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Gas-phase electronic absorption spectra of metallocene dihydrides $M(\eta^5\text{-}C_5H_5)_2H_2$ (M = Mo, W)

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Abstract

The gas-phase electronic absorption spectrum of $MoCp_2H_2$ ($Cp = \eta^5\text{-}C_5H_5$) reveals an intense peak at 35 500 cm^{-1} which is absent in the spectrum measured in *n*-pentane solution. The spectrum of WCp_2H_2 shows a shoulder at 35 000 cm^{-1} which disappears on going from the gas to the condensed phase. The term values of these features (16 100 and 16 600 cm^{-1}, respectively) are appropriate for their assignment as the transitions from the HOMO to the lowest Rydberg p-orbitals. The gas-phase spectra of $MoCp_2H_2$ and WCp_2H_2 give the first examples of clearly defined Rydberg transitions in the organometallic molecules with σ-bonded ligands. Appearance of Rydberg bands confirms that the HOMO of these complexes is really non-bonding.

Keywords: Metallocene hydrides; Molybdenum; Tungsten; Electronic absorption spectra; Rydberg transitions

1. Introduction

Transition metal sandwich complexes with planar parallel carbocycles are known as the first class of organometallics showing clearly defined Rydberg transitions in the gas-phase absorption spectra [1–9]. These transitions originate at the non-bonding MO representing the almost pure metal d_{z^2}-orbital and terminate at the Rydberg s, p and d MOs. Rydberg bands disappear on going to the condensed media of low electron mobility because of large sizes of Rydberg orbitals [10]. This results in dramatic differences between the absorption spectra of sandwich compounds measured in the gas-phase and in organic solvents [1–9].

The parameters of Rydberg bands in the spectra of sandwich molecules give valuable information on the ionisation characteristics [1–9,11,12] and photodissociation dynamics [11,12]. Each Rydberg excitation can be characterised by the term value *T* equal to the difference between the corresponding ionisation potential and the Rydberg frequency. The *T* magnitude represents the binding energy of a Rydberg electron. Low-lying Rydberg excitations in sandwich molecules have similar term values for each type of Rydberg orbitals [2–9]. Knowledge of the typical *T* magnitudes for the 'classical' sandwiches makes it possible to find and assign less resolved Rydberg bands in the spectra of other related organometallics. Such bands have been found in the spectra of the 'open metallocenes' and 'half-open metallocenes' [13,14]. In this work the first attempt is undertaken to reveal Rydberg transitions in the spectra of metallocene dihydrides MCp_2H_2 (M = Mo, W).

2. Experimental

The preparations were carried out in vacuo or under inert atmosphere of Ar using standard techniques. Bis(η^5-cyclopentadienyl)dihydridomolybdenum was prepared [15] from $MoCl_5$, NaCp, and $NaBH_4$. Bis(η^5-cyclopentadienyl)dihydridotungsten was purchased from Synor Co. The complexes were purified by

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repeated vacuum sublimation. The electronic absorption spectra were measured with a Specord UV–vis (Carl Zeiss, Jena) spectrometer. The gas-phase spectra were recorded in an evacuated quartz cell heated to 100–120 °C. These spectra were compared with those measured in n-C_5H_{12} solution in a vacuum cell at room temperature in order to reveal Rydberg bands. The solution spectra obtained in this work are in an excellent agreement with those reported earlier [16].

3. Results and discussion

The spectra of MCp_2H_2 show clearly defined features which disappear on going from the gas to the condensed phase (Figs. 1 and 2). In the gas-phase spectrum of $MoCp_2H_2$ (Fig. 1) an intense peak at 35 500 cm^{-1} and a broad shoulder in the 37 000–38 000 cm^{-1} region are observed while the spectrum recorded in n-pentane solution reveals only one intense ($\varepsilon = 4800$ l mol^{-1} cm^{-1} [16]) broad absorption band with the maximum at 36 300 cm^{-1}. The valence-shell transitions in polyatomic molecules are usually red-shifted when one goes from the gas to the solution phase [10]. The red shift has been observed for intravalency excitations in the spectra of sandwich complexes [1,3] so it is reasonable to suppose that the 36 300-cm^{-1} band in the solution spectrum of $MoCp_2H_2$ corresponds to the shoulder at 37 000–38 000 cm^{-1} in the gas-phase spectrum. Then one can conclude that the peak at 35 500 cm^{-1} disappears on going from the gas to the condensed phase. This feature should be assigned, therefore, to Rydberg transitions. Such assignment can be confirmed by determination of the term value.

The 35 500-cm^{-1} absorption peak is separated by 16 100 cm^{-1} from the first ionisation potential of $MoCp_2H_2$ (6.4 eV or ca. 51 600 cm^{-1} [17]). This magnitude agrees very well with the term values of the lowest Rydberg p excitations in non-substituted d^6 metallocenes (15 500–16 000 cm^{-1} for the p_z and 16 800–17 500 cm^{-1} for the $p_{x,y}$-orbitals [4]). The peak at 35 500 cm^{-1} arises, therefore, from the transitions originating at the HOMO of $MoCp_2H_2$ and terminating at the lowest Rydberg p levels. This interpretation is supported strongly by analysis of the WCp_2H_2 spectrum.

