Electronic structure of monosubstituted benzenes and X-ray emission spectroscopy

1. Benzaldehyde

V. D. Yumatov[a]* *and N. F. Salakhutdinov*[b]

[a]*Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Sciences,*
3 prosp. Akad. Lavrent'eva, 630090 Novosibirsk, Russian Federation.
Fax: +7 (383) 235 5960
[b]*Institute of Organic Chemistry, Siberian Branch of the Russian Academy of Sciences,*
9 prosp. Akad. Lavrent'eva, 630090 Novosibirsk, Russian Federation.
Fax: +7 (383) 235 4752

The electronic structure of the benzaldehyde molecule has been studied by X-ray emission spectroscopy. The gas-phase O-Kα- and C-Kα-spectra of this compound have been obtained. MNDO quantum-chemical calculations have been carried out. The structure of the MO's of benzaldehyde has been compared with those of benzene and formaldehyde molecules. The character of the p_π-p_π interaction of the phenyl and formyl fragments has been considered. The contribution of the latter to the highest occupied molecular orbitals of the π-system has been shown to be small.

Key words: X-ray emission; benzaldehyde, O-Kα— and C-Kα—spectra; MNDO.

This paper opens a series of studies of monosubstituted benzenes by X-ray emission spectroscopy. This method makes it possible to observe electronic transitions from the filled electronic levels of a molecule to some internal ones. In the case under study the latter are the 1s levels of oxygen or carbon atoms. Analysis of X-ray spectra of these atoms (O-Kα- and C-Kα-spectra) sheds some light on the structure of the molecular electronic wave functions.[1] Here we paid special attention to the interaction of the phenyl nucleus with the substituent, namely, to the influence of the latter on the structure of the highest occupied molecular orbitals (HOMO).

Experimental

X-ray spectra in the ultrasoft region were recorded using a Stearat spectrometer.[2] The substance under investigation, introduced into the X-ray tube as a gas jet, was subjected to electron impact and the emitted X-ray radiation was collected on a crystal analyzer using a system of focusing and aperture slits. For the detection of the O-Kα- and C-Kα-spectra, RbAP ($2d$ = 2.612 nm)[3] and NH_4AP ($2d$ = 5.228 nm)[4] crystals were employed, respectively.

The monochromatic radiation reflected by a crystal was directed to a proportional counter with a methane filler. The window transmitting X-rays into the counter was closed by a metal gauge coated with Formvar film. The X-ray photons monitored by the counter produced electric pulses which passed to an NTA-1024 multichannel analyzer in the time-resolved regime. The spectra so obtained were accumulated in the analyzer's memory and summed up.

The spectra were analyzed using an EMG-666 computer connected to the analyzer according to the scheme of Savitzky and Golay.[5] The smoothing interval was selected using the approach recommended in Ref. 6. In addition, the C-Kα-spectrum was corrected to the efficiency of the crystal-analyzer, as described in detail elsewhere.[7]

The O-Kα- and C-Kα-spectra were calibrated against the $\mathrm{Cr}L\alpha_{1,2}$ and $\mathrm{V}L\alpha_{1,2}$ lines of the pure metals[8] (by their second-order reflection in case of C-Kα-spectrum). The root-mean-square deviation of the dominant line origin of the X-ray spectra was found to be ±0.2 eV.

Theoretical spectra were simulated with the help of MNDO quantum-chemical calculations using an approximation considered previously.[1] Using this assumption the sum of the squared coefficients at the 2p atomic orbitals (AO) of oxygen (for the O-Kα-spectrum) or carbon (for the C-Kα-spectrum) in the LCAO expansion of a given molecular orbital (MO) determined the intensity of the electronic transition from this MO to the 1s AO of O(C). These intensities were used to evaluate the lines associated with various MO's and the corresponding Lorentzian curves which were then summed up. The full widths at half maximum for the separate lines deduced from the experimental spectra were ≈1.0 and ≈1.2 eV for the O-Kα- and C-Kα-spectra, respectively. All calculations were carried out using the MNDO-86 program, a modified version of MNDO-85 program.[9]

Results and Discussion

Before discussing the electron density distribution in the C_6H_5CHO molecule, let us consider the molecule of H_2CO (C_{2v} symmetry group) as a prototype of the formyl fragment of benzaldehyde. The electronic struc-

---

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 6, pp. 1033—1037, June, 1994.

