Vibronic Analysis and Symmetry of the Lowest Energy Ultraviolet Transition of Thiophen

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High resolution and temperature dependence measurements have been recorded for the lowest energy u.v transition of thiophen. Based on the new observations of the hot bands the vibronic fine structure has been reassigned. The new assignment can be fitted well to the spectra of deuteriated derivatives. The first band system of the u.v. spectrum is assigned to the $\psi_4 \longleftarrow \psi_3$ (B_2) transition. This conclusion is supported by a comparison of the ionization potentials and transition energies of some five-membered heterocycles.

THOUGH thiophen is one of the simplest aromatic heterocycles its u.v. spectrum has not yet been unambiguously interpreted. The first reliable vapour spectrum was published by Di Lonardo *et al.*[1] They found two band systems at 200—240 nm. Price and Walsh [2] interpreted one, while Milazzo [3] described three transitions in the same spectral range. The existence of two band systems was confirmed by Norden *et al.*[4] on the basis of magnetic circular dichroism spectral data. Having recorded the vapour-phase spectrum of thiophen we arrived at the same conclusion.

The symmetry of the lowest energy transition is a fundamental question which has been investigated before, but without any definite answer being found. The possible transitions in the investigated spectral range are as follows where ψ_1—ψ_5 represent the valence π orbitals $1b_1$, $2b_1$, $1a_2$, $3b_1$, and $2a_2$.

$$\psi_4 \longleftarrow \psi_3;\ \text{symmetry } B_2 \longleftarrow A_1$$
$$\psi_4 \longleftarrow \psi_2;\ \text{symmetry } A_1 \longleftarrow A_1$$
$$\psi_5 \longleftarrow \psi_3;\ \text{symmetry } A_1 \longleftarrow A_1$$

The problem was dealt with by quantum chemical calculations. By modifying the parametrization the order of the transitions can be inverted.[5-12] Also, the intensities of the band systems can be computed and compared to the experimental data; this process is, however, not quite reliable.

Di Lonardo *et al.*[1] tried to evaluate the vibronic structure by assuming only a_1 type vibrations, but their assignment contained several contradictions.

In order to clarify the first band system we investigated and reassigned the vibronic structure of the first u.v. band of thiophen. Our results were supported by comparisons of the u.v. photoelectron (u.p.s.) and u.v. spectral properties of five-membered heteroaromatic systems containing a heteroatom of Group VIA.

EXPERIMENTAL

The u.v. spectra were recorded with a Zeiss Specord u.v.–visible spectrophotometer in the 40 000—50 000 cm^{-1} region (Figure 1). High resolution measurements were carried out in the 40 000—42 500 cm^{-1} region. Measurements were performed with an NLM–E2M spectrometer equipped with an Echelette grating in a 2 m Czerny–Turner mount. The incident light from an Ostram 450 W regulated xenon arc lamp was chopped at 720 Hz, the light passing through the sample being detected by a combination of an HTV R376 photomultiplier tube and an NF LI–572 lock-in amplifier.

The longest wavelength u.v. band of thiophen was recorded with a Zeiss Specord u.v.–visible spectrophotometer in the temperature range 20—100 °C (Figure 2). Thiophen (Merck) was distilled several times before use to give a chromatographically pure product.

The spectrum obtained was in agreement with those observed earlier [1] with the exception of an additional band at 41 265 cm^{-1}. The 41 975 cm^{-1} band reported by Di Lonardo *et al.* was not observed.

RESULTS AND DISCUSSION

1. *The Vibronic Structure of the U.v. Spectrum.*—The most informative band system of the thiophen spectrum is that of lowest energy (Figure 1). In accord with the earlier investigations the 965 cm^{-1} progression has been found to dominate.[1,2] This progression is due to the totally symmetric vibration 6. The numbering and

