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## Ultraviolet vapour-phase absorption spectra of $d^6$ metallocenes

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### Abstract

The electronic absorption spectra of vaporous  $Cp_2M$ ,  $Cp_2^*M$  ( $Cp = \eta^5-C_5H_5$ ,  $Cp^* = \eta^5-C_5Me_5$ ;  $M = Fe, Ru, Os$ ) and  $CpRuCp^*$  have been investigated and compared with those of complexes in pentane solution. Vapour-phase spectra differ strongly from those measured in solution. This is due to the presence of Rydberg excitations in the spectra of vaporous metallocenes. The  $Cp_2M$  spectra show two sharp absorption bands which disappear on going from the vapour phase to the solution phase. They have been unambiguously assigned to the symmetry allowed  $nd(a_{1g}) \rightarrow R(n+1)p(e_{1u})$  and  $nd(a_{1g}) \rightarrow R(n+1)p(a_{2u})$  Rydberg transitions ( $n = 3, 4, 5$  for  $M = Fe, Ru, Os$ , respectively). One peak in the vapour-phase spectra of  $Cp_2^*M$  corresponds to these promotions. Two Rydberg bands have been found in the spectrum of vaporous  $CpRuCp^*$ . The excitations from the  $4d(a_1)$  nonbonding orbital to the  $R5s$  and  $R5p$  Rydberg orbitals are responsible for these bands. The electronic absorption spectra of  $d^6$  metallocenes in the vapour phase, in contrast to those in solution, appear to be sensitive to the changes in molecular symmetry.

### Introduction

The study of the absorption of vaporous  $d^6$  metallocenes in the UV region is an area of special interest. The ionization potentials ( $IP$ 's) of these compounds are unusually low (6–8 eV [1–6]), so the lowest Rydberg transitions lie at energies corresponding to absorption in the 20000–50000  $cm^{-1}$  range. Rydberg excitations can appear as sharp, narrow bands in the vapour phase, but they are broadened beyond detection when these compounds are dissolved in the more common solvents [7,8]. Hence, the UV absorption spectra of  $d^6$  metallocenes may be quite different from the well-known solution spectra [9,10].

In the first report on the electronic absorption spectrum of vaporous ferrocene [11] as well as in several recent works [12,13], the possibility of Rydberg excitations was not considered. Such a possibility was taken into account by Richer and Sandorfy [14] who recorded the  $Cp_2Fe$  vapour-phase spectrum in the UV and far UV regions with low resolution. These authors pointed out that some peaks could well represent Rydberg excitation. However, they failed to give a definite assignment. Only recently has the vapour-phase spectrum of  $Cp_2Fe$  been compared with

that obtained in solution [15]. Comparison has shown that two sharp band systems disappeared on going from the vapour phase to the solution phase. The long-wavelength system was interpreted as the  $3d(a_{1g}) \rightarrow R4p$  Rydberg transition. Additional information is however necessary for the assignment of the second band system. Such information can be obtained from the analysis of the  $Cp_2Ru$  and  $Cp_2Os$  vapour-phase UV absorption spectra which have not been investigated up to now. So we decided to record the electronic absorption spectra of vaporous ferrocene, ruthenocene and osmocene under the same conditions and to compare them with the solution spectra. In addition, we have undertaken the study of corresponding decamethylmetallocenes,  $Cp_2^*M$ , as well as of the asymmetrical sandwich  $CpRuCp^*$ , since this could give interesting results concerning the influence of methyl substituents and molecular symmetry on the electronic absorption spectra of  $d^6$  metallocenes.

### Experimental section

We used  $d^6$  metallocenes prepared by previously reported routes [16–23] and purified by repeated vacuum sublimation.

The vapour-phase spectra were measured in a quartz vacuum cell with a Specord UV–Vis spectrometer (Carl Zeiss, Jena, Germany) at 70–150°C. Temperatures were maintained by a coil of resistance wire wrapped around the quartz cell holder. Under these conditions, we could not observe the symmetry-forbidden  $d-d$  transitions because of their low intensity. For comparison, the absorption spectra of the complexes in *n*-pentane solutions were recorded on the same spectrometer at room temperature.

