Rydberg transitions in the near-ultraviolet vapor-phase absorption spectra of 3d metallocenes

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Abstract

The electronic absorption spectra of Cp_2M (M = V, Cr, Mn, Fe, Co, Ni; $Cp = \eta^5\text{-}C_5H_5$), Cp'_2Fe ($Cp' = \eta^5\text{-}C_5H_4Me$) and Cp^*_2Mn ($Cp^* = \eta^5\text{-}C_5Me_5$) in the vapor phase have been investigated. Vapor-phase spectra differ from the solution ones. In the most cases, this is caused by the presence of Rydberg bands in the vapor-phase absorption spectra. These bands disappear on going to the spectra of solutions. The $3d(a_{1g}) \rightarrow Rnp$ Rydberg transitions are revealed most clearly. The bands at 40 700, 41 000, 41 240, 41 570 cm^{-1} in the spectrum of Cp_2Fe and the band at 39 650 cm^{-1} in the spectrum of Cp'_2Fe are unambiguously assigned to the $3d(a_{1g}) \rightarrow R4p$ transition which displays a vibrational structure for ferrocene (0,0 transition at 41 000 cm^{-1}). In addition, the vapor-phase spectrum of ferrocene shows bands at 42 490 and 42 800 cm^{-1} which can be assigned to the second component of the $3d(a_{1g}) \rightarrow R4p$ transition. The peaks at 39 400 and 46 470 cm^{-1} in the spectrum of vaporous vanadocene correspond to the two first members of the Rydberg series: $3d(a_{1g}) \rightarrow R4p$ and $3d(a_{1g}) \rightarrow R5p$. Analogous assignment for the bands at 35 000 and 45 000 cm^{-1} in the vapor-phase spectrum of nickelocene seems to be reasonable. For Cp^*_2Mn, the $3d(a_{1g}) \rightarrow Rnp$ (n = 4, 5, 6) Rydberg series is observed. The energy of ionization from the $3d(a_{1g})$ orbital of Cp^*_2Mn (5.4 eV) has been determined as a convergence limit of the series. The shoulder at 48 450 cm^{-1} in the spectrum of vaporous chromocene may be interpreted as one of the first members of the Rydberg *np* series. The intensity of the band at 47 000 cm^{-1} in the spectrum of cobaltocene changes when going from the vapor phase to solution. This can be explained by the contribution of the $3d(a_{1g}) \rightarrow R4p$ Rydberg transition.

Introduction

Electronic absorption spectroscopy plays an important role in the investigation of the electronic structure of 3d metallocenes. The ultraviolet and visible spectra of 3d metallocenes in solutions are well known [1]. However, these spectra give little information. As a rule, they show broad structureless bands which correspond to the d–d or charge-transfer transitions. It is difficult to make a concrete assignment for the strong bands in these spectra. The vapor-phase electronic absorption spectra of 3d metallocenes may be more interesting. The ionization potentials (*IP*) of Cp_2M are low [2–5]. So the bands corresponding to the Rydberg transitions from the upper occupied molecular orbitals (MO) may be observed in the near-UV spectra of vaporous metallocenes. The ionization potentials can be estimated from the frequencies of Rydberg bands. Hence, near-

UV vapor-phase absorption spectra of metallocenes may give information to supplement the photoelectron spectroscopy data. The electronic absorption spectra of Cp_2V, Cp_2Cr and Cp_2Mn in the vapor phase have not been investigated up to now. The spectrum of vaporous ferrocene was studied by McGlynn and co-workers [6] more than 20 years ago. However, these authors did not consider the possibility of the presence of Rydberg bands. Such a possibility was taken into account by Richer and Sandorfy and co-workers [7, 8] when analysing the spectra of Cp_2Fe, Cp_2Co and Cp_2Ni in the vapor phase. They pointed out that the peaks at 41 000 and 41 500 cm^{-1} in the Cp_2Fe spectrum could well be Rydberg. However, they failed to give a more concrete assignment. The sharp Rydberg bands were not revealed in the spectra of vaporous Cp_2Co and Cp_2Ni [7, 8].

Some Rydberg series were found in the multi-photon dissociation/ionization spectra of similar organometallic compounds [9, 10]. However, these series arose not from the organometallic molecules themselves but from the metal atoms which were formed in the process of multiphoton dissociation.

On the other hand, we have recently found the Rydberg series in the vapor-phase absorption spectra of bisarene complexes of vanadium [11, 12], chromium [12–14] and molybdenum [15]. The convergence limits corresponded to the ionization from the $3d(a_{1g})$ non-bonding orbital. These works have demonstrated that the electronic absorption spectra of sandwich complexes in the vapor phase and in solution must be compared in order to reveal Rydberg transitions. Rydberg bands disappeared on going from the vapor phase to the solution.

This situation prompted us to investigate the electronic absorption spectra of vaporous 3d metallocenes and to compare them with the solution spectra as well as with the spectra of bisarene complexes in the vapor phase [11–15].

Experimental

Ferrocene was obtained from commercial sources. Other metallocenes as well as 1,1'-dimethylferrocene and decamethylmanganocene were prepared by previously reported routes [16–18]. All compounds were purified by repeated vacuum sublimation.

Vapor-phase electronic absorption spectra were recorded using a vacuum cell on a Specord UV–Vis (Carl Zeiss, Jena, F.R.G.) spectrometer at 50–150 °C. For comparison, the absorption spectra of some 3d metallocenes in n-pentane solution were recorded on the same spectrometer at room temperature. Error in determination of the band positions was 50–100 cm^{-1} for the narrow bands and 150–250 cm^{-1} for the broad bands and shoulders. We could not observe the bands corresponding to the symmetry forbidden d–d transitions in the vapor-phase spectra because of their low intensity.

