

The Electronic Spectra of Acenaphthylene and Fluoranthene A Comment on the Classification of Electronic Spectra

EDGAR HEILBRONNER and JEAN-PIERRE WEBER

Laboratorium für Organische Chemie, Eidg. Technische Hochschule, Zürich

JOSEF MICHL and RUDOLF ZAHRADNÍK

Institute of Physical Chemistry, Czechoslovak Academy of Sciences, Prague

Received June 3, 1966

Acenaphthylene (I) and fluoranthene (II) in their electronic ground state are often regarded as consisting of two weakly interacting subsystems (naphthylene/ethylene or naphthalene/benzene), which conserve much of their individuality. This seems to suggest that the lower electronically excited states of I and II can also be linked in a simple fashion to the low energy L_b , L_a , B_b and B_a states of naphthalene and of benzene in II and of naphthalene in I, according to either SIMPSON's "Independent System Approach" or the "Molecules in Molecules" scheme proposed by LONGUET-HIGGINS and MURRELL. Contrary to expectation this approach fails even for the lowest excited states of I and II, because of the extensive mixing of high energy locally excited and charge transfer configurations. These involve molecular orbitals of the subsystems naphthalene/ethylene or naphthalene/benzene, which do not contribute to their low energy L_b , L_a , B_b or B_a states.

Es wird oft angenommen, daß sich Acenaphthylen (I) und Fluoranthen (II) in ihrem elektronischen Grundzustand in guter Näherung so verhalten, wie wenn sie sich aus zwei nur locker miteinander gekoppelten Teilsystemen (Naphthalin/Aethylen, bzw. Naphthalin/Benzol) zusammensetzen würden. Dies legt zunächst die Vermutung nahe, daß auch die niedrigst liegenden elektronisch angeregten Zustände von I und II in einfacher Weise mit den L_b , L_a , B_b und B_a Zuständen des Naphthalins und des Benzols in Beziehung setzen lassen, indem man sich des von SIMPSON vorgeschlagenen „Independent System Approach“ oder des „Molecules in Molecules“ Verfahrens von LONGUET-HIGGINS und MURRELL bedient. Es zeigt sich aber, daß dies nicht der Fall ist.

Der Grund für das Versagen der genannten Betrachtungsweise ist darin zu suchen, daß sowohl in I als auch in II bereits in den elektronisch angeregten Zuständen niedrigster Energie lokal angeregte Konfigurationen der Teilsysteme eine Rolle spielen, die nicht zu deren L_b , L_a , B_b und B_a Zuständen beitragen, sondern zu Zuständen höherer Energie.

On suppose souvent que dans leurs états électroniques fondamentaux, l'acénaphthylène (I) et le fluoranthène (II) se comportent pratiquement comme s'ils étaient composés de deux systèmes partiels faiblement couplés (naphthalène/éthylène, respectivement naphthalène/benzène).

On peut alors croire que les premiers états électroniques excités de I et de II peuvent être simplement mis en rapport avec les états L_b , L_a , B_b et B_a du naphthalène et du benzène, par exemple en se servant de la méthode «Independent System Approach» proposée par SIMPSON ou de la méthode «Molecules in Molecules» proposée par LONGUET-HIGGINS et MURRELL.

Contrairement à cette attente, l'approximation mentionnée n'est plus valable, même pour les états excités de plus basse énergie. Ceci est dû au fait que des configurations d'excitation locale et de transfert de charge qui contribuent à ces états, et qui ont une énergie élevée, sont basées sur des orbitales moléculaires des systèmes partiels — naphthalène/éthylène ou naphthalène/benzène — qui ne contribuent pas aux états d'excitation locale de basse énergie, L_b , L_a , B_b ou B_a , de chacun de ces systèmes.

There are in the main four types of classification currently used for the interpretation of the electronic spectra of aromatic hydrocarbons and their derivatives:

1. Clar's empirical classification [1]

This has been deduced from "spectral resemblances" [2] between the electronic spectra of series of benzologous aromatic hydrocarbons. Bands which show similar intensities and vibrational fine structure and which react in a similar fashion to substitution or "annelation" (that is to the enlargement of the π -electron system by additional ortho-condensed benzene rings) are given the same label: e.g. p -band, α -band, β -band, β' -band [3].

2. Platt's classification (for catacondensed π -electron systems) [4]

The basis of this classification is a simple free electron model (or an equivalent one-electron MO-model) for the peripheral chain of atomic orbitals of catacondensed π -electron systems. The cross bonds in these systems are treated as perturbations. The labels for the electronic transitions which can be calculated for the fully symmetrical unperturbed perimeter are chosen according to the change in total angular momentum which results when an electron is promoted to a higher state. These labels are then carried over to the corresponding transitions of the perturbed i.e. crosslinked π -electron systems and matched in essence with those obtained empirically by CLAR: e.g. $\alpha \rightarrow {}^1L_b$, $p \rightarrow {}^1L_a$, $\beta \rightarrow {}^1B_b$, $\beta' \rightarrow {}^1B_a$; see however [5]. The Platt classification yields, therefore, an explanation for the empirical rules observed by Clar and allows for a more systematic extrapolation of the "spectral resemblance"-scheme to new systems.

3. The independent system classification of BURAWOY [6]

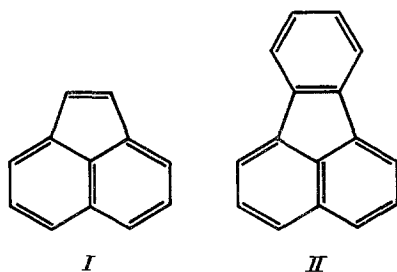
Interest in this classification, which has been neglected for a long time, has been revived through the theoretical investigations of SIMPSON [7] and of LONGUET-HIGGINS and MURRELL [8]. In these the electronically excited states of a loosely coupled system $R \cdots S$ are described in terms of locally excited states of the individual parts R , S and in terms of charge transfer or charge resonance states. Absorption bands which correspond primarily to a locally excited state in one of the subsystems R or S are called R -bands (or B -bands) by Burawoy, those which show high charge transfer or charge resonance character, K -bands. This nomenclature is now obsolete in view of the more precise way in which the transitions can be characterised through the theoretical treatments indicated above [7, 8]. The fundamental contribution of Burawoy to this subject should nevertheless be recognised.

4. Classification according to symmetry [9]

This classification characterises each band in the electronic spectrum according to the direct product of the irreducible representations $\Gamma^{(i)}$, $\Gamma^{(j)}$ (symmetry types) of the two states Ψ_i , Ψ_j involved in the transition $\Psi_i \rightarrow \Psi_j$. It is the only classification which can fully be subjected to an experimental verification. The selection rules for the electronic excitation of the system and the orientation of the transition moment of the allowed transitions depend in a unique way on the symmetry

types $I^{(i)}$, $I^{(j)}$ of the states involved. The classification is therefore largely independent of the choice of a particular model for the π -electron system. However, the classification has the drawback that bands in systems belonging to different symmetry groups can not always be correlated.

Classification 1. has stimulated a considerable amount of experimental and theoretical work. It is invaluable for predicting the gross structure and the shape of electronic spectra of many unknown π -electron systems, as long as the implicitly underlying assumptions are fulfilled. Among other things, the system should be alternant or only "weakly" non-alternant, which means that it consists of alternant subunits linked by non-essential double bonds [10] in such a way that although alternancy is lost for the compound system, the subunits retain much of their individuality. As we shall see later, a system may sometimes be classified as "weakly" nonalternant as far as its ground-state properties are concerned, while exhibiting "strong" non-alternant behaviour in its electronically excited states (e.g. acenaphthylene and fluoranthene). 2. and 3. are really attempts to correlate in different aromatic systems those bands which correspond to similar electronic



mechanisms of excitation. In this attempt 2. and 3. represent in a way two extreme points of view: 2. has proved to be an excellent approximation for cata-condensed, tightly conjugated systems while 3. is only adequate for loosely coupled systems $R - S$ where the link between R and S can be treated, even for the excited states of $R - S$, as a small perturbation. In intermediate cases both classifications fail if taken individually. However, use of both of them, together with a CI-model of the PARISER-PARR-POPLE type [11] will yield a reasonably good insight into the electronic mechanism underlying the spectra of such systems. This is exemplified by the following analysis of the electronic spectra of acenaphthylene (I) and fluoranthene (II).

