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Photoabsorption study of electronic excited states of (η^5-cyclopentadienyl)(η^6-arene)manganese

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Abstract

The electronic absorption spectra of the (Cp)(arene)Mn compounds (Cp = η^5-C_5H_5, arene = η^6-C_6H_6, η^6-$C_6H_6CH_3$, η^6-1,3-$C_6H_4(CH_3)_2$) in the vapour phase and in pentane solution have been investigated for the first time. Most of the sharp bands revealed by vapour-phase photoabsorption disappear from the solution spectra. Electronic excited states corresponding to these bands have a Rydberg origin. The vapour-phase spectra show electron transitions from the non-bonding 3d(σ^+) orbital to *n*s, *n*p, and *n*d Rydberg levels (n = 4, 5, 6). These excitations have been assigned on the basis of their quantum defects and term values. The Rydberg structure in the spectrum of (η^5-cyclopentadienyl)(η^6-benzene)manganese can be adequately described under the $C_{\infty v}$ point group. The introduction of methyl substituents into the benzene ring disturbs the axial symmetry. This is indicated by the splitting of the Rydberg degenerate 4p(π) orbital. On methyl substitution, the energy of the lowest *R*4s(σ^+) state is shifted in a way which is parallel to that of the neutral-molecule ground electronic state. At the same time, *R*5p, *R*5d, and *R*6p levels change in line with the ground electronic state of the [(Cp)(arene)Mn]$^+$ cation. These facts have been interpreted in terms of the size and the penetrating properties of the Rydberg orbitals.

Key words: Manganese; Arene; Cyclopentadienyl; Photoabsorption; Electronic

1. Introduction

In recent years, interesting results have been achieved from investigation of the electronic excited states of transition-metal bisarene complexes [1–4] and metallocenes [5,6]. UV and visible absorption spectra of these compounds in the vapour phase can differ strongly from those in the solution phase and this is due to the presence of Rydberg transitions. Rydberg excitations are manifested as sharp bands in vapour-phase photoabsorption but they are broadened beyond detection in the spectra of the sandwich compounds which appear in the solution state. This broadening is caused by the short relaxation time and the scattering of a Rydberg electron in the condensed media with low electron mobility [7].

As in atoms, Rydberg orbitals in molecules are characterized by the principal quantum number n and they can be of the s, p, d, *etc.* type depending on the angular orbital moment. The transitions of an electron from the occupied molecular orbital (MO) to the Rydberg levels of each type with increasing n form a series converging at the ionization threshold. Each series can be described by the well-known Rydberg formula

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

where ν_n is the transition frequency (cm^{-1}), I is the ionization potential (cm^{-1}) which corresponds to detachment of an electron from the occupied MO participating in the Rydberg excitation, R is the Rydberg constant (109737 cm^{-1} for large polyatomic molecules), n is the principal quantum number of a Rydberg orbital, δ represents the quantum defect which remains nearly constant in the given series and T is the term value equal to the binding energy of a Rydberg electron.

A series can be assigned to type (s, p, d, *etc.*) on the basis of its quantum defect. The spectra of polyatomic molecules often show only the lowest members of a Rydberg series [7–9]. In that case, the term values are used for the assignment of Rydberg bands. The T magnitude for the lowest Rydberg orbital of each type is nearly constant within a class of closely related molecules [7–9].

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In previous work [1–6], the Rydberg excitations in the vapour-phase spectra of symmetric transition-metal complexes bearing two η^6-arene or two η^5-cyclopentadienyl ligands have been investigated in detail. The entire Rydberg transitions in photoabsorption of vaporous sandwiches appeared to originate at a totally symmetric non-bonding d_{z^2} metal orbital. The sharpest Rydberg excitations were found in "18 electron" complexes $(\eta^6\text{-arene})_2M$ (M = Cr, Mo) [1–4] and $(\eta^5\text{-}C_5H_5)_2M$ (M = Fe, Ru, Os) [6].

