

Electronic spectra of radical cations and their correlation with photoelectron spectra—III. Perylenes and coronenes

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Abstract—Radical cations of perylene, 1,12-benzoperylene, coronene, 1,2-benzocoronene, and naphtho-(2',3':1,2)coronene are produced by photooxidation in boric acid matrix and their electronic absorption spectra are measured. The results are discussed in terms of Longuet-Higgins-Pople and Wasilewski type Open-Shell SCF-MO calculations and the u.v. photoelectron spectra of the parent molecules. The correspondence between optical and photoelectron spectra is found to be fairly good. A correlation diagram for the electronic transitions for some of the molecular ions is presented to demonstrate their movement from one system to another. Finally, an expression showing the relationship between the first ionization potentials of the parent molecules and *A*-type electronic band energies in the cation spectra is given from which the first IP's of the hydrocarbons may be estimated.

INTRODUCTION

In the previous papers of this series [1, 2], the optical spectroscopy of radical cations of some catacondensed systems was studied in detail and correlation with u.v. photoelectron spectroscopy established. Here, we extend such investigations to the molecular ions of perylenes and coronenes. The landmark work in this area was carried out by HOIJTINK and coworkers in 1957–60. Recently, large polycyclic aromatics like coronenes have become of interest to astrophysicists because of their discovery in interstellar matter [3]. Impetus for study of the positive ions is provided since a large fraction of such hydrocarbons is considered as singly ionized [4].

EXPERIMENTAL

Perylene of puriss grade was obtained from Fluka (Switzerland). Other hydrocarbons were from the collection of Professor E. CLAR. The boric acid crystals used in the experiment were acquired from E. MERCK. All the chemicals were used without further purification. The method for the preparation of boric acid films is the same as discussed earlier [5] where a measured quantity of boric acid crystals was heated in a crucible to about 400°C in a temperature-controlled oven. A small quantity (concentration ~ 0.002–0.02 wt. %) was thoroughly mixed with the melt. The melt was then sandwiched between two glass plates placed 1 or 2 mm apart. After cooling to room temperature, the hydrocarbon-doped boric acid formed a rigid transparent glass. To produce hydrocarbon radical cations, the doped glasses were irradiated with a 120 W high-pressure mercury lamp using a 313 nm filter. The exposure time was chosen to be such that further irradiation did not result in any significant change in the colouring of the glasses. Electronic absorption spectra in the region 200–800 nm were measured on a Zeiss DMR 10 spectrometer and those above 800 nm on a Cary 17 spectrometer. In the case of perylene, however, no filters were used during u.v. irradiation and the measurements were made on a Perkin-Elmer 552 u.v.-VIS Spectrophotometer.

CALCULATIONS

The cation electronic transition energies were calculated using Longuet-Higgins-Pople (LHP) [6] and Wasilewski [7] open-shell SCF-MO methods with limited configuration interaction (LCI). For the CI calculations in the LHP model, the matrix elements given by ZAHRADNIK and CARSKY [8] were used. A detailed discussion of parameters and evaluation of integrals is given in [1, 2]. The computation was done on a CDC Cyber 170/730 computer at the National Informatics Centre, Electronics Commission, New Delhi.

RESULTS AND DISCUSSION

The figures display the electronic spectra of perylene and coronene radical cations. The transition energies for cations inferred from u.v. photoelectron spectra (PES) of the parent hydrocarbons [9] are given at the top of each figure. The results of the LHP and Wasilewski calculations are shown as stick diagrams showing the polarization of the allowed transitions. Forbidden transitions are represented by dotted lines. Electronic transitions are usually designated by "one-letter" symbols. Unless specifically mentioned, the results are discussed in the light of the LHP method as the predictions of both the theoretical models are largely identical.

(i) Perylene radical cation

In the past, a variety of methods have been used to produce perylene anions [10–12] and cations [12–18] and their electronic absorption spectra have been measured. The first successful effort to interpret the spectrum of perylene mononegative ions was made by HOIJTINK *et al.* [11] using a simplified MO approach. Improved calculations using a SCF-MO method were later carried out by SHIDA and IWATA [12], but the

