Electronic structure of monosubstituted benzenes and X-ray emission spectroscopy

4. Phenol

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The electronic structure of the phenol molecule in the gas phase was studied by X-ray emission spectroscopy (using the O-Kα and C-Kα spectra). MNDO calculations were performed, which made it possible to construct theoretical spectra and interpret experimental spectra. The structure of the molecular orbitals of phenol was compared with those of benzene and water. The π-interaction of the phenyl fragment with the oxygen-containing substituent was investigated. The contribution of the 2p atomic orbital of the oxygen atom to the π-HOMO of phenol is considerably less than that to lower-lying orbitals.

Key words: X-ray emission; O-Kα spectra, C-Kα spectra; MNDO; phenol.

Previously,[2] we have performed an X-ray spectral study of conjugation between the phenyl ring and the lone electron pair of the sulfur or phosphorus atom in the Ph_2S and Ph_3P molecules. However, no clear idea of its nature was formulated. As a simple model system, phenol makes it possible to analyze the nature of this conjugation in detail. Unlike the benzaldehyde molecule,[3] the orbitals of the oxygen atom in the phenol molecule directly interact with the orbitals of the benzene ring. The experimental conditions and procedure for constructing theoretical spectra from the results of the MNDO calculations have been reported previously.[3]

Results and Discussion

Let us consider the structure of the molecular orbitals (MOs) of phenol by comparing it with those of MOs of the benzene and water molecules. The orbitals of the first and second molecules are close in type to those of the phenyl ring and the oxygen-containing substituent, respectively. The electronic structure of the benzene molecule (D_{6h} symmetry) obtained from data of photoelectron spectroscopy and X-ray spectral studies has been reported in many works (see, for instance, Ref. 4). The photoelectron (PES) and X-ray spectra of the water molecule (C_{2v} symmetry) have also been reported (see Refs. 5 and 6—10, respectively). The PES and X-ray spectra of water in the gaseous state are shown in Fig. 1. The spectrum obtained on a unique spectrometer with a diffraction grating[10] is reproduced for comparison. As in Ref. 10, we used the electron impact (EI) technique to excite the X-ray radiation of the molecules. At the same time, the photoionization technique was also used. As was already mentioned in Ref. 3, we used a spectrometer with an analyzer crystal as dispersive element in our experiments. The resolution of the spectra reported in this work is not poorer than that obtained by other authors[10] (see Fig. 1). The spectra of water in the gaseous state were reduced to an energy scale of ionization potentials (*I*) using the position of the inner O1s energy level determined by X-ray electron spectroscopy.[11] The most intense line of the spectrum of water corresponds to the $1b_1$ MO, which is an orbital of the lone electron pair of the oxygen atom. The two orbitals (the $3a_1$ and $1b_2$ MOs) lying higher on an energy scale (or on an ionization potentials scale) (see Fig. 1) correspond to the orbitals of the σ-bond between the oxygen and hydrogen atoms. The high-energy region spectra is a group of maxima due to transitions in doubly ionized molecules.[10] Along with these maxima, an intense *S* satellite is present in the spectrum recorded on the spectrometer with the analyzer crystal (EI). This satellite is absent in the spectrum obtained by the authors of Ref. 10 or in that we obtained using the photoionization technique and reported in Ref. 3 (see Fig. 1). It can be assumed that the *S* line is due to several effects: X-ray transitions in doubly ionized molecules (multiple ionization satellites), whose intensities depend on the energy of excitation (an analogous problem we considered

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* For Part 3, see Ref. 1.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 12, pp. 2187—2193, December, 1997.

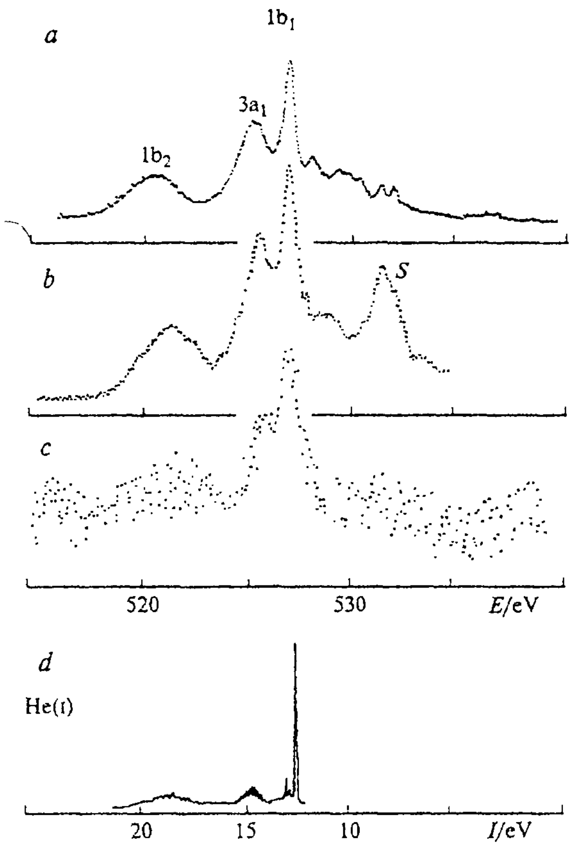

Fig. 1. The X-ray (*a—c*) and photoelectron (He(I))[5] (*d*) spectra of the water molecule in the gas phase: the O-Kα spectrum (*a*) reported previously[10] and those obtained in this work by EI (*b*) and photoionization technique (*c*).

