Optical absorption study of "half-open ferrocene" and "open ferrocene"

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Abstract

The electronic absorption spectra of vaporous (η^5-cyclopentadienyl)(η^5-2,4-dimethylpentadienyl)iron (1) and bis(η^5-2,4-dimethylpentadienyl)iron (2) have been measured and compared with those of the complexes in pentane solution as well as with the vapor-phase spectrum of 1,1'-dimethylferrocene (3). The photoabsorption of vaporous 1 shows two shoulders at 33 000 and 35 400 cm^{-1} which disappear on going to the condensed phase and have the term values appropriate for their assignment as the lowest ns and np Rydberg transitions, respectively. These excitations originate at the molecular orbital (MO) corresponding to the first peak in the photoelectron spectrum of 1. The data obtained indicate that "half-open ferrocene" (1) is between "open ferrocene" (2) and "closed ferrocene" (3) with respect to the 3d character of their MO's.

*Keywords:* Iron; Pentadienyl complexes; Photoabsorption; Rydberg transitions

1. Introduction

The electronic structures of transition metal–pentadienyl complexes have recently been of great interest, especially relative to those of their well-known cyclopentadienyl counterparts [1–4]. It has been previously shown [5,6] that the electronic absorption spectra of vaporous "closed ferrocene" and other d^6 metallocenes reveal intriguing features which correspond to the Rydberg excitations originating at the metal d$_{z^2}$ orbital. These features disappeared on going from the vapor to the solution phase. Valuable information concerning the ionization energies and bonding properties of MO's can be obtained when analyzing the parameters of Rydberg bands [5–12]. The present study was undertaken in order to determine the effect that successive openings of the two η^5-cyclopentadienyl rings would have on the appearance of the Rydberg transitions. With this aim, the UV and visible absorption spectra of vaporous "half-open ferrocene", (Cp)-(C$_7$H$_{11}$)Fe (1), (Cp = η^5-C$_5$H$_5$, C$_7$H$_{11}$ = η^5-2,4-Me$_2$-

C$_5$H$_5$) and "open ferrocene", (C$_7$H$_{11}$)$_2$Fe (2), were measured and compared with those of 1 and 2 in *n*-pentane solution.

2. Experimental section

Complexes 1 and 2 were synthesized by previously reported routes [2,13] and purified by repeated vacuum sublimation. The electronic absorption spectra of vaporous compounds were recorded using a heated quartz vacuum cell on a 'Specord UV Vis' (Carl Zeiss, Jena) spectrometer at 50–80°C. The spectra of 1 and 2 in pentane solution were measured on the same spectrometer in vacuo at room temperature. For comparison, the spectrum of "closed ferrocene" (C$_5$H$_4$Me)$_2$Fe (3), was recorded in the vapor and solution phases under the same conditions.

1　　　　2　　　　3

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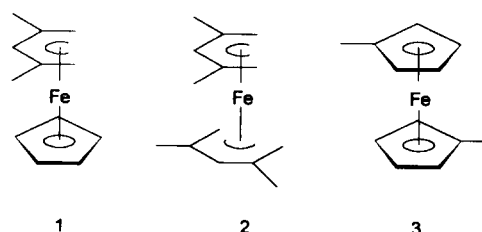
* Corresponding author.

3. Results and discussion

The photoabsorption spectrum of vaporous 3 (Fig. 1(a)) shows a sharp peak A at 39650 cm^{-1} which disappears on going to the solution phase (Fig. 1(b)). This band has been previously assigned to the $3d_{z^2} \rightarrow$ $R4p_{x,y}$ Rydberg excitation on the basis of its term value (T = 17290 cm^{-1}). The term value of a Rydberg transition is equal to the energy separation between the Rydberg state and the ionic state corresponding to the detachment of a Rydberg electron [11,12]. Photoabsorption study of a large number of transition metal sandwich compounds [5–10] has demonstrated that the term values for the lowest Rydberg excitations of each type (s, p or d) are nearly constant within this class of molecules. Thus the magnitude of T provides a reliable criterion for the interpretation of a Rydberg transition in a sandwich molecule. The term value for peak A is very close to those for the lowest Rydberg $p_{x,y}$ excitations of other d^6 metallocenes [5]. This fact confirms the assignment suggested.

