Journal of Fluorine Chemistry, *28* (1985) 257–272

Received: August 20, 1984; accepted: February 11, 1985

THE OXYGEN K_α X-RAY EMISSION SPECTRA OF FLUORINATED ANISOLES AND PENTAFLUOROPHENOL

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SUMMARY

Oxygen and fluorine K_α X-ray emission spectra have been obtained for a number of oxygen-containing compounds: H_2O, CH_3OH, C_6H_5OH, $C_6H_5OCH_3$, C_6F_5OH and $4\text{-}XC_6F_4OCH_3$ (X = F, OCH_3, CF_3) in the solid or gaseous states and interpreted on the basis of the UV photoelectron and ESCA data and the results of MINDO/3 calculations. The mixing of the oxygen 2p-AO with the highest occupied π-orbitals of the benzene ring is concluded to be small. The main contribution of the 2p(O)-AO is shown to be to the system of σ-levels and lower-lying π-levels. CH_3OH is assumed to have hyperconjugation. Comparison of the electronic structures of oxygen in phenol and anisole with those in their polyfluorinated analogues shows the reduced effectiveness of oxygen 2p-AO conjugation with the π-system of the benzene ring in the latter cases.

INTRODUCTION

Our recent [1] X-ray studies of fluorine electronic structures in fluorinated compounds have shown that the contribution of the fluorine 2p-AO to the highest occupied π-orbitals of the benzene ring and π-orbital of the ethylene bond is small and that the major contribution is to the system of σ-levels and lower-lying π-levels. At the same time, changes in the HOMO

0022-1139/85/$3.30

energies and the charges on the carbon atoms, on introduction of fluorine to the benzene ring, revealed by the physical methods, suggest changes in the electronic structures of atoms of functional groups bonded to the polyfluorinated benzene ring. Our UV photoelectron and X-ray fluorescent studies of the aromatic sulphides and phosphines [2,3] indicate decreased HOMO energies, increased positive charges on the sulphur and phosphorus atoms and a reduced efficiency of p-π-conjugation of the non-bonding electron pairs sulphur or phosphorus with the π-system of the fluorinated benzene ring in comparison with non-fluorinated analogues. If the efficiency of interaction of the 2p-electrons of these elements with the π-system of the benzene ring depends on their energy position, the contribution of oxygen 2p-electrons to the highest occupied π-level of the molecule is expected to be small for oxygen aromatic derivatives, as in the cases of fluoroaromatic compounds (for example, according to [4], the ionization potentials of hypothetical lone-electron pairs of fluorine and oxygen in hydrogen fluoride and water are equal to 16.06 and 12.62 eV; cf. with the e_{1g}-level of benzene 9.24 eV). The analysis of the oxygen K_α X-ray emission spectrum of β-naphthol in [5] showed a very low intensity of X-ray signals corresponding to transitions from the highest occupied π-orbitals of that compound. The authors attributed this to strong delocalization of the electron density from the lone electron pairs of the oxygen atom, due to overlap with the aromatic π-orbitals, which we consider to be doubtful.

In the present work, the oxygen K_α X-ray emission spectra of some aromatic and polyfluoroaromatic derivatives of oxygen are interpreted to reveal oxygen 2p-AO distribution in MOs, the effects of fluorine atoms introduced into the benzene ring on the efficiency of p-π-interaction of oxygen non-bonding electron pairs with the π-system of the benzene ring, and to obtain data on the nature of p-π-interactions of oxygen with an unsaturated fragment. We used the X-ray spectroscopy method, since it gives information on the distribution of element 2p-electrons in MOs [6]. The oxygen K_α X-ray emission spectra, where the energy position, form and intensity of emission peaks depend on the character of the chemical bond, give important information for predicting the reactivities of organic compounds.

Earlier, such information has been obtained from the oxygen K_α X-ray emission spectra of dialkyl ethers and alcohols, and was used for predicting their extractive ability [7].