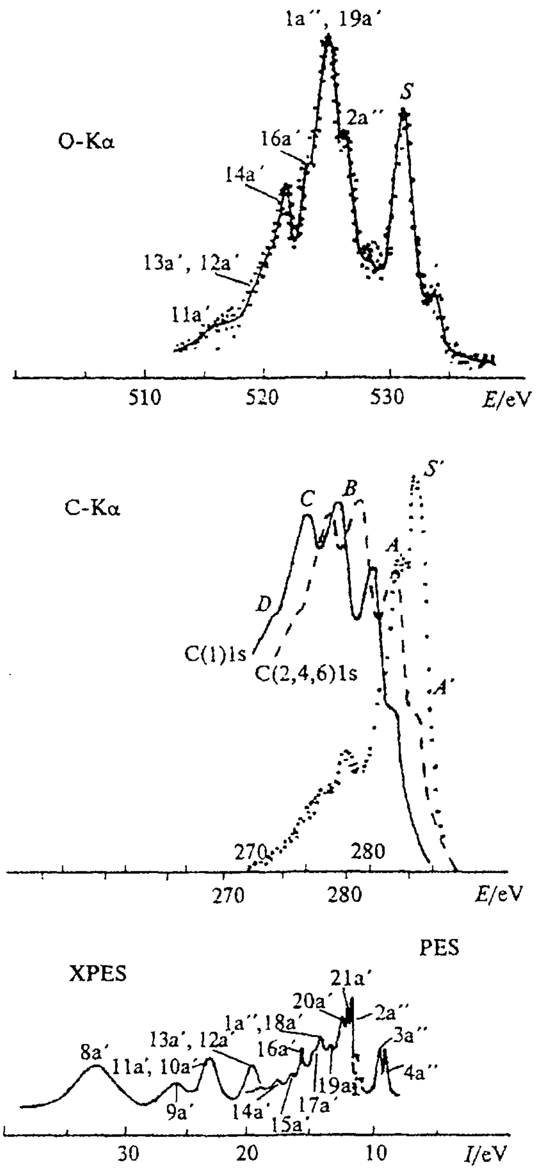

Fig. 2. The X-ray spectra of the gas phase, photoelectron spectrum (He(I)),[5] and the high-energy region of the XPES (Al-K$\alpha_{1,2}$)[16] of the PhOH molecule: experimental spectra are shown as dots; solid and dashed lines correspond to smoothed spectra (the C-Kα spectrum was corrected taking into account the efficiency of the analyzer crystal).

using the example of the F-Kα spectra[1]), the intrinsic fluorescence of the analyzer crystal, as well as the anomalous (non-Bragg) reflection. This maximum is present in all spectra of oxygen-containing compounds studied in this series of works.

The phenol molecule (the point symmetry group C_s) has been studied by quantum-chemical methods,[5,12—16] photoelectron spectroscopy,[5,12,13,17—22] X-ray photoelectron spectroscopy,[16] and X-ray electron spectroscopy.[11,15,16,23] The O1s satellite lines caused by multielectron processes have been studied theoretically and experimentally.[15,16,23] Previously,[4,24] we have obtained X-ray emission spectra of somewhat lower resolution and lower intensity (they were not interpreted).

The X-ray emission spectra (EI) (Fig. 2) were compared with one another taking into account the positions of the inner levels on a unified scale of ionization potentials and matched with the PES (see Ref. 5) and the high-energy region of the X-ray photoelectron spectra (XPES).[16] The C-Kα spectrum was referenced to the scale of ionization potentials using the C(1)1s level (solid line in Fig. 2). Other C1s levels (C(2,6)1s, C(3,5)1s, and C(4)1s) can also be used. In this case, the spectrum is shifted along the scale of ionization potentials. The energies of these levels have been determined previously.[11] (Since the data on the C(2,6)1s and C(4)1s levels are identical, they will be denoted as C(2,4,6)1s levels.) The C-Kα spectrum referenced using the C(2,4,6)1s level is shown in Fig. 2 as a dotted line. The use of the C(3,5)1s level for the reference would result in an X-ray spectrum of carbon which would be shifted only by 0.4 eV relative to the preceding spectrum; for this reason, it is not shown