Results and discussion

Consideration of the molecular symmetry is important for the interpretation of the electronic absorption spectra. The structures of 3d metallocenes were determined in X-ray and electron diffraction studies [19–28]. The geometry of the Cp_2M molecules (M = V, Co, Ni) in crystals is staggered (the D_{5d} point group) [19, 22, 23], whereas the structure of
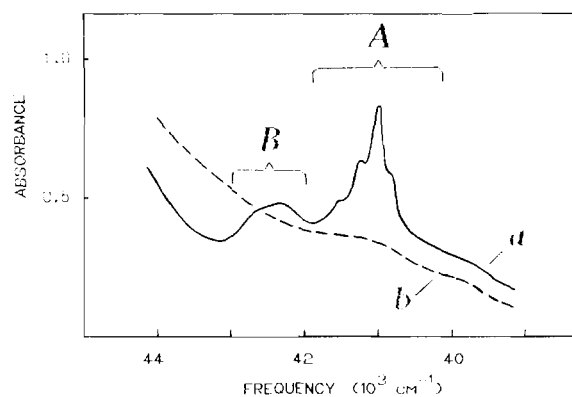

Fig. 1. The electronic absorption spectrum of ferrocene in the vapor phase (a) and in the pentane solution (b).
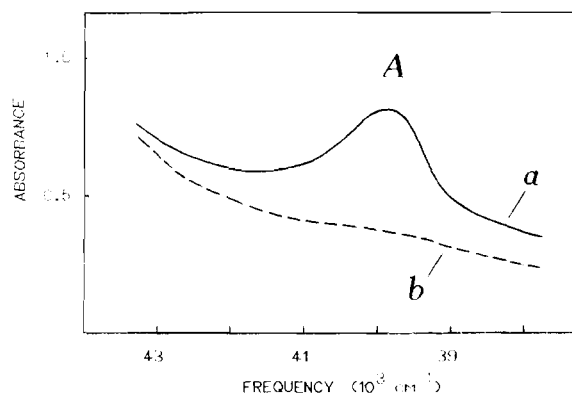

Fig. 2. The electronic absorption spectrum of Cp'_2Fe in the vapor phase (a) and in the pentane solution (b).

unsubstituted 3d metallocenes in the vapor phase is in a better accordance with the eclipsed (D_{5h}) conformation [24–28]. Decamethylmanganocene displays the D_{5d} symmetry both in the crystal [29] and in the vapor phase [30]. Hence, the analysis of the electronic transitions in the metallocene molecules should be carried out under D_{5d} or D_{5h} symmetry. Use of the D_{5d} group is traditional [1–8]. Since each cyclopentadienyl ring rotates easily [31], the Cp_2M complexes are considered sometimes under D_5 [32] or $C_{\infty v}$ [33] symmetry. However, an analysis shows that the selection rules for the electronic transitions considered in our work are identical in all point groups mentioned. So we use traditionally the D_{5d} irreducible representations to designate the symmetry of MOs and electronic states of metallocenes.

The electronic absorption spectra obtained are presented in Figs. 1–9. The spectra are given in that sequence which corresponds to the logic of further detailed analysis. The comparison of vapor-phase spectra with the well-known data for solutions [1]
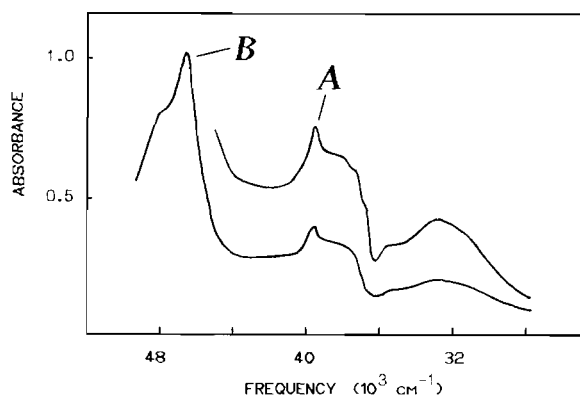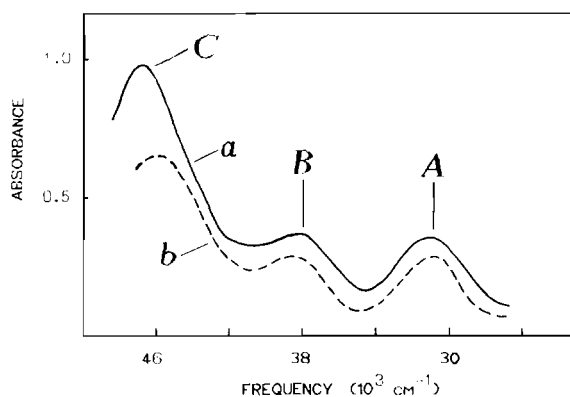
Fig. 3. The vapor-phase absorption spectrum of Cp$_2$V.

Fig. 6. The electronic absorption spectrum of Cp$_2$Co in the vapor phase (a) and in the pentane solution (b).

