X-RAY EMISSION SPECTROSCOPY AND ELECTRONIC. STRUCTURE OF HETEROCYCLIC COMPOUNDS

2*. THIOPHENE

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The electronic structure of has been studied by X-ray spectroscopy. SK_β-, $SL_{2,3}$- *and* CK_α-*spectra were obtained. Theoretical spectra were constructed on the basis of* ab initio *and MNDO calculations and the experimental results were interpreted. The HOMO is an orbital in which the electron density is localized on the carbon atoms. Conclusions about the occupancy of the lowest 3d orbital were reached from the experimental results.*

There are a large number of papers concerned with the study of the electronic structure of thiophene by photoelectron spectroscopy and quantum chemical calculations (see [2] and references cited therein). X-ray photoelectron spectra have been obtained previously [3,4]. X-ray emission spectroscopy is the subject of a number of papers [5-9] in which the SK_β- [5-8] and the $SL_{2,3}$-spectra [6, 7, 9] have been reported. However the carbon emission spectrum of the thiophene molecule has not yet been reported.

The object of the present study was a complete X-ray spectroscopic investigation of the filled orbitals of the thiophene molecule. We have recorded the SK_β- and $SL_{2,3}$-spectra again and the CK_α-emission for the first time (Fig. 1). The spectra are presented on an ionization potential (I) scale by a method described, for example, in ref.[10]. The photoelectron spectrum obtained with the HeI excitation line (from [11]) and the high energy part of the X-ray photoelectron spectrum excited by the MgK_α line (from [3]) are also given here.

The ground state of the thiophene molecule (point group C_{2v}) was calculated *ab initio* and by the MNDO method. The X-ray spectra synthesized on the basis of these calculations are shown in Fig. 2) (see also Table 1).

The experimental spectra could be interpreted from the theoretical results. Note that molecular orbitals (MO) of a_1 and b_2 symmetry belong to the σ-system (they lie in the plane of the molecule), while MO of a_2 and b_1 symmetry belong to the π-system (perpendicular to the plane of the molecule).

The highest occupied level of the molecule is $1a_2$. According to symmetry rules, sulfur wave functions of *s*- and *p*-type are not involved in this orbital which is formed from carbon $2p_\pi$ atomic orbitals (AO). Electronic transitions from $1a_2$ to carbon 1*s orbitals* ($1a_2 \rightarrow C_{2,5}1s$ and $1a_2 \rightarrow C_{3,4}1s$) appear as line A in the CK_α spectrum. The energy difference between these transitions is not large, since the experimental distance between $C_{2,5}1s$ and $C_{3,4}1s$ is about 0.34 eV [3].

Next in order of increasing energy of electron bonding (I scale) is the $3b_1$ level populated by sulfur $3p_\pi$ and carbon $2p_\pi$ electrons. Transitions from this level appear in both the CK_α- and SK_β-spectra. Consequently line A results from the superposition of four transitions: from the $1a_2$ and $3b_1$ MO to $C_{2,5}1s$ and $C_{3,4}1s$ (see Figs. 1 and 2). It coincides with the high energy line (transition energy scale, E) in the SK_β-spectrum and with the first two bands of the photoelectron spectrum. The transition energy of this line in the SK_β-spectrum is ≈ 2468.1 ± 0.1 eV which corresponds to ≈ 9.4 ± 0.2 eV on the ionization potential scale. Thus it can be said to coincide with two photoelectron spectral lines (I = 9.5 eV [2]). I = 8.9 eV for the first band [2]. As noted previously, line S in the CK_α-spectrum is not associated with an MO but results from characteristic fluorescence of the analyzer crystal.

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*For Communcation 1, see [1].

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TABLE 1. Identification of Individual Lines of the Theoretical CK_α-Spectra Shown in Fig. 2

