Journal of Fluorine Chemistry, 35 (1987) 627–641

Received July 30, 1986; accepted. December 14, 1986

PHOTOELECTRON SPECTROSCOPY OF MONOSUBSTITUTED BENZENES AND 4H-TETRAFLUOROBENZENES : THE EFFECTS OF INTRODUCTION OF FLUORINE IN THE PARA-POSITION AND SYMMETRY OF HIGHEST OCCUPIED π-LEVELS

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SUMMARY

Experimental determination of symmetry of the highest occupied molecular π-levels can be realized by means of UV photoelectron spectroscopy in the cases of the benzene monofunctional derivatives C_6H_5X and 4-HC_6F_4X ($X = NH_2$, NO_2, NSO, NO), possessing C_{2v} or pseudo-C_{2v} symmetry, and for the compounds obtained by introduction of fluorine substituents into the ring para-position 4-FC_6H_4X and C_6F_5X. MNDO calculations in accordance with the model, derived earlier by second-order perturbation theory, show the ionization potential of an a_2 (π) MO to be systematically more sensitive to fluorine introduction than that of a b_1 (π) MO.

INTRODUCTION

Formulation of the problem

Frontier orbital theory connects reactivities of molecules with the energies of highest occupied and lowest virtual MO s, the squares of the coefficients at the AO s of atomic reaction centres in these MO s and the charges on these atoms [1]. Enumerated para-

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0022-1139/87/$3.50

meters of molecular electronic structure can be obtain both theoretically - by means of computational methods of quantum chemistry - and experimentally - by means of UV photoelectron (UPS), X-ray photoelectron and X-ray spectroscopy [2].

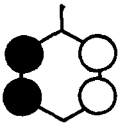
Quantum chemical calculations, especially semiempirical, are more readily available, but often lead to wrong orbital ordering [2]. The aniline molecule can be considered as an example, since two nonempirical calculations predict the different symmetry of its HOMO [3,4]. Hence, additional criteria are greatly desirable.

These are available. For example, the analysis of the vibronic structure of UPS bands and comparison of photoelectron and X-ray emission spectra are very useful [2]. Unfortunately, the vibronic structures of UPS bands of sufficiently complex molecules, as a rule, are not fully resolved, and correct comparison of X-ray and photoelectron spectra is not always possible (the example is again aniline, see [5] and below). The data of [6] on fluorobenzene show the anisotropy parameter, characterizing the angular distribution of photoelectrons, to have different values for the two first UPS bands (b_1 and a_2 MO s), being the experimental criterion of HOMO symmetry. However, systematic investigations in that field have probably not been carried out.

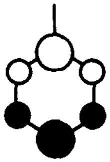
The purpose of the present work is consideration of the possibility of experimental determination of HOMO symmetry by means of UPS in a series of benzene monofunctional derivatives, possessing C_{2v} or pseudo-C_{2v} symmetry, and in compounds obtained by introduction of a fluorine substituent into the ring para-position.

Formulation and analysis of the models

The highest occupied level of a benzene molecule is doubly degenerate and corresponds to π-MO s of e_{1g}-symmetry. On passing to monofunctional derivatives C_6H_5X, molecular symmetry reduces to C_{2v} ($X = NO_2$) [7,8] or C_s ($X = NH_2$, NO, NSO) [4,9-11] and MO's e_{1g} transform into a_2 (π) and b_1 (π) orbitals (in terms of irreducible representations of C_{2v} group). These orbitals differ from each other, in particular, by the contribution of 2p-AO s of the ipso- and para-carbon atoms, being equal to zero to a_2 MO. In the cases when symmetry of monosubstituted molecules is reduced to C_s, according to non-empirical calculations [3] the symmetry of π-MO s within the ring remains high and these MO s may be classified in terms



a_2



b_1

of irreducible representations of C_{2v} group (pseudo-C_{2v} symmetry). The illustration of it again is the aniline molecule. Since the amino group hydrogen atoms do not lie in the plane of the C_6H_5N fragment [4,9], the symmetry of the molecule is C_s. However, π-MOs are formed by 2p-AOs of the carbon and nitrogen atoms of that fragment, which in good approximation possesses C_{2v} symmetry [4,9].

