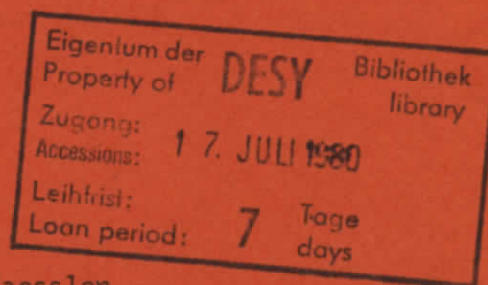X-RAY SPECTROSCOPIC STUDY OF THE ELECTRONIC STRUCTURE

OF BENZENE, MONOFLUORO- AND MONOCHLOROBENZENE

by

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X-Ray Spectroscopic Study of the Electronic Structure

of Benzene, Monofluoro- and Monochlorobenzene

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Abstract

*The C 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
C K-spectrum of benzene is interpreted on the basis of MO-
calculations for the free molecule, and the intensity distri-
bution is compared with a theoretical line spectrum represen-
tation of the X-ray emission.*

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1. Introduction

Since benzene and its derivatives are of fundamental importance
in organic chemistry, the electronic structure of these compounds
has been frequently the subject of experimental and theoretical
investigations. On the experimental side especially photo-electron
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 com-
position 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 spectro-
scopy. As a consequence of the dipole selection rules only the elec-
trons with p-like symmetry of the atom under consideration contribute
to the K-emission spectra.

Unfortunately, in the region of ultrasoft X-rays ($\lambda > 20$ Å) the appli-
cation of X-ray emission spectroscopy to organic compounds has not
provided very satisfactory results up to now. Using primary excitation
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 C_6H_5F and monochloro-
benzene C_6H_5Cl 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.

2. Experiment

The X-ray spectra were excited in fluorescence using the synchrotron
radiation of the storage ring DORIS at Hamburg. Details of the experi-
mental set-up are described elsewhere[1].

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
halogeno benzenes the resolution was 0.5 eV 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 decom-
position can be observed by watching the change of the visible
fluorescence light. After about 20 minutes exposure to the synchrotron
radiation the first changes in the intensity distribution of the X-ray
spectrum became apparent. To get spectra unaffected by products of de-
composition, 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 C K-emission spectra of benzene, monofluoro- and monochloro-
benzene are shown in fig. 1. As can be seen the main characte-
ristics of the benzene spectrum are also present in the spectra
of the halogenated benzenes: between 274 eV 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 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 further down.

The C K-emission spectra of the halogenated benzenes are reported
here for the first time. The C K-emission band of benzene has al-
ready been measured by several authors[2-4], but our spectrum was
measured with considerably improved resolution. Some of the earlier
measurements show features not present in our spectrum, which we
suppose to be connected with decomposition products, as these spectra
were measured primary excitation. In fig. 3 a plot of the originally
obtained data for benzene is shown. After we had finished the measure-
ments[5], our result was confirmed by Gilberg et al.[6] 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 fig. 2 the C K-emission band of benzene is shown together with
available photoelectron spectra[7-9]. The X-ray spectrum and the photo-
electron spectra are aligned by the binding energy of the C 1s-level
determined in the XPS-measurement[9].

The energies of the upper valence orbitals and their identification are known very accurately particularly from UPS-measurements 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 ± 0.1 eV [8]. 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 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 eV to 1.2 eV is obtained. It therefore may 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 fig.2 shows 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 fig. 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 MOs of benzene have been calculated by numerous authors (9-11 and references in 11). In the top part of fig. 2 the theoretical results of Niessen et al.[11] 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 reorganization 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 emphasized, 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 fig. 2 is shown the atomic composition of the orbitals according to Stevens et al.[12]. 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[13].

The composition of the orbitals is reflected by the intensity distribution of the various spectra. The 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[14]. 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 ψ_i can be represented by a
linear combination of the atomic orbitals φ_j:

$$\psi_i = \Sigma_j \, c_{ji} \, \varphi_j$$

The contribution of the molecular orbitals ψ_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 $\phi_{C\ 2p}$ of the six
carbon atoms[14]:

$$I(E)_i \sim E^4 \Sigma_{j=C\ 2p} \, c_{ji}^2$$

The C K-emission spectrum then results from

$$I(E)_{CK} = \Sigma_i \, I(E)_i$$

For a quantitative comparison with the theoretical results the C K-
emission was plotted as $I(E)/E^4$ vs. E, and then decomposed into
Lorentzians, positioned at the orbital energies determined in fig. 2.
This decomposition is shown in fig. 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 ionization energy.

Table 1 shows the comparison of the integral intensities of the
Lorentzians with two theoretical results[12,14].

