\nu_{24}$, it is possible to use the measured relative intensity of these modes (1.0 : 3.2, Table 3) to identify the analogous, but higher frequency, antisymmetric (op) vibrations $\nu_{23}$ and $\nu_{25}$ in the b.f.d. spectrum. The measured intensity of the transition at 451 cm$^{-1}$ relative to that at 503 cm$^{-1}$ (6.3 : 1.5, Table 3) therefore leads to the assignment of the band at 451 cm$^{-1}$ to $\nu_{25}$ and that at 503 cm$^{-1}$ to $\nu_{23}$, in agreement with the scheme of Fritz and Fischer.[16] The experimentally determined intensity ratios of the ring-tilting modes ($\nu_{24}$ and $\nu_{25}$) relative to the stretches ($\nu_{21}$ and $\nu_{23}$) are not, however, in agreement with the calculated values shown in Table 4. Indeed comparison of Tables 3 and 4 shows that, in the most extreme case, the measured intensity ratio of $\nu_{24}$ relative to $\nu_{21}$ is only slightly over half that anticipated. Nevertheless, at least in qualitative agreement with prediction, the bands assigned to $\nu_{21}$ and $\nu_{23}$ are less intense than those assigned to $\nu_{24}$ and $\nu_{25}$.

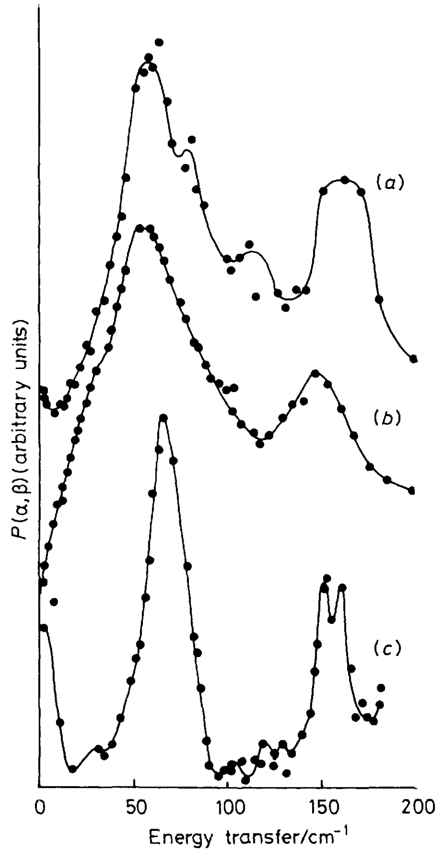

FIGURE 2 T.o.f. spectra of (*a*) [Cr($\eta^6$-$C_6H_6$)$_2$], 4H5 spectrometer (233 K), scattering angle of 82°; (*b*) [Cr($\eta^6$-$C_6H_6$)$_2$]I, 4H5 spectrometer (233 K), scattering angle of 82°; (*c*) [Cr($\eta^6$-$C_6H_6$)$_2$]I IN4 spectrometer (10 K), scattering angle of 91°

This leaves $\nu_{26}$ and $\nu_{22}$ unassigned. From the work of Campbell *et al.*[25] it is expected that $\nu_{22}$ will represent the torsional modes of two essentially independent tops. Employing the activation enthalpy calculated by Campbell *et al.* (19.1 kJ mol$^{-1}$), and assuming both a six-fold periodicity and the high barrier approximation,[31] a wavenumber for $\nu_{22}$ of ≈73 cm$^{-1}$ is calculated. Since the t.o.f. spectra (Figure 2) display better resolution below 250 cm$^{-1}$, we will discuss the region of the b.f.d. spectrum in which $\nu_{22}$ is predicted to occur in conjunction with these.

