Optical Determination of Pair Correlation in π-Electron System

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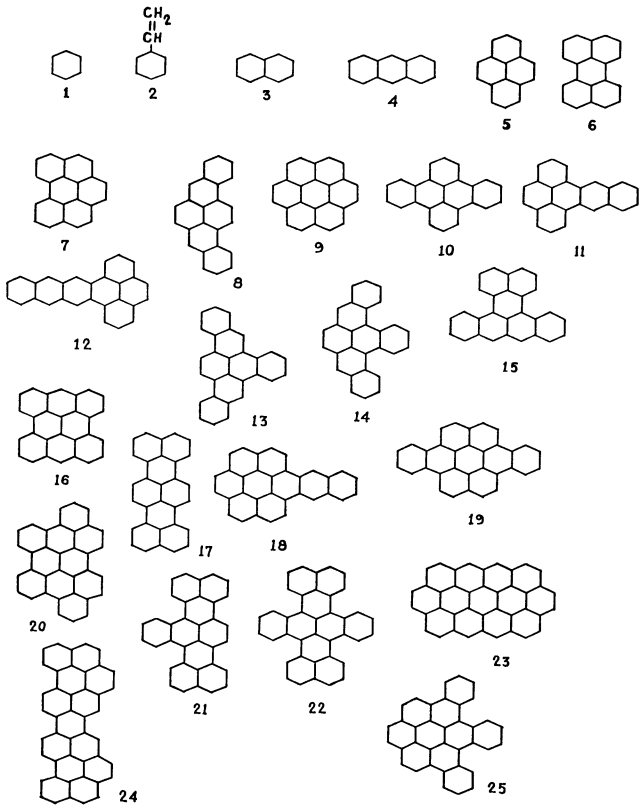
Synopsis. α, p, and β bands in the electronic spectra of polynuclear aromatic hydrocarbons have been found to converge to a limiting value. This has been ascribed to pair correlation effect arising from interaction of π-electrons with σ-framework and with molecular vibrations of appropriate symmetry.

Pair correlation effect plays an extremely important role in systems consisting of a large number of Fermi particles. This effect is caused by the presence of attractive force between Fermi particles and are manifested in diverse fields. Thus pair correlation in metals and degenerate semiconductors leads to the development of superconductivity. The pair correlation between nucleons in atomic nucleus explains the regularities observed in the nuclear moment of inertia. The problem of pair correlation of π-electrons in aromatic hydrocarbon has been theoretically analysed by Kresin.[1] Kresin[2] has also shown that such pair correlation is responsible for the characteristic difference in the electronic spectra of perylene and its mono- and dianions.[2] The pair correlation between π-electrons in linear polyene chains has been shown to give rise to convergence in the longest wavelength electron transition with the length of the conjugated chain, *i.e.*, number of π-electrons.[3] This means that pair correlation in π-electron systems may be demonstrated optically. The object of the present note is to analyse if pair correlation could be detected optically in polynuclear aromatic compounds. Clar[4] has prepared hundreds of polynuclear aromatic hydrocarbons where the number or π-electrons ranges from 6 to over 50. Clar has also documented the electronic spectra, which have been divided into α, p, and β regions, for most of these compounds. Since the attraction between electrons is maximum when they have opposite projection quantum numbers, we have selected molecules which have at least one symmetry axis. The frequency of spectral transition (ν) for the α, p, and β bands as well as the number of π-electrons present in the molecules (n) selected are summarised in Table 1. The plot of $\nu(\mathrm{cm}^{-1})$ *vs.* n is given in Fig. 1, where the curves have been drawn by a method of curve fitting.



It may be observed that all the three bands α, p, and β converge to a limiting value. The convergence is faster for the β and α bands but much slower for the p band. In presence of pair correlation, the single particle excitation spectrum is given as[1]

$$E = \sqrt{\xi^2 + \Delta^2}, \tag{1}$$

Table 1. Absorption bands in polynuclear aromatic hydrocarbons

Compound	n[a]	ν/cm^{-1}		
		α band	p band	β band
1	6	38000	48050	54500
2	8	34000	38000	46500
3	10	32000	34000	45400
4	14	26400	—	39000
5	16	26900	29985	36765
6	20	29629	23045	39840
7	22	24000	25806	33003
8	24	23094	25188	33670
9	24	23364	29283	32787
10	24	26881	30487	34722
11	24	24539	28985	31153
12	28	—	22624	28169
13	28	23923	25974	33727
14	28	21691	25445	29629
15	28	23419	16474	33112
16	28	23584	15094	32051
17	30	17857	—	37037
18	32	22522	23640	—
19	32	22988	24937	30303
20	34	21459	23980	27932
21	34	25510	15540	33557
22	38	23529	13559	31250
23	40	20243	16339	25000
24	44	—	17331	29069
25	36	21551	24570	28248

a) n denotes the number of π-electrons.