Line	Transition		Line	Transition	
	STO-3G	MNDO		STO-3G	MNDO
1	$1a_2 \rightarrow C_{2,5}1s$	$1a_2 \rightarrow C_{2,5}1s$	14	$6b_2 \rightarrow C_{3,4}1s$	$6b_2 \rightarrow C_{3,4}1s$
2	$1a_2 \rightarrow C_{3,4}1s$	$1a_2 \rightarrow C_{3,4}1s$	15	$9a_1 \rightarrow C_{2,5}1s$	$9a_1 \rightarrow C_{2,5}1s$
3	$3b_1 \rightarrow C_{2,5}1s$	$3b_1 \rightarrow C_{2,5}1s$	16	$9a_1 \rightarrow C_{3,4}1s$	$9a_1 \rightarrow C_{3,4}1s$
4	$3b_1 \rightarrow C_{3,4}1s$	$3b_1 \rightarrow C_{3,4}1s$	17	$5b_2 \rightarrow C_{2,5}1s$	$5b_2 \rightarrow C_{2,5}1s$
5	$11a_1 \rightarrow C_{2,5}1s$	$11a_1 \rightarrow C_{2,5}1s$	18	$5b_2 \rightarrow C_{3,4}1s$	$5b_2 \rightarrow C_{3,4}1s$
6	$11a_1 \rightarrow C_{3,4}1s$	$11a_1 \rightarrow C_{3,4}1s$	19	$8a_1 \rightarrow C_{2,5}1s$	$8a_1 \rightarrow C_{2,5}1s$
7	$7b_2 \rightarrow C_{2,5}1s$	$2b_1 \rightarrow C_{2,5}1s$	20	$8a_1 \rightarrow C_{3,4}1s$	$8a_1 \rightarrow C_{3,4}1s$
8	$7b_2 \rightarrow C_{3,4}1s$	$2b_1 \rightarrow C_{3,4}1s$	21	$4b_2 \rightarrow C_{2,5}1s$	$7a_1 \rightarrow C_{2,5}1s$
9	$2b_1 \rightarrow C_{2,5}1s$	$7b_2 \rightarrow C_{2,5}1s$	22	$7a_1 \rightarrow C_{2,5}1s$	$7a_1 \rightarrow C_{3,4}1s$
10	$2b_1 \rightarrow C_{3,4}1s$	$7b_2 \rightarrow C_{3,4}1s$	23	$4b_2 \rightarrow C_{3,4}1s$	$4b_2 \rightarrow C_{2,5}1s$
11	$10a_1 \rightarrow C_{2,5}1s$	$10a_1 \rightarrow C_{2,5}1s$	24	$7a_1 \rightarrow C_{3,4}1s$	$4b_2 \rightarrow C_{3,4}1s$
12	$10a_1 \rightarrow C_{3,4}1s$	$6b_2 \rightarrow C_{2,5}1s$	25	$6a_1 \rightarrow C_{2,5}1s$	$6a_1 \rightarrow C_{2,5}1s$
13	$6b_2 \rightarrow C_{2,5}1s$	$10a_1 \rightarrow C_{3,4}1s$	26	$6a_1 \rightarrow C_{3,4}1s$	$6a_1 \rightarrow C_{3,4}1s$

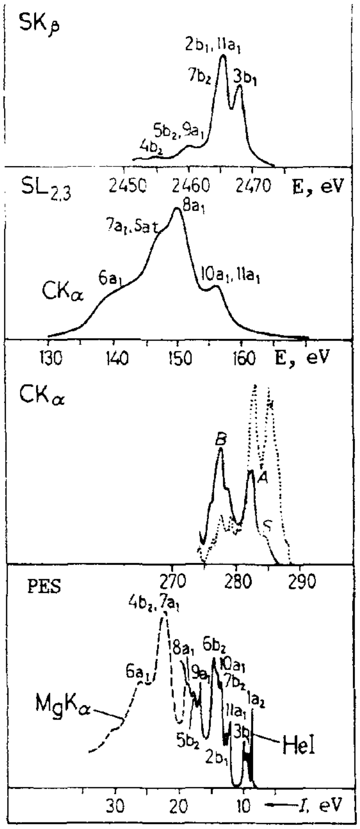

Fig. 1. X-ray and photoelectron spectra of thiophene. SK_β- and $SL_{2,3}$-spectra: - - smoothed; CK_α-spectrum: ..... experimental, - - smoothed and corrected for the effectiveness of the analyzer crystal.

