Electronic Spectra of Radical Cations and Their Correlation with Photoelectron Spectra.

II. Dibenzotetraphene and Pentaphenes*

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Absorption measurements on the radical cations of 3.4,8.9-dibenzotetraphene, pentaphene, 3.4-benzopentaphene, 6.7-benzopentaphene, and naphtho-(2′.3′:6.7)pentaphene are made in the spectral region 7–50 kK. Electronic spectra of the cations are calculated using the Longuet-Higgins-Pople and Wasilewski type Open-Shell SCF-MO methods with limited configuration interaction. A detailed discussion of the absorption bands is given in the light of the calculations and the electronic transition energies of the cations derived from the ultraviolet photoelectron spectra of the parent hydrocarbons. The correlation between the optical and photoelectron spectra is closely examined and it is found to be excellent.

Introduction

In continuation of previous work on the correlation between the optical and photoelectron spectra of polycyclic aromatics [1], we have extended our investigations to other closely related cata-condensed systems, viz., dibenzotetraphene and pentaphenes. The correspondence between the photoelectron spectra (PES) of the hydrocarbons and the electronic spectra of their radical cations is found to be excellent. The matrix shift between the two types of spectra is also negligibly small. The assignment of the electronic transitions is discussed in the light of the PES data and the Open-Shell SCF-MO-LCI calculations.

Experimental

Most of the aromatic hydrocarbons were from the collection of Professor E. Clar and the boric acid crystals were obtained from E. Merck. All the chemicals were used without further purification. The boric acid glasses were prepared according to the method discussed in [1]. The solute concentrations varied between 0.002 and 0.02 wt% and the same irradiation technique was adopted as in the previous paper.

Calculations

For the calculation of electronic transition energies and intensities for radical cations, the Longuet-Higgins and Pople (LHP) [2] and Wasilewski [3] type open-shell SCF-MO methods were used. All the hydrocarbons were assumed to be planar, having hexagonal geometries with a constant bond-length of 1.4 Å. The resonance integrals for the bonded carbon atoms were taken as −2.318 eV, and zero otherwise. The one-centre Coulomb repulsion integrals were chosen to have a constant value of 10.53 eV, while the two-centre integrals were evaluated according to the Mataga-Nishimoto approximation [4]. For configuration interaction calculations, in the framework of the LHP method, formulas for matrix elements published by Ishitani and Nagakura [5] and Zahradnik and Carsky [6] were used. For the other method, the corrected version of the formulas given by Wasilewski [3, 7] were employed. Based on these methods, a computer program was written using a CI scheme with a sufficiently large but limited number of low-energy configurations. The calculations were made on a CDC Cyber 170/730 computer at the National Informatics Centre, Electronics Commission, New Delhi.

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* For part I, see Ref. [1].

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Results and Discussion

The electronic absorption spectra of the radical cations of dibenzotetraphene and the pentaphenes, which have not been reported before, are displayed in the following figures. At the top of each figure, the transition energies for the cations, as inferred from the PE spectra [8] of the corresponding hydrocarbons, are shown. The results of the open-shell SCF-MO-LCI calculations for the LHP and Wasilewski methods are given at the bottom as "sticks" whose lengths are measures of the calculated oscillator strengths of the electronic transitions. Wherever relevant, the calculated polarizations of the transitions are also given. At the bottom of the stick diagrams, the designation of each electronic transition is mentioned. Usually, "one-letter" symbols are adopted for designating the transitions to avoid crowdedness, but in some cases "two-letter" symbols [9] are also used. Forbidden transitions are shown by dotted lines. As both types of calculations give almost identical results, especially for the lower-energy transitions, we have usually employed the LHP method for the interpretation of the spectra. However, specific mention is made in the text whenever the other method is used. A detailed discussion of each of the spectra is given in the following.