The calculated and the experimentally determined intensities are
normalized 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 orbitals further investgations 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 $1e_{1g}$ 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
$1a_{2u}$ orbital. Both are π-orbitals which for symmetry reasons can
only contain C $2p_z$ components, the $1e_{1g}$ orbital being occupied
with four π-electrons, and the $1a_{2u}$ orbital with two. The predictions
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

$$< \phi(C1s)_A \, |e\vec{r}| \, \phi(C2p)_B >$$

where A and B are adjacent atoms. When wave functions with inclusion
of overlap are used, the contributions of such terms to the overall
calculated intensity will not be, as was assumed by Manne[14], negligible.
It is remarkable that the experimental result is easily understood in
terms of simple electron counting, i.e. e_{1g} : 4 C $2p_z$ - and a_{2u} : 2 C $2p_z$-
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_{6h} to C_{2v}, which results in 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 partially is 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 monohalogeno 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 fig. 1). The C 1s-levels of the carbon atoms which are bound to the halogen atom are shifted to higher binding energies compared to 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[15,16]. 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 C_6H_5Cl and about 2.6 eV for C_6H_5F, 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 C_6H_5F 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 fig. 4 are shown the C K-emission spectrum of solid monochlorobenzene together with the Cl Kβ-emission spectrum measured by Gilberg[17] and an UP-spectrum measured by Murrell and Suffolk[18]. The two latter measurements refer to gaseous samples.

As can be seen the C K- and the Cl K-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 1s 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 $2p_{1/2,3/2}$ energies which are available from XPS-measurements[16] and the Cl $K\alpha_{1,2}$ doublet[19]. 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 detail in the photoemission spectrum is also present in the X-ray spectra; the vertical lines in fig. 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 Kβ-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 Kβ - 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 are not resolved which possibly
are present on both sides of the main peak. The two X-ray spectra
together with an UPS-measurement of gaseous monofluorobenzene[20]
are shown in fig. 5. Other available UP-spectra[18,21] were measured
also with gaseous samples, and are quite similar with the one shown
in fig. 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[15].

By comparing figs. 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 ioni-
zation 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[22-25],
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 different kinds of atoms
X-ray spectroscopy is a powerful method to provide information
concerning the atomic origin of the individual molecular orbitals,
which cannot be obtained by other spectroscopic methods.
Thus for C_6H_5F and C_6H_5Cl the lone pair halogen p-orbitals clearly
were 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 theore-
tical results for these C 2p-components lead to the assumption that
for a better interpretation of the C K-emission spectrum of benzene
also configuration interaction and cross transition effects should
be taken into account.

Acknowledgements

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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[14]	Stevens et al.[12]
$2a_{1g}$	1.7 ± 0.9	0	0.4
$2e_{1u}$	3.3 ± 1.3	0.3	1.9
$2e_{2g}$	7.1 ± 0.9	4.4	6.3
$3a_{1g}$	6.8 ± 0.8	5.1	5.4
$2b_{1u}$	2.3 ± 1.3	3.4	2.9
$1b_{2u}$	13.5 ± 2.5	11.0	10.8
$3e_{1u}$	14.1 ± 2.5	14.6	14.6
$1a_{2u}$	12.3 ± 2.5	10.6	10.8
$3e_{2g}$	17.8 ± 2.5	22.4	19.0
$1e_{1g}$	21.6 ± 1.2	27.9	27.8

Figure Captions:

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

Fig. 2 C K-emission spectrum of solid benzene together with UPS-measurements of solid[7] and gaseous[8] benzene, an XPS-measurement of solid benzene[9], theoretical orbital energies[11] and calculated orbital composition[12].

Fig. 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 line: sum of Lorentzians; dotted curve: experimental data.

Fig. 4 C K-emission spectrum of solid monochlorobenzene C_6H_5Cl together with Cl Kβ-spectrum[17] and UP-spectrum[18] of gaseous monochlorbenzene.