1066-5285/94/4306-0968 $12.50

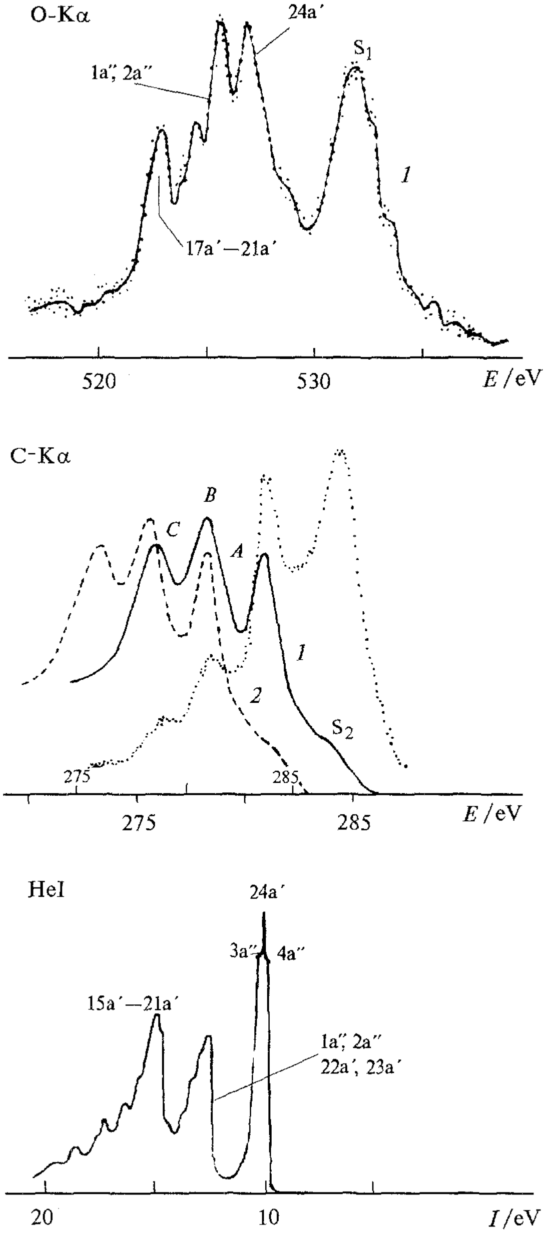

Fig. 1. X-ray (O-Kα and C-Kα) and photoelectron (HeI) spectra of C_6H_5CHO. Points — experiment; (*1*) smoothed spectra (a correction for the efficiency of the crystal-analyzeris is introduced for the C-Kα-spectrum); (*2*) C-Kα-spectrum (upper scale *E*) adjusted to the C_O1s level.