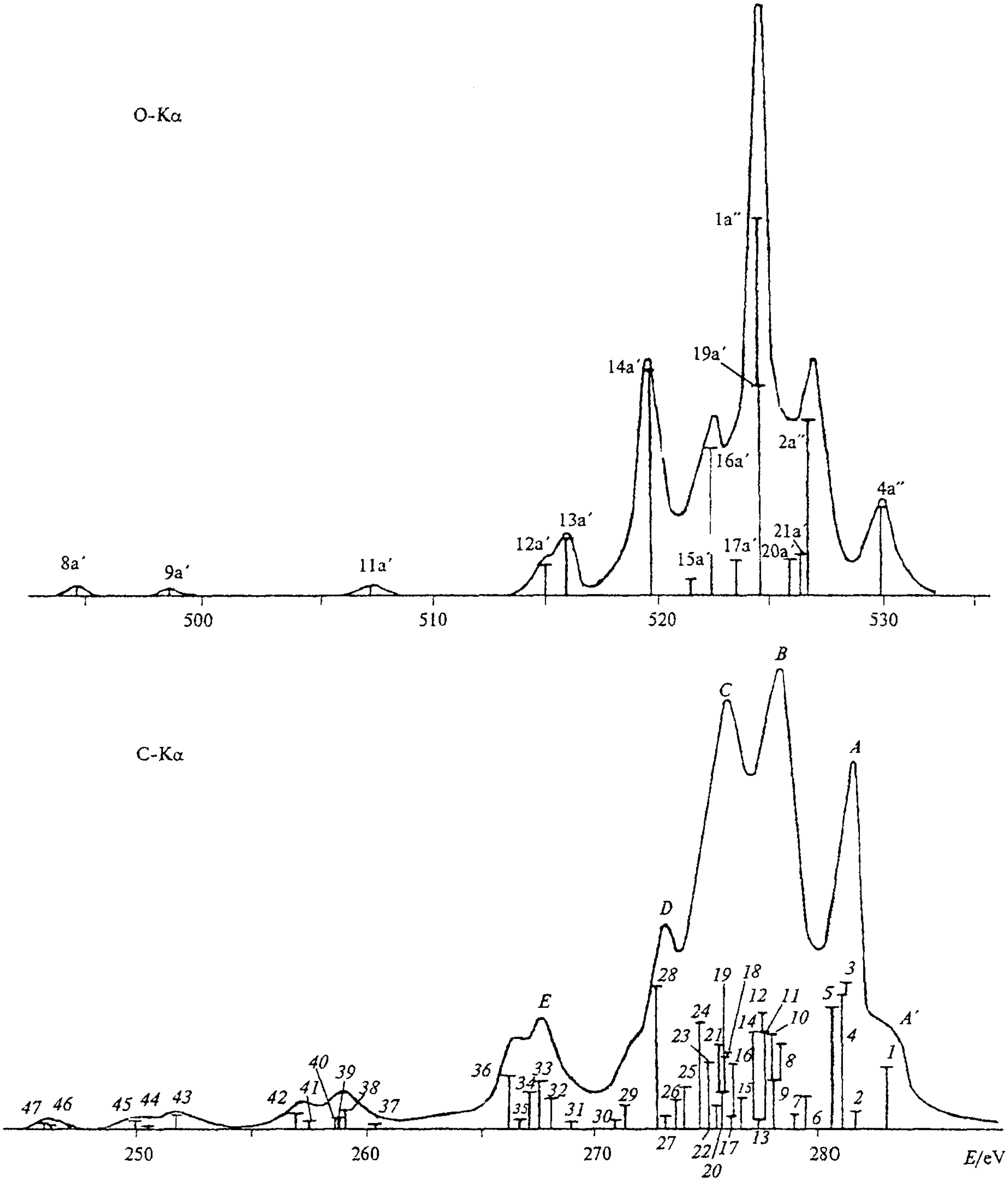

Fig. 3. Theoretical X-ray spectra of PhOH constructed on the basis of the MNDO calculations (assignment of lines is given in Table 1).

in Fig. 2. Theoretical spectra constructed using the results of the MNDO calculations are presented in Fig. 3. They were assigned using the C(1)1s level as a reference. The C-Kα spectrum was constructed using the experimental X-ray electron spectra.

