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## X-ray spectroscopic study of the electronic structure of benzene, monofluoro- and monochlorobenzene

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## X-ray spectroscopic study of the electronic structure of benzene, monofluoro- and monochlorobenzene

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**Abstract.** The carbon K-emission spectra of solid benzene, monofluoro- and monochlorobenzene were measured. These spectra together with photoelectron spectra and additional x-ray spectra enabled detailed information on the composition of molecular orbitals in terms of their atomic components to be obtained. The carbon K spectrum of benzene is interpreted on the basis of molecular orbital (MO) calculations for the free molecule and the intensity distribution is compared with a theoretical line spectrum representation of the x-ray emission.

### 1. Introduction

Since benzene and its derivatives are of fundamental importance in organic chemistry, the electronic structure of these compounds has frequently been the subject of experimental and theoretical investigations. On the experimental side especially photoelectron spectroscopy has considerably contributed to the elucidation of the electronic structure. By this method the binding energies of the individual orbitals can be determined accurately, but the composition of valence orbitals in terms of their atomic components is indicated only in an indirect way. One of the few methods which yield direct information on orbital composition is x-ray emission spectroscopy. As a consequence of the dipole selection rules only the electrons with p-like symmetry of the atom under consideration contribute to the K-emission spectra.

Unfortunately, in the region of ultrasoft x-rays ( $\lambda > 20 \text{ \AA}$ ) the application of x-ray emission spectroscopy to organic compounds has not provided very satisfactory results up to now. Using primary excitation, i.e. by electron bombardment, organic materials generally are decomposed very quickly. This difficulty can be overcome to a large extent by using synchrotron radiation for excitation. With this kind of excitation the x-ray K-emission spectra of carbon in solid benzene, monofluorobenzene  $\text{C}_6\text{H}_5\text{F}$  and monochlorobenzene  $\text{C}_6\text{H}_5\text{Cl}$  were obtained. The spectra are discussed together with available photoelectron spectra and in the particular case of benzene quantitative information on the C 2p components of the individual orbitals is obtained.

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## 2. Experiment

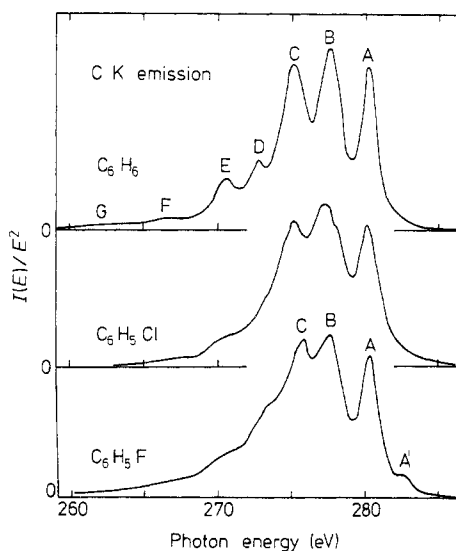
The x-ray spectra were excited in fluorescence using the synchrotron radiation of the storage ring DORIS at Hamburg. Details of the experimental set-up are described elsewhere (Kosuch *et al* 1978).

The samples were prepared *in situ* as thin films by condensing the gaseous substance on the sample holder cooled with liquid nitrogen. During the measurements the pressure in the sample chamber was about  $10^{-8}$  mbar. For the main parts of the spectra of benzene and for the halogen benzenes the resolution was 0.5 and 0.7 eV, respectively. The resolution was only about 2 eV in the low-energy region of the spectra (<270 eV) due to low intensities.

It was observed that the samples decomposed slowly even though synchrotron radiation was used for excitation. The process of decomposition can be observed by watching the change of the visible fluorescence light. After about twenty minutes exposure to the synchrotron radiation the first changes in the intensity distribution of the x-ray spectrum became apparent. To obtain spectra unaffected by products of decomposition, the samples were changed every five minutes. The final spectrum is built up from many (about 50) such short-time sections of the spectrum.