The electronic spectra of acenaphthylene and fluoranthene

The electronic spectra and the fluorescence polarisation spectra of acenaphthylene (I) and of fluoranthene (II) are shown in Fig. 1 and 2. (For previous results concerning these spectra see Ref. [12]). Characteristic values ($\tilde{\nu}$ in cm^{-1} , λ in nm, E in eV and intensities in $\log \epsilon$ units) are collected in Tab. 1 and 2.

The relative directions of polarisation of the individual absorption bands have been determined according to the well known method of measuring the degree of polarisation, P , of the fluorescence emission at $\tilde{\nu}_F$ relative to that of the polarised excitation radiation $\tilde{\nu}$, the molecules being trapped in a rigid matrix of ethanol

glass at 100° K [13]. The measurement is carried out for light emitted at the fixed wavenumber position $\tilde{\nu}_F$ indicated by a vertical arrow in Fig. 1 and 2, that is at 19000 cm^{-1} for I and at 21500 cm^{-1} for II. These values correspond to the location of the intensity maxima of the fluorescence emission bands. P is a function of $\tilde{\nu}$, the wavenumber of the exciting radiation and is computed according to:

$$P(\tilde{\nu}) = (I_{\parallel} - I_{\perp}) / (I_{\parallel} + I_{\perp}).$$

I_{\parallel} and I_{\perp} are the intensities of the components of the emitted radiation ($\tilde{\nu}_F$) polarised parallel (I_{\parallel}) or perpendicular (I_{\perp}) to the plane of polarisation of the radiation $\tilde{\nu}$ absorbed by the trapped molecules. In Fig. 1 and 2 the curve representing the function $P(\tilde{\nu})$ is superimposed on the electronic spectra (curve $AP(F)$ = polarisation of fluorescence at variable absorption wavelength). For details of the experimental procedure the reader is referred to the original literature [14]. P depends on the orientation of the transition moment $\vec{\mu}(\tilde{\nu})$ of the state to which the molecule is excited by the absorbed radiation $\tilde{\nu}$, relative to the transition moment $\vec{\mu}(\tilde{\nu}_F)$ of the fluorescent state. If ω is the angle encompassed by $\vec{\mu}(\tilde{\nu})$ and $\vec{\mu}(\tilde{\nu}_F)$, then

$$P = (3 \cos^2 \omega - 1) / (\cos^2 \omega + 3).$$

For $\omega = 0$ we have $P = \frac{1}{2}$; for $\omega = \pi/2$, $P = -\frac{1}{3}$. The experimental results are interpreted as follows:

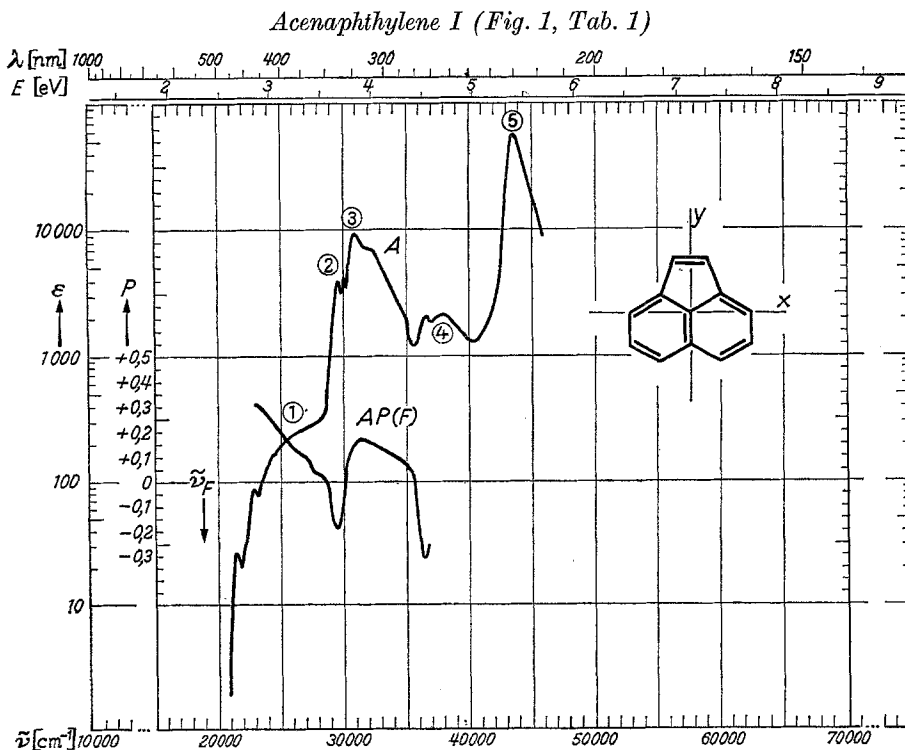


Fig. 1. Electronic spectrum (A) and fluorescence polarisation spectrum [AP (F)] of acenaphthylene (I). Solvent: ethanol. A: room temperature; AP (F): 100° K. Concentration for AP (F): $2 \cdot 10^{-3}$ M. Vertical arrow: maximum of fluorescence intensity ($\tilde{\nu}_F = 19000 \text{ cm}^{-1}$). The numbering of the bands refers to Tab. 1.

Table 1. *Electronic spectrum of acenaphthylene I* (c.f. fig. 1)

Band	$\tilde{\nu}$ (cm^{-1})	λ (nm)	E (eV)	$\log \epsilon$	Rel. Pol. ^a
①	(21500) ^b	(466) ^b	(2.66) ^b	(1.4) ^b	([]) ^{b c} x^d
②	29500	339	3.66	3.7	\perp y
③	31000	322	3.84	4.0	x
④	36400	275	4.51	3.5	\perp y
⑤	43500	230	5.39	4.7	x

^a Rel. Pol. = relative polarisation (i.e. relative to first band).

^b Values in brackets refer to shoulders.

^c Assigned reference orientation.

^d Assignment according to EGGERS [17].

The drop (with increasing $\tilde{\nu}$) in the AP (F) curve underneath the first weak band ① (21000 to 28000 cm^{-1} , $\epsilon \approx 200$) is typical for a strong vibronic coupling with an intense band, here the band ② at 29000 cm^{-1} ($\epsilon \approx 6000$). This band ② gives rise to a sharp minimum in the AP (F) curve at 29500 cm^{-1} and is therefore polarised perpendicular to the first band ①. As the AP (F) curve indicates the third intense band ③ in the region from 31000 to 35000 cm^{-1} ($\epsilon \approx 10000$), which dominates the preceding second band ② and to which the general shape of the electronic spectrum in this region (29000 – 35000 cm^{-1}) is due, is polarised parallel to the first band (positive value of P). The steady decrease of the AP (F) curve (from 31000 to 35000 cm^{-1}) is in all probability due again to vibronic coupling with the following fourth transition (band ④) at 36000 to 38000 cm^{-1} . This fourth band ($\epsilon \approx 3000$) is polarised perpendicular to ① and hence to ③, as can be seen from the pronounced dip in the AP (F) curve at 37000 cm^{-1} .

