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

4.* PYRIDINE

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The electronic structure of the pyridine molecule has been investigated by x-ray emission spectroscopy. The $NK_{\alpha y}$ *and* $CK_{\alpha y}$ *emission spectra have been measured.* Ab initio *and MNDO calculations have been carried out and individual bands in the spectra have been identified subsequently. The calculations produce spectral contours which approximate those of the experimental spectra.*

A considerable number of publications are concerned with studies of the pyridine molecule by photoelectron spectroscopy and quantum chemical calculations and the results have been reviewed (see [2, 3] and references cited therein). Data on the x-ray electronic spectrum of pyridine have been reported [4].

The objective of the present work was to study the electronic structure of pyridine by quantum chemical methods and to investigate any peculiarities in its x-ray emission spectra. As noted in the preceding paper [1], a basic problem in work of this type is the need to develop to methods for the x-ray spectroscopy of nitrogen. Only after a method was developed to record the $NK\alpha$ spectrum did it become possible to carry out a full x-ray spectroscopic investigation of nitrogen-containing compounds. Clearly it is unsatisfactory to produce a general picture of the electronic structure of a nitrogen-containing compound without information from the $NK\alpha$ emission spectrum.

The x-ray emission spectra of pyridine are shown in Fig. 1 together the photoelectron spectrum reproduced from [5]. The spectra have been transferred to a common energetic scale based on the ionization potentials (I) by a known method [6] using the energies of inner levels determined by photoelectron spectroscopy. Unfortunately only the value for the N1s level of pyridine in the gas phase is recorded in the literature (I(N1s) = 404.9 eV) [4]. Since this information is lacking for C1s , its value was taken from a paper on the electron energy loss spectrum [7]. The value I(C1s) = 290.8 eV obtained in this way is a mean value for carbon atoms with different geometric positions relative to the nitrogen atom.

Theoretical spectra constructed on the basis of *(i) ab initio* calculations with the GAUSSIAN-80 program (V. L. Gugaenko, V. G. Zakzhevskii and N. B. Kuz'minskii's version) using 4-31G and STO-3G basis sets and (ii) MNDO calculations are presented in Fig. 3 and Table 1.

We now identify the spectra obtained. The pyridine molecule belongs to point group C_{2v}. Orbitals of symmetry a_2 and b_1 form the π-system of the molecule (perpendicular to the plane of the ring) while orbitals of symmetry a_1 and b_2 belong to the σ-system (in the plane of the ring). According to the quantum chemical calculations, the molecular orbitals (MO) falling the following order of increasing one electron bond energy (I scale): $1a_2$, $2b_1$ and $11a_1$ (see Fig. 1 and 3). The order of $2b_1$ and $11a_1$ remains indefinite. Orbital $1a_2$ is composed of C2$p\pi$−AO only, while involvement of N2$p\pi$−AO is forbidden on symmetry grounds. The N2$p\pi$−AO contributes to the $2b_1$ MO together with C2$p\pi$. Finally the $11a_1$ MO has its major contribution from the N2$p\pi$−AO. It approximates an unshared electron pair. All three orbitals appear in the $CK\alpha$ spectrum as line A. The contribution of the N2$p\pi$−AO to the wave functions of levels $2b_1$ and $11a_1$ means that electron transitions from

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[*] For Communication 3 see [1].

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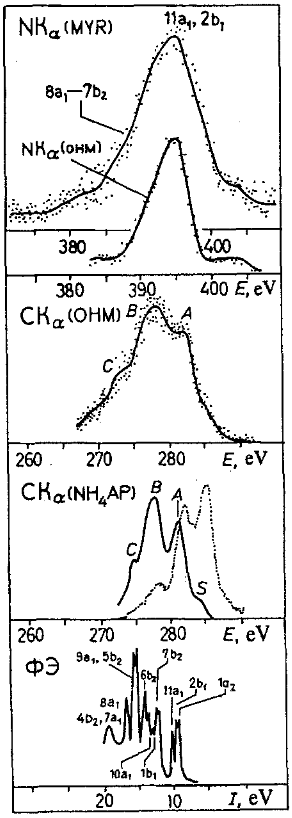

