Electronic structure of monosubstituted benzenes and X-ray emission spectroscopy

3.* Fluorobenzene

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The electronic structure of fluorobenzene was investigated by X-ray emission spectroscopy (using the F-Kα- and C-Kα-spectra) and quantum-chemical MNDO calculations. Molecular orbitals of fluorobenzene were compared with those of benzene and hydrogen fluoride. The p_π—p_π-interaction between the phenyl ring and the fluorine atom in the fluorobenzene molecule is weak for both the outer and inner π levels.

Key words: X-ray emission; F-Kα spectra and C-Kα spectra; MNDO; fluorobenzene.

Since the first ionization potential of hydrogen fluoride is equal to 16.05 eV,[2] one can expect that in the case of fluorobenzene the p_π—p_π-interaction between the substituent and the phenyl ring will be weak for both the higher occupied orbitals and low-lying π orbitals. In this work, the electronic structure of the fluorobenzene molecule was studied by the ultrasoft X-ray spectroscopy.

Experimental

Experimental procedure for obtaining C-Kα- [3,4] and F-Kα-spectra[3,5] has been described previously. The MNDO calculations of the theoretical C-Kα spectrum of fluorobenzene have been reported in Ref. 4. The F-Kα spectrum was constructed analogously using the experimentally established FWHM value of ~0.8 eV for the individual spectral line. In this case, the line in the X-ray spectrum corresponding to the 1π molecular orbital (MO) of the F-Kα spectrum of the HF molecule was used.[3,5,6]

Results and Discussion

As in the previous works,[1,4] we will consider the electronic structure of the fluorobenzene molecule by analyzing correlations of its MOs with the orbitals of benzene and HF molecules (the point symmetry groups D_{6h} and $C_{\infty v}$, respectively).

The electronic structure of the fluorobenzene molecule has been investigated by quantum-chemical methods,[2,6—16] He(I)[2,7,8,11,17] and He(II)-photoelectron spectroscopy (PES),[11,12] Penning ionization electron spectroscopy,[14] by studying angular dependences of the relative intensities of individual lines in the photoelectron spectra,[18] and X-ray photoelectron spectroscopy (XPS).[19] Theoretical X-ray emission spectra were simulated by using the CNDO/2 calculations.[9] Transitions from the same MO to the C1s levels of carbon atoms occupying different (nonequivalent) positions with respect to the substituent have not been taken into account to construct the C-Kα-spectrum. This drawback was removed in the MNDO calculations of the spectra[6] where experimental data on the energies of inner levels were taken into account; however, only spectral patterns were described[6,16] without specifying the contributions of individual atomic orbitals (AOs) to the MOs. One of the first F-Kα-spectra of the solid fluorobenzene was obtained[9] by using an analyzer crystal as dispersive element for spectral dispersion of X-ray radiation of the sample. We have also reported the F-Kα spectra of fluorobenzene in both the solid and gaseous states.[3,6,20,21] The X-ray spectra of fluorobenzene in the solid phase were investigated[22] on a spectrometer with a diffraction grating (with synchrotron radiation as the excitation source). The resolution of the F-Kα-spectrum reported in Ref. 22 was poorer than that we had obtained, whereas the C-Kα-spectra were of nearly the same resolution (see Ref. 3). The X-ray spectra of fluorobenzene were not analyzed.

The X-ray spectra of the C_6H_5F molecule are shown in Fig. 1. They were reduced to a unified energy scale of ionization potentials (*I*) using experimental data on the

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* For Part 2, see Ref. 1.

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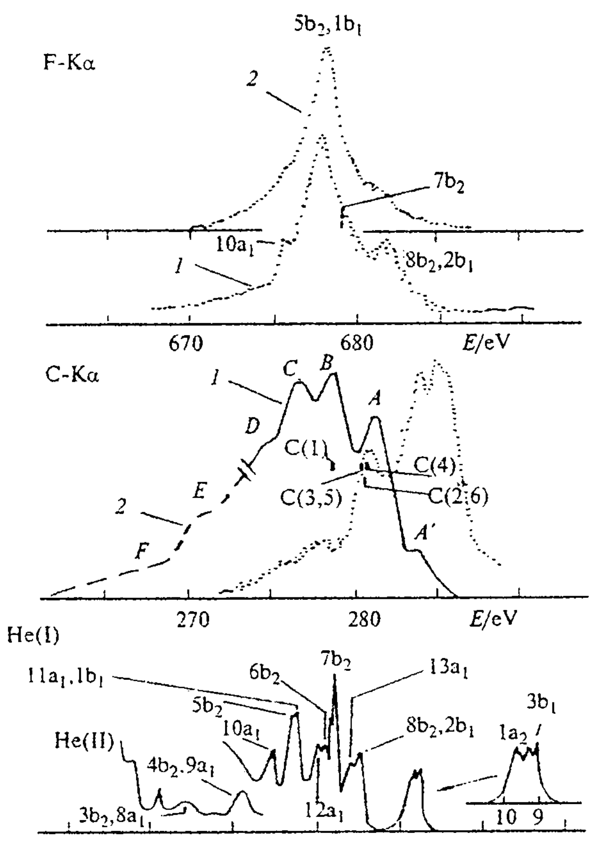