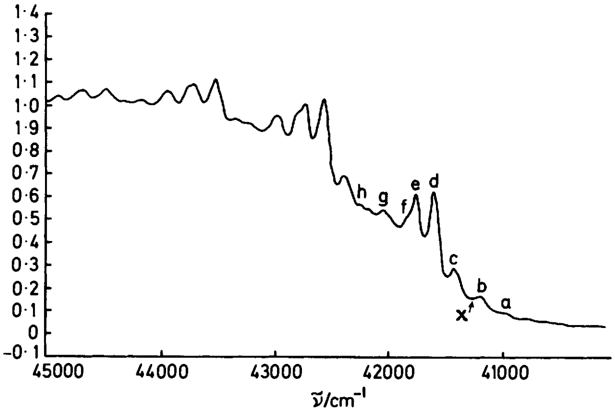

FIGURE 1 The lowest energy band system of thiophen. x, Not present in ref. 1

assignment of some relevant ground state frequencies according to Rico *et al.*[13] can be seen in Table 1. In that work vibrations 6 and 7 were inverted in the case of the deuteriated compounds. Our assignment is proved by the fact that the progression forming mode has a maximum for thiophen (965 cm^{-1}), 2,5-dideuteriothiophen (995 cm^{-1}), and tetradeuteriothiophen (835 cm^{-1}). From this trend it may also be concluded (in agreement with valence force field calculations[14]) that the β-carbon atoms oscillate with larger amplitude. In the case of the tetradeuterio-compound the spacing of the progression is 835 cm^{-1} and it can be assigned to the 896 cm^{-1} ground state wavenumber. The frequency decrease in the excited state is 51 and 61 cm^{-1} for the deuterio-compounds and 71 cm^{-1} in the case of thiophen.

TABLE 1

Assignment of fundamentals (cm^{-1})

No.	Symmetry	Thiophen	2,5-Dideuteriothiophen	Tetradeuteriothiophen
3	a_1	839	754	731
6	a_1	1 083	884	785
7	a_1	1 036	1 046	896
8	a_1	608	590	585
11	a_2	565	528	484
14	b_1	452	419	414
18	b_2	751	740	711

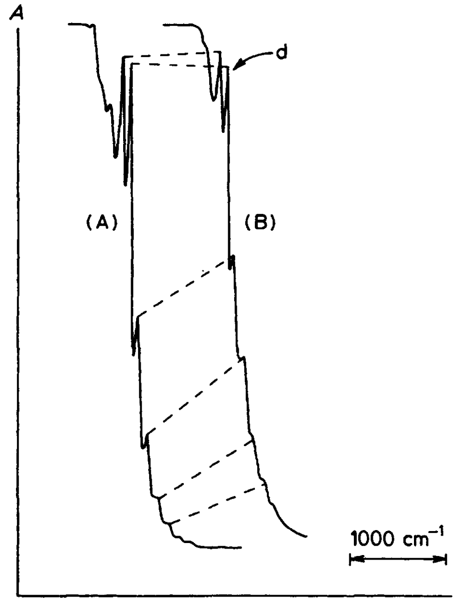

FIGURE 2 The bands of the first progression (A) at 20 °C and (B) at 100 °C

Bands of the first progression are marked by different letters on Figure 1. The first progression, measured at two different temperatures, is in Figure 2.

Di Lonardo *et al.*[1] assigned the d band as the 0–0 band. This is supported by our measurements since it is the lowest energy transition without significant intensity enhancement upon increasing the temperature (Figure 2).

Table 2 contains the mutual spacings of the bands.

For the interpretation of the electronic transition, band e is of fundamental importance. It was assigned as a hot band[1] but from studying the temperature dependence we have found that this band cannot belong to a 1–*n* transition. The enhancement of the intensity is much less than the calculated value using the Boltzmann formula and it can be explained by the increasing continuous background of the band system. The hot band assumption is unlikely given the high intensity of this band. Therefore band e can be assigned as a 0–1 transition. In this case one of the fundamental frequencies has to be decreased significantly (a similar effect can be found *e.g.* for benzene where the frequency of vibration 16 decreases drastically from 404 to 240 cm^{-1}).[15] The two lowest fundamental frequencies [14(b_1) and 11(a_2)] belong to out-of-plane bending modes. As in the C_{2v} point group A_2 type transitions are forbidden, the a_2 vibration is forbidden with an $A_1 \longleftarrow A_1$ electronic transition, while the b_1 vibration is forbidden with a $B_2 \longleftarrow A_1$ transition. Therefore, if band e belongs to the b_1 type 452 cm^{-1} vibration the electronic transition is of A_1 type; in the other case it is of B_2 type.

If band e is assigned to the a_2 vibration, the 1–0 and the 1–1 transitions are expected at −565 and at −410 cm^{-1} (by comparison with band d) [if band e belonged to the 452 cm^{-1} (b_1) vibration the 1–0 band should be at −452 cm^{-1}, the 1–1 band at −297 cm^{-1}; these bands do not appear in the spectrum]. The 1–1 band can be found at −390 cm^{-1} (subtracting the continuous background absorption; the distance from the 0–0 band must be greater), while the 1–0 transition can hardly be separated from the −615 cm^{-1} band. In the other progressions the excited state frequency of these vibrations is somewhat higher. This shift cannot be explained by the hot band assumption.