(i) *3.4,8.9-Dibenzotetraphene Radical Cation*

The electronic spectrum of 3.4,8.9-dibenzotetraphene radical cation is presented in Fig. 1 and is compared with the PES diagram and the results of the calculations. In ionic systems, the lower-energy transitions are of great significance as they characterize such species and also because they have a direct correlation with the PE spectrum of the hydrocarbon. To get a better insight into these transitions, we reproduce in the following the major configurations for the first twelve doublet excited states of the cation along with the calculated oscillator strengths of the electronic transitions. These, in the light of the LHP calculations, are:

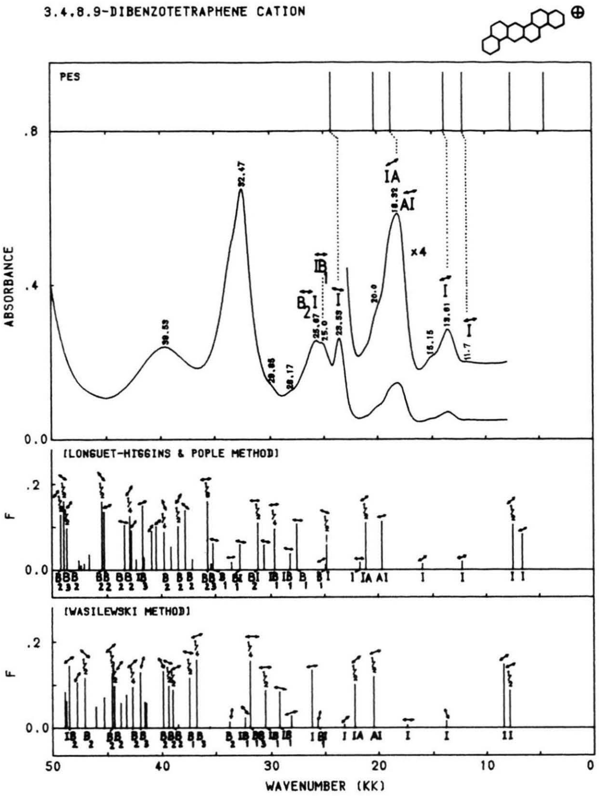

Fig. 1. Electronic absorption spectrum of 3.4,8.9-dibenzotetraphene radical cation and its comparison with the calculated spectrum and the transition energies estimated from the photoelectron spectrum (PES).

(1) $I\,[0.803(\Phi_{12} \rightarrow \Phi_{13}) + 0.534(\Phi_{11} \rightarrow \Phi_{13})]$, 0.083;

(2) $I\,[0.795(\Phi_{11} \rightarrow \Phi_{13}) - 0.537(\Phi_{12} \rightarrow \Phi_{13})]$, 0.209;

(3) $I\,[0.923(\Phi_{10} \rightarrow \Phi_{13})]$, 0.019;

(4) $I\,[0.939(\Phi_{9} \rightarrow \Phi_{13})]$, 0.013;

(5) $AI\,[0.649(\Phi_{13} \rightarrow \Phi_{14}) + 0.607(\Phi_{8} \rightarrow \Phi_{13})]$, 0.112;

(6) $IA\,[-0.689(\Phi_{8} \rightarrow \Phi_{13}) + 0.583(\Phi_{13} \rightarrow \Phi_{14})]$, 0.217;

(7) $I\,[0.875(\Phi_{7} \rightarrow \Phi_{13})]$, 0.016;

(8) $I\,[0.855(\Phi_{6} \rightarrow \Phi_{13})]$, 0.160;

(9) $B_1 I\,[0.581(\Phi_{13} \rightarrow \Phi_{16}) + 0.436(\Phi_{5} \rightarrow \Phi_{13})]$, 0.011;

(10) $B_1 B_2\,[0.571(\Phi_{13} \rightarrow \Phi_{15}) + 0.564(\Phi_{11} \rightarrow \Phi_{14})]$, 0.106;

(11) $IB_1\,[-0.658(\Phi_{5} \rightarrow \Phi_{13}) + 0.240(\Phi_{13} \rightarrow \Phi_{16}) + 0.229(\Phi_{13} \rightarrow \Phi_{15})]$, 0.036;

(12) $IB_1\,[-0.412(\Phi_{4} \rightarrow \Phi_{13}) + 0.342(\Phi_{5} \rightarrow \Phi_{13}) + 0.419(\Phi_{13} \rightarrow \Phi_{15})]$, 0.378.