Fig. 1. X-ray spectra of C_6H_5F in the gas (*1*) and solid (*2*) phase: dotted, solid, and dashed lines correspond to experimental data, the C-Kα spectrum smoothed and corrected taking into account the efficiency of the analyzer crystal (see Ref. 3), and the low-energy region of the C-Kα spectrum (see Ref. 22), respectively. The He(I)[2] and He(II)[12] photoelectron spectra reported previously are also presented. In this experiment, the C-Kα spectra for the gas and solid phase nearly coincide.

positions of the inner energy levels.[19] The low-energy region (the *E* scale of the transition energy) of the C-Kα spectrum of fluorobenzene in the solid state,[22] inaccessible when using our procedure because of low efficiency of the analyzer crystal in this spectral region, is also reproduced in Fig. 1. In this work, as well as in the previous works,[1,4] differences in the charges of carbon atoms (caused by their nonequivalent positions with respect to the fluorine atom) were taken into account in the analysis of the C-Kα spectrum. This nonequivalence manifests itself in different energies of the C1s levels of different carbon atoms in the phenyl ring.[19] Since published data on the energies of the inner levels for the same atoms are slightly different, we averaged these data. The C-Kα spectrum was referenced to the scale of ionization potentials using the C(1)1s level. The theoretical spectra shown in Fig. 2 were also matched using the energy of this level. However, other C1s levels can also be used. In Fig. 1, the position of the *B* maximum of the C-Kα spectrum, obtained by referencing with the use of different C1s levels of fluorobenzene, corresponds to short vertical lines.

The fluorobenzene MOs with the a_2 and b_1 symmetry belong to the $\pi_\perp$-system (they consist of 2p-orbitals perpendicular to the molecular plane), while MOs with the a_1 and b_2 symmetry are composed of the 2s AOs and 2p AOs lying in the molecular plane. The character of the interaction between the C(1) atom and the fluorine atom allows one to assign MOs with the a_1 and b_2 symmetry to the orbitals of the σ-bond and the π-bond between these atoms in the molecular plane (or $\pi_\parallel$-bond), respectively.

The first three broad bands with a finer structure in the PES of fluorobenzene lie in the same energy intervals as those in the PES of benzene.[2] The X-ray spectra of these molecules are also similar.[3,6,22]

According to quantum-chemical calculations, the $3b_1$ orbital is the highest occupied MO (HOMO) of fluorobenzene. It consists mainly of carbon $2p_\perp$ AOs and correlates with the $1e_{1g}S$ MO of benzene. The $2p_\perp$ AO of fluorine makes a small contribution to this orbital (~7% according to the MNDO calculations, see Figs. 2 and 3), which is due to a great difference in the energies

