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ON THE VIBRATIONAL ASSIGNMENTS OF FERROCENE, RUTHENOCENE AND OSMOCENE

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Summary

The solution Raman spectra of ferrocene, ruthenocene and osmocene have been reinvestigated. Polarization measurements in general support previous assignments for Cp_2Fe (Cp = cyclopentadienyl), but the weak line at 1186 cm^{-1} was found to be polarized and a new assignment for this vibration is discussed. An assignment of the skeletal modes for Cp_2Os is made and patterns in the frequencies and force constants in the series Cp_2M (M = Fe, Ru, Os) are discussed.

The vibrational spectra of ferrocene (Cp_2Fe), ruthenocene (Cp_2Ru) and osmocene (Cp_2Os) (Cp = cyclopentadienyl) have been discussed repeatedly in the literature [1-16]. The IR spectra of Cp_2Fe as a gas, solution and solid at ambient and low temperatures have been studied, as have the deutero derivative in the IR and far IR regions, and the Raman spectra of Cp_2Fe and Cp_2Fe-d_{10}. An assignment of the ring and skeletal modes has been given. The first Raman spectrum of a metallocene to be measured was that of Cp_2Fe [1], but no polarization measurements were made in this study because the lines were too weak. The results of such measurements have since been given [16] but only for the strong lines. The Raman spectra of a solution of Cp_2Fe has been obtained [5], but polarization data were not given and, therefore, the assignment of some weak Raman lines may be ambiguous.

In the present study the solution Raman spectra of Cp_2Fe are reinvestigated and our data in general support previous assignments. All Raman lines, assigned to A_{1g} modes, are polarized. In particular, of two weak lines at 812 and 834 cm^{-1} which are assigned to the out-of-plane CH modes of the Cp ring the former was found polarized in CH_3I solution and the latter depolarized (Fig. 1), but unexpectedly the weak line at 1186 cm^{-1}, which is usually assigned to an in-plane CH bending mode $\nu_{24}(E_{2g})$, was found to be polarized in CCl_4 solution (Fig. 1). Earlier we found that the corresponding line of the Cp

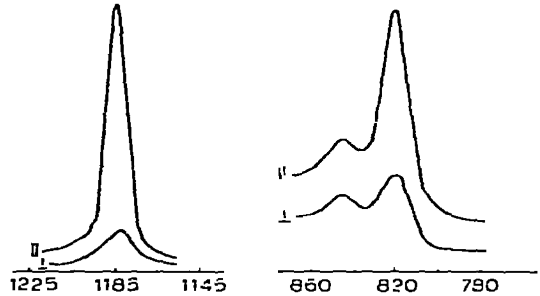

Fig. 1. Raman spectra of Cp_2Fe in the 800 cm^{-1} (CH_3I solution) and 1200 cm^{-1} (CCl_4 solution) regions. ∥, polarized., ⊥, non-polarized.

ring in cyclopentadienylmanganese tricarbonyl is also polarized [19]. This observation is at variance with the previous assignment and the mode is probably the overtone of ν_{28} (out-of-plane Cp mode at about 600 cm^{-1}). In this case the overtone symmetry is $2 \times E_{2g} = A_{1g} + A_{2g} + E_{1g}$. This line may be polarized if the principal contribution to the intensity is made by the A_{1g} component. For instance in the Raman spectrum of Cp_2Ru this line is depolarized [9], but this may be due to different contributions of A_{1g} and E_{1g} components to this line. We were unable to measure the polarization of this line for Cp_2Os because of its low intensity and the low solubility of the compound.

Of special interest for Cp_2M compounds are the skeletal modes. Symmetric (A_{1g}, Raman) and asymmetric (A_{2u}, IR) stretching modes Cp—M, and symmetric and asymmetric ring tilts (E_{2g}, Raman, and E_{1u}, IR respectively) and CpMCp bending modes are expected in the region below 500 cm^{-1} for sandwich complexes. Polarization data have been obtained for the Raman active modes of Cp_2Fe and Cp_2Ru and the assignment is unambiguous. For Cp_2Os Raman data were only available for the solid state [14]. We have now obtained the polarized Raman spectrum of Cp_2Os in CH_3I solution, and we assigned the strong polarized line at 356 cm^{-1} to $\nu_4(A_{1g})$ and the line at 415 cm^{-1} to $\nu_{16}(E_{1g})$. Thus a systematic increase in ν_4 takes place in the series $Cp_2Fe < Cp_2Ru < Cp_2Os$. This regularity can only be explained by an increase in the force constant of the Cp—M bond, because the frequency of $\nu_4(A_{1g})$ does not depend on the mass of the metal atom. It has been shown by crystal splitting in the low-temperature IR spectra of Cp_2Fe that the band at 478 cm^{-1} may be assigned to $\nu_{11}(A_{2u})$ and that at 492 cm^{-1} to $\nu_{21}(E_{1u})$(ring tilt) [14]. For Cp_2Ru and Cp_2Os, the weak bands at 530 cm^{-1} observed only for the solids were earlier assigned to $\nu_{21}(E_{1u})$[4, 14], but the spectra below 400 cm^{-1} were not investigated and the strong IR bands at 380 cm^{-1} (Cp_2Ru) and 353 cm^{-1} (Cp_2Os) were therefore not observed. However, we and other authors [9, 10] observed no bands in the 530 cm^{-1} region for Cp_2Ru and Cp_2Os either in the solid state at room temperature (KBr pellets, Nujol) or in solution, and neither was splitting of the skeletal modes of Cp_2Ru and Cp_2Os in the IR spectra of the solids at low temperatures observed [9, 10]. On the basis of model calculations for Cp_2Ru [9] the band at 446 cm^{-1} is assigned to ν_{11} and that at 380 cm^{-1} to ν_{21}. Thus a change in the order found for Cp_2Fe ($\nu_{21} > \nu_{11}$) is suggested. For the in-phase modes of all three complexes the stretching mode ν_4 is always at a lower frequency than the ring tilt ν_{16}. On