Before we begin interpreting the spectra, let us note that MOs wih the a″ symmetry belong to the $\pi_{\perp}$-system (the 2p atomic orbitals (AOs) are perpendicular to the molecular plane), while MOs with the a′ symmetry consist of the 2p AOs lying in the molecular plane. These orbitals can also be divided into two types. The first type (the $\pi_{\parallel}$-system) includes such MOs of the phenyl ring in which the C(1)2p AO is perpendicular to the axis of the bond containing the first atom of the

Table 1. Assignment of the lines of the theoretical C-Kα spectrum of the phenol molecule (see Fig. 3)

Line	Transition	Line	Transition
1	4a″ → C(1)1s	*24*	17a′ → C(2,4,6)1s
2	4a″ → C(3,5)1s	*25*	16a′ → C(3,5)1s
3	4a″ → C(2,4,6)1s	*26*	16a′ → C(2,4,6)1s
4	3a″ → C(3,5)1s	*27*	15a′ → C(3,5)1s
5	3a″ → C(2,4,6)1s	*28*	14a′ → C(1)1s,
6	21a′ → C(1)1s		15a′ → C(2,4,6)1s
7	20a′ → C(1)1s	*29*	14a′ → C(3,5)1s
8	2a″ → C(3,5)1s	*30*	14a′ → C(2,4,6)1s
9	21a′ → C(3,5)1s	*31*	13a′ → C(1)1s
10	2a″ → C(2,4,6)1s	*32*	12a′ → C(1)1s
11	19a′ → C(1)1s,	*33*	13a′ → C(3,5)1s
	21a′ → C(2,4,6)1s	*34*	13a′ → C(2,4,6)1s
12	1a″ → C(1)1s,	*35*	12a′ → C(3,5)1s
	20a′ → C(3,5)1s	*36*	12a′ → C(2,4,6)1s
13	18a′ → C(1)1s	*37*	11a′ → C(1)1s
14	20a′ → C(2,4,6)1s	*38*	11a′ → C(3,5)1s
15	17a′ → C(1)1s	*39*	10a′ → C(1)1s
16	19a′ → C(3,5)1s	*40*	11a′ → C(2,4,6)1s
17	1a″ → C(3,5)1s	*41*	10a′ → C(3,5)1s
18	18a′ → C(3,5)1s	*42*	10a′ → C(2,4,6)1s
19	19a′ → C(2,4,6)1s	*43*	9a′ → C(1)1s
20	1a″ → C(2,4,6)1s	*44*	9a′ → C(3,5)1s
21	18a′ → C(2,4,6)1s	*45*	9a′ → C(2,4,6)1s
22	16a′ → C(1)1s	*46*	8a′ → C(3,5)1s
23	17a′ → C(3,5)1s	*47*	8a′ → C(2,4,6)1s

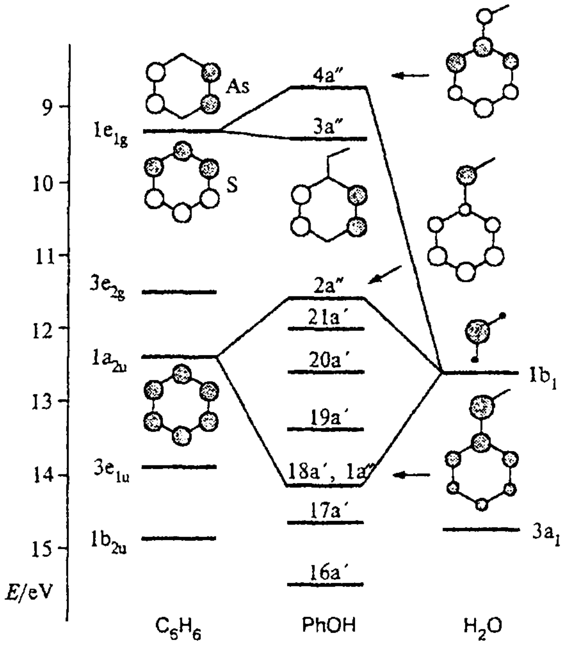

Fig. 4. Correlation of the $\pi_\perp$ molecular orbitals (using ionization potentials reported previously,[5] the structure of MOs was obtained from the MNDO calculations).

fragment (the orbitals of the π-bond in the molecular plane). The second type (the σ-system) includes MOs, in which the C(1)2p AO lies along the above bond axis.

The 4a″ MO is the highest occupied molecular orbital of phenol (Fig. 4). According to the data of the MNDO calculations, the contribution of the 2p AO of the oxygen atom to this orbital is small (see below). The 4a″ MO is formed as a result of the interaction between the orbital of the phenyl ring that correlates with the $1e_{1g}S$ MO of the benzene molecule and the orbital of the oxygen-containing fragment with the a″ symmetry that is correlated with the $1b_1$ MO of the water molecule.

The 3a″ MO with the same structure as the $1e_{1g}As$ MO of benzene (see Fig. 4) is the closest to the HOMO on a scale of bonding energies (or *I*). The first broad split band in the PES corresponds to the MOs considered (see Fig. 2). It is difficult to find a line analogous to the 4a″ MO in the O-Kα spectrum because of the small contribution of the 2p-AO of the oxygen atom to this MO and the superposition of an intense *S* satellite. The C-Kα spectrum of phenol uncorrected for the efficiency of the analyzer crystal (see Fig. 2) also contains a pronounced *S′* line. Its nature is close to that considered above for the *S* line of the O-Kα spectrum. When the C(1)1s level is used as a reference, the first PES band matches the *A′* "swelling" of the C-Kα spectrum (see Fig. 2). Hence, this "swelling" can be assigned to the highest-energy (the *E* scale) transition from the 4a″ MO to the C(1)1s level. The MNDO calculations make it possible to give the same explanation for the structure of the C-Kα spectrum (see Fig. 3). Referencing with the use of other C1s levels matches the first line in the PES (the 4a″ and 3a″ MOs) and the *A* maximum of the C-Kα spectrum. The theory confirms that this maximum is composed of transitions from the 4a″ and 3a″ MOs to these inner levels (see Fig. 3).