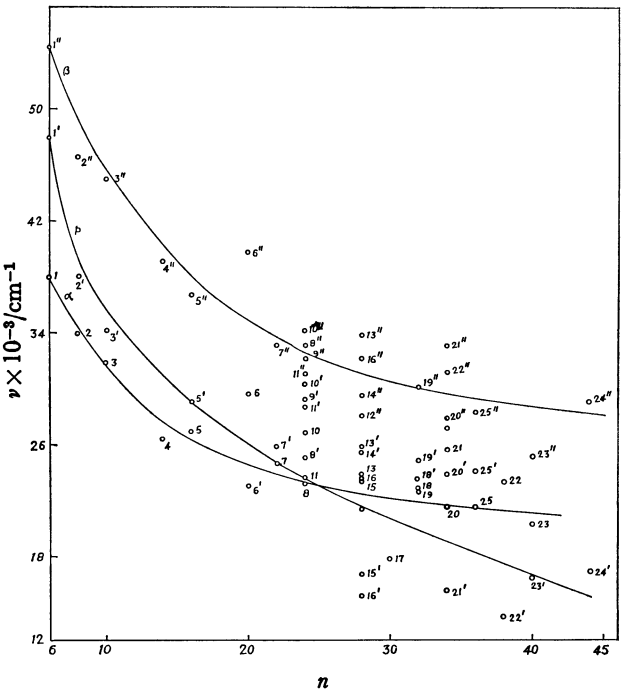


Fig. 1. Longest wavelength transition peaks of the α, p, and β bands in the absorption spectra of poly nuclear aromatic hydrocarbons. The numbers in the figure refer to the serial number in Table 1. Unprimed numbers refer to α, singly primed to p and doubly primed to β transitions.

where $\xi=\varepsilon_b-\varepsilon_a$, ε_b and ε_a being HF energy of an unoccupied and an occupied orbital respectively in absence of pair correlation and Δ is a gap parameter which gives the minimum excitation energy which separates the first excited state from the ground level and it is related to pair correlation energy between electrons having projection quantum numbers of opposite sign. As the number of electrons goes to infinity, ξ goes to zero, and the excitation energy goes to Δ, *i.e.*, Δ gives the convergence limit of the excitation spectrum. From Fig. 1 we get the convergence limit for β, α, and p transitions as 22666, 17333, and 10166 cm^{-1} respectively. The pair correlation energy is largest for a β-transition and smallest for a p-transition, with an α-transition in between. Before searching for a cause for this difference let us first analyse how pair correlation arises in π-electron system.

The major factor which determines the appearance of correlation effect and the energy gap is the presence of attractive force between π-electrons. The primary cause is the polarization of 6-framework, in the field of which the π-electrons move. Due to Coulombic interaction π-electrons cause transition of a σ-electron to a virtual orbital. On return of the σ-electron to the original orbital the energy liberated is transmitted to the π-electrons, which can surmount the repulsive force between similarly charged particles to some extent and the net result is effective attraction between π-electrons. This mechanism will be most effective for allowed π-transitions which have large oscillator strength and can polarise σ-framework. The second mechanism is the interaction of electronic energy with the molecular vibrational quanta. Virtual vibration will be excited and when the oscillator returns to the ground state, the energy transferred to the π-electron will lead to effective attraction. It is obvious that the vibrational quanta is of much lower energy than the electronic quanta, so the first effect will cause stronger correlation than the second.

The various bands observed in the hydrocarbons listed in Table 1 have not been assigned completely. Only for lower members the assignment is agreed upon. If we assume that assignment for the lower members also holds for higher members, then we may propose the following tentative explanation for pair correlation energy.

The presently accepted explanation[5] of the α-band is that they are symmetry forbidden transitions. They are made allowed by simultaneous excitation of some vibrational mode of the molecule so that the product function has proper symmetry to make the transition allowed. It may be suggested that pair correlation in the α-band arises from the interaction of electron with vibrational quanta. The β-bands are orbitally allowed transitions and have high oscillator strength. The polarization of σ-framework therefore may be responsible for pair correlation observed. The p-band is also orbitally forbidden singlet transition made allowed by combination with excited vibrational state. This band is rather diffuse. The pair correlation effect in this band also arises from the interaction of electrons with vibrational quanta, but because of the lower probability of interaction of ground electronic state with excited vibrational state, the correlation energy is low. This phenomenological analysis of the convergence in the absorption bands of various polynuclear aromatic hydrocarbons appears to indicate that a detailed theoretical analysis of the problem must be taken up to establish if the convergence is really due to pair correlation effect as suggested.

References

1) V. Z. Kresin, *Dokl. Akad. Nauk SSSR*, **177**, 1306 (1967).
2) V. Z. Kresin, *Zh. Strukt. Khim.*, **12**, 745 (1971).
3) S. Basu, *Adv. Quant. Chem.*, **11**, 33 (1978) and references cited there.
4) E. Clar, "Polycyclic Hydrocarbons," Academic Press, N. Y. (1964).
5) K. S. Pitzer, "Quantum Chemistry," Prentice Hall, Inc. (1977), p. 293, and references cited there.