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

V. D. Yumatov, N. P. Erchak and É. Lukevits

The electronic structure of the pyrrole molecule has been investigated by X-ray emission spectroscopy. The NK_α *and* CK_α *spectra have been recorded. The theoretical spectra were prepared on the basis of non-empirical calculations. The structure of the HOMO was investigated similarly. The particularly high resolution in the* CK_α *spectrum permitted the identification of the X-ray transitions from the upper orbitals to the atomic orbitals of carbon atoms in different positions relative to the nitrogen atom.*

The results of studies of the electron structure of pyrrole by photoelectron spectroscopy and quantum chemistry have been well discussed in a number of reviews (e.g., [2-5] and the references cited therein). The relative positions of the internal (atomic) energy levels have been studied by X-ray electron spectroscopy and reported [6, 7].

The present work is concerned with the analysis of the electronic structure of pyrrole and the observation of its X-ray emission spectra. The basic problem is to obtain the K_α spectrum of nitrogen (NK_α). NK_α emissions have been successfully recorded for only a small number of relatively simple molecules (e.g., [8]). The results of our work to develop a method for obtaining nitrogen K_α spectra have been described in detail [9, 10].

The NK_α and CK_α spectra of pyrrole are shown in Fig. 1. The spectra are displayed on the same ionization potential (I) energy scale using a known method (e.g., see [11]). However this procedure with the carbon spectrum leads to some indeterminacy since two C1*s* levels are present ($C_{2,5}1s$ and $C_{3,4}1s$). A similar problem was encountered in the case of the furan molecule [12]. The CK_α spectrum in Fig. 1 is superimposed on the general ionization potential scale using the $C_{3,4}1s$ level. Also shown are the HeI photoelectron spectrum (from [13]) and the high energy part of the X-ray photoelectron spectrum (MgK_α exciting line), reproduced from [6].

Spectra are presented in Fig. 2 which were obtained by *ab initio* quantum chemical calculations with 4-31G and STO-3G basis sets using the GAUSSIAN-80 program (V. L. Bugaenko, V. G. Zakzhevskii and N. B. Kuz'minskii's version). According to this calculation the HOMO of pyrrole (point group symmetry C_{2v}**) is an orbital of symmetry $1a_2$ which consists of carbon $2p\pi$ AO (atomic orbitals), with the contribution from the $C_{2,5}2p\pi$ AO approximately twice as large as that from the $C_{3,4}2p\pi$ AO. The $2p\pi$ AO of the central nitrogen atom does not participate in this MO for symmetry reasons. This is expressed in the X-ray spectrum as follows: the first line in the photoelectron spectrum coincides with the maximum A, if the $C_{2,5}1s$ level is used, and with the shoulder B, if the $C_{3,4}1s$ level is used. Consequently line A may correspond to the transition $1a_2 \rightarrow C_{2,5}1s$, which is the highest energy transition (on the transition energy scale E) and the shoulder B to the $1a_2 \rightarrow C_{3,4}1s$ transition (see Fig. 2 and 3).

Since the contribution of the $C_{2,5}2p\pi$ AO to the $1a_2$ orbital is greater than that of the $C_{3,4}2p\pi$ AO, the intensity of the transition to $C_{2,5}1s$ is greater than that of the transition to $C_{3,4}1s$.

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*For Communication 2, see [1].

**Orbitals of symmetry a_2 and b_1 belong to the π-system (perpendicular to the plane of the molecule) and orbitals of symmetry a_1 and b_2 to the σ-system (in the plane of the molecule).

Institute of Inorganic Chemistry. Siberian Branch, Russian Academy of Sciences, Novosibirsk, 630090. Latvian Institute of Organic Chemistry, Riga, LV-1006. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 10, pp. 1333-1338, October, 1993. Original article submitted April 19, 1993.