## 3. Results

The carbon K-emission spectra (C K-emission spectra) of benzene, monofluoro- and monochlorobenzene are shown in figure 1. As can be seen the main characteristics of the benzene spectrum are also present in the spectra of the halogenated benzenes: between 274 and 281 eV the spectra exhibit three intense peaks (A–C); towards lower energies four more features follow (D–G), but F and G are very weak. In general, the minima are less pronounced in the spectra of the halogenated benzenes. In the



**Figure 1.** C K-emission spectra of solid benzene, monochlorobenzene  $C_6H_5Cl$  and monofluorobenzene  $C_6H_5F$ .

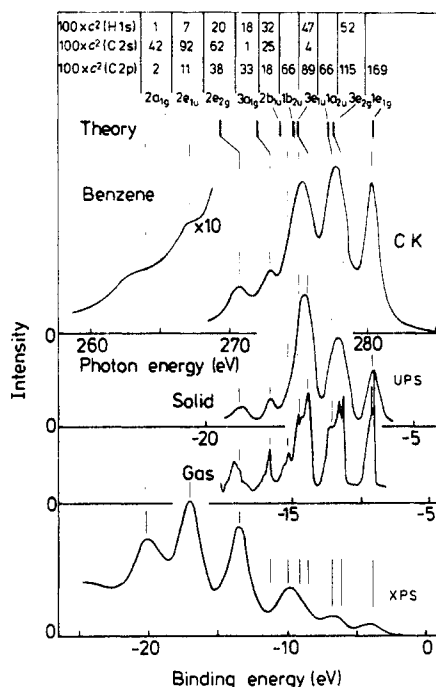
spectrum of monofluorobenzene the maximum C has clearly shifted towards higher energies; at the high-energy limit of the spectrum an additional feature A' shows up which will be discussed below.

The C K-emission spectra of the halogenated benzenes are reported here for the first time. The C K-emission band of benzene has already been measured by several authors (Mattson and Ehlert 1968, Werme *et al* 1973, Khel'mer *et al* 1976), but our spectrum was measured with considerably improved resolution. Some of the earlier measurements show features not present in our spectrum. We suppose that these additional features are caused by decomposition products, since these spectra were measured using primary excitation. In figure 3 a plot of the originally obtained data for benzene is shown. After we had finished the measurements (Tegeler *et al* 1978), our result was confirmed by Gilberg *et al* (1978) who measured the spectrum also in fluorescence using the radiation of a rotating anode high-power x-ray tube.

## 4. The electronic structure of benzene

### 4.1. Interpretation of the x-ray and photoelectron measurements

In figure 2 the C K-emission band of benzene is shown together with available photoelectron spectra (Demuth and Eastman 1974, Grobman and Koch 1979, Riga *et al* 1977). The x-ray spectrum and the photoelectron spectra are aligned by the binding energy of the C 1s level determined by x-ray photoelectron spectroscopy (XPS).



**Figure 2.** C K-emission spectrum of solid benzene together with UPS measurements of solid (Demuth and Eastman 1974) and gaseous (Grobman and Koch 1979) benzene, an XPS measurement of solid benzene (Riga *et al* 1977) theoretical orbital energies (von Niessen *et al* 1976) and calculated orbital composition (Stevens *et al* 1971).

The energies of the upper valence orbitals and their identification are known very accurately particularly from ultraviolet photoelectron spectroscopy (UPS) studies of gaseous benzene. A comparison with UPS measurements for solid benzene shows that in the solid state all orbitals are shifted to smaller binding energies by  $1.15 \pm 0.1$  eV (Grobman and Koch 1979). Since all orbitals are shifted by the same amount, the electronic structure of the benzene molecule remains, on the whole, unchanged by solidification, the molecule being bound by weak van der Waals forces.

It is remarkable that the ultraviolet photoelectron (UP) spectrum of solid benzene (resolution 0.1 eV) does not show sharper or additional structural features as compared with the C K-emission spectrum (resolution 0.5 eV). Taking into account the experimental resolution, from both spectra the same natural width of the features of 1.1 to 1.2 eV is obtained. It may therefore be anticipated that even if there were considerable improvements in the instrumental resolution the shape of the C K spectrum would scarcely be changed.

