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CARBON K-EMISSION SPECTRA AND ELECTRONIC STRUCTURE OF SOLID NAPHTHALENE AND ANTHRACENE

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Abstract

The carbon K-emission spectra of polycrystalline naphthalene and anthracene were measured. For naphthalene single crystals the carbon K-emission spectrum was also measured as a function of the take-off angle. The angular dependent intensity distribution of the spectra allows the contribution of the π- and σ-valence orbitals to be determined. As the size of the molecules increases the carbon K-spectra approach the spectrum of graphite. The experimental results are compared with photoelectron spectra and are discussed on the basis of MO-calculations for the free molecules.

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1. Introduction

In a preceeding paper we reported X-ray emission spectroscopic studies of the electronic structure of benzene and its halogenated derivatives (1). The present paper deals with corresponding investigations of naphthalene and anthracene.

As the size of the molecule is increased, the number of occupied orbitals increases rapidly. For instance in naphthalene there are 24 occupied orbitals (19 σ- and 5 π-orbitals) compared with 15 (12 σ- and 3 π-orbitals) in benzene. In general, experience suggests that the valence orbitals, for any particular molecule, cover an energy range of about 10 eV to 20 eV, so that for larger molecules the spacings between the orbitals get smaller and the spectral lines become blended together. This is particularly true for the condensed phase, where the spectra are broadened due to solid state effects.

For an unambiguous identification of the molecular orbitals, and for a reliable interpretation of the spectroscopic data, the application of various and complementary spectroscopic methods is necessary, such as, for instance, X-ray and ultraviolet photoelectron spectroscopy (XPS and UPS) and X-ray spectroscopy.

Because of the strong dipole selection rules X-ray emission spectroscopy enables the atomic composition of the electronic structure of valence band orbitals to be studied directly. Still more detailed information can be obtained, if the anisotropic emission of single crystals is studied by measuring the spectra at several directions of observation. By this means it is possible to separate the π- and σ-parts of the valence electrons. In the case of aromatic hydrocarbons this procedure is somewhat difficult, since these compounds form monoclinic crystals in which the two molecules of the unit cell are not parallel to each other, but as will be shown in this paper, a quantitative decomposition of the π- and σ-parts can still be achieved.

We observed that the overall shape of the spectra systematically changes with increasing molecular size towards that characteristic of solids. This can clearly be seen when comparing the spectra of the sequence benzene, naphthalene, anthracene, and graphite.

2. Experimental

For the investigation of the X-ray K-emission spectra of carbon (C K-emission spectra) the experimental set-up of FLEUR at the storage ring DORIS in Hamburg was used. For details of the spectrometer see ref. (2); the sample preparation has been described in a preceeding paper (1).

Special precautions were taken when the samples of naphthalene single crystals were mounted on the sample holder. To avoid surface contamination, or at least to reduce it to a tolerable amount, cooling with liquid nitrogen was not started unless the sample chamber was pumped down to less than 0.1 mbar. The orientation of the single crystals will be described below.

The resolution was 0.5 eV for the polycrystalline samples, and 0.7 eV for the naphthalene single crystals.

3. The anisotropic emission of naphthalene single crystals

The naphthalene molecule belongs to the point group D_{2h}. As a consequence of this symmetry the emission of the carbon K-radiation of a naphthalene molecule is anisotropic. It therefore is possible to separate the π- and σ-contributions from each other by measuring the C K-spectrum at different take-off angles (= angle between the plane of the molecules and the direction of observation). This procedure has already successfully been applied to other materials, in particular to layer crystals (3 - 6), and also - as in the present case - to molecular single crystals (7, 8).

For studies of the anisotropic emission single crystals have to be used, or at least textured samples (5). In the case of naphthalene such investigations are somewhat more complicated because naphthalene forms monoclinic crystals (space group C^5_{2h}) (9). The unit cell contains two planar molecules as shown in fig. 1. The angle between the planes of the molecules is 52.6°.

