Nature of low-lying electron excited states of (η^5-cyclopentadienyl)(η^7-cycloheptatrienyl)niobium

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Electron absorption spectra of (η^5-cyclopentadienyl)(η^7-cycloheptatrienyl)niobium in solution and in the vapor phase have been measured for the first time. Possible variants of the band assignment for the spectrum of the complex in a solution have been considered. In the spectrum of the vaporous compound the bands at 29570, 31730, and 34630 cm^{-1} correspond to the electron transitions from the 4d(σ^+) orbital to the lowest Rydberg p- and d-levels. The values of Rydberg transition terms and symmetry of p-states have been determined.

Key words: (η^5-cyclopentadienyl)(η^7-cycloheptatrienyl)niobium, electron absorption spectrum, electron excited states, Rydberg levels, electron transitions.

According to the data of photoelectron spectroscopy (PES)[1–4] and quantum chemical calculations,[5–7] d(σ^+)- and d(δ)-orbitals of the metal atom make the main contribution to the higher occupied molecular orbitals (MO) of the majority of 17- and 18-electron sandwich complexes of transition metals of the type (η^n-C_nH_n)$_2$M and (η^n-C_nH_n) (η^m-C_mH_m)M (irreducible representations of point groups $C_{\infty v}$ are used for designation of the symmetry of orbitals). The orbitals of the π-type localized predominantly at hydrocarbon ligands are arranged lower (Fig. 1). Lower vacant MO of such complexes look like π-MO with a considerable contribution of the d-orbital of the metal atom and the σ-MO consisting mainly of vacant orbitals of ligands.[5–8] The valent electron transitions of sandwich compounds lowest in energy correspond to the considered MO. These transitions can be conditionally defined as 1) d—d, 2) with ligand—metal or metal—ligand charge transfer, and 3) of the ligand—ligand type. These are the transitions that may cause the bands observed in the absorption spectra of the solutions of sandwich compounds in the visible and UV regions.[6–13]

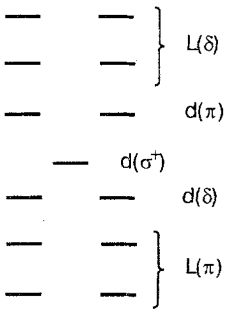

Fig. 1. Scheme of highest occupied and lowest vacant energy levels of MO of the complexes (η^n-C_nH_n)$_2$M and (η^n-C_nH_n) (η^m-C_mH_m)M (M is a transition metal atom).

In addition to valent excitations, the transitions from the nonbonding d(σ^+)-levels to the Rydberg levels can be seen in electron absorption spectra of vaporous sandwich complexes.[14–20] The atomic orbitals (AO) corresponding to these levels have a higher value of their principal quantum number than AO participating in the formation of the valent shell of the molecule.[21,22] Similarly to atomic orbitals, the Rydberg orbitals may be characterized by the principal and orbital quantum numbers. The bond energy of a Rydberg electron with a molecular frame is determined by the value of the term

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

where R is the Rydberg constant (109737 cm^{-1}), n is the principal quantum number, Δ is a quantum defect, I is the energy required to remove an electron from an occupied MO participating in the Rydberg transition with the frequency ν_n. The term values for the Rydberg transitions of molecules of the same type that have the similar structures differ slightly and may be used for interpretation of spectra.[14–22] As can be seen from Eq. (1), the transition frequency ν_n is determined by the difference between I and T. For the majority of organic molecules, the values of ν_n correspond to the UV spectrum in the vacuum region.[21,22] The appearance of the Rydberg bands in visible and UV spectra of sandwich complexes of transition metals[14–20] is associated with the very low energy of the removal of d-electrons from molecules of these compounds.[1-4]

The strong change in the form of the electron absorption spectrum on going from the vaporous phase to condensed media with a low electron mobility is one of the properties indicating the presence of Rydberg