Comparison of the frequencies attributed to $\nu_{26}$ and $\nu_{22}$ from solid-phase far-i.r. studies[16] [171 (159 cm$^{-1}$ in $CS_2$ solution) and 152 cm$^{-1}$ respectively] with those derived from the i.n.s. spectrum apparently reveals that a transition equivalent to the band at 171 cm$^{-1}$ is absent. However, it should be noted that in this region of the spectrum the resolution of both the b.f.d. and 4H5 spectrometers is poor (≈35—42 cm$^{-1}$ b.f.d., >19 cm$^{-1}$ 4H5), being in the former case very much greater than, and in the latter comparable with, the reported separation of the bands in the i.r. spectrum. It must therefore be considered whether both modes could be present within the profile of the band at 155 cm$^{-1}$ (b.f.d.) (which has a distinct shoulder to higher frequency at 202 cm$^{-1}$) and its analogue in the t.o.f. spectra at 158.0 cm$^{-1}$ (which possesses no shoulder to either higher or lower frequency). We can dismiss the possibility that the shoulder at 202 cm$^{-1}$ (b.f.d.) represents either $\nu_{26}$ or $\nu_{22}$. Assignment to $\nu_{26}$ may be ruled out both because no equivalent band is observed in the far-i.r., and because the measured intensity of the b.f.d. band is comparable with that of $\nu_{21}$ (a singly degenerate translational mode) rather than twice as great (as predicted for a doubly degenerate translational mode, Table 4). Equally, assignment to $\nu_{22}$ is unacceptable firstly because this torsional frequency is unreasonably high when compared with that predicted (≈73 cm$^{-1}$), or indeed those found, for example, in [Fe(CO)$_3$($\eta$-$C_4H_4$)][32] (≈60 cm$^{-1}$) and in [Fe($\eta^5$-$C_5H_5$)$_2$][33] (≈45 cm$^{-1}$), and secondly because the intensity of the band at 202 cm$^{-1}$ is too small (Table 3). In the absence of any remaining normal modes of [Cr($\eta^6$-$C_6H_6$)$_2$] expected to occur in this region of the spectrum, the transition at 202 cm$^{-1}$ may be attributed to either a combination band (158.0 + 59.5 cm$^{-1}$, see later) or an effect of order contamination[29] (0.25 × 863 cm$^{-1}$).

Considering the b.f.d. band at 155 cm$^{-1}$ (158.0 cm$^{-1}$ t.o.f.), it may be seen from Table 4 that if $\nu_{22}$ and $\nu_{26}$ exist beneath the same band profile then the intensity displayed is predicted to be 4.6 times that of a singly degenerate translational mode, for example $\nu_{21}$. Allowing for the poor agreement between predicted and observed relative intensities found for the ring-tilt modes ($\nu_{24}$ and $\nu_{25}$), we cannot immediately discount the possibility that $\nu_{22}$ and

TABLE 3

The i.n.s. and optical spectroscopic wavenumbers (cm$^{-1}$) and assignments of [Cr($\eta^6$-$C_6H_6)_2$] and [Cr($\eta^6$-$C_6H_6)_2$]I ($D_{6h}$ symmetry assumed for both complexes)

