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X-RAY EMISSION SPECTROSCOPY AND ELECTRONIC STRUCTURE OF HETEROCYCLIC COMPOUNDS. 1. FURAN

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The electronic structure of the furan molecule was investigated by x-ray spectroscopy. A quantum-chemical calculation (ab initio) was undertaken, and the results were compared with the experimental data. The interpretation of the x-ray spectra of the molecule, the carbon atoms of which have a different energy position for the 1s levels, is discussed in detail. The electronic transitions from the MO to these core levels are clearly recorded in the carbon x-ray spectrum. It was shown experimentally that the HOMO is an orbital in which the electron density is localized at the carbon atoms.

The present work begins a cycle of articles devoted to the investigation of a series of heterocyclic compounds by x-ray spectroscopy. The furan molecule has been studied in detail by quantum chemistry and photoelectron spectroscopy (PES) (e.g., see [1-3] and the references in them) and also by x-ray electron spectroscopy (XES) [4, 5]. The investigations have made it possible to obtain a fairly full picture of the electronic structure of furan, i.e., the energy position of the MO and the structure of the wave functions. Since the latter was only established on the basis of theoretical calculations, it was necessary to determine it experimentally. X-ray spectroscopy was used for this purpose. There are no such data in the literature, and the aim of the present work was therefore to investigate the electronic structure of the furan molecule from the standpoint of its x-ray emission spectra.

We obtained the OK_{α} and CK_{α} spectra (the x-ray emission spectra of oxygen and carbon respectively for furan) (Fig. 1). The experimental and smoothed spectra were reduced to the single energy scale of ionization potentials using the energy position of the inner O1s and C1s levels,* taken from [4,5]. However, whereas the OK_{α} spectrum is reduced to a single scale in the usual way, e.g., by the method in [6], for the CK_{α} spectrum it becomes indeterminate on account of the presence of two types of carbon atoms in the furan molecule (in relation to the oxygen) and, accordingly, two C1s levels. The CK_{α} spectrum, reduced to the scale of ionization potentials by means of the $C_{3,4}1s$ level, is shown in Fig. 1 by the solid line (the lower scale of electron transition energies, E), while the spectrum obtained by means of the $C_{2,5}1s$ level is represented by the dotted line (the upper scale of transition energies). The photoelectron spectrum (HeI), presented in the same figure was reproduced from [2]. The x-ray spectra were synthesized on the basis of the *ab initio* calculation that we made (Fig. 2). The identification of the intensities of the individual x-ray transitions is given in Fig. 2 and in Table 1.

*The ionization potentials of the C1s orbitals: $I(C_{2,5}1s) = I(C_{3,4}1s)$; $I(C_31s) = I(C_41s) = I(C_{3,4}1s)$.