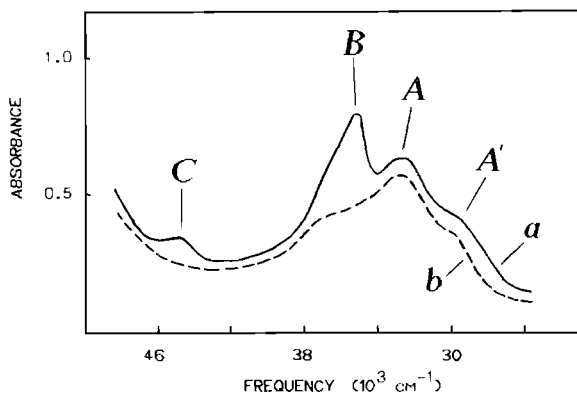

Fig. 4. The electronic absorption spectrum of Cp$_2$Ni in the vapor phase (a) and in the pentane solution (b).
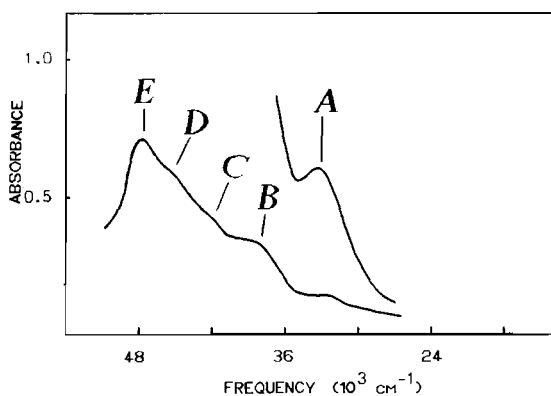
Fig. 7. The vapor-phase absorption spectrum of Cp$_2$Mn.
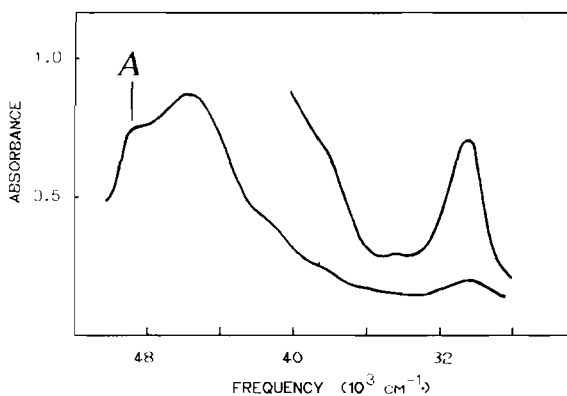
Fig. 5. The vapor-phase absorption spectrum of Cp$_2$Cr.
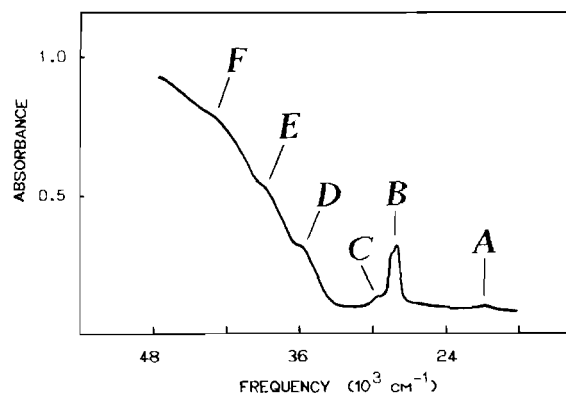
Fig. 8. The vapor-phase absorption spectrum of Cp*$_2$Mn.

as well as with the solution spectra recorded in this work shows that a number of absorption bands disappear on going from the vapor to the condensed phase. This can be indicative of the Rydberg origin of such bands [34, 35].

Rydberg transitions are easily identified when the electronic absorption spectrum shows a series converging to the ionization limit. The frequencies of the series' members are given by the Rydberg formula

$$\nu_n = I - R/(n - \delta)^2 \qquad (1)$$

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Fig. 9. The electronic absorption spectrum of Cp*$_2$Mn in the pentane solution.

where I is an ionization limit, R the Rydberg constant, n is a principal quantum number and δ the quantum defect. The long series were observed in the vapor-phase spectra of bisarene complexes [11–15]. The spectra of 3d metallocenes however show only one or two bands which disappear on going from the vapor phase to solution. The employment of the Rydberg formula is not effective in this case.
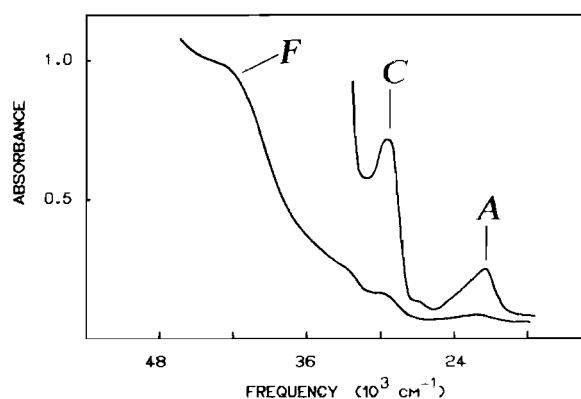
Another criterion can be used however for the assignment of an absorption band to the Rydberg transition. This is the term value (i.e. the difference between the energy of ionization from a MO and the energy of the Rydberg transition from the same MO). The term value for the lowest Rydberg orbital of each type (s, p, d,...) in the similar molecules is nearly constant [34, 35]. This can be used for the identification of the Rydberg bands in the spectra of 3d metallocenes.

The term values for the lowest Rydberg transitions in the spectra of (η^6-arene)$_2$M (M = V, Cr) are known [12, 13]. Since the molecular structures of Cp$_2$M and (η^6-arene)$_2$M are similar, one can expect that the Rydberg term values for 3d metallocenes will be close to those for bisarene complexes. The vapor-phase spectra of (η^6-arene)$_2$M show the Rydberg bands originating from the 3d(a_{1g}) orbital only [11–15]. So the energy of ionization from the 3d(a_{1g}) MO ($IP_{a_{1g}}$) should be used in the first place to calculate the term values for the Rydberg bands in the spectra of 3d metallocenes.

Ionization energies of the metallocenes considered were determined in photoelectron studies [2–5]. However, an unequivocal interpretation of the metal d ionization structure was only given for Cp$_2$Fe, Cp'$_2$Fe, Cp$_2$V and Cp*$_2$Mn. Several alternative assignments were suggested for the bands in the photoelectron spectra of Cp$_2$Cr, Cp$_2$Mn, Cp$_2$Co and Cp$_2$Ni [2–4]. So we have calculated first the term values for the long-wave absorption bands which disap-

peared on going from the vapor-phase spectra of ferrocene, 1,1'-dimethylferrocene, vanadocene and decamethylmanganocene to the solution ones (Table 1). It can be seen from Table 1 that the values obtained are indeed very close to the lowest Rydberg term values for Bz$_2$V and Bz$_2$Cr (Bz = η^6-benzene). This supports strongly the assignment of the disappearing absorption bands to the Rydberg transitions. The detailed analysis of each metallocene spectrum should be carried out for the more concrete interpretation of Rydberg bands. We begin our analysis with the spectrum of Cp$_2$Fe since the electronic structure of this complex is very similar to that of Bz$_2$Cr for which the Rydberg transitions were thoroughly investigated [12, 13].