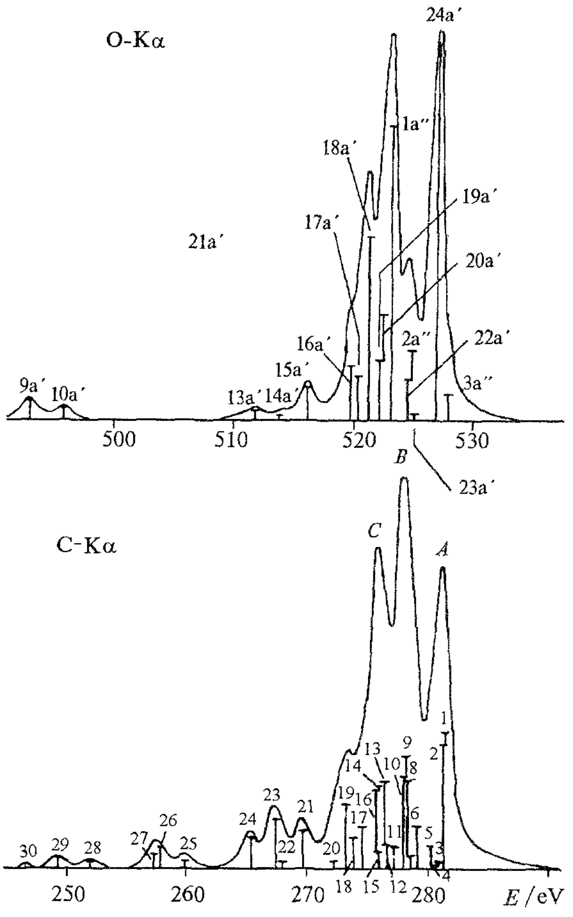

Fig. 2. Theoretical X-ray emission spectra of C_6H_5CHO (see Table 1 for line identification).

ture of formaldehyde has been investigated by photoelectron spectroscopy (PES) and quantum-chemical methods.[10] According to these results, HOMO $2b_2$ corresponds to a lone pair which predominantly consists of the 2p AO's of the oxygen atom lying in the molecular plane. The nearest neighbor of the HOMO is the $1b_1$ MO whose electrons are responsible for the π-bond between the oxygen and carbon atoms (AO's are perpendicular to the molecular plane). The corresponding σ-bond is formed by the lower $5a_1$ MO, while the $1b_2$ MO is responsible for the σ-bond between the carbon and hydrogen atoms. The $4a_1$ and $3a_1$ MO's with lower energies have significant 2s AO contributions, whereas the lowest occupied $2a_1$ and $1a_1$ orbitals have a purely atomic character associated with the 1s AO's of carbon and oxygen, respectively. The electronic structure of benzene (D_{6h} symmetry) has been described in sufficient detail,[10] while that of benzaldehyde has been the subject of PES[11—13] and X-ray electron spectroscopy (XES)[14] studies. The data of quantum-chemical calculations were presented in Ref. 11.

The X-ray O-Kα and C-Kα emission spectra and the photoelectron spectra (HeI)[11] of benzaldehyde are shown in Fig. 1 using a uniform energy scale referred to the ionization potential (*I*). The XES data from Ref. 14 were used for connecting the scales by a method described elsewhere.[1] Figure 2 and Table 1 contain the characteristics of theoretical spectra obtained on the basis of MNDO calculations. These spectra were also reduced to the transition energy scale using the measured positions of the internal energy levels.[14]

The photoelectron spectra of the benzene and benzaldehyde molecules[10,11] are quite close to each other and exhibit three broad bands which, in turn, have a

Table 1. Identifications of the lines of the theoretical C-Kα-spectrum of benzaldehyde

Line	Transition	Line	Transition
1	$4a'' \rightarrow C_B1s$	15	$16a' \rightarrow C_O1s$
2	$3a'' \rightarrow C_B1s$	16	$19a' \rightarrow C_B1s$
3	$2a'' \rightarrow C_O1s$	17	$18a' \rightarrow C_B1s$
	$23a' \rightarrow C_O1s$	18	$17a' \rightarrow C_B1s$
4	$22a' \rightarrow C_O1s$	19	$16a' \rightarrow C_B1s$
5	$24a' \rightarrow C_B1s$	20	$16a' \rightarrow C_O1s$
6	$1a'' \rightarrow C_O1s$	21	$15a' \rightarrow C_B1s$
7	$20a' \rightarrow C_O1s$	22	$13a' \rightarrow C_O1s$
8	$23a' \rightarrow C_B1s$	23	$14a' \rightarrow C_B1s$
	$19a' \rightarrow C_O1s$	24	$13a' \rightarrow C_B1s$
9	$2a'' \rightarrow C_B1s$	25	$11a' \rightarrow C_O1s$
10	$22a' \rightarrow C_B1s$	26	$12a' \rightarrow C_B1s$
11	$18a' \rightarrow C_O1s$	27	$11a' \rightarrow C_B1s$
12	$1a'' \rightarrow C_B1s$	28	$10a' \rightarrow C_O1s$
13	$21a' \rightarrow C_B1s$	29	$10a' \rightarrow C_B1s$
	$17a' \rightarrow C_O1s$		$9a' \rightarrow C_O1s$
14	$20a' \rightarrow C_B1s$	30	$9a' \rightarrow C_B1s$