| [Cr($\eta^6$-$C_6H_6)_2$] | | | | [Cr($\eta^6$-($C_6H_6)_2$]I | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| I.n.s. value | | Relative intensities in b.f.d. | Assignment | Optical value | | I.n.s. value | | | Relative intensities in b.f.d. | Assignment |
| B.f.d. | 4H5 T.o.f. | | | I.r. | Raman | B.f.d. | 4H5 T.o.f. | IN4 T.o.f. | | |
| | | | | | | | 30.0 ± 1.5 | 29.5 ± 3.0 | | Lattice mode |
| | 59.5 ± 2.5 | | Composite band containing $\nu_{22}$ | 52 | 60<br>54 | | 55.0 ± 2.5 | 66.0 ± 2.5 | | Composite band containing $\nu_{22}$ |
| | 82.0 ± 3.5 | | Lattice mode? | | | | | 78.5 ± 2.0 | | Lattice mode? |
| | 108.5 ± 5.0 | | Combination band/ overtone | | 111 | | | 106.0 ± 1.5<br>119.5 ± 1.5<br>129.0 ± 1.0 | | Combination bands/ overtones |
| 155 ± 8 | 158.0 ± 8.0 | 4.1 | $\nu_{26}$ | 149<br>142 | | 149 ± 8 | 150.0 ± 7.5 | 159.5 ± 0.5<br>152.0 ± 0.5 | 3.5 | $\nu_{26}$ |
| 202 ± 8 | | 0.8 | Combination band | | | 212 ± 8 | | | 1.4 | Combination band |
| 271 ± 8 | | 1.0 | $\nu_{21}$ | | 285 | 275 ± 8 | | | 1.0 | $\nu_{21}$ |
| 348 ± 8 | | 3.2 | $\nu_{24}$ | | 342 | 345 ± 8 | | | 3.3 | $\nu_{24}$ |
| 383 ± 8 | | 2.9 | $\nu_{16}^{ip}$, $\nu_{16}^{op}$ | 412 | | 422 ± 8 | | | 3.3 | $\nu_{16}^{ip}$, $\nu_{16}^{op}$ |
| 451 ± 8 | | 6.3 | $\nu_{25}$ | 465 | | 448 ± 8 | | | 6.7 | $\nu_{25}$ |
| 503 ± 8 | | 1.5 | $\nu_{23}$ | | | 503 ± 8 | | | 1.0 | $\nu_{23}$ |
| | | | | | | 546 ± 8 | | | | Combination band |
| 633 ± 8 | | | $\nu_6^{ip}$, $\nu_6^{ip}$ | | | 633 ± 8 | | | | $\nu_6^{ip}$, $\nu_6^{op}$ |
| 714 ± 8 | | | $\nu_4^{ip}$, $\nu_4^{op}$ | | | 719 ± 8 | | | | $\nu_4^{ip}$, $\nu_4^{op}$ |
| 807 ± 8 | | | $\nu_{11}^{ip}$, $\nu_{11}^{op}$ | 798 | | 813 ± 8 | | | | $\nu_{11}^{ip}$, $\nu_{11}^{op}$ |
| 863 ± 8 | | | $\nu_{10}^{ip}$, $\nu_{10}^{op}$ | | | | | | | |

$\nu_{26}$ both exist beneath the b.f.d. band centred at 155 cm$^{-1}$. However, in view of the frequency (≈73 cm$^{-1}$) that we calculated for $\nu_{22}$ from the n.m.r. data[25] it is very unlikely that this mode will be present beneath this band. It is much more likely that the b.f.d. band at 155 cm$^{-1}$ (158.0 cm$^{-1}$ t.o.f.) is simply due to $\nu_{26}$. Furthermore, this is supported by evidence from the complex [Cr($\eta^6$-$C_6H_6)_2$]I (which will be reviewed later) where a band analogous to the t.o.f. band at 158.0 cm$^{-1}$ in [Cr($\eta^6$-$C_6H_6)_2$] is seen in higher resolution t.o.f. (IN4) spectra to be split into components centred at 152.0 and 159.5 cm$^{-1}$. These are of equal intensity and may be unambiguously assigned to $\nu_{26}$. As a consequence, it must follow that the i.r. band at 159 cm$^{-1}$ observed for [Cr($\eta^6$-$C_6H_6)_2$] in $CS_2$ solution[16] has been wrongly correlated with the band of the solid at 171 cm$^{-1}$ and should be correlated with the transition at 152 cm$^{-1}$.

TABLE 4

Predicted relative intensities for internal vibrations of [Cr($\eta^6$-$C_6H_6)_2$] or [Cr($\eta^6$-$C_6H_6)_2$]$^+$ involving motion of the benzene ligands relative to the chromium atom

| Mode * | Predicted relative intensity |
|---|---|
| Torsion ($C_6H_6$–Cr–$C_6H_6$) ($\nu_{22}$) | 2.6 |
| Symmetric ring tilt ($\nu_{24}$) | 5.2 |
| Antisymmetric ring tilt ($\nu_{25}$) | 5.2 |
| $\delta$($C_6H_6$–Cr–$C_6H_6$) ($\nu_{26}$) | 2.0 |
| $\nu_{sym}$($C_6H_6$–Cr–$C_6H_6$) ($\nu_{21}$) | 1.0 |
| $\nu_{asym}$($C_6H_6$–Cr–$C_6H_6$) ($\nu_{23}$) | 1.0 |

