The Vibrational Spectrum of Ruthenocene

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The complex Raman and i.r. spectra of ruthenocene at ambient and liquid-nitrogen temperatures have been interpreted with the aid of solution and Raman single-crystal data to yield a complete assignment, including inactive modes. The polarisation property of the π(C–H) modes in ferrocene has been determined for the first time. Contrary to the accepted order, the i.r.-active ring ' tilt ' mode of ruthenocene comes at lower frequency than the M–ring bond stretch.

As the prototype ' sandwich ' organometallic molecule, ferrocene has been the object of many vibrational spectroscopic studies.[1-6] Even so, its spectrum is still not fully understood. In particular, the π(C–H) modes have not been assigned with an adequate degree of proof; the i.r. M–ring modes need further study; and the inactive modes have not been determined with completeness. Ferrocene crystallises in a monoclinic space group which has several unattractive features insofar as attempts at proof of assignment are concerned. However, ruthenocene, Ru(π-$C_5H_5)_2$, crystallises in the orthorhombic group *Pnma* (D_{2h}^{16}), $Z = 4$,[7] which is more satisfactory for single-crystal spectroscopy. We have re-investigated the vibrational spectrum of ruthenocene, the only previous study being that of Lippincott and Nelson [1] which pre-dated laser-Raman equipment. During our work Bodenheimer reported, in summary, a single-crystal Raman study.[8]

Selection Rules.—In solution the barrier to rotation of the rings is low. Bunker has shown that the molecular symmetry is then more correctly described in terms of the double group G_{100}, the representation including *G*-type quadridegenerate symmetry species.[9] The i.r.–Raman coincidences required for the G_{1s} species will be removed if there is coupling between the two rings, with the result that either D_{5h} (rings eclipsed) or D_{5d} (rings staggered) selection rules then apply. The rules are summarised, and their inter-relations shown, in Table 1.

In the solid each molecule has approximately D_{5h} symmetry and is located on a C_s site [the plane retained is (*zx*)]. Unit-cell analysis [10] and the correlation scheme are shown in Table 2. We note in particular that all of the inactive molecular species become active in the crystal.

Assignment.—Solution spectra.—A_1' modes. Lippincott and Nelson did not obtain Raman polarisation data for their solutions. We find strong polarised bands at 3111, 1101, and 329 cm^{-1}, similar to values reported for ferrocene and the cobalticinium ion. The fourth totally symmetric mode, ν_2 π(C–H), is exceedingly weak; the low intensity has been explained by Hartley and Ware.[5] Ruthenocene is less readily soluble in common solvents than ferrocene; on the reasonable assumption that the π(C–H) modes ν_2 and ν_{14} will follow the same order for both molecules, we showed (for the first time) that the 812 cm^{-1} band of ferrocene is polarised in nitromethane solution and accordingly assign ν_2 at 806 and ν_{14} at 832 for ruthenocene.

A_2'' modes. These will be close to those of a_1' type if coupling beteeen the rings is negligible since the two species correspond to out-of-plane and in-plane motions

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of the rings respectively. Three i.r. (solution) bands can be so assigned (Table 3); the fourth is not expected to be particularly close to its a_1' counterpart as it is a skeletal mode. It could be at either 381 or 446 cm^{-1}.

E_1' and E_1'' modes. E_1' modes can now be assigned readily as they generate the only remaining i.r. (solution) bands. Unfortunately an ambiguity arises because one more than the theoretical number of bands is found. This is important as the sort of e_1'' and e_2' Raman-active modes must be made on the basis of the expected proximity of e_1' and e_1'' modes. Suspicion falls upon the 1050 cm^{-1} i.r. (solution) band, also observed by Lippincott and Nelson, as it is both weak and broad whereas the other presumed-e_1' bands are all strong: they found that it was absent from the spectrum of the vapour. On this assumption, the e_1'' Raman modes must be assigned as in Table 3. The a_2''–e_1' ambiguity remains over assignment of the skeletal modes ν_{11} and ν_{21} for which the values 381 and 446 cm^{-1} are available.