Arene and cyclopentadienyl species can form another class of sandwich molecules — mixed compounds $(\eta^5\text{-}C_5H_5)(\eta^6\text{-arene})M$. Among the neutral complexes of this class, the compounds of manganese and rhenium have an "18 electron" configuration. The energy of ionization from d_{z^2} orbital for $(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6H_6)Mn$ is comparatively low (6.36 eV or 51290 cm^{-1} [10]). UV photoabsorption of $(\eta^5\text{-}C_5H_5)(\eta^6\text{-arene})Mn$ may therefore reveal Rydberg bands which disappear on going from the vapour to the condensed phase. This situation prompted investigation of the vapour-phase electronic absorption spectra of such compounds and comparing them with the solution spectra, using cyclopentadienyl manganese complexes bearing benzene, toluene, or *m*-xylene as the second ligand.

2. Experimental section

All manipulations were carried out *in vacuo*. The compounds (Cp)(Bz)Mn, (Cp)(Tol)Mn, and (Cp)(Xyl) Mn (Cp = $\eta^5\text{-}C_5H_5$, Bz = $\eta^6\text{-}C_6H_6$, Tol = $\eta^6\text{-}C_6H_5CH_3$, Xyl = $\eta^6\text{-}1,3\text{-}C_6H_4(CH_3)_2$) were prepared by low-temperature co-condensation of atomic metal with a vaporous mixture of cyclopentadiene and corresponding arene [11,12]. This method is most appropriate for the synthesis of mixed manganese sandwich complexes. The co-condensation leads to the individual asymmetric compound alone because atomic manganese does not react with cyclopentadiene or arene taken separately, giving manganocene or bis(η^6-arene)manganese, respectively [11,13].

In a typical experiment, manganese (~ 1 g) sublimed from a resistively heated tungsten basket was co-condensed with an excess of cyclopentadiene (~ 25 g) and arene (~ 50 g) in the liquid-nitrogen cooled reactor described earlier [14] over a period of 2 h. Each ligand was evaporated from a separate ampoule. After warming to room temperature the reaction mixture was filtered and collected. Excess cyclopentadiene and arene were then removed *in vacuo*. Subsequent vacuum sublimation (80–100°C/0.01 Torr) afforded a pink-red crystalline complex (yield 0.5–1.0% based on manganese) which decomposed above 150°C with formation of cyclopentadiene and the corresponding arene. The complexes obtained were washed with cold pentane and purified by repeated vacuum sublimation.

The vapour-phase photoabsorption spectra were recorded using a vacuum cell on a "Specord UV VIS" (Carl Zeiss, Jena) spectrometer at 80–110°C. Temperatures were maintained by a coil of resistance wire wrapped around the quartz cell holder. For comparison, the spectra of complexes in n-pentane solutions were measured on the same spectrometer *in vacuo* at room temperature.

3. Results and discussion

As with symmetric "18 electron" sandwiches [1–6], the absorption spectra of (Cp)(arene)Mn change strongly when one goes from the vapour phase to the solution (Figs. 1–3) (from now on the "η^6-" designation for the arene ligand is omitted). Photoabsorption of vaporous complexes shows comparatively narrow bands 1–10 which are absent from the solution spectra. Such a behaviour can be indicative of a Rydberg nature for the corresponding transitions. Drawing a parallel with $(arene)_2M$ [1–4] and $(Cp)_2M$ [5,6], we can assign peaks 1–10 (Figs. 1–3) to Rydberg transitions from the $3d(\sigma^+)$ orbital which is the uppermost occupied MO in the molecules of (Cp)(arene)Mn [10].

The irreducible representations of the $C_{\infty v}$ point group are used here to designate the symmetry of the (Cp)(Bz)Mn orbitals. The $(Cp'(\eta^n\text{-}C_nH_n)M$ molecules (n = 4–8) display formally very low symmetry (C_1 or C_s). Nevertheless, both experimental data [15–19] and calculations [20–22] indicate that their electronic structure can be treated under the axial $C_{\infty v}$ symmetry. For