* $\nu_{22}$ may be considered to represent a singly degenerate rotational mode and $\nu_{24}$ and $\nu_{25}$ doubly degenerate rotational modes. $\nu_{26}$ may be considered to represent a doubly degenerate translational mode and $\nu_{21}$ and $\nu_{23}$ singly degenerate translational modes.

To lower frequency in the t.o.f. spectra (Figure 2), the only band of sufficient intensity to contain $\nu_{22}$ is that situated at 59.5 cm$^{-1}$. The remaining bands in the t.o.f. spectra, at 82.0 and 108.5 cm$^{-1}$, must, in view of our assignment of all the intramolecular modes predicted to occur in this region of the spectrum, represent either overtone or combination bands of the transitions present within the composite band at 59.5 cm$^{-1}$, or lattice modes. Evidence from [Cr($\eta^6$-$C_6H_6)_2$]I (which will be reviewed later) suggests that, in all probability, the band at 82.0 cm$^{-1}$ arises from the latter and that at 108.5 cm$^{-1}$ from one of the former causes.

(*b*) [Cr($\eta^6$-$C_6H_6)_2$]I.—I.n.s. spectra of [Cr($\eta^6$-$C_6H_6)_2$]I are shown in Figures 2 and 3 and the transition frequencies derived are summarised in Table 3.

Taking the assignments of [Cr($\eta^6$-$C_6H_6)_2$], together with those of [Cr($\eta^6$-$C_6H_6)_2$]I suggested from optical spectroscopy[11,12,27] and n.c.a.,[17,24] the higher frequency (>250 cm$^{-1}$) b.f.d. spectrum (Figure 3) of the cationic species may, for the most part, be readily assigned. However, assignment of the modes $\nu_{16}^{op}$ and $\nu_{16}^{ip}$ will be discussed since previous work has placed the former at 420 cm$^{-1}$ in the Raman spectrum, whilst the latter has been considered from combination-band analysis of the i.r. spectrum to lie at 543 cm$^{-1}$ (refs. 11, 12). Certainly, the i.n.s. band at 422 cm$^{-1}$ may be attributed to $\nu_{16}^{op}$, in accordance, not only with the aforementioned optical work carried out on [Cr($\eta^6$-$C_6H_6)_2$]I[11,12] but also with observed (400 cm$^{-1}$)[17] and calculated (399—409 cm$^{-1}$)[21-2]

frequencies of the vibration in $[\mathrm{Cr}(\eta^6\text{-}\mathrm{C_6H_6})_2]$. Correlation of $\nu_{16}^{\mathrm{ip}}$ with the b.f.d. band at 546 cm$^{-1}$, however, appears more conjectural in view of the exceedingly large frequency splitting which would exist between the in-phase and out-of-phase motions of the charged compared with the neutral species (where both modes are believed from n.c.a. to be of equal frequency [21–23]). This splitting would be greater than that found for any other internal benzene ligand mode in our b.f.d. spectra of either $[\mathrm{Cr}(\eta^6\text{-}\mathrm{C_6H_6})_2]$ or $[\mathrm{Cr}(\eta^6\text{-}\mathrm{C_6H_6})_2]\mathrm{I}$, where it has proved impossible to resolve the in-phase and out-of-phase components. Conversely, the transition at 546 cm$^{-1}$ is present in the i.n.s. spectrum of $[\mathrm{Cr}(\eta^6\text{-}\mathrm{C_6H_6})_2]\mathrm{I}$ but is absent from that of $[\mathrm{Cr}(\eta^6\text{-}\mathrm{C_6H_6})_2]$. It is reasonable to assume that the assignment of $\nu_{16}^{\mathrm{ip}}$ and $\nu_{16}^{\mathrm{op}}$ to similar frequencies, as has been suggested for $[\mathrm{Cr}(\eta^6\text{-}\mathrm{C_6H_6})_2]$,[21–23] is also likely to hold for $[\mathrm{Cr}(\eta^6\text{-}\mathrm{C_6H_6})_2]\mathrm{I}$. We therefore assign the b.f.d. band at 422 cm$^{-1}$ to both $\nu_{16}^{\mathrm{ip}}$ and $\nu_{16}^{\mathrm{op}}$ and, as a consequence, attribute the transition at 546 cm$^{-1}$ to a combination band [perhaps that resulting from the band located at 503 cm$^{-1}$ (b.f.d.) and that resolved at 66.0 cm$^{-1}$ (IN4 t.o.f. spectra) (see later)].