Note. The sum of the transitions with the same line number contributes to this line.

fairly complex structure. At this time, fairly definite assignments have been made for the benzene spectrum: The first band corresponds to the $1e_{1g}$ MO, the second — to the $3e_{2g}$ and $1a_{2u}$ MO's, and the third — to the $3e_{1u}$, $1b_{2u}$, and $2b_{1u}$ MO's, see Ref. 10. It is likely that the compositions and energies of numerous MO's of the benzene and benzaldehyde (C_s symmetry) molecules are similar, *i.e.*, the MO's of C_6H_5CHO are close to the parent MO's of C_6H_6. As a consequence, the orbitals associated with one or another band of the benzene photoelectron spectrum should correlate with those responsible for the analogous band in the benzaldehyde spectrum. Hence, it is possible to estimate the energies of the benzaldehyde orbitals by comparison with those of benzene.

We carried out the identification of the recorded spectra of benzaldehyde. It should be noted that the MO's of a' symmetry belong to the σ-system, whereas those of a" symmetry form the π-system. According to the theoretical calculations, the three highest occupied MO's should be identified as 24a', 4a", and 3a". The first one (24a') is formed predominantly of 2p oxygen AO's (*ca.* 61 % as follows from MNDO calculations) and may be correlated with the $2b_2$ MO of formaldehyde. Its structure resembles the lone pair of an oxygen atom, while the 4a" and 3a" MO's are close to the $1e_{1g}$As and $1e_{1g}$S MO's of benzene. The oxygen $2p_\pi$ AO does not participate in 4a" MO by symmetry, but contributes a little to the 3a" MO (≈5 % according to MNDO results). The $2p_\pi$ AO of the formyl carbon atom contributes almost nothing to these MO's. The fact that the 2p AO's make the greatest contribution to the 24a' MO should be reflected in the O-Kα-spectrum, *i.e.*, the most intense high-energy band (in the transition energy scale *E*) should be assigned to the 24a' → O 1s transition. The bands S_1 and S_2 in Fig. 1 are likely a consequence of the fluorescence of the crystal-analyzer induced by the X-ray emission by the compound under study.

The MO's 4a" and 3a" consist mainly of the $2p_\pi$ AO of the carbon atom of the phenyl fragment, which is confirmed by the appearance of the *A* line in the C-Kα-spectrum which, like the line of the O-Kα-spectrum corresponding to the 24a' MO, coincides in the same scale with the first band of the photoelectron spectrum having three maxima, see Fig. 1. This coincidence takes place if the scales are connected based on the position of the C_B1s level, *i.e.*, the core level of a carbon atom belonging to the phenyl ring. This fact leads to the conclusion that the *A* line of the C-Kα-spectrum is due to transitions from MO's containing $2p_\pi$ AO's of phenyl carbon atoms.