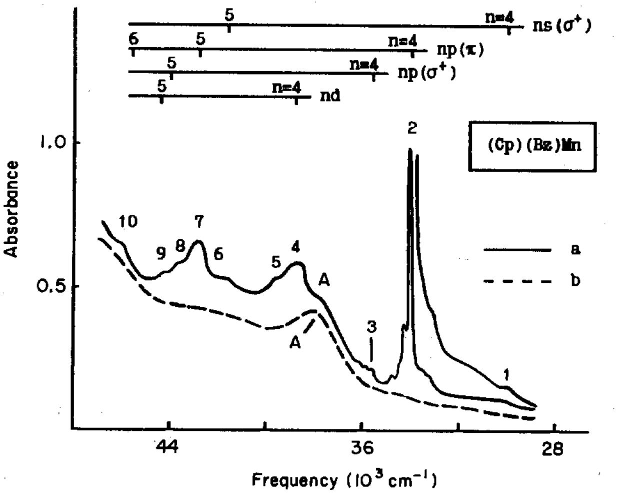

Fig. 1. The electronic absorption spectrum of (η^5-cyclopentadienyl)-(η^6-benzene)manganese in the vapour phase (a) and in pentane solution (b).

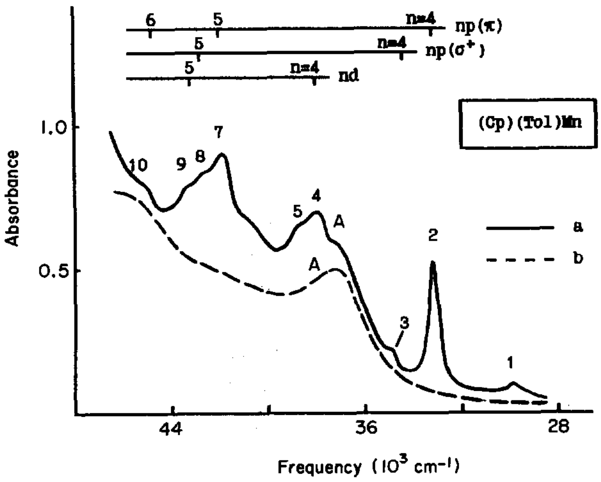

Fig. 2. The electronic absorption spectrum of (η^5-cyclopentadienyl)(η^6-toluene)manganese in the vapour phase (a) and in pentane solution (b).

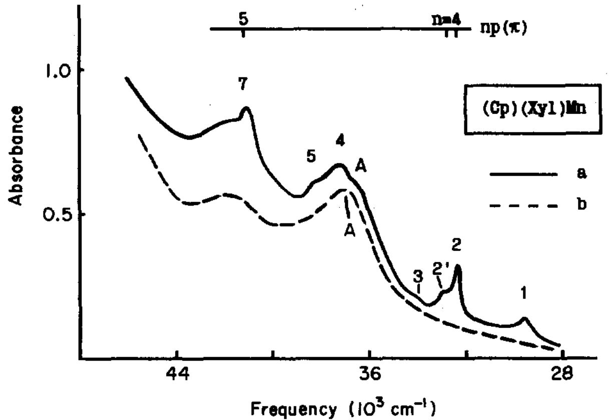

Fig. 3. The electronic absorption spectrum of (η^5-cyclopentadienyl)(η^6-*m*-xylene)manganese in the vapour phase (a) and in pentane solution (b).

convenience, the $C_{\infty v}$ group notation is retained here for (Cp)(Tol)Mn and (Cp)(Xyl)Mn where axial symmetry is disturbed by the presence of methyl substituents in the benzene ring. Calculations [21,22] show that MO 3d(σ^+) in the mixed sandwich complexes (Cp)(η^n-C_nH_n)M (M is a first-row transition metal) is an almost pure metal d_{z^2} orbital.

Long-wavelength Rydberg excitations in the spectra of vaporous manganese sandwich complexes can be interpreted when comparing their term values with the known *T* magnitudes of Rydberg transitions in symmetric sandwich compounds [1–6]. To calculate the term values for bands 1–10 (Figs. 1–3) it is necessary to know the energy of ionization from the 3d(σ^+) orbital in (Cp)(arene)Mn. For (Cp)(Bz)Mn, this energy corresponds to the first band at 6.36 eV (51290 cm^{-1}) in the photoelectron spectrum of the compound [10]. It should be noted that the present value is very close to the arithmetic mean of the 3d(σ^+) ionization energies in bis(benzene)chromium [1] and ferrocene [23] ((5.45 + 7.23)/2 = 6.34 eV). This makes it possible to determine the ionization potentials corresponding to the detachment of 3d(σ^+) electron in (Cp)(Tol)Mn and (Cp)(Xyl)Mn for which the photoelectron spectra have not been measured up to now. One must use the ionization potentials of $(Tol)_2Cr$ (5.29 eV [1]) and $(Xyl)_2Cr$ (5.14 eV [1]), respectively, together with that of $(Cp)_2Fe$ [23].