In second-order perturbation theory the change in one-electron energy of an arene molecule π-MO, $\Delta\varepsilon$, caused by introduction of a substituent, may be described [12-14] by the type (1) equation, where $\Delta\alpha$ and γ are inductive and mesomeric perturbation parameters, respectively; c are coefficients at 2p-AOs of carbon atoms in ipso-, ortho- and ortho'-positions in given MO; factor m is the measure of inductive effect reduction on passing from ipso- to ortho-positions (usually accepted equal to 0.33 [12,15]).

$$\Delta\varepsilon = (c_i^2 + m\cdot c_o^2 + m\cdot c_{o'}^2)\Delta\alpha + c_i^2\gamma \qquad (1)$$

$$\Delta\varepsilon = (c_i^2 + m\cdot c_o^2 + m\cdot c_{o'}^2)\Delta\alpha \qquad (2)$$

$$\Delta\varepsilon = c_i^2\,\Delta\alpha \qquad (3)$$

It has been shown that, in such models, in the case of fluorine, mesomeric and inductive terms partly compensate each other [14]. However, in the case of fluorine introduced into the ring para-position of a benzene monofunctional derivative, possessing C_{2v} or pseudo-C_{2v} symmetry, such compensation is possible only for a b_1 orbital and is not possible for an a_2 orbital. As a result, values of $\Delta\varepsilon$ must be different for these MOs and for an a_2 orbital must be greater than for b_1. Koopmans' theorem in SCF MO theory connects one-electron energies of canonical orbitals with values of appropriate vertical IPs ($\varepsilon_j = -IP_j$) [2]. Hence, if the compensational model (1) is true, for compounds under consideration, values of Δ IP's, caused by introduction of a fluorine substituent into the ring para-position, have diagnostic character, and make it possible to distinguish the highest b_1 (π) MO from an a_2 (π) MO.

On the other hand there is a widespread conclusion that the fluorine 2p-AO does not overlap with arene highest occupied π-MO s owing to the great energy gap and the π - fluoro effect well-known in UPS has electrostatic nature [16].

The comparison of available UV photoelectron, FK_α and CK_α spectra of benzene fluoro derivatives does not allow us to reach unambiguous conclusions about the fluorine 2p-AO contribution to the highest occupied π - MO s; it is only obvious that its possible value cannot be greater of a few percent [17,18].

Under conditions when the fluorine 2p-AO does not contribute to the highest occupied π - MO s [16], the mesomeric term of equation (1) is equal to zero and it is transformed into equation (2). Accordingly [19], on passing from benzene to fluorobenzene the change in 1s- electron binding energy of a carbon ortho-atom is about 15 percent of that of an ipso-atom. These changes in binding energies are caused by the changes in electrostatic potentials at given carbon atom nuclei, but in the simplest approximation they can be taken as caused by the changes in atomic charges [20]. This makes it possible to simplify the equation (2) additionally, namely, to consider the factor $\underline{m}$ as being very small and, by neglect of corresponding terms, to transform equation (2) into equation (3). In model (3) the diagnostic character of Δ IP s, caused by introduction of a fluorine substituent into the ring, is retained, but behaviour of a_2 and b_1 orbitals is opposite to that in model (1), since in model (3) Δ IP for an a_2 MO must be greater than for a b_1 MO.

RESULTS AND DISCUSSION

Table 1 presents vertical IP s in pairs of compounds C_6H_5X-4-FC_6H_4X and 4-HC_6F_4X- C_6F_5X obtained by He(I) UPS. Some of them were measured earlier [3,15,21-23]. Substituents X include both donor (NH_2) and acceptor (NO_2, NO) groups and one changing in character from acceptor to donor on passing from hydrocarbon analogues to polyfluoro derivatives (NSO [24]). Table 2 lists some results of MNDO calculations of compounds above.