assignment of the individual absorption bands was not discussed by these authors. However, optical data for perylene anion are now available in the region 9–45 kK and those for the cation in the 10–44 kK region. It appears that in spite of their great resemblance, some spectral differences do exist. Firstly, the cation bands are blue-shifted from those of the anion and, secondly, the anion spectrum shows a strong absorption in the region 28–35 kK, compared to the moderate intensity two cation absorption peaks in the same region. Apart from this, there seems to be some discrepancy in the early assignment of the anion spectrum by HOJTINK *et al.* which we have attempted to settle in the light of photoelectron spectroscopic data and open-shell calculations. With this objective, we have carried out a detailed investigation of the electronic spectrum of perylene cation. At first, the experiment was performed

in the usual way, i.e. exposing the perylene-doped boric acid glass with the u.v. light using a 313 nm filter. As the ion formation was found to be insufficient, irradiation was performed without a filter. This resulted in considerable improvement in the spectrum (Fig. 1). Except for the absorption in the 22–28 kK region, which is due to presence of the neutral species, the spectrum characterizes the perylene cation. Figure 1 also shows the results of calculations and estimates of cation transition energies from the PE spectrum of the molecule.

The calculations reveal that the first and fifth states arise as a result of strong mixing between the configurations $\phi_9 \rightarrow \phi_{10}$ and $\phi_{10} \rightarrow \phi_{11}$ and are assigned as *IA* and *AI*, respectively. Due to its extremely small oscillator strength, the first of these transitions has not been observed. In the spectrum of perylene negative

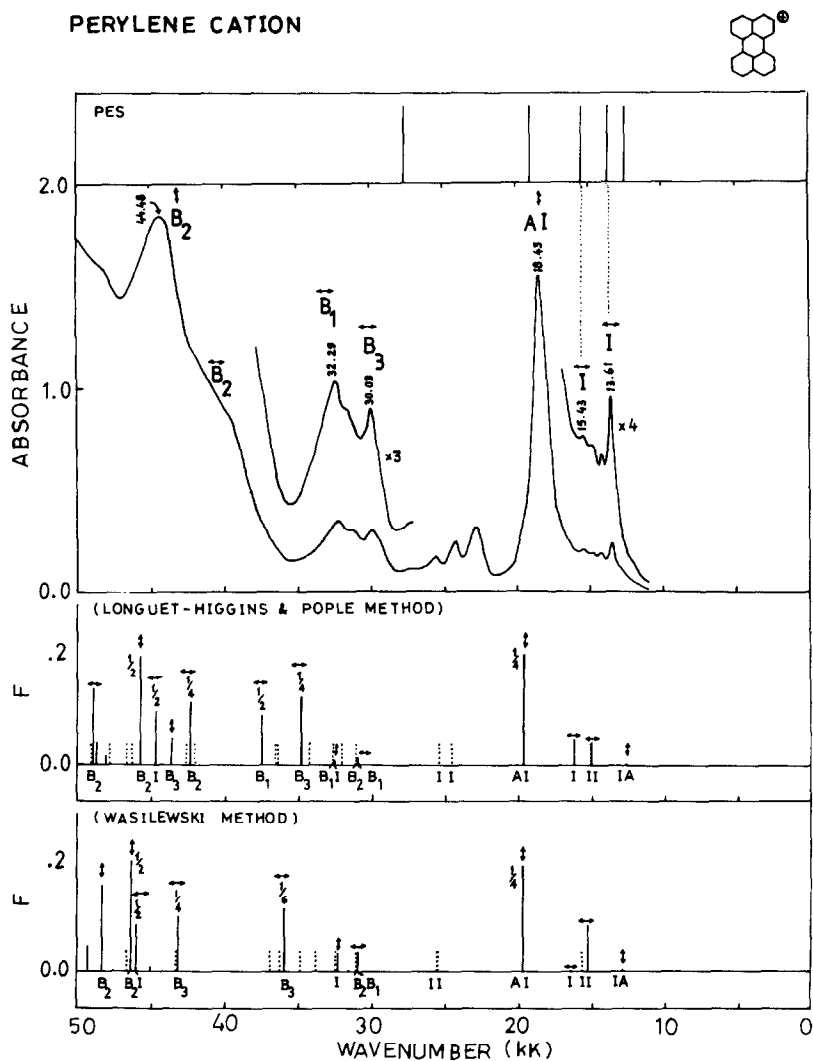


Fig. 1. Electronic absorption spectrum of perylene radical cation and its comparison with the calculated spectrum and the transition energies estimated from the PE spectrum of the parent molecule. In the optical spectrum, calculated polarizations of the individual electronic bands are given. The dotted lines in the lower half of the figure correspond to the forbidden transitions and the fractional notations show the amount by which the actual oscillator strengths have been reduced in the diagram.