Ferrocene and 1,1'-dimethylferrocene

The spectrum of ferrocene in the vapor phase recorded in the present work (Fig. 1(a)) is in a good agreement with the results of McGlynn and co-workers [6] and Richer and Sandorfy [7]. The relative intensities of the bands in this spectrum differ from those obtained in the synchrotron studies [36, 37]. The electronic absorption spectrum of vaporous ferrocene (Fig. 1(a)) shows a broad shoulder at $\sim 37\,700$ cm^{-1} and the systems of bands A and B corresponding to the VII–XI systems revealed in ref. 6. System A consists of the bands at $\sim 40\,700$ (shoulder), 41 000, 41 240 and $\sim 41\,570$ (shoulder) cm^{-1}, the peak at 41 000 cm^{-1} being the strongest. The average distance between the neighbouring bands in system A (290 cm^{-1}) corresponds to the frequency of the symmetric ring–metal stretch ν_4 (303 cm^{-1} for ferrocene in the ground electronic state [38]). System A disappears on going from the vapor-phase spectrum (Fig. 1(a)) to the solution one (Fig. 1(b)). So it may be supposed that the Rydberg transition is responsible for this system.

The electronic configuration of ferrocene in the ground state is $^1A_{1g}$: ...$[\pi(e_{1g})]^4[\pi(e_{1u})]^4$-$[3d(a_{1g})]^2[3d(e_{2g})]^4$ [3–5]. Two first bands in the photoelectron spectrum of Cp$_2$Fe are assigned to the 3d(e_{2g}) and 3d(a_{1g}) orbitals [3–5] (corresponding ionization potentials are 6.88 ($IP_{e_{2g}}$) and 7.23 ($IP_{a_{1g}}$) eV [3]). Obviously, one of these orbitals participates in the Rydberg transition corresponding to system A (Fig. 1(a)). Only 3d(a_{1g}) → Rnp Rydberg transitions are observed in the spectrum of vaporous Bz$_2$Cr. So it may be presumed that system A in the spectrum of Cp$_2$Fe corresponds to the Rydberg transition from the 3d(a_{1g}) MO as well. Indeed, the difference between the $IP_{a_{1g}}$ value and the frequency of the strongest band of system A ($\nu = 41\,000$ cm^{-1}) appears to be practically equal to the term value for the 3d(a_{1g}) → R4p 0,0 transition in Bz$_2$Cr (Table 1). Thus,

TABLE 1. Frequencies ν (cm^{-1}) and term values T^a (cm^{-1}) for the long-wave absorption bands which disappear on going from the vapor-phase spectra of Cp$_2$Fe, Cp$'_2$Fe, Cp$_2$V and Cp$^*_2$Mn to the solution ones. For comparison, the frequencies and the term values of the 3d(a$_{1g}$)→R4p Rydberg transitions in the spectra of Bz$_2$V^b and Bz$_2$Cr [12] are given

Complex	Cp$_2$Fe		Cp$'_2$Fe	Cp$_2$V	Cp$^*_2$Mn		Bz$_2$V		Bz$_2$Cr
Band^c	A	B	A	A	B	B			
ν	41000^d	42490^d	39650	39400	27800	28100	32130	34030	26700^d
T	17350	15860	17320	15280	15190	14890	17550	15650	17290

^{a}Term values were calculated using $IP_{a_{1g}}$ [3, 4]. ^{b}Bz = η^6-C$_6$H$_6$. ^{c}The bands are designated according to Figs. 1–3, 8. ^{d}The strongest peak in the vibrational progression.

system A can be unambiguously assigned to the allowed 3d(a$_{1g}$)→R4p Rydberg transition. The strongest band of system A corresponds to the 0,0 transition as it was for Bz$_2$Cr [12, 13]. This is in agreement with the non-bonding character of the 3d(a$_{1g}$) orbital [32]. The shoulder at 40 700 cm^{-1} (Fig. 1(a)) is evidently a hot band (the excitation of the ν_4(a$_{1g}$) vibration in the ground state). The bands at 41 240 and 41 570 cm^{-1} are the members of a vibrational progression. Similar hot band and progression are present in the system of bands corresponding to the 3d(a$_{1g}$)→R4p transition in the Bz$_2$Cr vapor-phase spectrum [12, 13].

System A in the spectrum of vaporous 1,1'-dimethylferrocene (Fig. 2(a)) is observed as a comparatively broad band (maximum at 39 650 cm^{-1}) disappearing on going to the solution spectrum (Fig. 2(b)). The absence of vibrational structure is, obviously, caused by the increase in the number of allowed vibronic transitions. This increase is a result of the symmetry reduction. A similar effect takes place in the spectra of alkylsubstituted derivatives of Bz$_2$Cr [12, 13]. The difference between $IP_{a_{1g}}$ and the frequency of band A for Cp$'_2$Fe (Table 1) is very close to the term value of the 3d(a$_{1g}$)→R4p 0,0 transition in the spectra of ferrocene and Bz$_2$Cr. The intensity maximum of system A is red shifted by 1350 cm^{-1} on going from Cp$_2$Fe to Cp$'_2$Fe. A similar shift (1170 cm^{-1}) was observed for the 3d(a$_{1g}$)→R4p 0,0 transition in the spectra of bis(η^6-benzene)chromium and bis(η^6-toluene)chromium [12, 13]. All these facts confirm the suggested assignment of system A.