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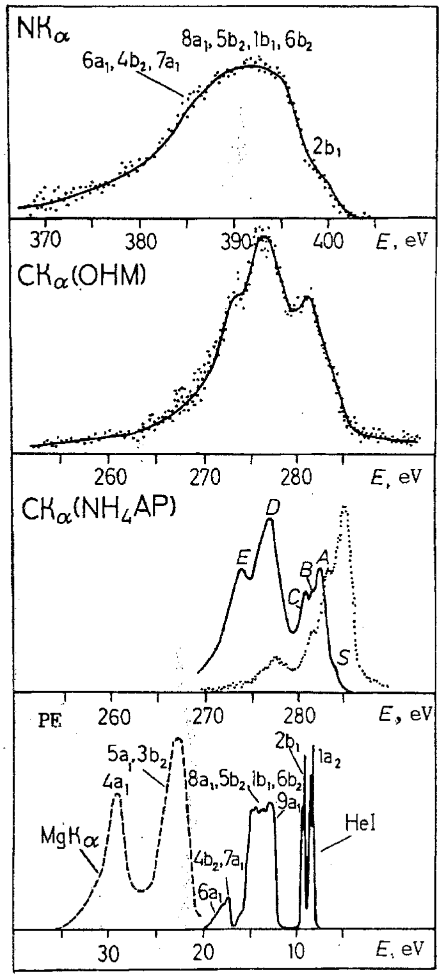

Fig. 1. X-ray and photoelectron spectra of pyrrole NK_α and CK_α(ONM) spectra: ......) experimental; _____) smoothed spectrum. $CK_\alpha(NH_4AP)$ spectrum:....) experimental; _______) smoothed and corrected for the effectiveness of the analyzer crystal.

The second MO with high orbital energy (*I* scale) is $2b_1$. It is composed of carbon and nitrogen $2p\pi$ AO. Since, according to the calculations, the contribution of the $C_{2,5}2p\pi$ AO is small, the transition $2b_1 \rightarrow C_{2,5}1s$ should have negligible intensity. Shoulder B should be assigned to this transition; since it is tied to the use of the $C_{2,5}1s$ level it coincides with the second band in the photoelectron spectrum which, in its turn, corresponds to the $2b_1$ MO (see Fig. 3). Hence line B in the CK_α spectrum corresponds basically to the $1a_2 \rightarrow C_{3,4}1s$ transition with a very small contribution from the $2b_1 \rightarrow C_{3,4}1s$ transition. Association through the $C_{3,4}1s$ level leads to the coincidence of the second band of the photoelectron spectrum with line C. Consequently the latter may be compared with the $2b_1 \rightarrow C_{3,4}1s$ transition. The contribution of the $N2p\pi$ AO to the $2b_1$ MO leads to its appearance in the K_α spectrum as a high energy (*E* scale) shoulder on the basic maximum. This band coincides with the second band of the photoelectron spectrum which corresponds to the $2b_1$ MO.

The structure of the CK_α spectrum, which reflects transitions from the $1a_2$ and $2b_1$ HOMO to the C1*s* level, is shown in Fig. 3 where it is compared with results from the basic photoelectron study [6]. Line S of the CK_α spectrum is evidently connected with radiation from the analyzer crystal and is not associated with transitions from pyrrole MOs.

The group of σ-bond levels $9a_1$, $6b_2$, $5b_2$ and $8a_1$ and one π-bond level $1b_1$ correspond to higher orbital energies. Transitions from MO of this group may correspond with intense lines in the NK_α and line D in the CK_α spectrum which coincide. Moreover they coincide with the broad band in the photoelectron spectrum which, in its turn, has much fine structure (See Fig. 1 and 2).

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

Line	Transition		Line	Transition	
	4-31G	STO-3G		4-31G	STO-3G
1	$1a_2 \rightarrow C_{2,5}1s$	$1a_2 \rightarrow C_{2,5}1s$	12	$1b_1 \rightarrow C_{3,4}1s$	$1b_1 \rightarrow C_{3,4}1s$
2	$2b_1 \rightarrow C_{2,5}1s$	$2b_1 \rightarrow C_{2,5}1s$	13	$8\mathrm{a}_1 \rightarrow C_{3,4}1s$	$8a_1 \rightarrow C_{3,4}1s$
3	$1a_2 \rightarrow C_{3,4}1s$	$1a_2 \rightarrow C_{3,4}1s$	14	$7a_1 \rightarrow C_{2,5}1s$	$7a_1 \rightarrow C_{2,5}1s$
4	$2b_1 \rightarrow C_{3,4}1s$	$2b_1 \rightarrow C_{3,4}1s$	15	$4b_2 \rightarrow C_{2,5}1s$	$4b_2 \rightarrow C_{2,5}1s$
5	$9a_1 \rightarrow C_{2,5}1s$	$9a_1 \rightarrow C_{2,5}1s$	16	$6\mathrm{a}_1 \rightarrow C_{2,5}1s$	$7a_1 \rightarrow C_{3,4}1s$
6	$6b_2 \rightarrow C_{2,5}1s$	$6b_2 \rightarrow C_{2,5}1s$	17	$7a_1 \rightarrow C_{3,4}1s$	$4b_2 \rightarrow C_{3,4}1s$
7	$1b_1 \rightarrow C_{2,5}1s$	$9a_1 \rightarrow C_{3,4}1s$	18	$4b_2 \rightarrow C_{3,4}1s$	$6a_1 \rightarrow C_{3,4}1s$
8	$9a_1 \rightarrow C_{3,4}1s$	$1b_1 \rightarrow C_{2,5}1s$	19	$3b_2 \rightarrow C_{3,4}1s$	$3b_2 \rightarrow C_{3,4}1s$
9	$5b_2 \rightarrow C_{2,5}1s$	$5b_2 \rightarrow C_{2,5}1s$	20	$5a_1 \rightarrow C_{2,5}1s$	$5a_1 \rightarrow C_{2,5}1s$
10	$8a_1 \rightarrow C_{2,5}1s$	$8a_1 \rightarrow C_{2,5}1s$	21	$5a_1 \rightarrow C_{3,4}1s$	$5a_1 \rightarrow C_{3,4}1s$
11	$6b_2 \rightarrow C_{3,4}1s$	$6b_2 \rightarrow C_{3,4}1s$	22	$4\mathrm{a}_1 \rightarrow C_{2,5}1s$	$4a_1 \rightarrow C_{2,5}1s$

