THE RAMAN SPECTRA OF FERROCENE

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Raman spectra of ferrocene single crystals are presented and their assignment given. Some of the controversies regarding different assignments given by Lippincott and Nelson and by Stammreich are resolved.

The molecule $(C_5H_5)_2Fe$ has been of interest as a relatively simple dicyclopentadienyl compound [1]. It has a sandwich structure in which the iron ion is located at the center between two rings and has point symmetry D_{5d}. One would expect two types of spectra, one corresponding to the intra-ring vibrations and another corresponding to the inter-ring vibrations, altogether 34 modes of which 15 are Raman active.

In the crystal one expects in addition a third type of spectrum, near the exciting line, caused by the intermolecular vibrations. The space symmetry of the crystal is C_{2h}^5. Every Raman active mode of the molecule is doubled in the crystal (for non-degenerate modes) or quadrupled (for degenerate modes). Also a forbidden line of A_{2g} symmetry in the molecule becomes Raman active in the crystal.

The Raman spectra of ferrocene have in the past been studied in solution. Lippincott and Nelson [2] have made a detailed assignment of their observed spectra, and predicted a few unobserved lines. Stammreich [3] has made a different assignment of some of the lines, based to a large extent on his observation of a polarized line at 1390 cm^{-1} which he assigns to the A_{1g} ring breathing mode.

Single crystal data can discriminate better between the assignments because of the dependence of the polarizability on orientation of the crystal with respect to scattering geometry. We list in this paper, in table 1, the frequencies of the observed spectra on single crystals of ferrocene. The studies were made at room temperature, and between 180 and 200°K, using a He Ne laser (20 mW at 6328Å), Spex double monochromator and a Philips XP1117 (s-20) photomultiplier.

The accuracy of the measured frequencies is better than ± 2 cm^{-1}. Below 169°K there is a phase transition which is being investigated at present.

Table 1 gives the data of Lippincott and Nelson, Stammreich and the present work. The following should be noticed. In the solid, all lines are of A_g and B_g symmetries, whereas in solution the lines are of the symmetries A_{1g}, E_{1g}, E_{2g}. We indeed resolved the broad line near 310 cm^{-1} corresponding to ring-metal stretch, into one A_g and one B_g split by 7 cm^{-1}. Similarly, the E_{1g} line corresponding to symmetric ring tilt is split into 4 lines, of which two are clearly resolved and the other two indicated in the line profile. Many other lines are also resolved or the structure discernible within the linewidth

The four lines predicted by Lippincott between 500-900 cm^{-1} have been observed by us and assigned to the appropriate vibration. Two of these have also been observed by Stammreich. Stammreich, however, observed lines at 1105 and 1390 cm^{-1} to be polarized, and assigns the latter to the ring breathing mode. On the basis of this he reassigns many of the other lines between 1000-1400 cm^{-1}. Lippincott has not observed the line near 1390 cm^{-1} and we have also not been able to confirm the existence of this line. In addition, the observation of the CH bending (⊥) and ring distortion (ıı) at 843.5 and 897 cm^{-1} invalidate Stammreich's assignment of these lines to fall at 1105 and 1054 cm^{-1}. Hence the assignments of Lippincott and Nelson are confirmed by our measurements. We therefore assign the line at 814.5 cm^{-1} to be the A_{1g} CH bending (⊥).

The strong line at 1102 cm^{-1}, which is now assigned to the ring breathing mode, shows a

Table 1
Observed Raman spectra of ferrocene in solution and single crystals

Lippincott and Nelson [2] (solution)	Stammreich [3] (solution)	Present work (crystals)
–	–	60 cm^{-1} intermolecular vibrations several unresolved lines.
303 A_{1g} ring-metal stretch	306	309, $A_g + B_g$, split 7 cm^{-1}
388 E_{1g} symmetry ring tilt	390	389, at least 2, probably 4 lines, split 5 cm^{-1}
(569) E_{2g} ring distortion ($\perp$)	591	597
(800) E_{1g} CH bending ($\perp$)	818	814.5
(804) A_{1g} CH bending ($\perp$)	–	843.5
(885) E_{2g} ring distortion (∥)	–	897
1010 E_{1g} CH bending (∥)	998	997.5
1050 E_{2g} CH bending ($\perp$)	1054 E_{2g} ring distortion (∥)	1058.5 CH bending ($\perp$) at least 3 probably 4 lines, split 7 cm^{-1}
–	–	1096 CH bending (∥) inactive in solution
1105 A_{1g} ring breathing	1105 A_{1g} CH bending ($\perp$)	1102 ring breathing
1178 E_{2g} CH bending (∥)	1184 E_{2g} CH bending ($\perp$)	1191 CH bending (∥)
303 + 1050 combination	1361 E_{2g} CH bending (∥)	1356 CC stretch
–	1390 A_{2g} ring breathing	–
1408 E_{1g} CC stretch	1412	1410
1560 E_{2g} CC stretch	1527	–
3085 E_{2g} CH stretch / E_{1g} CH stretch	3045 / 3089	3088 / 3100
3099 A_{1g} CH stretch	3110	3109

The brackets in Lippincott and Nelson's assignment refer to the predicted but unobserved lines.
The units are in cm^{-1}.

shoulder of about 1/12 intensity at 1096 cm^{-1} which appears to have the same polarization characteristics, but is absent in solution. We propose tentatively that this corresponds to the CH bending (∥) of A_{2g} symmetry, which is inactive in solution, but becomes Raman active in the solid. This needs further confirmation.

It is to be noticed that we have not been able to observe the line at 1560 cm^{-1}, however, we assign the line at 1356 cm^{-1} to be the missing C-C stretching mode.

Of interest are several unresolved bands near 60 cm^{-1} which we assigned to intermolecular vibrations between the two molecules in the unit cell.

Note added: Our attention has been drawn to the fact that Ferrocene Raman spectra have recently been measured in solution by T. V. Long and F. R. Huege in Chem. Commun. 20 (1968) 1239. Their results confirm as well the assignment of Lippincott and Nelson.

REFERENCES

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