On the basis of the similarity between the photoelecton and C-Kα spectra (see Ref. 3) of benzene and those of phenol, one can expect that the 4a″ and 3a″ MOs originate from removal of the degeneracy of the $1e_{1g}$ MO of benzene and the symmetry change ($D_{6h} \rightarrow C_s$) that occurs on going from benzene to phenol: $1e_{1g} \rightarrow 1e_{1g}S + 1e_{1g}As \rightarrow 4a'' + 3a''$. The first line in the PES and that in the C-Kα spectrum of benzene corresponds to the $1e_{1g}$ MO. They have the same energies as the first lines of the corresponding spectra of phenol. This fact enables us to conclude that the first split band in the PES of phenol corresponds to the 4a″ and 3a″-MOs, while the first band in the C-Kα spectrum (the *A′* "swelling" and the *A* line, see Fig. 2) is composed of transitions from these orbitals to the inner levels.

The second broad band in the PES corresponds to the next group of MOs (the 2a″, and 21a′ and 20a′ orbitals) close to the group of MOs discussed above and corresponding to a higher bonding energy (see Fig. 2). It might be considered that they appear as follows on going from benzene to phenol: $1a_{2u} \rightarrow 2a''$, and $3e_{2g} \rightarrow 3e_{2g}$As + $3e_{2g}$S → 21a′ + 20a′. The 2a″ orbital should be considered as an antibonding orbital. It appears as a result of the interaction between the MO of the phenyl fragment that correlates with the $1a_{2u}$ MO of benzene and the orbital of the substituent corresponding to the $1b_1$ MO of water. In the case of interaction of such a type, the 1a″ MO is a bonding orbital, while the 2a″ MO is an antibonding orbital (see Fig. 4). According to the published data,[5] the 21a′ MO belonging to the $\pi_{\|}$-system of the molecule corresponds to the $3e_{2g}$As MO of benzene. The 20a′ MO analogous to the $3e_{2g}$S AO of benzene belongs to the σ-system of the molecule of phenol and one would expect mixing of the orbitals of the C(1) and oxygen atoms; however, the wave function of the 20a′ MO has a node on the C(1) atom. The MNDO calculation also shows that the electron density on this atom is low. Referencing matches the second broad band in the PES corresponding to these orbitals and the high-energy (the *E* scale) "swelling" of the O-Kα spectrum (see Fig. 2). The corresponding theoretical spectrum shows that the contributions of the 21a′ and 20a′ MOs to this "swelling" are low because of low populations of the O2p levels and a line that can be assigned to the 2a″ MO plays a key role (see Fig. 3).

The orbitals of the substituent that correlate with the $3a_1$ and $1b_2$ MOs of the water molecule correspond to all orbitals of phenol with the a′ symmetry. For this reason, it is impossible to determine which of them makes the predominant contribution to any of the MOs of this molecule.

Mutual referencing of the spectra shows that the second broad band in the PES corresponding to the 2a″, 21a′, and 20′ MOs matches mainly the *B* band of the C-Kα spectrum. Hence, the latter is mainly composed of lines that appear as a result of transitions from these MOs, which is also confirmed by theoretical investigations (see Fig. 3).

The second broad band in the PES and the second line of the C-Kα spectrum of benzene corresponds to the $3e_{2g}$ and $1a_{2u}$ MOs (see Ref. 4). Their energies are equal to those of the second broad band in the PES of phenol and the second band of the C-Kα spectrum (line *B*, see Fig. 2). Taking into account the correlation of the orbitals on going from benzene to phenol, it should be expected that this band in the PES of phenol is composed of the 2a″, 21a′, and 20a′ MOs. The second band of the C-Kα spectrum is formed by transitions from these orbitals to the inner levels.