In the following discussion anisotropic emission will be considered as a molecular effect; i.e. a single crystal will be treated as consisting of two groups of molecules with characteristic orientation and the interaction between molecules in the crystal is neglected. The anisotropy of the emission is most easily detected by measurements in directions which are nearly parallel or perpendicular to the two planes of molecules in the unit cell. There is a direction which runs parallel to the planes of both molecules, since two planes always intersect in one line. When the spectrum is measured in that direction, the π-band should be enhanced by a factor of two, compared with the spectrum of a polycrystalline sample with anisotropic distribution of the crystallites (5). But as there is no direction which is perpendicular to the plane of both molecules, it is not possible to eliminate completely the π-band of the X-ray spectrum. The π-band is expected to have a minimum intensity when observed along the angular bisectrix between the two normals. Applying the formulae of ref. (5) we calculated that in this case the intensity of the π-band should be reduced by a factor of 0.22 compared to the intensity observed for a polycrystal, the σ-band being normalized to the same intensity in all cases.

The theoretical values just mentioned for the anisotropy of the spectra of naphthalene are upper limits. These could not be achieved in practice due to limitations on the mechanical alignment of the sample. The crystals were drawn from the melt*. The measurements were made on samples freshly cleaved along the ab-plane. The C K-spectrum was measured for two different directions, in both cases the take-off angle with respect to the ab-plane was 57° (fig. 1). Both directions were situated within the ac-plane, and the radiation was observed along the direction of the $\vec{c}$-axis, and at an angle of 66° towards the $\vec{c}$-axis. In fig. 1 these two directions are denoted as "position 1" and "position 2". Theoretically the π-band intensity should be enhanced by a factor of 1.85 along the $\vec{c}$-axis, and along the other direction it should be reduced to 0.64, compared with the intensity of the π-band of a polycrystal.

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Fig. 2 shows the spectra measured for the single crystal together with the spectrum obtained for frozen (polycrystalline) naphthalene. The spectrum of the polycrystalline sample did not show any angular dependence. In all cases the measured values are connected by a solid line. Unfortunately the synchrotron radiation causes chemical decomposition of the sample, and hence the statistics of the single crystal spectra is limited. Nevertheless it is possible to distinguish the π- and σ-bands in the spectra.

A graphical method (5) was used for this separation. The results are presented in fig. 2, the π- and σ-band being drawn as dotted curves. The sum of these two curves (dashed line) is in agreement with the measured spectra within the statistical error. When the two spectra from the single crystal are compared to the spectrum of the polycrystalline naphthalene it is found that the intensity of the π-band is enhanced by a factor of 1.5 in one case and reduced by a factor of 0.85 in the other. This discrepancy between the experimental results and the theoretically expected values (1.85 and 0.64, respectively) may be due to small errors in the sample alignment and to possible perturbations produced in the surface of the sample by cleaving.

4. The electronic structure of naphthalene

The C K-emission spectrum of frozen (polycrystalline) naphthalene with its π- and σ-bands is presented in fig. 3 together with the photoelectron spectra (UPS (10, 11) and XPS (12)) of solid and gaseous naphthalene. The spectra were set to a common energy scale by means of the energy of the C 1s level (12).

All these spectra reflect the composition of the valence electron system, yet with differing weight of the contributions from the individual atomic components. Because of the dipole selection rules the X-ray spectrum contains only contributions of C 2p → C 1s transitions, the π-band containing those of the C $2p_z$-electrons and the σ-band those of the C $2p_x$- and C $2p_y$-electrons. In the UP-spectra the main contributions originate from C 2p-electrons, though H 1s-electrons and, to a considerably smaller extent, C 2s-electrons also contribute to the photoelectron spectrum. In the XP-spectrum C 2s-electrons are predominant because of their large cross section, whilst the cross-sections of H 1s- and C 2p-electrons are considerably smaller (13, 14).