The arithmetic mean equals 6.26 eV (50490 cm^{-1}) for (Cp)(Tol)Mn and 6.19 eV (49920 cm^{-1}) for (Cp)(Xyl)Mn. These magnitudes were used for calculation of the *T* and ($n - \delta$) parameters presented in Table 1 together with the frequencies of bands 1–10. It is seen in Table 1 that the peaks of the same number

TABLE 1. Frequencies ν, term values *T*, ($n - \delta$) parameters (see eqn. 1), and excited states corresponding to bands 1–10 in the vapour-phase spectra of (Cp)(Bz)Mn (I), (Cp)(Tol)Mn (II), and (Cp)(Xyl)Mn (III) (Figs. 1–3)

Band	ν (cm^{-1})			T (cm^{-1})			($n - \delta$)			Excited state
	I	II	III	I	II	III	I	II	III	
1	29900 *	29950	29830	21390	20540	20090	2.26	2.31	2.34	$R4s(\sigma^+)$
2	33740	33180	32530	17550	17310	17350	2.50	2.52	2.51	$R4p(\pi)$
2′	–	–	33160 *	–	–	16820	–	–	2.55	
3	35370	34950 *	34350 *	15920	15540	15570	2.63	2.66	2.65	$R4p(\sigma^+)$
4	38400	38050	37500	12890	12440	12420	2,92	2.97	2.97	$R4d$
5	39280 *	38850 *	38300	12010	11640	11620	3.02	3.07	3.07	$R4d$
6	41730 *	–	–	9560	–	–	3.39	–	–	$R5s(\sigma^+)$
7	42750	42030	41200	8540	8460	8720	3.58	3.60	3.55	$R5p(\pi)$
8	43530 *	42750 *	–	7760	7740	–	3.76	3.77	–	$R5p(\sigma^+)$
9	44110 *	43310 *	–	7180	7180	–	3.91	3.91	–	$R5d$
10	46050 *	45300 *	–	5240	5190	–	4.58	4.60	–	$R6p(\pi)$

* Shoulder.

are characterized by similar magnitudes of T and $(n - \delta)$. This indicates that such peaks arise from the transitions terminating at the same Rydberg orbital.

In the spectrum of vaporous (Cp)(Bz)Mn (Fig. 1(a)) peak 2 is the strongest band. Its term value (Table 1) is very close to the T magnitude for the lowest member of the Rnp(π) series in $(Bz)_2Cr$ (17290 cm^{-1} [1]) and $(Cp)_2Fe$ (17350 cm^{-1} [5]). So peak 2 should be assigned to the 3d(σ^+) → R4p(π) excitation. This band is mainly associated with the 0,0 transition. On either side of peak 2 there are several weak features forming a vibrational structure of the Rydberg excitation.

The presence of resolved vibronic features at temperatures exceeding 100°C represents an intriguing peculiarity of the vapour-phase photoabsorption of "18 electron" transition-metal sandwich complexes with no substituents in the aromatic rings [1–6]. In the condensed phase, the electronic spectra of such compounds reveal broad structureless bands arising from valence-shell excitations. Vibrational structure is observed only in the photoabsorption of $(Cp)_2Fe$ [24] and photoemission of $(Cp)_2Ru$ [25,26] at low temperatures. The appearance of vibronic features in the photoabsorption of vaporous sandwich compounds confirms the non-bonding character of the 3d(σ^+) orbital and Rydberg MO's.