The relative order of the three HOMO's seems still questionable since the energy spacing between them is quite small (≈1 eV according to PES[11]). A reasonable sequence of these MO's (4a", 24a', and 3a" in order of increasing ionization potential) was suggested in Ref. 11 using the data on intensity redistribution among the lines of the first PES band in C_6H_5CHO and $C_6H_5CH_2CHO$ molecules. The structure of the 4a" and 3a" MO's is also controversial. As follows from CNDO/2 and INDO calculations,[11] these MO's correlate with the $1e_{1g}$S and $1e_{1g}$As MO's of benzene, respectively, while the MNDO approach predicts the opposite situation.

The next (deeplying) orbitals of C_6H_5CHO are 2a" and 1a", the π-MO's formed by the interaction of the π-MO of the formyl fragment (the counterpart of the $1b_1$ MO of formaldehyde) with the corresponding orbital of the phenyl fragment, which can be related to the $1a_{2u}$ MO of benzene. According to MNDO data, the 23a' and 22a' MO's of the the σ-system originate from lifting the degeneracy of the $3e_{2g}$ MO of benzene in benzaldehyde ($3e_{2g} \rightarrow 23a' + 22a'$). These two MO's, as well as the 2a" and 1a" MO's, are responsible for the second band of PES, see Fig. 1. Transitions from the four MO's manifest themselves in the C-Kα-spectrum mainly as a *B* line. It is difficult to relate these orbitals to the patterns of the O-Kα-spectrum. The two maxima of this spectrum which coincide with the second PES band may be assigned to the 2a", 1a", 23a', and 22a' MO's.

In the theoretical spectrum this group of MO's appears to be close to the next two orbitals, 20a' and 19a' (the contribution of the oxygen 2p AO's to the 21a' MO is very small so it does not manifest itself in the O-Kα-spectrum). However, the comparison of benzene and benzaldehyde photoelectron spectra as well as the existence of four maxima in the second band of the latter make it possible to conclude that it is the 2a", 1a", 23a', and 22a' MO's that are responsible for the two lines of the experimental O-Kα-spectrum under study. The order of these MO's is of course questionable, since, according to the theory, the contributions of the 23a' and 22a' MO's to the O-Kα-spectrum is not large (they are not marked in Fig. 1).

The next MO's in order of increasing energy (*I* scale) are 21a' and 17a'. They belong to the molecular σ-system and correspond to the third broad band of PES, which, like the two previous ones, has a sufficiently rich structure. The composition of these MO's may be established from the orbital correlations between the C_6H_6 and C_6H_5CHO molecules. As follows from the calculations, the $3e_{1u}$As of benzene correlates with the 21a' MO of benzaldehyde, while the bonding and antibonding 20a' and 19a' MO's originate from the interaction of the benzene $3e_{1u}$S MO with the 2p AO's of the formyl fragment (their combination is likely to be most like the $1b_2$ MO of formaldehyde).

The electron density distribution in the phenyl fragment formed by the 18a' and 17a' MO's of benzaldehyde is close to that formed by the $1b_{2u}$ and $2b_{1u}$ MO's of benzene. The lowest maximum in the O-Kα-spectrum (*E*-scale), which coincides with the last band of the PES, should be assigned to electronic transitions from this group of MO's. Apparently, the dominant contribution to this maximum stems from the 18a' → O1s transition, as follows from MNDO calculations (*cf.* Figs. 1 and 2). The *C* band in the C-Kα-spectrum, which also coincides with the last PES band, corresponds to the 21a'-17a' MO's. According to the calculations, the 15a'-9a' MO's consist mainly of 2s AO's of oxygen and carbon atoms. The close resemblance of the C-Kα-spectra of benzene[15] and benzaldehyde reveals the similarity of electron density distributions in the benzene rings of these molecules. The carbon atom of the substituent has practically no effect on the shape of the C-Kα-spectrum, as is evident from the calculations.