As far as the experimental resolution permits a separation of structural details, all spectra yield the same binding energies for corresponding orbitals (features A - L). This means that from all the spectroscopic data an entirely consistent picture of the valence electron structure is obtained. It must be remembered, however, that, compared to the gaseous samples, in the solid samples the energies of all orbitals are uniformly shifted to smaller binding energies by 1.2 eV relative to the vacuum level (10). In spite of the fact that in solids all structural features are broadened, it is possible, as a first approximation, to interpret the spectra by using MO-calculations for the free molecule.

The UP-spectrum of solid naphthalene was measured with considerably higher resolution (≤ 0.1 eV) than the X-ray spectrum (0.5 eV).Nevertheless the resolution available in the present X-ray experiment was sufficient to show all the structural details seen in the photoelectron spectrum (with the exception of feature C), although some features are present only as a shoulder. Therefore, if an X-ray spectrum of solid naphthalene were to be measured with a much better resolution, considerably improved information should not be expected.

At the top of fig. 3 are listed the binding energies of the occupied valence orbitals as calculated by Hayashi and Nakajima (15), the two uppermost orbitals being fitted to the experimental data. Each of the available MO-calculations provides five occupied π-orbitals (12, 15 - 20). However, there exist discrepancies with regard to the relative energetic positions of the orbitals, especially for the lowest π-orbital.

As fig. 3 shows the π-band of the C K-spectrum also exhibits five structural features, the uppermost of which, however, is present only as a weak shoulder on the high energy side of the main maximum. There is good agreement between the relative energies of the structural features in the π-band and the calculated positions of the π-orbitals. This measurement for the first time gives clear indication that the lowest π-orbital has the comparatively high binding energy of about 15 eV with reference to the vacuum level of gaseous naphthalene. In the UP-spectrum the structures A, B and C are to be attributed to the three uppermost π-orbitals. Structures E and H cannot be identified in the photoelectron spectrum because of a strong overlap with σ-orbitals.

Compared to the X-ray spectrum the uppermost features (A, B, C) in the UP-spectrum of solid naphthalene are of comparatively low intensity. On the other hand in the energy region of the σ-band good agreement is found between the relative intensities within the σ-band and the UP-spectrum. The agreement here is considerably better than between the shape of the UP-spectrum and the whole spectrum of the C K-emission. It therefore seems as if in the UPS-measurements the cross-sections were larger for C 2p-electrons with σ-symmetry than for those with π-symmetry. A similar effect has previously been observed for graphite by Bianconi et al. (21).

We observed that in the C K-emission spectrum the contributions of the individual π-orbitals to the spectrum differ considerably in intensity, decreasing with increasing binding energy, despite the fact that all the π-orbitals contain two electrons with exclusively C $2p_z$-character. Unfortunately no LCAO-calculations are available which predict to what extent the particular atomic components do contribute to the molecular orbitals.

Therefore a quantitative discussion of the relative intensities is rather difficult. Qualitatively this decrease can be explained as follows. For the deeper lying orbitals the bonding character is more pronounced, being associated with a larger overlap of the contributions of the individual atomic orbitals. Hence the probability of finding a π-electron in the vicinity of a 1s-hole is reduced, as is the contribution of the orbital to the X-ray spectrum. Calculations of the orbital composition of the π-orbitals would be of particular interest: this case is a test for the intensities in X-ray emission spectra resulting from electron transitions of delocalized orbitals.

5. The electronic structure of anthracene

The C K-emission spectrum of frozen anthracene is presented in fig. 4 together with UP- (10) and XP-spectra (12). To align the spectra the binding energy of the C 1s-level (12) was used.

The above interpretation of the naphthalene spectra can by analogy also be applied to anthracene; here too the spectroscopic data provide a consistent description of the electronic structure (features A - M). From a comparison of the UPS-measurement and the X-ray spectrum we conclude that features A - C (and perhaps also D) originate from π-orbitals. The high intensity of structure I in the UP-spectrum indicates that the H 1s-electrons are concentrated in this energy region.