In addition to band A, a weak shoulder B at 36900 cm^{-1}, which disappears on going from the vapor to the solution, has been found in this work (Fig. 1). Band B is separated by 20040 cm^{-1} from the energy of the $3d_{z^2}$ ionization of 3 (7.06 eV or 56940 cm^{-1} [14]). This term value is close to the magnitude of T for the lowest Rydberg ns transition in isoelectronic bis(η^6-toluene)chromium (T = 19810 cm^{-1} [7]). Therefore shoulder B may be assigned to the $3d_{z^2} \rightarrow R4s$ excitation. This transition is symmetry-forbidden for unsubstituted "closed sandwiches" but it becomes allowed for the complexes bearing substituents or open rings.
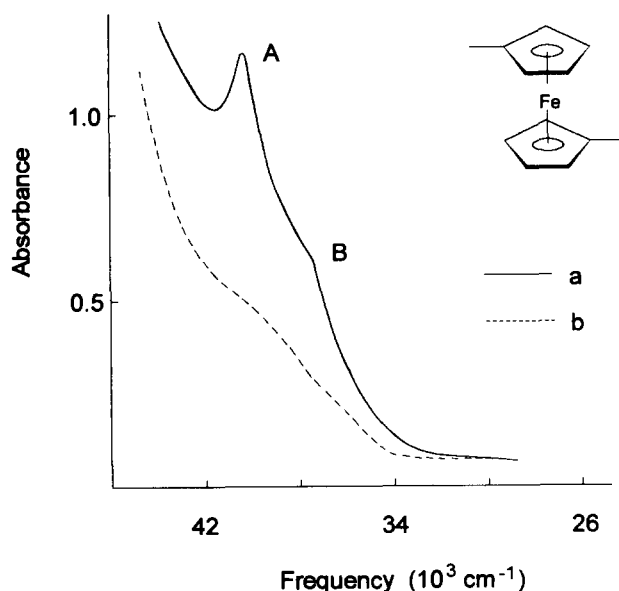

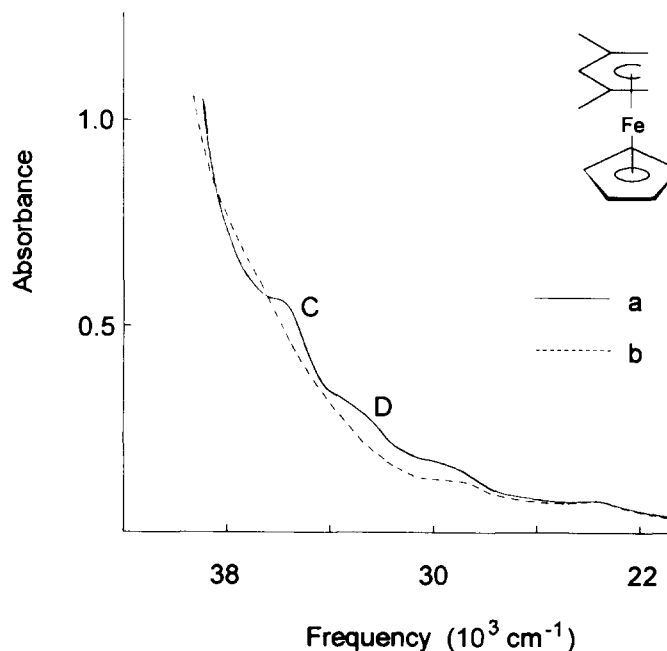Fig. 1. Electronic absorption spectrum of 3 in the vapor phase (a) and in pentane solution (b).

Fig. 2. Electronic absorption spectrum of 1 in the vapor phase (a) and in pentane solution (b).

Similar bands were observed in the spectra of vaporous ferrocenophanes and 1,1'-diethylferrocene [15].

The spectrum of vaporous 1 (Fig. 2(a)) shows two features near 30000 and 24000 cm^{-1} which remain practically unchanged on going to the solution spectrum (Fig. 2(b)) and correspond to the valence-shell transitions. In addition to these long-wavelength bands, the vapor-phase photoabsorption of 1 reveals a rather sharp shoulder C and a weaker feature D which are absent from the solution spectrum. Their frequencies are given in Table 1. The disappearance of absorption bands when one goes from the vapor to the condensed phase is usually indicative of their Rydberg origin [5–12]. It can therefore be presumed that bands C and D arise from Rydberg transitions. For their detailed assignments, knowledge of the term values is necessary. The magnitudes T_1, T_2, and T_3, which were calculated with use of the ionization potentials corresponding to the three first peaks in the photoelectron spectrum (PES) of 1 (IP_1 = 6.65 eV or 53330 cm^{-1}; IP_2 = 6.9 eV or 55650 cm^{-1}; IP_3 = 7.3 eV or 58870 cm^{-1} [4]), are given in Table 1. It is seen that the T_1 magnitudes for

Table 1
Frequencies ν (cm^{-1}) and the term values T^a (cm^{-1}) of bands C and D in the electronic absorption spectrum of vaporous 1 (Fig. 2(a))

Band	ν	T_1	T_2	T_3
C	35400	17930	20250	23470
D	33000	20330	22650	25870

^{a} $T_1 = IP_1 - \nu$, $T_2 = IP_2 - \nu$, $T_3 = IP_3 - \nu$, where IP_1, IP_2, IP_3 correspond to the three first peaks in the PES of 1 [4].

the shoulders C and D are close to the term values for bands A and B respectively in the spectrum of **3**. Thus it is quite reasonable to conclude that shoulders C and D in the vapor-phase spectrum of **1** are due to transitions from the MO, which is responsible for the first ionization potential of **1**, to the lowest Rydberg $p_{x,y}$ and s levels, respectively.