Model , similar (3) and (2), was employed earlier for assignment of the UV photoelectron spectrum of fluorobenzene. The first UPS band with IP value of 9.25 eV undergoes splitting into two bands with IP's values of 9.35 and 9.75 eV on passing from benzene to fluoro-

TABLE 1

Vertical IP s of studied compounds, eV, and assignment of IP_1 and IP_2 on the basis of model (1) and quantum chemical calculations

X	C_6H_5X		4-FC_6H_4X		4-HC_6F_4X		C_6F_5X	
NH_2	8.05	b_1	8.18	b_1	8.9	b_1	8.9	b_1
	9.21	a_2	9.57	a_2	9.48	a_2	9.7	a_2
	10.81		10.91		11.51		11.49	
	11.79		12.08		13.71		13.09	
	12.4		12.51		14.59		13.6	
NO_2	9.92	a_2+b_1	10.06	b_1	10.15	a_2	10.66	a_2+b_1
	11.23		10.45	a_2	10.62	b_1	12.1	
	12.75		11.23		11.96		13.42	
	13.3		12.95		13.45		14.38	
	14.9		14.67		14.49		15.38	
	15.4		15.38		15.47			
NSO	9.06	b_1	9.12	b_1	9.71	a_2+b_1	9.97	a_2+b_1
	9.52	a_2	9.96	a_2	11.77		11.78	
	10.38		10.66		13.04		12.29	
	10.87		11.26		14.03		13.19	
	11.18		12.61		14.93		13.98	
	12.26		13.63					
	12.85		14.49					
	13.75		15.32					
NO	8.9	n^*_{NO}	9.01	n^*_{NO}	9.42	n^*_{NO}	9.53	n^*_{NO}
	9.84	b_1	9.87	b_1	10.02	a_2	10.15	a_2
	10.15	a_2	10.4	a_2	10.71	b_1	10.75	b_1
	12.2	n_{NO}	12.57	n_{NO}	12.74	n_{NO}	12.85	n_{NO}
	12.41		13.78		14.02		14.16	
							14.95	

TABLE 2

Some results of MNDO calculations. Highest occupied MO s of studied compounds

X	Energy*, eV, and symmetry of MO			
	C_6H_5X	$4\text{-}FC_6H_4X$	$4\text{-}HC_6F_4X$	C_6F_5X
H	9.39 e_{1g}	9.48 b_1 9.83 a_2		
NH_2	8.85 b_1 9.51 a_2	9.02 b_1 9.93 a_2	10.03 b_1 10.29 a_2	10.19 b_1 10.67 a_2
NO_2	10.38 a_2 10.56 b_1	10.64 b_1 10.77 a_2	11.04 a_2 11.74 b_1	11.37 a_2 11.82 b_1
NSO	9.0 b_1 9.82 a_2	9.17 b_1 10.23 a_2	10.02 a_2 10.66 b_1	10.35 a_2 10.84 b_1
NO	9.84 a_2 9.96 b_1	10.13 b_1 10.34 a_2	10.57 a_2 11.19 b_1	10.99 a_2 11.32 b_1

* with opposite sign

benzene, assigned to ionization from MO s a_2 and b_1 respectively [25]. This assignment is in controversy with results of non-empirical [3,6] and MNDO (Table 2) calculations which establish the opposite ordering of these MO s in accordance with model (1).

It is worthwhile to start consideration of the experimental data of this work with anilines. The NK_α spectrum of aniline is known [5], but its comparison with the UV photoelectron spectrum does not allow us to make unambiguous conclusions about HOMO symmetry, because the broadened first band of the NK_α spectrum corresponds to both first and second UPS bands. MNDO calculations simulate the experimental NK_α spectrum quite well (see below) and predict b_1 and a_2 symmetry for aniline MO_1 and MO_2 respectively, being in accordance with non-empirical calculations [3,5] (throughout the work the number of MO s corresponds to number of IP s).

On passing from aniline to its 4-fluoro derivative, the ΔIP_2 is about 2.8 ΔIP_1. This result is in agreement with model (1) and in controversy with models (3) and (2) (throughout the work the coefficients $\underline{c}$ were taken from MNDO calculations and factor $\underline{m}$ was accepted as equal to 0.33).