Of these, the first two transitions, which show some mixing, have not been observed due to experimental limitations. The next two transitions are pure one-electron excitations as the mixing with other configurations is negligibly small and these have been well identified. Again, mixing becomes prominent in the fifth and sixth transitions which are designated as *AI* and *IA*, respectively. They appear to be superimposed and lie within the broad absorption at 18.32 kK. The next *I*-transition is too weak to be observed and is likely to be hidden in the vibrational structure of the *IA* transition. The absorption band at 23.53 kK is easily recognized as an *I*-type transition. Except for slight red-shifts, the electronic transitions obtained from the optical absorption spectrum are in excellent accord with those inferred from the PE spectrum. We observe yet another absorption at 25.0 kK which corresponds to the twelfth transition in the above list and is assigned as IB_1. This seems to correspond to the small absorption at 10.5 eV in the PE spectrum of the hydrocarbon (not shown in the PES diagram).

(ii) *Pentaphene Radical Cation*

Figure 2 displays the electronic absorption spectrum of the pentaphene radical cation and its comparison with the calculated spectrum and the transition energies estimated from the PE spectrum of the hydrocarbon. The main configurations for some of the lower-energy excited doublet states of the cation and the intensities of the corresponding electronic transitions are:

(1) $I\,[0.967\,(\Phi_{10} \rightarrow \Phi_{11})]$, 0.056;

(2) $I\,[0.952\,(\Phi_9 \rightarrow \Phi_{11})]$, 0.124;

(3) $I\,[0.950\,(\Phi_8 \rightarrow \Phi_{11})]$, 0.025;

(4) $AB_3\,[0.732\,(\Phi_{11} \rightarrow \Phi_{12}) - 0.515\,(\Phi_{10} \rightarrow \Phi_{13})]$, 0.192;

(5) $I\,[0.885\,(\Phi_7 \rightarrow \Phi_{11})]$, 0.072;

(6) $I\,[0.916\,(\Phi_6 \rightarrow \Phi_{11})]$, 0.041;

(7) $B_1 B_3\,[0.695\,(\Phi_{11} \rightarrow \Phi_{13}) - 0.412\,(\Phi_{10} \rightarrow \Phi_{12})]$, 0.013;

(8) $I\,[-0.854\,(\Phi_5 \rightarrow \Phi_{11})]$, 0.008;

(9) $IA\,[0.666\,(\Phi_4 \rightarrow \Phi_{11}) + 0.494\,(\Phi_{11} \rightarrow \Phi_{12})]$, 0.330.

The first transition, which is supposed to occur in the infrared region, is beyond the range of our measurements. All other major transitions have been observed and assigned. As compared to the transitions estimated from the PE spectrum, some of the optical bands are blue-shifted. The hydrocarbon is not well photo-oxidized as a result of which all the absoprtion bands of the parent hydrocarbon are present in the cation spectrum, but with reduced intensity. This is particularly true for the absorption bands with energies > 30 kK.

