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Vapor-phase and solution-phase UV spectroscopic studies of η^5-pentadienyl derivatives of iron and ruthenium

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Abstract

The electronic absorption spectra of the 'half-open metallocenes', $(Cp)(C_7H_{11})Fe$, $(Cp)(C_7H_{11})Ru$, $(Cp^*)(C_7H_{11})Ru$ (Cp = η^5-cyclopentadienyl, Cp* = η^5-pentamethylcyclopentadienyl, C_7H_{11} = η^5-2,4-dimethylpentadienyl), and 'open metallocenes', $(C_7H_{11})_2Fe$, $(C_7H_{11})_2Ru$, have been measured in the vapor phase and in *n*-pentane solution and have been compared with the spectrum of the 'closed ferrocene' (Cp)(Cp*)Fe. The vapor-phase spectrum of (Cp)(Cp*)Fe reveals two sharp absorption bands arising from the $3d_z2 \rightarrow R4s$ and $3d_z2 \rightarrow R4d$ transitions. These bands are absent in the solution spectrum. Similarly, the spectra of iron and ruthenium η^5-pentadienyl complexes show absorption features which disappear on going from the vapor to the solution phase. These features were interpreted as being due to Rydberg excitations originating at the metal d_z2 orbital. The estimated term values indicate that Rydberg bands in the spectra of 'half-open metallocenes' and 'open metallocenes' most likely correspond to transitions from the molecular orbital responsible for the first ionization peak in the photoelectron spectra to the lowest Rydberg s, p, and d levels. Gaussian analysis shows that Rydberg bands are successively broadened on going from the 'closed ferrocene' to 'half-open metallocenes' and then to 'open metallocenes'. This broadening can be interpreted as a result of an increase in mixing of the metal d_z2 orbital with ligand functions in this group of compounds. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Pentadienyl derivatives; Iron; Ruthenium; Electronic absorption spectra; Rydberg transitions

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1. Introduction

The high chemical and catalytic reactivities of transition-metal η^5-pentadienyl derivatives [1] has stimulated a currently considerable interest in the electronic structures of such compounds especially relative to their counterparts containing closed η^5-cyclopentadienyl ligands. Both theoretical and experimental techniques including INDO MO calculations [2,3], photoelectron (PE) [2–4] and ESR [5] spectroscopy have been employed to analyze the influence of opening the 5-membered carbocyclic ring on the compositions and energies of the highest occupied molecular orbitals (MOs) of iron-group metallocenes. The interpretations of low-lying bands in the PE spectra of 'half-open metallocenes' [3] and 'open metallocenes' [2,4] appeared to be, however, more complicated than those for their closed-ring analogues [6–8].

Insight into the nature of the highest filled MOs of the η^5-pentadienyl complexes may be obtained from their vapor-phase UV absorption spectra, which can reveal promotions of electrons to Rydberg levels. Rydberg MOs of a polyatomic molecule are formally constructed from atomic orbitals having principal quantum numbers greater than those of the valence shell levels. Molecular Rydberg orbitals are characterized by the quantum numbers *n* and *l* similar to atomic orbitals. In general, a series of Rydberg transitions may be observed, involving successively higher values of *n* and leading to convergence at the ionization threshold. The

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frequencies of the series members obey the well-known Rydberg formula,

$$\nu = I - \mathrm{R}/(n-\delta)^2 = I - T$$

for which I is the ionization potential for detachment of an electron from the occupied MO participating in the Rydberg excitation, R is the Rydberg constant, δ represents the quantum defect which is nearly constant for a given series, and T is the term value equal to the binding energy of the Rydberg electron.

Closed-ring sandwich compounds appear to comprise the first class of organometallic species which show clearly defined Rydberg transitions in their absorption spectra [9–19]. These transitions originate at an orbital having high metal d_z2 character. Rydberg bands might also be observable in the vapor-phase electronic absorption spectra of the transition metal η^5-pentadienyl derivatives having metal-localized HOMOs. Since the frequencies of Rydberg excitations depend on ionization potentials [20], analyses of Rydberg band parameters for η^5-pentadienyl complexes would make it possible to determine the ionization energies corresponding to the MOs with high metal d_z2 character. It therefore became of interest to investigate open pentadienyl ligand analogues, partly to gain a better understanding of their electronic structures, but partly also to attempt to find at least a second class of organometallic compounds that exhibits Rydberg spectra. We have indeed found that the iron group open and half-open metallocenes show Rydberg transitions in their vapor-phase absorption spectra.

Rydberg bands disappear from the spectra of the closed-ring sandwiches [9–19] on going from the vapor to the solution phase, this effect being due to scattering of a Rydberg electron in media of low electron mobility [20]. The spectra of gas-phase iron and ruthenium η^5-pentadienyl derivatives have therefore been compared in this work with those of the complexes in pentane solution to reveal Rydberg features. For comparison we have recorded the spectra of closed-ring (η^5-cyclopentadienyl)(η^5-pentamethylcyclopentadienyl)iron in the vapor and solution phases as well. A preliminary description of part of the iron work has been briefly reported earlier [21].