As shown in figure 2, the energetic positions of the structural features in the various spectra agree fairly well and therefore permit the determination of the orbital binding energies in an unambiguous way. Thus from x-ray and photoelectron spectra a consistent picture of the electronic structure is obtained. The orbital energies of the ten occupied valence orbitals in figure 2 are marked by vertical lines. For closely adjacent orbitals the determination of the orbital energies is based on the UP spectrum of gaseous benzene.

The MO of benzene have been calculated by numerous authors (Riga *et al* 1977, Bigelow 1977, von Niessen *et al* 1976 and references therein). In the top part of figure 2 the theoretical results of Von Niessen *et al* (1976) are indicated by vertical bars; the positions refer to the energy scale of gaseous benzene. The calculations of these authors are based on an *ab initio* many-body approach and include the effects of electron correlation and reorganisation beyond the one-particle approximation; such detailed calculations were not carried out for the two lowest orbitals,  $2a_{1g}$  and  $2e_{1u}$ . The theoretical results concerning energy position and assignment of the structural features are confirmed by our measurements. In this connection it should be emphasised that photoemission and x-ray emission result in the same energy position of the structural features, though the physical process leading to this features is different.

At the top of figure 2 is shown the atomic composition of the orbitals according to Stevens *et al* (1971). In this paper the molecular orbitals are represented as a linear combination of the atomic orbitals and the numbers in the table refer to the sum of the squared coefficients  $c^2$  of the atomic contributions with H 1s, C 2s and C 2p character. Similar results for the composition of the orbitals were published by Hoffmann (1963).

The composition of the orbitals is reflected by the intensity distribution of the various spectra. The x-ray photoelectron (xp) spectrum of benzene is dominated by C 2s character. Accordingly in this spectrum the more tightly bound orbitals are the most intense. By contrast in the UPS measurements the cross section for photoemission is largest for C 2p electrons. Therefore this spectrum resembles much more closely the x-ray C K-emission spectrum which reflects pure C 2p character (Manne 1970). For a more quantitative comparison, however, the energy-dependent transmission of the energy analyser used for the UP spectrum must be taken into account. It should be pointed out that, even after these corrections have been made, it would appear that the low-lying orbitals of the UP spectrum are still rather more intense than in the C K x-ray spectrum. This point needs further consideration.

#### 4.2. Intensity distribution of the C K-emission spectrum

In MO theory the molecular orbitals  $\psi_i$  can be represented by a linear combination of the atomic orbitals  $\phi_j$ :

$$\psi_i = \sum_j C_{ji} \phi_j.$$

The contribution of the molecular orbitals  $\psi_i$  to the C K-emission spectrum of benzene is then given by the sum of the squares of the coefficients of the C 2p atomic orbitals  $\phi_{C2p}$  of the six carbon atoms (Manne 1970):

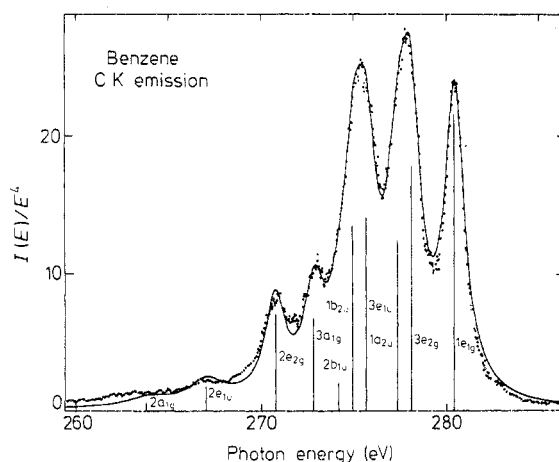
$$I(E)_i \sim E^4 \sum_{j=C2p} C_{ji}^2.$$