### Results and discussion

The molecular symmetries and the electronic structures of  $d^6$  metallocenes must be briefly considered before analysing their UV absorption spectra. Molecular geometries of  $d^6$  metallocenes were determined both in the crystal [22,24–29] and in the gas phase [30–32]. Most of the  $Cp_2M$  and  $Cp_2^*M$  molecules adopt an eclipsed conformation (the  $D_{5h}$  point group). Only for  $Cp_2^*Fe$  was staggered geometry (the  $D_{5d}$  point group) found both in the solid [28,29] and in the gas phase [31]. Hence, the analysis of electronic excitations in most  $d^6$  metallocenes should be carried out under  $D_{5h}$  symmetry. Nevertheless, the use of the  $D_{5d}$  irreducible representations is traditional when considering the electronic structure of these compounds [1–6]. Inasmuch as the sets of the  $D_{5d}$  and  $D_{5h}$  representations may be correlated and interchanged with ease [33], and the selection rules for the electronic transitions considered in our work are practically identical in both points groups, we use here the  $D_{5d}$  notation to designate the molecular orbitals (MO's) and electronic states of  $Cp_2M$  and  $Cp_2^*M$ . For  $CpRuCp^*$ , the eclipsed conformation, which is more stable [34], corresponds to the  $C_{5v}$  point group. So we consider the spectrum of this compound under the  $C_{5v}$  symmetry.

According to photoelectron spectroscopy data [1–6], the electronic configuration of ground-state  $d^6$  metallocenes is  ${}^1A_{1g}: \dots[\pi(e_{1g})]^4[\pi(e_{1u})]^4[nd(a_{1g})]^2[nd(e_{2g})]^4$  ( $n = 3, 4, 5$  for  $M = Fe, Ru, Os$ , respectively). As for any polyatomic molecule, the unoccupied orbitals of a metallocene may have an intravalence or Rydberg char-

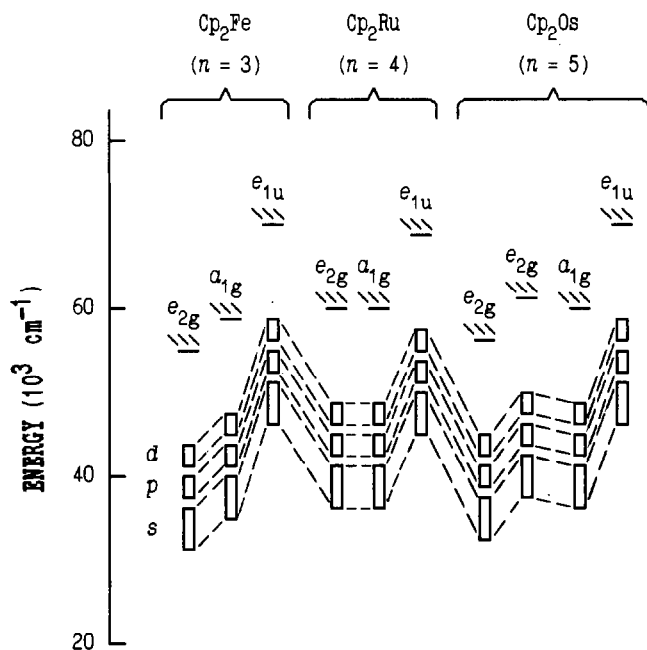


Fig. 1. Energies of ionization from three highest occupied MO's of  $d^6$  metallocenes ( $nd(e_{2g})$ ,  $nd(a_{1g})$  and  $\pi(e_{1u})$ ) and possible energy ranges for Rydberg transitions from these orbitals to the  $R(n+1)s$ ,  $R(n+1)p$  and  $R(n+1)d$  MO's (see text). Two values of  $IP_{e_{2g}}$  for osmocene correspond to the spin-orbit splitting of the  $Cp_2Os^+$  cation  ${}^2E_{2g}$  state into the  ${}^2E_{2(3/2)}$  and  ${}^2E_{2(5/2)}$  components [6].

acter. The orbital set having atomic components with principal quantum numbers larger by 1 or more than those in the outer-shell set constitutes the Rydberg manifold of the molecule [7,8]. Correspondingly, the excited states of  $d^6$  metallocenes can be classified into valence-shell and Rydberg states. Rydberg state is characterized by the term value which represents the binding energy of the Rydberg electron. The term value is equal to the energy separation between the Rydberg transition and the corresponding  $IP$  and is given by the formula [7]:

$$T = R / (n - \delta)^2 \quad (1)$$

where  $R$  is the Rydberg constant ( $109737 \text{ cm}^{-1}$ ),  $n$  is a principal quantum number and  $\delta$  the quantum defect.

The term value for the lowest Rydberg orbital of each type ( $s$ ,  $p$ ,  $d$ , ...) in similar molecules is nearly constant [7,8]. Hence, one can estimate the energies of the Rydberg excitations in  $Cp_2M$  using the  $IP$ 's of metallocenes from photoelectron spectra [1-6] and the term values of Rydberg transitions which have been determined previously [35-39] for bisarene complexes of vanadium, chromium and molybdenum (the molecular structures of these compounds [40,41] are very similar to those of  $d^6$  metallocenes).