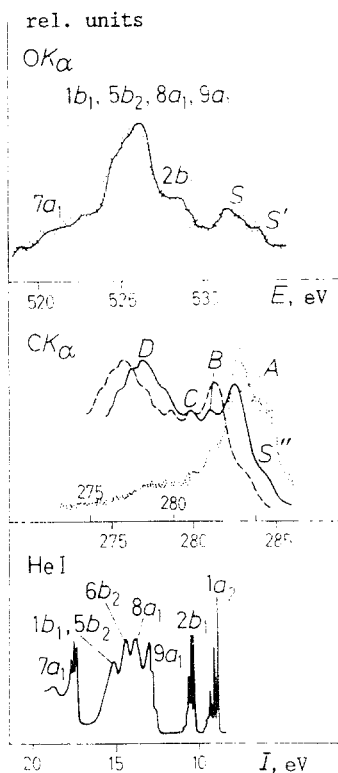


Fig. 1

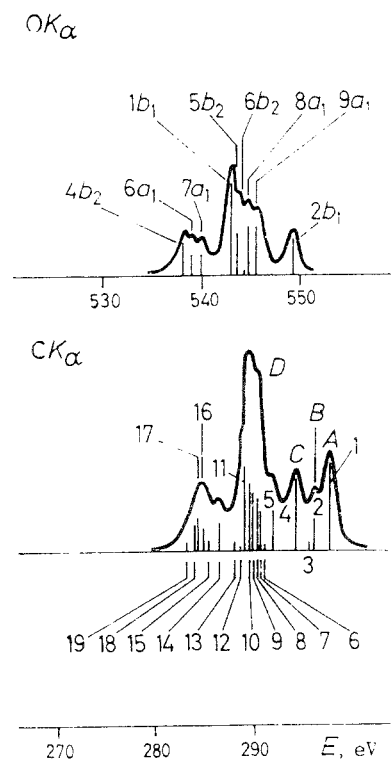


Fig. 2

Fig. 1. X-ray and photoelectron spectra of furan. OK_{α} spectrum: dotted line represents the experimental spectrum, and solid line represents the smoothed spectrum. CK_{α} spectrum: dotted line represents the experimental spectrum, and solid line represents the smooth spectrum corrected for the efficiency of the crystal analyzer.

Fig. 2. Theoretical x-ray spectra of furan. The vertical lines represent the intensities of the individual x-ray transitions.

Below we give the interpretation of the obtained spectra. According to the theoretical investigations, the HOMO of furan is the $1a_2$ orbital, belonging to a π system. On the basis of symmetry operations (the C_{2v} symmetry group) the MO of the a_2 type does not contain the $2p_{\pi}$ AOs of oxygen. According to quantum-chemical calculations, the contribution from the $C_{3,4}2p_{\pi}$ -AO to this orbital is approximately half the contribution from the $C_{2,5}2p_{\pi}$ -AO.

We will now consider the appearance of $1a_2$ in the x-ray spectra. As already mentioned, the contribution from the AO of oxygen to the $1a_2$ MO is absent, and consequently there is no analog of this orbital in the OK_{α} x-ray spectrum (Fig. 1). Although the nature of the S and S' lines is debatable, it can be stated that they are not associated with the occupied MOs. A similar judgement can be made about the S'' line of the CK_{α} spectrum. When treated by means of $C_{2,5}1s$ level the band of the photoelectron spectrum corresponding to the $1a_2$ orbital coincides with the maximum A of the CK_{α} spectrum, and when treated by means of the $C_{3,4}1s$ level it coincides with maximum B. Consequently, lines A and B correspond to the appearance of the $1a_2$ orbital in the CK_{α} spectrum. Since it is stronger and is lower in energy,* the maximum A must be compared with the $1a_2 \rightarrow C_{2,5}1s$ transition or in the MO scheme $1a_2 \rightarrow 2a_1$ and $1a_2 \rightarrow 1b_2$, while maximum B corresponds to the $1a_2 \rightarrow C_{3,4}1s$ transition or in the MO scheme $1a_2 \rightarrow 3a_1$ and $1a_2 \rightarrow 2b_2$. The foregoing can also be substantiated by the fact that the last transitions have lower energy than $1a_2 \rightarrow C_{2,5}1s$ and must consequently appear in the more low-energy region (the E scale) of line A. In addition, the intensity of the x-ray band corresponding to the $1a_2 \rightarrow C_{2,5}1s$ transition must be higher than $1a_2 \rightarrow C_{3,4}1s$, since the contribution from the $C_{2,5}2p_{\pi}$ -AO to the $1a_2$ orbital is approximately twice the contribution from the $C_{3,4}2p_{\pi}$ -AO (Figs. 1 and 2).

*Here and subsequently, except where indicated otherwise, we are concerned with the scale of ionization potentials (I).

TABLE 1. Identification of the Individual Lines in the Theoretical CK_{α} Spectrum, Given in Fig. 2

Designation of the transitions in the figure	Transition	Designation of the transitions in the figure	Transition
1	$1a_2 \rightarrow C_{2,5}1s$	11	$6b_2 \rightarrow C_{3,4}1s$
2	$1a_2 \rightarrow C_{3,4}1s$	12	$1b_1 \rightarrow C_{2,5}1s$
3	$2b_1 \rightarrow C_{2,5}1s$		$5b_2 \rightarrow C_{3,4}1s$
4	$2b_1 \rightarrow C_{3,4}1s$	13	$1b_1 \rightarrow C_{3,4}1s$
5	$9a_1 \rightarrow C_{2,5}1s$	14	$7a_1 \rightarrow C_{2,5}1s$
6	$8a_1 \rightarrow C_{2,5}1s$	15	$6a_1 \rightarrow C_{2,5}1s$
7	$6b_2 \rightarrow C_{2,5}1s$	16	$7a_1 \rightarrow C_{3,4}1s$
8	$9a_1 \rightarrow C_{3,4}1s$	17	$4b_2 \rightarrow C_{2,5}1s$
9	$5b_2 \rightarrow C_{2,5}1s$	18	$6a_1 \rightarrow C_{3,4}1s$
10	$8a_1 \rightarrow C_{3,4}1s$	19	$4b_2 \rightarrow C_{3,4}1s$

