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PHOTOELECTRON SPECTRA OF POLYCYCLIC AROMATIC HYDROCARBONS. PYRENE AND CORONENE[1]

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Aromatic hydrocarbons are particularly attractive objects of investigation for the photoelectron spectroscopist, in that they possess loosely bound π electrons which in many cases give rise to characteristic, easily recognisable PE bands. With the exception of the lower homologues benzene[2], naphthalene[2] and azulene[3], however, no high-resolution PE research has as yet been carried out on this class of compounds.

PE spectra are presented in this note for pyrene and coronene. Our objectives are to identify the first few π bands and to gain information on the onset of the σ band system - a point about which there has been much controversy until recently (cf. the discussion on the second π IP of benzene[2,4]). Consequently only the low-energy section of the spectra is reproduced in the figure. Both spectra have been recorded on a Perkin-Elmer PS-16 spectrometer, which was equipped with a heated probe, at 118 ± 1 and 225 ± 1°C respectively.

In the absence of accurate ab-initio calculations for hydrocarbons larger than naphthalene[5], our analysis of the spectra is necessarily provisional as it rests solely on phenomenological criteria, e.g. band shapes and intensities, and the results of standard HMO, PPP, EHT and MINDO/2 calculations, the geometrical parameters of which were taken from the known X-ray structures.[6] Since semi-empirical all-electron procedures of the EHT and MINDO/2 type notoriously place σ levels at too high energies relative to the π MO's (according to our experience[1] in large molecules by 1.5 - 2.0 eV), only the π orbital energies are quoted in the table. In each molecule the four treatments yield the same π level ordering[7] and nearly identical wave functions; we believe that this conformity is not fortuitous, but a consequence of the high symmetry and the relatively small degree of double bond fixation in both hydrocarbons, the orbital sequence then being largely dictated by topology.

Relative band intensities, estimated under the assumption that the area underneath a particular PE band is proportional to the orbital occupation and inversely proportional to the kinetic energy of the ejected photoelectrons, are as follows (beginning with band 1): pyrene 1.00, 0.96, 2.09, 1.01; coronene 2.00, ca. 4.0. Thus the double band in the pyrene spectrum centred at ca. 9.2 eV has to accommodate two MO's; likewise the comparatively high intensities of the second and third bands in the coronene spectrum must be due to a coincidence of two or more orbitals, because all the MO treatments agree that the first band originates from a degenerate e_{2u} MO.

If a steep band onset, that is dominance of the 0-0 vibrational component and a slow intensity fall-off, are taken to be indicative of a π ionisation, we are tempted to conclude that the five highest occupied MO's in pyrene are of the π type, belonging to symmetry species $2b_{3g}$, $2b_{2g}$, $3b_{1u}$, $1a_u$ and $2b_{1u}$ in order of decreasing energy. This would place the onset of

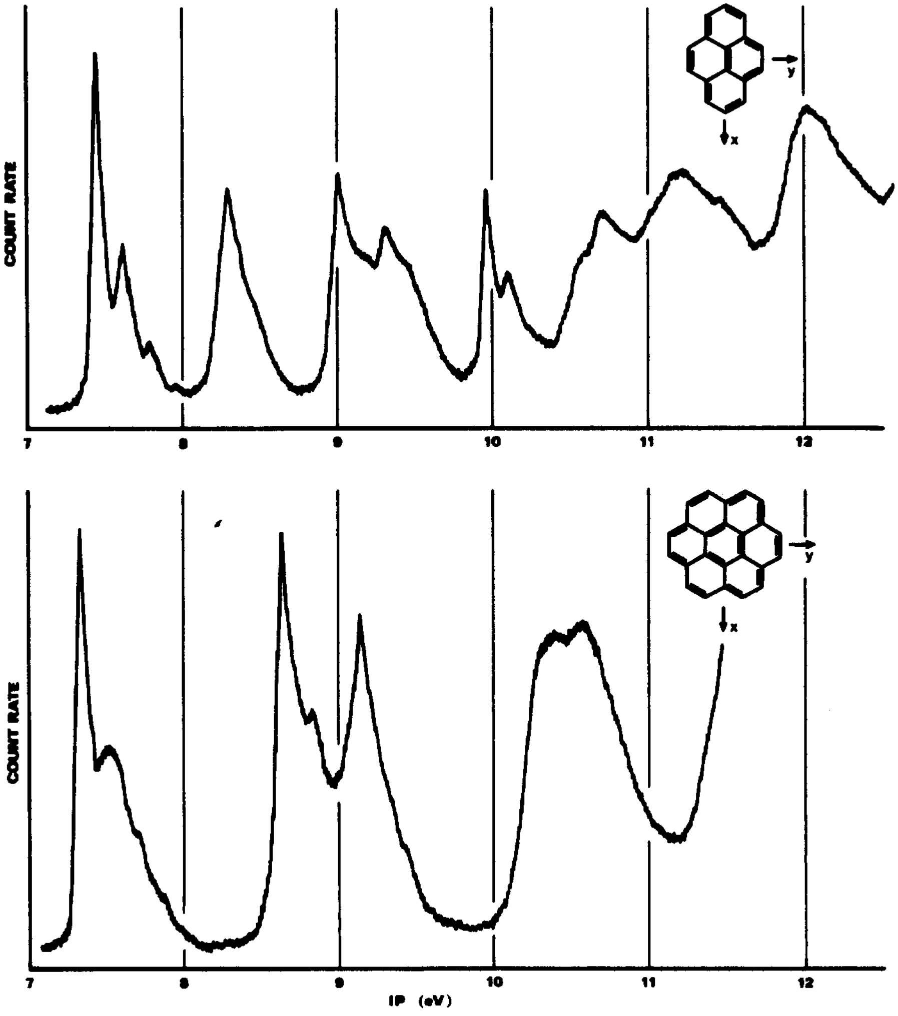

Figure. Expanded recordings of the first photoelectron bands of pyrene[8] (vertical IP's 7.4_1 8.2_6, 9.0_0, 9.2_9, 9.9_6, 10.7, 11.2, 12.0 eV) and coronene (vertical IP's 7.3_4, 8.6_4, 9.1_5, 10.4, 10.5_5, 11.6 eV).