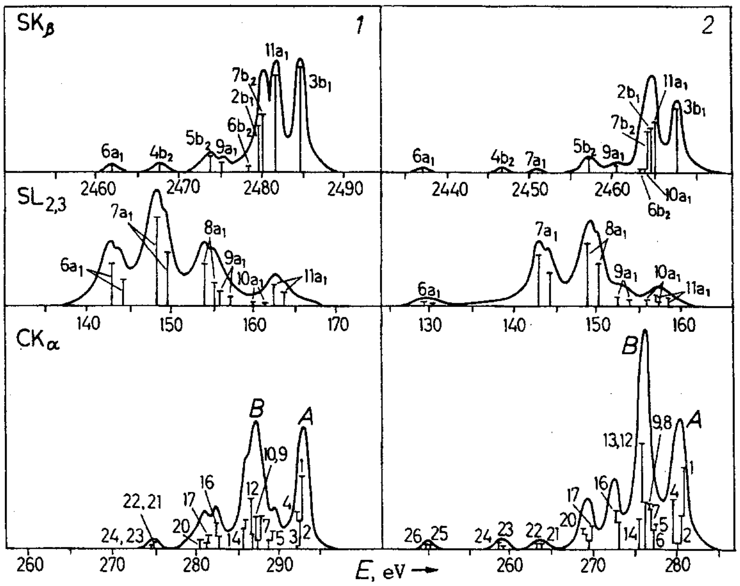

Fig. 2. Theoretical X-ray spectra of thiophene: STO-3G basis set (1); MNDO (2). In the $SL_{2,3}$-spectrum, the higher intensity line of a pair corresponding to the same MO represents the transition to $S2p_{3/2}$ and the lower intensity line to $S2p_{1/2}$. In the CK_α-spectrum, the unnumbered lines correspond to transitions identified in sequential order in Table 1. A single line with two numbers corresponds to the sum of two transitions differing by less than 0.1 eV on the energy scale.

A group of levels can be separated which lie within a narrow energy range at ≈ 2.8 eV (PES results [2]). These are the MO $11a_1$, $2b_1$, $7b_2$, $10a_1$ and $6b_2$. Different calculations place them in the same sequence. A detailed quantum chemical analysis of the constitution of these MO has been published [2]. We shall use this sequence which we consider most reliable.

The wave functions of orbitals $11a_1$, $2b_1$ and $7b_2$ have considerable contributions from $3p$ AO so that transitions to the corresponding levels appear in the SK_β-spectrum as lines with maximum intensity (Figs. 1 and 2). Orbitals $10a_1$ and $6b_2$ consist predominantly of contributions from $2p$ AO so their participation in SK_β-emissions is negligible. The sulfur $3s$ AO contributes to the $11a_1$ and $10a_1$ orbitals and consequently these MO have their analogs in the $SL_{2,3}$-spectrum (Figs. 1 and 2).

Note that two transitions from the same bonding MO ($\mathrm{MO}(a_1) \to S2p_{3/2}(L_3)$ and $\mathrm{MO}(a_1) \to S2p_{1/2}(L_2)$) were taken into account in constructing the theoretical $SL_{2,3}$-spectrum. The energy difference between them, obtained from the photoelectron spectrum [3], is ≈ 1.25 eV and the intensity ratio SL_3/SL_2 is ≈ 1.6. The ratio was calculated as the average value from a series of high resolution spectra for compounds of elements of period 3 [12-15] (see Fig. 2).

This group of orbitals appears as line B in the CK_α- spectrum (Figs. 1 and 2). All of the bands in the X-ray spectrum corresponding to the MO $11a_1$, $2b_1$, $7b_2$, $10a_1$ and $6b_2$ coincide and this also occurs in the photoelectron spectrum (Fig. 1).

The $9a_1$, $5b_2$, $8a_1$, $4b_2$, $7a_1$ and $6a_1$ MO are based on contributions from the sulfur $3s$ AO and the carbon $2s$ AO. This sulfur AO does not contribute to MO of type b_2 for symmetry reasons. Some MO appear in the SK_β-spectrum because of small contributions from the $S3p$ AO. According to *ab initio* calculations the contribution of the sulfur $3s$ AO is greater for the $7a_1$ and $6a_1$ MO than for the $8a_1$, although, as Fig. 1 shows, the experimental results lead to the opposite conclusion. The MNDO results are closer to the experimental (Figs. 1 and 2). The lines corresponding to $7a_1$ and $6a_1$ in the $SL_{2,3}$-spectrum coincide with the X-ray photoelectron spectrum. Note that the line corresponding to the $7a_1$ MO is a superposition of the transitions $7a_1 \to 2p_{3/2,1/2}$ and the satellite (S_{at}). The nature of the latter is in dispute. It frequently appears in X-ray spectra of this type (e.g., [8]). In a detailed examination of the nature of so-called satellite X-ray lines it was concluded that these lines in the $L_{2,3}$-spectrum correspond to second order reflections of the carbon K_α emission [16].