Anthracene has 33 occupied valence orbitals (26 σ- and 7 π-orbitals). The number of experimentally observed structural features is, however, much lower. The correlation of features with orbitals is therefore extremely difficult. According to the MO-calculation of Lipari and Duke (19) part of the spacings between the individual orbitals are extremely small ($\leqq$ 0.05 eV). However, an MO-calculation which provides only orbital energies is of limited use in interpreting a photoelectron spectrum or an X-ray emission spectrum. For an X-ray emission spectrum in particular it would be desirable to have available calculations which would at least give the C 2p-components of the molecular orbitals, so that the shape of the C K-emission spectrum could be estimated.

6. The C K-emission spectra of solid acenes

With increasing size the number of occupied orbitals in an aromatic hydrocarbon is also increased. Since this increase is not accompanied by a corresponding increase in the width of the spectrum, the orbitals come closer together than in benzene. As a consequence it is not possible to resolve the individual orbitals in the X-ray emission spectra of higher hydrocarbons. The changes in the C K-emission spectra when going from benzene (1) to naphthalene and anthracene can clearly be seen in fig 5. For comparison the C K-spectrum of graphite (22) has also been included. As can be seen, the principal structural features of benzene on the whole remain unchanged in their position. There appear some additional weak features with the result that the minima in the spectra of the higher hydrocarbons are smeared out, and therefore are less pronounced.

It is interesting to observe that with increasing molecular size the structural features at about 275 eV become more accentuated as compared to those at about 280 eV. This behaviour can be understood from the MO-calculations for benzene (23): the orbitals corresponding to structural features at 275 eV comprise a relatively large amount of H 1s, which in part is replaced by the C 2p-components of carbon atoms, as the molecule is increased.

In the π-region at about 280 eV the relative intensity of the peaks falls rather slowly as the molecular size increases, and the breadth of the π-band increases; this is presumably due to interactions between the increasing number of π-orbitals.

It is remarkable that the C K-emission spectrum of graphite does fit so well into the sequence of the spectra of the aromatic hydrocarbons. This suggests that for an understanding of the spectrum of graphite it is not necessary to have band structure calculations. One may therefore optimistically hope that, for an interpretation of X-ray spectra of layer crystals, MO-calculations for clusters of molecules will be sufficient, as have been calculated for instance by Zunger (24) for hexagonal boron nitride.

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Figure captions

fig. 1 Crystal structure of naphthalene, and take-off directions of X-rays for studies of the anisotropic emission (pos. 1 and pos. 2)

fig. 2 C K-emission spectra of naphthalene single crystals (a and c) and of frozen naphthalene (b).

Take-off direction of the radiation:

in a: parallel to the $\vec{c}$-axis of the crystal

in c: within ac-plane and 66° to $\vec{c}$-axis of the crystal

——: experiment; -----: sum of components;

·····: π- and σ-components

fig. 3 C K-emission spectrum of polycrystalline naphthalene and its decomposition into π- and σ-bands, together with the UP-spectra of solid (10) and gaseous naphthalene (11), and the XP-spectrum of solid naphthalene (12).

Top: Calculated energies for the π- and σ-orbitals (15)

fig. 4 C K-emission spectrum of solid anthracene together with UP-spectrum (10) and XP-spectrum (12)

fig. 5 C K-emission spectra of solid benzene (1), naphthalene, anthracene, and graphite (22).