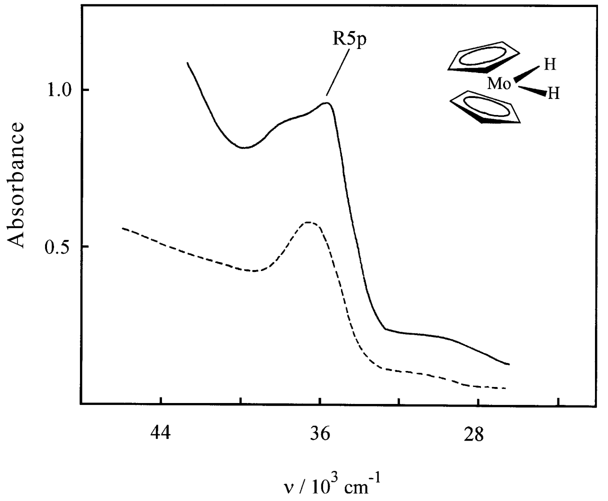

Fig. 1. Electronic absorption spectrum of $MoCp_2H_2$ in the gas-phase (full line) and in n-pentane solution (dashed line). The peak assigned to the $4d_{x^2}$ → R5p Rydberg transitions is denoted.

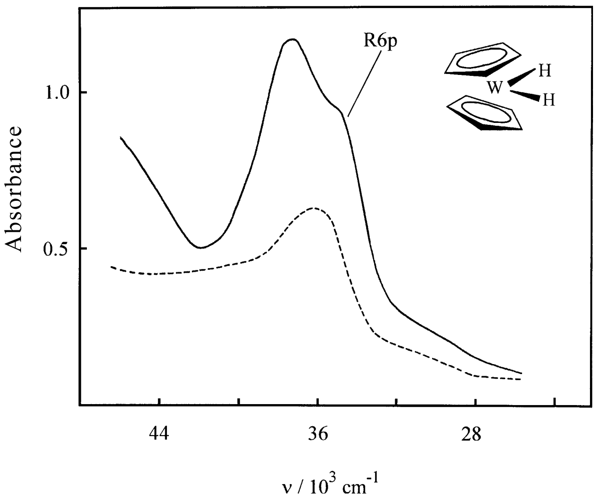

Fig. 2. Electronic absorption spectrum of WCp_2H_2 in the gas-phase (full line) and in n-pentane solution (dashed line). The shoulder assigned to the $5d_{x^2}$ → R6p Rydberg transitions is denoted.

The electronic absorption spectrum of WCp_2H_2 in n-pentane solution (Fig. 2) is very similar to that of $MoCp_2H_2$. Only one broad intense band ($\varepsilon = 5000$ l mol^{-1} cm^{-1} [16]) with the maximum at 36 000 cm^{-1} is observed. In the gas-phase, however, two intense features are revealed. There are a peak at 37 200 cm^{-1} and a clearly defined shoulder at 35 000 cm^{-1} (Fig. 2). The peak shifts to long wavelengths on going to the solution spectrum and transforms into the 36 000-cm^{-1} band arising from symmetry-allowed valence-shell excitations. This band in the spectra of $MoCp_2H_2$ and WCp_2H_2 was tentatively interpreted as a charge-transfer transition from the metal to the cyclopentadienyl ligands [16]. The shoulder at 35 000 cm^{-1} disappears when one goes to the condensed phase and should be assigned to Rydberg excitations.

The Rydberg term values for sandwich molecules change very little on replacing molybdenum with tungsten [18] so one should expect that the T magnitudes for the low-lying Rydberg transitions in $MoCp_2H_2$ and WCp_2H_2 will be similar. Indeed, the term value of the 35 000-cm^{-1} feature in the WCp_2H_2 gas-phase spectrum calculated on the basis of the first ionisation potential (6.4 eV [17]) equals 16 600 cm^{-1}. This T magnitude is appropriate for the lowest Rydberg p excitations originating at the HOMO. Thus, the Rydberg frequency and the term value for WCp_2H_2 are very close to those for $MoCp_2H_2$ as it should be expected. The different shapes of gas-phase absorption spectra of $MoCp_2H_2$ and WCp_2H_2 in the 34 000–38 000 cm^{-1} region (Figs. 1 and 2) can well be a result of changes in relative intensities of the valence-shell and Rydberg transitions on replacing molybdenum with tungsten in the metallocene complex.