The C K-emission spectrum then results from

$$I(E)_{CK} = \sum_i I(E)_i.$$

For a quantitative comparison with the theoretical results the C K-emission was plotted as  $I(E)/E^4$  against  $E$  and then decomposed into Lorentzians positioned at the orbital energies determined in figure 2. This decomposition is shown in figure 3 where the vertical lines indicate energy position and height of the Lorentzians and the solid line is the sum of all Lorentzians; the dots represent the measured data. For the upper eight orbitals the Lorentzians have a halfwidth (FWHM) of 1.3 eV. For the two lowest orbitals the halfwidth is 2.5 eV. The broadening of the lower orbitals is caused by lower experimental resolution (only 2.0 eV) and Auger broadening which increases with increasing ionisation energy. Table 1 shows the comparison of the integral intensities of the Lorentzians with two theoretical results (Stevens *et al* 1971, Manne 1970).

The calculated and the experimentally determined intensities are normalised so that the sum of the contributions of all orbitals is 100. Generally there is agreement between the theoretical and the experimental results; but for the two lowest orbitals,  $2a_{1g}$  and  $2e_{1u}$ , smaller intensities are predicted by theory than are observed. For these two



**Figure 3.** Decomposition of the C K-emission spectrum of solid benzene into Lorentzians positioned at the experimentally determined MO energies; vertical lines: position and height of Lorentzians; full curve: sum of Lorentzians; dotted curve: experimental data.

**Table 1.** Experimentally determined and calculated contributions of the individual molecular orbitals to the C K-emission spectrum of benzene.

Orbital	Experiment	Theory	
		R Manne (1970)	Stevens <i>et al</i> (1971)
2a <sub>1g</sub>	1.7 ± 0.9	0	0.4
2e <sub>1u</sub>	3.3 ± 1.3	0.3	1.9
2e <sub>2g</sub>	7.1 ± 0.9	4.4	6.3
3a <sub>1g</sub>	6.8 ± 0.8	5.1	5.4
2b <sub>1u</sub>	2.3 ± 1.3	3.4	2.9
1b <sub>2u</sub>	13.5 ± 2.5	11.0	10.8
3e <sub>1u</sub>	14.1 ± 2.5	14.6	14.6
1a <sub>2u</sub>	12.3 ± 2.5	10.6	10.8
3e <sub>2g</sub>	17.8 ± 2.5	22.4	19.0
1e <sub>1g</sub>	21.6 ± 1.2	27.9	27.8

orbitals further investigations are required to determine the importance of configuration interaction effects which might produce rather more intense peaks in the C K-emission spectrum than those anticipated from the C 2p components alone.

At rather smaller binding energies it should be noticed that the orbital 1e<sub>1g</sub> is contributing much less to the x-ray emission spectrum than predicted by theory. This discrepancy seems the more remarkable because the agreement between theory and experiment is much better for the 1a<sub>2u</sub> orbital. Both are  $\pi$  orbitals which for symmetry reasons can only contain C 2p<sub>z</sub> components, the 1e<sub>1g</sub> orbital being occupied with four  $\pi$  electrons and the 1a<sub>2u</sub> orbital with two. The prediction of the relative intensities of the x-ray peaks for the two orbitals is about 2.6:1, but experimentally a value of only (1.8 ± 0.4):1 is observed. This difference is probably due to the neglect of cross terms of the type

$$\langle \phi(\text{C } 1s)_A | e r | \phi(\text{C } 2p)_B \rangle$$

where A and B are adjacent atoms. When wavefunctions with inclusion of overlap are used, the contributions of such terms to the overall calculated intensity will not be negligible as was assumed by Manne (1970). It is remarkable that the experimental result is easily understood in terms of simple electron counting, i.e. e<sub>1g</sub>: 4 C 2p<sub>z</sub>—and a<sub>2u</sub>: 2 C p<sub>z</sub>—electrons.