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excitation. Usually, this change results in the disappearance of Rydberg bands, which is related to the scattering of optically excited electrons.[21] Therefore, spectra of vaporous sandwich complexes and their solutions should be compared in studying electron excited states of different natures. The Rydberg bands in the absorption spectra of several *bis*-arene compounds,[14—16] metallocenes,[17,18] and mixed sandwiches[19,20] were revealed by just this method. Complexes of metals in the 3d-row have been mainly studied in these works. The excited states of the sandwich compounds of heavier transition metals are significantly less known. In the present work, the electron absorption spectrum of the sandwich niobium complex in the vaporous phase, specifically, the 17-electron complex (η^5-Cp)(η^7-C_7H_7)Nb (**1**) was chosen, in which the nonbonding d(σ)-orbital is occupied by one electron (ground electron state $^2\Sigma^+$: ...$[C_7H_7(\pi)]^4$ $[Cp(\pi)]^4$ $[4d(\delta)]^4$ $[4d(\sigma^+)]^1$...), has been studied for the first time.[3,4]

Experimental

Complex 1 was synthesized according to the known procedure[23] from $NbCl_5$, CpNa, and cycloheptatriene in the presence of *i*-PrMgBr. The structure of the compound was confirmed by the ESR spectrum of 10 lines corresponding to the splitting at the ^{93}Nb (I = 9/2) nucleus. The value of the hfs constant (a_{Nb} = 3.33 mT) agrees well with the literature data.[4,23] The complex was purified by two sublimations *in vacuo.*

The electron absorption spectrum of **1** in the vaporous phase was recorded on a Specord UV VIS spectrometer at 80—120 °C. An evacuated heated cuvette with windows of optical quartz was used. A spectrum of a solution of the complex was registered *in vacuo* by the same spectrometer at room temperature (*n*-pentane was used as the solvent).

Results and Discussion

The electron absorption spectrum of a solution of **1** in *n*-pentane (Fig. 2) is a set of broad structureless bands typical of sandwich complexes. Two weak shoulders **A** and **B** are observed in the visible range, and a more intense shoulder **C** and a strong band **D** are in the UV part of the spectrum. The frequencies of the **A**- **D** bands are listed in Table 1. The great width of the bands and the absence of the vibrational structure do not allow us to interpret unambiguously the absorption spectrum of a solution of **1**, however, we can make a suppositional assignment based on the scheme of the arrangement of the MO levels (Fig. 1), the data of PES,[4] and identification of the absorption bands in spectra of several metallocenes,[9,10] *bis*(η^6-benzene)vanadium (**2**),[7,12] and mixed complexes.[8,11,13]

In terms of the point group $C_{\infty v}$ the selection rules allow all transitions between the levels presented in Fig.1, except the transitions $d(\delta)\rightarrow d(\sigma^+)$ and $d(\sigma^+)\rightarrow L(\delta)$. Weak long-wave bands in the spectra of sandwich compounds are usually assigned to d—d-transitions, and intense short-wave bands are assigned to transitions with charge transfer.[6—13] Since the energies of the highest occupied and lowest vacant MO of the aromatic ligand C_mH_m (m = 5—8) decrease as m increases,[5] in molecule **1** the metal→ligand transition with participation of the orbital of C_7H_7 and the ligand→metal transition with participation of MO localized on Cp have a lower energy.

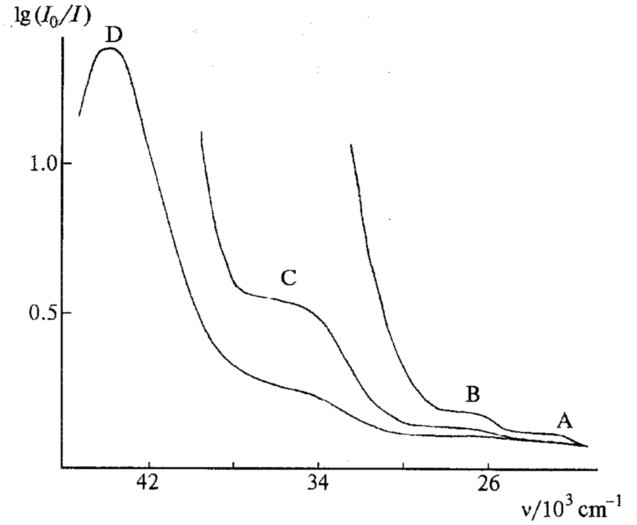

Fig. 2. Electron absorption spectrum of **1** in *n*-pentane.