Little can be said concerning the direction of polarisation of the very intense ($\epsilon \approx 70000$) fifth band ⑤ at 43000 cm^{-1} . The fluorescence intensity was too weak to allow a reliable measurement for $\tilde{\nu}$ -values higher than 38000 cm^{-1} . However, the onset of a steep increase in the AP (F) curve at that point seems to indicate that ⑤ is polarised parallel to ①. The existence of the five independent electronic transitions ① to ⑤ has also been inferred from a study of the substituent effects [16].

These results are collected in Tab. 1, where the polarisation of each band relative to the first weak band ① are given in the last column.

Fluoranthene II (Fig. 2, Tab. 2)

The AP (F) curve for this system measured at $\tilde{\nu}_F = 21500 \text{ cm}^{-1}$ (solid line in Fig. 2) is flat and without prominent features, which renders an assignment of relative orientations of the transition moments impossible on the basis of this information alone. Moreover it would suggest that the band ② at 27800 cm^{-1} corresponds to the transition of lowest energy in II.

In contrast, a careful investigation (the details of which shall be reported at a later date [15]) of the electronic spectrum of II and its methyl- and aza-derivatives, recorded at the temperature of liquid nitrogen in a solid solution of 3-methylpentane, allows the assignment of seven transitions to the spectral region between 26000 and 43000 cm^{-1} . It clearly indicates that three transitions (①, ②

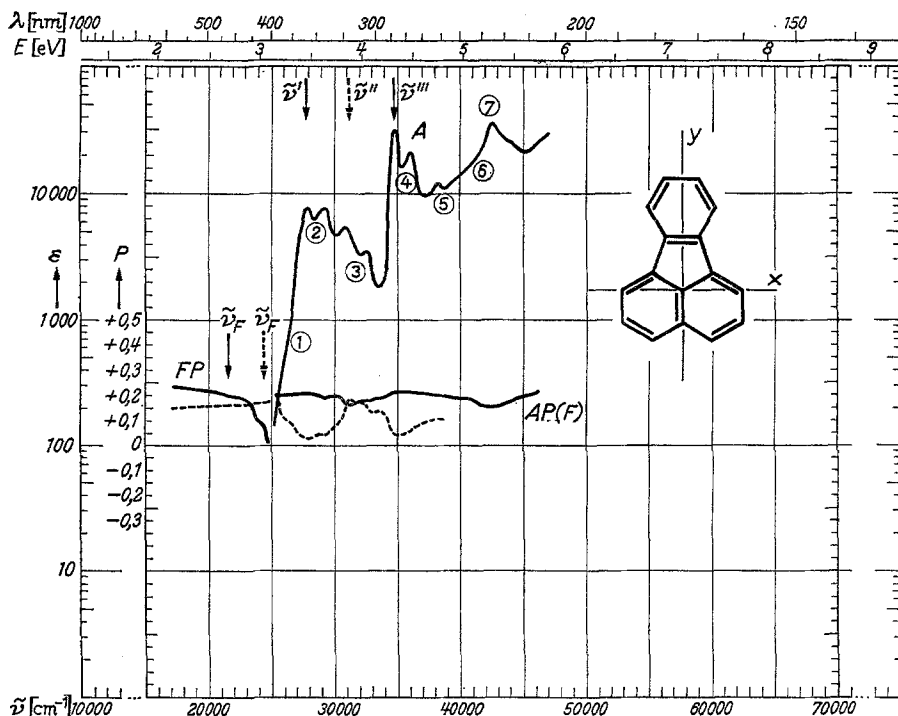


Fig. 2. Electronic spectrum (A) and fluorescence polarisation spectra [FP and AP (F)] of fluoranthene (II). Solvent: ethanol. A: room temperature; FP and AP (F): 100° K. Concentration for FP and AP (F): $1 \cdot 10^{-5}$ M. The numbering of the bands refers to Tab. 2. AP (F): a) solid line, measured at $\tilde{\nu}_F = 21500 \text{ cm}^{-1}$; b) broken line, measured at $\tilde{\nu}_F = 24500 \text{ cm}^{-1}$. FP: a) solid line, measured at either $\tilde{\nu}' = 27800 \text{ cm}^{-1}$ or $\tilde{\nu}'' = 34900 \text{ cm}^{-1}$; b) broken line measured at $\tilde{\nu}'' = 31300 \text{ cm}^{-1}$

Table 2. *Electronic spectrum of fluoranthene (c.f. fig. 2)*

Band	$\tilde{\nu}$ (cm^{-1})	λ (nm)	E (ev)	log ϵ	Rel. Pol. ^a		
					d	e	t
①	(~ 26000) ^b	(~ 390) ^b	(~ 3.2) ^b	(~ 2) ^b			[] ^c
②	27800	359	3.45	4.0	y	[] ^c	⊥
③	30800	324	3.82	3.8	x	⊥	
④	34800	287	4.32	4.7	y		⊥
⑤	38200	262	4.74	4.1	y	?	⊥?
⑥	(40000) ^b	(250) ^b	(4.96) ^b	(4.2) ^b	(?)	(?)	(?)
⑦	42400	236	5.25	4.7	x	⊥	

^a Rel. Pol. = relative polarisation (i.e. relative to first band).

^b Values in brackets refer to shoulders.

^c Assigned reference orientation.

^d Assignment according to EGGERS [17].

^e Assignment according to AP(F) curve of Fig. 2 ($\tilde{\nu}_F = 21500 \text{ cm}^{-1}$).

^t Assignment according to AP (F) curve of Fig. 2 ($\tilde{\nu}_F = 24500 \text{ cm}^{-1}$).

and ③) are responsible for the broad, fine-structured maximum extending from 26000 cm^{-1} to 31000 cm^{-1} , i.e. that it is composed of three bands. (See also ref. [12]). Note that these conclusions are in perfect agreement with theoretical predic-

tions [18], such as those contained in Tab. 4. The numbering of the individual bands in Fig. 2 and in Tab. 2 corresponds to these results, which — of course — yield no information concerning the relative polarisation of these transitions.

Such information has been obtained for II by EGGERS, using the stretched film technique [17]. In this procedure one measures the dichroism of a stretched polyethylene film, in which host molecules, dissolved in the film, are partially oriented with their long axis parallel to the stretch direction. The assignment is as follows: The bands ② (27000 to 30000 cm^{-1}), ④ (34000 to 37000 cm^{-1}), ⑤ (around 38000 cm^{-1}) and the high energy part of ⑦ (shoulder at 44000 cm^{-1}) have their transition moments oriented parallel to the twofold axis (y) of the fluoranthene molecule. The bands ③ (30000 to 34000 cm^{-1}) and ⑦ (at 42000 cm^{-1}) are polarised perpendicular to the molecular y -axis. The information concerning the low intensity bands ① and ⑥ (at 26000 and 40000 cm^{-1} respectively) is inconclusive because of the proximity of the overlapping high intensity bands ② and ⑦.

While there is no doubt that the assignment based on the low-temperature spectra, the substituent effects and the stretched-film dichroism is the correct one, there remains the question, why the AP (F) curve recorded at $\tilde{\nu}_F = 21500 \text{ cm}^{-1}$ (i.e. at the position of maximum fluorescence intensity normally used for this type of measurement) fails to give any indication concerning the composite nature of the longwave part of the spectrum. Furthermore, as the fluorescence radiation is due to the transition from the lowest electronically excited state, corresponding to the band ① at 26000 cm^{-1} to the ground state, the AP (F) curve seems to indicate that the second transition (band ② at 27800 cm^{-1}) is polarised parallel to the first transition (band ①). This is in sharp contrast to the experimental results obtained by EGGERS [17] and to the theoretical predictions.