On passing from 2,3,5,6-tetrafluoroaniline to pentafluoroaniline, IP_1 does not change, but IP_2 increases to 0.22 eV. Using model (3) and (2) this means the a_2 symmetry of MO_1 and b_1 symmetry of MO_2 in these compounds. Model (1) and MNDO calculations lead to the opposite conclusion.

On passing from nitrobenzene to 4-fluoronitrobenzene the first UPS band undergoes splitting into two. As a result there is an IP_1 of 4-fluoronitrobenzene which differs from the IP_1 of nitrobenzene insignificantly, there is IP_3 of the former which does not differ from IP_2 of the latter, and there is a new IP, namely, IP_2 of 4-fluoronitrobenzene between them (Table 1). These data indicate that IP_1 of nitrobenzene corresponds to nearly degenerated MO s a_2 and b_1. On passing to the 4-fluoro derivative, the degeneracy is removed. In models (3) and (2) the symmetry of MO_1 and MO_2 of 4-fluoronitrobenzene is a_2 and b_1 respectively, but in model (1) the symmetry of MO_1 is b_1 and the symmetry of MO_2 is a_2.

It follows from non-empirical [3] and MNDO calculations that the group NO_2 does not contribute to the highest occupied MO s b_1 and a_2 of nitrobenzene which are indeed almost degenerated. The next occupied MO is nonbonding combination of oxygen 2p-AO s with a_2 symmetry. It also follows from MNDO calculations that the ordering of highest occupied π-MO s of 4-fluoronitrobenzene corresponds to that predicted by model (1).

On passing from 2,3,5,6-tetrafluoronitrobenzene to pentafluoronitrobenzene the IP_3 of the former changes insignificantly, but transforms into IP_2 of the latter, because the first UPS band of pentafluoronitrobenzene is broadened and corresponds probably to ionization from two neighbouring levels. Its intensity maximum lies very close to that of the second UPS band of 2,3,5,6-tetrafluoronitrobenzene. Within model (3) these data indicate the next ordering of three highest occupied MO s of 2,3,5,6-tetrafluoronitrobenzene : b_1 (MO_1, ring), a_2 (MO_2, ring), a_2 (MO_3, NO_2). On passing to pentafluoronitrobenzene, MO_1 and MO_2 become again nearly degenerated as in the case of its hydrocarbon analogue. MNDO calculations support this conclusion. Model (2) leads to the same orbital ordering as model (3), whereas model (1) in accordance with MNDO calculations leads to an opposite orbital ordering placing ring the a_2 MO of tetrafluoro derivative higher than the b_1 MO.

The N-sulfinyl group is the thio-analogue of the nitro group (possessing, like all known thio-analogues of nitrogen-oxygen functional groups [26], different group topology). It has been shown by means of CNDO/S calculations and comparison of He(I) and He(II) photoelectron spectra that IP_1 and IP_2 of N-sulfinylaniline correspond to ionization from π-MO s [15]. On passing from N-sulfinylaniline to its 4-fluoro derivative ΔIP_2 is about 7.3 ΔIP_1. Within models (3) and (2) it indicates 'a_2' symmetry of MO_1 and 'b_1' symmetry of MO_2 [23](throughout the work inverted commas designate pseudo-C_{2v} symmetry). However, model (1) in accordance with the results of MNDO (Table 2) and CNDO/S [15] calculations establish the opposite ordering of these MO s.

In the He(I) photoelectron spectrum of N-sulfinylpentafluoroaniline, the first band intensity maximum is shifted to higher energies by 0.26 eV, whereas the second band is split into two, with IP s values of 11.78 and 12.29 eV, compared with the spectrum of N-sulfinyl-2,3,5,6-tetrafluoroaniline. Values of second IP s of N-sulfinyl derivatives of both 2,3,5,6-tetrafluoro- and pentafluoroanilines are very close to the value of IP_1 of HNSO (11.6 eV [15]), whereas IP_3 of N-sulfinylpentafluoroaniline is very close to the value of IP_2 of HNSO (12.59 eV [15]). These data make it possible to suppose, unlike the mistaken interpretation, given earlier [23], that IP_1 of both N-sulfinyl-2,3,5,6-tetrafluoro- and N-sulfinylpentafluoro-anilines correspond to ionization from near-lying a_2 and b_1 levels, as in the case of pentafluoronitrobenzene. Results of MNDO calculations support this supposition.