Table 1. Theoretical C-Kα spectrum of fluorobenzene

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

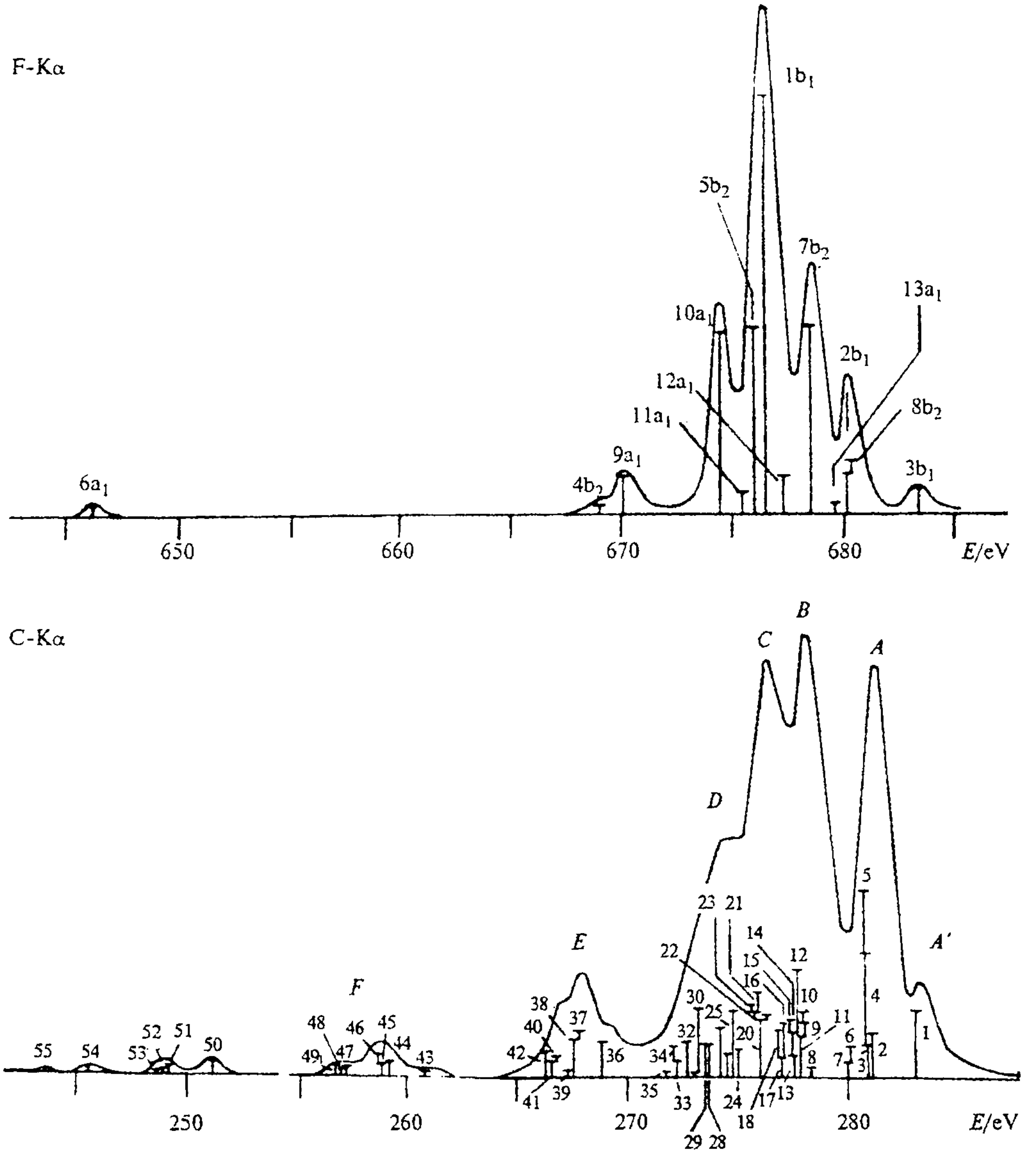

Fig. 2. Theoretical X-ray spectra of C_6H_5F (see Table 1).

between the $1e_{1g}S$ MO of benzene and the 1π MO of hydrogen fluoride (~6.8 eV according to the PES data,[2] see Fig. 3).

The line in the PES of fluorobenzene corresponding to the HOMO matches the *A'* line in the C-Kα spectrum when the spectra are referenced using the C(1)1s level, thus confirming that this line is due to the $3b_1 \to C(1)1s$ transition (see Figs. 1 and 2). Referencing with the use of other inner levels (namely, the C(2,6)1s, C(3,5)1s, and C(4)1s levels) matches this line in the PES to the *A* line of the C-Kα spectrum. Theoretical data also indicate that transitions from the $3b_1$ MO to the above-mentioned inner levels of carbon atoms participate in the formation of the *A* line. It is difficult to find an exact analog of the $3b_1$ MO in the F-Kα spectrum because of the small contribution of the $F2p_\perp$ AO. The theoretical spectrum shown in Fig. 2 gives an indication to the ratio between the intensity of the line corresponding to the given MO and intensities of other lines.