System B in the Cp$_2$Fe vapor-phase spectrum (Fig. 1(a)) consists of the band at 42 490 cm^{-1} and the shoulder at ~42 800 cm^{-1}. This system disappears on going to the solution spectrum, so it can arise from the Rydberg transition. The term value for the band at 42 490 cm^{-1} (Table 1) is very close to that for the 3d(a$_{1g}$)→R4p transition in the Bz$_2$V spectrum

[12]. Thus, system B in the spectrum of vaporous ferrocene can be assigned to the 3d(a$_{1g}$)→R4p Rydberg transition as is system A. The presence of two 3d(a$_{1g}$)→R4p transitions is caused by the splitting of the R4p Rydberg orbital into MOs of the e$_{1u}$ and a$_{2u}$ type under D_{5d} symmetry. For benzene (D_{6h} point group), the np(a$_{2u}$) Rydberg orbitals lie at higher energies than the np(e$_{1u}$) MOs [35]. So we believe that the assignment of systems A and B to the 3d(a$_{1g}$)→R4p(e$_{1u}$) and 3d(a$_{1g}$)→R4p(a$_{2u}$) transitions, respectively, is the most probable. Table 1 shows that the R4p(a$_{2u}$) − R4p(e$_{1u}$) energy separation in Cp$_2$Fe is very close to that in Bz$_2$V.

Thus, the analysis of the term values seems to be helpful for the assignment of Rydberg bands in the spectra of ferrocene and 1,1'-dimethylferrocene.

Vanadocene and nickelocene

The ground electronic state of these metallocenes is A$_{2g}$. The configuration of ground state vanadocene is ^{4}A$_{2g}$: ...[π(e$_{1g}$)]^4[π(e$_{1u}$)]^4[3d(a$_{1g}$)]^1[3d(e$_{2g}$)]^2 [3–5]. The electronic absorption spectrum of vaporous Cp$_2$V is given in Fig. 3. There is an intensive band with maximum at 33 700 cm^{-1} and shoulders at ~35 500, ~39 000 and ~47 700 cm^{-1} which correspond to the peaks at 33 330, 35 400, 38 920 and 47 390 cm^{-1} in the spectrum of the Cp$_2$V solution [1]. Besides these bands, however, the comparatively narrow peaks A and B with the maxima at 39 400 and 46 470 cm^{-1}, respectively, are observed in the vapor-phase spectrum of vanadocene (Fig. 3). The solution spectrum [1] does not show such bands. So we can suppose that Rydberg transitions are responsible for peaks A and B.

The first band in the photoelectron spectrum of Cp$_2$V lies at 6.78 eV (54 680 cm^{-1}) and corresponds to ionization from the 3d(a$_{1g}$) and 3d(e$_{2g}$) MOs [3]. The difference between this value and the A band frequency (Table 1) is very close to the term value

of the $3d(a_{1g}) \rightarrow R4p$ transition in the spectrum of Bz_2V. So the A band can be considered as the first member of the np Rydberg series.

The difference between the first IP of Cp_2V and the frequency of band B in the vanadocene spectrum (8210 cm^{-1}) coincides with the $3d(a_{1g}) \rightarrow R5p$ term value for Bz_2Cr (8300 cm^{-1} [12, 13]). Hence, the B band (Fig. 3) can be assigned to the second member of the np series converging to the first IP. Indeed, the use of A and B frequencies in eqn. (1) leads to $I = 54\,500 \text{ cm}^{-1}$, $\delta = 1.3$. The ionization limit is very close to the first IP of vanadocene ($54\,680 \text{ cm}^{-1}$ [3]), the quantum defect being typical for the np series in the $(\eta^6\text{-arene})_2M$ spectra [11–13]. Thus, bands A and B (Fig. 3) can be confidently assigned to the symmetry allowed $3d(a_{1g}) \rightarrow R4p$ and $3d(a_{1g}) \rightarrow R5p$ transitions, respectively.

The sequence of the nickelocene occupied orbitals is $...[\pi(e_{1g})]^4[\pi(e_{1u})]^4[3d(a_{1g})]^2[3d(e_{2g})]^4[3d(e_{1g})]^2$ [3–5]. The ground state term is $^3A_{2g}$. The intensive peaks A and B are at $32\,500$ and $35\,000 \text{ cm}^{-1}$, respectively, the weak band C is at $45\,000 \text{ cm}^{-1}$ and the shoulder A' at $\sim 29\,800 \text{ cm}^{-1}$ in the Cp_2Ni vapor-phase absorption spectrum (Fig. 4(a)). The presence of the band at $32\,500 \text{ cm}^{-1}$ in the spectrum of vaporous nickelocene turns down the assumption [39] that this peak arises from the impurity of the Cp_2Ni^+ cation. On going from the vapor-phase spectrum (Fig. 4(a)) to the solution one (Fig. 4(b)), band A and shoulder A' remain practically unchanged, band B becomes weaker and transfers to the shoulder at $\sim 36\,000 \text{ cm}^{-1}$, band C disappears. In accordance with such changes of the spectrum, it may be supposed that bands B and C (Fig. 4(a)) correspond to the Rydberg transitions. The difference between the C and B frequencies ($10\,000 \text{ cm}^{-1}$) is close to that between the frequencies of two first members of np series in the spectrum of Bz_2Cr (9000 cm^{-1} [12, 13]). So these bands may be interpreted as the first and second members of the np Rydberg series corresponding to the transitions from the $3d(a_{1g})$ MO, by analogy with bisarene complexes and Cp_2V.