TABLE 1

Selection rules for bis-(π-cyclopentadienyl)metal complexes

Point group	Numbering [a] and representation							
	ν_{1-4}	ν_7	ν_{17-22}	ν_{23-28}	ν_{5-6}	ν_{8-11}	ν_{12-16}	ν_{29-34}
D_{5d}	$4A_{1g}$	$+ A_{2g}$	$+ 6E_{1u}$	$+ 6E_{2g}$	$+ 2A_{1u}$	$+ 4A_{2u}$	$+ 5E_{1g}$	$+ 6E_{2u}$
Activity	R		Ir	R		Ir	R	
D_{5h}	$4A_1'$	$+ A_2'$	$+ 6E_1'$	$+ 6E_2'$	$+ 2A_1''$	$+ 4A_2''$	$+ 5E_1''$	$+ 6E_2''$
G_{100} (ref. 9)	$4A_{1s}$	$+ A_{2s}$	$+ \begin{cases} 5G_{1s} \\ 1E_{6d} \end{cases}$	$+ 6G_{4s}$	$+ 1A_{3s}$ [b]	$+ 4A_{4s}$		
Activity	R		$\begin{cases} \text{R,Ir} \\ \text{Ir} \end{cases}$	R		Ir		

[a] The numbering of Hartley and Ware (ref. 5) is retained. [b] No torsional mode in G_{100}.

TABLE 2

Unit-cell analysis and correlation scheme for solid ruthenocene

D_{2h}^{16}	N_T	A	T	R	N_i	Activity
A_g	34		2	1	31	xx, yy, zz
B_{1g}	29		1	2	26	xy
B_{2g}	34		2	1	31	zx
B_{3g}	29		1	2	26	yz
A_u	29		1	2	26	
B_{1u}	34	1	1	1	31	z
B_{2u}	29	1	0	2	26	y
B_{3u}	34	1	1	1	31	x

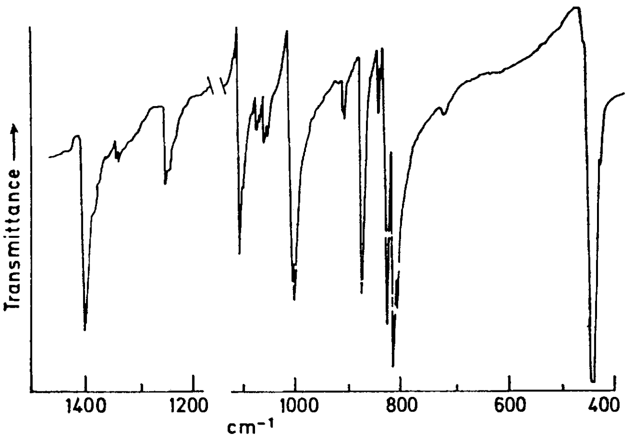
Molecule	Site	Crystal
D_{5h}	$C_s(\sigma_{zx}) \xrightarrow{\times 4}$	D_{2h}
A_1'	A'	$A_g + B_{2g} + B_{1u} + B_{3u}$
A_2'	A''	$B_{1g} + B_{3g} + A_u + B_{2u}$
A_1''	A''	(As above)
A_2''	A'	
$E_p{}^{\sigma}$	$A' + A''$	$A_g + B_{1g} + B_{2g} + B_{3g} + A_u + B_{1u} + B_{2u} + B_{3u}$

N_T = Total number of modes; A = acoustic; T = translatory; R = rotatory; N_i = internal modes.

E_2' modes. These are assigned to the only remaining unlabelled Raman bands, *viz.*, 3100, 1361, 1193, 1055, 895, and 602 cm^{-1}; the number of bands is correct and their frequencies are those expected on qualitative grounds. E_2' modes are generally weak for this molecule: the bands at 895 and 602 cm^{-1} have not been observed previously.

A_2', A_1'', and E_2'' modes. These are all inactive. Since the a_1', a_2'' and e_1', e_1'' pairs are almost coincident (for ring modes) we can confidently attribute e_2'' values by analogy with those of e_2': this is done below in connection with crystal data. The sole remaining undetermined modes are an a_1'', a_2' pair which will be effectively coincident and with frequency/cm^{-1} in the 1000—1300 region, since they are δ(C–H) modes. A second a_1'' mode is a torsional motion, only possible in the solid state, which will certainly lie below 200 cm^{-1}.