The objects of our investigation were the simplest aromatic derivatives of oxygen: phenol, anisole, substituted polyfluoroaromatic anisoles $4\text{-}XC_6F_4OCH_3$ (X = F, OCH_3, CF_3), pentafluorophenol; also the model compounds for this series - water and methanol in the gaseous and solid states.

RESULTS AND DISCUSSION

Let us consider the X-ray and UV photoelectron spectra of the simplest oxygen derivative, water, in various physical states. The electronic structure of its molecule is well-known There is a large number of quantum-chemical calculations. The photoelectron spectra of water have been analysed [8-12], as have the X-ray spectra [13-16], and ESCA [17]. These studies formed the basis for rationalising the nature of the chemical bond in the molecule of water. The oxygen K_α X-ray emission spectrum and the UV photoelectron spectrum of gaseous water matched in a single scale of ionization potentials are given in Fig.1 (the oxygen K_α X-ray emission spectrum was obtained by the electron impact method for water vapour). The spectra were superimposed with respect to the internal O_{1s} level taken from [17].

Identification of the X-ray spectral transitions corresponding to emission peaks is shown in Fig.1. The highest occupied level of water is $1b_1$ (unshared electron pair localised on oxygen). The molecular orbital wave function corresponding to that level involves a single 2p-AO of oxygen. This MO corresponds to the most intensive maximum A in the X-ray spectrum, which coincides, when the spectra are superimposed one upon another, with the lowest energy (ionization potential scale) and the most intensive signal A' of the UV photoelectron spectrum (Fig.1). The next level is an MO of a_1-symmetry ($3a_1$) which consists of oxygen 2p- and 2s-AO and hydrogen 1s-AO. Therefore, the intensity of the X-ray transition corresponding to that MO will be lower. In the region of higher energies (ionization potential scale), the A signal is followed by the less intensive B signal, which should be assigned to the $3a_1$ MO. The $1b_2$ orbital, which consists of oxygen 2p-AO and hydrogen 1s-AO, shows itself as maximum C in the X-ray spectrum. In the UV photoelectron spectrum, the two latter MOs correspond to signals B' and C'. The most low-lying valent level is the $2a_1$ level, the MO of which consists mainly of oxygen 2s-AO. The X-ray spectra do not show this level. Each of maxima A, B and C of the X-ray spectrum has a complex structure involving a number of signals which seem to result from vibrations of the molecule and multi-electron transitions in the X-ray spectra [18].

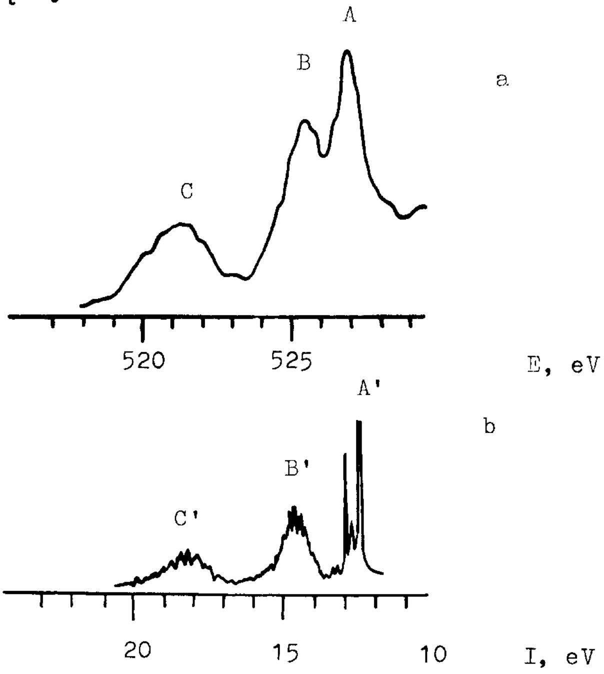

Fig.1. The oxygen K_α X-ray emission spectrum of gaseous water (a) and the He (I) photoelectron spectrum of water (b).