The first IP of nickelocene (6.51 eV or $52\,500 \text{ cm}^{-1}$ [3]) is $17\,500 \text{ cm}^{-1}$ higher than the B band frequency. The value of $17\,500 \text{ cm}^{-1}$ is a typical term value for the first member of the np series [12, 13, 34, 35]. The first IP of Cp_2Ni corresponds however to the ionization not from the $3d(a_{1g})$ MO but from the $3d(e_{1g})$ orbital [3]. The $3d(e_{1g})$ MO in the Cp_2Ni molecule is antibonding [32, 39]. The ligand orbitals take a large part (34% [39]) in the building of this MO. So it is unlikely that the transitions from the $3d(e_{1g})$ orbital can be responsible for the sharp Rydberg bands. We believe that the assignment of bands B and C (Fig. 4(a)) to the $3d(a_{1g}) \rightarrow R4p$ and

$3d(a_{1g}) \rightarrow R5p$ transitions is more reasonable though this is at variance with the interpretation of the Cp_2Ni photoelectron spectrum [4]. Use of the B and C frequencies in the Rydberg formula gives $IP_{a_{1g}} = 6.8$ eV. In this case, the asymmetry of the first band in the Cp_2Ni photoelectron spectrum [3] can be caused by the contribution of the ionization from the $3d(a_{1g})$ orbital. However, the energy of the Cp_2Ni^+ $^4A_{2g}$ state calculated by Green and co-workers [4] is 1.65 eV higher than that of the ground state, i.e. $IP_{a_{1g}} = 8.15$ eV. The investigation of the cobaltocene vapor-phase spectrum may be helpful for ascertaining the origin of bands B and C (Fig. 4(a)). For Cp_2Co, the $3d(e_{1g})$ ionization energy is very low (5.56 eV [3]). If the sharp Rydberg bands correspond to the transitions from the $3d(e_{1g})$ MO, then a Rydberg series converging to the ionization limit must be observed in the near-UV vapor-phase absorption spectrum of cobaltocene.

Chromocene and cobaltocene

In contrast to the metallocenes considered above, Cp_2Cr and Cp_2Co possess the degenerate ground electronic states. The configuration of ground state chromocene is $^3E_{2g}$: $...[\pi(e_{1g})]^4[\pi(e_{1u})]^4[3d(a_{1g})]^1[3d(e_{2g})]^3$ [3–5]. The absorption spectrum of vaporous Cp_2Cr (Fig. 5) shows broad intensive bands at $30\,000$ and $45\,540 \text{ cm}^{-1}$ corresponding to the peaks at $29\,590$ and $44\,640 \text{ cm}^{-1}$ in the spectrum of the Cp_2Cr solution [1]. In addition, there are weak features at $\sim 38\,200$ and $\sim 41\,200 \text{ cm}^{-1}$ and the sharp shoulder A at $48\,450 \text{ cm}^{-1}$ in the vapor-phase spectrum (Fig. 5). The features at $\sim 38\,200$ and $41\,200 \text{ cm}^{-1}$ correspond apparently to the shoulder at $\sim 40\,000 \text{ cm}^{-1}$ in the Cp_2Cr solution spectrum [1]. Band A in the spectrum of the Cp_2Cr solution [1] is absent, so the Rydberg transition may be responsible for this band. By analogy with bisarene complexes [11–15] and the metallocenes considered above, we can suppose that this is the $3d(a_{1g}) \rightarrow Rnp$ transition. For verification of such a supposition, it is necessary to use the photoelectron spectroscopy data.

Green and co-workers [4] investigated the band intensity in the He(I) and He(II) photoelectron spectra of Cp_2Cr and they concluded that the ionization of the $3d(a_{1g})$ electron was responsible for the band at 7.20 eV. The difference between this value and the frequency of band A (Fig. 5) is 9620 cm^{-1} which corresponds to $n = 5$ and $\delta = 1.62$. The quantum defect is close to that of the np series in the spectra of polyatomic molecules [34, 35]. In that case, band A can be interpreted as the second member of the np Rydberg series. The calculation shows that the first member of this series lies at $\sim 38\,700 \text{ cm}^{-1}$.

The shoulder at $\sim 38\,200$ cm^{-1} may correspond to this transition. The interpretation of band A (Fig. 5) as the first member of the np Rydberg series cannot however be excepted. In this case, $IP_{a_{1g}}$ lies in the 8.0–8.3 eV region. This confirms one of the possible interpretations of the Cp$_2$Cr photoelectron spectrum [3]. Thus, the assignment of band A (Fig. 5) to the $3d(a_{1g}) \rightarrow R4p$ or $3d(a_{1g}) \rightarrow R5p$ transition does not contradict with the photoelectron spectroscopy data.

One can undoubtedly conclude that the vapor-phase spectrum of chromocene does not show the Rydberg bands corresponding to the transitions from the $3d(e_{2g})$ orbital. The first band in the photoelectron spectrum of Cp$_2$Cr (5.70 eV [4]) arises from the $3d(e_{2g})$ ionization. Rydberg transitions from this MO must form a series in the 28 000–44 000 cm^{-1} region. Such a series is absent in the spectrum of vaporous Cp$_2$Cr (Fig. 5).

The cobaltocene ground state is $^2E_{1g}$: $\ldots[\pi(e_{1g})]^4[\pi(e_{1u})]^4[3d(a_{1g})]^2[3d(e_{2g})]^4[3d(e_{1g})]^1$ [3–5]. The Cp$_2$Co vapor-phase spectrum obtained in our work (Fig. 6(a)) is in a good agreement with the data of refs. 7 and 8. This spectrum changes little on going to the Cp$_2$Co solution (Fig. 6(b)). There are the bands A and B of approximately equal intensity (maxima at 30 700 and 38 400 cm^{-1}, respectively) and the more intensive band C (maximum at 47 000 cm^{-1} in the vapor-phase spectrum and at 46 000 cm^{-1} in the solution one). The Rydberg series converging to the first IP of cobaltocene ($IP_{e_{1g}}=5.56$ eV [3]) in the vapor-phase spectrum (Fig. 6(a)) is absent. Consequently, it is unlikely that the Rydberg transitions from the $3d(e_{1g})$ orbital can be responsible for the sharp absorption bands. This is an argument in favour of our assignment of bands B and C in the nickelocene vapor-phase spectrum (Fig. 4a) to the transitions from the $3d(a_{1g})$ orbital. It should be taken into account however that the dynamic Jahn–Teller effect may be important for the Cp$_2$Co molecule [27, 40].

