Electronic structures of monosubstituted benzenes and X-ray emission spectroscopy
5.* Nitrobenzene

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The electronic structure of nitrobenzene was studied by X-ray emission spectroscopy. The O-Kα, N-Kα, and C-Kα spectra of the title compound in the gas and solid phases were obtained. Based on the results of quantum chemical MNDO calculations, theoretical spectra were constructed. An interpretation of the experimental spectra is given. π-Interaction between phenyl fragment and nitro group in nitrobenzene is weak.

Key words: X-ray emission; nitrobenzene; O-Kα, N-Kα, and C-Kα spectra; quantum chemical calculations.

UV-Photoelectron spectroscopy (UPS)[2—12] and X-ray photoelectron spectroscopy (XPS)[13] were repeatedly used in studies of the electronic structure of nitrobenzene molecule (C_{2v} point symmetry group). The UPS data were interpreted using semiempirical quantum chemical calculations[3—6,12] of $C_6H_5NO_2$. The electronic structure of nitrobenzene molecule was also studied[14] by fragment analysis in the MNDO and MINDO/3 approximations.

Ab initio quantum chemical calculations of the nitrobenzene molecule in the DZ, MB, and STO-3G (see Ref. 8) and 6-31G* (see Ref. 9) basis sets were carried out. Based on the results of *ab initio* calculations with the 6-21G* basis set, theoretical spectra of nitrobenzene were constructed,[15] but no correspondence between particular MOs (and their symmetry) and spectral lines was reported.

In this study the X-ray emission spectra (XES) of nitrobenzene in the gas and crystalline phases were investigated and interpreted using the results of MNDO calculations.

The experimental XES are shown in Fig. 1. All of them were referenced to a uniform scale of ionization potentials (IP) using the energy positions of the core levels,[13] the C(1)1s level being used for the C-Kα spectrum. The use of the C(2,6)1s, C(3,5)1s, or C(4)1s levels causes a slight (by at most ~1 eV) shift of the spectrum toward higher transition energies (E) (see Fig. 1). Since different authors report different experimental energies of the 1s levels (see Ref. 13), we used averaged values.

When optimizing the geometry in the framework of the MNDO method, the angle between the planes in which the phenyl fragment and nitro group lie was set to zero in accordance with the data of gas-phase electron difraction studies.[17] The theoretical spectra constructed based on the results of these calculations are shown in Fig. 2 and in the Table 1. They were referenced to the energy scale of X-ray transitions using the average values of the experimental ionization potentials obtained by XPS.[13] The procedure for constructing theoretical spectra based on the results of semiempirical quantum chemical calculations was reported earlier (see, *e.g.*, Ref. 18). The X-ray photoelectron spectrum of nitrobenzene was interpreted by comparing it with the theoretical spectra and with the X-ray spectra of nitrogen dioxide anion and benzene. These two compounds can be considered as reasonably correct models for the nitro substituent and phenyl fragment, respectively. The MO composition of NO_2^- anion (point symmetry group C_{2v}) and its manifestation in the X-ray spectra was analyzed elsewhere.[19]