Consider the X-ray spectrum of water as ice, reported earlier [13,16]. The X-ray spectra of water in a solid state differ from those of gaseous water both in the number of maxima and their relative intensities (Fig.2). For the purpose of comparison, Fig. 2 shows also the X-ray fluorescent spectrum of liquid water obtained by us. Changes in the X-ray spectra of water as a solid may be attributed to changes in the nearest environment of the oxygen atom [15]. The X-ray spectra of ice and liquid water resemble the sulphur K_α X-ray emission spectra of a number of period III compounds, where the environment of the sulphur atom represents a distorted tetrahedron. The structure of ice is known [15] to be determined by the tetrahedrally directed bonds at the oxygen atom. Due to non-equivalence of the O-H bonds the tetrahedron gets distorted, which shows itself in our spectrum.

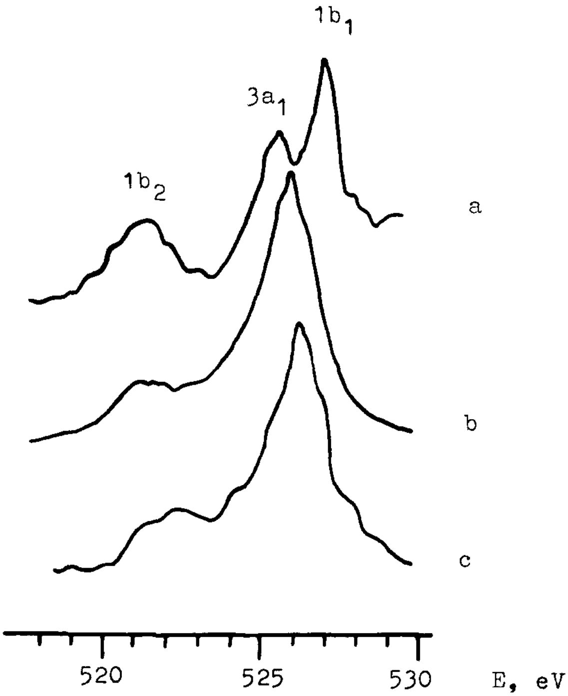

Fig.2. The oxygen K_α X-ray emission spectra of water as a: gas (a), solid (b), liquid (c).

We compared the X-ray spectra of gaseous and solid water to clarify whether the UV photoelectron spectra and the calculation results for gaseous water are useful in interpretations. This analysis allowed us to conclude that the X-ray spectra of solids are substantially affected by intermolecular interactions (for example, hydrogen bonding), which leads to considerable differences between them and the spectra of gaseous compounds.

The electronic structure of another model compound, CH_3O has also been extensively studied (quantum-chemical calculations [19-22], UV photoelectron [22-25], X-ray photoelectron [17] and X-ray [16] spectroscopy). These methods allow us to interpret the oxygen and carbon K_α X-ray emission spectra of CH_3OH, represented in Fig.3 in a single scale of ionization potentials, together with the UV photoelectron (He (I)[25]) spectrum.

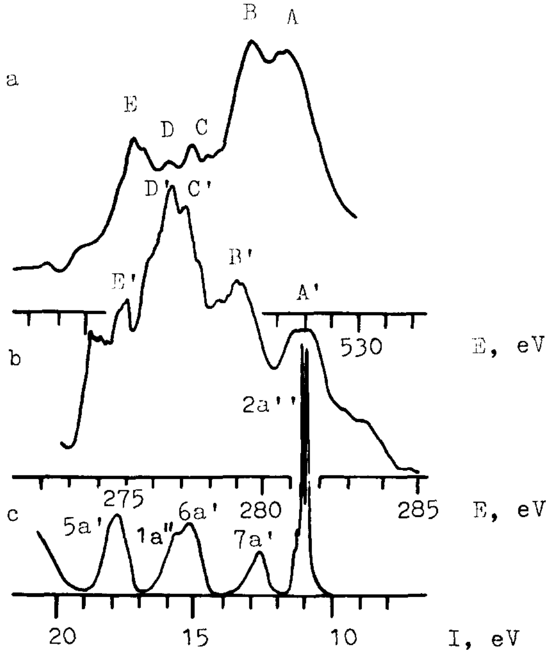

Fig.3. The oxygen K_α X-ray emission spectrum of gaseous methanol (a), the carbon K_α X-ray emission spectrum of gaseous methanol (b) and the He (I) photoelectron spectrum of methanol (c).