An indication as to why our AP (F) curve fails to yield the correct information, can be obtained by rerecording it at $\tilde{\nu}_F = 24500 \text{ cm}^{-1}$ (dashed curve in Fig. 2), that is nearer to the 0-0-position of the first transition ①. This curve is no longer flat and featureless, but shows the first two transitions ① and ② with their correct relative directions of polarisation, thus confirming the previous assignment (c.f. Tab. 2, last column). Also the direction of polarisation of the bands following ② at higher energies are now in agreement with those quoted above.

This result can be interpreted as follows: while the 0-0-transition moment of the first transition ① is polarised parallel to the x -axis, this is not necessarily the case for the 0- v -transitions, where v is a higher vibrational quantum number of the ground state. Such transitions could easily exhibit substantial y -components, in view of the weakness of the electronic transition moment. This would let us expect strong vibronic coupling with the second y -polarised transition. As a result the emitting transition-moment at $\tilde{\nu}_F = 21500 \text{ cm}^{-1}$ could well be in-plane polarised, but not isotropically, which would explain the inversion of the polarisation directions shown by the AP (F) curve recorded at $\tilde{\nu}_F = 21500 \text{ cm}^{-1}$, that is at a position corresponding to higher vibrational levels of the ground state. In fact calculations show that such an assumption would limit the $P(\tilde{\nu})$ -values to the range from $P = +0,05$ (for y -polarised transitions) to $P = +0,25$ (for x -polarised transitions). The strong overlap between the individual bands in the spectrum of II [17] is the reason why the value $+0,05$ is never reached.

Configuration interaction models of acenaphthylene and fluoranthene

As a basis for the discussion, configuration interaction models of the PARISER-PARR-POPPE type [11] have been calculated independently in Zurich (A, B) and in Prague (C, D), using HÜCKEL MOs (A, C) or SCF-MOs (B, D) as basis functions and the following sets of parameters:

Models A and B:

$$\beta = - 2.37 \text{ eV}$$

$$\gamma_{\mu\mu} = 10.96 \text{ eV}$$

$$\gamma_{\mu\nu} = 6.79 \text{ eV for bonded centers } \mu, \nu$$

$$\gamma_{\mu\nu} = \frac{328.77 + R}{30.0 + 12.341 R + R^2} \quad \text{for nonbonded centers } \mu, \nu \text{ if } R \leq 6 \text{ \AA}$$

$$\gamma_{\mu\nu} = 14.395 / R \quad \text{for nonbonded centers } \mu, \nu \text{ if } R > 6 \text{ \AA}$$

Models C and D:

$$\beta = - 2.32$$

$$\gamma_{\mu\mu} = 10.84$$

$$\gamma_{\mu\nu} = \frac{14.399}{R + 1.3283} \quad \text{for all pairs of centers } \mu \neq \nu.$$

The following sets of ground-state configuration (I) and singly excited configurations ($\psi_J^{-1} \psi_K$) have been used in our calculations:

Acenaphthylene (I): Models A and B, 21 configurations; Model C, 13 configurations [18]; Model D, 28 configurations. Fluoranthene (II): Models A and B, 17 configurations; Model C, 23 configurations [18, 19]; Model D, 28 configurations.

In all cases the interatomic distance between bonded centers has been assumed to be 1.40 Å and the geometry is the most regular one that can be obtained under this restriction.

Notwithstanding the differences in the choice of parameters and of basis functions, the theoretical results agree satisfactorily with each other. In particular the same symmetry sequence has been found for the low energy states and good agreement was obtained for the oscillator strengths of the corresponding transitions (see Tab. 3 and 4). Furthermore the low lying states have been found to be dominated by the same configurations $\psi_J^{-1} \psi_K$ in all three models.

For both I and II the calculated sequence of transitions matches the one found experimentally and the relative intensities as given by the corresponding f -values are also in fair agreement with observations, as can be seen from Fig. 3. In this connection it should be remembered that $\log \varepsilon$ -values do not necessarily reflect the oscillator strengths, especially when weak bands are overlapped by strong bands (e.g. bands ⑤ and ⑥ of II). Furthermore, the theoretical values of the oscillator strengths, $f_{0 \rightarrow j}$, depend in a critical way on the coefficients of the configurations $\psi_J^{-1} \psi_K$ in the linear combination Ψ_j . Finally, significant changes in the f -values could be produced by taking into consideration higher energy configurations and multiply-excited ones. The theoretical excitation energies, i.e. the theoretical predictions for the band positions, show deviations from the experimental values which are of the order expected for the kind of treatment used.

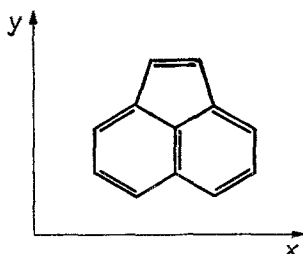


Table 3. CI-models for acenaphthylene I

Ψ_j^a	A		B		C		D		Pol. ^d
	E_j^b	$f_{0 \rightarrow j}^c$	E_j^b	$f_{0 \rightarrow j}^c$	E_j^b	$f_{0 \rightarrow j}^c$	E_j^b	$f_{0 \rightarrow j}^c$	
Ψ_1	2.70	0.04	2.86	0.05	2.61	0.04	2.75	0.04	<i>x</i>
Ψ_2	3.82	0.25	3.83	0.29	3.70	0.24	3.75	0.31	<i>y</i>
Ψ_3	4.05	0.13	3.93	0.18	3.93	0.16	3.83	0.22	<i>x</i>
Ψ_4	4.84	0.00	5.01	0.00	4.55	0.04	4.75	0.00	<i>y</i>
Ψ_5	5.86	0.78	5.82	0.94	5.63	1.08	5.56	1.21	<i>x</i>

^a Ψ_j = electronically excited state.

^b E_j = excitation energy in ev.

^c $f_{0 \rightarrow j}$ = oscillator strength for the transition $\Psi_0 \rightarrow \Psi_j$.

^d Pol. = direction of polarisation relative to the axis given above.

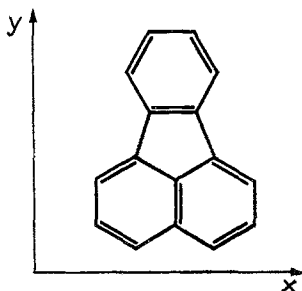


Table 4. CI-models for fluoranthene II

Ψ_j^a	A		B		C		D		Pol. ^d according to Model			
	E_j^b	$f_{0 \rightarrow j}^c$	E_j^b	$f_{0 \rightarrow j}^c$	E_j^b	$f_{0 \rightarrow j}^c$	E_j^b	$f_{0 \rightarrow j}^c$	A	B	C	D
Ψ_1	3.41	0.02	3.56	0.02	3.33	0.02	3.32	0.01	<i>x</i>	<i>x</i>	<i>x</i>	<i>x</i>
Ψ_2	3.66	0.47	3.68	0.52	3.58	0.64	3.51	0.52	<i>y</i>	<i>y</i>	<i>y</i>	<i>y</i>
Ψ_3	4.16	0.05	4.13	0.06	4.09	0.07	3.93	0.08	<i>x</i>	<i>x</i>	<i>x</i>	<i>x</i>
Ψ_4	4.89	0.11	4.83	0.13	4.70	0.20	4.48	0.22	<i>y</i>	<i>y</i>	<i>y</i>	<i>y</i>
Ψ_5	5.40	0.01	5.42	0.00	5.20	0.03	5.08	0.01	<i>x</i>	<i>x</i>	<i>x</i>	<i>y</i>
Ψ_6	5.62	0.01	5.73	0.86	5.25	0.00	5.13	0.05	<i>y</i>	<i>y</i>	<i>y</i>	<i>x</i>
Ψ_7	5.72	0.73	5.80	0.03			5.26	0.60	<i>y</i>	<i>y</i>		<i>y</i>
Ψ_8	5.87	1.51	5.81	1.51			5.39	1.28	<i>x</i>	<i>x</i>		<i>x</i>

^a Ψ_j = electronically excited state.