On the high-frequency side, peak 2 (Fig. 1(a)) is accompanied by a short 250 cm^{-1} progression associated with the σ^+ vibration which corresponds to the symmetric metal–ring stretch in bis(benzene)chromium and ferrocene (the ground-state frequencies are 277 and 311 cm^{-1}, respectively [27,28]). In addition, a weak band at 34590 cm^{-1} is observed in the spectrum of vaporous (Cp)(Bz)Mn. This band is separated by 850 cm^{-1} from the 0,0 transition and can be assigned to the excitation of totally symmetric C–H bending vibrations in the R4p(π) state (Rydberg states are designated here by the labels of those Rydberg orbitals which are populated by the electronic transition originating at MO 3d(σ^+), *i.e.* the R4s(σ^+) state corresponds to the $[3d(\sigma^+)]^1[R4s(\sigma^+)]^1$ configuration). These vibrations are responsible for the features at 762 and 808 cm^{-1} in the IR spectrum of (Cp)(Bz)Mn [16].

On the long-wavelength side of peak 2 there are several hot bands which correspond to excitation of the symmetric metal–ring stretching mode in the ground electronic state of (Cp)(Bz)Mn. A similar vibrational structure is shown by the 3d(σ^+) → R4p(π) transition in the vapour-phase spectrum of $(Bz)_2Cr$ [1].

Some broadening of peak 2 is observed when one goes from (Cp)(Bz)Mn (Fig. 1(a)) to (Cp)(Tol)Mn (Fig. 2(a)). A few ill-resolved shoulders spaced by ~200 cm^{-1} are revealed on the wings of peak 2 in the spectrum of vaporous (Cp)(Tol)Mn. They can be assigned to the vibronic transitions associated with excitation of symmetric metal–ring stretch. For (Cp)(Xyl)Mn, a splitting of the R4p(π) level takes place. In addition to band 2, peak 2′, arising from an individual electronic excitation, appears in the (Cp)(Xyl)Mn vapour-phase spectrum (Fig. 3(a)). A similar picture is observed in $(Xyl)_2Cr$ [1,3]. Such a splitting is caused by the removal of degeneracy of the 4p(π) Rydberg orbital which transforms into the $R4p_x(a')$ and $R4p_y(a'')$ components on reducing the symmetry from $C_{\infty v}$ to C_s (σ_{xz} is chosen here as the mirror plane). The $4p_x(a')$ and $4p_y(a'')$ Rydberg states in (Cp)(Xyl)Mn are separated in energy by the interval of 530 cm^{-1} which is somewhat larger than that in $(Xyl)_2Cr$ (350 cm^{-1} [3]). Obviously, the broadening of peak 2 on going from (Cp)(Bz)Mn to (Cp)(Tol)Mn arises also from the splitting of the R4p(π) orbital. All these facts confirm unambiguously the assignment of band 2 (Table 1).

The $R4p_z$ orbital corresponds to the totally symmetric irreducible representation in the $C_{\infty v}$ point group. The 3d(σ^+) → R4p(σ^+) excitation is symmetry-allowed and it is responsible for the band 3 (Figs. 1(a)–3(a)). In (Cp)(Bz)Mn this transition shows a poorly resolved vibrational structure displaying 250 cm^{-1} metal–ring stretching mode. For (Cp)(Xyl)Mn, band 3 is appreciably broadened as a result of the mixing of the Rydberg state with a higher-lying intravalency level. Such a mixing takes place in $(Bz)_2Cr$ where the 3d(σ^+) → R4p(σ^+) transition is so broadened as to be unobservable [1–3]. The excitation considered is revealed by $(Bz)_2V$ [1] and $(Cp)_2Fe$ [5] with term values of 15650 and 15860 cm^{-1}, respectively, which are very close to the magnitudes of T for band 3 (Table 1).

As shown in Table 1, something of a decrease in the R4p term values occurs as methyl groups are introduced into benzene ring of (Cp)(Bz)Mn. A similar trend is observed in $(arene)_2Cr$ [1–3].