The comparison of Fig. 6(a) and (b) shows that the C/B intensity ratio decreases from ~ 3.7 to ~ 2.5 on going from the spectrum of vaporous Cp$_2$Co to that of solution whereas the A/B intensity ratio remains practically unchanged. The difference between the C band molar absorption coefficients in the vapor phase and in solution is $\sim 18\,000$ l mol^{-1} cm^{-1} [1, 7]. This value corresponds to the intensity of a symmetry allowed transition. As one of the possible explanations, it may be suggested that the $3d(a_{1g}) \rightarrow R4p$ Rydberg transition contributes to band C. For this transition (the first member of the np series), the term value of 15 000–20 000 cm^{-1} is typical [7, 12, 13, 34, 35]. So $IP_{a_{1g}}$ of Cp$_2$Co is

expected to lie at 62 000–67 000 cm^{-1}, or 7.7–8.3 eV. This is in a good agreement with the assignment of the band at 8.01 eV in the cobaltocene photoelectron spectrum to the ionization from the $3d(a_{1g})$ orbital [3]. If Rydberg bands in the Cp$_2$Co and Cp$_2$Ni absorption spectra are characterized by similar quantum defects, the second member of the np series in the Cp$_2$Co spectrum should be at 57 000 cm^{-1}. Indeed, there is a sharp shoulder at 57 000 cm^{-1} in the far-UV vapor-phase absorption spectrum of cobaltocene [7, 8]. Thus, Rydberg transitions from the $3d(a_{1g})$ orbital can be responsible for some peculiarities in the Cp$_2$Cr and Cp$_2$Co vapor-phase absorption spectra.

Manganocene and decamethylmanganocene

Manganocene and its substituted derivatives are the most unusual compounds among 3d metallocenes. This is associated with the fact that biscyclopentadienyl compounds of manganese display both high-spin ($^6A_{1g}$: $\ldots[\pi(e_{1g})]^4[\pi(e_{1u})]^4[3d(a_{1g})]^1[3d(e_{2g})]^2[3d(e_{1g})]^2$) and low-spin ($^2E_{2g}$: $\ldots[\pi(e_{1g})]^4[\pi(e_{1u})]^4[3d(a_{1g})]^2[3d(e_{2g})]^3$) ground electronic states. For Cp$_2$Mn in the vapor phase and in solution, the $^6A_{1g}$ ground state is observed [1, 3, 4, 25, 41, 42]. Only a very small percentage of the Cp$_2$Mn molecules in the $^2E_{2g}$ state was found in the photoelectron study [3, 4]. For 1,1'-dimethylmanganocene, however, a thermal equilibrium takes place, the low-spin form being more stable both in solution [1, 41, 42] and in the vapor phase [4, 43]. Cp*$_2$Mn displays the $^2E_{2g}$ state only [4, 18, 30, 42]. Thus, Cp$_2$Mn and Cp*$_2$Mn represent 3d^5 metallocenes displaying the high-spin and low-spin ground state, respectively. The difference in the ground states must undoubtedly affect the electronic absorption spectra of these compounds.

The spectrum of vaporous manganocene is given in Fig. 7. There are the broad bands A and E with maxima at 32 800 and 47 700 cm^{-1}, the sharp shoulder B at $\sim 38\,000$ cm^{-1} and the weak shoulders C and D at $\sim 42\,700$ and $\sim 45\,700$ cm^{-1}. Peak A (Fig. 7) corresponds to the band at 33 000 cm^{-1} in the spectrum of the Cp$_2$Mn solution [1]. Bands C, D and E transfer apparently into the shoulder at 42 370 cm^{-1} and the band at 46 950 cm^{-1} in the solution spectrum [1]. Comparison of the Cp$_2$Mn vapor-phase spectrum with the data of Gordon and Warren [1] shows that the shoulder B (Fig. 7) disappears on going from the vapor phase to solution. Such a behaviour may indicate that the corresponding transition is Rydberg in origin [11–15, 34, 35]. The difference between the manganocene first IP (6.91 eV or 55 730 cm^{-1} [3]) and the frequency of band B is 17 730 cm^{-1}. This difference is very close to

the term value of the first member of the np series in the spectra of Bz_2Cr and Cp_2Fe (Table 1). However, the first IP of Cp_2Mn corresponds to the ionization from the $3d(e_{1g})$ orbital as it was for nickelocene. For the reason given above, it is unlikely that Rydberg transitions from the $3d(e_{1g})$ MO can be responsible for the sharp absorption bands. So the assignment of band B (Fig. 7) to the $3d(e_{1g}) \rightarrow R4p$ transition is hardly probable. The interpretation of this band as $3d(a_{1g}) \rightarrow R4p$ is also unlikely. Green [5] assigned the peak at 10.1 eV in the photoelectron spectrum of Cp_2Mn to the $3d(a_{1g})$ ionization. In this case, the $3d(a_{1g}) \rightarrow R4p$ transition must be in the far-UV region. It cannot be excluded that the band B (Fig. 7) corresponds to the valence-shell transition. The difference between the Cp_2Mn spectra in the vapor phase and in solution can be caused by the presence of dimer and oligomer particles, which represent the remains of the zigzag polymer chains forming the Cp_2Mn crystal structure [20], in the manganocene solution. Some data obtained in the NMR investigation are indicative of the availability of such particles [42].