^b E_j = excitation energy in ev.

^c $f_{0 \rightarrow j}$ = oscillator strength for the transition $\Psi_0 \rightarrow \Psi_j$.

^d Pol. = direction of polarisation relative to the axis given above.

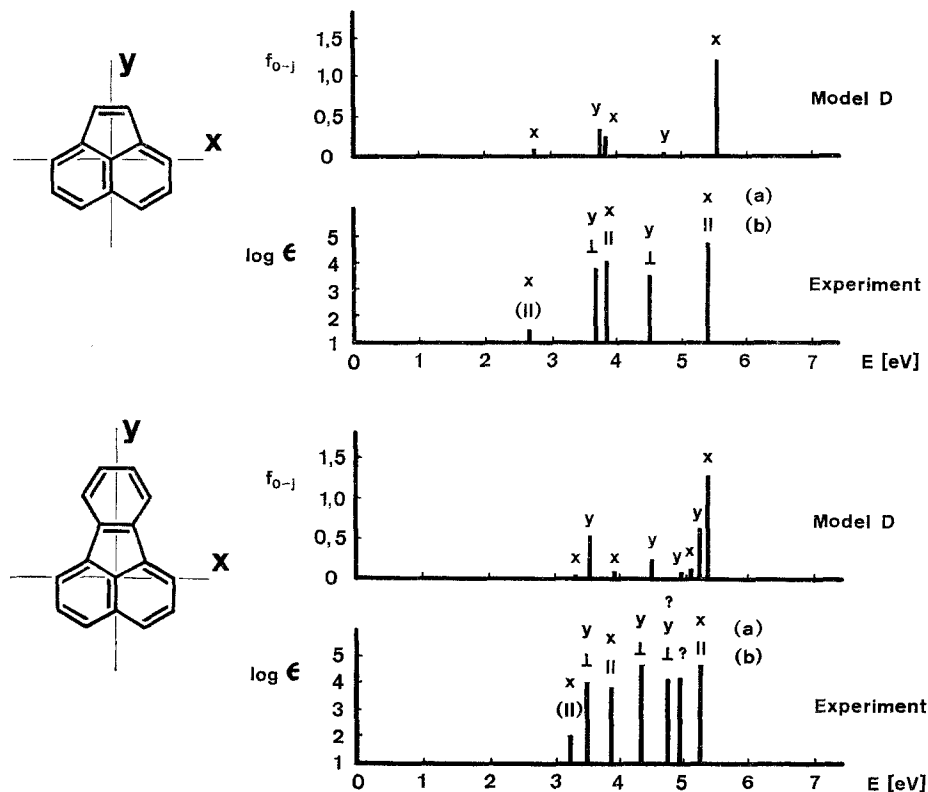


Fig. 3. Comparison of observed and predicted band positions and band intensities for acenaphthylene and fluoranthene. x, y refer to the axis given in Figs. 1 and 2. The experimental x, y polarisations are those given by EGGERS [17]; \parallel, \perp from the AP (F) curves of Figs. 1 and 2

Discussion

Some of the chemical evidence and zero order HMO calculations seem to indicate, that I and II are best regarded as systems in which a naphthalene unit is weakly coupled with a strongly localised double bond (I) or an essentially unperturbed benzene ring (II) [23]. This would suggest that SIMPSON's "Independent systems approach" (ISA) [7] or the MIM-treatment (= Molecules in Molecules) proposed by LONGUET-HIGGINS and MURRELL [8] — which underlie the classification scheme C — are the methods of choice for correlating the electronic transitions observed for I and II with those of the subsystems naphthalene/ethylene or naphthalene/benzene. Calculations carried out along these lines have however shown that not even qualitative agreement with observation can be obtained, when the locally excited states ${}^1L_a, {}^1L_b, {}^1B_a, {}^1B_b$ of naphthalene are mixed with the corresponding four states in benzene (for II), or the locally excited B-state of ethylene (for I). Inclusion of the relevant charge transfer or charge resonance states in the MIM scheme does not materially improve this situation.

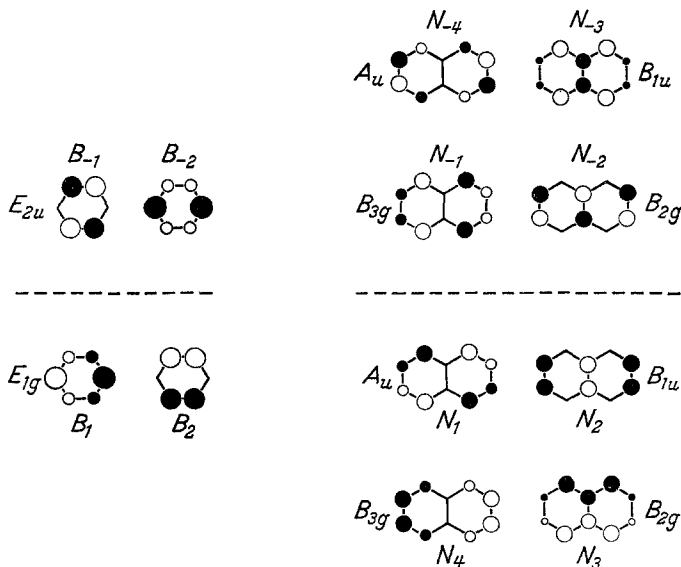
The aim of this treatment was to allow the states of I and II to be labelled according to those locally excited states of the subsystems which contribute with greatest weight to the hybrid state of the joint system. The reason for its failure,

despite its apparent appropriateness to the systems under discussion, is revealed through an analysis of the CI-results given in the previous paragraph and in the appendix. (We shall limit our discussion to model A which is based on simple HMO-LCAO orbitals.)

Fig. 4 is a graphical representation of the upper bonding and lower anti-bonding HMOs

$$\psi_J = \sum_{\mu=1}^n c_{J\mu} \phi_{\mu}$$

of naphthalene and of benzene. (Open and shaded circles represent coefficients $c_{J\mu}$ of opposite sign; their diameters are proportional to the absolute value $|c_{J\mu}|$).



The ground states of our systems — taking naphthalene as an example — will be represented by a Slater-determinant

$$\Gamma(N) = || N_3 \bar{N}_3 N_2 \bar{N}_2 N_1 \bar{N}_1 || .$$

N_J and \bar{N}_J standing for naphthalene orbitals occupied by electrons with spin α or β .

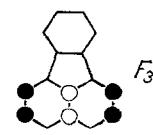
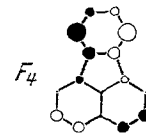
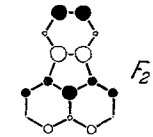
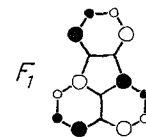
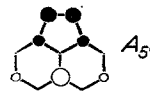
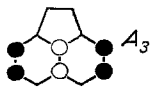
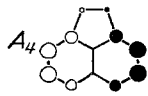
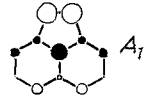
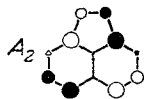
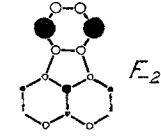
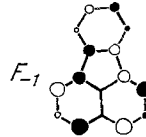
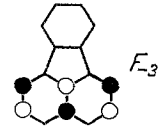
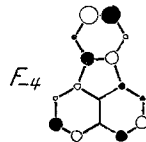
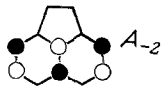
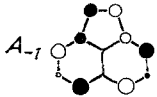
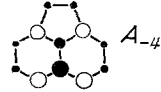
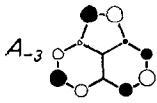
Electronically excited singlet configurations $\psi_J^{-1} \psi_K$ where an electron has been promoted from ψ_J to ψ_K are defined relative to Γ , as shown here for our example naphthalene:

$$N_2^{-1} N_{-1} = \frac{1}{\sqrt{2}} \{ || N_3 \bar{N}_3 N_2 \bar{N}_{-1} N_1 \bar{N}_1 || + || N_3 \bar{N}_3 N_{-1} \bar{N}_2 N_1 \bar{N}_1 || \} .$$

The locally excited states of ethylene, benzene and naphthalene can be represented in a fair approximation by the linear combinations of configurations given in Tab. 5 [20]. In this table the locally excited states are labelled according to the Platt nomenclature and matched with the corresponding absorption bands observed in the electronic spectra of the subsystems, e.g. ethylene, benzene and naphthalene.