Typical term values for the lowest member of the  $s$ ,  $p$  and  $d$  Rydberg series in the spectra of bisarene compounds are 20000-24000, 15000-18000 and 11000-14000  $\text{cm}^{-1}$ , respectively [35-39]. The possible energy ranges for the lowest Rydberg excitations from the three highest occupied MO's of  $Cp_2M$ , calculated from these data and  $IP$ 's [2-6], are given in Fig. 1. It is seen that the transitions from the

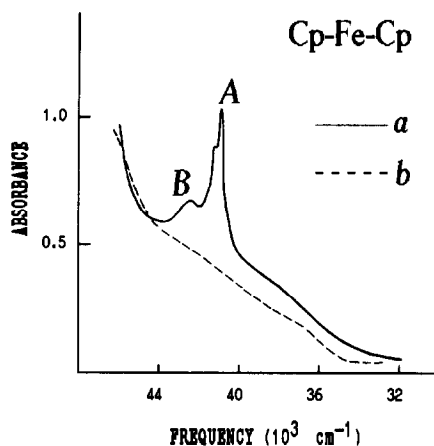


Fig. 2. Electronic absorption spectrum of ferrocene in the vapour phase (a) and in pentane solution (b).

$nd(e_{2g})$  and  $nd(a_{1g})$  MO's to the Rydberg  $(n+1)s$ ,  $(n+1)p$  and  $(n+1)d$  levels as well as the  $\pi(e_{1u}) \rightarrow R(n+1)s$  excitation lie at energies corresponding to absorption in the spectral region investigated in this work (20000–50000  $\text{cm}^{-1}$ ).

The  $nd(e_{2g}) \rightarrow R(n+1)p(e_{1u})$ ,  $nd(a_{1g}) \rightarrow R(n+1)p(e_{1u})$ ,  $nd(a_{1g}) \rightarrow R(n+1)p(a_{2u})$  and  $\pi(e_{1u}) \rightarrow R(n+1)s(a_{1g})$  transitions are symmetry-allowed under the  $D_{5d}$  point group. In addition, the  $nd(e_{2g}) \rightarrow R(n+1)d(e_{2g})$  promotion becomes allowed on going to the  $D_{5h}$  symmetry. These Rydberg excitations can be responsible for the intense absorption bands disappearing when one goes from the vapour-phase UV spectra of  $d^6$  metallocenes to the solution spectra. We have found such bands in all spectra obtained in this work.

The electronic absorption spectra of  $\text{Cp}_2\text{M}$  are given in Figs. 2–4. As for ferrocene, the vapour-phase spectra of ruthenocene and osmocene appear to be quite different from the solution spectra. Two comparatively narrow, intense bands A and B represent the prominent features in the absorption of vaporous  $\text{Cp}_2\text{M}$

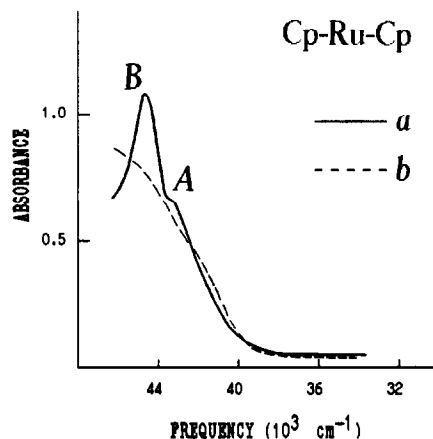


Fig. 3. Electronic absorption spectrum of ruthenocene in the vapour phase (a) and in pentane solution (b).

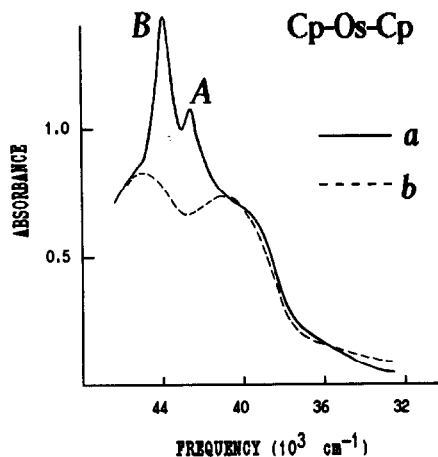


Fig. 4. Electronic absorption spectrum of osmocene in the vapour phase (a) and in pentane solution (b).