The difference between the energy of removing an electron from the 4d(δ) orbital and removing an electron from the 4d(σ^+) orbital is small for **1** (1.15 eV, or 9270 cm^{-1}).[4] Therefore, the forbidden transition $4d(\delta)\rightarrow 4d(\sigma^+)$ should be expected in the IR region, and of the other transitions, the $d(\sigma^+)\rightarrow d(\pi)$ transition, which may cause the long-wave shoulder **A** (Fig. 2), has the smallest energy capacity in 17- and 18-electron sandwiches.[6—9] The calculated energy of the analogous

Table 1. Frequencies and suggested assignment of bands in the electron absorption spectrum of **1** in *n*-pentane.

Band	ν/cm^{-1}	Assignment	
		Variant I	Variant II
A*	~ 21000	$4d(\sigma^+) \rightarrow 4d(\pi)$	$^{**}4d(\delta) \rightarrow 4d(\pi)^1$
B*	~ 25000	$^{**}4d(\delta) \rightarrow 4d(\pi)^1$ $Cp(\pi) \rightarrow 4d(\sigma^+)$	$Cp(\pi) \rightarrow 4d(\sigma^+)$ $^{**}4d(\delta) \rightarrow 4d(\pi)^2$ $4d(\delta) \rightarrow C_7H_7(\delta)$
C*	~ 33000	$^{**}4d(\delta) \rightarrow 4d(\pi)^2$ $4d(\delta) \rightarrow C_7H_7(\delta)$ $C_7H_7(\pi) \rightarrow 4d(\sigma^+)$	$Cp(\pi) \rightarrow C_7H_7(\delta)$ $Cp(\pi) \rightarrow 4d(\pi)$ $C_7H_7(\pi) \rightarrow 4d(\sigma^+)$
D	41700	$Cp(\pi) \rightarrow C_7H_7(\delta)$ $Cp(\pi) \rightarrow 4d(\pi)$ $4d(\delta) \rightarrow Cp(\delta)$	$C_7H_7(\pi) \rightarrow C_7H_7(\delta)$ $C_7H_7(\pi) \rightarrow 4d(\pi)$ $4d(\delta) \rightarrow Cp(\delta)$

* Shoulder.

** Two components of the $4d(\delta)\rightarrow 4d(\pi)$ transition were taken into account.

excitation in **2** (22540 cm^{-1})[7] agrees well with the frequency of the band of **A** (Table 1). In the spectrum of ferrocene, the $3d(\sigma^+)\rightarrow 3d(\pi)$ transition also has a similar frequency (21800 cm^{-1}).[9] The forbidden transition $4d(\sigma^+)\rightarrow C_7H_7(\delta)$ may appear in the range of shoulder **A**, because the δ levels of MO of C_7H_7 and of the orbital $d(\pi)$ may be close.[24]

The $d(\delta)\rightarrow d(\pi)$ excitation falls in the higher energy range. Two components of this transition appear in the spectra of 18-electron metallocenes.[9] The frequency of the long-wave component is higher than that for the $d(\sigma^+)\rightarrow d(\pi)$ transition by 2000—3000 cm^{-1}, and for the short-wave component by 7000—9000 cm^{-1}. Based on the mutual arrangement of the **A**, **B**, and **C** bands, it may be suggested that the low-frequency component of the $4d(\delta)\rightarrow 4d(\pi)$ transition contributes to the **B** shoulder, and the high-frequency component contributes to the long-wave shoulder of the **C** band.