A correlation MO diagram based on the density functional calculations [19] is given in Fig. 3 for the frontier orbitals of the parallel-ring metallocenes, bent metallocenes, and metallocene dihydrides. As the metallocene molecule bends the metal d-orbitals of a_{1g} and e_{2g} symmetry give two totally symmetric MOs ($3a_1$ and $4a_1$) and the $2b_1$ level. When forming a dihydride, the $2b_1$ and $4a_1$ orbitals mix with the two linear combinations of the hydrogen 1s AOs. The non-bonding $3a_1$ orbital is the HOMO of $MoCp_2H_2$ and WCp_2H_2. The isosurface of this MO [19] shows that it is formed mainly by the metal d_{x^2} AO, being in accord with an ESR study of d^1 complexes [20]. The Rydberg transitions observed in the spectra of $MoCp_2H_2$ and WCp_2H_2 are assigned, therefore, as $4d_{x^2} \rightarrow$ R5p and $5d_{x^2} \rightarrow$ R6p, respectively. All the three components (p_x, p_y, and p_z) are allowed by the selection rules and can contribute to the Rydberg features revealed (Figs. 1 and 2).

In the non-substituted parallel-ring sandwich systems the first two members of the Rydberg p series are separated by ca. 9000 cm^{-1} [1,3,18] so the $nd_{x^2} \rightarrow R(n+2)p$ transition in the spectra of $MoCp_2H_2$ and WCp_2H_2 is expected to lie in the 44 000–44 500 cm^{-1} region. The spectra of the metallocene dihydrides show no clearly defined features in this region but there is a noticeable increase in the relative intensity of photoabsorption in the gas-phase as compared with the solution phase (Figs. 1 and 2). This can well be caused by the contribution of the Rydberg transitions.

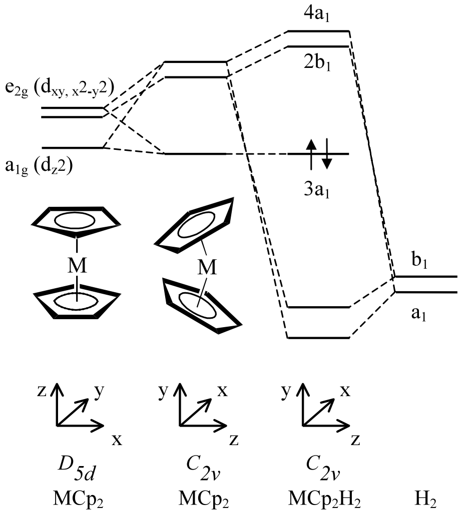

Fig. 3. MO correlation diagram for the frontier orbitals of parallel-ring metallocenes, bent metallocenes, and metallocene dihydrides. The axis system corresponds to that assumed for the density functional calculations [19], the symmetry point groups being indicated for each type of the complexes. The HOMO of metallocene dihydrides $MoCp_2H_2$ and WCp_2H_2 is denoted by a double arrow.

The excitations of the d_{x^2}-electron to the Rydberg s- and d-orbitals are also allowed for MCp_2H_2. The lowest Rydberg s and d transitions in MCp_2H_2 (M = Mo, W) are expected to lie at ca. 30 000 cm^{-1} and ca. 39 000 cm^{-1}, respectively, but they are too weak to be revealed in the gas-phase spectra (Figs. 1 and 2). The intensities of allowed Rydberg s and d transitions in the spectra of $(\eta^6\text{-}C_6H_5CH_3)_2M$ (M = V, Cr, Mo, and W) [1,3,18] are also much less than those of lower Rydberg p excitations.

Appearance of Rydberg p excitations in the gas-phase spectra of $MoCp_2H_2$ and WCp_2H_2 confirms the non-bonding character of the $3a_1$ MO (Fig. 3). The spectra of the parallel-ring sandwich compounds [1–9] reveal only those Rydberg transitions which originate at the strongly non-bonding d_{z^2} (a_{1g}) orbital. For ferrocene, ruthenocene and osmocene [2,4] no Rydberg excitations from the e_{2g} level were observed though various MO calculations carried out for Cp_2Fe [19,21–23] including recent works based on the density functional theory [19,23] show that this orbital consists mainly of the metal d_{xy,x^2-y^2} AOs. Surprisingly, the Rydberg feature in the spectra of $MoCp_2H_2$ and WCp_2H_2 is resolved better than those in the spectra of the ‘open metallocenes’ and even of the ‘half-open metalocenes’ [13,14]. However, on going from the ‘classical’ parallel-ring sandwich complexes [1–9] to $MoCp_2H_2$ and WCp_2H_2 a considerable broadening of Rydberg bands is observed. This can be explained by less localisation of the HOMO in MCp_2H_2 as compared with the d_{z^2}-orbital in the parallel-ring sandwich molecules.

The gas-phase spectra of $MoCp_2H_2$ and WCp_2H_2 give the first (to our knowledge) examples of clearly defined Rydberg transitions in the organometallic molecules with σ-bonded ligands. Rydberg states can play an important role in photodissociation of sandwich molecules [11,12] so the gas-phase metallocene dihydrides may appear to have some specific photophysical and photochemical properties in the region of the Rydberg transitions revealed (35 000–36 000 cm^{-1}). The results obtained in this work show that Rydberg features can be expected to appear in the gas-phase electronic absorption spectra of bent metallocene complexes with such ligands as CH_3, CO and C_2H_4. The shapes of the first band in the photoelectron spectra of these compounds [17] resemble those for $MoCp_2H_2$ and WCp_2H_2. This similarity is indicative of non-bonding character of the HOMO in such molecules.

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