TABLE 2

The band distances of the lowest energy band system (cm^{-1})

	a	b	x	c	d	e	f	g	h
a		225	285	440	615	770	830	1 050	1 265
b			71	213	399	559	626	826	1 039
x				142	328	487	554	756	967
c					186	346	412	615	826
d						160	226	429	640
e							67	269	480
f								202	413
g									211
h									

Band a is the 1–0 transition of vibration 8 (a_1). Band c can be assigned to the 1–1 transition of the low frequency vibration 14 (b_1) because of its high intensity.

TABLE 3

The assignment of the first band system of thiophen and deuteriated thiophens (cm^{-1})

Thiophen					2,5-Dideuteriothiophen				Tetradeuteriothiophen			
Band	low resolution	high resolution	This work	Ref. 1	Band	[l]	This work	Ref. 1	Band	[l]	This work	Ref. 1
a	40 980		8_1^0	8_1^0	a	41 080	8_1^0	8_1^0	a	41 150	8_1^0	8_1^0
						41 160	11_1^0	?				
b	41 205	41 193	11_1^1	$7_1^0 3_0^1$	b	41 315	11_1^1	?	b	41 350	11_1^1	$3_0^1 18_1^0$
x		41 265	$8_1^0 18_0^1$									
c	41 420	41 406	14_1^1	3_1^1	c	41 490	14_1^1	3_1^1	c	41 550	14_1^1	3_1^1
d	41 595	41 592	0	0	d	41 680	0	0	d	41 750	0	0
e	41 750	41 752	11_0^1	$6_0^1 3_1^0$	e	41 825	11_0^1	$6_0^1 3_1^0$	e	41 880	11_0^1	$7_0^1 6_1^0$
f	41 810	41 818	$18_1^1 8_0^1$	$7_1^0 3_0^2$	f	41 890	$18_1^1 8_0^1$	?				
g	42 030	42 021	8_0^1	3_1^2	g	42 095	8_0^1	$6_0^1 8_1^0$				
					i	42 170	$7_0^1 11_1^0$	?				
h	42 245	42 232	3_0^1	3_0^1	h	42 315	3_0^1	3_0^1	h	42 330	3_0^1	3_0^1
k	42 380	42 362	$7_0^1 14_1^1$	$6_0^1 3_1^1$	k	42 520	$7_0^1 14_1^1$	$6_0^1 3_1^1$	k	42 430	$7_0^1 14_1^1$	$6_0^1 3_1^1$
l	42 560	42 556	7_0^1	6_0^1	l	42 675	7_0^1	6_0^1	l	42 585	7_0^1	6_0^1
m	42 725	42 719	$7_0^1 11_0^1$	$6_0^2 3_1^0$	m	42 830	$7_0^1 11_0^1$	$6_0^2 3_1^0$	m	42 775	$7_0^1 11_0^1$	$6_0^2 7_1^0$
i	42 785		$7_0^1 18_1^1 3_0^1$	$6_0^1 3_1^0$		42 940	$7_0^1 11_1^1 3_0^1$	3_0^2				
j	42 985		$7_0^1 8_0^1$	$6_0^1 3_1^2$	r	43 155	$7_0^1 3_1^1 14_1^1$	$6_0^2 8_1^0$	r	42 950	$7_0^1 3_0^1 14_1^1$	$6_0^2 8_1^0$
n	43 215		$7_0^1 3_0^1$	$6_0^1 3_0^1$	n	43 330	$7_0^1 3_0^1$	$6_0^1 3_0^1$	n	43 140	$7_0^1 3_0^1$	$6_0^1 3_0^1$
o	43 355		$7_0^2 14_1^1$	$6_0^2 3_1^1$	o	43 520	$7_0^2 14_1^1$	$6_0^2 3_1^1$	o	43 290	$7_0^2 14_1^1$	$6_0^1 7_0^1$
p	43 525		7_0^2	6_0^2	p	43 655	7_0^2	6_0^2	p	43 640	7_0^2	6_0^2
	43 710		$7_0^2 11_0^1$	$6_0^3 3_1^0$						43 645	$7_0^2 11_0^1$	$6_0^3 7_1^0$
	43 755		$7_0^2 18_1^1 8_0^1$	$6_0^2 7_1^0 3_0^2$								
	43 945		$7_0^2 8_1^0$	$6_0^2 3_1^2$						43 795	$7_0^2 3_0^1 14_1^1$	$6_0^3 8_1^0$
	44 170		$7_0^2 3_0^1$	$6_0^2 3_0^1$						43 995	$7_0^2 3_0^1$	$6_0^2 3_1^0$
	44 330		$7_0^3 14_1^1$	$6_0^3 3_1^1$								
	44 490		7_0^3	6_0^3								
	44 910		$7_0^3 8_0^1$	$6_0^3 3_1^2$								
	45 130		$7_0^3 3_0^1$	$6_0^3 3_0^1$								
	45 430		7_0^4	6_0^4								

[l] = low resolution.