Table. Computed π level ordering in pyrene (D_{2h}) and coronene (D_{6h}). For orientation of the axes see figure. All energies in eV, except HMO eigenvalue coefficients x_{HMO} which are dimensionless. The PPP orbital energies refer to an arbitrary zero point.

Pyrene	$2b_{3g}$	$2b_{2g}$	$3b_{1u}$	$1a_u$	$2b_{1u}$	$1b_{3g}$	$1b_{2g}$	$1b_{1u}$
HMO	0.445	0.879	1.000	1.247	1.347	1.802	2.000	2.532
PPP	2.015	0.713	0.041	-0.490	-0.986	-2.294	-2.861	-4.295
EHT	-11.80	-12.48	-12.73	-13.00	-13.47	-14.06	-14.42	-15.08
MINDO/2	-7.94	-8.90	-9.64	-9.82	-10.82	-12.08	-13.01	-14.82

Coronene	$2e_{2u}$	$2e_{1g}$	$1b_{1g}$	$1b_{2g}$	$2a_{2u}$	$1e_{2u}$	$1e_{1g}$	$1a_{2u}$
HMO	0.539	1.000	1.000	1.214	1.539	1.675	2.214	2.675
PPP	1.846	0.187	0.022	-0.297	-1.496	-1.890	-3.426	-4.650
EHT	-11.86	-12.60	-12.93	-12.94	-13.63	-13.88	-14.65	-15.19
MINDO/2	-7.80	-9.27	-9.84	-9.62	-11.15	-11.69	-13.57	-15.18

the σ band system at ca. 10.5 eV, a conclusion which correlates well with the corresponding findings in naphthalene[2, 5] (σ onset at ca. 10.8 eV, ionisation from $9a_g$) and benzene[4] (11.4 eV, $3e_{2g}$). Increasing annelation in alternant aromatic hydrocarbons thus shifts the onset of the π band system approximately twice as fast to lower IP's as the onset of the σ bands.

The third band in the coronene spectrum extending from 10 to 11 eV appears therefore to be - at least partly - due to σ ionisation. However the second split band centred at 8.9 eV can confidently be attributed to ionisation from the π levels $2e_{1g}$, $1b_{1g}$ and $1b_{2g}$. Since the computed gap between these three MO's is only a few tenths of an eV, their ordering is open to debate; the observed intensity pattern within this band however seems to confirm the theoretical prediction that $1b_{1g}$ and $1b_{2g}$ are very close in energy (cf. table).

Supporting evidence for the π assignments proposed above is provided by a least square regression of the vertical π IP's of benzene, naphthalene, pyrene and coronene on the calculated π orbital energies. The PPP, EHT and MINDO/2 energies yield equally excellent overall linear correlations. If HMO orbital energies are used, the resulting correlation,

$$\text{IP (eV)} = (3.034 \pm 0.330)\, x_{HMO} + (5.892 \pm 0.377),$$

(90 % security level, 13 degrees of freedom) is much worse, but nevertheless sufficient to allow an identification of the π IP's of molecules whose levels are not too closely spaced. However, owing to the large amount of scatter, the HMO regression does not allow, at least not on a 90 % security level, to decide between the two conflicting interpretations which have been advanced for the second PE band of benzene. If the statistical test is carried out on the same security level with the aid of the MINDO/2 data, the result is clear-cut and fully corroborates Lindholm's interpretation[4]: only the second band component with IP of ca. 12.2 eV lies within the upper and lower confidence limits of the regression.

Further arguments supporting our assignment of the highest occupied MO of pyrene arise from the ESR spectrum[9] of the radical cation which is most readily interpreted on the basis of a half-filled b_{3g} orbital, and from the vibrational fine structure of the first PE band which appears to be dominated by a single progression with frequency 1390 ± 30 cm^{-1}. Similar spacings have been observed in many electronic absorption bands of cata- and peri-condensed hydrocarbons, and interpreted in terms of an alternate lengthening and shortening of the vertical and transversal CC bonds. A glance at the computed wave functions shows that this kind of nuclear motion is likely to be excited if the photoelectron vacates the $2b_{3g}$ MO. Ionisation from $2b_{2g}$, $3b_{1u}$ or $1a_u$, on the other hand, is expected to excite in addition to this high-frequency CC "stretching" vibration other low-frequency "breathing" modes. This mixing must necessarily broaden the vibrational components of the 1400 cm^{-1} progression, as can be seen in the second and third PE bands. However this simple picture fails to explain the appearance of only one progression in the fourth band, which we ascribe to $2b_{1u}$ - a progression whose frequency (1130 ± 40 cm^{-1}) is furthermore significantly lower.

Both the complex envelope of the first PE band of coronene, which points to the excitation of non-totally symmetric vibrational modes, and the ESR spectrum of the cation[10] which exhibits unusually broad hyper-fine lines, are consistent with a degenerate ground state of the cation; the coupling constants are furthermore as expected for a half-occupied $2e_{2u}$ MO.

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