In nitrosobenzene, the group NO, as follows from MNDO calculations, does not contribute to the nearly degenerated MO_1 and MO_2 with 'a_2' and 'b_1' symmetry respectively, whereas MO_3 is an antibonding combination of nitrogen and oxygen lone-pairs, lying in the plane of the σ-framework, n^*_{NO}. The non-empirical [27] and CNDO/S [28] calculations establish the same relative sequence of 'a_2' and 'b_1', but different absolute orbital ordering, namely, n^*_{NO} (MO_1), 'a_2' (MO_2), 'b_1' (MO_3), bonding combination of lone-pairs n_{NO} (MO_4), etc. Comparison of the value of nitrosobenzene

IP_1 and that of benzene supports its assignment to ionization from n^*_{NO}.

On passing from nitrosobenzene to 4-fluoronitrosobenzene, IP_2 practically does not change, whereas ΔIP_3 is equal to 0,25 eV. It means 'b_1' and 'a_2' symmetry of MO_2 and MO_3 of these compounds respectively within model (1). In the case of nitrosobenzene this assignment is in controversy with results of all quantum chemical calculations mentioned above, but in the case of 4-fluoronitrosobenzene relative ordering of 'b_1' and 'a_2' correspond to that predicted by MNDO calculations. Models (3) and (2) lead to the opposite assignment of MO_2 and MO_3 which in the case of nitrosobenzene is in agreement with the results of non-empirical and CNDO/S calculations [27, 28].

On passing from 2,3,5,6-tetrafluoronitrosobenzene to pentafluoronitrosobenzene ΔIP_2 is about 3,3 ΔIP_3. Within model (1) it indicates 'a_2' and 'b_1' symmetry of MO_2 and MO_3 respectively and this relative orbital ordering is in agreement with results of MNDO calculations. It also follows from calculations that 'a_2' MO of 2,3,5,6-tetrafluoronitrosobenzene is more sensitive to replacing of the hydrogen atom by fluorine than 'b_1' MO, as is predicted by model (1). The use of models (2) and (3) leads to an opposite assignment of MO_2 and MO_3.

Thus in the compounds under consideration one of the two highest occupied π-MO s is consistently more sensitive than the other to the introduction of a fluorine substituent in the ring para-position, as is clear from the values of appropriate ΔIP s. In all cases above, MNDO calculations being in accordance with model (1) indicate the a_2 MO to be more sensitive to replacing a para-hydrogen atom by fluorine. Results, obtained within model (3), as is predetermined by its formulation, are opposite to those obtained within model (1). The use of model (2) leads in all cases to the same result as with model (3).

MNDO calculations of hymeric molecules C_6H_5A and C_6H_5D, where A and D are the pseudo-atoms, make it possible to estimate the inductive influence of a substituent on the energies of arene highest occupied π-MO s. In these calculations values of all semiempirical parameters were accepted as equal to that of the hydrogen atom with the exception of the core parameter U_s, which value was accepted equal to - 13.906 and - 9.906 eV for A and D respectively, in comparison with - 11.906 eV for the hydrogen atom. Since increase of U_s module leads to increase of both atomic IP and proton affinity, the passing from H to A or to D corresponds to passing to a more acceptor or a more donor substituent respectively, in comparison with the hydrogen atom. Since A and D pseudo-atoms have no 2p-AO s, like hydrogen atoms, effects of p_π- conjugation are excluded and correct estimation of substituent inductive influence on the energies of π - MO s is possible.

The results of MNDO calculations of C_6H_6, C_6H_5A and C_6H_5D are presented in Table 3. As follows from this data introduction of A or D into the benzene molecule changes the charge on the carbon ipso-atom significantly, but does not lead to removing of HOMO degeneracy. On passing from C_6H_6 to C_6H_5A or C_6H_5D the energy shift of a_2 and b_1 levels is practically the same and is more than its splitting by an order of magnitude. This result leads to the conclusion that models of type (3) or (2) are inadequate.