2. Experimental section

The complexes (Cp)(Cp*)Fe (**1**) [22], (Cp)(C_7H_{11})Fe (**2**) [5], (Cp)(C_7H_{11})Ru (**3**) [3], (Cp*)(C_7H_{11})Ru (**4**) [23], $(C_7H_{11})_2$Fe (**5**) [24], and $(C_7H_{11})_2$Ru (**6**) [25] (Cp = η^5-cyclopentadienyl, Cp* = η^5-pentamethylcyclopentadienyl, C_7H_{11} = η^5-2,4-dimethylpentadienyl) chosen for spectroscopic study in this work were synthesized by previously reported routes. Each compound was purified by recrystallyzation from pentane and subsequent vacuum sublimation. Sample purities were checked by elemental analysis and NMR.

The UV absorption spectra of the gas-phase complexes were recorded using a quartz vacuum cell with a Specord UV–vis spectrometer (Carl Zeiss, Yena) at 50–80°C. Temperatures were maintained by a coil of resistance wire wrapped around the quartz cell holder. The spectra of **1**–**6** in n-pentane solution were measured on the same spectrometer in vacuo at r.t.

3. Results and discussion

The electronic absorption spectra of **1**–**6** in the vapor phase appear to differ from those recorded in n-pentane solution (Figs. 1–6), similar to observations for the closed-ring sandwich compounds investigated earlier [9–19]. In particular, the spectra of the gas-phase compounds show some features which disappear on going to the solution spectra. They are labeled by the letters A–L in Figs. 1–6. Such behavior suggests that these features arise from Rydberg transitions [20]. To determine the frequencies corresponding to the maxima of bands A–L more accurately, we decomposed the vapor-phase spectra of **1**–**6** in into sums of symmetric Gaussian peaks. The results of these decompositions are shown in the insets (Figs. 1–6). The peak parameters so obtained are given in Table 1.

The vapor-phase spectrum of **1** (Fig. 1) reveals two sharp bands, A and B. By analogy with other iron-group closed-ring metallocenes [9,10] these features can

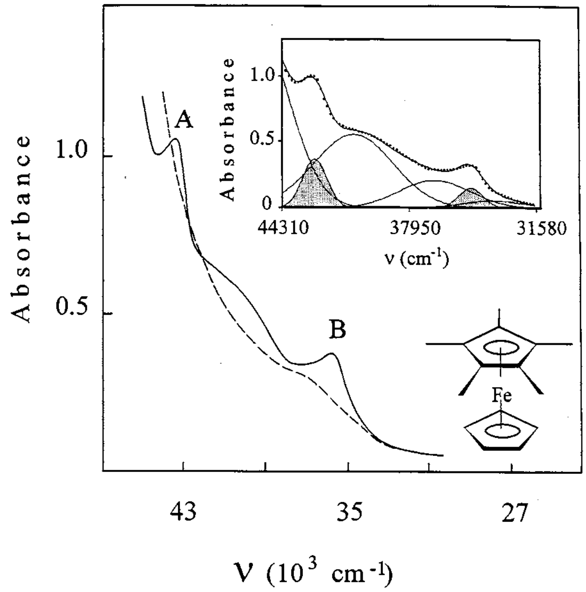


Fig. 1. Electronic absorption spectrum of **1** in the vapor phase (solid line) and in n-pentane solution (dashed line). The inset shows the decomposition of the vapor-phase spectrum into a sum of symmetric Gaussian peaks. The experimental curve is given by points. Shadings indicate the peaks assigned to Rydberg transitions.

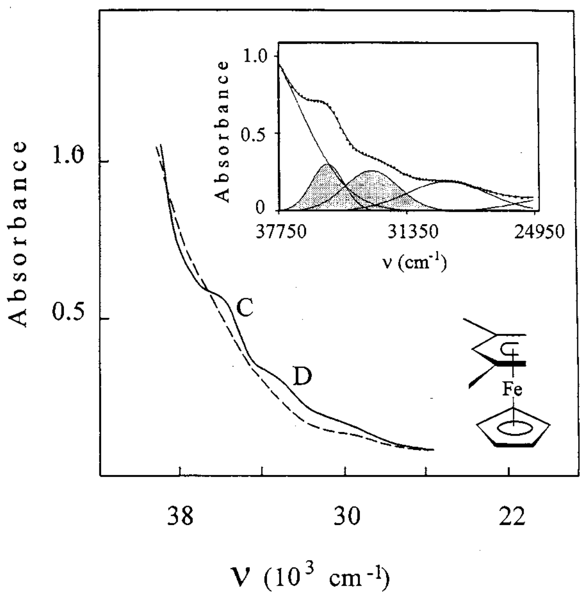


Fig. 2. Electronic absorption spectrum of **2** in the vapor phase (solid line) and in *n*-pentane solution (dashed line). The inset shows the decomposition of the vapor-phase spectrum into a sum of symmetric Gaussian peaks. The experimental curve is given by points. Shadings indicate the peaks assigned to Rydberg transitions.

be unambiguously interpreted as being due to the Rydberg transitions originating at the totally-symmetric occupied MO which represents almost 'pure' Fe $3d_{z^2}$ orbital [26,27].