ion, HOIJTINK *et al.* assigned a weak absorption on the longer wavelength side to the *AI* band as the *y*-polarized *IA*-transition. The computer based calculations show however that the absorption bands at 13.61 and 15.43 kK correspond to the second and third lines in the PES diagram. The *AI*-transition is easily identified due to its strong intensity. From the PE spectrum two more *I*-type transitions are expected, the first of which is presumably hidden in the strong *AI* absorption while the other is forbidden and has evaded detection. On intensity considerations, the absorption peaks at 30.03 and 32.29 kK are assigned as $B_3(x)$ and $B_1(x)$, respectively. In the anion spectrum, these are

replaced by a single absorption at ~ 31.3 kK. On the higher-energy side of the cation spectrum, the strong absorption at 44.48 kK is recognized as the $B_2(y)$ transition. A similar band occurs at ~ 43.6 kK in the spectrum of perylene anion.

(ii) 1,12-Benzoperylene radical cation

The optical absorption spectrum of 1,12-benzoperylene radical cation is presented in Fig. 2. As the hydrocarbon is only partially converted to the positive ion on exposure to u.v. radiation, the absorption bands above 25 kK are primarily due to the presence of the parent molecule, although some intensity changes

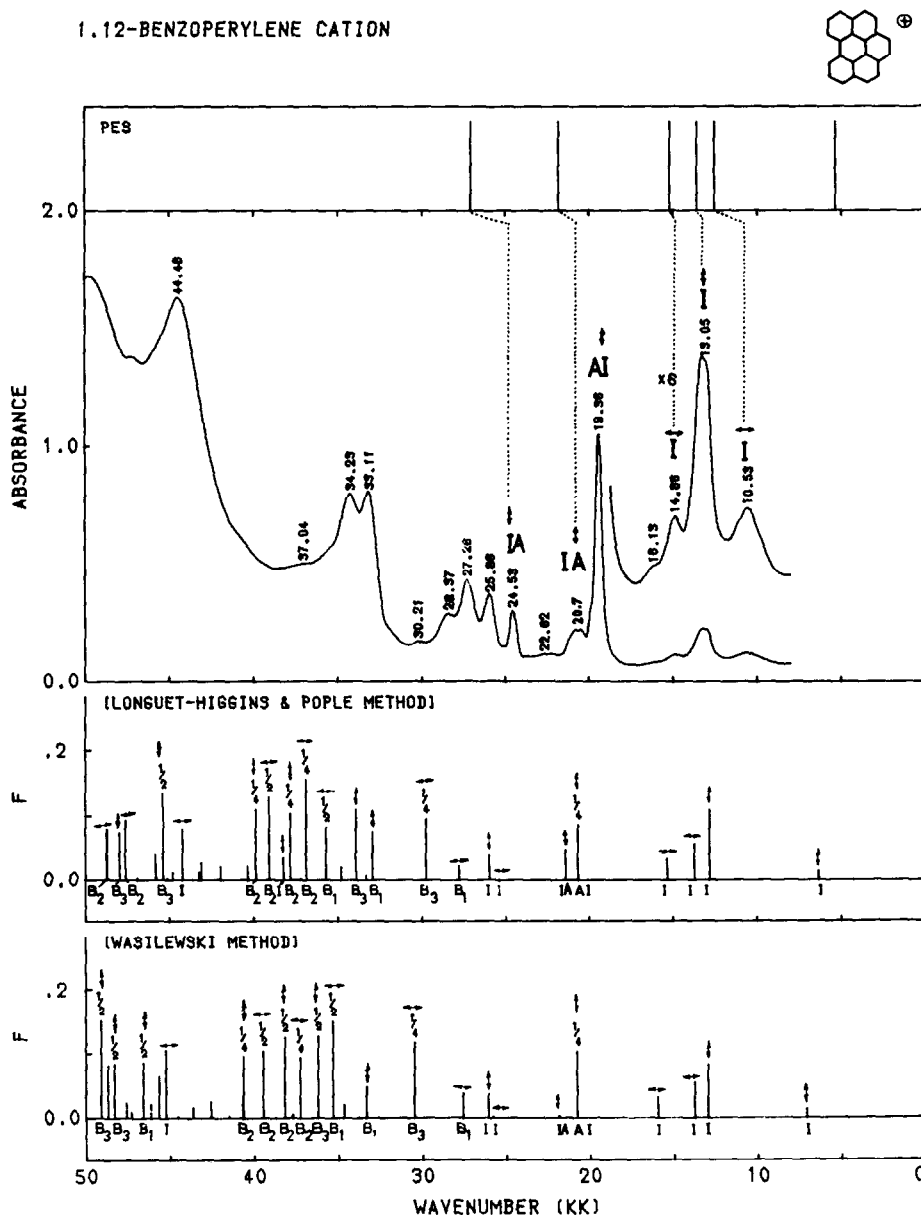


Fig. 2. Electronic absorption spectrum of 1,12-benzoperylene radical cation and its comparison with the calculated spectrum and the transition energies estimated from the PE spectrum of the parent molecule. For other details, see caption to Fig. 1.

are noticed. The only other report on the electronic spectra of this species is that of SHIDA and IWATA [12], who produced the anions and cations by different methods, and measured their spectra in the 10–28 kK region, but without giving any interpretation.

The calculations reveal that the first four transitions are almost pure one-electron excitations. Of these, the lowest-energy transition falls beyond our measurement range. In the lower part of the spectrum, a strong absorption occurs at 13.05 kK which, on the basis of its calculated intensity, is assigned as the γ -polarized I -transition. This assignment is made on the hypothesis that the energy of the third I -transition has been

overestimated by the theory. This also agrees with the assignment of the relevant photoelectron peaks of the parent hydrocarbon by BOSCHI *et al.* [19]. The absorption band at 10.53 kK, which belongs to the class $I(x)$, may be correlated with the second line in the PES diagram. The large deviation between the optical and PE spectroscopic results is not unique to this transition only; a similar variation is also noticed for the higher I -type transitions. The next $I(x)$ transition has low intensity and is probably buried in the vibrational structure at 14.86 kK. The next two transitions arise from mixing between configurations $\phi_{11} \rightarrow \phi_{12}$, $\phi_6 \rightarrow \phi_{11}$, and $\phi_9 \rightarrow \phi_{11}$. This gives rise to a