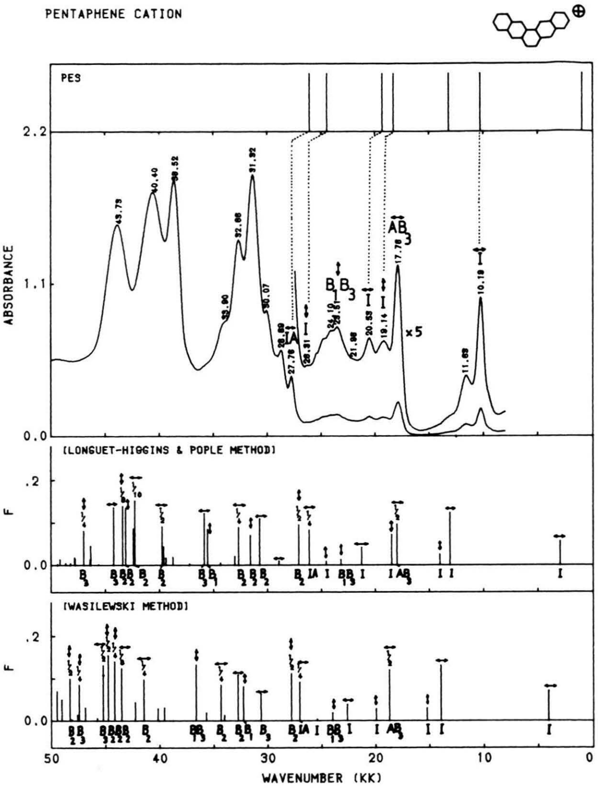

Fig. 2. Electronic absorption spectrum of pentaphene radical cation and its comparison with the calculated spectrum and the transition energies estimated from the photoelectron spectrum (PES).

(iii) *3.4-Benzopentaphene Radical Cation*

A complete picture of the observed and calculated spectrum of the 3.4-benzopentaphene radical cation is depicted in Figure 3. In view of the importance of its lower-energy excited states, we reproduce in the following the main configurations for the first twelve states along with the oscillator strengths of the electronic transitions:

(1) $I\,[0.915\,(\Phi_{12} \rightarrow \Phi_{13})]$, 0.065;

(2) $I\,[0.896\,(\Phi_{11} \rightarrow \Phi_{13})]$, 0.224;

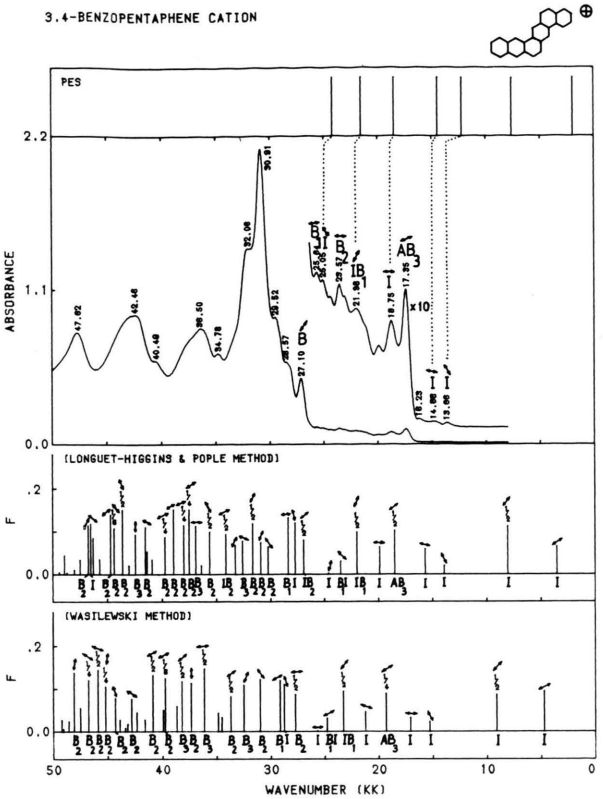

Fig. 3. Electronic absorption spectrum of 3.4-benzopentaphene radical cation and its comparison with the calculated spectrum and the transition energies estimated from the photoelectron spectrum (PES).

(3) $I\,[0.945\,(\Phi_{10} \rightarrow \Phi_{13})]$, 0.020;

(4) $I\,[0.939\,(\Phi_9 \rightarrow \Phi_{13})]$, 0.059;

(5) $AB_3\,[-0.747\,(\Phi_{13} \rightarrow \Phi_{14}) + 0.390\,(\Phi_{12} \rightarrow \Phi_{15})]$, 0.203;

(6) $I\,[0.892\,(\Phi_8 \rightarrow \Phi_{13})]$, 0.064;

(7) $IB_1\,[0.712\,(\Phi_7 \rightarrow \Phi_{13}) - 0.370\,(\Phi_{13} \rightarrow \Phi_{15})]$, 0.196;

(8) $B_1 I\,[0.565\,(\Phi_{13} \rightarrow \Phi_{15}) + 0.480\,(\Phi_7 \rightarrow \Phi_{13})]$, 0.030;