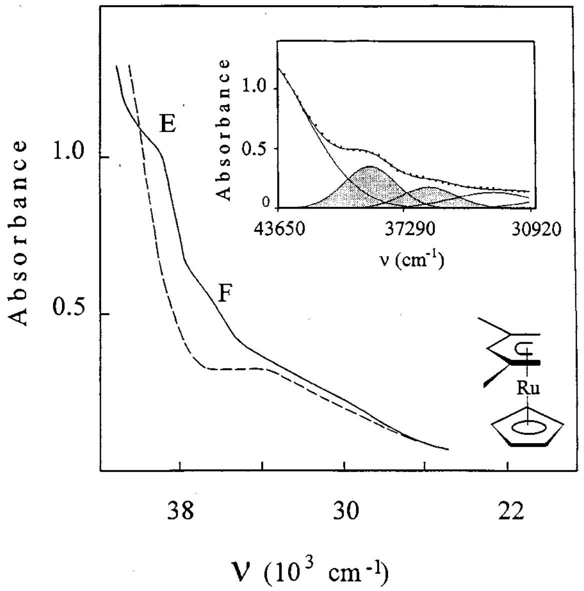


Fig. 3. Electronic absorption spectrum of **3** in the vapor phase (solid line) and in *n*-pentane solution (dashed line). The inset shows the decomposition of the vapor-phase spectrum into a sum of symmetric Gaussian peaks. The experimental curve is given by points. Shadings indicate the peaks assigned to Rydberg transitions.

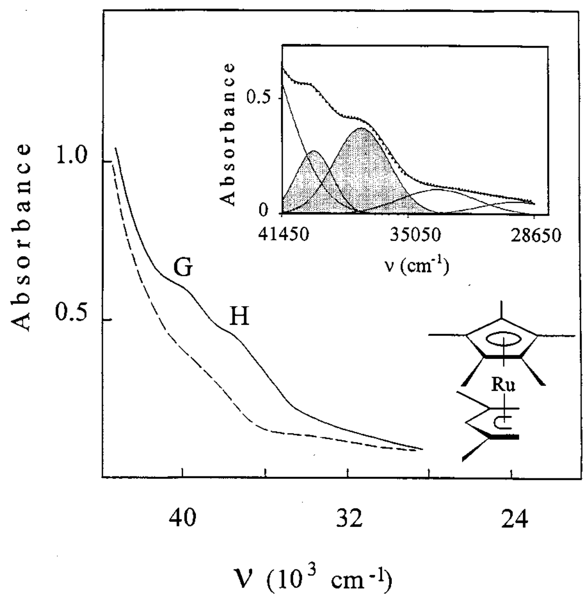


Fig. 4. Electronic absorption spectrum of **4** in the vapor phase (solid line) and in *n*-pentane solution (dashed line). The inset shows the decomposition of the vapor-phase spectrum into a sum of symmetric Gaussian peaks. The experimental curve is given by points. Shadings indicate the peaks assigned to Rydberg transitions.

Each of these Rydberg excitations is characterized by the term value *T* which is equal to the difference between the energy of ionization from the occupied MO participating in the Rydberg transition and the transition energy [20]. The magnitude of *T* provides a rather reliable criterion for assignment of a Rydberg transition. It has been demonstrated earlier [9–19] that the term values of the lowest Rydberg excitations

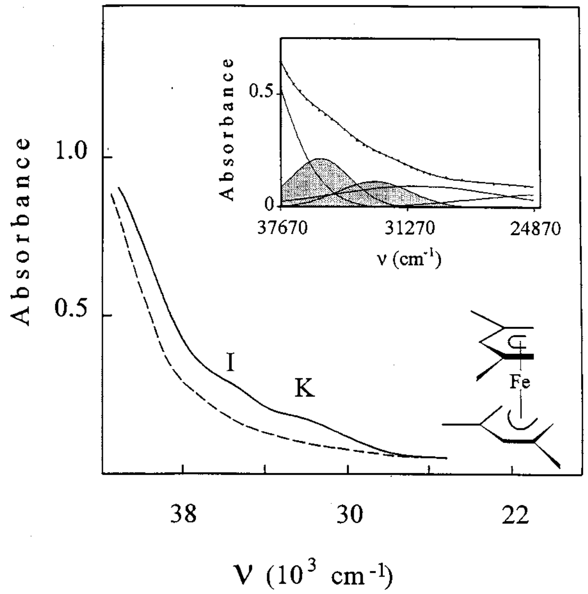


Fig. 5. Electronic absorption spectrum of **5** in the vapor phase (solid line) and in *n*-pentane solution (dashed line). The inset shows the decomposition of the vapor-phase spectrum into a sum of symmetric Gaussian peaks. The experimental curve is given by points. Shadings indicate the peaks assigned to Rydberg transitions.