As shown by the above-mentioned quantum-chemical calculations and the UV photoelectron data, the highest occupied level of methanol is that of a'' (2a'') symmetry and the contribution of oxygen 2p-AO to that level is 80%. The carbon 2p-AO contribution indicates π-bonding between oxygen and carbon (hyperconjugation effect). The electron transition from that level shows itself in the oxygen K_α X-ray emission spectrum as maximum A, in the carbon K_α X-ray emission spectrum as maximum A', which coincides with the 2a'' bond in the UV photoelectron spectrum when the spectra are superimposed. Then follow the higher energy level 7a', the electrons of which are responsible for the formation of a σ-bond of oxygen with carbon and hydrogen. In the oxygen K_α X-ray emission spectrum it corresponds to maximum B, in the carbon K_α X-ray emission spectrum to maximum B'. Levels 6a' and 1a'' may be defined as the carbon-hydrogen σ-bond levels. The presence of C and D maxima in the oxygen K_α X-ray emission spectrum corresponding to these levels indicates the hyperconjugation effect. In the carbon K_α X-ray emission spectrum transitions $6a' \longrightarrow C_{1s}$ and $1a'' \longrightarrow C_{1s}$ show themselves as the most intensive maxima C' and D'. Molecular orbital 5a', electrons of which are responsible for the formation of a σ-bond between oxygen, carbon and hydrogen atoms, shows itself as maximum E in the oxygen K_α X-ray emission spectrum and as maximum E' in the carbon K_α X-ray emission spectrum. Levels 4a' and 3a' consist mainly of oxygen and carbon 2p-AO respectively and partly of hydrogen 1s. Levels 2a' and 1a' involve carbon 1s-AO and oxygen 1s-AO respectively and are, therefore, of atomic character. Their energy position may be determined by X-ray photoelectron spectroscopy [17].

Figure 4 shows the oxygen K_α X-ray emission spectra of gaseous and solid methanol. The molecule of solid methanol has a strong hydrogen bond. Differences between the oxygen K_α X-ray emission spectra of gaseous and of solid methanol arise mainly from differences in the highest levels of the molecules. The spectra, as in the case of water, show merging of maxima A and B (the lone-pair of oxygen and MOs of σ-bond of oxygen with carbon and hydrogen).

Thus for systems with a stong hydrogen bond (H_2O, CH_3OH), molecular crystal approximation in the analysis of the electronic structure is not valid.

The oxygen and carbon K_α X-ray emission spectra of phenol, (see Fig.5) provide a guide to the interpretation of the

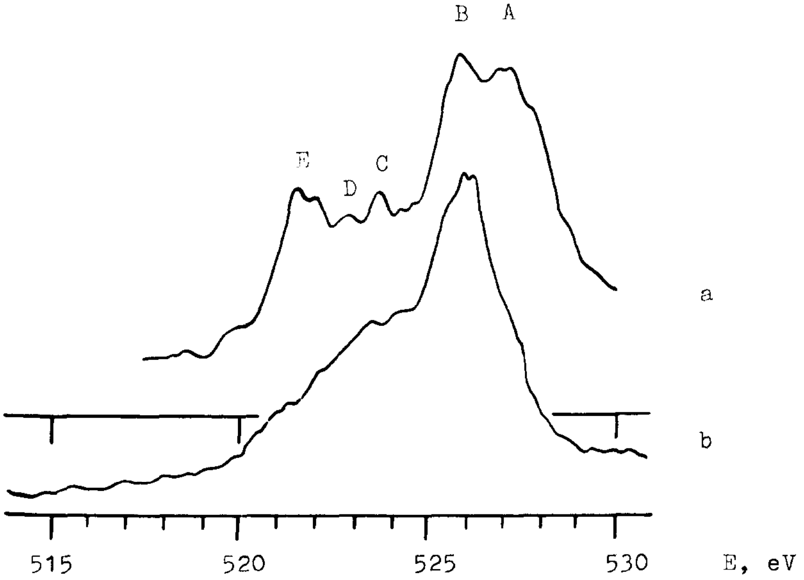

Fig.4. The oxygen Kα X-ray emission spectra of methanol as a: gas (a), solid (b).