## 5. The electronic structure of monochloro- and monofluorobenzene

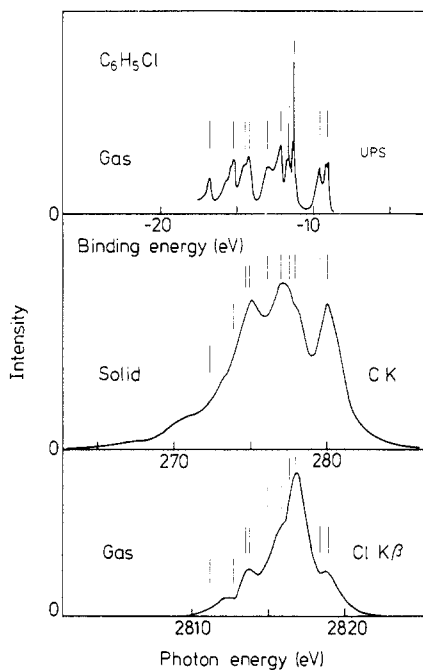
If in benzene one hydrogen atom is replaced by a halogen atom, the symmetry of the molecule is reduced from D<sub>6h</sub> to C<sub>2v</sub>, which results in the lifting of degeneracy of some orbitals. This, together with the increased number of electrons, causes the number of independent energy levels to be increased from 10 to 18. Particularly for those orbitals in which the contribution of the hydrogen atoms is partially replaced by that of the halogen atom, an increase of the binding energy is to be expected. Most of the halogen p electrons are concentrated as lone pairs, the energy position of which depends upon the particular halogen.



In the monohalogen derivatives of benzene there are differently bound carbon atoms and this may, to some extent, cause the minima in the halogenated benzenes to be less pronounced than in those of benzene (see figure 1). The C 1s levels of the carbon atoms which are bound to the halogen atom are shifted to higher binding energies compared with the C 1s levels of the other carbon atoms. As is known from xps measurements this chemical shift is also transmitted to the carbon atoms bound to the hydrogen atoms and causes a variation of the C 1s binding energy of some tenths of an electron volt (Clark *et al* 1972a, 1975). The C 1s level of the carbon atom bound to the halogen atom, compared to the other carbon atoms, is shifted to higher binding energies by about 1.4 eV for  $\text{C}_6\text{H}_5\text{Cl}$  and about 2.6 eV for  $\text{C}_6\text{H}_5\text{F}$ , on the average. Therefore, transitions from the same valence orbital to a C 1s vacancy in the x-ray spectrum can appear with photon energies which differ by these energies. Since maximum A' on the high-energy side of the C K spectrum of  $\text{C}_6\text{H}_5\text{F}$  is separated by about 2.6 eV from maximum A, it therefore may be interpreted as a transition from the same valence orbital to the most tightly bound C 1s level. In the case of chlorobenzene one observes a less steep decrease in intensity to the high-energy end of the spectrum than for benzene. Since, however, the energy difference is only 1.4 eV no additional feature in the spectrum is observed.

### 5.1. Monochlorobenzene

In figure 4 are shown the C K-emission spectrum of solid monochlorobenzene together with the chlorine  $\text{K}\beta$ -emission spectrum ( $\text{Cl K}\beta$ ) measured by Gilberg (1970) and a UP



**Figure 4.** C K-emission spectrum of solid monochlorobenzene  $\text{C}_6\text{H}_5\text{Cl}$  together with Cl  $\text{K}\beta$  spectrum (Gilberg 1970) and UP spectrum (Murrell and Suffolk 1972) of gaseous monochlorobenzene.

spectrum measured by Murrell and Suffolk (1972). The two latter measurements refer to gaseous samples.

As can be seen the C K and the Cl K $\beta$ -spectrum are quite different in their shapes. This strikingly illustrates that x-ray spectra are strongly governed by selection rules and as they probe the region of the 1 s atomic state of the atom under consideration they are closely related to the local partial density of states; consequently, distinctive statements about valence orbital composition can be made. The alignment of the two x-ray spectra to a common energy scale can be achieved unambiguously with the help of the C 1s and Cl 2p<sub>1/2,3/2</sub> energies which are available from XPS measurements (Clark *et al* 1975) and the Cl K $\alpha_{1,2}$  doublet (Gilberg 1969). The alignment of the x-ray spectra and the UP spectrum was performed using the positions of the structural features.