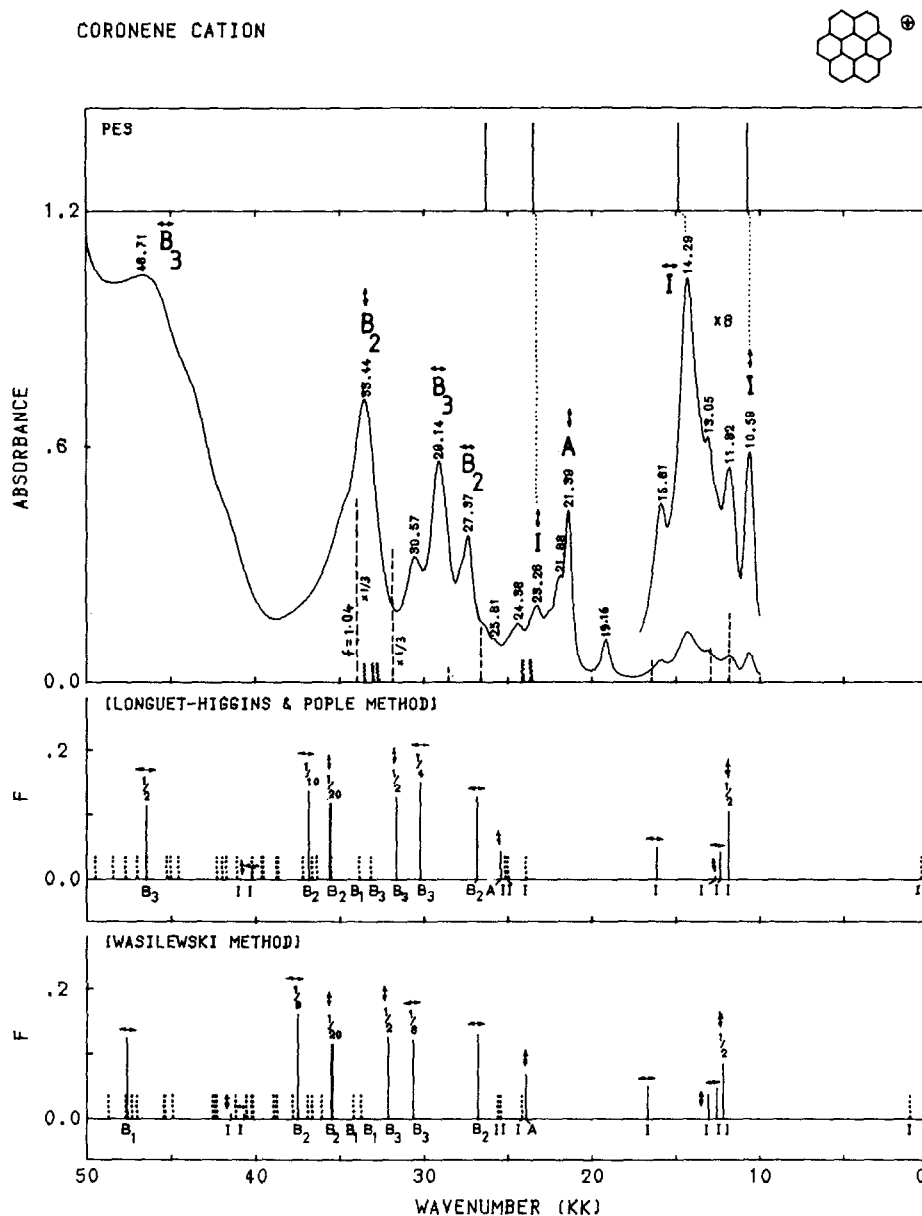


Fig. 3. Electronic absorption spectrum of coronene radical cation and its comparison with the calculated spectrum and the transition energies estimated from the PE spectrum of the parent molecule. For other details, see caption to Fig. 1.

strong *AI* transition and a weak *IA* transition, both polarized along the y -axis of the molecular ion. Their identification is straightforward as the *AI* transition does not appear in the PES diagram. The calculations predict yet another y -polarized *I*-transition which is located at 24.53 kK in the absorption spectrum. This again is in accord with the assignment of the peaks in the photoelectron spectrum of the molecule [19].

(iii) *Coronene radical cation*

Unlike other molecular ions of the series, coronene has a degenerate ground state and is thus susceptible to Jahn-Teller distortion. The study of its ion-radicals is

therefore of considerable interest. Although the optical spectroscopy of coronene anions and cations has been subjected to several studies [12, 15, 20], the literature is not altogether free from ambiguities. It is, therefore, desirable to study the ion spectrum in detail.

The observed electronic spectrum of coronene cation is displayed in Fig. 3. At the bottom of the absorption curve, the calculations of KUHNS *et al.* [21] are reproduced (allowed and forbidden transitions are shown by dashed and wavy lines, respectively). These calculations are based on the "half-electron" (HE) method which explicitly considers the degeneracy of the ground state. On u.v. irradiation, the molecular