corresponding UV photoelectron spectrum [26]. Identification of the first ionization potentials of phenol has been carried out [26-28]. Using intensity arguments, based on an MINDO/3 calculation of the one-center X-ray intensities, the $1b_1$ and $3a_1$ (O_{2p} lone pair) orbitals could be identified in the oxygen Kα X-ray emission spectrum. As shown in [4], the position of the oxygen non-reacting lone-pair is close to the bonding a_{2u} π-level of benzene. The contribution of oxygen to the highest occupied π-level of the molecule is small. As follows from the oxygen Kα X-ray emission spectrum of phenol, the 2p-electron density of oxygen and HOMO-shows itself as a low-energy (ionization potential scale) main maximum (line A'). The values of inner O_{1s} and C_{1s} levels are taken from [17,29]. In the carbon Kα X-ray emission spectrum the two HOMOs are represented by maximum A. Then, as show by the calculation results, follows a higher-energy group of levels that may be correlated based on its origin with $1a_{2u}$ and $3e_{2g}$ of benzene and $1b_1$ of water (the lone electron pair). In the oxygen Kσ X-ray emission spectrum,

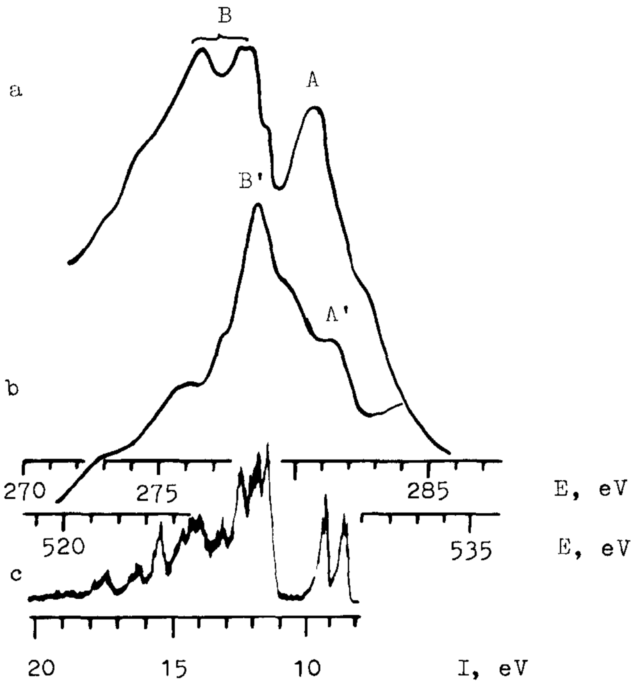

Fig.5. The carbon K$_\alpha$ X-ray emission spectrum of gaseous phenol (a), the oxygen K$_\alpha$ X-ray emission spectrum of gaseous phenol (b) and the He (I) photoelectron spectrum of phenol (c).

these levels show themselves as maximum B', in the carbon K$_\alpha$ X-ray emission spectrum as maximum B coinciding with B' when the spectra are superimposed one upon another.

Figure 6 represents the oxygen K$_\alpha$ X-ray emission spectra of phenol in solid and gaseous states. The spectra show very slight variations in structure as opposed to large variations for water and methanol. This seems to be connected with the reduced hydrogen bonding for the phenol molecule. Thus it be concluded that the electronic structure of oxygen aromatic derivatives in the solid state may be analysed using the oxygen K$_\alpha$ X-ray emission spectra. Further treatment involves interpretation of the fluorescent oxygen K$_\alpha$ X-ray emission spectra of some oxygen derivatives in the solid state.