Part of the abundant structural details in the photoemission spectrum is also present in the x-ray spectra; the vertical lines in figure 4 indicate corresponding energies. The spike-shaped maximum in the UP spectrum at a binding energy of -11.5 eV has no analogy in the spectrum of benzene and since it corresponds with the main maximum of the Cl K $\beta$  spectrum, it must be attributed to the Cl 3p electrons. The C K spectrum of benzene is not greatly altered by the introduction of a chlorine atom even in the region of the main peak B. This shows that the intense Cl 3p components hardly modify the distribution of carbon 2p character at all. One therefore may assume that the main maximum of the Cl K $\beta$  spectrum has its origin in lone pair valence electrons of chlorine.

## 5.2. Monofluorobenzene

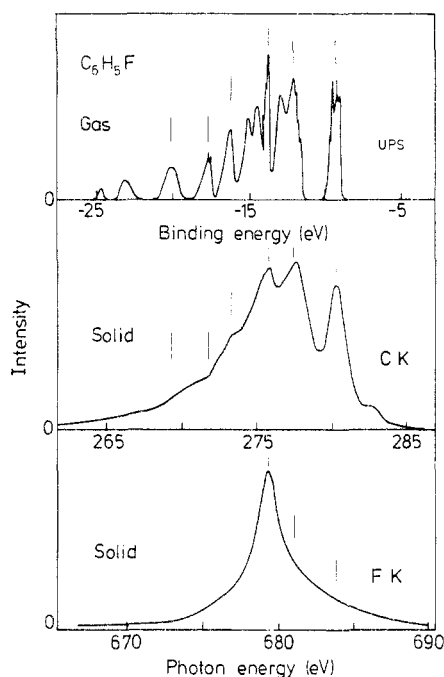
For solid monofluorobenzene both the C K and the F K spectrum have been measured. Since the resolution in the F K spectrum is only 1.3 eV, structural features which possibly are present on both sides of the main peak are not resolved. The two x-ray spectra together with an UPS measurement of gaseous monofluorobenzene (Potts *et al* 1972) are shown in figure 5. Other available UP spectra (Murrell and Suffolk 1972, Debies and Rabalais 1972) were measured also with gaseous samples and are quite similar with the one shown in figure 5. An alignment of all spectra is accomplished by means of the C 1s (of carbon not bound to fluorine) and F 1s energies obtained from XPS measurements (Clark *et al* 1972a).

By comparing figures 4 and 5 it is obvious that, with reference to the energy scale of the carbon spectra, the maximum of the F K spectrum is positioned at smaller energies (i.e. at higher ionisation energies) than the maximum of the chlorine spectrum. The same is also true for the most intense peaks of the UP spectra which represent the halogen p components. This is because the lone pair electrons in fluorine are more tightly bound than in chlorine.

For monochlorobenzene a number of MO calculations is available (Clark *et al* 1972b, Almlöf *et al* 1973, Yadav *et al* 1973a, b, Duke *et al* 1977), but the results refer only to the orbital energies and not to their compositions. Since for an experimental determination of the orbital energies the available UPS results are most suitable, the experimental and theoretical results will not be compared here.

## 6. Conclusions

The present work shows that it is possible to obtain emission spectra of organic compounds even in the ultrasoft x-ray region. In particular, for larger molecules with



**Figure 5.** C K and F K-emission spectrum of a solid monofluorobenzene together with an UP spectrum of a gaseous sample (Potts *et al* 1972).

different kinds of atoms x-ray spectroscopy is a powerful method of providing information concerning the atomic origin of the individual molecular orbitals which cannot be obtained by other spectroscopic methods. Thus for  $\text{C}_6\text{H}_5\text{F}$  and  $\text{C}_6\text{H}_5\text{Cl}$  the lone pair halogen p orbitals were clearly identified. In the case of benzene not only the identification of the valence orbitals was confirmed, but also the C 2p components of the orbitals were determined and compared quantitatively with theoretical results. Discrepancies between experimental and theoretical results for these C 2p components lead to the assumption that for a better interpretation of the C K emission spectrum of benzene, configuration interaction and cross transition effects should also be taken into account.

### Acknowledgments

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