Table 5. *Locally excited states of ethylene, benzene and naphthalene* [20]

State	Function	Sym.	E (in ev)	<i>f</i>
Ethylene				
1B	$E_1^{-1} E_{-1}$		7.0	0.3
Benzene				
1L_b	$\frac{1}{\sqrt{2}} (B_1^{-1} B_{-2} - B_2^{-1} B_{-1})$	B_{2u}	4.9	
1L_a	$\frac{1}{\sqrt{2}} (B_1^{-1} B_{-1} + B_2^{-1} B_{-2})$	B_{1u}	6.1	
1B_b	$\frac{1}{\sqrt{2}} (B_1^{-1} B_{-2} + B_2^{-1} B_{-1})$	} E_{1u}	6.9	
1B_a	$\frac{1}{\sqrt{2}} (B_1^{-1} B_{-1} - B_2^{-1} B_{-2})$			
Naphthalene				
1L_b	$\frac{1}{\sqrt{2}} (N_1^{-1} N_{-2} - N_2^{-1} N_{-1})$	B_{3u}	4.1	
1L_a	$N_1^{-1} N_{-1}$	B_{2u}	4.5	
1B_b	$\frac{1}{\sqrt{2}} (N_1^{-1} N_{-2} + N_2^{-1} N_{-1})$	B_{3u}	5.6	
1B_a	$N_2^{-1} N_{-2}$	B_{2u}	6.1	



The bonding and antibonding HMOs of I and II are represented in Fig. 5 and 6. These are the orbitals used in our CI treatment (model A: For I, all pairs of configurations $A_J^{-1} A_K$ with $J = 1, 2, 3, 4$; $K = -1, -2, -3, -4$ and the four configurations $A_5^{-1} A_K$ with $K = -1, -2, -3, -4$. For II, all pairs of configurations $F_J^{-1} F_K$ with $J = 1, 2, 3, 4$; $K = -1, -2, -3, -4$.)

The Tabs. 9 and 10 given in the appendix show that the lower electronically excited states Ψ_j of I and II can be represented to a good first approximation by only one or two configurations $\psi_J^{-1} \psi_K$ namely by those with the highest coefficients $C_{j,JK}$ in the linear combination Ψ_j . The weights given in the following Tab. 6 are the squares of the corresponding coefficients $C_{j,JK}$, expressed in percent. (The same conclusions, with minor changes in the absolute values of the weights, can be drawn from models B, C and D.)

Table 6. Major contributing configurations to the low energy states Ψ_j of acenaphthylene (I) and fluoranthene (II)

Configurations and weights in brackets refer to the second, most important, component. Minor components (weight < 10%) are not listed.

State	Acenaphthylene	Weight %	Fluoranthene	Weight %
	Configuration $\psi_J^{-1} \psi_K$		Configuration $\psi_J^{-1} \psi_K$	
Ψ_0	$\Gamma (A)$	97	$\Gamma (F)$	99
Ψ_1	$A_1^{-1} A_{-1}$	91	$F_2^{-1} F_{-1}$	90
Ψ_2	$A_2^{-1} A_{-1}$	86	$F_4^{-1} F_{-1}$	90
Ψ_3	$A_3^{-1} A_{-1}; (A_2^{-1} A_{-2})$	65; (25)	$F_3^{-1} F_{-1}; (F_1^{-1} F_{-3})$	57; (31)
Ψ_4	$A_1^{-1} A_{-2}$	93	$F_4^{-1} F_{-1}; (F_2^{-1} F_{-2})$	52; (31)
Ψ_5	$A_2^{-1} A_{-2}$	51	$F_1^{-1} F_{-2}$	81
	$(A_1^{-1} A_{-3}; A_3^{-1} A_{-1}; A_5^{-1} A_{-1})$	(10; 13; 16)		
Ψ_6			$F_2^{-1} F_{-3}$	88
Ψ_7			$F_2^{-1} F_{-2}; F_4^{-1} F_{-1}$	45; 39
Ψ_8			$F_1^{-1} F_{-3}; (F_3^{-1} F_{-1})$	62; (28)

The configurations listed in Tab. 6 can be correlated with those given in Tab. 5 for the subsystems ethylene, benzene and naphthalene using an "HMO resemblance scheme" originally proposed by SANDORFY [21] and which also underlies the well known LCMO approximation of DEWAR [22] (LCMO = Linear Combination of Molecular Orbitals). Comparing the schematic representations of the basis HMOs of naphthalene and ethylene (Fig. 4) with those of acenaphthylene (Fig. 5) shows that the HMOs of the subsystems have retained much of their individuality in those of the compound system I. This is of course a direct consequence of the fact that the HMOs of I could be obtained in a fair approximation through Dewar's LCMO scheme using only two energetically nearest HMOs in a second order perturbation calculation. The correlation suggested in this way is shown graphically in the schematic Fig. 7 for the system I. An analogous comparison based on Figs. 4 and 6 will yield the HMO correlation diagram for fluoranthene shown in Fig. 8.

The correlation diagrams of Figs. 7 and 8 make it possible to determine in a unique way which locally excited configurations $\psi_J^{-1} \psi_K$ of the subsystems [and therefore which locally excited states (Tab. 5)] contribute mainly to the low-energy states Ψ_j of I and II. The result of this analysis is given in Tab. 7.

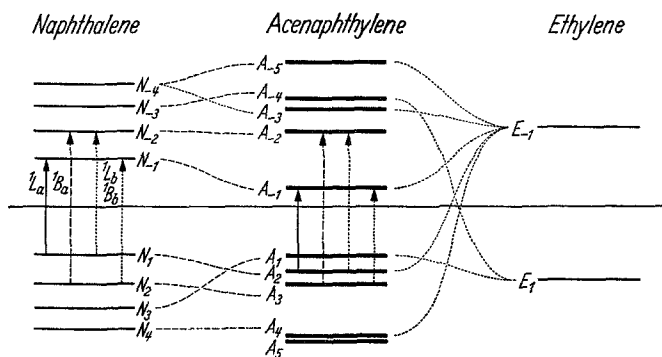


Fig. 7. Correlation diagram for the contribution of locally excited states of naphthalene and ethylene to the low energy configurations of acenaphthylene

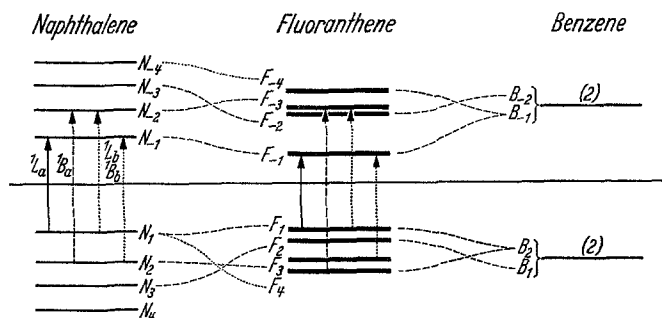


Fig. 8. Correlation diagram for the contribution of locally excited states of naphthalene and benzene to the low energy configurations of fluoranthene