(Figs. 2–4 (a)). These peaks are absent in the solution spectra which exhibit only very broad structureless features (Figs. 2–4 (b)). The A and B frequencies are summarised in Table 1. In  $\text{Cp}_2\text{Fe}$  (Fig. 2 (a)), these bands display a vibrational structure. Short progressions in the symmetric metal–ring stretching frequency,  $\nu_4'$ , were found in ref. 15.

Table 1

Frequencies  $\nu$  ( $\text{cm}^{-1}$ ) for bands which disappear from the spectra of  $d^6$  metallocenes on going from the vapour phase into solution (Figs. 2–8). The term values  $T$  ( $\text{cm}^{-1}$ ) calculated using the energies of ionization from three highest occupied MO's ( $IP_{1g}$ ,  $IP_{e_{2g}}$ ,  $IP_{e_{1u}}$ ) [2–6] and the band assignments are presented

Band	Complex	$\nu$	$T_{e_{2g}}^a$	$T_{a_{1g}}^a$	$T_{e_{1u}}^a$	Assignment
A	$\text{Cp}_2\text{Fe}$	41000	14580	17480	29580	$3d(a_{1g}) \rightarrow R4p(e_{1u})$
	$\text{Cp}_2\text{Ru}$	43300	16780	16780	25010	$4d(a_{1g}) \rightarrow R5p(e_{1u})$
	$\text{Cp}_2\text{Os}$	42520	15140	17350	27060	$5d(a_{1g}) \rightarrow R6p(e_{1u})$
			20460 <sup>b</sup>			
B	$\text{Cp}_2\text{Fe}$	42500	13080	15980	28080	$3d(a_{1g}) \rightarrow R4p(a_{2u})$
	$\text{Cp}_2\text{Ru}$	44600	15480	15480	23710	$4d(a_{1g}) \rightarrow R5p(a_{2u})$
	$\text{Cp}_2\text{Os}$	44040	13620	15830	25540	$5d(a_{1g}) \rightarrow R6p(a_{2u})$
			18940 <sup>b</sup>			
C	$\text{Cp}_2^*\text{Fe}$	36000	11420	14650	22960	$3d(a_{1g}) \rightarrow R4p(e_{1u}, a_{2u})$
	$\text{Cp}_2^*\text{Ru}$	39070	15290	15290	20130	$4d(a_{1g}) \rightarrow R5p(e_{1u}, a_{2u})$
	$\text{Cp}_2^*\text{Os}$	38840	12450	15290	20360	$5d(a_{1g}) \rightarrow R6p(e_{1u}, a_{2u})$
			17620 <sup>b</sup>			
D	$\text{CpRuCp}^*$	37200	20060	20060	–	$4d(a_1) \rightarrow R5s(a_1)$
E	$\text{CpRuCp}^*$	40700	16560	16560	–	$4d(a_1) \rightarrow R5p(e_1, a_1)$

<sup>a</sup>  $T_{e_{2g}} = IP_{e_{2g}} - \nu$ ,  $T_{a_{1g}} = IP_{a_{1g}} - \nu$ ,  $T_{e_{1u}} = IP_{e_{1u}} - \nu$ . <sup>b</sup> Two term values are due to the splitting of the  ${}^2E_{2g}$  state of the  $\text{Cp}_2\text{Os}^+$  and  $\text{Cp}_2^*\text{Os}^+$  cations into the  ${}^2E_{2(3/2)}$  and  ${}^2E_{2(5/2)}$  components as a result of spin–orbit coupling [5,6].

Using the data on the vapour pressure of  $d^6$  metallocenes [42,43], we have estimated the molar extinction coefficients at the A and B maxima to be 3000–5000  $\text{l mol}^{-1} \text{cm}^{-1}$ . Taking into account the contribution from the broad features, on which the narrow peaks are superimposed (Figs. 2–4 (a)), we have received for bands A and B the “pure”  $\epsilon$  values of 1000–3000  $\text{l mol}^{-1} \text{cm}^{-1}$ . These magnitudes correspond to the symmetry allowed transitions.

The disappearance of absorption bands on going from the vapour to the dense phase may be indicative of their Rydberg nature [7,8]. In fact, band A in  $\text{Cp}_2\text{Fe}$  was assigned as the symmetry allowed  $3d(a_{1g}) \rightarrow R4p$  Rydberg excitation [15]. This assignment can be verified by the calculation of the A-band term values for  $\text{Cp}_2\text{Ru}$  and  $\text{Cp}_2\text{Os}$ . The investigations of Rydberg excitations in  $(\eta^6\text{-Arene})_2\text{Cr}$  and  $(\eta^6\text{-Arene})_2\text{Mo}$  [38,39] have demonstrated that the term value of the  $nd(a_{1g}) \rightarrow R(n+1)p$  transition did not change on going down a group in the periodic table. Hence, if the assignment from ref. 15 is correct, separations between the energy of ionization from the  $nd(a_{1g})$  MO ( $IP_{a_{1g}}$ ) and the A-band frequency ( $\nu_A$ ) would be expected to be very similar in ferrocene, ruthenocene and osmocene.