The $1a_2$ orbital (the closest to the HOMO) correlates with the $1e_{1g}As$ MO of the benzene molecule (see Fig. 3); according to the symmetry rules, it cannot interact with MOs of the substituent. For this reason, it should energetically correspond to the $1e_{1g}$ HOMO of benzene; however, it becomes by ~0.56 eV more stable than the HOMO.[2] We also observed a similar effect for other benzene derivatives;[1,4] this was associated with the

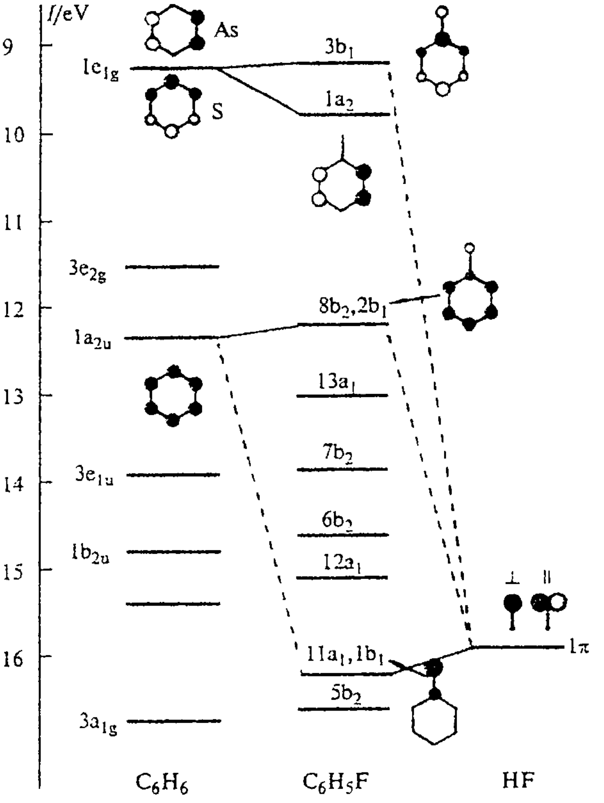

Fig. 3. Correlation of the $\pi_\perp$ molecular orbitals (using ionization potentials reported previously;[2] the structure of MOs was obtained from the MNDO calculations).

inductive effect of the substituent rather than with the result of the covalent interaction between the MOs of the phenyl ring and the substituent. As was already mentioned above, the $1a_2$ orbital MO of fluorobenzene is composed of the C(2,6)$2p_\perp$ and C(3,5)$2p_\perp$ AOs, and transitions from this orbital to the 1s levels of these atoms are only revealed in the C-Kα spectrum. According to calculations, they participate in the formation of the *A* line in this spectrum (see Fig. 2). Experimental data show that when the C(2,6)1s and C(3,5)1s levels of fluorobenzene are used for referencing, the PES line corresponding to the $1a_2$ MO matches the *A* line of the C-Kα spectrum thus confirming theoretical consideration.

The similarity between the photoelectron spectra and particularly between the C-Kα spectra of fluorobenzene and those of benzene suggest that the first maximum of the PES and the *A* maximum of the C-Kα spectrum of C_6H_5F are composed of MOs, whose structures are similar to those of the orbitals that give rise to analogous maxima of benzene spectra.[2,3,6,22] In fact, these lines in the benzene spectra correspond to the $1e_{1g}$ MO. The molecular symmetry changes ($D_{6h} \rightarrow C_{2v}$) on going from benzene to fluorobenzene result in the splitting of this orbital: $1e_{1g} \rightarrow 1e_{1g}S + 1e_{1g}As \rightarrow 3b_1 + 1a_2$. Hence, it should be expected that the analogous band in the PES of fluorobenzene will correspond to two MOs ($3b_1$ and $1a_2$), whereas the *A* line of its C-Kα spectrum (similar to the analogous line of the X-ray spectrum of benzene) will be composed of the totality of transitions from the $3b_1$ and $1a_2$ MOs to the C1s levels.

The second broad line (see Fig. 1) in the PES corresponds to the group of $8b_2$, $2b_1$ and $13a_1$ orbitals. The $8b_2$ MO is composed of two orbitals: an orbital of the phenyl ring similar to the $3e_{2g}$As MO of benzene and an orbital of the substituent that correlates with the $1\pi_\parallel$ MO of hydrogen fluoride (see Fig. 3). The bond between the C(1) and F atoms has a $\pi_\parallel$-antibonding character.[2,7,14] According to the fragment analysis,[15] the contribution of the phenyl ring MO to this MO is equal to ~88%.

According to quantum-chemical calculations, the $2b_1$ MO belonging to the system of the $\pi_\perp$-bonds is composed of a phenyl ring orbital similar to the benzene $1a_{2u}$ MO and of the fluorine F$2p_\perp$ AO that is correlated with the $1\pi_\perp$ MO of hydrogen fluoride (see Fig. 3). According to the MNDO calculations and the fragment analysis,[15] the contribution of the carbon AO to this orbital is equal to ~9.7% and 11%, respectively.