It has been shown previously [5–10] that all of the Rydberg transitions observed in photoabsorption studies of d^6 metallocenes, bisarene compounds and mixed sandwich complexes originate at the non-bonding MO which is almost a pure metal d_{z^2} orbital. No Rydberg excitations were found originating from the MO formed by the d_{xy} and $d_{x^2-y^2}$ metal orbitals, even though calculations [16] predict this MO to be nearly non-bonding in metallocenes. Thus the assignment of bands C and D to the transitions $3d_{z^2} \to R4p_{x,y}$ and $3d_{z^2} \to R4s$, respectively, seems to be the most probable. In that case, the first band in the PES of **1** should be interpreted as being due to the $3d_{z^2}$ ionization (the MO $17a'$ under the C_s point group notation [4]). This differs to some extent from the previous interpretation [4], in which the third peak at 7.3 eV was assigned to MO $17a'$, but the assignment suggested in this work is in good agreement with ESR data indicating that for the $\mathbf{1}^{+\cdot}$ and $\mathbf{2}^{+\cdot}$ radical cations the singly occupied MO could be almost exclusively derived from the Fe $3d_{z^2}$ orbital [2]. On the other hand, the magnitude of T_2 for shoulder C (Table 1) is close to the term values of the lowest Rydberg ns excitation in sandwich molecules. Hence, there is a possibility that the transition from the MO responsible for IP_2 to the R4s level contributes to band C. The T_3 values (Table 1), however, are appreciably larger than the term values of the lowest Rydberg excitations in sandwich molecules [5–10]. It is therefore unlikely that the Rydberg transitions originating at the MO corresponding to the third peak in PES of **1** [4] are responsible for features C and D.

Shoulders C and D in the absorption spectrum of **1** (Fig. 2(a)) are appreciably broadened relative to bands A and B (Fig. 1(a)). This is apparently due to an increased interaction between the iron $3d_{z^2}$ orbital and ligand MO's when one goes from the "closed ferrocene" to the "half-open ferrocene". Such a supposition is in accord with an increase in the width of the $3d_{z^2}$ ionization PES band on going from **3** to **1** [4,14].

Upon opening the second cyclopentadienyl ring, further broadening of the d-orbital ionization bands is observed in the PES [1,4]. This can be indicative of a subsequent increase in metal-ligand orbital mixing on going to the "open ferrocene". One can therefore expect the Rydberg transitions in **2** to be more broad than in **1**. Indeed, the absorption spectrum of vaporous **2** (Fig. 3(a)) shows no sharp Rydberg bands. There are only very broad, weak features E and F at 35 200 and 32 000 cm^{-1}, respectively, which are absent in the
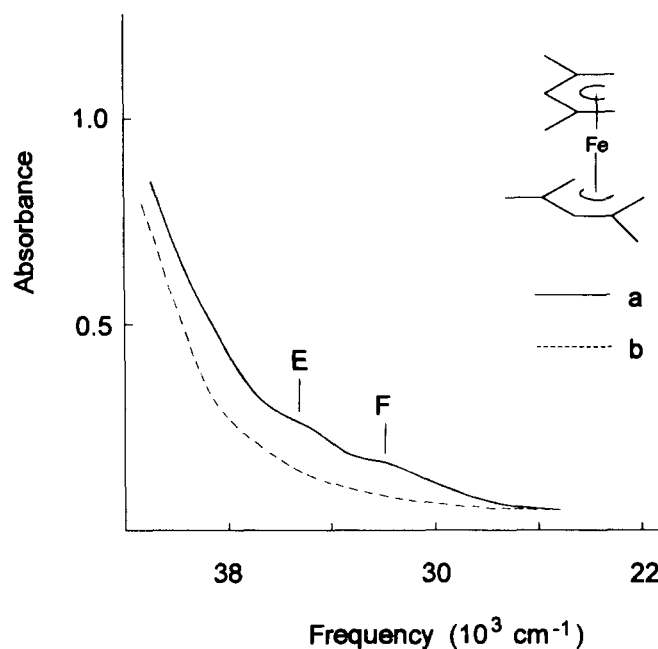

Fig. 3. Electronic absorption spectrum of **2** in the vapor phase (a) and in pentane solution (b).

solution spectrum (Fig. 3(b)). These bands are separated from the first ionization potential of **2** (6.6 eV or 53 200 cm^{-1} [1]) by 18 000 and 21 200 cm^{-1}, respectively. Such separations are close in magnitude to the term values of the lowest Rydberg $np_{x,y}$ and ns excitations, respectively [5–10]. Hence, it is quite possible that these Rydberg transitions are responsible for features E and F. On the other hand, these features are as broad as the valence-shell bands. Thus assignment of E and F to intravalency transitions is also possible. In that case, the absence of E and F in the solution spectrum can be explained by small shifts of their positions on going from the vapor to the condensed phase, and their occlusion in the background of more intense valence-shell bands.

In any event, a comparison of the vapor-phase absorption spectra of **1** and **2** (Figs. 2,3(a)) shows that the Rydberg bands are broadened when opening the cyclopentadienyl ring of the "half-open ferrocene". This could be due to a decrease in the metal 3d character of the occupied MO participating in the Rydberg transitions. Thus, the results obtained in this work are in accord with the prediction [4] that "half-open ferrocene" is between "open ferrocene" and "closed ferrocene" with respect to the 3d characters of their wave functions.

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