(9) $I\,[0.877\,(\Phi_6 \rightarrow \Phi_{13})]$, 0.002;

(10) $IB_2\,[0.548\,(\Phi_5 \rightarrow \Phi_{13}) + 0.513\,(\Phi_{12} \rightarrow \Phi_{14})]$, 0.160;

(11) $IB_2\,[-0.568\,(\Phi_5 \rightarrow \Phi_{13}) + 0.405\,(\Phi_{12} \rightarrow \Phi_{14})]$, 0.120;

(12) $B_1 B_3\,[-0.385\,(\Phi_{13} \rightarrow \Phi_{16}) + 0.369\,(\Phi_{12} \rightarrow \Phi_{15})]$, 0.131.

In the above, the first four states are pure and mixing first becomes significant for the fifth state. Except for the first two transitions, all other I-transitions have been observed and are in good accord with the energies estimated from the PE spectrum, but show a blue-shift as compared to the latter. The identification of the absorption band at 23.57 kK is not clear as the LHP and Wasilewski methods put it in different classes, namely in IB_2 and B_2, respectively. But, since there is no corresponding line in the PES digram, the former classification is ruled out.

As the hydrocarbon is very poorly oxidized, the spectrum above 30 kK represents solely that of the parent molecule. For this reason, the absorption bands in this region have not been assigned.

(iv) *6.7-Benzopentaphene Radical Cation*

Figure 4 displays the electronic spectrum of 6.7-benzopentaphene radical cation and its comparison with the calculated spectrum and the PES diagram. The prominent configurations for the first ten doublet excited states of the cation and the intensities of the corresponding electronic transitions are:

(1) $I\,[0.964\,(\Phi_{12} \rightarrow \Phi_{13})]$, 0.027;

(2) $I\,[0.965\,(\Phi_{11} \rightarrow \Phi_{13})]$, 0.081;

(3) $I\,[0.975\,(\Phi_{10} \rightarrow \Phi_{13})]$, 0.068;

(4) $I\,[0.966\,(\Phi_9 \rightarrow \Phi_{13})]$, 0.067;

(5) $I\,[0.948\,(\Phi_8 \rightarrow \Phi_{13})]$, 0.136;

(6) $IB_3\,[0.786\,(\Phi_7 \rightarrow \Phi_{13}) + 0.393\,(\Phi_{12} \rightarrow \Phi_{15})]$, 0.002;

(7) $I\,[0.951\,(\Phi_6 \rightarrow \Phi_{13})]$, 0.016;

(8) $IA\,[0.550\,(\Phi_7 \rightarrow \Phi_{13}) - 0.381\,(\Phi_5 \rightarrow \Phi_{13}) + 0.553\,(\Phi_{13} \rightarrow \Phi_{14})]$, 0.119;

(9) $B_1 B_3\,[0.684\,(\Phi_{13} \rightarrow \Phi_{15}) - 0.495\,(\Phi_{12} \rightarrow \Phi_{14})]$, 0.008;

(10) $IA\,[0.750\,(\Phi_5 \rightarrow \Phi_{13}) + 0.497\,(\Phi_{13} \rightarrow \Phi_{14})]$, 0.234.

In the above, the first five and the seventh I-transitions are pure one-electrton excitations. For the eighth state, the largest contribution comes from $\Phi_{13} \rightarrow \Phi_{14}$, and this should accordingly be assigned as *AI*. But keeping in mind that the combined contribution from $\Phi_7 \rightarrow \Phi_{13}$ and $\Phi_5 \rightarrow \Phi_{13}$ exceeds the contribution from the former, we classify it as *IA*. It corresponds to the absorption peak at 21.05 kK and agrees well with the PES diagram. Barring the