Solid-state spectra. At liquid-nitrogen temperature both i.r. and Raman spectra are of considerable complexity, showing many band splittings (see Figure).



I.r. spectrum (KBr disc) of ruthenocene at liquid-nitrogen temperature, showing weakly allowed ' inactive ' modes

On the basis of two very reasonable assumptions (negligible interaction between rings; that the weak 1050 cm^{-1} i.r. band is not a fundamental) an assignment for almost all of the internal modes of ruthenocene in solution was deduced with some certainty. We seek confirmation from the crystal spectra.

ν(C–H) region. We found six ν(C–H) Raman bands but Bodenheimer, working at 80 K, was able to resolve

planation to be that D_{5h} Raman-active modes only show in the solid-state spectrum, and that they exhibit full site and correlation splitting (requiring ten bands in all).

TABLE 3

Vibrational frequencies/cm^{-1} and assignment for ruthenocene

I.r.			Raman			
Solid at liquid-nitrogen temp.	Solution	D_{5h} Molecular assignment	Solution	Crystal at liquid-nitrogen temp.	Crystal at ambient temp.	Crystal assignment D_{2h}
138w		a_1'',ν_6		130vw	111vw	$B_{1g} + B_{3g}$
165wm 172wm		e'_1,ν_{22}				
		a_1',ν_4	329s,P	329s 337vs	327s 335vs	$A_g + B_{2g}$
381s		e_1',ν_{21}				
		e_1'',ν_{16}	400m,dP	394w 400m 402w 406m	400m 403w 406m	$A_g + B_{1g} + B_{2g} + B_{3g}$
450vs	446m	a_2'',ν_{11}				
		e_2',ν_{28} $(+e_2'',\nu_{31}?)$	602vw,dP	602w 606w	601w 604w	$A_g + B_{1g} + B_{2g} + B_{3g}$
		a_1',ν_2	~806vw	818w	817w	$A_g + B_{2g}$
804m 812s	807s	a_2'',ν_9				
821m 823m 833vw 838w	835w	e_1',ν_{19}				
		e_1'',ν_{14}	~832vvw	833w 840w 845w	832w 843w	$A_g + B_{1g} + B_{2g} + B_{3g}$
868m		e_2'',ν_{33}				
898w		e_2',ν_{27}	895vw,dP	896vvw 909vvw	908vvw	B_{1g}
		e_1'',ν_{13}	995w,dP	991vw 996vw 1003vw 1012vw	993vw 1003vw 1011vw	$A_g + B_{1g} + B_{2g} + B_{3g}$
998s 1002sh	1002s	e_1',ν_{18}				
1047w 1052w	1050w,br	e_2'',ν_{13}		1050w	1049w	$A_g + B_{1g} + B_{2g}$
1060w 1066w		e_2',ν_{25}	1055wm,dP	1062m 1065wm	1061m 1063sh	$A_g + B_{1g} + B_{2g} + B_{3g}$
		a_1',ν_3	1101s,P	1092w 1099vs	1093w 1099vs	$A_g + B_{2g}$
1098sh 1100s	1102s	a_2'',ν_{10}		1101vw,sh		
		e_2',ν_{24} and e_2'',ν_{30}	1193w,dP	1182ww 1193vvw 1204vvw 1208vvw	1192vvw 1203vvw	$A_g + B_{1g} + B_{2g} + B_{3g}$
1248sh 1255m		a_1'',ν_5; a_2',ν_7				
1340vw 1345vw		e_2'',ν_{32}				
		e_2',ν_{26}	1361m,dP	1359w 1364w	1359w 1362w	$A_g + B_{1g} + B_{2g} + B_{3g}$
1400sh 1410m	1412m	e_1'',ν_{15}				
		e_1',ν_{20}	1412s,dP	1406wm 1411w	1406wm 1409w	$A_g + B_{1g} + B_{2g} + B_{3g}$
	3100m	a_2'',ν_8				
		e_2',ν_{23} e_1'',ν_{12}	3100w,dP	3076w 3084w 3092vw 3097vw	3076w 3084w 3095w	$A_g + B_{1g} + B_{2g} + B_{3g}$
				3104m	3104m	$A_g + B_{1g} + B_{2g} + B_{3g}$
		a_1',ν_1	3111s,P	3112m	3111m	$A_g + B_{2g}$

nine. Even this is less than half the number required by unit-cell analysis. There are several alternative assignments but the evidence is insufficient to distinguish between them. We consider the most probable ex-

ν_{15} and ν_{20}; ν_{26} and ν_{32}. ν_{15},e_1'' and ν_{20},e_1' Occur in both i.r. and Raman solution spectra at 1412 cm^{-1}; both are present as doublets in low-temperature solid-state spectra, the Raman polarisations being those expected for an *e*-mode. The i.r. doublet is at slightly different frequency from the Raman doublet but the overall splitting is small.