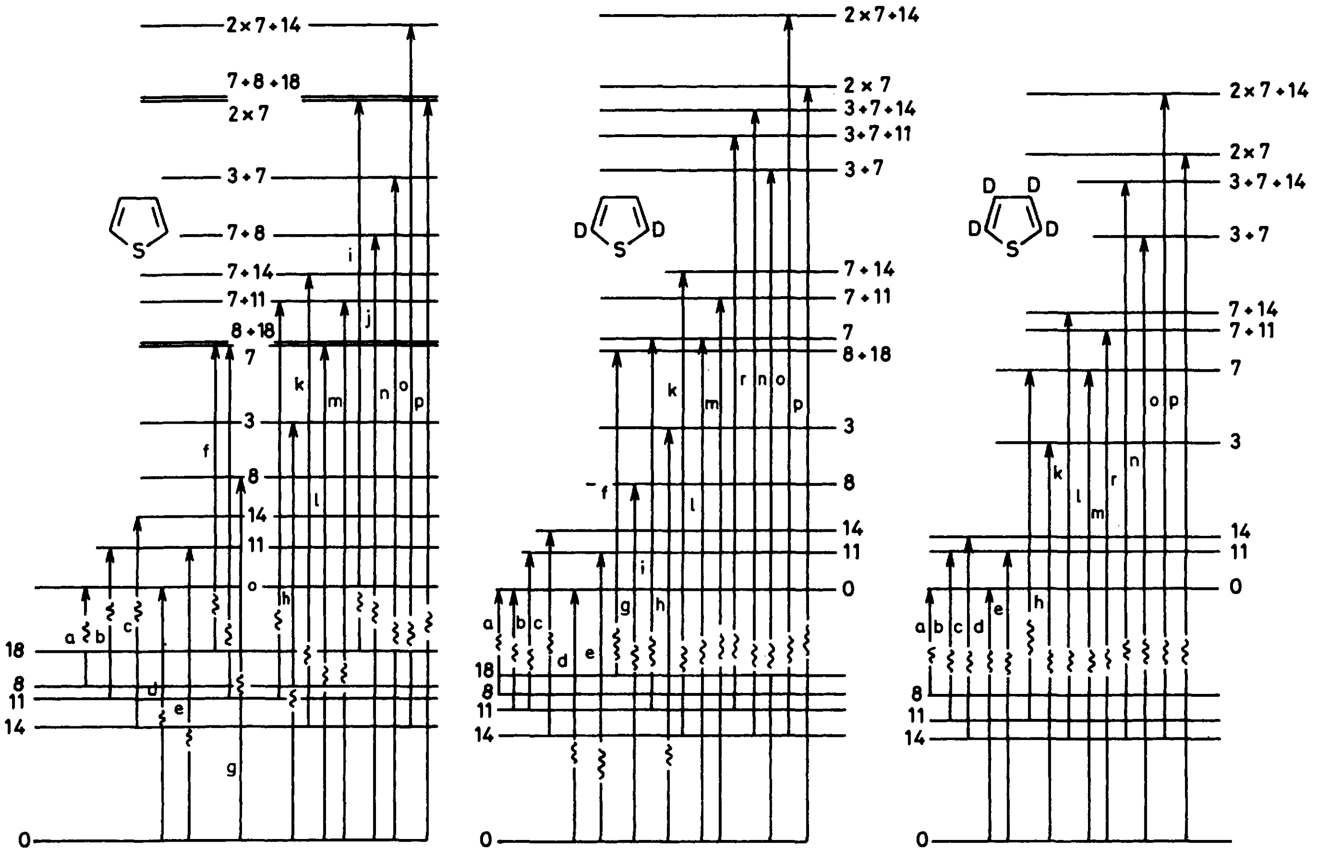

FIGURE 3 The transitions of the vibronic spectra of some deuteriated thiophens

Band g is probably a 0–1 transition of the 608 cm^{-1} vibration (a_1). Shoulder f is a 1–1 band accompanying the 8_0^1 transition. It probably belongs to the lowest frequency in-plane skeletal vibration 18 (b_2). Band h, in agreement with Di Lonardo *et al.*, is the 3_0^1 transition.