Let us consider another feature of the X-ray spectra of benzaldehyde. As has been already mentioned, the C-Kα-spectrum is adjusted to the ionization potential scale using the energy of the C_B1s level. However, the C_O1s level, *i.e.*, the core level of the carbon atom of the substituent group, may be used for adjustment as well. Then the benzaldehyde C-Kα-spectrum appears to be shifted relative to PES (Fig.1, dotted line) so that the *A* line coincides with the second band of the latter, *B* with the third one, and the *C* line is superimposed on the weak PES band at ≈17eV. This alternative adjustment makes it possible to identify the lines of the C-Kα-spectrum that correspond to electronic transitions from MO's containing 2p AO's of carbon to the C_O1s level. Hence, matching the second PES band with the *A* line (using the adjustment at hand) enables one to assign this line to the MO's with a contribution (probably not large) from the 2p AO's of the formyl carbon atom. Indeed, as follows from the theoretical spectrum, the 2a" → C_O1s, 23a' → C_O1s, and 22a' → C_O1s transitions are reflected in this line together with the 4a" → C_B1s and 3a" → C_B1s transitions (see Fig. 1 and Table 2), although the three former transitions have very low intensity due to the small weights of the 2p AO's of the formyl carbon atom in the corresponding MO's. Analogous treatment is applicable to the *B* and *C* bands of the C-Kα-spectrum, which also contain lines arising from electron transitions to the C_O1s level.

In order to obtain a more detailed description of the π-interaction in the benzaldehyde molecule one can employ the two-orbital model, which precludes the formation of bonding and antibonding combinations of two interacting fragment orbitals. This interaction is stronger when the energies of the initial levels are closer. In our case such levels correspond to the deeplying π-MO of the phenyl ring (similar to the $1a_{2u}$ MO of benzene) and the π-MO of the formyl fragment (analog of the formaldehyde $1b_1$ orbital). Indeed, the ionization potentials of the benzene $1a_{2u}$ and formaldehyde $1b_1$ MO's are 12.38 and 14.5 eV, respectively.[10] Therefore, the counterparts of these MO's localized on the phenyl and formyl fragments of the benzaldehyde molecule should strongly interact with each other. This conjugation results in a bonding 1a" MO which is similar to the formaldehyde $1b_1$ MO and the antibonding 2a" MO correlating with the benzene $1a_{2u}$ orbital. Figure 3 shows π-MO's and the corresponding energy levels. The higher stability of the benzaldehyde 4a" and 3a" MO's with respect to the $1e_{1g}$ MO of benzene may be explained by the inductive effect of the substituent. Indeed, the phenyl carbon atoms in benzaldehyde are charged more positively than those of benzene due to the transfer of electron density toward the oxygen atom. One can easily notice this feature by comparing the energies of the C1s levels of benzene with those of the benzaldehyde molecule.[14] The dependence of the atomic charges of a molecule on the energy of the core levels determined by X-ray spectroscopy has been

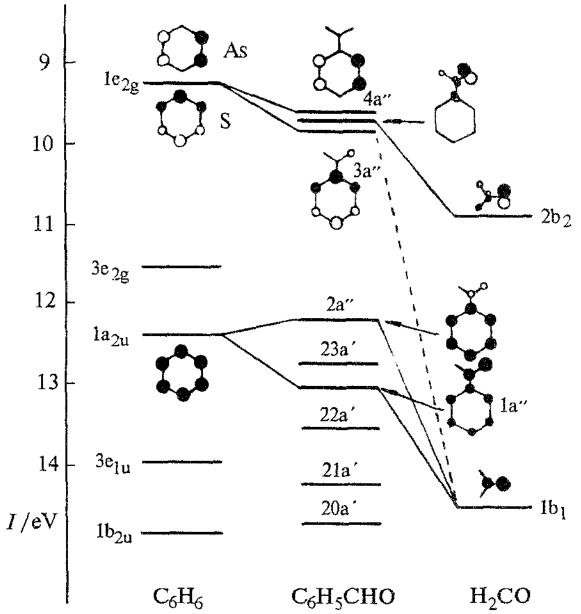

Fig. 3. Correlations of π-orbital energies. Ionization potentials are taken from Refs. 10, 11 and the structures of the MO's are determined by the MNDO method.