A second variant of the energy distribution of d—d-excitations in **1** is also possible. The $4d(\sigma^+)\rightarrow 4d(\pi)$ transition may occur in a more long-wave range and may not be observed due to its low intensity. (In the spectrum of **2**,[12] the band at 13000 cm^{-1} was assigned to the $3d(\sigma^+)\rightarrow 4d(\pi)$ excitation). Then the **A** and **B** bands correspond to two components of the $4d(\delta)\rightarrow 4d(\pi)$ transition. In this case, there is a transition with charge transfer $4d(\delta)\rightarrow C_7H_7(\delta)$ in the region of the **B** shoulder.

The higher intensity of the **B** band compared to that of **A**, seems to also be caused by a contribution of the allowed $Cp(\pi)\rightarrow 4d(\sigma^+)$ transition with charge transfer. The bands assigned to the analogous excitation in the 17-electron complexes **2** (22300 cm^{-1})[12] and $(\eta^5\text{-}C_5Me_5)(\eta^8\text{-}C_8H_8)Zr$ (**3**) (24100 cm^{-1})[11] are in the same range as the **B** shoulder (Table 1). The values of the difference of the energies to remove electrons from $Cp(\pi)$ and $d(\sigma^+)$ MO of these compounds (27100 cm^{-1} for **2**[2] and 23900 cm^{-1} for **3**[11]) also correspond to this spectral range. Therefore, the similarity of the **B** band frequency (Table 1) to the difference of the ionization energies of $Cp(\pi)$- and $4d(\sigma^+)$-MO in **1** (23550 cm^{-1})[4] also attests to the contribution of the $Cp(\pi)\rightarrow 4d(\sigma^+)$ transition.

The ultraviolet part of the spectrum of **1** in solution (Fig. 2) looks very similar to the previously studied but not interpreted spectrum of $(\eta^5\text{-}Cp)(\eta^7\text{-}C_7H_7)V$[25] containing a shoulder in the range of 35700 cm^{-1} and an intense peak with a maximum at 41900 cm^{-1} corresponding to the **C** and **D** bands (Table 1). The frequency of the **C** band may correspond to the $C_7H_7(\pi)\rightarrow 4d(\sigma^+)$ transition. The difference in the ionization energies of the $C_7H_7(\pi)$- and $4d(\sigma^+)$-MO for **1** is 4.37 eV (35240 cm^{-1}).[4] Generally speaking, the difference in the ionization potentials of a neutral molecule is an equivalent to the energy of the transition between the corresponding electron states of the monocharged cation rather than to the energy of excitation of an electron of the neutral molecule. Nevertheless, from the example of the $Cp(\pi)\rightarrow d(\sigma^+)$ transition considered above one can see that the difference between the excitation energies of the valent shell of the molecule and its cation is not very large.

The first of the variants of the sequence of d—d-transitions considered above assumes that the $4d(\delta)\rightarrow C_7H_7(\delta)$ excitation, which is close in energy to $4d(\delta)\rightarrow 4d(\pi)$, is related to the **C** band. The calculated energy value of the $3d(\delta)\rightarrow C_6H_6(\delta)$ transition in **2** (31550 cm^{-1})[7] lies in the same range. According to this variant, the transitions $Cp(\pi)\rightarrow C_7H_7(\delta)$, $Cp(\pi)\rightarrow 4d(\pi)$, and $4d(\delta)\rightarrow Cp(\delta)$, which may cause the intense peak **D**, should be assigned to the higher frequency range. The excitation bands $C_7H_7(\pi)\rightarrow C_7H_7(\delta)$, $C_7H_7(\pi)\rightarrow 4d(\pi)$, $Cp(\pi)\rightarrow Cp(\delta)$, and $C_7H_7(\pi)\rightarrow Cp(\delta)$ with higher energies lie in this case beyond the range studied.