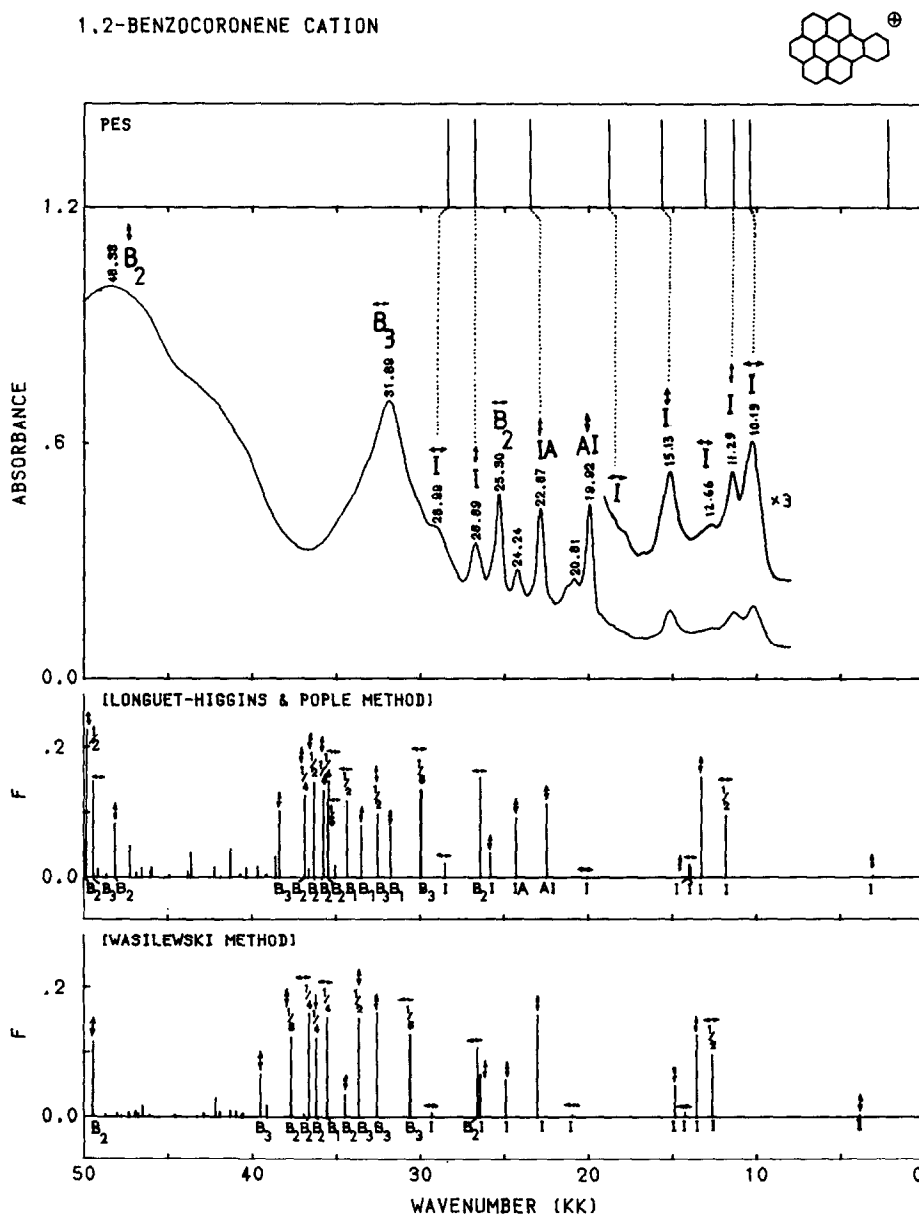


Fig. 4. Electronic absorption spectrum of 1,2-benzocoronene radical cation and its comparison with the calculated spectrum and the transition energies estimated from the PE spectrum of the parent molecule. For other details, see caption to Fig. 1.

spectrum is almost completely transformed, but the cation spectrum retains two absorption bands at ~ 29 and ~ 33 kK slightly shifted from the molecular spectrum. The present spectrum closely resembles the spectra of the cations and anions produced by other methods. This makes us fairly convinced that in the present experiment, the conversion to monovalent ions is almost 100%.

The LHP and Wasilewski like calculations for coronene cation are based on the assumption that the ground state is non-degenerate. Therefore, it should not be surprising if their predictions are somewhat

erroneous. The first *I*-transition, which in practice is not feasible, is the result of this inadequacy. This problem has, however, been overcome in the calculations of KUHN *et al.* [21]. The transitions (2–5) are almost pure, the first three of which form a cluster with decreasing intensity. In the HE method, this cluster of bands is replaced by two closely-separated transitions: $2e_{1g} \rightarrow 2e_{2u}$ and $1b_{1g} \rightarrow 2e_{2u}$ [21], respectively. In all the calculations, the next *I*-transition, $1b_{2g} \rightarrow 2e_{2u}$ is distinct in energy as well as intensity. This allows us to assign the absorption peaks at 10.59 and 14.29 kK which show a striking correspondence with the first