Fig. 1

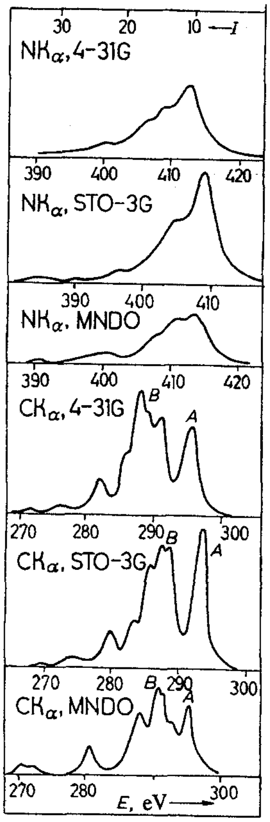

Fig. 2

Fig. 1. x-ray and photoelectron spectra of pyridine; ....) experimental and --------------) smoothed spectra. Note: in the CKα(NH_4AP) spectrum a correction for the effectiveness of the crystal analyzer was introduced in addition to the curve smoothing.

Fig. 2. Comparison of the theoretical x-ray spectra for pyridine constructed on the basis of various calculations: *ab initio* with 4-31G and STO-3G basis sets, and MNDO.

them to N1*s* have their analogs in the N*K*α spectrum. As a result of these interrelations, line *A* in the C*K*α spectrum coincides with the maximum intensity line in the N*K*α spectrum and the first three bands in the photoelectron spectrum (see Fig. 1 and 3). Line *S* in the C*K*α spectrum is apparently connected to characteristic fluorescence of the analyzer crystal and is not associated with MO transitions.

The group of orbitals $7b_2$, $1b_1$, $10a_1$ and $6b_2$ is the basis for band *B* and the orbitals $5b_2$ and $9a_1$ of band *C* in the C*K*α spectrum, and these correspond to the low energy part (*E* scale) of the principal maximum of the N*K*α spectrum.

The deeper orbitals — $8a_1$, $4b_2$, $7a_1$, $3b_2$, $6a_1$ and $5a_1$ — are constructed predominantly from the 2*s* AO of carbon and nitrogen. They show up as elongated low energy structures (*E* scale) in the N*K*α and C*K*α spectra as a result of small admixtures of carbon and nitrogen 2*p* AO in the composition of these MO.

The following orbitals are basically atomic in character: $4a_1$ ($C_4 1s$), $2b_2$ ($C_{3,5} 1s$), $3a_1$ ($C_{3,5} 1s$), $2a_1$ ($C_{2,6} 1s$), $1b_2$ ($C_{2,6} 1s$) and $1a_1$ (N1*s*).

Thus on the basis of both the experimental and theoretical x-ray spectral results it can be concluded that the highest occupied molecular orbitals of pyridine are two orbitals of the π-system and one orbital which is similar in structure to an unshared pair of electrons on the nitrogen atom. Theoretical spectra based on various calculations satisfactorily reproduce the experimental spectra (except for a few details) (see Fig. 1-3).

TABLE 1. Identification of Individual Lines of the Theoretical C$K\alpha$ Spectrum Shown in Fig. 3.