TABLE 3

Some results of MNDO calculations : C_6H_5X molecules

X	Charge on atom		MO energy*, eV		$\Delta\varepsilon = \lvert\varepsilon(b_1) - \varepsilon(a_2)\rvert$
	ipso-C	X	a_2	b_1	
H	- 0.059	0.059	9.392	9.392	0.000
A	0.014	- 0.109	9.582	9.567	0.015
D	- 0.216	0.219	9.304	9.314	0.010

* with opposite sign

It follows from MNDO calculations that highest occupied π-MO s of the fluorinated compounds under study contain non-negligible contributions of fluorine 2p-AO s which overlap with carbon 2p-AO s in an antibonding manner. For example, the contribution of para-fluorine 2p-AO to the highest b_1 MO s vary in the range from 4 to 8 percent with the smallest value obtained in the case of N-sulfinyl-4-fluoroaniline and the greatest value obtained in the cases of both 4-fluoro- and pentafluoronitrobenzenes. This is in agreement with the results of more rigorous consideration of some fluorinated alkenes, alkynes and arenes based on non-empirical calculations in double-dzeta basis, completed with manybody Green function calculations to include the effects of electron correlation and relaxation [29-31]. It should be pointed out that relative small values of fluorine contributions to the highest occupied π-MO s does not mean weak mesomeric interaction and is not in controversy with previous data [14]. Because fluorine is more electronegative than carbon, it gives a great contribution to bonding π-combinations and a small contribution to antibonding ones, corresponding to the highest occupied π-MO s of compounds under consideration (on this common rule see, for example, ref. [1]). It is the situation that is reflected by the experimental FK_α spectra and MNDO calculations.

Comparison of experimental data and that obtained from MNDO calculations of theoretical X-ray emission spectra is the real criterion of the calculation's quality with respect to MO s structure. Because the available experimental FK_α spectra are poorly resolved and possess the simple form, the much more complex NK_α spectrum of aniline [5] and SK_β spectrum of its N-sulfinyl derivative [32] were chosen for this purpose, besides the FK_α spectrum of fluorobenzene [18]. It is clear from the Figure that agreement between experimental and theoretical spectra is quite good, especially in short-wave sides in which occur transitions from π-MO s.

The whole of the data obtained in this work reject the electrostatic interpretation of the π-fluoro effect, proposed in [16], and thus models (3) and (2), as used in earlier work [23,25]. The agreement between the results of MNDO calculations and those obtained within the compensational model (1), confirm mutually its truth and lead to the conclusion that in the cases of benzene monofunctional derivatives, possessing C_{2v} or pseudo-C_{2v} symmetry, it is possible to determine the symmetry of highest occupied π-MO s by means of UPS and introduction of fluorine substituents into the ring para-position. It follows from the data presented that one of the two highest occupied π-levels, for which the IP under such introduction changes least, possesses b_1 symmetry and the other one, for which the IP changes more, possesses a_2 symmetry.

EXPERIMENTAL

All compounds studied were obtained by known methods; their purities were controlled by means of GLC, ^1H and ^{19}F NMR and elemental analysis.