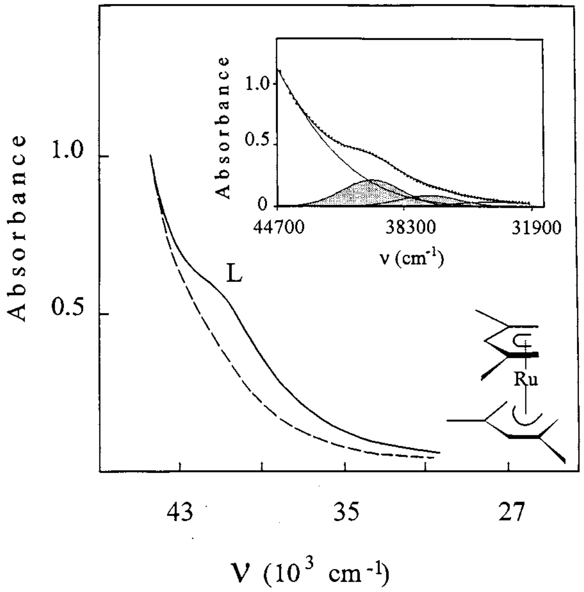
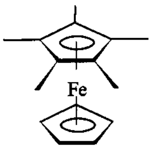


Fig. 6. Electronic absorption spectrum of **6** in the vapor phase (solid line) and in *n*-pentane solution (dashed line). The inset shows the decomposition of the vapor-phase spectrum into a sum of symmetric Gaussian peaks. The experimental curve is given by points. Shadings indicate the peaks assigned to Rydberg transitions.

change very little on going from one transition-metal sandwich to another. To assign bands A, B in the spectrum of **1** to individual Rydberg transitions, it is therefore necessary to determine the corresponding *T* values.



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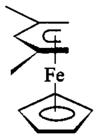

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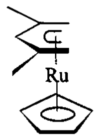

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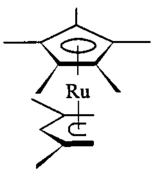

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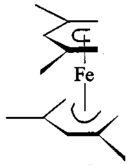

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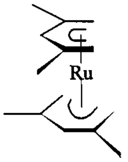

6

The ionization from the iron $3d_z2$ orbital is responsible for the second band in the PE spectra of closed-ring ferrocenes [6,8]. The $3d_z2$ ionization energy for **1** has recently been measured [28] to be 6.77 ± 0.01 eV (54600 cm^{-1}), very close to the value of 6.75 eV (54480 cm^{-1}) which could be estimated from the average of the $3d_z2$ ionization potentials of $(Cp)_2Fe$ [6] and $(Cp^*)_2Fe$ [8]. The close agreement reflects the fact that there is a linear correlation between the d-electron ionization potentials and the number of methyl groups in the cyclopentadienyl ligands of d^6 metallocenes [29]. The value of 54600 cm^{-1} will therefore be taken for the estimation of the term values corresponding to peaks A and B (Fig. 1). The transition responsible for band A has a *T* value of 11730 cm^{-1} which is close to those of the lowest R*n*d excitations in bisarene and mixed sandwich complexes [11–19] (11600–12900 cm^{-1}). This band should therefore be assigned to the $3d_z2 \rightarrow R4d$ promotion. It is worth mentioning that (Cp)(Cp*)Fe represents the first example of a d^6 metallocene showing a clearly defined R*n*d excitation.

The molecule of **1** belongs to the C_{5v} point group [30]. In the C_{5v} ligand field the metal and Rydberg d orbitals split into three sets, d_z2 (a_1), d_{xz}, d_{yz} (e_1) and $d_{x2-y}2$, d_{xy} (e_2), and the transitions from Fe $3d_z2$ to the a_1 and e_1 Rydberg orbitals are symmetry allowed. By comparison to related species [19], peak A in the spectrum of **1** can be interpreted as arising from the $3d_z2 \rightarrow R4d_{xz,yz}$ transition.

The difference between the $3d_z2$ ionization energy of **1** and the frequency of band B (Fig. 1) equals 19560 cm^{-1} which is close to the term values of the lowest Rydberg s excitation in (Cp)(Cp*)Ru [10] (20060 cm^{-1}), (η^6-1,3-$C_6H_4Me_2$)(Cp)Mn [16] (20090 cm^{-1}), (η^6-1,3-$C_6H_4Me_2)_2Cr$ [12] (19000 cm^{-1}) and (η^6-1,3-$C_6H_4Me_2)_2Mo$ [14] (19130 cm^{-1}). Peak B can therefore be consistently assigned to the symmetry allowed $3d_z2 \rightarrow R4s$ transition.

Surprisingly, the vapor-phase spectrum of **1** shows no clearly-defined transitions terminating at the lowest Rydberg p orbital. In the spectra of transition-metal sandwich complexes [9–19], including the iron-group metallocenes [13,14], the symmetry allowed Rydberg p (R*n*p) excitations usually lead to strong and sharp bands. Assuming that the term value of the lowest R*n*p transition in **1** is close to that in (Cp)(Cp*)Ru [10] (16560 cm^{-1}), we can predict the corresponding band to appear in the vapor-phase spectrum of **1** at ca. 38000 cm^{-1}. There are, however, no sharp features in this region (Fig. 1). The lowest R*n*p transition in **1** therefore must be broadened beyond detection. Such broadening is indicative of an interaction between the Rydberg state and valence-shell excited levels [20]. Thus, comparison of the spectrum of **1** with that of (Cp)(Cp*)Ru [10] demonstrates that, despite the similarity in the term values of their Rydberg transitions, the Rydberg structures in the spectra of closely related sandwich complexes can well be different due to changes in the Rydberg-valence mixing.