ν_{26},e_2' has no i.r. counterpart: it also shows as a doublet in the Raman crystal spectrum (1364, 1359 cm^{-1}) with the correct symmetry labels. A weak doublet is found at 1345, 1340 cm^{-1} in the i.r. spectrum of the solid. This could be due to either (*a*) the i.r. part of the correlation and site split ν_{26} or (*b*) ν_{32}, inactive in solution but allowed in the solid. Since the centres of the i.r. and Raman doublets are *ca.* 20 cm^{-1} apart we prefer to assign the i.r. doublet to ν_{32}.

ν_5 and ν_6. The i.r. spectrum (solid) shows a weak doublet at 1255, 1248 cm^{-1} not present in solution and well removed from any Raman-active frequencies. It is therefore most probably due to an inactive mode(s); its position suggests that it is δ(C–H) and it is accordingly attributed to both ν_7, a_2' and ν_5, a_1''.

ν_{24} and ν_{30}. ν_{24}, e_2' has been assigned to a weak Raman solution line at 1193 cm^{-1}. It does not show through in the i.r. spectrum of the solid and is present in the Raman spectrum of the crystal as a very weak multiplet: we observe four lines whilst Bodenheimer found two more possible lines at 80 K. In view of the breadth of the multiplet we are inclined to attribute it to ν_{24} *and* ν_{30} rather than ν_{24} alone.

ν_3 and ν_{10}. ν_3 (Raman) and ν_{10} (i.r.) are degenerate in solution. The i.r. (solid) spectrum shows an intense band with a weak shoulder, consistent with the ν_{10} assignment. The Raman spectrum shows three lines, 1101, 1099, and 1092; only two of these can come from ν_3 (see correlation scheme) so we must conclude that another mode is showing through, *viz.*, ν_{10}. We reject Bodenheimer's suggestion that the 1092 cm^{-1} line is due to ν_5 and ν_6 as we consider it better to assign them to the relatively more prominent i.r. group as above.

ν_{25} and ν_{31}. Between 1000 and 1100 cm^{-1} there are two doublets in both i.r. and Raman spectra of the solid, whereas the solutions show only one band each. (The 1050 cm^{-1} i.r. band was considered above *not* to be a fundamental.) The i.r.–Raman doublets centred near 1063 cm^{-1} are *ca.* 8 cm^{-1} higher than the ν_{25} solution value and the Raman doublet is quite strong: we therefore attribute it to ν_{25} (the Raman crystal-symmetry labels are correct). The lower doublet is reasonably assigned to ν_{31}, although the i.r. counterpart may be linked in origin with the 1050 cm^{-1} solution band.

We note that rather large solution to solid upward shifts appear to be associated with π(C–H) modes; also, if our assignments of ν_{25}, ν_{31} are correct, this is the largest of the differences between components of G_4.

ν_{13} and ν_{18}. The Raman and i.r. multiplets between 940 and 1040 cm^{-1} are most probably associated with ν_{13} and ν_{18} as no inactive modes are expected in this region. Since *two* of the Raman lines bear A_g labels we conclude that ν_{18} has become weakly allowed in the Raman spectrum (as expected).

ν_{27} and ν_{33}. ν_{27} and ν_{33} are really skeletal modes and need not be expected in as close proximity as other e_2', e_2'' pairs. ν_{27} was found at 895 cm^{-1} in solution and corresponds to the 896—909 cm^{-1} pair in the Raman spectrum of the crystal. It remains to assign the prominent 868 cm^{-1} i.r. band which has no solution counterpart. We consider this to be ν_{33}.