The very weak long-wavelength band 1 in the spectrum of vaporous (Cp)(Bz)Mn (Fig. 1a) arises from the 3d(σ^+) → R4s(σ^+) transition. The R4s(σ^+) orbital is the lowest Rydberg MO in (Cp)(arene)Mn. The difference between the 3d(σ^+) ionization energy and the frequency of this band equals 21390 cm^{-1} coinciding with the term value of the first member of the Rns series in the spectrum of asymmetric "18 electron" sandwich $(Cp)(\eta^7\text{-}C_7H_7)Cr$ [19]. The 3d(σ^+) → R4s(σ^+) transition is symmetry-forbidden for $(Cp)_2M$ and $(Bz)_2M$ (the $D_{\infty h}$ point group), but it becomes allowed for (Cp)(Bz)Mn (the $C_{\infty v}$ group). Nevertheless, the relative intensity of band 1 in the spectrum of unsubstituted complex (Fig. 1(a)) is very low. Its intensity increases appreciably as methyl groups appear in the benzene ring (Figs. 2(a), 3(a)). In the spectra of (Cp)(Tol)Mn and (Cp)(Xyl)Mn, band 1 is characterized by the term values (Table 1) which are very close to those of the $3d(\sigma^+) \rightarrow R4s(\sigma^+)$ excitation in $(Tol)_2Cr$ (19810 cm^{-1} [3]) and $4d(\sigma^+) \rightarrow R5s(\sigma^+)$ excitation in $(Tol)_2Mo$ (20100 cm^{-1} [4]). This fact confirms the interpretation of band 1 as the lowest Rns transition.

The T magnitude of the $3d(\sigma^+) \rightarrow R4s(\sigma^+)$ excitation changes more on methyl substitution than that of the lowest Rydberg np transitions (Table 1). It decreases to almost the same extent as the $3d(\sigma^+)$ ionization energy does. So the frequency of peak 1 is nearly constant in all three manganese compounds.

Bands 4–10 in the spectra of vaporous complexes are superimposed on the intense absorption which remains practically unchanged when one goes from the vapour to the solution phase (Figs. 1–3) and corresponds to the valence-shell excitations. The comparatively sharp and intense peak A stands out against broad intravalency photoabsorption. Its maximum lies at 37600, 37200, and 36800 cm^{-1} in the solution spectra of (Cp)(Bz)Mn, (Cp)(Tol)Mn, and (Cp)(Xyl)Mn, respectively (Figs. 1–3). The position of peak A in respect to Rydberg excitations resembles that of the intense band at 32900 cm^{-1} in the spectrum of $(Bz)_2Cr$ [1,3] which was assigned to the charge-transfer transition $3d(\delta) \rightarrow Bz(\delta)$ on the basis of SCF MS X_α calculation [29]. However, the red shift of this band on methyl substitution [3] indicates that the electron is transferred rather from the arene ligand to the metal [30].

Features 4 and 5 have the term values (Table 1) appropriate for their interpretation as the first members of two Rydberg nd series. The electronic transitions from MO $3d(\sigma^+)$ to the $Rnd(\sigma^+)$ and $Rnd(\pi)$ levels are allowed under the $C_{\infty v}$ symmetry. The second member of the more intense long-wavelength d series corresponds to shoulder 9 which is characterized by the quantum defect equal to that of peak 4 and the principal quantum number $n = 5$ (Table 1).

Shoulder 6 in the spectrum of vaporous (Cp)(Bz)Mn can be assigned to the second member of the Rns series on the basis of its $(n - \delta)$ value. Something of a decrease of the quantum defect on going from the first member of this series (band 1) to the second (shoulder 6) is a typical phenomenon for sandwich complexes [1–4,19].

The δ magnitude for peak 7 coincides with that for shoulder 10 (Table 1). Hence, these features belong to one and the same Rydberg series. The quantum defect equals 1.42 for (Cp)(Bz)Mn and 1.40 for (Cp)(Tol)Mn. These values are very close to the quantum defect of the np(π) Rydberg series in $(Bz)_2Cr$ and $(Tol)_2Cr$ (1.35 and 1.40, respectively [1–3]). Bands 7 and 10 should therefore be assigned to the $3d(\sigma^+) \rightarrow R5p(\pi)$ and $3d(\sigma^+) \rightarrow R6p(\pi)$ excitations, respectively. The first member of this series corresponds to peak 2. Shoulder 8, revealed in the spectra of (Cp)(Bz)Mn and (Cp)(Tol)Mn, can be interpreted as the second member of the $Rnp(\sigma^+)$ series. Thus all the absorption bands, disappearing when one goes from the vapour-phase spectra of (Cp)(arene)Mn to the solution spectra (Figs. 1–3), have been assigned in the present work to the concrete Rydberg excitations.