The vapor-phase spectra of 'half-open metallocenes' **2**–**4** reveal shoulders C–H (Figs. 2–4) which disappear on going to the solution phase and may therefore arise from Rydberg excitations. For their assignment it is necessary to estimate the term values. Taking into consideration the ionization energies of the iron-group 'half-open metallocenes' [3,31], we can conclude that only those orbitals which correspond to the first three

Table 1
Gaussian fit analysis[a], term values[b] and assignments of Rydberg bands in the vapor-phase spectra of **1**–**6**

Complex	Band	ν_{max} cm^{-1}	$\Delta_{1/2}$ cm^{-1}	T_1 cm^{-1}	T_2 cm^{-1}	T_3 cm^{-1}	Assignment
1	A	42 870	730	–	11 730	–	$3d_z2 \rightarrow R4d_{xz,yz}$
1	B	35 040	740	–	19 560	–	$3d_z2 \rightarrow R4s$
2	C	35 400	960	17 900	20 200	23 500	$3d_z2 \rightarrow R4p_{x,y}$
2	D	33 100	1610	20 200	22 500	25 800	$3d_z2 \rightarrow R4s$
3	E	39 200	1570	17 700	19 700	24 600	$4d_z2 \rightarrow R5p_{x,y}$
3	F	36 200	1630	20 700	22 700	27 600	$4d_z2 \rightarrow R5s$
4	G	39 900	1110	12 500	15 000	22 300	$4d_z2 \rightarrow R5d$
4	H	37 500	1660	14 900	17 400	24 700	$4d_z2 \rightarrow R5p$
5	I	35 700	1780	17 800	18 400	22 400	$3d_z2 \rightarrow R4p_{x,y}$
5	K	33 000	2180	20 500	21 100	25 100	$3d_z2 \rightarrow R4s$
6	L	39 900	1810	16 900	20 200	21 400	$4d_z2 \rightarrow R5p_{x,y}$
6	–	37 000	1830	19 800	23 100	24 300	$4d_z2 \rightarrow R5s$

[a] Gaussians are of the form $\varepsilon = \varepsilon_{max}\exp[-\ln 2\ (\nu - \nu_{max})^2/\Delta^2_{1/2}]$, for which ε and ν are absorbance and frequency, respectively, ε_{max} and ν_{max} correspond to the peak maximum, and $\Delta_{1/2}$ is the half-width at half-height.

[b] The term values T_1, T_2, T_3 were calculated on the basis of the ionization energies I_1, I_2, I_3, respectively, corresponding to the three first bands in the photoelectron spectra of **1**–**6** [2–4,31].

bands in the PE spectra of these compounds can participate in the Rydberg transitions lying below 45000 cm^{-1}. These PE bands are assigned to the MOs derived mainly from the metal d_z2, d_{xy} and $d_x2_{-y}2$ orbitals [3]. Notably, all of the Rydberg transitions revealed by the spectra of d^6 metallocenes [9,10], bisarene compounds [11–14] and mixed sandwich complexes [15–19] originate at the highly non-bonding MO of metal d_z2 character. No Rydberg excitations were found originating at the MO formed by the d_{xy} and $d_x2_{-y}2$ metal orbitals. This circumstance was interpreted [10,14] as being a consequence of the presence of stronger interactions of the ligand MOs with the metal dxy and $d_x2_{-y}2$ levels as compared to the metal d_z2 orbital. Since it would be unreasonable for the opening of the cyclopentadienyl ring to lead to a decrease in the metal–ligand orbital mixing [2], it seems therefore to be most probable that the Rydberg transitions observed in the spectra of the iron and ruthenium pentadienyl derivatives, similar to those shown by the spectra of closed-ring sandwiches, originate at the MO with substantial metal d_z2 character. Thus, the d_z2 ionization energy should be used to estimate the term values of the Rydberg transitions in **2**–**4**. It is, however, difficult to determine which low-lying band in the PE spectra of 'half-open metallocenes' [3,31] corresponds to the MO of d_z2 character. According to an INDO calculation [3], the ionization energies from the three metal-localized MOs of **2** are very close. We therefore estimated in this work the energy separations between the frequencies of Gaussian peaks' maxima and the ionization potentials I_1, I_2 and I_3 corresponding to the first three bands in the PE spectra of **2**–**4** [3,31] to determine the possible term values of the Rydberg transitions responsible for the shoulders C–H (Figs. 2–4). The resulting magnitudes of T_1, T_2 and T_3 are presented in Table 1. For comparison, the term values of the Rydberg excitations observed in the spectrum of **1** are given as well. Since ionization from the Fe $3d_z2$ orbital is responsible for the second band in the PE spectra of 'closed ferrocenes' [6–8], these term values are placed in the T_2 column of Table 1.