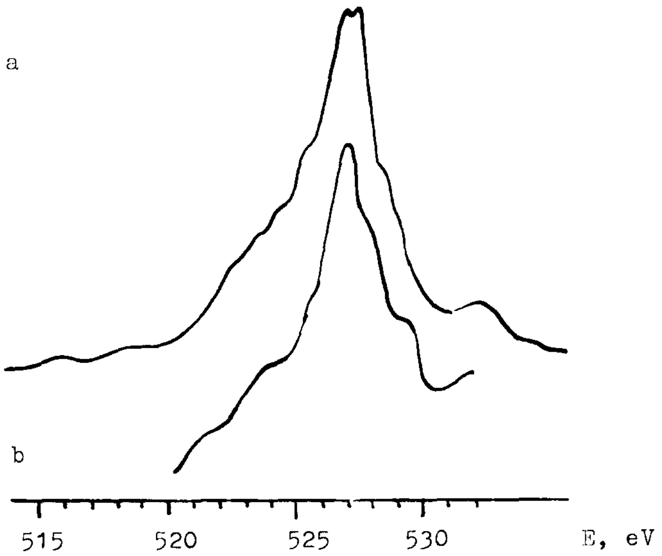

Fig.6. The oxygen K_α X-ray emission spectra of phenol as a: solid (a), gas (b).

Figure 7 shows the oxygen K_α X-ray emission and UV photoelectron spectra of anisole, the UV photoelectron spectrum from [27]. The two HOMOs are the π-type orbitals correlating with $1e_{1g}$ of benzene. The contribution of oxygen 2p-AO to these MOs is small, which shows itself in the low-energy structure of the main maximum.

How will introduction of fluorine into the benzene ring affect the oxygen K_α X-ray emission spectrum ? Figure 8 represents the oxygen K_α X-ray emission and the UV photoelectron spectrum of pentafluorophenol, superimposed relative to the values of O_{1s} level (taken from [30], the UV photoelectron spectrum from [31]). The same Figure shows also the oxygen K_α X-ray emission spectrum of pentafluorophenol.

According to the MINDO/3 results, the highest occupied levels of the molecule are those correlating with the $1e_{1g}$ level of the fluorinated benzene ring, as was the case with the phenol molecule. The next level is the π-bond level (correlating with the a_{2u} level of hexafluorobenzene). As shown

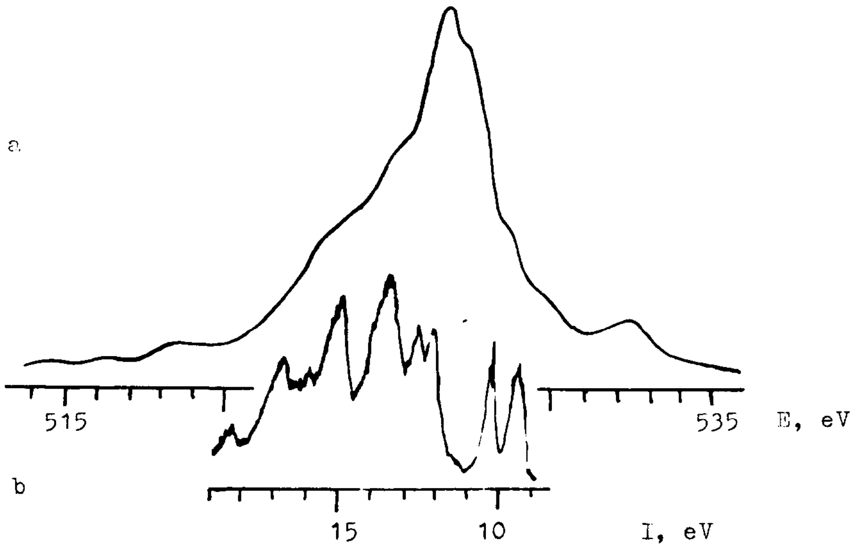

Fig.7. The oxygen K_α X-ray emission spectrum of solid anisole (a) and the He (I) photoelectron spectrum of anisole (b).