The orbitals $1b_1$ ($S2p_z$), $3b_2$ ($S2p_y$), $5a_1$ ($S2p_x$), $4a_1$ ($S2s$), $2b_2$ ($C_{3,4}1s$), $3a_1$ ($C_{3,4}1s$), $1b_2$ ($C_{2,5}1s$), $2a_1$ ($C_{2,5}1s$), $1a_1$ ($S1s$) are atomic. Their energetic positions were determined by photoelectron spectroscopy (e.g., [3]).

Finally we turn to the role of the vacant sulfur $3d$ orbitals in chemical bond formation in thiophene. A necessary condition for the participation of $S3d$ AO in chemical bonding in any compound is the formation of a positive charge on the

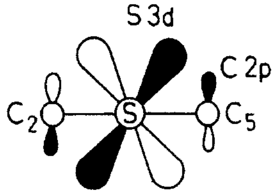

Fig. 3. Diagram of p_{π}-d_{π} interaction in the thiophene molecule.

sulfur atom. This is achieved, for example, by electron density transfer through the σ-system to the neighboring atoms which should be highly electronegative. As a result of such electron density redistribution, the S3*d* AO becomes less diffuse and this in its turn facilitates overlap with the π-system of the surrounding atoms and electron population of the 3*d* orbitals [10]. This somewhat pictorial hypothesis provides a mechanism for the participation of sulfur 3*d* AO in chemical bonds. However the first prerequisite condition does not occur in the thiophene molecule. According to X-ray spectroscopy the charge on the sulfur atom is close to zero [10]. In contrast, in SO_4^{2-} , which in theory has the most highly populated S 3*d* orbitals [17], the charge on sulfur is $\approx$ 2.6*e* [10].

On symmetry grounds the thiophene $1a_2$ orbital may be constructed from the carbon $2p_{\pi}$ AO and the sulfur $3d_{\pi}$ AO (Fig. 3). However the small positive charge on the sulfur atom makes overlap of the $S3d_{\pi}$ and $C2p_{\pi}$ orbitals impossible. If the sulfur 3*d* orbitals were occupied, lines corresponding to the $1a_2 \rightarrow 2p_{3/2,1/2}$ transitions should appear at $\approx$ 161 eV (*E* scale) in the experimental $SL_{2,3}$-spectrum (see Fig. 1).

Thus the sulfur 3*d* AO make no contribution to contribution to chemical bonding in the thiophene molecule, in other words $S3d_{\pi}$-$C2p_{\pi}$ bonding was not observed experimentally.

EXPERIMENTAL

The X-ray spectroscopic apparatus has been described elsewhere [7]. The $SL_{2,3}$-spectrum of solid thiophene was obtained as described in that paper [7]. The sulfur $K\alpha_{1,2}$- and $K\beta$-spectra were measured for gas phase thiophene (the role of the $SK_{\alpha_{1,2}}$ lines is discussed below). X-ray emission was excited by electron bombardment. Calibration for sulfur has been described elsewhere [18].

CK_{α} emission was obtained by electron bombardment in the gas phase as described elsewhere [19]. Second order reflexion $CrL\alpha_{1,2}$ and $VL\alpha_{1,2}$ lines from the pure metals were used for calibration; the energy levels were taken from [20]. An algorithm for correcting the spectrum for the effectiveness of the analyzer crystal was developed previously [19].

The rms deviations for the energies of the main lines in the $SK_{\alpha_{1,2}}$-, SK_{β}-, $SL_{2,3}$ and CK_{α}-spectra were ±0.1, ±0.1, ±0.3 and ±0.2 eV respectively. The intensity deviation did not exceed $\approx$3 to 5%.

All spectra were smoothed by a known method [21]. The smoothing intervals were chosen experimentally based on the halfwidths (width at half height) of individual lines, estimated experimentally, in a particular spectrum. The halfwidths were 1.3, 1.8 and 1.2 eV respectively for SK_{β}, $SL_{2,3}$ and CK_{α} emissions.

The ionization potential of the lowest orbital $1a_1$ (S1*s*), used as the basis for the SK_{β}-spectrum, was determined as the sum of the energies of the $S2p_{3/2}$ level [3] and the SK_{α_1} line (2307.8 ± 0.1 eV) and had the value 2477.7 ± 0.2 eV. This parameter has a value of 2477.6 eV based on the sulfur *K* absorption spectrum [8].