discussed in detail elsewhere.[16] It was established that the higher energy of the internal atomic level the more positive atomic charge corresponds. Owing to the positive charges of the phenyl carbon atoms, the 4a" and 3a" MO's are more stable than the corresponding $1e_{1g}$ orbitals of benzene. At the same time, the O1s and C_O1s levels of C_6H_5CHO molecules are less stable than their analogs in formaldehyde.[10] This means that the negative charges on the carbon and oxygen atoms of the substituent are higher than those of formaldehyde.

References

1. L. N. Mazalov and V. D. Yumatov, *Elektronnoe stroenie ekstragentov* [*Electronic Structure of Extragents*], Nauka, Novosibirsk, 1984, 26 (in Russian).
2. V. D. Yumatov, Ph. D. Chem. Thesis, Inst. Neorganicheskoi Khimii SO AN SSSR, Novosibirsk, 1976 (in Russian).
3. D. M. Barrus, R. L. Blake, H. Felthauser, E. E. Fenimore, and A. J. Burek, in *Low Energy X-Ray Diagnostics - 1981*, Eds. D. T. Attwood and B. L. Henke, American Institute of Physics, New York, 1981, 115.
4. Y.Okaya and R. Pepinsky, *Acta Crystallogr.*, 1957, **10**, 324.
5. A. Savitzky and M. J. E. Golay, *Anal. Chem.*, 1964, **36**, 1627.
6. P. M. A. Sherwood, in *Practical Surface Analysis by Auger and X-Ray Photoelectron Spectroscopy*, Eds. D. Briggs and M. P. Seach, John Wiley & Sons, Chichester, New York, 1983.
7. V. D. Yumatov, A. V. Okotrub, L. N. Mazalov, G. S. Belikova, and T. M. Okhrimenko, *Zh. Strukt. Khim.*, 1985, **26**, 59 [*J. Struct. Chem.*, 1985, **26** (Engl. Transl.)].
8. J. A. Bearden, *Rev. Mod. Phys.*, 1967, **39**, 78.
9. A. A. Bliznyuk and A. A. Voityuk, *Zh. Strukt. Khim.*, 1986, **27**, 190 [*J. Struct. Chem.*, 1986, **27** (Engl. Transl.)].
10. K. Kimura, S. Katsumata, Y. Achiba, T. Yamazaki, and S. Iwata, *Handbook of HeI Photoelectron Spectra of Fundamental Organic Molecules,* Japan Scientific Societies Press, Tokyo, Halsted Press, New York, 1981, 270 p.
11. J. W. Rabalais and R. J. Coltron, *J. Electron Spectrosc. and Relat. Phenom.*, 1972/73, **1**, 83.
12. L. Klasnic, B. Kovac, and H. Gusten, *Pure and Appl. Chem.*, 1983, **55**, 289.
13. J. P. Tolic, B. Kovac, L. Klasnic, S. M. Shevchenko, and M. C. McGlynn, *Int. J. Quantum. Chem., Symp.*, 1990, **24**, 789.
14. W. L. Jolly, K. D. Bomben, and C. J. Eyermann, *Atom. Data and Nucl. Data Tables*, 1984, **31**, 433.
15. G. G. Furin, A. V. Zibarev, L. N. Mazalov, and V. D. Yumatov, *Elektronnaya struktura ftororganicheskih soedinenii* [*Electronic Structure of Fluoroorganic Compounds*], Nauka, Novosibirsk, 1988, 210 p. (in Russian).
16. V. I. Nefedov, *Rentgenoelektronnaya spektroskopiya khimicheskikh soedinenii* [*X-Ray Electron Spectroscopy of Chemical Compounds*], Khimiya, Moscow, 1984, 43 (in Russian).

Received March 13, 1993,
in revised form February 15, 1994