The next orbital, close in its energy to those considered above, is the 19a′ MO. According to the data of MNDO calculations, the contribution of the 2p AO of oxygen to this orbital is ~30%. It is considered as an orbital of the lone electron pair of the oxygen atom.[13] Most likely, the portion of this MO of phenol corresponding to the carbon atoms is a combination of several orbitals of the phenyl fragment corresponding to different MOs of benzene. Additionally, this MO is a combination of orbitals corresponding to the $3a_1$ and $1b_2$ MOs of water. The structure of the 19a′ MO is such that no mixing of the AOs of the phenyl fragment and those of the substituent occurs due to the presence of the node of the wave function on the C(1) atom.[5] Matching of the PES and O-Kα spectrum shows that the 19a′ MO corresponds to the line of maximum intensity (see Fig. 2); according to the data of MNDO calculations (see Fig. 3), this line is a superposition of the lines corresponding to the 19a′ and 1a″ MOs. In this case, the contribution of the 2p AO of the oxygen atom to the 1a″ MO is approximately twice as large as that to the 19a′ MO. Referencing the PES and the C-Kα spectrum using the C(1)1s level matches the line in the PES corresponding to the 19a′ MO and the *B* line of the C-Kα spectrum. When other C1s levels are used as references, the above line in the PES matches the *C* line. The data of calculations show also that the transition from the 19a′ MO to the C(1)1s level participates in the formation of the *B* line along with other transitions, while those to the C(2,4,6)1s and C(3,5) levels participate in the formation of the *C* line of the C-Kα spectrum.

The bonding 1a″ MO is a combination of the orbital of the phenyl ring that correlates with the $1a_{2u}$ MO of benzene and the orbital of the substituent corresponding to the $1b_1$ MO of water. A comparison of the PES and C-Kα spectrum suggests that the line corresponding to the 1a″ → C(1)1s transition participates in the formation of the *B* maximum of the C-Kα spectrum, while lines composed of transitions to other inner levels of the ring participate in the formation of the *C* maximum (see Fig. 3).

The 18a′ MO correlates with the orbital of the phenyl ring analogous to the $3e_{1u}$As MO of benzene. According to the *ab initio*[5] and MNDO calculations performed in this work, this orbital must not appear in the O-Kα spectrum because of the small contribution of the 2p AO of oxygen (see Fig. 3). It follows from the above calculations that the contributions of the C(1)2p and C(4)2p AOs to the 18a′ MO are close to zero. The fact that this orbital correlates with the $3e_{1u}$As MO of the benzene molecule, which has nodes of the wave function on the same atoms, makes it possible to draw the same conclusion. Referencing with the use of the C(2,4,6)1s and C(3,5)1s levels matches the analog of the 18a′ MO in the PES and the *C* line of the C-Kα spectrum. A theoretical spectrum constructed on the basis of results of MNDO calculations confirms the participation of the 18a′ → C(2,4,6)1s and 18a′ → C(3,5)1s transitions in the formation of the *C* line (see Fig. 3).

The next (considering the *I* scale), the 17a′ MO, correlates with an orbital of the phenyl fragment similar to the $3e_{1u}$S MO of benzene and can be considered as an orbital of the σ-bond between the fragments (see, for instance, Ref. 5). According to the MNDO calculations, the contribution of the 2p AO of oxygen to this orbital is relatively small (see Fig. 2). Referencing PES and the C-Kα spectrum with the use of the C(1)1s level makes it possible to determine the position of the transition from the 17a′ MO to the C(1)1s level that matches the minimum between the *B* and *C* lines on the energy scale. The line obtained from the MNDO calculations has the same position (see Fig. 3). When other inner levels are used as reference, the line in the PES corresponding to the 17a′ MO matches the *C* line of the X-ray spectrum of the carbon atom. Hence, transitions from the 17a′ MO to the C(2,4,6)1s and C(3,5)1s levels participate in the formation of the *C* maximum along with other transitions, as is predicted by theory.

According to calculations (see, for instance, Ref. 5), the 16a′ MO close to the MOs discussed above belongs to the system of $\pi_{\parallel}$-orbitals and correlates with the $1b_{2u}$ MO of the benzene molecule. Referencing the PES and the O-Kα spectrum makes it possible to argue that the low-energy "swelling" (the *E* scale) of the dominant line of the X-ray spectrum of oxygen is an analog of the 16a′ MO (see Figs. 2 and 3), while referencing the PES and the C-Kα spectrum shows that the 16a′ → C(1)1s transition participates in the formation of the *C* line of the latter. This is confirmed by the theoretical spectrum (see Figs. 2 and 3). Both experimental and theoretical data show that along with other transitions, those from the 16a′ MO to other inner levels of the phenyl fragment are responsible for the appearance of the *C* and *D* lines of the C-Kα spectrum.

The 15a′ MO that correlates with the orbital of the phenyl fragment, which in turn coresponds to the $2b_{1u}$ MO of the benzene molecule, makes a small contribution to the O-Kα spectrum of phenol (see Fig. 3). Both the experiment and theory show unambiguously that the 15a′ MO has a lower energy as compared to the 16a′ MO and that in this spectrum it lies in the low-energy region (the *E* scale) relative to the line corresponding to the 16a′ MO (see Figs. 2 and 3). According to the *ab initio* calculation,[5] the wave function of the orbital in question has a node on the C(1) atom. Based on the experimental and theoretical data, one can conclude that transitions from the 15a′ MO to the C(2,4,6)1s and C(3,5)1s levels also participate in the formation of the *D* line and that the first transition makes the dominant contribution.