The $S2p_{2,3}$ level with an energy of 109.9 eV [3] was used to connect the $SL_{2,3}$ spectrum to the ionization energy scale. The theoretical and experimental CK_{α}-spectra were reconciled using the $C_{3,4}1s$ level, the experimental value for which [3] was used for spectra calculated by the MNDO method.

Ab initio calculations used the GAUSSIAN-80 program (V. L. Bugaenko, V. G. Zakzhevskii and N. B. Kuz'minskii's version) with the STO-3G basis set, omitting 3*d* functions. Semi-empirical calculations were carried out with the MNDO-86 program which is alter development of MNDO-85 [22].

Theoretical curves were synthesized as the sum of Lorentzian curves with the halfwidths discussed above. For the semi-empirical calculations the heights of individual lines corresponded to the squares of the contributions of the AO to the MO [6], while for the non-empirical calculations the line intensities were calculated via the matrix elements of the X-ray transitions using the frozen orbital approximation [6].

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REFERENCES

1. V. D. Yumatov, V. V. Murakhtanov, A. V. Okotrub, N. P. Erchak and É. Lukevits, Khim. Geterotsikl. Soedin., No. 12, 1631 (1991).
2. W. Von Niessen, W. P. Kramer and L. Cederbaum, J. Electron Spectrosc. Related Phenom., **8**, 179 (1976).
3. U. Gelius, C. J. Allan, G. Johansson, H. Siegbahn, D. A. Allison and K. Siegbahn, Phys. Scripta, **3**, 237 (1971).
4. S. A. Chambers and T. D. Thomas, J. Chem. Phys., **67**, 2596 (1977).
5. D. R. Phillips and G. Andermann, Phys. Fenn., **9**, Suppl., 141 (1974).
6. L. N. Mazalov, V. D. Yumatov, V. V. Murokhtanov, F. Kh. Gel'mukhanov, G. N. Dolenko, E. S. Gluskin and A. V. Kondratenko. X-Ray Spectra of Molecules [in Russian], Nauka, Novosibirsk (1977), p.280.
7. V. D. Yumatov. Study of the Electronic Spectra of Extractant Molecules by Longwave and Ultra Longwave X-Ray Spectroscopy. Diss. Cand. Chem. Sci., Novosibirsk (1977), p. 57.
8. R. C. C. Perea and R. E. LaVilla, J. Chem. Phys., **84**, 4234 (1986).
9. K. Taniguchi and B. L. Henke, J. Chem. Phys., **64**, 3021 (1976).
10. L. N. Mazalov and V. D. Yumatov. Electronic Structure of Extractants [in Russian], Nauka, Novosibirsk (1984), p. 29.
11. P. J. Derrick, L. Å. Asbrink, O. Edqvist, B. -Ö. Jonnson and E. Lindholm, Int. J. Mass Spectrom. Ion Phys., **6**, 177 (1971).
12. G. Andermann, B. Henke, D. S. Urch and G. Wiech, Japan J. Appl. Phys., **17**, Suppl.17-2, 428 (1978).
13. E. Gilberg, M. J. Hanus and B. Foltz, Rev. Sci. Instr., **52**, 62 (1981).
14. H. Ågren, J. Nordgren, L. Selander, C. Nordling and K. Siegbahn, Phys. Scripta, **18**, 499 (1978).
15. J. Nordgren, H. Ågren, C. Nordling and K. Siegbahn, Phys. Scripta, **19**, 5 (1979).
16. A. Maizel', G. Leonkhardt and R. Sargan. X-Ray Spectra and Chemical Bonds [in Russian], Naukova Dumka, Kiev (1981), p. 45.
17. V. V. Murkhtanov, J. Electron Spectrosc. Related Phenom., **56**, 297 (1991).
18. V. D. Yumatov, L. N. Mazalov, A. V. Okotrub and I. A. Topol', Zh. S. Khim., **25**, No.5, 63 (1984).
19. V. D. Yumatov, A. V. Okotrub, L. N. Mazalov, G. S. Belikova and T. M. Okhrimenko, Zh. S. Khim., **26**, No.4, 59 (1985).
20. J. A. Bearden, Rev. Mod. Phys., **39**, 78 (1967).
21. A. Savitsky and M. J. E. Golay, Anal. Chem., **36**, 1627 (1964).
22. A. A. Bliznyuk and A. A. Voitnyuk, Zh. S. Khim., **27**, No.4, 190 (1986).