The size and geometry of the molecular cores of the iron-group 'half-open metallocenes' [1,3] and 'open metallocenes' [32–34] are very similar to those of their closed-ring counterparts [30,35–39]. Thus the term values of the Rydberg transitions in **2**–**6** are expected to be close to the typical magnitudes of T found for the sandwich complexes investigated earlier. The separations of bands D and F (Figs. 2 and 3) from the corresponding first ionization potentials (20200 and 20700 cm^{-1}, respectively) are appropriate for assignment of these features to the lowest Rydberg s transition. The T_2 and T_3 magnitudes for these bands (Table 1) are appreciably larger than the usual term values of low-lying Rydberg excitations in sandwich molecules. We can then conclude that the first peak in the PE spectra of **2** and **3** corresponds to the MO with substantial iron $3d_z2$ character. This conclusion agrees well with the ESR data [5] indicating that for the $\mathbf{2}^{+\bullet}$ and $\mathbf{5}^{+\bullet}$ radical cations the singly occupied MO could be almost exclusively derived from the Fe $3d_z2$ orbital.

The T_1 magnitudes for shoulders C and E (Table 1) are similar to the typical term values of the lowest Rnp transition in closed-ring sandwich compounds (e.g. 17480, 17290, 17290, 17150 and 17550 cm^{-1} for $(Cp)_2Fe$ [9,10], $(\eta^5\text{-}C_5H_4Me)_2Fe$ [9,21], $(\eta^6\text{-}C_6H_6)_2Cr$ [12,13], $(\eta^6\text{-}C_6H_5Me)_2Cr$ [12,13] and $(\eta^6\text{-}C_6H_6)(Cp)Mn$ [15,16], respectively). In unsubstituted sandwiches the lowest Rnp level represents degenerate Rydberg p_x and

p_y orbitals [10–19]. This level is split into two closely-lying components on ring methylation [12–14,16]. Bands C and E in the spectra of **2** and **3** are too broad to reveal such splitting. In comparison, the term values of the lowest Rydberg pz excitation in sandwich molecules are ca. 1500–2000 cm^{-1} lower than those of the px,y components [10,15–18]. On the basis of the T_1 values, bands C and E can therefore be assigned to the $nd_z2 \rightarrow R(n+1)p_{x,y}$ transitions ($n = 3$ for Fe, 4 for Ru). The absence of the $R(n+1)p_z$ component in the vapor-phase spectra of **2** and **3** is explained either by its low intensity or from Rydberg-valence mixing. The $R4p_z$ transition was also not observed in the spectra of 1,1′-dimethylferrocene [9,21] or 1,1′-diethylferrocene [40].

On the other hand, the magnitudes of T_2 (C) and T_2 (E) (Table 1) are typical for the lowest Rydberg s excitation. This fact makes possible an alternative interpretation of bands C and E as being due to the promotion from the MO responsible for I_2 to the lowest Rydberg s orbital. However, metal d_z2 character can not dominate both MOs corresponding to the first two peaks in the PE spectra of **2** and **3**. As a result, the assignment of shoulders C, D, E and F to Rydberg transitions originating at the MO responsible for I_1 is preferable. The T_3 magnitudes for bands C and E are too large to allow their interpretation as term values of the lowest Rydberg excitations in a sandwich molecule.

The situation changes when one goes from **2** and **3** to **4**. The T_1 values for the bands G and H in the spectrum of **4** are appreciably lower than those for features C–F (Table 1). Though the results obtained for $(Cp)_2M$ and $(Cp^*)_2M$ (M = Fe, Ru, Os) [10] revealed that decreases in the term values of the Rydberg transitions are expected on methylation of the Cp ring in **3**, the difference between the first ionization potential of **4** [31] (6.5 eV or 52400 cm^{-1}) and the H frequency is too low to be correlated with the R5s term value. The T_1 magnitude for this band is much closer to the term values of the lowest Rydberg p excitations in decamethylmetallocenes [10] (14650, 15290, and 15290 cm^{-1} for $(Cp^*)_2Fe$, $(Cp^*)_2Ru$ and $(Cp^*)_2Os$, respectively). Thus, the shoulder H in the spectrum of **4** may arise from the $4d_z2 \rightarrow R5p$ transitions. Interestingly, in contrast to $(Cp)_2M$ (M = Fe, Ru, Os), whose spectra show both $Rnp_{x,y}$ and Rnp_z excitations, the permethylated d^6 metallocenes reveal only one peak attributable to the Rydberg p transitions [10]. This is presumably due to a mutual convergence of the $Rnp_{x,y}$ and Rnp_z term values that accompanies ring methylation. The T_1 magnitude for band H can then correspond well to any of the $4d_z2 \rightarrow R5p$ components, unlike the T_1(C) and T_1(E) values which are too large for the lowest Rydberg p_z excitation. The separation between the G frequency and I_1 (Table 1) is appropriate for assignment of this band to one of the R5d excitations.