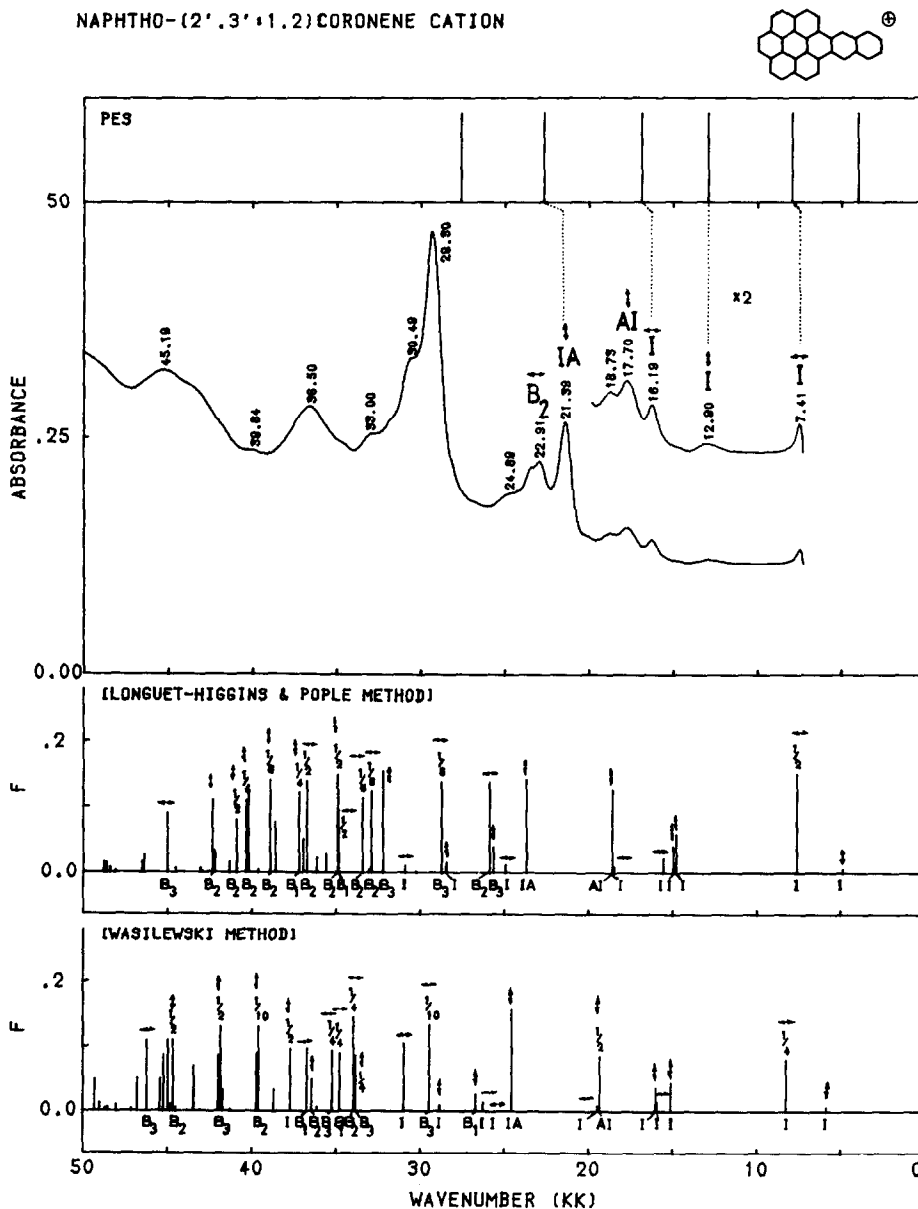


Fig. 5. Electronic absorption spectrum of naphtho-(2',3':1,2)-coronene radical cation and its comparison with the calculated spectrum and the transition energies estimated from the PE spectrum of the parent molecule. For other details, see caption to Fig. 1.

two lines in the PES diagram. The calculations reveal that it is the pi levels $2e_{1g}$ and $1b_{1g}$ that are close in energy rather than $1b_{1g}$ and $1b_{2g}$ [22].

In the absence of any theoretical evidence, it is difficult to draw a definite conclusion about the nature of the 19.16 kK absorption. The absorption band at 21.39 kK has no counterpart in the PES diagram and in conformity with the Wasilewski calculations it is assigned as the *A*-type transition. The other two calculations overestimate its energy and put it in the reverse ordering. The variation in the calculated and observed intensities for this as well as for some other transitions is perhaps due to Jahn–Teller distortion. The third electronic peak obtained from the PE spectrum corresponds to the *I*-type absorption band at 23.26 kK. Although the predictions of the LHP and Wasilewski calculations make it difficult to identify the higher-energy transitions, it is at least in principle possible to make a tentative assignment of the bands on the basis of the HE calculations.

(iv) 1,2-Benzocoronene radical cation

Figure 4 presents a complete picture of the previously unobserved and calculated spectrum of 1,2-benzocoronene monocation. The parent molecule is completely ionized on u.v. irradiation. The absorption bands at 10.19, 11.29, and 12.66 kK show a good correlation with the lines in the PES diagram. For the next *I*-band at 15.13 kK, the situation is slightly different; the energy and the intensity are underestimated by both calculations. The *AI* and *IA* transitions arise due to mixing between $\phi_7 \rightarrow \phi_{14}$ and $\phi_{14} \rightarrow \phi_{15}$ configurations. As the former of these transitions does not appear in the PES diagram, its identification is straightforward. The spectrum reveals that the ninth (*I*-type) and tenth (B_2 -type) transitions, which are predicted to be in close proximity, are reversed in ordering by the calculations. The most intense band in the spectrum occurs at 31.89 kK which is assigned as the *x*-polarized B_3 -transition. Similarly, the absorption band at 48.33 kK is identified as the $B_2(y)$ transition in accordance with the calculations.