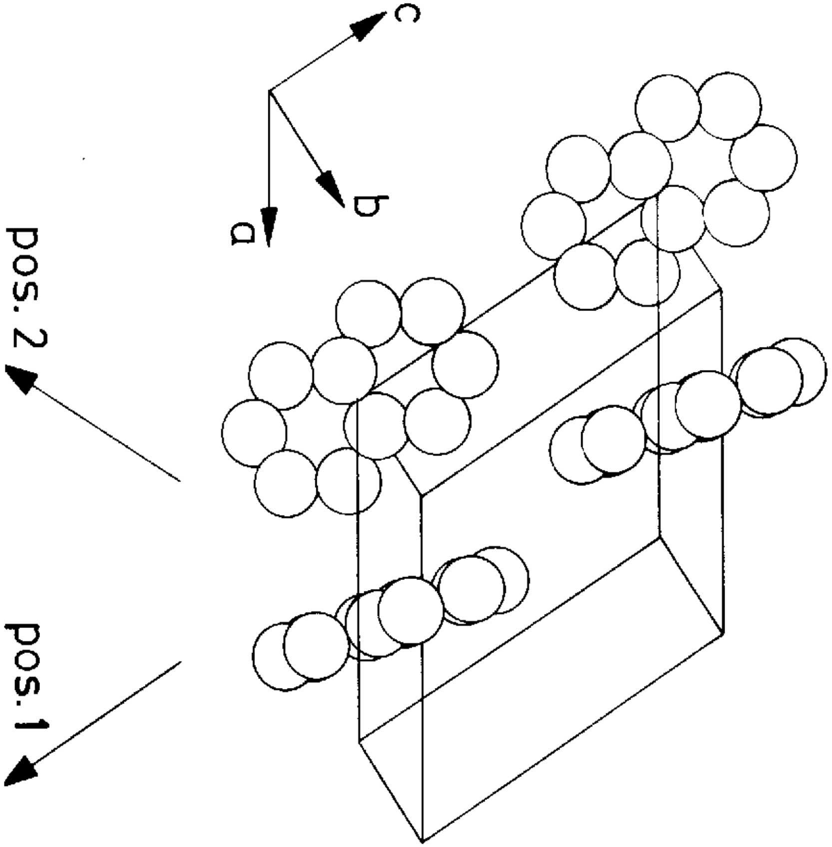
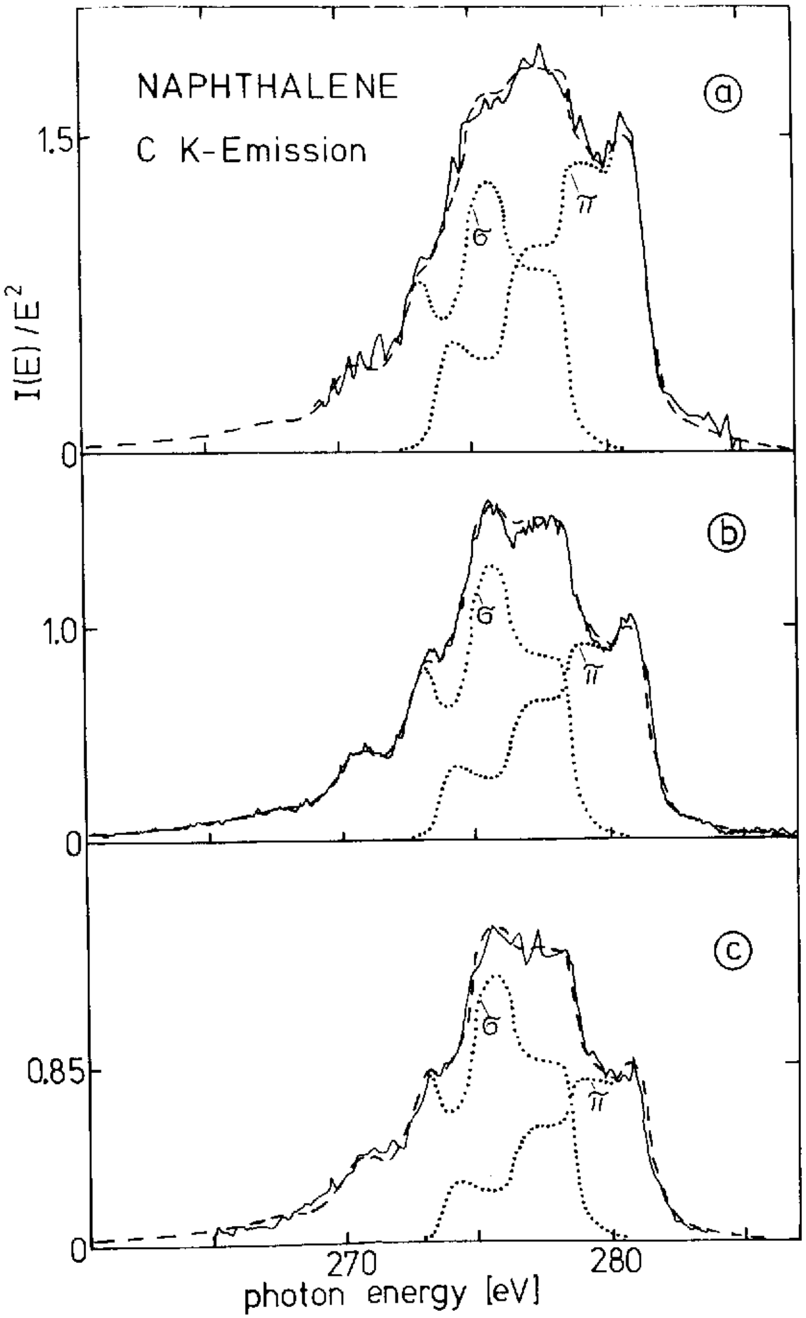