Our assumptions can be checked by similar assignments of the vibronic spectra of deuteriated thiophens. Table 3 contains the observed frequencies and our assignments for thiophen and deuteriated thiophen, as well as the high resolution spectral data of the first progression for thiophen, compared to those of Di Lonardo *et al.* The transitions are shown on Figure 3. It appears that our assignments are correct for both deuteriated compounds. The ground state frequencies (i.r. and Raman data) of deuteriated thiophens agree well with those calculated from the vibronic spectrum.

2. *The Five-membered Heterocycles of Group* VIA.—The first two u.v. transitions of thiophen, selenophen, and tellurophen are $\psi_4 \longleftarrow \psi_3$ (B_2) or $\psi_4 \longleftarrow \psi_2$ (A_1). The first transition of furan is of the $\psi_4 \longleftarrow \psi_3$ type [4,5] but the assignment of the second is doubtful. Several authors [2,16] assigned this band system as a Rydberg transition but they do not preclude the possibility of an unchanged principal quantum number.

It may be established from Table 4 that all the heterocycles have a strong band system between 6.2 and 6.6 eV (the spectra of selenophen and tellurophen were recorded only up to 6.2 eV) which is assigned as a Rydberg transition.[2,16] Nevertheless, it has been demonstrated [1] that the mentioned band cannot be of Rydberg type for thiophen. Consequently the transition is $\psi_5 \longleftarrow \psi_3$ (A_1). Because neither the ψ_3 (a_2) nor ψ_5 (a_2) orbitals contain the heteroatom, it may be assumed that their energy does not change significantly with changing the heteroatom. This is supported by u.p.s. data [21–28] and by the calculations of Norden *et al.*[4]

TABLE 4

Transition energies of $\overbrace{\text{CH:CH·CH:CH}}^{\text{X}}$-like molecules in eV

X	O [2,17,18]	S [1,2]	Se [4,19]	Te [4,20]	NH [2,21]	CH_2 [2,21]
	6.48	6.60			6.63	6.23
				5.35		
		5.83	5.23	4.44		
	5.88	5.19	5.05	5.12	5.87	4.96

TABLE 5

The difference of the first two IP and transition energies of thiophen, selenophen, and tellurophen (eV)

	Thiophen	Selenophen	Tellurophen
ΔIP	0.62	0.26	0.48
ΔE_{tr}	0.64	0.18	0.68

The $\psi_4 \longleftarrow \psi_3$ transition is close in energy to the $\psi_5 \longleftarrow \psi_3$ transition in the case of furan. This can be understood by the fact that on changing the heteroatom to higher electronegativity the energy of the ψ_4 orbital increases.[29]

Based on Koopmans' theorem [30] the energies of the two highest occupied molecular orbitals are known from u.p.s. data.[21–28] When the electron is excited to the ψ_4 orbital, the difference in the transition energies has to be correlated with that of the orbital energies because of the similar molecular structure. The $\psi_4 \longleftarrow \psi_2$ transition of furan cannot be found in the spectrum, therefore the correlation was investigated only for the other three heterocycles (Table 5).

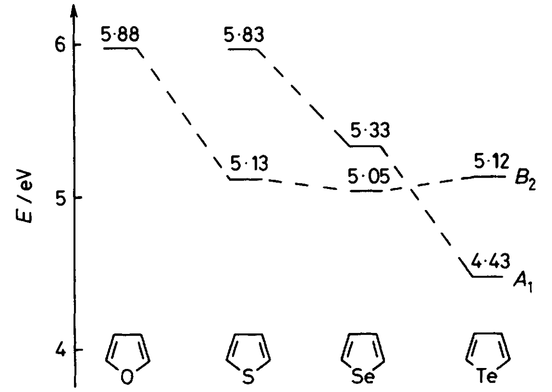

FIGURE 4 The electronic transitions of five-membered heterocycles

Assuming that the orbital and transition energies change in parallel with each other we obtained a straight line with a correlation coefficient 0.999. This finding supports the conclusion that the lowest energy transition of thiophen is $\psi_4 \longleftarrow \psi_3$ (B_2) and that the second one is $\psi_4 \longleftarrow \psi_2$ (A_1). The order of the transition is given in Figure 4.

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