The second variant of the sequence of the d—d-transitions assumes that the excitations $Cp(\pi)\rightarrow C_7H_7(\delta)$ and $Cp(\pi)\rightarrow 4d(\pi)$ contribute not to the **D** band, but to the **C** shoulder. Despite the great calculated value of the frequency of the $C_6H_6(\pi)\rightarrow 3d(\pi)$ transition in molecule **2** (55490 cm^{-1}),[7] the band at 31250 cm^{-1} in the spectrum of **2** in solution[12] is assigned to this transition (the bathochromic shift of the band after the introduction of methyl substituents into the benzene rings support this). The calculated frequency of the $Cp(\pi)\rightarrow 3d(\pi)$ transition in the $(\eta^5\text{-}Cp)(\eta^6\text{-}C_6H_6)Fe^+$ cation (35890 cm^{-1})[8] is comparable with that of band **C** (Table 1). The assumption that the $Cp(\pi)\rightarrow 4d(\pi)$ excitation contributes to the **C** band agrees poorly with the first variant of the assignment of the **A** shoulder (Table 1), because in this case the sum of the frequencies of the $Cp(\pi)\rightarrow 4d(\sigma^+)$ and $4d(\sigma^+)\rightarrow 4d(\pi)$ transitions would exceed the frequency of the $Cp(\pi)\rightarrow 4d(\pi)$ transition by 12000 cm^{-1}.

The difference in the ionization energies of $C_7H_7(\pi)$ and $Cp(\pi)$ MO for **1** is 1—1.5 eV.[4] Therefore, the estimates of the frequencies of the transitions from these MO to the same vacant MO may differ by approximately 8000—12000 cm^{-1}. If transitions involving $Cp(\pi)$ MO occur in the region of the **C** shoulder, the analogous excitations involving a $C_7H_7(\pi)$ MO may correspond to the **D** band. Thus, the second variant of the interpretation of the spectrum of **1** in solution suggests the assignment of the **D** peak to $C_7H_7(\pi)\rightarrow C_7H_7(\delta)$, $C_7H_7(\pi)\rightarrow 4d(\pi)$, and $4d(\delta)\rightarrow Cp(\delta)$ transitions. In this case, the transitions $Cp(\pi)\rightarrow Cp(\delta)$ and $C_7H_7(\pi)\rightarrow Cp(\delta)$ remain beyond the studied spectral range.

Both of the considered variants of the band assignment in the spectrum of **1** in solution are presented in Table 1. Currently available experimental and calculated data do not allow one to make a more unambiguous interpretation. Information about the influence of various factors (size of the aromatic ring, introduction of substituents, *etc.*) on the position of the absorption bands in the spectra of mixed sandwich complexes is necessary for the interpretation. Additional data may be obtained from electron absorption spectra in low-temperature matrices and spectra of circular dichroism studies, as was done in the case of compound **2**.[12]

Nevertheless, even this information were available, the unambiguous assignment of the broad structureless bands corresponding to valent electron transitions in sandwich complexes would be unsuccessful in the nearest future. On the other hand, the Rydberg bands in the absorption spectra of sandwich compounds can be interpreted with sufficient accuracy on the basis of the values of their terms.[14—22] These bands are observed in the spectra of vaporous complexes and disappear in the spectra of their solutions. Three such bands are distinguished in the case of compound **1**.

There is a shoulder in the range of 25000 cm^{-1} and a broad intense peak with the maximum at 43000 cm^{-1} in the spectrum of **1** in the vaporous phase which correspond to the absorption bands **B** and **D** of **1** in solution (Fig. 3) (the shoulder **A** is not observed in the vapor-phase spectrum due to its low intensity). At the same time, three strong quite narrow peaks **E**, **F**, and **G** are notable, which are absent in the spectrum of the **1** solution, while the weaker band **C** does not appear against their background. The frequencies of these peaks are listed in Table 2. The disappearance of the bands **E—G** on going from the vapor phase to a solution testify to their Rydberg character.[14—22]

As the Rydberg transitions in the spectra of all sandwich compounds studied previously were observed only from the nonbounding 4d(σ^+) MO, the peaks **E—G** should be also assigned to the Rydberg excitations involving the 4d(σ^+) MO. Knowing the energy required to remove a 4d(σ^+)-electron from a molecule of **1**, one can determine the values of the terms corresponding to the **E—G** bands. The first ionization potential of **1** corresponding to this energy is close to 5.98 eV [3] or 5.85 eV.[4] In this work, the *T* values listed in Table 2 were calculated using the results presented in Ref. 4.

