

## THE RAMAN SPECTRA OF RUTHENOCENE

J. BODENHEIMER*Microwave Division, Department of Physics,  
The Hebrew University, Jerusalem, Israel*

Received 6 July 1970

Raman spectra of ruthenocene single crystals are presented. Assignment in terms of the molecular normal modes is given.

The ruthenocene molecule  $(C_5H_5)_2Ru$  has a sandwich structure similar to that of ferrocene. The molecule has  $21 \times 3 - 6 = 57$  vibrational degrees of freedom, which give rise to 34 modes, of which 15 are Raman-active. Ruthenocene crystallizes in the orthorhombic space group  $D_{2h}^{16}$ , with four molecules per unit cell [1]. The cyclopentadienyl rings lie in an eclipsed configuration, so that the local symmetry of the molecule is  $D_{5h}$ , rather than  $D_{5d}$  in ferrocene. Unlike ferrocene, no phase transition has so far been reported in ruthenocene.

Vibrational spectra of ruthenocene in solution have been studied by Lippincott and Nelson [2], and assignments have been given. No crystal Raman spectra have been reported.

In the crystal one expects 228 modes from the intra-molecular vibrations, of which 114 are Raman-active: each non-degenerate vibration in the molecule gives rise to two Raman-active vibrations in the crystal, whereas each degenerate vibration gives four Raman-active vibrations. This includes also those modes which are inactive in the  $D_{5h}$  symmetry\*. Thus ruthenocene crystal Raman spectra are useful in testing assignments, since the inactive molecular normal vibrations may be expected to show up in the crystal Raman spectrum.

Single crystals were grown from solution in toluene at room temperature. Crystals of suitable dimensions were obtained without difficulty. Spectra were taken at room temperature and at  $80^\circ K$ , with a HeNe laser ( $6328\text{\AA}$ ) as well as an Argon ion laser ( $5145\text{\AA}$  and  $4880\text{\AA}$ ). The accuracy of the measured frequencies is better than  $\pm 2\text{ cm}^{-1}$ .

The results are given in table 1. The frequencies observed by Lippincott and Nelson, in Raman and infrared, are listed in the first and second columns respectively. The assignment in the third column is in general an extension of that given by those authors for their observed lines in solutions, corrected for  $D_{5h}$  symmetry, except for the line at  $1353\text{ cm}^{-1}$  which we have assigned to CC stretching. Lippincott and Nelson assign this line as a combination, and the CC stretching mode is assigned by them to a line at  $1560\text{ cm}^{-1}$ , which has not been observed in ruthenocene by them or by us.

The last column gives the experimental results of our present study. It is obvious that one observes many more lines and detailed structure in the particular assignments, as expected for single crystals. The frequencies listed are those measured at  $80^\circ K$ . The temperature shifts are mostly negligible; the main effect in reducing the temperature is in the line narrowing, thus improving resolution of this complex spectrum. A notable exception is the ring-metal-ring deformation at  $130\text{ cm}^{-1}$ . This frequency appears to shift at room temperatures to  $111.5\text{ cm}^{-1}$ . The explanation for this effect must be sought in the nature of the vibration.

Several weak bands near  $2740\text{ cm}^{-1}$  have been observed at room temperature only, and are assigned to difference bands. Studies on mixed crystals of ferrocene-ruthenocene are in progress.

The advice and assistance of Professor W. Low, and the technical assistance of Mr. A. Gabay and Mr. I. Wagner, are gratefully acknowledged.

\* A detailed analysis will be published.

Table 1  
Vibrational spectra of ruthenocene

Solution (Lippincott and Nelson)		Molecular description	Raman in crystals (80°K) (Present work)
Raman	Infrared		
	---	$E_2'$ ring-metal-ring deform band	130 cm <sup>-1</sup> , large temp. shift
330 cm <sup>-1</sup>	4	$A_1'$ metal-ring stretch	329, 336
402	16	$E_1''$ ring tilt	392, 394(?), 403, 404
	446	$A_2''$ metal-ring stretch	400, 407
	528	$E_1'$ ring tilt	---
---	28, 34	$E_2', E_2''$ ring deform (I) distorted	602, 607
	763	$A_1' + A_2''$ combination	
804	806	$A_1', A_2''$ CH deform (I) stretch band	818
	835	$E_1'', E_1'$ CH deform (I) bend	832, 834, 841, 846, 868
---	27, 33	$E_2', E_2''$ ring deform (II) distortion	896, 909
996	1002	$E_1'', E_1'$ CH deform (II) bend	991, 996, 998(?), 1003, 1012
1056	1050	$E_2', E_2''$ CH deform (I) bend	1049, 1062, 1065, 1068
	7, 5	$A_1'', A_2'$ CH deform (II) bend	1092
1104	1103	$A_1', A_2''$ ring breath	1099, 1101
1193	24, 30	$E_2', E_2''$ CH deform (II) bend	1169(?), 1176(?), 1184, 1194, 1203, 1208
1360	26, 32	$E_2', E_2''$ CC stretch	1359, 1365
1412	1413	$E_1'', E_1'$ CC stretch	1404, 1407, 1411, 1414
	1622		
	1651	Overtone and combination	
	1684	bands, involving	
	1727	CH modes	
	1774		
		difference bands	2736, 2739, 2746, at room temperature only
3089	12, 17	$E_1'', E_1'$ CH stretch	3076, 3083, 3085
3104	3100	$E_2', E_2''$ CH stretch	3092, 3098, 3102
	1, 8	$A_1', A_2''$ CH stretch	3104, 3112, 3113

## REFERENCES

- [1] G. L. Hardgrove and D. H. Templeton, Acta Cryst. 12 (1959) 28.  
 [2] E. R. Lippincott and R. D. Nelson, Spectrochim. Acta 10 (1958) 307.