Fig. 5 C K- and F K-emission spectrum of solid monofluorbenzene together with an UP-spectrum of a gaseous sample[20].
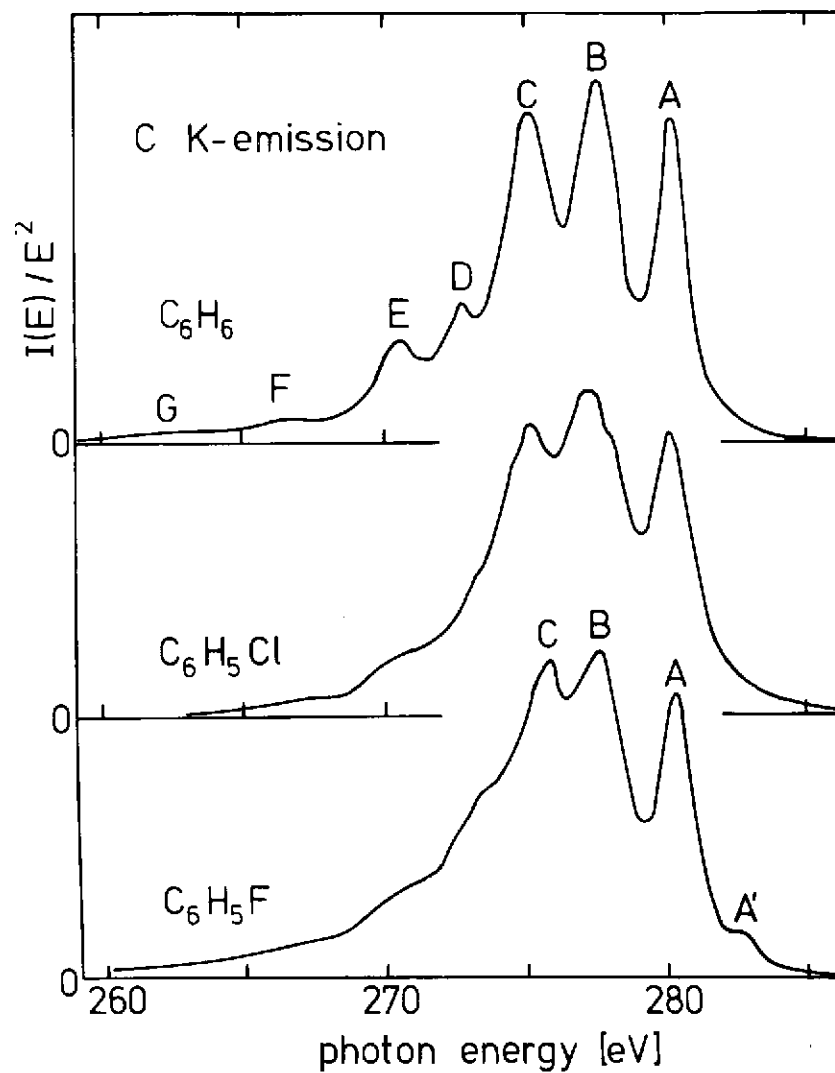