TABLE 1

SKELETAL MODES (cm^{-1}) AND FORCE CONSTANTS (mdyn/Å) FOR Cp_2M

M	$\nu_4(A_{1g})$	$\nu_{11}(A_{2u})$	$\nu_{16}(E_{1g})$	$\nu_{21}(E_{1u})$	$\nu_{22}(E_{1u})$	K(M—Cp)	H
Fe	303	478	388	492	170	3.04	0.48
Ru	329	385	402	446	162 172	3.33	0.85
Os	356	353	415	428	160 166	3.83	0.98

the other hand such an assumption for Cp_2Ru would signify that the in-phase tilt has a higher frequency than the out-of-phase one. This observation caused a change of assignment to ν_{11} 380 cm^{-1} and ν_{21} 446 cm^{-1} [10]. We are of the opinion that such an assignment is more likely and the IR spectra of Cp_2Ru at high pressure also seems to agree with this assignment [15]. Assuming that for Cp_2Os the order must not be changed we assign the band at 353 cm^{-1} to ν_{11} and that at 430 cm^{-1} to ν_{21}. Thus, in contradiction to ν_4, the ν_{11} frequencies decrease in the series $Cp_2Fe > Cp_2Ru > Cp_2Os$, a fact which may be explained by the increase in mass of the metal atom. A result of this is that for Cp_2Os the frequencies ν_4 and ν_{11} are virtually coincident (strong IR band 353 cm^{-1} and polarized Raman line 356 cm^{-1}). Taking into consideration that the mutual exclusion rule works well for Cp_2Ru and Cp_2Fe, IR and Raman bands occuring at the same frequency must be assigned to the different modes.

The force constants, calculated using a simple three mass model, are given in Table 1. In accordance with the ν_4 frequency order they increase in the series $Cp_2Fe < Cp_2Ru < Cp_2Os$.

The behaviour of the ring tilt vibrations is similar to that of the metal—ring stretching modes: the frequency of the in-phase mode increases and that for the out-of-phase mode decreases with increasing atomic weight of the metal atom. The CpMCp bending modes for all compounds in the solid state are located in approximately the same region (160-170 cm^{-1}) and are split because of crystal effects.

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References

1 E.R. Lippincott and R.D. Nelson, Spectrochim. Acta, 10 (1958) 307.
2 L.S. Mayantz, B.V. Lokshin and G.B. Shaltuper, Opt. Spektrosk., 13 (1962) 317.
3 W.K. Winter, B. Curnutte and S.E. Whitcomb, Spectrochim. Acta, 12 (1959) 1085.
4 H.P. Fritz, Advan. Organometal. Chem., 1 (1964) 239.
5 T.V. Long and F.R. Huege, Chem. Commun., 20 (1968) 1239.
6 D. Hartley and M.J. Ware, J. Chem. Soc. A, (1969) 138.
7 J.S. Bodenheimer, E. Loewenthal and W. Low, Chem. Phys. Lett., 3 (1969) 715.
8 J.S. Bodenheimer, Chem. Phys. Lett., 6 (1970) 519.
9 D.M. Adams and W.S. Fernando, J. Chem. Soc. Dalton Trans., (1972) 2507.
10 J.S. Bodenheimer and W. Low, Spectrochim. Acta, Part A, (1973) 1733.

11 R.T. Bailey, Spectrochim. Acta, Part A, 27 (1971) 199.
12 L.J. Hyams, Spectrochim. Acta, Part A, 29 (1973) 839.
13 L.J. Hyams, Chem. Phys. Lett., 18 (1973) 399.
14 J.M. Kimelfeld, E.M. Smirnova, V.T. Aleksanian and A.A. Lubovich, Zh. Strukt. Khim., 14 (1973) 826.
15 K. Nakamoto, C. Udovich, J.R. Ferraro and A. Quattrochi, Appl. Spectrosc., 24 (1970) 606.
16 A. Sado, R. West, H.P. Fritz and L. Schäfer, Spectrochim. Acta, 22 (1966) 509.
17 C. Postmus, K. Nakamoto and J.R. Ferraro, Inorg. Chem., 6 (1967) 2194.
18 J.R. Allkins, R.J. Obremski, C.W. Brown and E.R. Lippincott, Inorg. Chem., 8 (1969) 1450.
19 B.V. Lokshin, V.N. Setkina, E.B. Rusach and N.V. Pyshnograeva, J. Organometal. Chem., 77 (1974) 69.