Due to the fact that the T_2(G) and T_1(H) values are equal (Table 1), it is necessary to consider the possibility of assigning band G to the Rydberg p transition from the MO responsible for the second band in the PE spectrum of **4**. In that case, however, the H band should be interpreted as being due to the lowest Rydberg s excitation which seems to be unlikely because of low T_2(H) magnitude (Table 1). Thus the assignment of features G and H to the R5d and R5p transitions originating at the MO corresponding to the first ionization potential of **4** is more reasonable.The $\Delta_{1/2}$ parameters characterizing the widths of the Gaussians corresponding to Rydberg transitions in the spectra of **2**–**4** are substantially larger than those for **1** (Table 1). Such broadening of Rydberg bands can be caused either by Rydberg-valence mixing or an increased interaction between the metal d_z2 orbital and the ligand MOs when one goes from ‘closed metallocenes’ to ‘half-open metallocenes’. The absence of narrow Rydberg peaks in the vapor-phase spectra of **2**–**4** supports the latter supposition. Accordingly, an increase in the width of the $3d_z2$ ionization PE band is observed on going from $(Cp)_2Fe$ [6] to $(Cp)(C_7H_{11})Fe$ [3]. Though bands C–H are broadened in comparison with Rydberg peaks in the spectra of **1** and other closed-ring sandwiches, they appear to be more narrow than the features arising from valence-shell excitations in **2**–**4** (the Gaussians corresponding to intravalency transitions in the vapor-phase spectra of **2**–**4** are characterized by the $\Delta_{1/2}$ parameters of 2300–4600 cm^{-1}).

Further broadening of Rydberg bands is observed when one goes from ‘half-open metallocenes’ **2**–**4** to ‘open metallocenes’ **5** and **6** (Table 1). The vapor-phase spectra of **5** and **6** show shoulders I–L which disappear on going to the solution spectra (Figs. 5 and 6). By analogy with **1**–**4**, these features can be expected to arise from the Rydberg excitations originating at the MO of metal d_z2 character. The qualitative diagrams of the highest occupied MOs constructed on the basis of the PE spectral assignments for ‘closed ferrocene’ [6,29] and ‘open ferrocene’ [2,4] are compared in Fig. 7. The electronic structures of the iron-group ‘open metallocenes’ have been examined using the C_{2h} symmetry (*anti*-eclipsed form) [2,4] though X-ray crystal structures [32–34] of bis(η^5-pentadienyl) complexes revealed gauche-eclipsed conformations (the C_2 point group). So MOs of ‘open ferrocene’ are designated in Fig. 7 using the C_{2h} group notation.

The opening of two cyclopentadienyl rings of $(Cp)_2Fe$ results in splitting of the Fe e_{2g} (d_{xy}, $_x2_{-y}2$) level into the ag ($d_x2_{-y}2$) and bg (d_{xy}) components. According to semiempirical MO calculations [2], the Fe

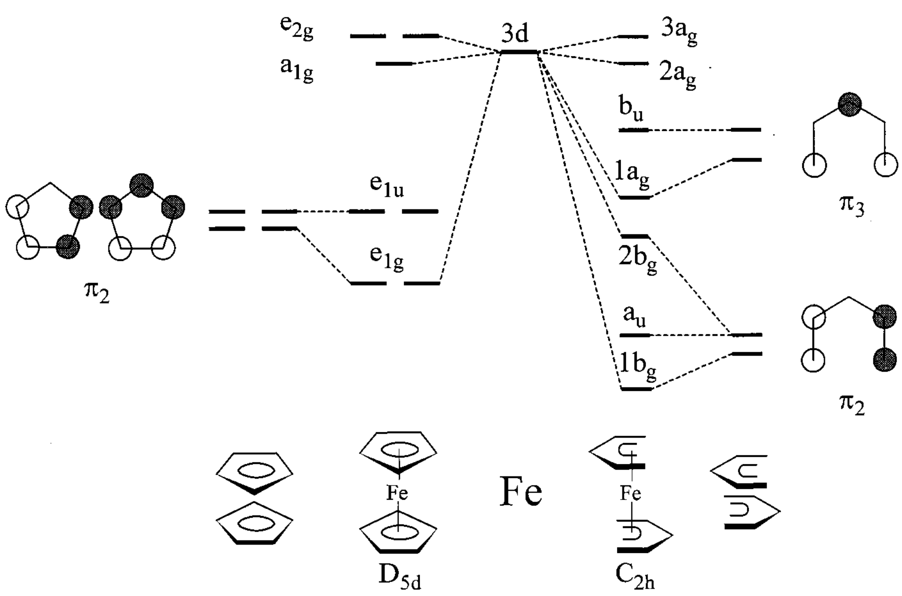

Fig. 7. Qualitative diagram of the highest occupied MOs of 'closed ferrocene' and 'open ferrocene' based on the assignments of ionization peaks in the PE spectra [2,6]. Shadings indicate the phases of the carbon $2p_z$ atomic orbitals. Only the highest filled MOs of ligands are shown.

$3d_{xy}$ orbital in bis(η^5-pentadienyl)iron is strongly coupled to ligand functions (the resulting orbitals are $1b_g$ and $2b_g$ in Fig. 7) while $3d_{z}2$ and $3d_{x}2_{-y}2$ are localized on the metal.