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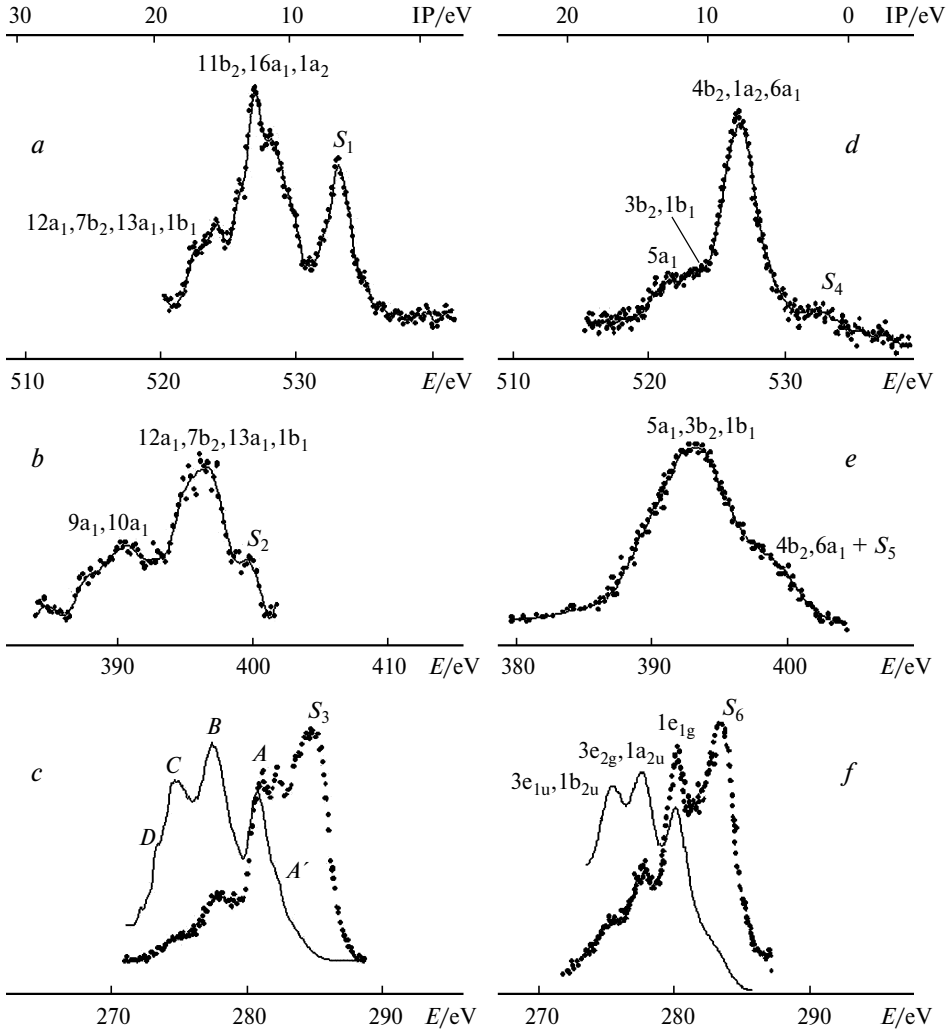

Fig. 1. X-Ray emission spectra of $C_6H_5NO_2$ (*a*—*c*), $NaNO_2$ (*d*, *e*), and C_6H_6 (*f*): O-Kα (*a*, *d*), N-Kα (*b*, *e*), C-Kα (*c*, *f*). Points denote experimental data and solid lines denote smoothed spectra; the C-K spectra were smoothed and corrected for the efficiency of reflection from the NH_4AP analyzer crystal (see Ref. 16). The lines S_1, S_2, S_3, S_4, S_5, and S_6 are satellites.

The relation between the electronic structure of benzene molecule (point symmetry group D_{6h}) and interpretation of the X-ray photoelectron spectra has long been debated (see, *e.g.*, Refs 16 and 20). Figure 1 presents the O-Kα and N-Kα X-ray emission spectra of sodium nitrite in the solid state and the C-Kα spectrum of benzene in the gas phase obtained in this study. Here we also give the interpretation of the spectra of NO_2^- anion (see Ref. 19) and benzene.[16,20] Since we were primarily interested in the nature of π-conjugation of the nitro substituent with the phenyl fragment, we will consider only the MOs composed of the AOs oriented normal to the phenyl ring plane. These are the $3b_1$, $2a_2$, $1a_2$, $2b_1$, and $1b_1$ MOs.

According to MNDO calculations, the $2a_2$ and $3b_1$ MOs are the highest occupied MOs of nitrobenzene. The appearance of these nitrobenzene orbitals can be associated with removal of degeneracy of the benzene $1e_{1g}$-MO on going to nitrobenzene molecule and with a change in the molecular symmetry, namely, $D_{6h} \rightarrow C_{2v}$, $1e_{1g} \rightarrow 2a_2 + 3b_1$. According to MNDO calculations, the $2a_2$ and $3b_1$ MOs are composed of C 2p-AOs. The contribution of the oxygen 2p-AO to the $2a_2$ and $3b_1$ MOs is negligible (0.004 and 3.415%, respectively). The wave functions of these orbitals have nodes on the nitrogen atom. Thus, electronic π-interaction between the phenyl ring and nitro group, which involves the $2a_2$ and $3b_1$ MOs, is relatively weak. A similar composition of the MOs in question is also indicated by the results of *ab initio*[8,9] and semiempirical[3—6,12] calculations. In the O-Kα and N-Kα spectra, transitions involving the $2a_2$ and $3b_1$ MOs are almost indistinguishable due to low contribution of the oxygen and nitrogen 2p-AOs (see Figs 1 and 2). One can expect that maximum *A* in the C-Kα spectrum is