The **E** band is characterized by a term value (Table 2) typical of the first term of the Rydberg *n*p(π)-series in sandwich complexes (17550, 17230, 16780, 17580, and 17550 cm^{-1} for **2**,[15] $(\eta^6\text{-C}_6\text{H}_6)\text{Mo}$,[16] $(\eta^5\text{-Cp})_2\text{Ru}$ (**4**),[18] $(\eta^5\text{-Cp})(\eta^7\text{-C}_7\text{H}_7)\text{Cr}$ (**5**),[19] and $(\eta^5\text{-Cp})(\eta^6\text{-C}_6\text{H}_6)\text{Mn}$ (**6**),[20] respectively), which allows one to assign it unambiguously to the 4d(σ^+)→*R*5p(π) excitation. This band has a weakly resolved vibrational structure in the form of a progression with a frequency of ~ 280 cm^{-1}. A similar progression is observed for some 18-electron sandwiches.[15—20]

In the case of metallocenes and *bis*-arene complexes, this band corresponds to the excitation of the completely symmetric metal—ring valent vibration. It should be mentioned that the **E** band is noticeably broadened compared to the lower terms of the *Rn*p(π)-series in the spectra of 18-electron complexes, so its maximum no longer corresponds to the 0,0-transition. Therefore, in the considered Rydberg state, the equilibrium metal—ring distance in **1** is changed more than in 18-electron sandwiches. This may be caused either by an increase in the contribution of the 4d(σ^+) MO of **1** to the formation of the metal—ligand bonds or by a mixture of a valent excited state of the same symmetry with the Rydberg state.

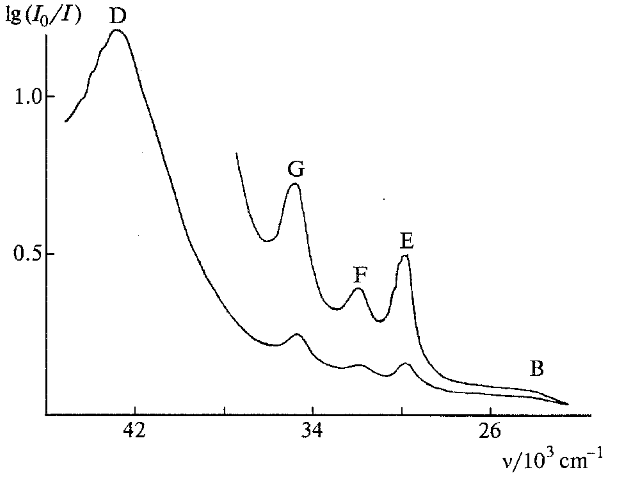

Fig. 3. Electron absorption spectrum of **1** in a vapor phase.

The *T* values for the **F** band (Table 2) and lower Rydberg *n*p(σ^+)-transition in compounds **2** (15650 cm^{-1}),[15] **4** (15480 cm^{-1}),[18] **5** (15490 cm^{-1}),[19] and **6** (15920 cm^{-1})[20] are similar. Therefore, this peak must be assigned unambiguously to the 4d(σ^+)→*R*5p(σ^+) excitation. The term value for the **G** band (Table 2) allows one to assign it to the 4d(σ^+)→*R*5d Rydberg transitions. These transitions are forbidden by the selection rules in nonsubstituted symmetric sandwich compounds $(\eta^5\text{-Cp})^2$M and $(\eta^6\text{-C}_6\text{H}_6)$M. But they are allowed for the complexes with substituents in the rings or for mixed sandwich compounds. In the absorption spectrum of **6**,[20] the lower *Rn*d-transitions have term values of ~ 129000 cm^{-1}, and in the spectrum of **5**,[19] the band with the maximum at 32440 cm^{-1} corresponding to T = 12750 cm^{-1} may be assigned to the first components of the *Rn*d-series. It seems impossible to unambiguously determine the symmetry of the excited state corresponding to the **G** band based on the data available. The transitions to *R*5d(π) and *R*5d(σ^+) levels are allowed in terms of the $C_{\infty v}$ point group.