The structure of the $13a_1$ orbital (see Refs. 2, 7, 11, and 14) is close to those of the $3e_{2g}$S MO of the benzene molecule and the 3σ MO of hydrogen fluoride. According to the symmetry rules, the electrons of this level should form the σ-bond between the phenyl ring and the fluorine atom. However, according to *ab initio*,[2,14] CNDO/2,[7] and MNDO calculations, a node of the wave function is on the C(1) atom (*i.e.*, the electron density is equal to zero). For this reason, the above interaction is improbable. The contribution from the F$2p_\sigma$ AO[7,14] to this MO is small, while its calculated value is equal to zero.[2] Based on the fragment analysis,[15] the structure of the $13a_1$ MO can be represented as a linear combination of the orbitals of the phenyl ring similar to the $3e_{1g}$S and the $3e_{2u}$S MOs of the benzene molecule with contributions of 9 and 87%, respectively. Therein lies a contradiction between Ref. 11, in which the $13a_1$ MO of fluorobenzene was correlated only with the $3e_{2g}$S MO of benzene, and Ref. 15, where the same fluorobenzene orbital was correlated with both the $3e_{2g}$S and the $3e_{1u}$S MOs of benzene. It is their antibonding linear combination that produces the zero electron density on the C(1) atom.

As was already mentioned, the $8b_2$, $2b_1$, and $13a_1$ MOs discussed above constitute the second weakly split band of the PES, which matches the first line of the F-Kα spectrum (see Fig. 1). The theoretical spectrum also contains one line corresponding to these MOs, the contribution of the F$2p_\sigma$ AO to the $13a_1$ MO being the smallest in this group (see Fig. 2). The relative intensity of the line under consideration in the experimental spectrum is somewhat higher than that in the theoretical spectrum; therefore, this line cannot be assigned only to the transition from this MO to the F1s level. Actually, a line due to the X-ray transitions of the doubly ionized molecule (a multiple ionization satellite) is observed in the same region (~681 eV).[23] This satellite is clearly seen[3,5,6] in the spectrum of the HF molecule. At the same time, an increase in the intensity of this band is observed on going from the solid fluorobenzene to the gaseous fluorobenzene (see Fig. 1); this fact allows one to consider this band as a superposition of two lines. Actually, we obtained the X-ray spectrum of solid C_6F_6 by the photoionization technique[24] (see Ref. 3) using the Cu-L$\alpha_{1,2}$ line with an energy of 929.7 eV, which is appreciably lower than the energy of the electron beam in the studies of the gas phase. The number of doubly ionized molecules, for which the X-ray transitions appear as high-energy satellites of the diagram lines (the *E* scale), increases as the energy of excitation of particles increases.[23] An increase in the intensity of the analogous satellite in the F-Kα spectrum of LiF with increasing energy of photons has been observed (see, for instance, Ref. 25). The same behavior of the multiple ionization satellite is characteristic of the O-Kα spectrum of water in the gas phase.[3] In this case the energy and hence the intensity of the satellite line in the first case were higher than those in the second case.

When the C(1)1s level is used as a reference, the PES band corresponding to the $8b_2$, $2b_1$, and $13a_1$ MOs matches the *A* line of the C-Kα spectrum. Therefore, one can suggest that this line is formed as a result of transitions from the above orbitals to the C(1)1s level. According to the theoretical calculation, the contribution of the $8b_2 \rightarrow$C(1)1s and $2b_1 \rightarrow$C(1)1s transitions is the largest. When other C1s levels are used as references, the PES band under consideration matches the *B* maximum of the C-Kα spectrum. The MNDO calculation indicate that this band is mainly composed of the lines that appear as a result of transitions from the $8b_2$, $2b_1$, and $13a_1$ MOs to these levels. Based on the similarity of the PES and the C-Kα spectra of benzene and fluorobenzene, one can trace how the MOs correlate. The second band in the benzene spectra consists of the $3e_{2g}$ and $1a_{2u}$ MOs.[2,3,6,22] On going from benzene to fluorobenzene, we get $3e_{2g} \rightarrow 3e_{2g}As + 3e_{2g}S \rightarrow 8b_2 + 13a_1$ and $1a_{2u} \rightarrow 2b_1$. Thus, one should expect that the second band of the fluorobenzene PES would correspond to the $8b_2$, $2b_1$, and $13a_1$ MOs, while the corresponding line in the C-Kα-spectrum (line *B*) would appear as a result of transitions from these MOs.