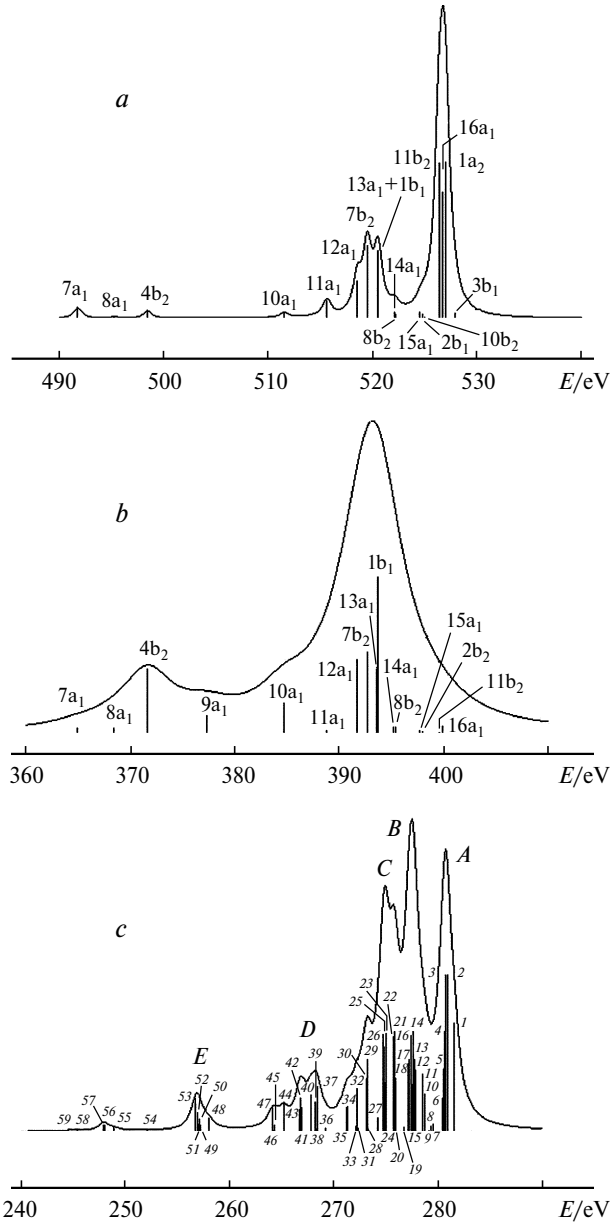

Fig. 2. Theoretical X-ray spectra of $C_6H_5NO_2$: O-Kα (*a*), N-Kα (*b*), and C-Kα (*c*).

composed by transitions from these MOs to C1s levels. This conclusion can be drawn upon comparing the C-Kα spectra of benzene and nitrobenzene. The first (or the highest-energy, scale *E*) band in the X-ray photoelectron spectrum of benzene was interpreted as transition from the $1e_{1g}$ MO.[20] Therefore, the corresponding line in the C-Kα spectrum of nitrobenzene should be assigned to a group of transitions from the $2a_2$ and $3b_1$ MOs to the C1s-levels (C(1)1s, C(2,6)1s, C(3,5)1s, and C(4)1s). This empirical procedure for the assignment of maximum *A* is confirmed by the theoretical spectrum (see Fig. 2), although here the component *A´* is not well defined. The

Table 1. Line assignment in theoretical C-Kα spectrum of nitrobenzene (see Fig. 2) to particular electronic transitions