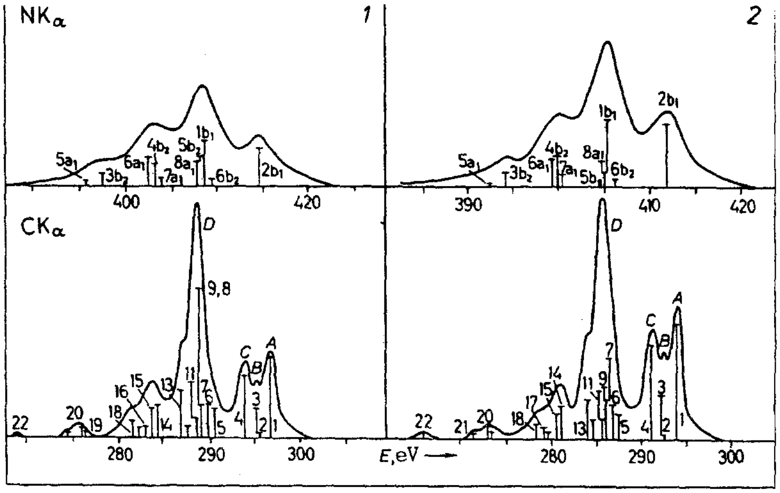

Fig. 2. Theoretical X-ray spectra of pyrrole. *Ab initio* calculations with 4-31G (*1*) and STO-3G (*2*) basis sets.

Orbitals $7a_1$, $4b_2$, $6a_1$, $3b_2$, $5a_1$ and $4a_1$ are reflected in the carbon and nitrogen K_α spectra as low energy (E scale) shoulders. They coincide with the remaining bands of the photoelectron and X-ray photoelectron spectra (see Fig. 1). These σ-bond MO are basically formed from the nitrogen and carbon $2s$ AO. They appear in the X-ray spectra as a result of a small contribution from the $2p\sigma$ AO.

The deeper lying orbitals $2b_2(C_{3,4}1s)$, $3a_1(C_{3,4}1s)$, $1b_{2(C_{2,5}1s)}$, $2a_1(C_{2,5}1s)$ and $1a_1(N1s)$ are completely atomic. As noted, their energies were determined by photoelectron spectroscopy.

We note in conclusion that transitions from the HOMO $1a_2$ and $2b_1$ to two $1s$ levels of carbon atoms in different positions with respect to the nitrogen atom ($C_{2,5}$ and $C_{3,4}$) were recorded experimentally for both the pyrrole and furan [12] molecules. The difference in energy between the two $C1s$ levels obtained from the X-ray experiment agreed with those from the photoelectron experiment within the limits of experimental error (see Fig. 3). The quantum chemical calculation reported here gave an energy difference between the $C1s$ levels of ~ 1.4 eV.

EXPERIMENTAL

A complete description of the X-ray spectroscopic apparatus used in this work has been given previously [14]. The NK_α spectrum was obtained for solid pyrrole at a temperature close to that of liquid nitrogen. The analyzer crystal used to disperse the X-ray radiation from the substances studied was an ONM crystal with planes $2d = 6.35$ nm [15].The spectra were calibrated using the $AlK\alpha_{1,2}$ (center of gravity) line in third and fourth order reflections.