The **F** and **G** bands are noticeably broader than the corresponding peaks in the spectrum of **5**.[19] As in the

Table 2. Frequencies, term values, and the assignment of the bands disappearing in the spectrum of **1** on going from a vaporous phase to a solution.

Band	ν/cm^{-1}	*T*/cm^{-1}	Assignment*
E	29570	17610	4d(σ^+) → *R*5p(π) [$^2\Pi$]
F	31730	15450	4d(σ^+) → *R*5p(σ^+) [$^2\Sigma^+$]
G	34630	12550	4d(σ^+) → *R*5d(σ^+,π) [$^2\Sigma^+$,^{2}P]

* The symmetry of the electron excited state is indicated in brackets.

case of the **E** band, this may be caused by the participation of the Nb 4d(σ^+)-orbital in the formation of a chemical bond or by the interaction between the Rydberg and valent levels. In the photoelectron spectra of **1**[4] and **5**,[26] the bands caused by the removal of a d(σ^+)-electron differ slightly in width. Therefore, it is unlikely that the contribution of the d(σ^+)-orbital to the chemical bonding increases considerably on going from **5** to **1**. However, in order to completely exclude this possibility, the comprehensive analysis of the band structure in the photoelectron spectra of **1** and **5** is necessary. The data on PES[3,4,26] available at the present time do not allow us to do this. It seems that mixing of the Rydberg and valent states plays the main role in the broadening of the **E**—**F** peaks. However, despite the possible role of the latter, the **E**—**F** bands, as a whole, must be characterized as Rydberg state as indicated by their disappearance on going from the vapor phase to a solution.

Of all of the Rydberg excitations of **1**, the $4d(\sigma^+) \rightarrow R5s(\sigma^+)$ transition possesses the lowest energy. The frequency of this transition calculated using the term value of the analogous excitation in compound **5** (21390 cm^{-1}) is 25790 cm^{-1}. This transition is allowed by the symmetry in the point group $C_{\infty v}$ but its intensity is too low to be observed against the background of the **B** shoulder (Fig. 3). The first component of the *Rn*-series was not manifested in the case of methylsubstituted derivatives of the 17-electron complex **2** as well,[15] although it is allowed by the selection rules.

We could not clearly detect the higher terms of the Rydberg series corresponding to $n > 5$ in the spectrum of the vaporous compound **1**. The transitions from the 4d(σ^+) orbital to the Rydberg MO with $n = 6$ and $n = 7$ are located between the **G** peak and the maximum of the **D** band, but they are so broadened that they do not appear in the spectrum. This is caused by strong mixing of the Rydberg levels with the valent excited states corresponding to the **D** band. Three very weak and quite narrow shoulders at 43440, 43760, and 44420 cm^{-1}, corresponding to $n = 8$ and $\Delta = 2.6$, 2.3, and 1.9, respectively, are observed at the short-wave wing of the **D** peak (Fig. 3). They can be assigned to the transitions from the 4d(σ^+) level to *R*8s, *R*8p, and *R*8d, respectively, on the basis of the values of the quantum defects. However, the weakly defined character of these bands as well as the low accuracy of the determination of the ionization potential of **1**,[3,4] and, hence, of the Δ values, force us to consider this assignment as just an assumption only. The transitions to the Rydberg levels from $n>8$ must be less intense and are not observed in the spectrum of **1**.

Thus, the Rydberg structure in the vaporous spectrum is less pronounced for the 17-electron niobium complex **1** than for the 18-electron sandwich chromium compound **5** with the same ligands. Extended Rydberg series having up to 9 components[19] are clearly seen in the spectrum of **5**. Nevertheless, our study shows that the peculiarities of the optical absorption of vapors of **1** in the near UV-region is caused by low-lying electron excitation levels of the Rydberg type.

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