ν_2 and ν_9; ν_{14} and ν_{19}. From 800 to 900 cm^{-1} both spectra are highly complex. The π(C–H) modes present in solution near 806 and 830 cm^{-1} show up clearly in both i.r. and Raman spectra, yielding multiplets which, for the Raman case, have symmetry labels in accord with predictions based upon the solution assignment. The frequency separation of these multiplets is a little greater than observed at higher frequencies, but these are π(C–H) motions and hence most likely to undergo stronger ring–ring and intermolecular interactions.

ν_{28} and ν_{34}. Between 450 and 712 cm^{-1} the i.r. spectrum of solid ruthenocene is clear but the Raman spectrum exhibits a doublet 606, 602 cm^{-1} bearing the labels $(A_g + B_{1g} + B_{2g} + B_{3g})$, consistent with its assignment as e_2',ν_{28} from solution spectra. The inactive e_2'',ν_{34} could in principle also show up here and may be coincident with ν_{28}.

ν_4, ν_{11}, ν_{16}, and ν_{21}. The four skeletal modes $\nu_4(a_1')$, $\nu_{11}(a_2'')$, $\nu_{16}(e_1'')$, and $\nu_{21}(e_1')$ are in the region 300—450 cm^{-1}. Assignment of ν_4 and ν_{16} is unequivocal and is supported by the single crystal Raman results in that ν_4 yields a doublet $(A_g + B_{2g})$ and ν_{16} a quartet. The 446 cm^{-1} i.r. band does not show through in the Raman spectrum and none of the Raman multiplet components appear in the i.r. spectrum. It could be argued that the Raman band at 394 cm^{-1} is part of the i.r. multiplet centred at 381 cm^{-1} but we think this unlikely in view of the other non-coincidences. ν_{11} should yield a doublet in the i.r. spectrum $(B_{1u} + B_{3u})$ whereas ν_{21} should become a triplet $(B_{1u} + B_{2u} + B_{3u})$. Unfortunately the splitting is not resolved on either of these bands and we reluctantly conclude that there is no *a priori* evidence for the order of ν_{11} and ν_{21} in ruthenocene: the same holds for ferrocene and the cobalticinium ion. However, we find that, at liquid-nitrogen temperature, the i.r. band of ferrocene centred at 497 cm^{-1} is approximately twice the width of that at 479 cm^{-1}. This is consistent with assignment of the higher band as ν_{21} and the lower one as ν_{11}. It is also consistent with the shifts consequent upon deuteriation of ferrocene, the basis upon which Lippincott and Nelson originally assigned $\nu_{21} > \nu_{11}$. For ruthenocene they made the assignment ν_{21} 528 and ν_{11} 446 cm^{-1}. As their i.r. observations were limited to 400 cm^{-1} they did not find the 381 cm^{-1} band; in contrast we cannot find the weak 528 cm^{-1} band and conclude that it was in some way associated with their solution work. Our KBr disc of ruthenocene showed no absorption in this region (Figure 1).

On the simplifying assumption that these molecules may be treated as pseudo-triatomic molecules, equation (1) applies. Since ν_4, a_1' is unequivocally established

$$\nu_{11} = \nu_4\left(1 + \frac{2M_{\text{ring}}}{M_{\text{metal}}}\right)^{\frac{1}{2}} \tag{1}$$

at 303 for ferrocene and 329 cm^{-1} for ruthenocene, ν_{11} is predicted at 553 (ferrocene), 497 cm^{-1} (ruthenocene). The ν_{11} value thus predicted for ferrocene is *ca.* 11% too high owing to inadequacies of the model; if the same assumption applies to ruthenocene the predicted figure is reduced to *ca.* 445 cm^{-1}, effectively coincident with the observed i.r. band at 446 cm^{-1}. This is basically the argument used by Lippincott and Nelson; we agree with it, but are then led to assign the remaining i.r. band (381 cm^{-1}) to ν_{21}, the ' tilt ' mode (*cf.* their erroneous assignment of ν_{21} as 528 cm^{-1}). Although the above triatomic model is oversimplified, we do not believe that it is so far in error as to predict ν_{11} at 497 cm^{-1} if the true value were 381 cm^{-1}. This is the first time that a ' tilt ' mode has been assigned at a lower frequency than the associated M–ring stretch.