The third band in the benzene PES is composed of transitions from the $3e_{1u}$, $1b_{2u}$, and $2b_{1u}$ MOs. A comparison of the PES of benzene and that of phenol shows that this band corresponds to several lines. Taking into account the correlation of orbitals on going from benzene to phenol, they can be identified as lines due to transitions from the 18a′, 17a′, 16a′, and 15a′ MOs. The third band of the C-Kα spectrum of benzene is identical to the *C* band of the corresponding spectrum of phenol (see Fig. 2) and is composed of transitions from these MOs.

The 14a′ MO of the phenol molecule correlates with an orbital of the phenyl ring analogous to the $3a_{1g}$ MO of benzene. This is an orbital of the σ-bond between the fragments (see Ref. 5). Its unambiguous analog in the O-Kα spectrum matches the corresponding line in the PES when referencing the spectra (see Figs. 2 and 3). When the PES and the C-Kα spectrum are referenced, transitions from this MO appear to participate in the formation of the *D* line. This conclusion agrees with theory (see Figs. 2 and 3).

The 13a′ MO that correlates with the orbital of the phenyl fragment similar to the $2e_{2g}S$ MO of the benzene molecule is the next orbital close in bonding energy. Correspondingly, the 12a′ MO correlates with the $2e_{2g}As$ MO. Transitions from these two orbitals of PhOH form one band in the XPES (see Fig. 2). The 2s AOs of the oxygen and carbon atoms make considerable contributions to these orbitals; therefore, since transitions from the 2p AOs make small contributions to the corresponding X-ray spectra, analogs of the 13a′ and 12a′ orbitals have low intensities (see Figs. 2 and 3). Referencing the XPES and the X-ray spectrum of oxygen suggests that lines corresponding to the 13a′ and 12a′ MOs form a small low-energy "swelling" (the *E* scale) of the intense line corresponding to the 14a′ MO. These MOs have not been investigated in the experimental C-Kα spectrum since attempts at recording a spectral region with a transition energy lower that ~270 eV failed (see Fig. 2) because of low reflectivity of the analyzer crystal in this region. (Previously,[6] this issue has been covered in the literature.) The *E* line in the theoretical X-ray emission spectrum of carbon corresponds to analogs of the 13a′ and 12a′ MOs (see Fig. 3).

One can establish the following correlation for the 11a′ and 10a′ MOs on going from benzene to phenol: $2e_{1u} \rightarrow 2e_{1u}S + 2e_{1u}As \rightarrow$ 11a′ + 10a′. These MOs, as well as the 13a′ and 12a′ orbitals discussed above, are mainly composed of the 2s AOs of the oxygen and carbon atoms. According to the MNDO data, one would expect them to be manifested in the X-ray spectra because of the small contributions of the 2p AOs of oxygen and carbon (see Fig. 3). Referencing the XPES and the O-Kα spectrum shows that the low-energy structure of the last line corresponding to the 14a′ MO in the O-Kα spectrum can be considered as an analog of the 11a′ MO. It is hardy probable to reveal the 10a′ MO in this spectrum, since the MNDO calculations show that the populations of the 2p levels of the oxygen atom are close to zero. It is also impossible to record transitions from the 11a′ and 10a′ MOs in the C-Kα spectrum because of the low efficiency of reflection of the analyzer crystal in the low-energy region. The degree of their participation in the formation of this spectrum can only be judged from the theoretical pattern (see Fig. 3). The 2s AOs of carbon atoms also make a considerable contribution to the orbital of benzene that correlates with the 11a′ and 10a′ MOs of phenol.[5] On the other hand, these orbitals also correlate with the $2a_1$ MO of the water molecule with a large contribution of the 2s AOs of oxygen.

The 9a′ and 8a′ MOs are the lowest-lying valence orbitals of the phenol molecule. The 9a′ orbital is an antibonding orbital while the 8a′ MO is a bonding orbital with respect to the combination of the orbital of the phenyl fragment corresponding to the $2a_{1g}$ MO of benzene and the orbital of the substituent correlated with the $2a_1$ MO of the water molecule. They participate in the σ-bond between the phenyl ring and the substituent and are mainly composed of the 2s AOs of the oxygen and carbon atoms, as well as their analogs in the benzene and water molecules. The 9a′ and 8a′ MOs almost do not participate in the formation of X-ray spectra because of the low contribution of the 2p AOs of the oxygen and carbon atoms (see Figs. 2 and 3). It was possible to record analogs of transitions from these subvalent MOs composed mainly of the 2s AOs of oxygen, for instance, in the O-Kα spectra of ice[25] and Li_3PO_4[26], due to the presence of a small contribution of the 2p AO of oxygen in these MOs.

