SYSTEMATIC INVESTIGATION OF THE NEAR ULTRAVIOLET SPECTRA OF CHLOROTHIOPHENES[*]

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The near ultraviolet (UV) spectra of all chlorothiophenes have been investigated in vapour phase and n-hexane solution. The Rydberg bands are shown to obliterate in condensed phase spectra and have an almost constant term value throughout the series of the investigated compounds. In order to assign the valence transitions CNDO/S calculations were carried out. The order of the transitions has been shown to be $\pi_4^* \leftarrow \pi_3$, $\pi_4^* \leftarrow \pi_2$ and $R_s \leftarrow \pi_3$ in each compound.

Introduction

In our previous works [1] the near UV spectra of thiophene and some of its substituted derivatives have been investigated. The result of our works was the identification of three electronic transitions as $\pi_4^* \leftarrow \pi_3$, $\pi_4^* \leftarrow \pi_2$, and $R_s \leftarrow \pi_3$ (Rydberg transition to an s type terminating orbital). The aim of the present work is to investigate all the chlorothiophenes in order to assign their spectra and to draw some conclusions about the electronic structure of these molecules.

Experimental

The investigated compounds were synthetised by known methods [2,3] and their purity was checked by gas chromatography. The spectra have been recorded using a Specord UV VIS spectrophotometer. For the assignment modified CNDO/S quantum-chemical calculations [4] have been carried out. Geometrical data were taken from the literature [5], the applied parameters were described earlier [4].

Results and discussion

The vapour and condensed phase spectra of the investigated compounds are shown in Fig. 1. In the 46–50000 cm^{-1} region a weak band-system is observable in the vapour spectrum of each compound. The effect of the condensed phase is to obliterate these structures as can be seen in Fig. 1. This behaviour is characteristic for Rydberg transitions [6].

Term values calculated from the adiabatic ionization energies [7] are listed in Table I. The observed term values are in good agreement with those calculated by Robin's method [6] for Rydberg orbitals of s type. The term values are roughly constant throughout the whole series as it is expected. Judging from the term value a transition to an s type terminating orbital is favourable. This transition is forbidden for molecules of C_{2v} symmetry ($A_2 \leftarrow A_1$), only a vibronic coupling can make it allowed. This might be the reason for the observed low intensity of the appropriate bands.
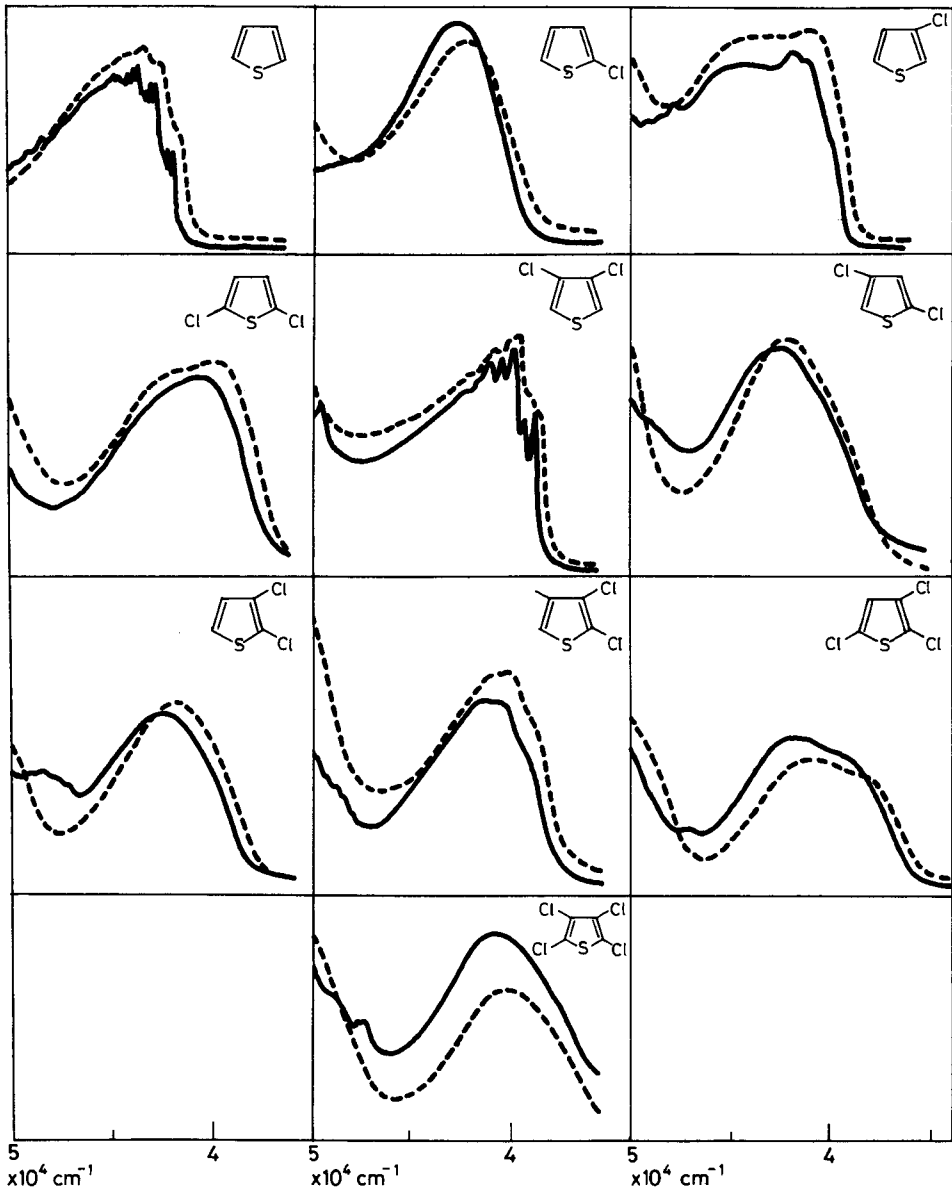