A group consisting of the $7b_2$, $6b_2$, and $12a_1$ MOs corresponds to the third band of the PES of fluorobenzene (see Fig. 1). The $7b_2$ orbital should be considered in combination with the $5b_2$ MO. These orbitals have closely related structures and are formed due to the interaction of the phenyl ring orbital similar to the $1b_{2u}$ MO of benzene and the fluorine AO similar to the $2\pi_{\parallel}$ MO of hydrogen fluoride. In this case, the $7b_2$ MO is an antibonding orbital, while the $5b_2$ MO is a bonding orbital with respect to the $\pi_{\parallel}$-bond between the C(1) and F atoms. The contributions of the phenyl ring MOs to the $7b_2$ and $5b_2$ MOs are equal to 46 and 52%, respectively.[15] Unlike other calculations, the zero electron density on the C(1) atom was obtained in Ref. 7 for the $7b_2$ MO.

The $6b_2$ MO can be correlated with the phenyl ring orbital, which, in turn, correlates with the $3e_{1u}As$ MO of benzene. According to the results of the fragment analysis,[15] the contribution of the latter orbital is equal to 99%. Unlike the results reported in Refs. 7 and 14, the *ab initio*[2] and MNDO (this work) calculations showed that the contribution of the F2$p_{\parallel}$ AO to this MO is close to zero. This orbital is antibonding with respect to the bond between the fragments.

The $12a_1$ MO can be correlated[2,7,14] with the phenyl ring orbital similar to the $3e_{1u}S$ MO of benzene and with the fluorine AO, which, in turn, correlates with the 3σ MO of hydrogen fluoride. The calculations show that this orbital is a bonding orbital with respect to the C(1) and F atoms. According to the results of the fragment analysis,[15] the contribution of the phenyl ring MO, which correlates with the $3e_{1u}S$ MO of benzene, to the $12a_1$ MO of fluorobenzene is equal to 7% (as was already mentioned, the $3e_{1u}S$ MO is closer to the $13a_1$ MO).

As can be seen in Fig. 2, the main contribution to the formation of the F-Kα spectrum of the fluorobenzene molecule comes from the $7b_2$ MO. A comparison of the PES and the F-Kα spectra and the theoretical consideration lead to the same result: the PES line corresponding to the $7b_2$ MO matches the high-energy region (the *E* scale) of the predominant line of the F-Kα spectrum (see Fig. 1).

The fact that the considered group of MOs corresponding to the third broad PES band matches the *B* maximum of the C-Kα spectrum (reference using the C(1)1s level) shows that transitions from the $7b_2$, $6b_2$, and $12a_1$ MOs to the C(1)1s level can participate in the formation of the C-Kα spectrum. However, according to the MNDO calculations, only the intensity of the $7b_2 \rightarrow$ C(1)1s transition is fairly high, whereas the intensities of transitions from the $6b_2$ and $13a_1$ MOs are very low. When other C1s levels are used as references, this PES band matches the *C* line of the C-Kα spectrum. Hence, this band is mainly formed by transitions from the $7b_2$, $6b_2$, and $13a_1$ MOs to the 1s levels of the carbon atoms not bonded to the fluorine atoms, which is confirmed by the MNDO calculation (see Fig. 2).

Let us consider the correlation of this group of MOs from the viewpoint of the similarity of the PES and the C-Kα spectra of benzene and fluorobenzene. The third band of the benzene PES is composed of the lines corresponding to the $3e_{1u}$, $1b_{2u}$, and $2b_{1u}$ MOs.[2] The third band of the C-Kα spectrum has an analogous structure.[3,6,22] On going from benzene to fluorobenzene, we get the following correlations: $3e_{1u} \rightarrow 3e_{1u}As + 3e_{1u}S \rightarrow 6b_2 + 12a_1$ and $1b_{2u} \rightarrow 7b_2$. Thus, the third band of the PES of fluorobenzene can be correlated with the $7b_2$, $6b_2$, and $12a_1$ MOs, while the *C* line of the C-Kα spectrum will be formed by transitions from these orbitals to the C1s levels.