The last three lines in the XPES of benzene (see Ref. 16) correspond to the $2e_{2g}$, $2e_{1u}$, and $2a_{1g}$ MOs. Their energies are close to those of the three lines of the analogous spectrum of phenol.[16] This makes it possible to assign them in accordance with the following correlation: $2e_{2g} \rightarrow 2e_{2g}S + 2e_{2g}As \rightarrow 13a' + 12a'$, $2e_{1u} \rightarrow 2e_{1u}S + 2e_{1u}As \rightarrow 11a' + 10a'$, and $2a_{1g} \rightarrow 9a'$. The last line in the XPES of phenol corresponds to transitions from the 8a′ MO (see Fig. 2) that also correlates with the $2a_{1g}$ MO of benzene.

The lower-lying orbitals are atomic orbitals, and their energies were determined by X-ray electron spectroscopy: 7a′, (C(4)1s); 6a′, 5a′(C(3,5)1s); 4a′, 3a′(C(2,6)1s); 2a′(C(1)1s), and 1a′(O1s). The energy of the C(4)1s level is equal to that of the C(2,6)1s level and is less than that of the C(3,5)1s level.

Let us consider an interaction over the $\pi_\perp$-system consisting of four MOs with the a″ symmetry (see Fig. 4). It is composed of three MOs of the phenyl ring that correlate with the $1e_{1g}$ and $1a_{2u}$ MOs of benzene and the $1b_1$ MO of water. The 3a″ MO of phenol correlates with the $1e_{1g}As$ MO of benzene and is occupied only by the electrons of carbon atoms. Its energy is 0.14 eV higher than that of the corresponding MO of benzene (according to PES data[5]), which is associated with the transfer of the electron density over the σ-system from the benzene ring to the electronegative oxygen atom (the inductive effect).[3] Thus, only three orbitals forming the 4a″, 2a″, and 1a″ MOs of phenol participate in the covalent interaction. The contribution of the 2p AO of oxygen to the antibonding 4a″ MO is ~14% (according to the MNDO calculations). The interaction occurs mainly between orbitals of the $1a_{2u}$ MO type of benzene and those of the $1b_1$ MO of water with the formation of the antibonding 2a″ and the bonding 1a″ MOs. The contribution of the 2p AO of oxygen to these orbitals is ~25% and ~56%, respectively.

Let us consider the theoretical conclusions from the viewpoint of the X-ray spectral experiment. Let us compare the O-Kα spectra of the water and phenol molecules (see Figs. 1 and 2). The high-energy line is the most intense in the spectrum of water (the *E* scale, the nature of the maxima of higher energies was considered above). Hence, it is due to transitions from the HOMO. Transitions from the 2p-AO of the oxygen atom make the largest contribution to this line as compared to other AOs. Analysis of the spectrum showed that the intense line should be correlated with the $1b_1$ MO, which is an orbital of the lone electron pair of the O atom. A transformation of the spectrum on going from the water molecule to the phenol molecule occurs in such a way that the most intense lines are not composed of transitions from the higher occupied MOs, but of those from the lower-lying orbitals (see Fig. 2). Matching of the X-ray spectra of phenol with eah other and with the PES leads to the conclusion that the $2p_\pi$ AOs of oxygen make the largest contribution to the 2a″ and 1a′ MOs (see Fig. 2). Decomposition of the experimental O-Kα spectrum into individual components (Lorentzian lines) shows that the ratio of the contributions of the $O2p_\pi$ AO to the 1a″ and 2a″ MOs is ~2.8, whereas the MNDO calculations lead to a value of ~2.2. According to X-ray spectral data, PES,[5] and *ab initio*[5] and MNDO calculations, the difference in the energies of these orbitals is ~1.6 eV, ~2.6 eV, ~2.9 eV, and ~2.2 eV, respectively.

A comparison of the O-Kα spectra of the water and phenol molecules shows that three orbitals (the 4a″, 2a″, and 1a″ orbitals) are mainly responsible for the contribution of the electron density of oxygen to the $1b_1$ MO if the hydrogen atom in the water molecule is replaced by a phenyl substituent. This is just the reason for decreasing the relative intensity of the line in the spectrum of the phenol molecule that can be correlated with the $1b_1$ MO of water.

Thus, the theoretically predicted increase in the conjugation between the phenyl ring and the substituent in the phenol molecule that occurs as the energy of the MOs of the $\pi_\perp$-system decreases was confirmed by the X-ray spectral experiment. Note that in the case of the phenol molecule and other molecules considered in this series of works,[1,3] the model of the mesomeric effect developed by C. K. Ingold[27] usually takes into account only the $\pi_\perp$-interaction between the phenyl ring and the substituent over the HOMO, ignoring that over lower-lying orbitals of the ring, which can be dominant in this case.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 96-03-33225a).

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Received March 3, 1997;
in revised form May 12, 1997