The $2b_1$ orbital, consisting of the $2p_{\pi}$ -AOs of oxygen and carbon, then follows in order of increasing bond energy. According to the calculation the contribution from the $C_{2,5}2p_{\pi}$ -AO is fairly small. It must be expected on this basis that the corresponding line of the CK_{α} spectrum (the $2b_1 \rightarrow C_{2,5}1s$ transition) has very low intensity. The $2b_1 \rightarrow C_{3,4}1s$ transition must be compared with the maximum C of the CK_{α} spectrum, since the second band of the photoelectron spectrum, corresponding to the $2b_1$ orbital, coincides with line C when treated by means of the $C_{3,4}1s$ level. In the OK_{α} spectrum the $2b_1$ orbital appears in the form of a low-energy extension on the dominant line. We note some discrepancy in the lines of the photoelectron and OK_{α} x-ray spectra, corresponding to the $2b_1$ orbital. This question has been discussed many times (see [7]) and may be due to the appearance of vibrational structure in the x-ray and photoelectron spectra. Thus, on the whole the low-energy structure of the experimental CK_{α} spectrum (lines A, B, and C) is fairly close to the analogous structure of the theoretical spectrum (Figs. 1 and 2). This part of the experimental CK_{α} spectrum was identified (Fig. 3).

This is followed, in order of increasing bond energy, by a group of levels in which the electrons form a σ bond: $9a_1$, $8a_1$, $6b_2$, and $5b_2$, and also a π bond ($1b_1$). By comparing the experimental and theoretical spectra it is possible to compare the above-mentioned orbitals with line D of the CK_{α} spectrum and the strongest maximum of the OK_{α} spectrum. A more detailed analysis of this group of MOs and identification with the individual maxima of the x-ray spectrum encounter considerable difficulties even for the OK_{α} spectrum. (The CK_{α} spectrum is even more complicated, since each MO appears in the form of two lines.) This can be attributed to the fact that the various calculations give a different sequence of orbitals for the given group, located in a narrow energy range of ≈ 3 eV, and also different populations of one and the same orbital (see [1,2] and the references therein).

The data from the x-ray spectral investigations of the energy position of the C1s levels are illustrated in Fig. 3, where they are compared with the XE experiment given in [4].

The energy distance between the two C1s levels on the basis of our calculation amounts to ≈ 1.55 eV, which is also close to the results given above.

In conclusion we note that in the furan molecule we were able to record experimentally the transition of electrons from the HOMO to the two C1s orbitals differing in energy position. These orbitals belong to carbon atoms having a different position in relation to the oxygen atom (the heteroatom). According to the x-ray spectral investigations, the HOMO is an orbital with electron density localized at the carbon atoms ($1a_2$). The electron density of the next, deeper, orbital ($1b_1$) is localized both at the carbon and at the oxygen atoms. The same conclusion can be reached on the basis of calculation, which with the exception of certain fine details describes the structure of the x-ray spectra satisfactorily.

EXPERIMENTAL

The x-ray emission spectra were obtained for the compound in the gas phase by electron impact. The spectra were recorded on a Stearat x-ray spectrometer. The procedure for the recording and calibration of the spectra was described in [8].

The experimental spectra were smoothed by least-squares treatment in relation to the central point [9]. The smoothing interval was 1.5 eV for the OK_{α} spectrum and 1.0 eV for the CK_{α} spectrum, and this amounts to ≈ 1.5 and ≈ 0.8 of the total width of the line at the half-height (the half-width). Such variation was made in connection with the search for the optimum smoothing interval. In [10], for example, it was considered that this value should amount to ≈ 0.7 of the half-width of the