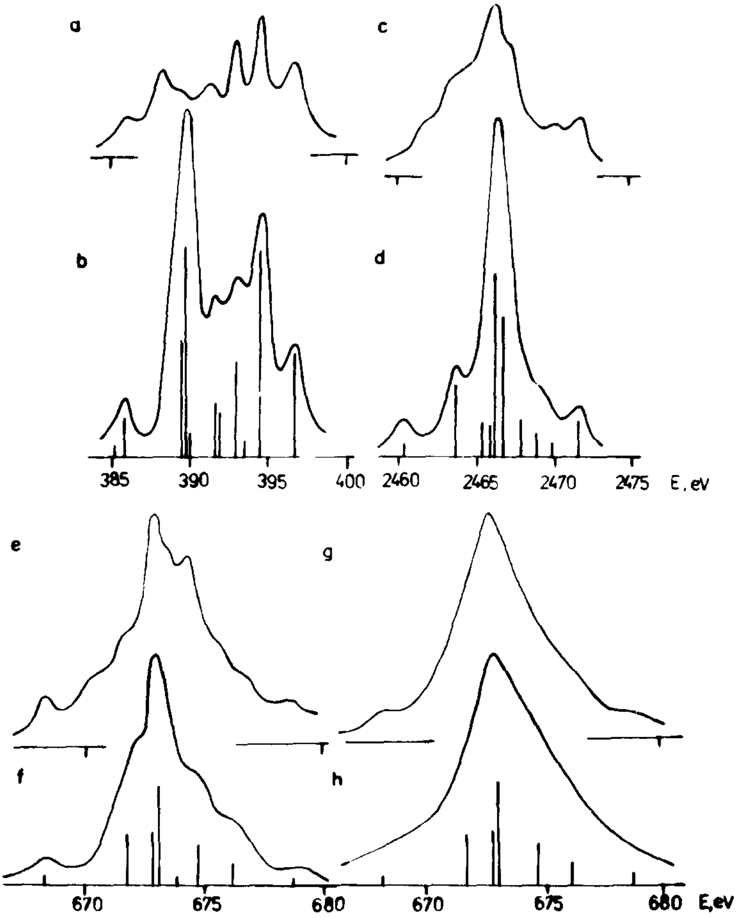


Fig. Experimental (a) and theoretical (b) NK$_\alpha$ spectra of aniline; experimental (c) and theoretical (d) SK$_\beta$ spectra of N-sulfinylaniline; experimental (e) and theoretical (f, g, h) FK$_\alpha$ spectra of fluorobenzene. Experimental spectra are taken from [5b, 18, 32]; (a) and (e) in gas phase, (c) in solid state. Theoretical spectra obtained from MNDO calculations under assumption that single spectral transition corresponds to gaussian band with full width at half height equal to 1.0 (b, d, f), 1.5 (g) or 2.0 (h) eV; (g) and (h) simulate the solid state spectra (see ref. [17, 18]). Relative intensities are inserted as bars.

He(I) photoelectron spectra were recorded on a spectrometer designed at Leningrad State University [33] which was built and located at the Institute of Chemistry in Ufa. The spectra were calibrated by Xe lines (IP_1 12.13, IP_2 13.43 eV). The accuracy of IP's is ± 0.02 eV (or for broad bands ± 0.05 eV). Detailed discussion of the spectra will be given elsewhere [34].

MNDO calculations with partial geometry optimization have been performed with standard parameters [35-37] with the MNDO-85 programm [38].

REFERENCES

1 I. Fleming, 'Frontier Orbitals and Organic Chemical Reactions', Wiley, London (1976).

2 V. I. Nefedov in, 'Structure of Molecules and Chemical Bonding' (in Russian), vol. 3, VINITI, Moscow (1975).

3a M. H. Palmer, W. Moyes, M. Spiers and J. N. A. Ridyard, J. Mol. Struct., 53 (1979) 235; 3b idem, ibid., 55 (1979) 243.

4 Z. Niu and J. E. Boggs, J. Mol. Struct., 109 (1984) 381.

5a J. Nordgren, L. Selander, L. Pettersson, R. Brommer, M. Backstrom, C. Nordling and H. Agren, Chem. Phys., 84 (1984) 333; 5b idem, Activity Report 1981/82, Institute of Physics (Fysik II), University of Uppsala, Uppsala, (1982) 16.

6 J. A. Sell, D. M. Mintz and A. Kuppermann, Chem. Phys. Lett., 58 (1978) 601.

7 J. H. Hog, L. Nygaard and G. O. Sorensen, J. Mol. Struct., 7 (1971) 111.

8 J. Trotter, Acta Cryst., 12 (1959) 884.

9 D. G. Lister, J. K. Tyler, J. H. Hog and N. W. Larsen, J. Mol. Struct., 23 (1974) 252.

10 Y. Hanyu and J. E. Boggs, J. Chem. Phys., 43 (1965) 3454.

11 R. Meij, A. Oskam and D. J. Stufkens, J. Mol. Struct., 51 (1979) 37.

12 E. Heilbronner, V. Hornung, F. H. Pinkerton and S. F. Thames, Helv. Chim. Acta, 55 (1972) 289.

13 D. G. Streets and G. P. Ceasar, Mol. Phys., 26 (1973) 1037.

14 D. G. Streets, Chem. Phys. Lett., 28 (1974) 555.

15 J. H. Louwen, H. van Dam, D. J. Stufkens, A. Oskam and H. H. Jaffe J. Electron Spectrsc. Relat. Phenom., 26 (1982) 235.