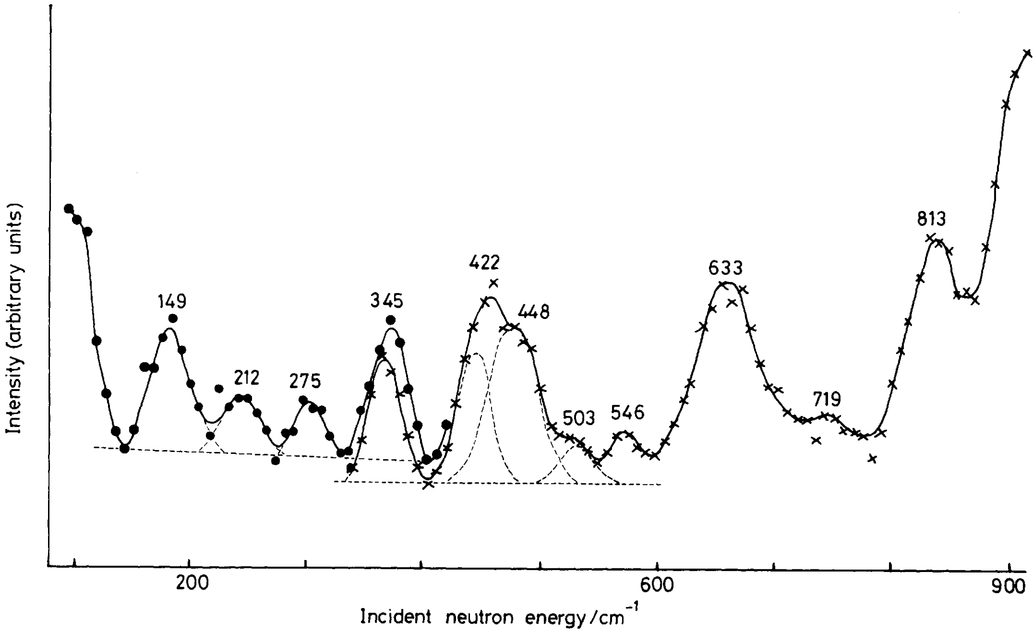

FIGURE 3 The Dido b.f.d. spectrum (12 K) of $[\mathrm{Cr}(\eta^6\text{-}\mathrm{C_6H_6})_2\mathrm{I}]$; details as in Figure 1

It is interesting to note that the $\nu_{16}$ vibrations, alone of the benzene ligand modes in the b.f.d. spectrum, occur to higher frequency in the spectrum of the charged compared with the uncharged species. This is perhaps surprising, given that $\nu_4^{\mathrm{ip}}$ and $\nu_4^{\mathrm{op}}$, which in common with $\nu_{16}^{\mathrm{ip}}$ and $\nu_{16}^{\mathrm{op}}$ represent out-of-plane C–C–C bends, remain essentially fixed in frequency.