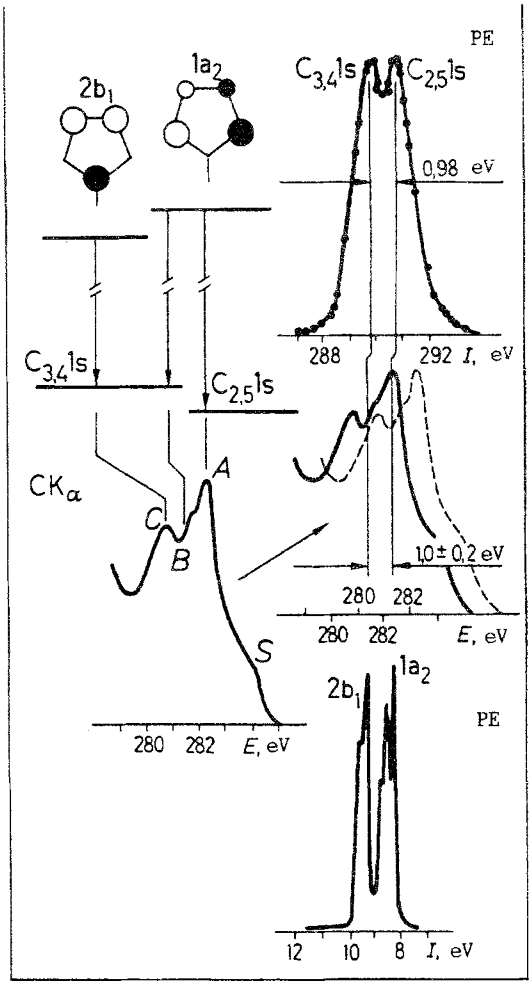

Fig. 3. Identification of the first lines in the X-ray CK_α spectrum of pyrrole and the corresponding lines from the photoelectron experiment. Connection to the low energy part of the photoelectron spectrum: ------ via the $C_{2,5}1s$ level; via the $C_{3,4}1s$ level. The upper energy scale (*E*) is given for the later type of connection.

CK_α(NH$_4$AP) spectrum was registered for gas phase pyrrole (Fig. 1). An NH$_4$AP crystal with $d = 5.288$ nm was used as the analyzer crystal [16]. Since the spectra were strongly distorted because of anomalous reflection, the spectra were corrected for effectiveness of the analyzer crystal (Fig. 1) by a known method [17]. Second order reflections of the $CrL\alpha_{1,2}$ and $VL\alpha_{1,2}$ lines of the pure metals were used to calibrate the spectra. The energies of all the calibration lines were taken from Bearden [18].

The CK_α(ONM) spectrum was registered for solid pyrrole using ONM as the analyzer crystal (Fig. 1). Additional recording was carried out by an approved method of comparison with the experimental spectrum obtained with an NH$_4$AP crystal, i.e, the CK_α(NH$_4$AP) spectrum. It makes no sense to use an ONM crystal to analyze the gas phase since it sharply reduces the intensities of all the bands without increasing the resolution. The methods for plotting the spectra of samples have been reported: gas phase [17], solid phase [14].

The least squares deviation in determining the energies of the lines using the ONM crystal was ± 0.4 eV and using the NH$_4$AP crystal ± 0.2 eV.

Spectra were smoothed by a known method [19, 20]. The smoothing interval was chosen in relation to the value of the full width at half height (FWHH) of individual lines of the X-ray spectrum and has a value of 0.7 FWHH. The experimental values for the FWHH for the NK_α spectra was 5 eV and for the CK_α spectrum was 1.2 eV. These values were used in the construction of the theoretical spectra which were synthesized as the sum of separate lines with Lorentzian shape, while the line intensities were calculated taking into account the matrix elements of the X-ray transitions in the frozen orbital approximation. The values of the FWHH mentioned above were used in the resolution of the $CK_{\alpha}(NH_4AP)$ spectrum into its separate components. This procedure was used for the precise determination of the energies of the X-ray transitions corresponding to the maxima A, B and C. These energies obtained from resolution of the spectrum are shown as vertical lines in Fig. 3.

The theoretical spectra were reconciled with the transition energy scale (*E*) using the N1*s* and $C_{2,5}1s$ levels, the values of which were taken from the calculated theoretical spectra.

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