ν_6 and ν_{22}. We have not yet considered the two very low-frequency modes ν_{22}, δ (ring–M–ring) and ν_6 (torsion). In both Raman and i.r. spectra there are many bands, due to lattice modes, below 100 cm^{-1}. But between 100 and 350 cm^{-1} we find only the following/cm^{-1}: Raman: 111w, ambient; shifting to 130 at liquid-nitrogen temperature; i.r.: 138w, 165w—m, 172w—m. ν_{22} is i.r.-active. ν_6,a_1'' is inactive in solution (it has zero frequency in Bunker's approximation) but in the solid it has the representation $B_{1g} + B_{3g}$ (Raman) $+ B_{2u}$ (i.r.). Accordingly we assign the 130—138 cm^{-1} bands to ν_6 and the 165—172 cm^{-1} pair to ν_{22}. The Raman polarisations of the 111 cm^{-1} band are $B_{1g} + B_{3g}$, as required. Its very large temperature shift is unique in this spectrum and seems consistent with our assignment of it as the torsional mode since this would be quite significantly affected by lattice contraction.

DISCUSSION

Our assignment is summarised in Table 4 in which frequencies have been taken from solid-state spectra. In the a_1', a_2''; a_2', a_1''; e_1'', e_1' pairs frequencies of corresponding ring modes are very close. The small differences apply to the solid state only and are seen to vanish if solution values are considered, consistent with Bunker's selection rules. Slightly larger differences are found in the e_2',e_2'' sets, but these are not sufficient to throw suspicion on the method of assignment. The only major reservation is attached to assignment of ν_{33}. One could argue, reasonably, that this is really a skeletal mode and there is therefore no reason why ν_{27} and ν_{33} should be particularly close. Nevertheless, knowledge of the symmetry species of the 868 cm^{-1} band would be helpful. If ν_{27} and ν_{33} are well separated, ν_{28} and ν_{34} should be even more so. Whilst the assignment of ν_{28} is well established, that for ν_{34} is only a suggestion. The weak 528 cm^{-1} band found by Lippincott and Nelson might be ν_{34}, but we were unable to locate it in our spectra.

Bodenheimer's assignment[8] differs slightly from ours; we had the benefit of low-temperature i.r. data which, taken together with the Raman spectra, led us to the conclusion of Table 4.

TABLE 4

Assignment for ruthenocene, D_{5h}, in the solid state (frequencies/cm^{-1})

a_1'	ν_1	3111	ν(C–H)	3100	a_2''	ν_8
	ν_2	818	π(C–H)	808		ν_9
	ν_3	1099	ν(C–C)	1099		ν_{10}
	ν_4	333	ν(Ru–ring)	450		ν_{11}
a_2'	ν_7	1251	δ(C–H)	1251	a_1''	ν_5
			Torsion	134		ν_6
e_1''	ν_{12}	3080	ν(C–H)	3080	e_1'	ν_{17}
	ν_{13}	1001	δ(C–H)	1000		ν_{18}
	ν_{14}	839	π(C–H)	829		ν_{19}
	ν_{15}	1410	ν(C–C)	1406		ν_{20}
	ν_{16}	400	Ring tilt	381		ν_{21}
			δ(Ring–Ru–Ring)	168		ν_{22}
e_2'	ν_{23}	3105	ν(C–H)	3095	e_2''	ν_{29}
	ν_{24}	1187	δ(C–H)	1206		ν_{30}
	ν_{25}	1063	π(C–H)	1049		ν_{31}
	ν_{26}	1361	ν(C–C)	1342		ν_{32}
	ν_{27}	902	δ(CCC)	868		ν_{33}
	ν_{28}	604	π(CCC)	604		ν_{34}

EXPERIMENTAL

Ruthenocene was prepared by the method of Bublitz, McEwen, and Kleinberg.[11] Large single crystals were grown by slow evaporation of toluene solutions. Axial directions were determined by both optical and *X*-ray methods. Faces were ground normal to the *a*- and *b*-axes for Raman single-crystal work. A stock sample of ferrocene was recrystallised before use.

I.r. spectra were determined by using a Perkin-Elmer 225 spectrometer and a Beckman-RIIC FS-620 interferometer. Raman work was done with Coderg PH1 and PH0 instruments with 632·8 and 488·0 nm excitation.

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