Line	Transition	Line	Transition
1	$3b_1 \rightarrow$ C(1)1s	*30*	$13a_1 \rightarrow$ C(4)1s
2	$2a_2 \rightarrow$ C(2,6)1s	*31*	$7b_2 \rightarrow$ C(2,6)1s
3	$2a_2 \rightarrow$ C(3,5)1s	*32*	$12a_1 \rightarrow$ C(1)1s
4	$3b_1 \rightarrow$ C(2,6)1s, $3b_1 \rightarrow$ C(4)1s	*33*	$7b_2 \rightarrow$ C(4)1s, $7b_2 \rightarrow$ C(3,5)1s
5	$3b_1 \rightarrow$ C(3,5)1s	*34*	$12a_1 \rightarrow$ C(2,6)1s
6	$16a_1 \rightarrow$ C(1)1s	*35*	$12a_1 \rightarrow$ C(3,5)1s
7	$16a_1 \rightarrow$ C(2,6)1s	*36*	$11a_1 \rightarrow$ C(1)1s
8	$16a_1 \rightarrow$ C(3,5)1s	*37*	$11a_1 \rightarrow$ C(2,6)1s
9	$11b_2 \rightarrow$ C(2,6)1s	*38*	$11a_1 \rightarrow$ C(4)1s
10	$10b_2 \rightarrow$ C(1)1s	*39*	$11a_1 \rightarrow$ C(3,5)1s
11	$2b_1 \rightarrow$ C(1)1s	*40*	$6b_2 \rightarrow$ C(1)1s
12	$10b_2 \rightarrow$ C(2,6)1s, $10b_2 \rightarrow$ C(4)1s	*41*	$6b_2 \rightarrow$ C(2,6)1s
		42	$6b_2 \rightarrow$ C(4)1s
13	$10b_2 \rightarrow$ C(3,5)1s	*43*	$6b_2 \rightarrow$ C(3,5)1s
14	$2b_1 \rightarrow$ C(2,6)1s	*44*	$10a_1 \rightarrow$ C(1)1s
15	$2b_1 \rightarrow$ C(4)1s	*45*	$10a_1 \rightarrow$ C(2,6)1s
16	$2b_1 \rightarrow$ C(3,5)1s	*46*	$10a_1 \rightarrow$ C(4)1s
17	$15a_1 \rightarrow$ C(2,6)1s	*47*	$10a_1 \rightarrow$ C(3,5)1s
18	$15a_1 \rightarrow$ C(4)1s, $15a_1 \rightarrow$ C(3,5)1s	*48*	$5b_2 \rightarrow$ C(1)1s
		49	$5b_2 \rightarrow$ C(2,6)1s
19	$9b_2 \rightarrow$ C(1)1s	*50*	$5b_2 \rightarrow$ C(4)1s
20	$8b_2 \rightarrow$ C(1)1s	*51*	$5b_2 \rightarrow$ C(3,5)1s
21	$9b_2 \rightarrow$ C(2,6)1s	*52*	$9a_1 \rightarrow$ C(2,6)1s
22	$9b_2 \rightarrow$ C(3,5)1s	*53*	$9a_1 \rightarrow$ C(3,5)1s
23	$8b_2 \rightarrow$ C(2,6)1s	*54*	$4b_2 \rightarrow$ C(1)1s
24	$8b_2 \rightarrow$ C(4)1s	*55*	$8a_1 \rightarrow$ C(1)1s
25	$8b_2 \rightarrow$ C(3,5)1s, $14a_1 \rightarrow$ C(2,6)1s	*56*	$8a_1 \rightarrow$ C(2,6)1s
		57	$8a_1 \rightarrow$ C(4)1s, $8a_1 \rightarrow$ C(3,5)1s
26	$14a_1 \rightarrow$ C(4)1s, $14a_1 \rightarrow$ C(3,5)1s	*58*	$7a_1 \rightarrow$ C(1)1s
27	$1b_1 \rightarrow$ C(1)1s	*59*	$7a_1 \rightarrow$ C(2,6)1s, $7a_1 \rightarrow$ C(3,5)1s
28	$1b_1 \rightarrow$ C(2,6)1s		
29	$13a_1 \rightarrow$ C(2,6)1s		

sequence order of the $2a_2$ and $3b_1$ MOs remains unclear. This is most likely due to the small separation between them on the energy scale (at most ~0.4 eV according to UPS data[3–12]).