The fourth band of fluorobenzene PES corresponds to the next group of MOs (the $11a_1$, $1b_1$, and $5b_2$ orbitals) close to the group of MOs discussed above (see Fig. 1). The $11a_1$ MO can be correlated with both the $2b_{1u}$ and $3a_{1g}$ MOs of benzene. According to the results of the fragment analysis,[15] the phenyl ring MO that correlates with the $3a_{1g}$ MO contributes 80% to the $11a_1$ orbital; however, other published data[11] indicate that the $11a_1$ orbital only correlates with the $2b_{1u}$ MO of benzene. The $11a_1$ MO of fluorobenzene is an orbital of the σ-bond, and the contribution of the $F2p_\sigma$-AO to this orbital is small (see, for instance, Fig. 2). According to the calculation,[2] a node of the wave function is on the C(1) atom; however, only nodes on the C(3, 5) atoms have been obtained.[7,14]

The $1b_1$ MO is the bonding orbital of the $\pi_\perp$-system. It consists mainly of the $F2p_\perp$ AO and correlates with the $\pi_\perp$ MO of hydrogen fluoride (see Fig. 3). According to the MNDO data, the contributions of the $F2p_\perp$ and the $C(1)2p_\perp$ AOs to this orbital are equal to ~80% and ~15%, respectively. The contributions of the $2p_\perp$ AOs of remaining carbon atoms do not exceed 2%. The calculations (see Fig. 2) allow one to conclude that the dominant maximum of the F-Kα spectrum is formed by the lines corresponding to the $1b_1$ and $5b_2$ MOs, which is confirmed experimentally (the corresponding PES band when referenced matches this maximum).

When the C-Kα spectrum of fluorobenzene is referenced to its photoelectron spectrum using the C(1)1s level, the PES band corresponding to the group of MOs under consideration matches the *C* line of the C-Kα spectrum. Hence, transitions from the $11a_1$, $1b_1$, and $5b_2$ MOs to the C(1)1s level can be revealed among other transitions participating in the formation of this line. However, according to the calculations (see Fig. 2), the intensities of only two transitions (from the $1b_1$ and $5b_2$ MOs) differ from zero. When other C1s levels are used as references, the fourth PES band matches the *D* maximum that, according to calculations, is formed by transitions from the $11a_1$, $1b_1$, and $5b_2$ MOs.

Analysis of the structures of the fourth broad PES band and the corresponding *D* line of the C-Kα spectrum of fluorobenzene (based on their similarity to analogous components in the benzene spectra) gives the following results. The $3a_{1g}$ MO corresponds to analogous lines in the PES and in the C-Kα spectrum of benzene. As was already mentioned above, the $3a_{1g}$ MO can be correlated only with the $11a_1$ MO of the fluorobenzene molecule. However, the $1b_1$ and $5b_2$ MOs that correlate with other benzene orbitals and appear in this energy region as a result of the interaction between the phenyl ring and substituent also participate in the formation of the corresponding lines in the C-Kα spectrum of fluorobenzene.

The $10a_1$ MO of fluorobenzene is composed of the phenyl ring orbital that correlates with the benzene $3a_{1g}$ MO and of the MO of the substituent that correlates with the 3σ MO of the HF molecule. The quantum-chemical calculations show that this orbital is a bonding σ-orbital (with respect to the C(1) and F atoms) with a node on the C(4) atom.[2,7,14] According to the results of the fragment analysis,[15] the contribution of benzene orbital to the $10a_1$ MO is equal to 18%. When the spectra are referenced, the PES line corresponding to the $10a_1$ MO matches the low-energy (the *E* scale) "swelling" of the dominant line of the F-Kα spectrum and the *D* line of the C-Kα spectrum (see Fig. 1). According to the MNDO calculations, the *D* line is formed by all transitions from this MO to the C1s levels.

Up to this point the similarity between the C-Kα spectra of fluorobenzene and the analogous benzene spectrum served as the basis for interpreting the spectra of C_6H_5F. However, the F-Kα spectra of fluorobenzene and hydrogen fluoride are also similar to some extent (see Refs. 3, 5, and 6). On going from $HF \rightarrow C_6H_5F$ (change in the symmetry $C_{\infty v} \rightarrow C_{2v}$), we get the following correlation of the orbitals: $1\pi \rightarrow 1\pi_\perp + 1\pi_\parallel \rightarrow 1b_1 + 7b_2 + 5b_2$ and $3\sigma \rightarrow 10a_1$. These four MOs mostly contribute to the formation of F-Kα spectrum of fluorobenzene. The most intense line in the spectrum of hydrogen fluoride corresponds to the 1π MO.[3,5,6] An analogous line in the F-Kα spectrum of fluorobenzene corresponds to the $7b_2$, $1b_1$, and $5b_2$ MOs (see Fig. 2); their correlations with the 1π MO of hydrogen fluoride were discussed above. The second (the less intense) line of the F-Kα spectrum of the HF molecule is characterized by a lower transition energy and might correspond to the 3σ MO.[3,5,6] Its analog in the F-Kα spectrum of fluorobenzene is a line corresponding to the $10a_1$ MO (see Fig. 2), whose electrons participate in the σ-interaction between the phenyl ring and the F atom.