Line	Transition	Line	Transition	Line	Transition
1	$1a_2 \rightarrow C_{2,6}1s$	15	$10a_1 \rightarrow C_{2,6}1s$	29	$8a_1 \rightarrow C_41s$
2	$2b_1 \rightarrow C_{2,6}1s$	16	$10a_1 \rightarrow C_{3,5}1s$	30	$4b_2 \rightarrow C_{2,6}1s$
3	$1a_2 \rightarrow C_{3,5}1s$	17	$10a_1 \rightarrow C_41s$	31	$7a_1 \rightarrow C_{2,6}1s$
4	$2b_1 \rightarrow C_{3,5}1s$	18	$6b_2 \rightarrow C_{2,6}1s$	32	$4b_2 \rightarrow C_{3,5}1s$
5	$11a_1 \rightarrow C_{2,6}1s$	19	$6b_2 \rightarrow C_{3,5}1s$	33	$4b_2 \rightarrow C_41s$
6	$2b_1 \rightarrow C_41s$	20	$6b_2 \rightarrow C_41s$	34	$7a_1 \rightarrow C_{3,5}1s$
7	$11a_1 \rightarrow C_{3,5}1s$	21	$9a_1 \rightarrow C_{2,6}1s$	35	$7a_1 \rightarrow C_41s$
8	$11a_1 \rightarrow C_41s$	22	$5b_2 \rightarrow C_{2,6}1s$	36	$3b_2 \rightarrow C_{2,6}1s$
9	$7b_2 \rightarrow C_{2,6}1s$	23	$9a_1 \rightarrow C_{3,5}1s$	37	$3b_2 \rightarrow C_{3,5}1s$
10	$1b_1 \rightarrow C_{2,6}1s$	24	$5b_2 \rightarrow C_{3,5}1s$	38	$3b_2 \rightarrow C_41s$
11	$7b_2 \rightarrow C_{3,5}1s$	25	$9a_1 \rightarrow C_41s$	39	$6a_1 \rightarrow C_{2,6}1s$
12	$1b_1 \rightarrow C_{3,5}1s$	26	$5b_2 \rightarrow C_41s$	40	$6a_1 \rightarrow C_{3,5}1s$
13	$7b_2 \rightarrow C_41s$	27	$8a_1 \rightarrow C_{2,6}1s$	41	$6a_1 \rightarrow C_41s$
14	$1b_1 \rightarrow C_41s$	28	$8a_1 \rightarrow C_{3,5}1s$		

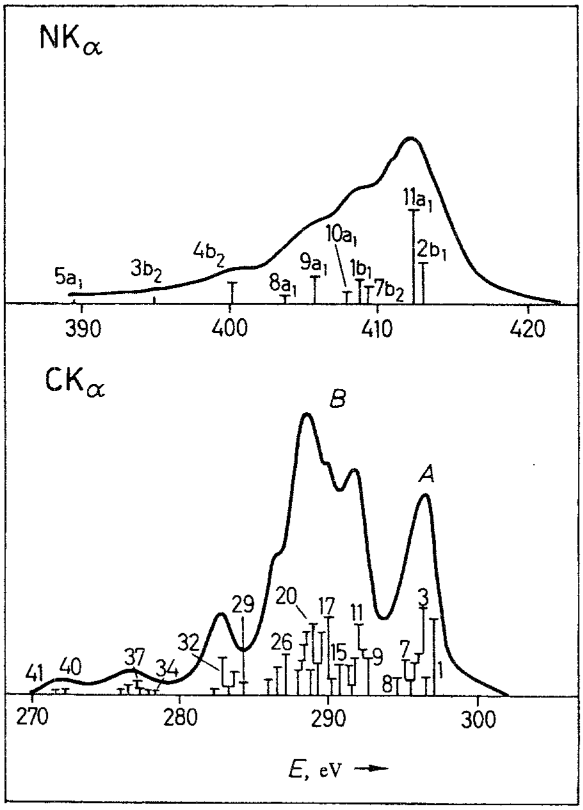

Fig. 3. Theoretical x-ray spectra of pyridine, calculated *ab initio* in the 4-31G basis set.

EXPERIMENTAL

ONM crystals were used to resolve the x-ray beam in the spectra. A detailed description of the use of this crystal and its characteristics has been published elsewhere [1]. The nitrogen spectrum was studied with a lead myristate pseudocrystal (N$K\alpha$(MYR)) with $2d = 8.05$ nm [9]. This spectrum showed some broadening in comparison with that obtained using an ONM crystal (N$K\alpha$(ONM)) (see Fig. 1). All these spectra were measured with solid compounds at a temperature close to the boiling point of nitrogen. The C$K\alpha$(NH_4AP) spectrum was measured in the gas phase, using an NH_4AP analyzer crystal. Details of working with this crystal, its characteristics and the methods of spectrum treatment and calibration are also given in [1].

To place the theoretical spectra derived from the *ab initio* calculations on the transition energy scale (*E*) the energies of the N1*s* and $C_{2,6}1s$ levels obtained from the same calculations were used, but since similar data are not obtained from the MNDO calculations results from the 4-31G basis sets were used.

In conclusion, the authors express their thanks to D.S.Urch (Queen Mary College, London) for donating ONM crystals and to N. A. Osmakov (Institute of Semiconductor Physics, Siberian Branch, Russian Academy of Sciences) for help with the calculations.

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