The next in order of increasing the binding energy (or ionization potential, IP) is the $1a_2$ MO of nitrobenzene; the corresponding electron density is concentrated on oxygen atoms in contrast to the $2a_2$ MO. According to fragment analysis data,[14] the $1a_2$-MO wave functions for nitrobenzene and nitrogen dioxide exactly match each other. This is also indicated by the results of quantum chemical calculations.[3–5,8,9] Among the X-ray photoelectron spectra of nitrobenzene, manifestation of transition from this orbital is expected only in the O-Kα spectrum. The theoretical O-Kα spectrum (see Fig. 2) shows that transitions from the $1a_2$, $16a_1$, and $11b_2$-MOs form the dominant line. Therefore, the most intense line in the experimental O-Kα spectrum should also be assigned to

transitions from these three MOs. This line can be compared with the corresponding line in the O-Kα spectrum of $NaNO_2$, which is composed by transitions from the MOs similar to the nitrobenzene MOs already considered (see Fig. 1).

The next in order of increasing IP is the $2b_1$ π-MO. According to MNDO calculations, it is mainly composed of carbon 2p-AOs. According to theoretical C-Kα spectrum, transitions from this MO manifest themselves in the experimental spectrum as line *B* (see Figs 1 and 2). This MO corresponds to the $1a_{2u}$ MO of benzene. In the benzene spectrum, this MO and the $3e_{2g}$ MO contribute to the second line (in order of decreasing the transition energy *E*). Based on similarity of the X-ray spectra of nitrobenzene and benzene, one can conclude that the $2b_1 \rightarrow C1s$ transition and transitions from other MOs (see Fig. 1), manifest themselves as line *B* in the C-Kα spectrum of nitrobenzene.

Finally, the lowest π-MO of nitrobenzene is the $1b_1$ MO. According to calculations, the corresponding electron density is mainly localized on the nitro substituent. The theoretical O-Kα spectrum shows that transitions from this orbital and other transitions contribute to the second, less intense line (see Fig. 2). Therefore, this orbital can be associated with a corresponding weak maximum in the experimental O-Kα spectrum (see Figs 1 and 2). Transition from this MO is best pronounced in the N-Kα spectrum; the nitrobenzene $1b_1$-MO is comparable with the same MO of the NO_2^- anion (see Fig. 1).

Thus, the π-system of the nitrobenzene molecule includes five MOs resulting from the interaction of the phenyl ring MOs similar to the benzene $1e_{1g}$ and $1a_{2u}$ MOs and the nitro substituent MO similar to the $1b_1$ MO of nitrogen dioxide. As shown above, this conjugation is relatively weak. This is clearly seen in the X-ray photoelectron spectra. As can be seen in Figs 1 and 2, the π-orbitals $3b_1$, $2a_2$, $1a_2$, $2b_1$, and $1b_1$ (lines *A* and *B* in the C-Kα spectrum) do not match one another when referenced to the intense (but lower-energy) lines in the N-Kα-spectrum (scale *E*). Indeed, would the N2p AO contribute largely to these MOs, the high-energy region of the N-Kα spectrum should exhibit rather intense maxima corresponding to lines *A* and *B* in the C-Kα spectrum when referenced.

Experimental

Spectra were recorded with a Stearat X-ray spectrometer designed at the A. V. Nikolaev Institute of Chemistry, Siberian Branch of the Russian Academy of Sciences, and built at the Experimental Plant, Siberian Branch of the Russian Academy of Sciences. A compound under study was introduced into a vacuum chamber as a gas stream and then subjected to electron impact. Solid substances were irradiated with copper bremsstrahlung radiation. X-ray emission thus excited was directed on the analyzer crystal using a system of slits. The O-Kα and C-Kα spectra were obtained using RbAP (rubidium hydrophthalate) and NH_4AP (ammonium hydrophthalate) crystals, respectively. The N-Kα spectrum was measured with an OHM (octadecylhydromaleate) crystal. The N-Kα spectrum was recorded for the compound in the solid phase. The use of the OHM analyzer crystal for analyzing the nitrobenzene emission in the gas phase was senseless because of an abrupt decrease in the intensity of the reflection from the crystal without noticeable increase in resolution. Many X-ray photoelectron spectra obtained with the Stearat spectrometer are at least competitive in resolution with those recorded with unique spectrometers based on diffraction gratings. Such a comparison was reported in our previous studies.[1,16,21] The procedure for recording the XES of chemical compounds was reported in more detail earlier.[16,18,22]

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