The term values calculated with use of  $IP_{e_{2g}}$ ,  $IP_{a_{1g}}$  and  $IP_{e_{1u}}$  [2–6] are listed in Table 1. In the photoelectron spectrum of  $\text{Cp}_2\text{Ru}$  [2], the bands arising from the  $4d(e_{2g})$  and  $4d(a_{1g})$  orbitals overlap, so the energy corresponding to the first photoelectron maximum (7.45 eV [2]) was taken here as both  $IP_{e_{2g}}$  and  $IP_{a_{1g}}$ . It is clearly seen from Table 1 that the  $(IP_{a_{1g}} - \nu_A)$  values for  $\text{Cp}_2\text{Ru}$  and  $\text{Cp}_2\text{Os}$  are indeed very close to that of  $\text{Cp}_2\text{Fe}$ , while there is an appreciable difference both in  $(IP_{e_{2g}} - \nu_A)$  and in  $(IP_{e_{1u}} - \nu_A)$ . Consequently, band A in the spectra of  $\text{Cp}_2\text{M}$  originates at the  $nd(a_{1g})$  MO, and only  $IP_{a_{1g}}$  should be used to calculate its true term value. The  $(IP_{a_{1g}} - \nu_A)$  magnitudes (Table 1) indicate that peak A arises from the excitation terminating at the lowest Rydberg  $p$  orbital. In other words, band A in the spectra of vaporous  $\text{Cp}_2\text{M}$  must be interpreted as the  $nd(a_{1g}) \rightarrow R(n+1)p$  transition. Thus, comparison of the vapour-phase absorption of  $\text{Cp}_2\text{Ru}$  and  $\text{Cp}_2\text{Os}$  with that of  $\text{Cp}_2\text{Fe}$  strongly supports the A-band assignment suggested previously [15].

Band B in the spectrum of vaporous  $\text{Cp}_2\text{Fe}$  has the term values (Table 1) appropriate for its interpretation as either  $3d(a_{1g}) \rightarrow R4p$  or  $3d(e_{2g}) \rightarrow R4d$  Rydberg excitation. However, the assignment of peak B to the transition from the  $3d(e_{2g})$  orbital can be ruled out on the basis of the B-band term values in  $\text{Cp}_2\text{Ru}$  and  $\text{Cp}_2\text{Os}$ . Table 1 shows the large differences in the  $(IP_{e_{2g}} - \nu_B)$  values for ferrocene, ruthenocene and osmocene, while the magnitudes of  $(IP_{a_{1g}} - \nu_B)$  are very similar. Thus, we are led to the conclusion that both band A and band B in the vapour-phase spectra of  $\text{Cp}_2\text{M}$  correspond to the  $nd(a_{1g}) \rightarrow R(n+1)p$  promotion. The existence of two peaks arising from this excitation is due to the splitting of the Rydberg  $p$  orbital into MO's of the  $a_{2u}$  and  $e_{1u}$  types under  $D_{5d}$  symmetry. The question is now what type of the upper orbital corresponds to each peak. The comparison with bisarene complexes appears to be helpful in solving this problem.

In  $\text{Bz}_2\text{Cr}$  and  $\text{Bz}_2\text{Mo}$  ( $\text{Bz} = \eta^6\text{-C}_6\text{H}_6$ ) which are isoelectronic to  $d^6$  metallocenes, the  $nd(a_{1g}) \rightarrow R(n+1)p$  excitation is responsible for one sharp structured band. This band is split into two components in bis( $\eta^6$ -xylene)chromium and bis( $\eta^6$ -xylene)molybdenum [38,39], indicating the degenerate upper state for the complexes with benzene ligands. Consequently, the spectra of  $\text{Bz}_2\text{Cr}$  and  $\text{Bz}_2\text{Mo}$  exhibit the  $nd(a_{1g}) \rightarrow R(n+1)p(e_{1u})$  transition. The term values for this excitation (17290 and