Since the ground electronic states of manganocene and decamethylmanganocene are different, the electronic absorption spectrum of Cp^*_2Mn must differ from that of Cp_2Mn. In reality, the vapor-phase spectra of Cp^*_2Mn (Fig. 8) and Cp_2Mn (Fig. 7) are not similar. System B consisting of the narrow bands at 27 800 and 28 100 cm^{-1} dominates in the longwave region of the Cp^*_2Mn vapor-phase spectrum. The weak shoulders A and C at $\sim 21\,000$ and $\sim 29\,000$ cm^{-1} stand out from the background of this system (Fig. 8). In addition, there are the shoulders D and E at $\sim 35\,400$ and $\sim 38\,300$ cm^{-1} as well as a very broad feature F in the 41 000 cm^{-1} region. The spectra in the vapor phase and in the solution should be compared to reveal the Rydberg bands.

The solution spectrum of Cp^*_2Mn has been little investigated. It was reported that this spectrum was obtained but neither the spectrum itself nor the band frequencies were presented [44]. Therefore we have investigated the solution spectrum of Cp^*_2Mn in the present work. This spectrum (Fig. 9) differs from that of vaporous Cp^*_2Mn. The B, D and E bands (Fig. 8) are absent in the solution spectrum but there are weak shoulders at $\sim 32\,500$ and $\sim 34\,000$ cm^{-1} which are not observed in the spectrum of vaporous Cp^*_2Mn against the background of the more intensive band D. The A and C bands in the spectrum of Cp^*_2Mn in pentane (Fig. 9) display the sharp maxima at 21 200 and 29 350 cm^{-1}, respectively. The feature F remains practically unchanged on going from the vapor phase to solution.

Note that the solution spectrum of Cp^*_2Mn (Fig. 9) is quite different from that of Cp_2Mn [1]. The presence of the longwave asymmetric band A is a characteristic feature of the Cp^*_2Mn solution spectrum. This band is absent in the manganocene spectrum [1]. On the other hand, such a band was found in the spectrum of the decamethylrenocene solution [45]. The spectroscopic investigation of Cp_2Re and Cp^*_2Re in the Ar and N_2 matrices [45, 46] revealed an excellently resolved vibrational structure of this band (0,0 transition at 20 421 and 16 572 cm^{-1} for Cp_2Re and Cp^*_2Re, respectively). The analysis of the vibrational structure permitted this band to be assigned to the symmetry allowed $\pi(e_{1u}) \rightarrow 5d(e_{2g})$ valence-shell transition [45, 46]. The electronic absorption, ESR and MCD spectra [45, 46] indicate that the ground state of the Cp_2Re and Cp^*_2Re molecules is $^2E_{2g}$: $...[\pi(e_{1g})]^4[\pi(e_{1u})]^4[5d(a_{1g})]^2-[5d(e_{2g})]^3$. Hence, these compounds are the analogues of Cp^*_2Mn. So the A band in the Cp^*_2Mn solution spectrum (Fig. 9) can be confidently assigned to the $\pi(e_{1u}) \rightarrow 3d(e_{2g})$ transition. The electronic absorption spectrum of the Cp_2Fe^+ cation ($^2E_{2g}$ ground state) also shows a similar band [47]. Thus, the Cp^*_2Mn solution spectrum is in agreement with the $^2E_{2g}$ ground state.

Comparison of Figs. 8 and 9 shows that the system B and bands D and E disappear on going from the vapor-phase spectrum of Cp^*_2Mn to the solution one. Consequently, these bands can arise from the Rydberg transitions. Indeed, we have established that the B, D and E bands represent a Rydberg series. The frequencies of these bands are given by eqn. (1) (Table 2). The energy of ionization from the Cp^*_2Mn $3d(a_{1g})$ orbital is 5.33 eV [4, 5]. This value is very close to the ionization threshold calculated as the convergence limit of the Rydberg series (Table 2). The quantum defect value of 1.36 (Table 2) is typical for the np series in the spectra of sandwich organometallics [11–15]. Hence, the bands B, D and E in the Cp^*_2Mn vapor-phase absorption spectrum can be unambiguously assigned to the $3d(a_{1g}) \rightarrow Rnp$ ($n = 4$, 5, 6) Rydberg series. System B corresponds to the $3d(a_{1g}) \rightarrow R4p$ transition.

TABLE 2. Calculated (using eqn. (1)) and observed ν (cm^{-1}) frequencies of the bands B, D and E in the vapor-phase spectrum of Cp^*_2Mn (Fig. 8). I (eV), n and δ (see eqn. (1)) are presented.

Band	n	ν_{calc}	ν_{obs}
B	4	27800	27800, 28100
D	5	35260	35400
E	6	38440	38300

$I = 5.40$, $\delta = 1.36$.

The presence of two bands in this system can be caused by the splitting of the R4p MO into the e_{1u} and a_{2u} orbitals under the D_{5d} symmetry as it was for Bz_2V [12] and Cp_2Fe. The term values for these bands are close to those for the first member of the np series in the spectra of Cp_2Fe, Cp_2V and Bz_2V (Table 1). So it can be concluded that our assignment of the B, D and E bands (Fig. 8) is correct.

Conclusions

Our investigation have shown that vapor-phase electronic absorption spectra of 3d metallocenes differ from the solution ones. As a rule, this difference arises from the presence of Rydberg bands which disappear on going from the vapor phase to solution. As for the bisarene complexes [11–15], the Rydberg bands corresponding to the allowed $3d(a_{1g}) \rightarrow R n p$ transitions are the most sharp. The sharp form of these Rydberg bands is due to the non-bonding character of the $3d(a_{1g})$ orbital. We did not find the peaks which can be unambiguously assigned to the Rydberg transitions from the $3d(e_{2g})$ or $3d(e_{1g})$ orbital. On the contrary, the spectrum of vaporous chromocene demonstrates the absence of the Rydberg bands corresponding to the transitions from the $3d(e_{2g})$ MO, and the vapor-phase spectrum of cobaltocene shows the absence of Rydberg bands corresponding to the transitions from the $3d(e_{1g})$ orbital. This is obviously due to the lower d character of the $3d(e_{2g})$ and $3d(e_{1g})$ orbitals in comparison with the $3d(a_{1g})$ MO.

Acknowledgements

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