Fig. 1. Near UV spectra of chlorothiophenes in vapour phase (———) and in
n-hexane solution (----)

Below 45 000 cm^{-1} an asymmetric band is observed for most of the compounds. However in
the case of 3-chloro-, 2,5-dichloro- and 2,3,5-trichlorothiophenes two bands can be clearly
distinguished. The bands generally do not show vibronic fine structures with the exception
of 3-chloro-, 2,5 dichloro-, 3,4-dichloro- and 2,3,4-trichlorothiophenes. The bands are seen

Table I

Ionization energies, transition energies and term values of chlorothiophenes

Compound	Adiabatic IE	Adiabatic transition energy	Term value	Term value Calc.[x]
Thiophene	71500	48300	23200	24200
2-Cl-thiophene	70800	46700	24100	24400
3-Cl-thiophene	71900	47900	24000	24400
2,5-Cl-thiophene	69400	46500	22900	24500
3,4-Cl-thiophene	73000	49400	23600	24500
2,4-Cl-thiophene	71300	47400	23900	24500
2,3-Cl-thiophene	70700	47000	23700	24500
2,3,5-Cl-thiophene	70200	46400	23800	24500
2,3,4-Cl-thiophene	71700	47200	24500	24500
2,3,4,5-Cl-thiophene	71000	47000	24000	24600

[x]Term values are calculated by Robin's method [6]

Table II

Calculated and observed band maxima and oscillator strengths for chlorothiophenes[x]

Compounds	$\pi_4^* \leftarrow \pi_3$	$\pi_4^* \leftarrow \pi_2$	$\pi_4^* \leftarrow n$	$\pi_5^* \leftarrow \pi_3$
Thiophene	43500 (0.18) 39700 (0.20)	44200 (0.04)	55800 (0.01)	56600 (0.60)
2-Cl	42700 (0.19) 39000 (0.24)	44100 (0.04)	55100 (0.06)	56000 (0.60)
3-Cl	41800 (0.11) 38500 (0.17)	45000 (0.10) 43000 (0.10)	52000 (0.00)	54800 (0.67)
2,5-Cl	40400 (0.25) 38500 (0.25)	42000 (0.24) 44000 (0.03)	54300 (0.00)	56000 (0.70)
3,4-Cl	40100 (0.10) 39500 (0.18)	41500 (0.08)	50500 (0.00)	54000 (0.80)
2,4-Cl	42000 (0.14) 42700 (0.31)	44600 (0.09)	59300 (0.00)	56000 (0.90)
2,3-Cl	42000 (0.13) 42700 (0.36)	44300 (0.05)	59000 (0.00)	55600 (0.88)
2,3,5-Cl	39600 (0.13) 37400 (0.21)	41800 (0.14) 41000 (0.04)	51100 (0.00)	53700 (0.72)
2,3,4-Cl	41400 (0.13) 42300 (0.32)	43200 (0.08)	58100 (0.00)	55100 (0.98)
2,3,4,5-Cl	40600 (0.21) 36900 (0.21)	41000 (0.06)	50200 (0.00)	52400 (0.32)

[x]The first rows represent the observed transition energies, the second rows the calculated ones. Oscillator strengths are in parentheses. Oscillator strengths were calculated by the formula used in Ref. [4]

in the solution spectra too having about 500–1000 cm^{-1} red shift compared to the vapour phase spectra. This behaviour confirms an assignment to a valence shell transition. In order to interpret these bands CNDO/S calculations were carried out. The results of the calculations together with the vertical transition energies are compiled in Table II.

According to the calculations the lowest energy transition is the $\pi_4^* \leftarrow \pi_3$ (the notation refers to the thiophene molecular orbitals) in each compound. The next transition at about 2–5000 cm^{-1} higher is a mixture of the $\pi_4^* \leftarrow \pi_2$ and the $\pi_5^* \leftarrow \pi_3$ transitions with a stronger $\pi_4^* \leftarrow \pi_2$ character. The order of the two transitions are the same in each compound regardless of whether they are observed in the spectra or not. The two above mentioned transitions are well separated from the $\pi^* \leftarrow n$ and $\pi_5^* \leftarrow \pi_3$ transitions by about 10000 cm^{-1}.

References

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