(v) Naphtho-(2',3':1,2)coronene radical cation

The optical absorption spectrum of the naphtho-(2',3':1,2)coronene radical cation, which has not been reported before, is presented in Fig. 5. As the solubility of the hydrocarbon in boric acid is low, the quality of the spectrum is poorer than for the other systems. The calculated spectrum above 30 kK is very crowded, but fortunately the number of electronic transitions in the higher-wavelength region is comparatively small which facilitates the assignment of the ionic bands. The lowest-energy transition of the cation occurs in the near i.r. which is inaccessible to our measurements, but the second transition is observed at 7.41 kK. The next three transitions forming a cluster are very close in energy with maximum intensity in the first. This leads to a tentative assignment of the absorption band at 12.90 kK. Keeping in view that the *A*-type transitions

do not show up in the PES diagram, the absorption at 17.70 kK is easily recognized. The fifth PES line corresponds to the electronic band at 21.39 kK. Its intensity is, however, overestimated by the theories. In the higher-energy region of the observed spectrum, only a few prominent peaks are observed. Although we are not sure about the nature of the electronic bands at 29.30 and 36.50 kK (which are present in the spectrum of the neutral molecule as well), the calculations do predict at least two electronic transitions, $B_3(x)$ and $B_2(y)$ with $f \geq 1$.

Correlation between the spectra

Figure 6 depicts the calculated lower-energy transitions of the radical cations of 1,12-benzoperylene, 1,2-benzocoronene, and naphtho-(2',3':1,2)coronene. Other molecular ions of the series have intentionally been left out as they belong to different point groups. The correlation diagram demonstrates the behaviour of the different bands in moving from one system to another. It is particularly interesting to notice the regular trend in the intensities of the *AI* and *IA* transitions which arise from strong mixing between the *A*-type (HOMO \rightarrow LUMO) configuration and one of the *I*-type configurations. In benzoperylene, the *AI*-transition steals most of the intensity. This trend changes as we move to benzocoronene and is almost reversed for naphthocoronene where the *IA* transition becomes more intense than the *AI* transition.

Yet another interesting feature is noticed for the *A*-type transitions, viz., they can be correlated with the first ionization potentials (IP_1 's) of the parent hydrocarbons. From the knowledge of the observed energies of the *A*-bands, E_A^{obs} , the first IP's may be estimated

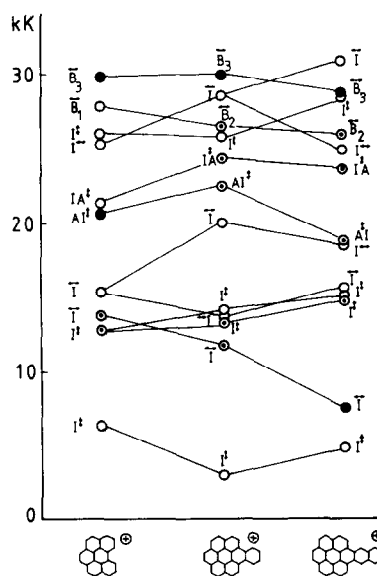


Fig. 6. Correlation diagram for the lower-energy transitions of some molecular ions belonging to the C_{2v} symmetry group. The circles show the relative oscillator strengths of the transitions: \circ $f < 0.05$; \odot $f = 0.05$ to 0.2 ; \bullet $f > 0.2$.

using the relation,

$$IP_1 = 5.114 + 0.820E_A^{obs}.$$

This expression is particularly valid for perylenes and coronenes and gives the calculated first IP's for perylene, 1,12-benzoperylene, coronene, 1,2-benzocoronene, and naphtho-(2',3':1,2)coronene as 6.99, 7.08, 7.29, 7.14, and 6.91 eV which compare well with the experimental values of 6.97, 7.15, 7.29, 7.08 and 6.88 eV [9], respectively.

CONCLUSIONS

This paper provides additional examples of correlation between the optical and photoelectron spectra. Efforts are made to assign absorption bands of radical cations. Except for 1,12-benzoperylene, where the results of the optical and PE spectra show comparatively large variations, the shifts for all other systems are negligibly small. It is also shown that there is a direct correlation between *A*-type absorption band energies in the cation spectra and the first IP's of the parent hydrocarbons.

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