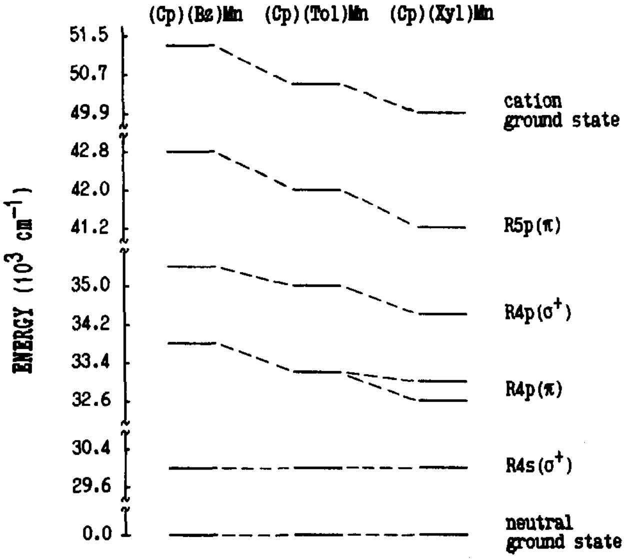

Fig. 4. Ground-state cation and 4s, 4p, 5p Rydberg state energy correlation for (Cp)(Bz)Mn, (Cp)(Tol)Mn, and (Cp)(Xyl)Mn (in each case energies are measured from the ground-state electronic level of a neutral molecule).

In contrast to the energy of the $3d(\sigma^+) \rightarrow R4s(\sigma^+)$ transition, which is nearly constant in all three (Cp)(arene)Mn compounds, the frequencies of the higher-lying excitations terminating at MO $R5p$, $R5d$, $R6p$ decrease appreciably on methyl substitution. At the same time, their term values remain practically unchanged (Table 1). This means that in the series of manganese compounds investigated the energy of the $R4s$ level is shifted in a way parallel with that of the neutral-molecule ground electronic state ($^1\Sigma^+$) while the energies of the $R5p$, $R5d$, $R6p$ states change in line with that of the cation ground state ($^2\Sigma^+$). The behaviour of the $R4p$ and $R4d$ levels is intermediate. This situation is illustrated in Fig. 4 for the 4s, 4p, and 5p Rydberg states.

The behaviour of Rydberg levels can be explained on the basis of the size and the penetrating properties of corresponding orbitals. For the electron moving around the nucleus with a positive charge Z, an average radius of the orbital with azimuthal quantum number l is given (in units of Bohr radius $a_0 = 0.529$ Å) by the formula [31]

$$\langle r \rangle = n^2\left[1.5 - 0.5l(l+1)/n^2\right]/Z \tag{2}$$

TABLE 2. The average radii of the (Cp)(arene)Mn Rydberg orbitals estimated with use of eqn. (2) on the basis of $(n-\delta)$ values (Table 1)

Rydberg MO	⟨r⟩ (Å)		
	(Cp)(Bz)Mn	(Cp)(Tol)Mn	(Cp)(Xyl)Mn
$R4s(\sigma^+)$	4.0	4.2	4.3
$R4p(\pi)$	4.8	4.8	4.8 4.9
$R4p(\sigma^+)$	5.2	5.4	5.3
$R4d$	5.9 6.3	6.1 6.5	6.1 6.5
$R5s(\sigma^+)$	9.1	–	–
$R5p(\pi)$	9.9	10.0	9.7
$R5p(\sigma^+)$	10.9	11.0	–
$R5d$	11.2	11.2	–
$R6p(\pi)$	16.3	16.5	–

The average radius of a Rydberg orbital in the neutral molecule can be estimated roughly using the effective charge $Z^\star = n^2/(n-\delta)^2$ instead of Z in eqn. (2) [9]. The ⟨r⟩ values of the (Cp)(arene)Mn Rydberg orbitals, obtained thus on the basis of the calculated $(n-\delta)$ magnitudes (Table 1), are given in Table 2. The average radius of a Rydberg MO is close to the distance corresponding to the strongest maximum of radial electron density [32].