17230  $\text{cm}^{-1}$  in bis( $\eta^6$ -benzene)chromium and bis( $\eta^6$ -benzene)molybdenum, respectively [38,39]) are very close to the  $(IP_{a_{1g}} - \nu_A)$  magnitudes (Table 1). So we conclude that the A absorption band populates the  $R(n+1)p(e_{1u})$  Rydberg orbital in  $\text{Cp}_2\text{M}$ . Hence, the excitation terminating at the  $R(n+1)p(a_{2u})$  MO is responsible for band B. The term values for peaks A and B (Table 1) are very similar to those for two components of the  $3d(a_{1g}) \rightarrow R4p$  transition in the spectrum of vaporous bis( $\eta^6$ -benzene)vanadium (17450 and 15650  $\text{cm}^{-1}$  [38]). This fact also supports our assignments of bands A and B in  $\text{Cp}_2\text{M}$ . These assignments are summarised in Table 1.

The vapour-phase spectra of  $\text{Bz}_2\text{Cr}$  and  $\text{Bz}_2\text{Mo}$  do not exhibit any sharp bands corresponding to the  $nd(a_{1g}) \rightarrow R(n+1)p(a_{2u})$  excitation [38,39]. This may be caused by mixing of the Rydberg state with valence excited states of the same symmetry [7,8]. On the other hand, the narrowness and vibrational structure of the band arising from the  $nd(a_{1g}) \rightarrow R(n+1)p(e_{1u})$  transition in  $\text{Bz}_2\text{Cr}$  and  $\text{Bz}_2\text{Mo}$  [35–39] indicate that the upper state has almost pure Rydberg character in this case. Bands A and B in the  $\text{Cp}_2\text{M}$  spectra (Figs. 2–4) are also comparatively narrow (width at half-height is 600–1100  $\text{cm}^{-1}$ ). In  $\text{Cp}_2\text{Fe}$ , the vibrational structure is observed. So one can conclude that both Rydberg states corresponding to the  $nd(a_{1g}) \rightarrow R(n+1)p$  excitation in  $\text{Cp}_2\text{M}$  do not mix with valence-shell excited states to any appreciable extent. This is further supported by the total disappearance of peaks A and B on going from the vapour phase into solution (Figs. 2–4) as well as by the very close similarity in term values (Table 1).

The  $nd(a_{1g}) \rightarrow R(n+1)p$  excitations are the lowest members of the Rydberg  $p$  series. The higher members of these series in  $\text{Cp}_2\text{M}$  lie beyond the spectral range investigated in this work. Transitions to higher Rydberg levels may be observed however in the UV absorption of decamethylmetallocenes,  $\text{Cp}_2^*\text{M}$ , since  $IP$ 's of these compounds are lower by  $\sim 1$  eV than those of  $\text{Cp}_2\text{M}$  [3–5]. The spectra of decamethylmetallocenes are given in Figs. 5–7. Vaporous  $\text{Cp}_2^*\text{M}$  shows only one sharp intense band C which disappears on going into solution. The positions of its maxima are listed in Table 1 together with the term values calculated in the same

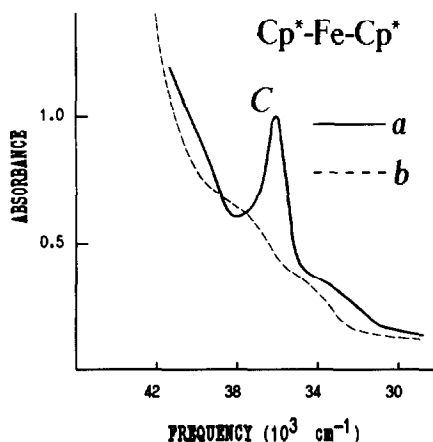


Fig. 5. Electronic absorption spectrum of decamethylferrocene in the vapour phase (a) and in pentane solution (b).

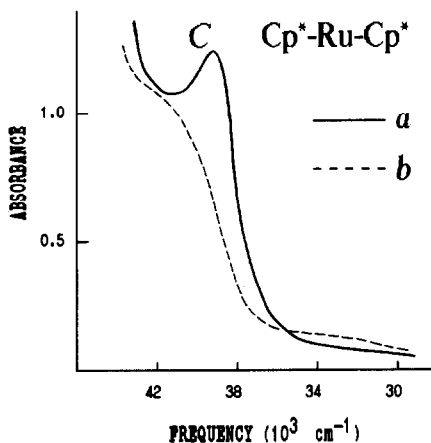


Fig. 6. Electronic absorption spectrum of decamethylruthenocene in the vapour phase (a) and in pentane solution (b).