Fig. 1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C K-Emission
ⓐ
ⓑ
ⓒ
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π
I(E)/E^2
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1.0
0.85
0
270
280
photon energy [eV]

Fig. 2

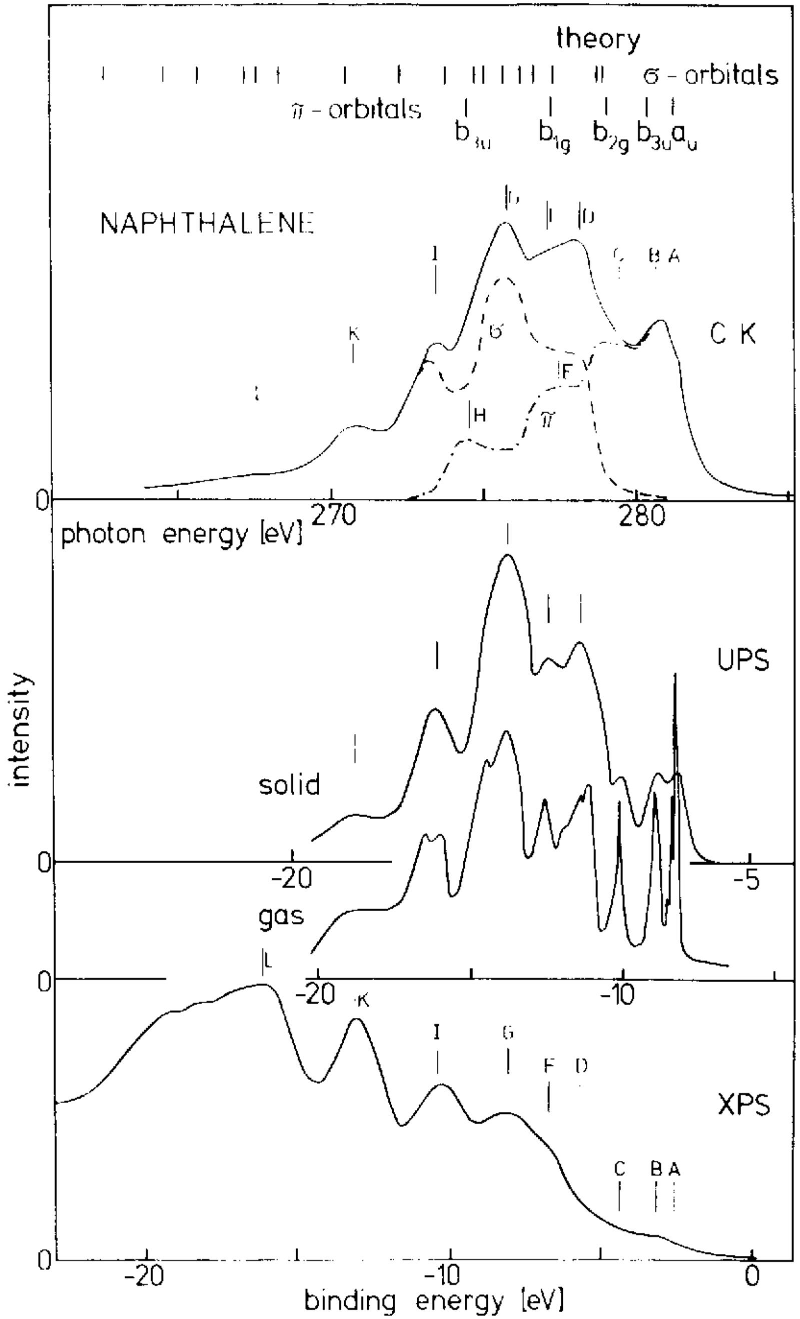