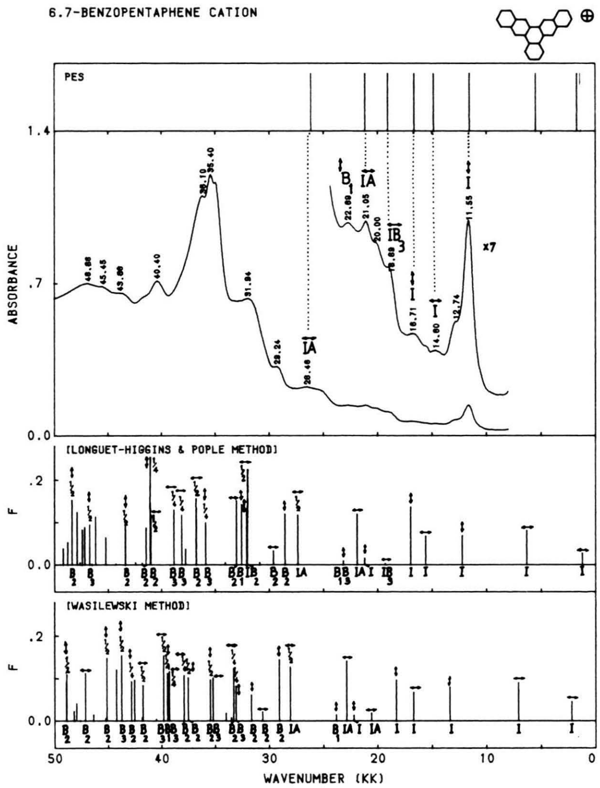

Fig. 4. Electronic absorption spectrum of 6.7-benzopentaphene radical cation and its comparison with the calculated spectrum and the transition energies estimated from the photoelectron spectrum (PES).

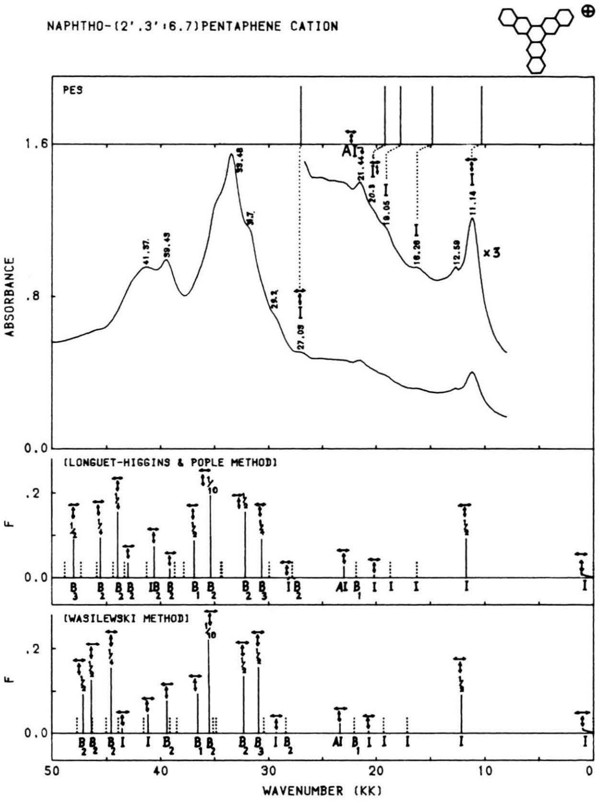

Fig. 5. Electronic absorption spectrum of naphtho-(2'.3' : 6.7)pentaphene radical cation and its comparison with the calculated spectrum and the transition energies derived from the photoelectron spectrum (PES).

first two transitions which fall beyond our measurement range, all other I-transitions have been identified.

(v) *Naphtho-(2'.3.':6.7)pentaphene Radical Cation*

The electronic absorption spectrum of naphtho-(2'.3':6.7)pentaphene cation is shown in Fig. 5 along with the energies for the cation inferred from the PE spectrum of the hydrocarbon. These experimental results are compared with the calculated spectrum of the cation. Calculations reveal that the prominent configurations for the lower-energy excited states of the cation together with the oscillator strengths for the electronic transitions are:

$$\begin{array}{ll} (1) & \left\{\begin{array}{l} I\,[0.982\,(\Phi_{14} \rightarrow \Phi_{15})],\ 0.005; \\ I\,[0.982\,(\Phi_{13} \rightarrow \Phi_{15})],\ 0.005; \end{array}\right. \\ (2) & \end{array}$$