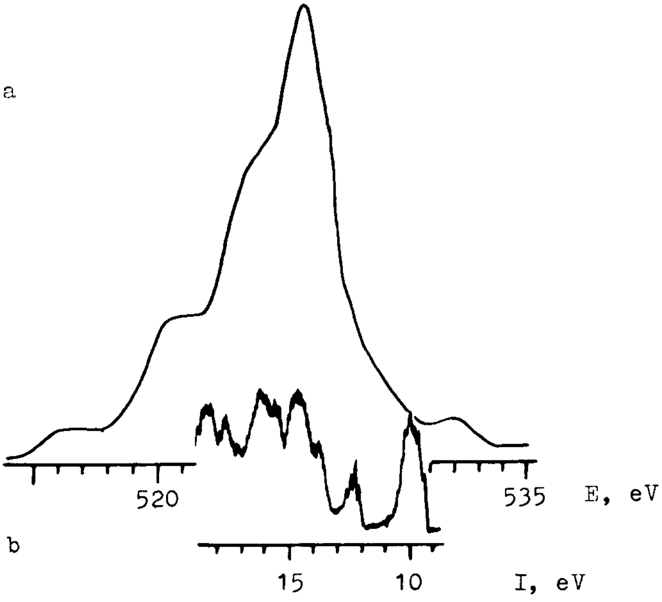

Fig.8. The oxygen K_α X-ray emission spectrum of solid pentafluorophenol (a) and the He (I) photoelectron spectrum of pentafluorophenol (b).

by the X-ray spectral data, the contribution of 2p(O)-AO to these MOs is small. As is perfluorination of the phenyl rings to prove the assignment of π-ionizations ('perfluoro effect' [32]). As shown by the calculations and X-ray spectral data for polyfluorinated phenol ⟶ phenol, the interaction of oxygen 2p-electrons with the 2p-electrons of the benzene ring is small. But the calculations also show that in fluorinated phenols the interactions of fluorine 2p-electrons with oxygen 2p-electrons are enhanced.

Figure 9 shows the oxygen and fluorine K_α X-ray emission and the UV photoelectron (taken from [31]) spectra of pentafluoroanisole (the values of inner O_{1s} and F_{1s} levels are tak from [30]). In this case the MINDO/3 calculations have also been carried out. These studies show a small contribution of oxygen $2p_\pi$-electron density in the highest π-level of the molecule (as in the case of anisole) and the substantial contribution of 2p(O)-AO in the π-levels of lower energy.

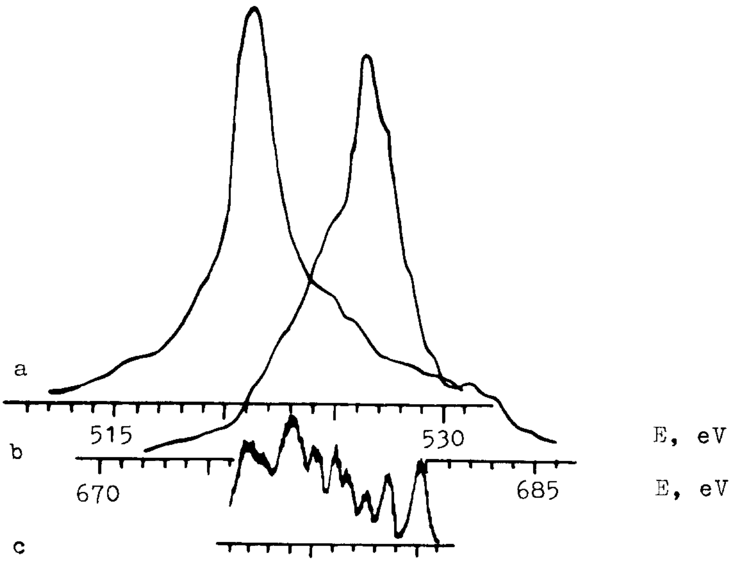

Fig.9. The oxygen K_α X-ray emission spectrum of solid pentafluoroanisole (a), the fluorine K_α X-ray emission spectrum of solid pentafluoroanisole (b) and the He (I) photoelectron spectrum of pentafluoroanisole (c).