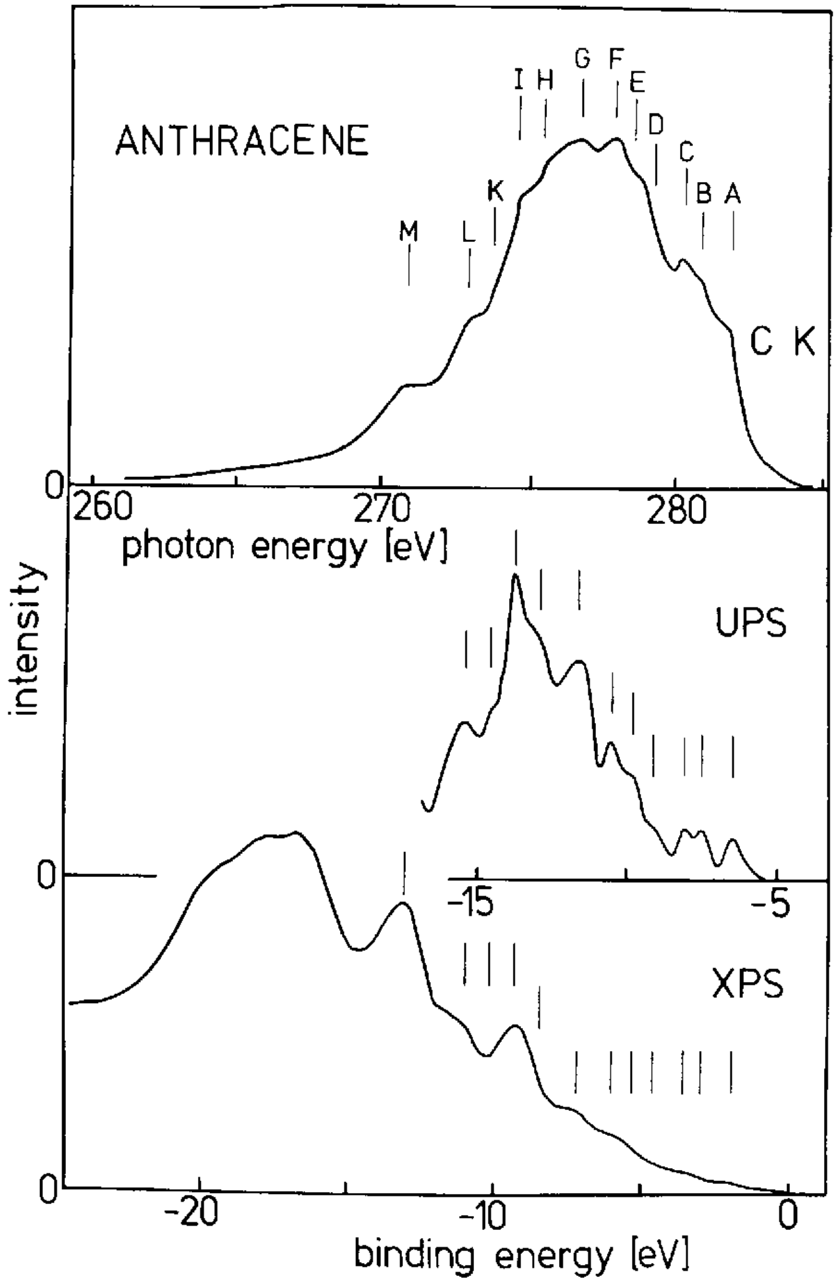

theory
σ - orbitals
π - orbitals
b_{3u}
b_{1g}
b_{2g}
b_{3u}
a_u
NAPHTHALENE
C K
σ
π
K
I
H
F
C
B
A
0
270
280
photon energy [eV]
intensity
UPS
solid
gas
0
-20
-5
-10
L
K
I
G
F
D
XPS
-20
-10
0
binding energy [eV]