Large widths of absorption bands I–L make the differences between the vapor-phase spectra and solution-phase spectra of **5** and **6** (Figs. 5 and 6) not so obvious as it was observed for the half-open counterparts, **2** and **3** (Figs. 2 and 3). We can not therefore exclude completely the possibility of assignment of bands I–L to valence-shell excitations (e.g. charge-transfer transitions). However, the analysis of the corresponding term values makes Rydberg assignments preferable.

The first two closely-lying bands (6.63 and 6.7 eV) in the PE spectrum of **5** [4] were assigned to the $2a_g$ and $3a_g$ MOs (Fig. 7) formed mainly by the Fe $3d_{z}2$ and $3d_{x}2_{-y}2$ orbitals. The third peak (7.2 eV) was interpreted as involving ionization from the pure ligand b_u orbital. The T_1(I) and T_1(K) magnitudes for **5** are very close to T_1(C) and T_1(D), respectively (Table 1). The assignments of bands I and K to the $3d_{z}2 \rightarrow R4p_{x,y}$ and $3d_{z}2 \rightarrow R4s$ transitions, respectively, are therefore quite reasonable. The difference between the T_1 and T_2 values for these features is small making it difficult to decide unambiguously which of the higher-lying a_g orbitals (Fig. 7) is of $3d_{z}2$ character. Taking into consideration the ESR data [5], it seems, however, to be likely that the Fe $3d_{z}2$ orbital corresponds to the 3ag, rather than to the $2a_g$, MO.

Shoulder L in the vapor-phase spectrum of 'open ruthenocene' **6** (Fig. 6) is characterized by the T_1 value (Table 1) appropriate for assignment of this band to the lowest Rydberg p transition. The Gaussian fit analysis of this spectrum shows that there is a peak centered at 37000 cm^{-1} which adjoins shoulder L. The magnitude of T_1 corresponding to this peak (Table 1) is typical for a term value of the first Rydberg s excitation. Thus, the bands centered at 39900 and 37000 cm^{-1} in the vapor-phase spectrum of **6** can be interpreted as being due to the $4d_{z}2 \rightarrow R5p_{x,y}$ and $4d_{z}2 \rightarrow R5s$ transitions, respectively. By analogy with features C and E in the spectra of **2** and **3**, the assignment of band L to the lowest Rydberg s excitation on the basis of its T_2 value (Table 2) seems to be less likely. Thus, the positions of the Rydberg bands in the vapor-phase absorption spectrum of **6** indicate that the MO with substantial $4d_{z}2$ character corresponds to the first, rather than second, peak in the PE spectrum of **6**.

A further increase in the $\Delta_{1/2}$ parameter characterizing Rydberg bands is observed when one goes from 'half-open metallocenes' **2**–**4** to 'open metallocenes' **5** and **6** (Table 1). This increase can be attributed to even stronger mixing between metal $d_{z}2$ and ligand functions in **5** and **6** compared with **2**–**4**. Thus, we are lead to conclude that the metallic character of the MO derived from the metal $d_{z}2$ orbital decreases successively on opening the two cyclopentadienyl rings of the iron-group 'closed metallocenes'. Although MO calculations suggest the extent of $d_{z}2$-ligand mixing is not large, it is possible that small differences could have significant effects on the widths of these peaks. This result is at least in general accord with the prediction made on the basis of INDO MO calculations [3] that the 'half-open ferrocene' lies between 'closed ferrocene' and 'open ferrocene' with respect to the 3d character of its wavefunctions.

4. Conclusions

The vapor-phase UV absorption spectrum of **1** shows clearly-defined $3d_z2 \rightarrow R4s$ and $3d_z2 \geq R4d_{xz, yz}$ Rydberg transitions, thereby providing the first example of an intense Rydberg d excitation in a metallocene molecule. Interestingly, the lowest Rydberg p transitions in (Cp)(Cp*)Fe are broadened beyond detection due to an admixture of valence-shell excitations.

The vapor-phase spectra of iron and ruthenium 'half-open metallocenes' **2**–**4,** and 'open metallocenes' **5** and **6,** reveal bands which disappear on going to the solution spectra. By analogy with earlier results for closed-ring sandwich compounds, these features can be assigned to Rydberg excitations originating at MO with substantial metal d_z2 character. Though the term values found for shoulders C–L on the basis of Gaussian fit analysis are less accurate than those for sharp Rydberg peaks in the spectra of closed-ring sandwich compounds, they lead us to a quite reasonable interpretation of the Rydberg structure in the spectra of **2**–**6**.

The term values indicate that bands C–L most likely correspond to the transitions from the MO responsible for the first ionization peak in the PE spectra of **2**–**6** to the lowest Rydberg s, p and d levels. Thus, the results reported in this work attest to metal d_z2 contribution in the singly occupied MO in the ground-state cations of the iron and ruthenium pentadienyl complexes studied.

Gaussian fit analyses of the vapor-phase spectra show that Rydberg bands are broadened on going from **1** to **2**–**4** and from **2**–**4** to **5** and **6**. This effect could well be due to increased mixing of the metal d_z2 orbital with ligand functions, indicating that the MO derived from d_z2 becomes successively less metal-localized when one and two cyclopentadienyl rings of ferrocene or ruthenocene are successively replaced by a η^5-pentadienyl ligand.

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