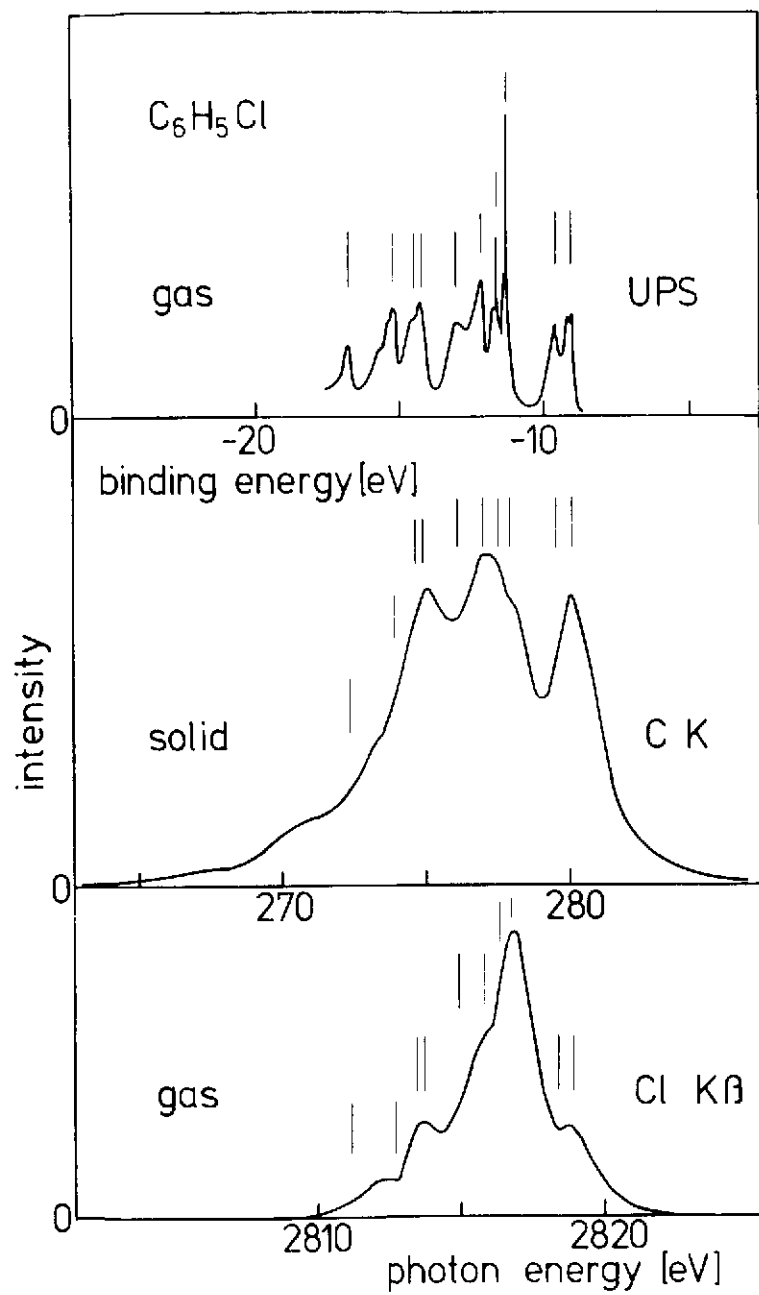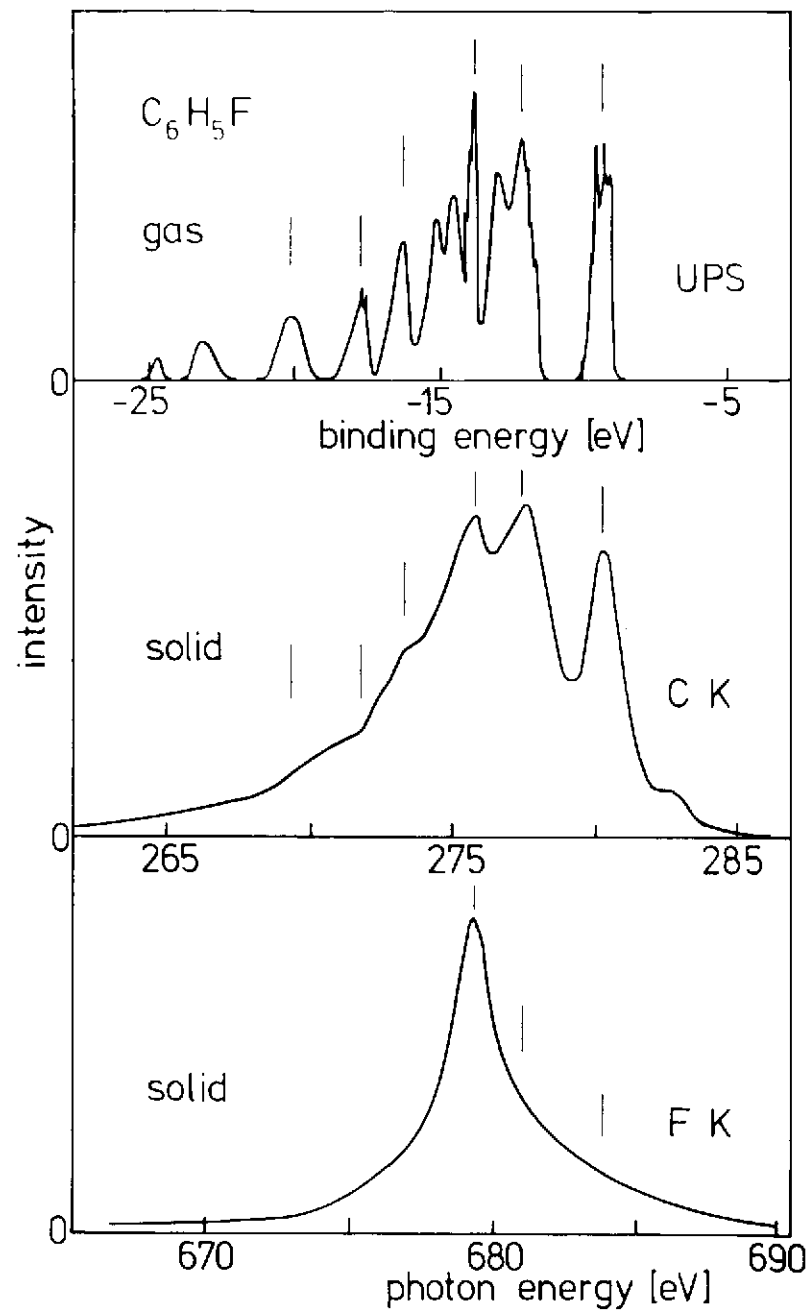

Fig. 1

Fig. 3

Fig. 2

Fig. 4

Fig. 5