Table 7. Correlation of configurations for acenaphthylene and fluoranthene with those of the naphthalene nucleus according to the diagrams of Fig. 6 and 1

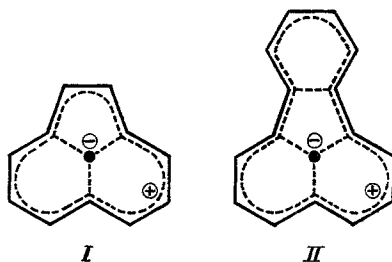
State	Acenaphthylene (I) Configuration	
Ψ_1	$A_1^{-1} A_{-1} \rightarrow N_3^{-1} N_{-1}$	(B_{1g})
Ψ_2	$A_2^{-1} A_{-1} \rightarrow N_1^{-1} N_{-1}$	$(B_{3u}; {}^1L_a)$
Ψ_3	$A_3^{-1} A_{-1} (A_2^{-1} A_{-2}) \rightarrow N_2^{-1} N_{-1} (N_1^{-1} N_{-2})$	$(B_{2u}; {}^1L_b, {}^1B_b)$
Ψ_4	$A_1^{-1} A_{-2} \rightarrow N_3^{-1} N_{-2}$	(A_g)
Ψ_5	$A_2^{-1} A_{-2} \rightarrow N_1^{-1} N_{-2}$	$(B_{2u}; {}^1L_b; {}^1B_b)$
State	Fluoranthene (II) Configuration	
Ψ_1	$F_2^{-1} F_{-1} \rightarrow N_3^{-1} N_{-1}$	(B_{1g})
Ψ_2	$F_1^{-1} F_{-1} \rightarrow N_1^{-1} N_{-1}$	$(B_{3u}; {}^1L_a)$
Ψ_3	$F_3^{-1} F_{-1} (F_1^{-1} F_{-3}) \rightarrow N_2^{-1} N_{-1} (N_1^{-1} N_{-2})$	$(B_{2u}; {}^1L_b, {}^1B_b)$
Ψ_4	$F_4^{-1} F_{-1} (F_2^{-1} F_{-2}) \rightarrow N_1^{-1} N_{-1} (N_3^{-1} N_{-3})$	$(B_{3u}; {}^1L_a)$
Ψ_5	$F_1^{-1} F_{-2} \rightarrow N_1^{-1} N_{-3}$	(B_{1g})
Ψ_6	$F_2^{-1} F_{-3} \rightarrow N_3^{-1} N_{-2}$	(A_g)
Ψ_7	$F_2^{-1} F_{-2}; F_4^{-1} F_{-1} \rightarrow N_3^{-1} N_{-3}; N_1^{-1} N_{-1}$	$(B_{3u}; {}^1B_a)$
Ψ_8	$F_1^{-1} F_{-3}; (F_3^{-1} F_{-1}) \rightarrow N_1^{-1} N_{-2} (N_2^{-1} N_{-1})$	$(B_{2u}; {}^1B_b, {}^1L_b)$

From this it is immediately evident why a description of the lower excited states Ψ_j of I and II in terms of the locally excited 1L_b , 1L_a , 1B_b , 1B_a -states of naphthalene and benzene will fail in both the ISA- and the MIM-method: The configuration $N_3^{-1} N_{-1}$ of the subsystem naphthalene necessary to describe satisfactorily the first excited band, i.e. the low energy states Ψ_1 of I and II, is one pertaining to a locally excited naphthalene state which is of higher energy than those given in Tab. 5. Such states are normally not included in MIM or ISA calculations for the simple reason that the relevant empirical data are not known. Furthermore the charge transfer configurations which would have to be included in an MIM-scheme demand a knowledge of higher ionisation potentials and electron affinities of the subsystems, and again there are no satisfactory empirical data for determining the energies of such configurations.

For example, in I, the configuration $A_1^{-1} A_{-1}$ which dominates Ψ_1 , includes the transfer of 0.32 of an electron from the double bond to the naphthalene system. This corresponds to the inclusion of the configurations $E_1^{-1} N_{-2}$ and $N_3^{-1} E_{-1}$, the latter involving the orbital N_3 . Ψ_5 of I, which has major components $A_1^{-1} A_{-3}$, $A_3^{-1} A_{-1}$ and $A_5^{-1} A_{-1}$, includes also some smaller amount of electron transfer from the double bond towards the naphthalene nucleus, which is due mainly to the incorporation and partial cancellation of transfer configurations $E_1^{-1} N_{-4}$, $N_3^{-1} E_{-1}$ (in $A_1^{-1} A_{-3}$), $N_2^{-1} E_{-1}$ (in $A_3^{-1} A_{-1}$) and of $N_4^{-1} E_{-1}$ (in $A_5^{-1} A_{-1}$). None of these can be introduced in a reasonable way into the MIM-treatment for lack of relevant empirical data.

In II the same situation prevails, although to a lesser degree. The lowest singlet excited state Ψ_1 , is mainly based on the $F_2^{-1} F_1$ configuration which involves transfer of 0.37 of an electron from the benzene to the naphthalene nucleus. This transfer is the resultant of $B_2^{-1} N_{-1}$ and $N_3^{-1} B_{-1}$, the latter of which involves a low lying HMO. Ψ_4 on the other hand needs for its description the inclusion of $N_3^{-1} B_{-2}$ and $B_2^{-1} N_{-3}$, both of which contribute to $F_2^{-1} F_{-2}$ included with a weight of 31% in Ψ_4 .

As a consequence of the above analysis, it becomes difficult to assign reasonable Platt-labels to the transitions from the ground state to the lower states of I or II. It would certainly be unreasonable to base such a classification on the states of the odd perimeter in these molecules — which would have to be charged positively to be a closed shell — perturbed by a central orbital of negative charge (I, II) and a cross bond (II):



This type of approximation would exaggerate greatly the non-alternant properties of both hydrocarbons and will not lead to a reasonable interpretation of the observed spectral data. If Burawoy's scheme (3.) is used in conjunction with the

results of our analysis (Tabs. 6 and 7) some of the bands can be characterised according to the Platt label of the major contributing locally excited state (or states) of the larger subsystem (= naphthalene). However, some bands will escape such a classification.

Clar's a posteriori assignment of α , p , β and β' labels to individual bands, according to their spectral behaviour under annelation and substitution, can of course be carried through. However, it should be recognised that the electronic mechanisms underlying such bands will be vastly different from those responsible for bands carrying the same designation in other hydrocarbons (e.g. the acenes).

To summarise: Even in hydrocarbons, such as I and II, which might be expected on chemical and structural grounds to behave as an ensemble of loosely coupled systems and therefore to exhibit to a good approximation their spectral characteristics, considerable mixing may occur in the excited states. This will obliterate to a large degree the individual spectral features of the subsystems and it can bring locally excited states into play which are not normally included in calculations according to the ISA- or MIM-schemes. This makes it difficult to label such bands according to the procedure advocated by BURAWOY [6].

