The Laser-Raman Spectrum of Ferrocene

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VIBRATIONAL spectroscopy has proved a versatile powerful technique in the characterization of both electronic and structural features of metallocenes.[1] Although a detailed analysis of the i.r. and Raman spectra of the most familiar congener of this series, ferrocene, has been given by Lippincott and Nelson,[2] a more recent study of the Raman spectrum reports[3,4] the observation of several additional bands and revises the frequency assignments. In an attempt to clarify this point, we used helium–neon laser excitation (Spectra-Physics Model 112) to measure the Raman spectrum of ferrocene in carbon tetrachloride, carbon disulphide, chloroform, nitromethane, and benzene solutions. It was also possible to record the spectrum of the highly-coloured, polycrystalline solid, free from solvent scattering. The previous studies were apparently restricted to solution, although no experimental details have been given. Our spectra were measured with a modular instrument employing a Spex Model 1400-11 double-monochromator spectrometer and an ITT FW-130 (S-20) photomultiplier.

The Table records a comparison between the Raman spectra observed in previous studies and those we observed in carbon tetrachloride. The frequency designation is that of ref. 2 based on a D_{5d} model of ferrocene (staggered).

Raman spectra of ferrocene and vibrational assignments

Symmetry and frequency designation	Ref. 2	Ref. 3	Present study	Description
A_{1g}				
ν_1	3099	3110	3100s[a]	*sym.* CH stretch[b].
ν_2		1105	812w[c]	*sym.* CH bend ($\perp$)
ν_3	1105	1390	1105s	*sym.* ring breathing
ν_4	303	306	301s	*sym.* ring-metal stretch.
E_{1g}				
ν_{12}	3085	3089	3085w	CH stretch.
ν_{13}	1010	998	999w	CH bend($\parallel$)
ν_{14}		818	835w[c]	CH bend($\perp$)
ν_{15}	1408	1412	1412m	*sym.* CC stretch.
ν_{16}	388	390	390s	*sym.* ring tilt .
E_{2g}				
ν_{23}	3085	3045	3070vw	Ch stretch.
ν_{24}	1178	1361	1175w	CH bend($\parallel$)
ν_{25}	1050	1184	1059m	CH bend($\perp$)
ν_{26}	1560	1527	1356w	CC stretch.
ν_{27}		1054	892w[d]	ring distortion($\parallel$)
ν_{28}		591	600w[e]	ring distortion($\perp$)

[a] Intensity designations based on uncorrected peak heights: s, strong; m, medium, w, weak; vw, very weak.

[b] $\parallel$ and $\perp$ refer to vibrations parallel and perpendicular to the five-fold symmetry axis.

[c] Observed in solid state and in nitromethane solution. Solvent band overlap otherwise prevents identification.

[d] Observed in solid and chloroform solution.

[e] Observed in solid only.

Our data are in general agreement with those of Lippincott and Nelson.[2] Stammreich and Forneris[3,4] report an intense, polarized band at 1390 cm.$^{-1}$, and this is assigned to the A_{1g} symmetric ring breathing mode. Although the spectral region between 1200 and 1700 cm.$^{-1}$ was carefully searched no band corresponding to this mode was evident. The peaks at 1412 and 1356 cm.$^{-1}$, also recorded in the earlier work,[2–4] appear well separated, and the region between these peaks is devoid of intensity above background. We retain the assignment of the most intense band in the spectrum at 1105 cm.$^{-1}$ to this mode. The fourth A_{1g} band, corresponding to a CH bending motion, was not observed by the previous workers[2] owing to solvent masking, but they assigned this mode a value of 804 cm.$^{-1}$ on the basis of the appearance of a peak in the spectrum of [^{2}H$_{10}$]ferrocene at 614 cm.$^{-1}$. In the solid spectrum, lines at 811 and 835 cm.$^{-1}$ are readily discerned, and the 811 cm.$^{-1}$ band, which we assign to ν_3, is also observed in the nitromethane solution spectrum. The normal co-ordinate analysis[2] predicts that ν_{14}, the CH bend ($\perp$) of E_{1g} symmetry, should appear at *ca.* 800 cm.$^{-1}$, and we assign this mode to the frequency at 835 cm.$^{-1}$. Absorptions which are analogous to ν_3 and ν_{14} are found in the i.r. spectrum at 811 (ν_g) and 834 cm.$^{-1}$ (ν_{19}).[2]

The class of E_{2g} vibrations exhibits the least intense scattering in the ferrocene spectrum. The ring-distortion modes, ν_{27} and ν_{28}, which were not found by Lippincott and Nelson,[2] were presumed to lie at 885 and 569 cm.$^{-1}$, respectively. We observed these at 892 and 600 cm.$^{-1}$ in good agreement with the i.r. single-crystal spectra.[5] The earlier workers[2,3] report the CC stretch, ν_{26}, to be in the region 1500—1600 cm.$^{-1}$. A thorough examination of this region reveals no corresponding band in the solid-state spectrum. In all cases, broad solvent bands, at least as intense as the other fundamental E_{1g} modes, are found in this region. For example, in the chloroform and carbon tetrachloride spectra the solvent overtone ($2 \times \nu_3$) is observed, while the formally Raman-forbidden band of carbon disulphide (ν_3) appears with considerable intensity centred at 1510 cm.$^{-1}$. No modification in these bands is apparent between neat solvent and ferrocene solution spectra, and they may represent the explanation for the marginally observed mode previously assigned. We identify the band at 1356 cm.$^{-1}$ with ν_{26}, for it is clearly revealed with an intensity comparable to that of the 1411 cm.$^{-1}$ band in all spectra. It is highly unlikely that a combination frequency ($\nu_4 + \nu_{25}$) would occur with this intensity while a fundamental went unobserved. A relatively strong i.r. absorption is found[5] at 1351 cm.$^{-1}$, and we believe this frequency should be reassigned to the similar infrared-active mode, ν_{32}. With this single exception, our data compare favourably with those of Lippincott and Nelson,[2] while differing from those of Stammreich and Forneris.[3,4]

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