way as for the A and B bands in  $\text{Cp}_2\text{M}$ . One can see from Table 1 that only use of  $IP_{a_{1g}}$  gives similar term values for band C in all the  $\text{Cp}_2^*\text{M}$  compounds. Arguing as for  $\text{Cp}_2\text{M}$ , we can interpret band C (Figs. 5–7) as the  $nd(a_{1g}) \rightarrow R(n+1)p$  Rydberg excitation without any doubt. The  $(IP_{a_{1g}} - \nu_C)$  magnitudes are close to the  $T_{a_{1g}}$  values for band B in  $\text{Cp}_2\text{M}$  (Table 1). So one may expect band C to arise from the transition terminating at the  $R(n+1)p(a_{2u})$  orbital. However, we believe the assignment of band C to both components of the  $nd(a_{1g}) \rightarrow R(n+1)p$  transition to be more reasonable. The data on chromium and molybdenum bisarene complexes [35–39] show that the methylation of the ring acts to decrease the term value for the  $nd(a_{1g}) \rightarrow R(n+1)p(e_{1u})$  excitation. The similar decreasing of term value for  $d^6$  metallocenes can result in large overlap of two  $nd(a_{1g}) \rightarrow R(n+1)p$  components in the absorption of  $\text{Cp}_2^*\text{M}$ . In that case, peak C (Figs. 5–7) corresponds to both Rydberg bands observed in  $\text{Cp}_2\text{M}$  (Figs. 2–4). Such an interpretation is supported

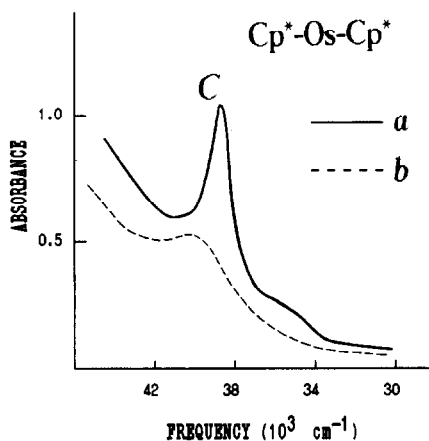


Fig. 7. Electronic absorption spectrum of decamethylosmocene in the vapour phase (a) and in pentane solution (b).



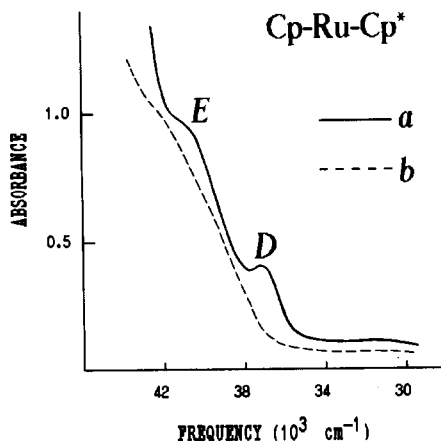


Fig. 8. Electronic absorption spectrum of  $(\eta^5\text{-cyclopentadienyl})(\eta^5\text{-pentamethylcyclopentadienyl})$  ruthenium in the vapour phase (a) and in pentane solution (b).

by some broadening of band C (its width at half-height is  $1200\text{--}1600 \text{ cm}^{-1}$ ) in comparison with the A and B bands.

From the data in Table 1 and by use of (eq. 1), one can calculate the quantum defects for band C in  $\text{Cp}_2^*\text{M}$ . On the basis of the  $\delta$  magnitudes, the term values and frequencies for higher members of the Rydberg  $p$  series can be determined. The  $nd(a_{1g}) \rightarrow R(n+2)p$  excitation is predicted to be at  $42800$ ,  $46250$  and  $46000 \text{ cm}^{-1}$  in  $\text{Cp}_2^*\text{Fe}$ ,  $\text{Cp}_2^*\text{Ru}$  and  $\text{Cp}_2^*\text{Os}$ , respectively. However, no sharp absorption bands correspond to this transition in the spectra of vaporous decamethylmetallocenes (Figs. 5–7). In the  $40000\text{--}50000 \text{ cm}^{-1}$  region, the absorption of  $\text{Cp}_2^*\text{M}$  in the vapour phase is nearly identical to that in solution. This can result from a low intensity of Rydberg transition as well as from mixing of the corresponding Rydberg state with valence excited states.