The $4b_2$ and $9a_1$ MOs are identical to the phenyl ring orbitals that correlate with the $2e_{2g}$ MOs of benzene. On going from benzene to fluorobenzene we get $2e_{2g} \rightarrow 2e_{2g}As + 2e_{2g}S \rightarrow 4b_2 + 9a_1$. According to the fragment analysis,[15] the contributions of the phenyl ring MOs (similar to the benzene orbitals mentioned above) to the $4b_2$ and $9a_1$ MOs of fluorobenzene are equal to 97 and 87%, respectively. The PES line corresponding to these orbitals matches the small low-energy (the *E* scale) "swelling" of the X-ray spectrum of C_6F_6 (see Fig. 1) when the X-ray spectrum is referenced to the PES. This fact allows one to conclude that the contribution of the F2p-AO to these MOs is small. Using different C1s levels for referencing the spectra, we can also conclude that the *E* band is mainly formed by transitions from the $9a_1$ and $4b_2$ MOs to the C1s levels and pertinent lines in the PES and in the C-Kα spectrum of benzene correspond to the $2e_{2g}$ MO.

The $3b_2$ and $8a_1$ MOs of fluorobenzene correlate with the $2e_{1u}$ MO of benzene:

$2e_{1u} \rightarrow 2e_{1u}As + 2e_{1u}S \rightarrow 3b_2 + 8a_1$. According to the fragment analysis,[15] the contributions of the phenyl substituent, whose MOs correlate with the benzene MOs indicated above, are equal to 100 and 88%, respectively. Consideration of the mutually referenced PES and F-Kα spectrum shows (see Fig. 1) that the $F2p_{\parallel}$ AO make small contributions to these MOs. Consideration of the mutually referenced PES and C-Kα spectrum indicates that transitions from the $3b_2$ and $8a_1$ MOs participate mainly in the formation of the *F* "swelling" of the C-Kα spectrum. In the theoretical spectra, individual maxima correspond to these transitions.

The lowest-lying valent MOs of fluorobenzene ($7a_1$ and $6a_1$) correlate with the $2a_{1g}$ MOs of benzene and with the 2σ MO of the HF molecule. They consist mainly of the 2s AOs of carbon and fluorine. According to the fragment analysis,[15] the phenyl ring MOs similar to the $2a_{1g}$ MO of benzene make contributions of 77% and 23% to the $7a_1$ and $6a_1$ MOs of fluorobenzene, respectively. The $C2p_{\sigma}$ and $F2p_{\sigma}$ AOs contribute insignificantly to the $7a_1$ and $6a_1$ MOs and are not revealed in the corresponding spectra. The lower-lying orbitals are atomic orbitals: $5a_1$(C(4)1s), $4a_1$,$2b_2$(C(3, 5)1s), $3a_1$,$1b_2$(C(2, 6)1s), $2a_1$(C(1)1s), and $1a_1$(F1s). Their energies were determined[19] by the XPS technique.

In conclusion, let us analyze the $\pi_{\perp}$-system of the fluorobenzene molecule. It consists of four MOs: $3b_1$, $1a_2$, $2b_1$, and $1b_1$ (see Fig. 3). As was already mentioned above, the contribution of $F2p_{\perp}$ AO to the first MO is small. Therefore, the $\pi_{\perp}$-interaction in the HOMO is weak. The electron density at the $1a_2$ MO is only localized on the C atoms. Since the contribution of the $F2p_{\perp}$ AO to the $2b_1$ MO is also small, the $\pi_{\perp}$-interaction with this orbital is also weak. The $F2p_{\perp}$ AO contributes mainly to the lowest-lying orbital of the $\pi_{\perp}$-system, namely, to the $1b_1$ MO orbital. For this reason, the mesomeric effect in the fluorobenzene molecule is insignificant even for the inner $\pi_{\perp}$ orbitals. This conclusion is confirmed by the X-ray spectral experiment. Actually, as can be seen from Fig. 1, referencing the X-ray spectra with the use of the scale of ionization potentials shows that the lines of the F-Kα spectrum correspond to the orbitals with relatively high bonding energies of the electrons, *i.e.*, that the F2p-electron density is mainly distributed over the low-lying valent orbitals.

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