Of those vibrations of $[\mathrm{Cr}(\eta^6\text{-}\mathrm{C_6H_6})_2]\mathrm{I}$ which involve motion of the benzene ligands relative to the chromium atom, $\nu_{21}$ and $\nu_{24}$ may be assigned to the b.f.d. bands at 275 and 345 cm$^{-1}$. In both cases, the frequencies obtained in the i.n.s. spectrum compare well with those reported in previous Raman studies (279 and 333 cm$^{-1}$ respectively).[11,12] Assignment of the antisymmetric (or out-of-phase) equivalents of $\nu_{21}$ and $\nu_{24}$ ($\nu_{23}$ and $\nu_{25}$ respectively) has been disputed, however, with i.r. work suggesting $\nu_{23}$ occurs at 415—418 cm$^{-1}$ and $\nu_{25}$ at 466—467 cm$^{-1}$ (refs. 11, 12, 27), and a partial n.c.a. indicating $\nu_{23}$ at 490 cm$^{-1}$ and $\nu_{25}$ at 459 cm$^{-1}$ (ref. 24).

In order to establish the correct assignments for $\nu_{23}$ and $\nu_{25}$ we have fitted [29] two Gaussians to the 422/448 cm$^{-1}$ b.f.d. band profile and another beneath the b.f.d. band at 503 cm$^{-1}$ using a Du Pont curve resolver. Although this procedure would involve considerable error if the component Gaussians each had three degrees of freedom (height, width, and position), we have reduced this error by making use of our b.f.d. data for $[\mathrm{Cr}(\eta^6\text{-}\mathrm{C_6H_6})_2]$. In the latter spectrum we have fitted a Gaussian to the band at 451 cm$^{-1}$ (using the lower energy side of the band to define its shape) and two Gaussians of equal half-widths to the incompletely resolved bands at 348 and 383 cm$^{-1}$. The half-widths of the bands at 383 and 451 cm$^{-1}$ {assigned to $\nu_{16}^{\mathrm{ip}}$, $\nu_{16}^{\mathrm{op}}$, and $\nu_{25}$ respectively in the $[\mathrm{Cr}(\eta^6\text{-}\mathrm{C_6H_6})_2]$ spectra} were measured, and by making the reasonable assumption that the half-widths of $\nu_{16}^{\mathrm{ip}}$, $\nu_{16}^{\mathrm{op}}$, and $\nu_{25}$ would be identical in the b.f.d. spectra of the two compounds, we have fitted the bands at 422 and 448 cm$^{-1}$ in the b.f.d. spectrum of $[\mathrm{Cr}(\eta^6\text{-}\mathrm{C_6H_6})_2]\mathrm{I}$. The components of the best fit are shown in Figure 3. It would appear that the band at 448 cm$^{-1}$ is considerably more intense than those at either 422 or 503 cm$^{-1}$ (Table 3). On intensity grounds therefore the band at 448 cm$^{-1}$ must be assigned to $\nu_{25}$ in reasonable agreement with the frequency attributed in both i.r. work (466—467 cm$^{-1}$) [11,12,27] and n.c.a. (459 cm$^{-1}$).[24] The total measured intensity of the $\nu_{16}^{\mathrm{ip}}$ and $\nu_{16}^{\mathrm{op}}$ bands relative to that of $\nu_{25}$ is, within experimental error, identical for both complexes. Consequently, it is unlikely that the b.f.d. band at 422 cm$^{-1}$ contains an additional unresolved band at 415 cm$^{-1}$ representing $\nu_{23}$, as suggested in i.r. studies.[11,12] Mode $\nu_{23}$ must therefore be represented by the i.n.s. transition at 503 cm$^{-1}$, in agreement with the n.c.a. of $[Cr(\eta^6\text{-}C_6H_6)_2]I$ (490 cm$^{-1}$) [24] and our findings for $[Cr(\eta^6\text{-}C_6H_6)_2]$. Given these assignments for $\nu_{25}$ and $\nu_{23}$, the measured intensity ratio is 6.7 : 1.0 (Table 3). This ratio, like that found for $[Cr(\eta^6\text{-}C_6H_6)_2]$, is in poor agreement with prediction (5.2 : 1.0) based upon $\nu_{25}$ corresponding to a doubly degenerate rotational mode and $\nu_{23}$ to a singly degenerate translational mode (Table 4).