It is of interest to compare the electronic absorption spectra of  $\text{Cp}_2\text{M}$  and  $\text{Cp}_2^*\text{M}$  with that of the asymmetric complex  $\text{CpRuCp}^*$ . The latter compound can exhibit new bands in absorption since some electronic transitions, which were forbidden by the selection rules in the  $D_{5h}$  point group, become allowed under the  $C_{5v}$  symmetry. However, the solution spectrum of  $\text{CpRuCp}^*$  (Fig. 8(b)) shows no new features in comparison with those of  $\text{Cp}_2\text{M}$  (Figs. 2–4(b)) and  $\text{Cp}_2^*\text{M}$  (Figs. 5–7(b)). Hence, the UV spectra of  $d^6$  metallocenes in solution are insensitive to the reduction of molecular symmetry from  $D_{5h}$  to  $C_{5v}$ .

The situation changes for the vapour-phase spectra. As with  $\text{Cp}_2\text{M}$ , the absorption of vaporous  $\text{CpRuCp}^*$  exhibits two bands which disappear on going into solution (bands D, E in Fig. 8(a)). Their frequencies are given in Table 1. By analogy with symmetric  $d^6$  metallocenes, one can assign these peaks to Rydberg excitations originating at the  $4d(a_1)$  orbital. However, the spacing between D and E bands is noticeably greater than that between the A and B peaks in  $\text{Cp}_2\text{M}$  (Table 1). For the interpretation of bands D and E, the term values must be calculated. Unfortunately, the photoelectron spectrum of  $\text{CpRuCp}^*$  has not been investigated. So the energy of ionization from the  $4d(a_1)$  MO is unknown. In spite of this, one can estimate  $IP_{a_1}$  of  $\text{CpRuCp}^*$  using the known ionization potentials of  $\text{Cp}_2\text{Ru}$  and

$\text{Cp}_2^*\text{Ru}$  [2,5]. There is a linear correlation between the  $d$ -electron ionization energy and the number of methyl groups in the cyclopentadienyl ligands of  $d^6$  metallocenes [4]. Hence, the arithmetic mean of the  $\text{Cp}_2\text{Ru}$  and  $\text{Cp}_2^*\text{Ru}$   $IP_{a_{1g}}$ 's, which equals  $7.10 \text{ eV}$  or  $57260 \text{ cm}^{-1}$ , can be taken as  $IP_{a_1}$  of  $\text{CpRuCp}^*$ . The differences between this value and the D and E frequencies are presented in Table 1. The term value for band E appears to be very close to  $T_{a_{1g}}$  for band A in  $\text{Cp}_2\text{Ru}$  (Table 1). This indicates that band E corresponds to the  $4d(a_1) \rightarrow R5p(e_1)$  Rydberg excitation. However, the comparatively low precision of estimation of  $IP_{a_1}$  makes it possible to interpret this feature as both components of the  $4d(a_1) \rightarrow R5p$  transition.

The term value for band D (Table 1) is too large to assign this peak as a Rydberg excitation terminating at the  $R5p$  orbital. This term value is very similar to that for the  $nd(a_{1g}) \rightarrow R(n+1)s(a_{1g})$  transition in methylated derivatives of  $\text{Bz}_2\text{Cr}$  and  $\text{Bz}_2\text{Mo}$  ( $19800 \text{ cm}^{-1}$  for bis( $\eta^6$ -toluene)chromium [37,38] and  $20100 \text{ cm}^{-1}$  for bis( $\eta^6$ -toluene)molybdenum [39]). The electronic transition from totally symmetric occupied orbital to totally symmetric empty MO is forbidden for  $d^6$  metallocenes under the  $D_{5h}$  and  $D_{5d}$  point groups, but it becomes allowed as symmetry is reduced to  $C_{5v}$ . Hence, band D (Fig. 8(a)) can be unambiguously interpreted as the  $4d(a_1) \rightarrow R5s(a_1)$  Rydberg excitation. The presence of this peak in absorption of vaporous  $\text{CpRuCp}^*$  demonstrates that the vapour-phase absorption spectra of  $d^6$  metallocenes are sensitive to changes in molecular symmetry, in contrast to the solution spectra.

In general, it should be noted that all the Rydberg transitions we have observed here originate in the totally symmetric  $nd$  orbital. The vapour-phase spectra of  $d^6$  metallocenes show no peaks corresponding to the lowest Rydberg excitations from the  $nd(e_{2g})$  MO though these excitations lie in the  $20000\text{--}50000 \text{ cm}^{-1}$  region (Fig. 1). In other words, Rydberg bands arising from the transitions, which originate in the  $nd(e_{2g})$  orbital of  $d^6$  metallocenes, are broadened beyond detection. This can be due to the somewhat enhanced bonding character of the  $nd(e_{2g})$  MO compared with the  $nd(a_{1g})$  orbital as well as to strong mixing of the Rydberg states, populated by promotions from the  $nd(e_{2g})$  MO, with manifold valence excited levels.

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