Fig. 3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M
L
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F
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D
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0
260
270
280
photon energy [eV]
intensity
UPS
0
-15
-5
XPS
0
-20
-10
0
binding energy [eV]

Fig. 4

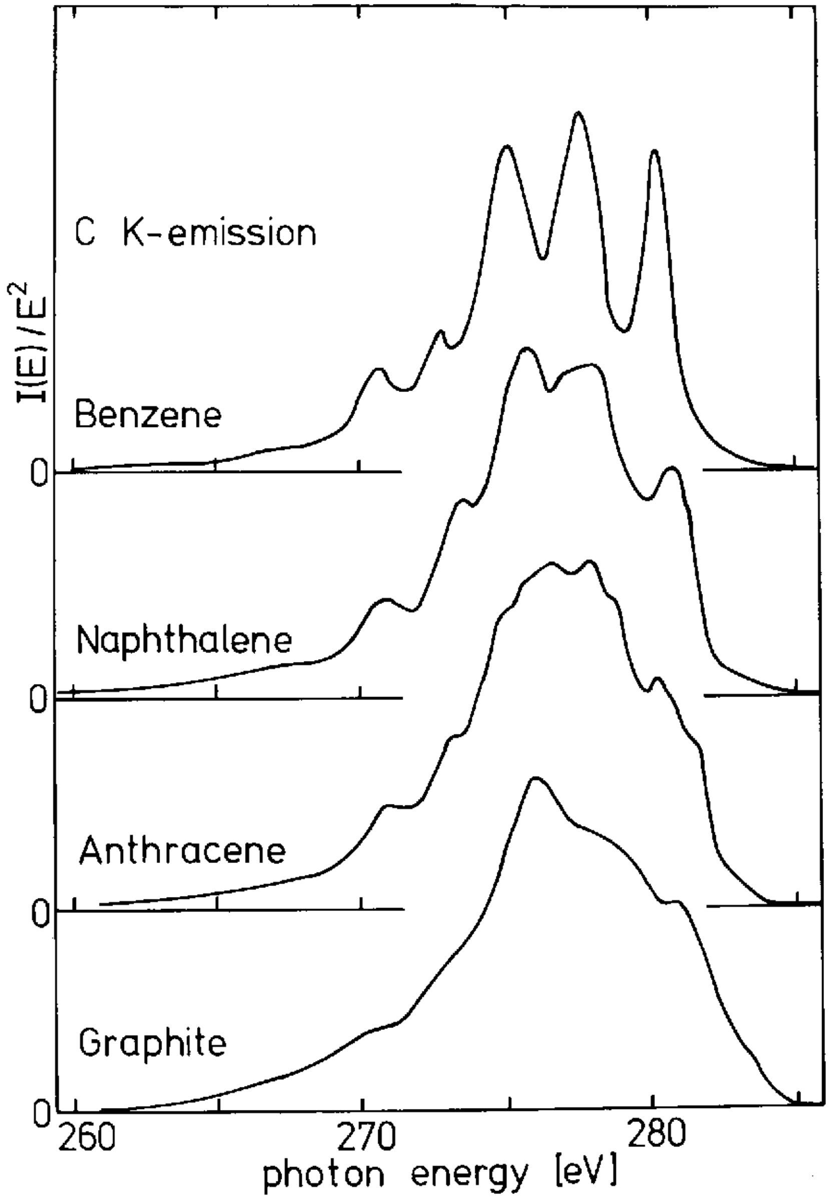
C K-emission
I(E)/E²
Benzene
0
Naphthalene
0
Anthracene
0
Graphite
0
260
270
280
photon energy [eV]

Fig. 5