The b.f.d. spectrum below 250 cm$^{-1}$ will be considered together with the t.o.f. spectra (Figure 2) which display better resolution in this region. The modes $\nu_{22}$ and $\nu_{26}$ are expected to occur in this area of the spectrum. However, no previous far-i.r. study has been carried out on $[Cr(\eta^6\text{-}C_6H_6)_2]I$ and the frequency quoted by Fritz *et al.*[11,12] for $\nu_{26}$ (144 cm$^{-1}$) has been derived from combination-band analysis. Likewise, a value of 303 cm$^{-1}$ has been suggested for $\nu_{22}$.[11,12] The latter assignment is clearly in error, not only because the frequency is unreasonably high but, more importantly, because there is no b.f.d. band at this frequency.

Our very high resolution t.o.f. (IN4) spectra (Figure 2) display a doublet at 152.0 and 159.5 cm$^{-1}$ (which is evident in all eight spectra collected at different scattering angles), whilst in the far-i.r. spectrum an equivalent doublet is observed at 142 and 149 cm$^{-1}$. It is unreasonable to expect that in the i.r. spectrum $\nu_{22}$ and $\nu_{26}$ should give rise to bands of comparable intensity because $\nu_{22}$ is formally inactive whilst $\nu_{26}$ is active. We therefore follow the evidence from our far-i.r. work, and from previous combination-band analysis (144 cm$^{-1}$),[11,12] and assign the i.n.s. doublet at 152.0 and 159.5 cm$^{-1}$ (142 and 149 cm$^{-1}$ i.r.) to $\nu_{26}$. This mode has had its degeneracy lifted, probably, by crystal-field effects. The frequencies found for the components of $\nu_{26}$ in $[Cr(\eta^6\text{-}C_6H_6)_2]I$ are therefore similar to that observed for the same mode in the i.n.s. spectrum of $[Cr(\eta^6\text{-}C_6H_6)_2]$ (158.0 cm$^{-1}$).

The remaining unassigned low-frequency intramolecular mode, $\nu_{22}$, on account of its great predicted intensity (Table 4), may only be assigned to the very intense IN4 t.o.f. band at 66.0 cm$^{-1}$. The half-width of this band is clearly greater than the resolution of the spectrometer indicating that several transitions must be present beneath its band profile. Of the remaining t.o.f. transitions, the shoulder at 78.5 cm$^{-1}$ and the weak band at 29.5 cm$^{-1}$ probably represent lattice modes, whilst the very weak bands at 106.0, 119.5, and 129.0 cm$^{-1}$ undoubtedly arise from overtone and combination bands of unresolved transitions occurring beneath the 66.0 cm$^{-1}$ band profile, possibly in association with the band at 29.5 cm$^{-1}$.

Finally, in view of the assignment of all the intramolecular modes of $[Cr(\eta^6\text{-}C_6H_6)_2]I$ predicted to be present below 830 cm$^{-1}$, the b.f.d. band at 212 cm$^{-1}$, which has no analogue in either t.o.f. or optical spectra, must either result from a combination band (*e.g.* 66.0 + 152.0 cm$^{-1}$) or from order contamination.[29]

(*c*) *Barrier Calculations*.—It has been shown by Campbell *et al.*[25] that the potential barrier to the rotation of the benzene ligands within $[Cr(\eta^6\text{-}C_6H_6)_2]$ about their hexad axes is six-fold. As in the preceding paper [29] we have calculated the barrier resulting from $\nu_{22}$ assuming a six-fold barrier ($V_6$), and employing the Simple Harmonic Oscillator Approximation. This calculation yields a value of 12.6 ± 1.1 kJ mol$^{-1}$ (233 K), which compares with an activation energy for benzene-ligand rotation determined from n.m.r. measurements of 19.1 kJ mol$^{-1}$ (ref. 25). Repeating this calculation for $[Cr(\eta^6\text{-}C_6H_6)_2]I$, making the same assumptions, yields a torsional barrier of 15.5 ± 1.2 kJ mol$^{-1}$.

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