Figure 10 represents the X-ray spectra of a number of substituted anisoles. The spectra of both the anisoles and the phenols show the tendency of oxygen electron density transfer to lower-lying π- and σ-orbitals. This is also confirmed by the calculation results. Taking into account that fluorination of the benzene ring does not result in any changes in its π-level position, the electron density transfer to lower-lying orbitals leads to the reduced contribution of oxygen 2p-electrons to the high-lying levels (or to the reduced efficiency of p_π-p_π-interaction).

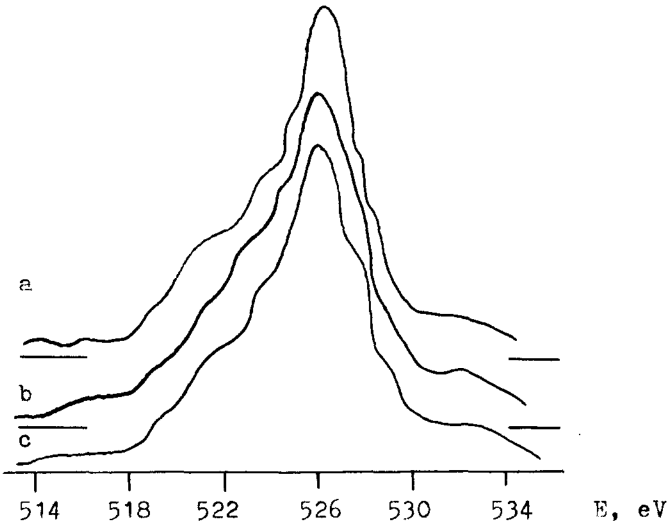

Fig.10. The oxygen K_α X-ray emission spectra of solid $4\text{-}CF_3C_6F_4OCH_3$ (a), $4\text{-}CH_3OC_6F_4OCH_3$ (b) and $C_6F_5OCH_3$ (c).

We attribute these changes to a decrease of the electron density on oxygen (as shown by the X-ray photoelectron data [30], on passing to polyfluorinated benzenes, the positions of internal O_{1s} levels are changed by 1-2 eV) as a result of the electron density transfer in the π-system to fluorine atoms.

EXPERIMENTAL

The oxygen and carbon K_α X-ray emission spectra have been obtained on the ultralong-wave X-ray spectrometer, using the organic acid salt monocrystal (2d = 26.6 and 52.4 Å) as a dispersing element. The Rowland circle radius - 0.25 m. The spectrometer resolution for an oxygen K_α X-ray emission spectrum - at least 0.25 eV, for a carbon K_α X-ray emission spectrum - at least 0.15 eV.

The X-ray spectra of solid samples have been obtained by fluorescent spectroscopy, using the method of freezing the sample vapours in vacuum ($\sim 10^{-6}$ torr) onto the secondary anode being cooled with liquid nitrogen. The spectra were initiated by breaking radiation of the copper anode. The X-ray tube setting: voltage 8 kV, current 0.5 A.

The gas-phase X-ray spectra have been obtained by the electron impact method. Electron energy 3-4 keV, current 0.5 A, the pressure of stream vapours - fractions of part torr. The spectra were registered by the proportional meter with methane filling under the pressure of 0.2-0.3 atm. The meter window was made of a polymer film. The intensity of the oxygen K_α X-ray emission spectra at maximum for solids $\sim 10^2$ pps, of the oxygen and carbon K_α X-ray emission spectra of gases ~ 10 pps. Approximation of superposition $\sim$ 0.2 eV.

The compounds used in this study have been obtained by the procedures described in [33].

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