Appendix

The Tabs. 8 and 9 contain the coefficients $C_{j,JK}$ of the individual configurations Γ and $\psi_J^{-1} \psi_K$ which enter the linear combinations

$$\Psi_j = C_{j,0} \Gamma + \sum_{JK} C_{j,JK} \psi_J^{-1} \psi_K$$

for the lower states of acenaphthylene (I) and fluoranthene (II), calculated according to the model A. The energy values E_j , measured relative to the energy $E_0 = 0$

Table 8. *Acenaphthylene* (I). *CI-states for model A*
Configurations $\psi_J^{-1} \psi_K$

	Ψ_0	Ψ_1	Ψ_2	Ψ_3	Ψ_4	Ψ_5
$J, K = 1, -1$	0	0.954	0	0.213	0	0.142
1, -2	0.013	0	-0.029	0	0.965	0
1, -3	0	-0.030	0	-0.162	0	-0.308
1, -4	-0.011	0	-0.188	0	0.019	0
2, -1	0.136	0	0.927	0	0.049	0
2, -2	0	-0.048	0	-0.500	0	0.713
2, -3	0.043	0	-0.091	0	0.053	0
2, -4	0	0.038	0	0	0	0.192
3, -1	0	-0.282	0	0.805	0	0.355
3, -2	-0.041	0	0.230	0	0.015	0
3, -3	0	0.048	0	-0.116	0	0.110
3, -4	-0.018	0	-0.018	0	-0.185	0
4, -1	0.048	0	0.141	0	-0.154	0
4, -2	0	-0.004	0	-0.036	0	0.200
4, -3	0.005	0	0.061	0	0.063	0
4, -4	0	-0.002	0	0.094	0	0.017
5, -1	0	-0.056	0	0.022	0	0.402
5, -2	0.035	0	0.048	0	0.011	0
5, -3	0	-0.034	0	-0.077	0	0.002
5, -4	0.025	0	0.030	0	-0.012	0
Γ	0.986	0	-0.126	0	-0.018	0

Table 9. Fluoranthene (II). CI-states for model A
Configurations $\psi_j^{-1}\psi_k$

	Ψ_0	Ψ_1	Ψ_2	Ψ_3	Ψ_4	Ψ_5	Ψ_6	Ψ_7	Ψ_8
$J, K = 1, -1$	0.051	0	0.949	0	-0.102	0	-0.047	0.153	0
1, -2	0	0.103	0	0.083	0	0.900	0	0	-0.095
1, -3	0	0.001	0	-0.560	0	0.151	0	0	0.786
1, -4	0.034	0	0.023	0	0.290	0	0.216	-0.235	0
2, -1	0	0.947	0	0.233	0	-0.100	0	0	0.179
2, -2	0.009	0	-0.198	0	-0.563	0	-0.112	0.668	0
2, -3	0.018	0	0.016	0	0.010	0	0.936	0.283	0
2, -4	0	0.034	0	-0.070	0	0.301	0	0	-0.225
3, -1	0	-0.296	0	0.757	0	0.060	0	0	0.529
3, -2	-0.015	0	-0.009	0	0.028	0	-0.135	0.041	0
3, -3	-0.025	0	0.189	0	-0.238	0	-0.022	-0.056	0
3, -4	0	0.053	0	-0.109	0	0.008	0	0	0.019
4, -1	-0.060	0	0.016	0	0.721	0	-0.200	0.621	0
4, -2	0	0.037	0	0.059	0	0.249	0	0	0.074
4, -3	0	0.008	0	0.182	0	-0.029	0	0	-0.067
4, -4	-0.011	0	0.149	0	0.096	0	0.047	-0.064	0
Γ	0.996	0	-0.040	0	0.039	0	-0.035	0.025	0

of the ground state Ψ_0 are given in Tabs. 3 and 4 together with the oscillator strength $f_{0 \rightarrow j}$ for the transitions $\Psi_0 \rightarrow \Psi_j$. The energy depressions of Ψ_0 relative to Γ are: -0.14 eV for I and -0.05 eV for II. For the π -contributions to the dipole moments $|\vec{\mu}_j|$ the values given in Tab. 10 have been found. In all cases the positive end of the dipole is situated on the side of the naphthalene nucleus.

Table 10. π -Contributions to the dipole moments of acenaphthylene and fluoranthene
in their ground and electronically excited states

Values in debye units. Positive end of dipole on the side of the naphthalene nucleus

State	I	II
Ψ_0	0.73	0.51
Ψ_1	2.91	4.31
Ψ_2	2.29	0.36
Ψ_3	2.12	1.42
Ψ_4	3.85	1.54
Ψ_5	1.18	5.17
Ψ_6		8.37
Ψ_7		2.75
Ψ_8		1.01

Acknowledgement. This work was supported by the Schweizerischer Nationalfonds (Projekt Nr. 3745). We thank Dr. J. H. EGGERS for making his results available to us and for the many suggestions and comments concerning their interpretation.

References

- [1] CLAR, E.: Polycyclic Hydrocarbons. New York: Academic-Press 1964.
- [2] KLEVENS, H. B., and J. R. PLATT: J. chem. Physics 17, 470 (1949).
- [3] FORBES, W. F.: Ultraviolet Absorption Spectroscopy. In: Interpretative Spectroscopy, FREEMAN, S. K., Editor. New York: Reinhold Publishing Corp. 1965.
- [4] PLATT, J. R.: J. chem. Physics 17, 484 (1949).
- [5] HEILBRONNER, E., and J. N. MURRELL: Molecular Physics 6, 1 (1963).

- [6] BURAWOY, A.: *J. chem. Soc.* **1939**, 1177.
- [7] SIMPSON, W. I.: *Theories of Electrons in Molecules*. New York: Prentice-Hall 1962.
- [8] LONGUET-HIGGINS, H. C., and J. N. MURRELL: *Proc. phys. Soc. (A)* **48**, 601 (1955).
- [9] COTTON, F. A.: *Chemical Applications of Group Theory*. New York: Wiley 1963.
- [10] HEILBRONNER, E.: *Molecular Orbitals in Chemistry, Physics and Biology* (B. Pullman and P. O. Löwdin, editors), p. 329. New York: Academic Press 1965.
- [11] PARR, R. G.: *Quantum Theory of Molecular Electronic Structure*. New York: Benjamin 1963.
- [12] FRIEDEL, R., and M. ORCHIN: *UV Spectra of arom. Compounds*. New York: Wiley 1951 (Acenaphthylene No. 234, Fluoranthene Nr. 439); *Organic Electronic Spectral Data*. New York: Interscience 1960—1963 (Acenaphthylene: I, 425; Fluoranthene: I, 646); see reference [18]; for Fluoranthene especially, see: STUBBS, H. W. D., and S. H. TUCKER: *J. Chem. Soc.* **1954**, 227; VAN DUUREN, B. L., and C. E. BARDI: *Anal. Chem.* **35**, 2200 (1963).
- [13] DÖRR, F., and M. HELD: *Angew. Chem.* **72**, 287 (1960).
- [14] — *Z. anal. Chem.* **197**, 241 (1963).
- [15] MICHL, J.: To be published.
- [16] MICHL, J., and R. ZAHRADNÍK: To be published.
- [17] EGGERS, J. H., and E. W. THULSTRUP: *Lecture: 8th European Congress on Molecular Spectroscopy* (1965).
- [18] KOUTECKY, J., P. HOCHMAN, and J. MICHL: *J. chem. Physics* **40**, 2439 (1964).
- [19] ZAHRADNÍK, R., J. MICHL, and J. KOUTECKY: *J. chem. Soc.* **1963**, 4998.
- [20] DEWAR, M. J. S., and H. C. LONGUET-HIGGINS: *Proc. phys. Soc. (A)* **67**, 795 (1954).
- [21] SANDORFY, C.: *Les spectres électroniques en chimie théorique*. Paris: Editions de la Revue d'Optique 1959.
- [22] DEWAR, M. J. S.: *Proc. Cambridge philos. Soc.* **45**, 638 (1949).
- [23] Recent experimental evidence concerning substituted fluoranthenes suggests however that in cases where conjugation in the system is enhanced by substituents, the system should be considered as markedly non alternating, even in the electronic ground state. [MICHL, J., and R. ZAHRADNÍK: *Coll. Czechoslov. Chem. Commun.* **31**, 3471, 3478 (1966).

Professor Dr. E. HEILBRONNER
Laboratorium für Organische Chemie
der Eidg. Technischen Hochschule
CH 8006 Zürich
Universitätsstraße 6