The ⟨r⟩ values given in Table 2 should be compared with the size of the (Cp)(arene)Mn molecular core. There are no structural data for these compounds. Nevertheless, one can estimate interatomic distances in (Cp)(arene)Mn on the basis of the known gas-phase molecular structures of the "18 electron" analogues—$(Bz)_2Cr$ [33], $(Cp)_2Fe$ [34], and $(\eta^5\text{-}C_5(CH_3)_5)_2Fe$ [35]. The longest Mn–H distances, equal to the minimal radius of the core, appear to be ~ 3.0 and ~ 4.2 Å in (Cp)(Bz)Mn and (Cp)(Tol)Mn, respectively, when the observed C(ring)–C(ring) (1.43 Å), C(ring)–C(methyl) (1.50 Å) and C–H (1.1 Å) bond lengths [33–35] are used together with the metal–C(ring) distance of 2.1 Å. Taking into account the van der Waals radius of the hydrogen atom (1.2 Å [36]), we find the largest core radius to be of ~ 4.2 and ~ 5.4 Å for (Cp)(Bz)Mn and its methylated derivatives, respectively. It is seen that the lowest Rydberg orbitals ($n = 4$) are comparable in size with the molecular core, while higher Rydberg MO's ($n = 5$, 6) are appreciably larger (Table 2).

In the $R4s(\sigma^+)$ state, where the orbital penetration is greatest, the Rydberg electron remains for the most part inside the core. From this point of view, the Rydberg 4s orbital is similar to an intravalency unoccupied non-bonding MO. So the energies of MO's $3d(\sigma^+)$ and $R4s(\sigma^+)$ are shifted equally and the frequency of the $3d(\sigma^+) \rightarrow R4s(\sigma^+)$ excitation is practically unchanged when methyl groups are introduced into benzene ring. It should be noted that the lowest Rydberg s orbital is nevertheless rather diffuse, so the $3d(\sigma^+) \rightarrow R4s(\sigma^+)$ transition is broadened beyond detection in the condensed phase. In that case, MO $R4s(\sigma^+)$ behaves like a typical Rydberg orbital [7].

The decrease in the $3d(\sigma^+)$ and $R4s(\sigma^+)$ ionization energies on methyl substitution is obviously caused by the change of the intracore charge distribution and the core geometry. The inductive effect of the CH_3 groups results in the increase of the electron density and, consequently, of the electron shielding and electron-electron repulsion in the central part of the sandwich molecule. This weakens the binding of the $3d(\sigma^+)$ and $R4s(\sigma^+)$ electrons to the core. Note that the growth of the core size on methyl substitution plays an important role in the decrease of the $R4s$ term value. The magnitude of T of $R4s$ shows no change when one goes from (Cp)(Bz)Mn to $(Cp)(\eta^7\text{-}C_7H_7)Cr$ [19] which has nearly the same core size. Regarded in that light, the behaviour of diffuse Rydberg MO $R4s$ differs from that of the metal-localized $3d(\sigma^+)$ orbital whose ionization energy decreases by 6100 cm^{-1} on going from (Cp)(Bz)Mn to $(Cp)(\eta^7\text{-}C_7H_7)Cr$ [19].

The penetration of the 4p and 4d Rydberg orbitals is not so extensive as that of $R4s$. For this reason, their term values change to a rather lesser extent on introduction of methyl substituents.

In the Rydberg p and d states characterized by the principal quantum numbers $n = 5$, 6, the Rydberg electron is remote and rather distant from the core which represents the ground-state $(^2\Sigma^+)$ cation $[(Cp)(arene)Mn]^+$. The penetration of the $R5p$, $R5d$, and $R6p$ orbitals into the core is small. So the change of intracore charge distribution and core geometry caused by methyl substitution does not influence to any appreciable extent the binding energy of the Rydberg electron in corresponding excited states. As a result, the levels with $n = 5$, 6 move in a way parallel with the energy of the cation ground state.

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