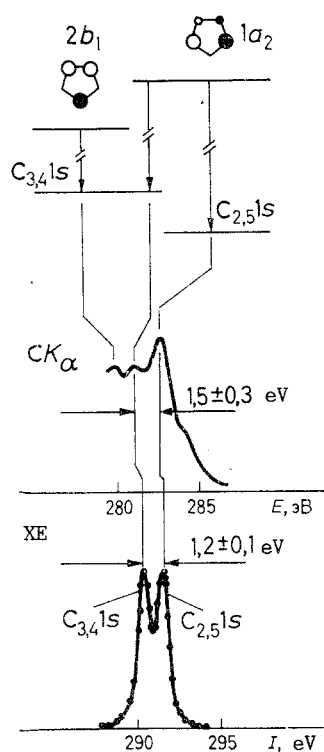


Fig. 3. Identification of the first lines of the CK_{α} x-ray spectrum of furan and comparison with the x-ray electron experiment.

individual spectral line. To determine the half-widths of the lines in the OK_{α} spectrum we used the analogous spectrum of water (≈ 1 eV) [11], and for the CK_{α} spectrum we used the spectrum of benzene (≈ 1.2 eV) [8]. These data were also used for the construction of the theoretical spectra, which represent the sum of individual lines of Lorentz form.

The error (mean-square deviation) in the determination of the intensity for the OK_{α} spectrum amounted to $\sim 3\%$ in relation to the maximum of the strongest line. For the experimental CK_{α} spectrum the error in the determination of the intensity was not less than 2% also in relation to the dominant line. Multiplication of the spectrum by the correction factor (the procedure was set out in detail in [8]) led to a nonuniform dependence of the error in the determination of the intensity on the energy of the transition, amounting to 2, 4, 6, and 13 % in relation to the maximum D for lines A, B, C, and D, respectively.

The error in the determination of the energy position of the individual lines in the OK_{α} spectrum amounted to about ± 0.2 eV, and the error for the CK_{α} spectrum amounted to about ± 0.3 eV.

Since different values of the ionization potentials for the inner levels of the molecule were given in [4,5], to reduce the OK_{α} and CK_{α} spectra to a common energy scale we used the following average values: $I(O1s) = 539.7 \pm 0.1$ eV; $I(C_{2,5}1s) = 291.6 \pm 0.2$ eV and $I(C_{3,4}1s) = 290.4 \pm 0.2$ eV.

The nonempirical *ab initio* calculations of the furan molecule were performed by the MONSTERGAUSS-81 program* in the standard 4-31G and STO-3G basis sets. The energies and intensities of the x-ray lines were calculated in the frozen orbital approximation. The appropriate program was written in order to determine the matrix elements of the x-ray transitions (in the 4-31G basis set). The agreement with experiment in the case of the 4-31G basis set was significantly better than for the STO basis set, and the results from calculation of the latter are not therefore given.

*The version of this program for the EC computer was by O. P. Charkin and coworkers.

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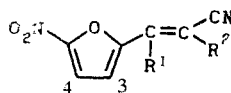
**FREE-RADICAL INTERMEDIATES IN THE
ELECTROCHEMICAL REDUCTION OF α,β
DERIVATIVES OF β -(5-NITRO-2-FURYL)- α -
CYANOETHYLENE**

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It was found by cyclic voltammetry and ESR that the excitation of the molecules of α,β derivatives of β -(5-nitro-2-furyl)- α -cyanoethylene in the radical-anion state by one-electron electrochemical reduction promotes chemical transformation of the other reaction centers, while preserving the nitrofuran group.

Earlier it was established that the products from one-electron reduction, i.e., radical-anions, were obtained during the electrochemical reduction of the 2-vinylene derivatives of 5-nitrofuran [1]. The formation of such radical-anions is due to the priority for the reduction of the nitro group. However, it is known [2] that the C=C bond of the vinylene group, conjugated with electron-withdrawing substituents and particularly with the cyano group, can also undergo electrochemical reduction, or the substituent may be removed electrochemically (with cleavage of the C-CN, C-Cl, or C-N⁺ bond) [3]. These effects can hinder the formation of radical-anions of the initial compounds sufficiently stable for study by ESR. Such features must also be expected in our investigated α,β derivatives of β -(5-nitro-2-furyl)- α -cyanoethylenes (I-VIII), the free radicals of which we attempted to generate in the present work.



I - VIII

I R¹=NMePh; II R¹=NH₂; III, VII R¹=NHPh; IV, VIII R¹=morpholino; V R¹=
=NH(CH₂)₂OH; VI R¹=Cl; I-V R²=CO₂Et; VI-VIII R²=CN

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