16 J. F. Liebman, P. Politzer and D. C. Rosen in P. Politzer and D. M. Truhlar (Eds), 'Chemical Applications of Atomic and Molecular Electrostatic Potentials', Plenum Press, London (1981), p.295.

17 E. Tegeler, G. Wiech and A. Faessler, J. Phys., B, 13 (1980) 4771.

18 G. G. Furin, G. G. Yakobson, V. D. Yumatov, L. N. Mazalov and A. V. Okotrub, J. Fluor. Chem., 28 (1985) 241.

19 T. Ohta, T. Fujikawa and H. Kuroda, Bull. Chem. Soc. Japan, 48 (1975) 2017.

20 V. I. Nefedov, 'X-Ray Photoelectron Spectroscopy of Chemical Compounds' (in Russian), Khimia, Moscow (1984), p.43-55 .

21 C. N. R. Rao, P. K. Basu and M. S. Hedge, Appl. Spectr. Rev., 15 (1979) 1.

22 G. G. Furin, M. A. Fedotov, G. G. Yakobson and A. V. Zibarev, J. Fluorine Chem., 28 (1985) 273.

23 A. V. Zibarev, A. Sh. Sultanov, G. G. Furin and I. I. Furley, Izv. Akad. Nauk SSSR, Ser. Khim., (1986) 474.

24 A. V. Zibarev, G. G. Furin, I. K. Korobeinicheva, M. A. Fedotov and G. G. Yakobson, Izv. Akad. Nauk SSSR, Ser. Khim., (1983) 2259.

25 M. Klessinger, Angew. Chem., 84 (1972) 544.

26 Y. Inagaki and R. Okazaki, J. Synth. Org. Chem. Japan, 36 (1980) 1.

27 F. P. Colonna, G. Distefano, D. Jones, A. Modelly and V. Galasso, Z. Naturforsch., A, 36 (1981) 385.

28 R. Egdell, J. R. Green, C. N. R. Rao, B. G. Gowenlock and J.J. Pfab, J. Chem. Soc., Faraday Trans, 2, 22 (1976) 988.

29 W. von Niessen, G. H. F. Dierksen and L. S. Cederbaum, Chem. Phys. Lett., 45 (1977) 295.

30 G. Bieri, A. Schmelzer, L. Asbrink and M. Jonsson, Chem. Phys., 49 (1980) 213.

31 G. Bieri, W. von Niessen, L. Asbrink and A. Svensson, Chem. Phys., 60 (1981) 61.

32 G. N. Dolenko, A. V. Zibarev, S. A. Krupoder, G. G. Furin and G. G. Yakobson, Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk, (1980) (6) 74.

33 N. E. Petrachenko, M. E. Akopyan, V. I. Kleymenov, M.V. Kleymenov, I. V. Korkoshko, M. M. Timoshenko and Yu. V. Chizhov, Vestnyk LGU, N 22, 4 (1983) 29.

34 G. G. Furin, A. Sh. Sultanov, I. I. Furley and G. A. Tolstikov, to be published.

35a M. J. S. Dewar and W. J. Thiel, J. Am. Chem. Soc., 99 (1977) 4899;
35b idem, ibid., 99 (1977) 4907.

36 M. J. S. Dewar and H. S. Rzepa, J. Am. Chem. Soc., 100 (1978) 58.

37 M. J. S. Dewar, M. L. McKee and H. S. Rzepa, J. Am. Chem. Soc., 100 (1978) 3607.

38 A. A. Bliznyuk and A. A. Voityuk, Zh. Struct. Khim., 27 (1986) 193.