$$\begin{array}{ll} (3) & \left\{\begin{array}{l} I\,[0.983\,(\Phi_{12} \rightarrow \Phi_{15})],\ 0.182; \\ I\,[0.983\,(\Phi_{11} \rightarrow \Phi_{15})],\ 0.183; \end{array}\right. \\ (4) & \end{array}$$

$$(5)\quad I\,[0.974\,(\Phi_{10} \rightarrow \Phi_{15})],\ 0.000;$$

$$(6)\quad I\,[0.983\,(\Phi_{9} \rightarrow \Phi_{15})],\ 0.000;$$

$$\begin{array}{ll} (7) & \left\{\begin{array}{l} I\,[0.940\,(\Phi_{8} \rightarrow \Phi_{15})],\ 0.005; \\ I\,[0.940\,(\Phi_{7} \rightarrow \Phi_{15})],\ 0.005; \end{array}\right. \\ (8) & \end{array}$$

$$(9)\quad B_1\,B_3\,[0.687\,(\Phi_{15} \rightarrow \Phi_{18}) + 0.464\,(\Phi_{14} \rightarrow \Phi_{16}) - 0.464\,(\Phi_{13} \rightarrow \Phi_{17})],\ 0.000;$$

$$\begin{array}{ll} (10) & \left\{\begin{array}{l} AI\,[-\,0.578\,(\Phi_{15} \rightarrow \Phi_{16}) + 0.451\,(\Phi_{6} \rightarrow \Phi_{15}) \\ \quad -\,0.263\,(\Phi_{7} \rightarrow \Phi_{15})],\ 0.025; \\ B_1\,I\,[0.578\,(\Phi_{15} \rightarrow \Phi_{17}) + 0.451\,(\Phi_{5} \rightarrow \Phi_{15}) \\ \quad +\,0.263\,(\Phi_{8} \rightarrow \Phi_{15})],\ 0.025; \end{array}\right. \\ (11) & \end{array}$$

$$(12)\quad B_2\,[0.665\,(\Phi_{13} \rightarrow \Phi_{16}) + 0.665\,(\Phi_{14} \rightarrow \Phi_{17})],\ 0.000;$$

$$\begin{array}{ll} (13) & \left\{\begin{array}{l} IB_2\,[0.823\,(\Phi_{6} \rightarrow \Phi_{15}) + 0.316\,(\Phi_{14} \rightarrow \Phi_{18})], \\ 0.001; \\ IB_2\,[0.823\,(\Phi_{5} \rightarrow \Phi_{15}) + 0.316\,(\Phi_{13} \rightarrow \Phi_{18})], \\ 0.001. \end{array}\right. \\ (14) & \end{array}$$

The paired states in the above are degenerate. This comes from the inadequacy of the theories used which are primarily meant for systems having non-degenerate ground states. Another short-coming of the methods becomes obvious from the fact that the first degenerate state is thrown below the ground state by both calculations. This, however, does not cause any serious problem as it is inaccessible to our measurements. The degeneracy shown above is in complete agreement with the assignment of the photoelectron peaks of the molecule [8]. In the PE spectrum, the first three *IP*'s are triply degenerate. Using the formula

$$E_n = IP_{n+1} - IP_1\,, \quad (n \geqq 1)\,,$$

one can therefore estimate the first two electronic bands of the cation to come at 0.00 kK. For this reason, these are not explicitly shown in the PES diagram. The calculations, together with the energies calculated from the PE spectrum, have successfully led to the assignment of the major absorption bands of the cation. Except for the slight blue-shift, the *I*-transitions show one-to-one correspondence with the lines in the PES diagram.

Conclusions

This work further strengthens our concept of the correlation between the optical and photoelectron spectra of polycyclic aromatics. The overall agreement between the experimental and theoretical results seems to be quite reasonable. However, due to poor conversion of these molecules to their radical cations, it is difficult to assign the bands above 30 kK. This suggests the desirability to look for other matrices which could be more efficient for cation formation.

Acknowledgements

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