

## Single and Double Ionization of Corannulene and Coronene

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Dedicated to *Edgar Heilbronner* on the occasion of his 80th birthday

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Electron-transfer processes that involve single and doubly charged cations of corannulene ( $C_{20}H_{10}$ ) and coronene ( $C_{24}H_{12}$ ) are examined by three different mass-spectrometric techniques. Photoionization studies give first-ionization energies of  $IE(C_{20}H_{10}) = 7.83 \pm 0.02$  eV and  $IE(C_{24}H_{12}) = 7.21 \pm 0.02$  eV. Photoionizations of the neutrals to the doubly charged cations occur at thresholds of  $20.1 \pm 0.2$  eV and  $18.5 \pm 0.2$  eV for corannulene and coronene, respectively. Energy-resolved charge-stripping mass spectrometry yields kinetic energy deficits of  $Q_{\min}(C_{20}H_{10}^{\cdot+}) = 13.8 \pm 0.3$  eV and  $Q_{\min}(C_{24}H_{12}^{\cdot+}) = 12.8 \pm 0.3$  eV for the transitions from the mono- to the corresponding dications in keV collisions. Reactivity studies of the  $C_{20}H_{10}^{\cdot+}$  and  $C_{24}H_{12}^{\cdot+}$  dications in a selected-ion flow-tube mass spectrometer are used to determine the onsets for the occurrence of single-electron transfer from several neutral reagents to the dications, affording two different monocationic products. With decreasing *IE*s of the neutral reagents, electron transfer to doubly charged corannulene is first observed with hexafluorobenzene ( $IE = 9.91$  eV), while neutrals with lower *IE*s are required in the case of the coronene dication, e.g.,  $NO_2$  ( $IE = 9.75$  eV). Density-functional theory is used to support the interpretation of the experimental data. The best estimates of the ionization energies evaluated are  $IE(C_{20}H_{10}) = 7.83 \pm 0.02$  eV and  $IE(C_{24}H_{12}) = 7.21 \pm 0.02$  eV for the neutral molecules, and  $IE(C_{20}H_{10}^{\cdot+}) = 12.3 \pm 0.2$  eV and  $IE(C_{24}H_{12}^{\cdot+}) = 11.3 \pm 0.2$  eV for the monocations.

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**Introduction.** – Polycyclic aromatic hydrocarbons (PAHs) are of environmental relevance due to their toxicity combined with their ubiquity as combustion products of organic material in fuel-rich flames [1]. Further, PAHs and their ions are believed to contribute to interstellar absorption bands in the infrared [2a] (for criticism of this hypothesis, however, see [2b]) [3]. For these and other reasons [4], the interest in PAHs has a long tradition [5].

As far as first- and second-ionization energies of PAHs are concerned, *Tobita et al.* provided a comprehensive survey for more than 20 different compounds, ranging from benzene to buckminsterfullerene [6]. However, the data available for the dications are not all unambiguous, and differences may spread over several eV. For example, the appearance energy measurements for the tetracene dication compiled by *Tobita et al.* range from  $18.6 \pm 0.2$  eV obtained with photoionization to  $20.1 \pm 0.5$  eV determined by charge stripping and  $22.1 \pm 0.2$  eV with electron ionization. Such a magnitude of uncertainties in the evaluation of second-ionization energies appears rather large, thus justifying a re-evaluation that aims at a more accurate determination of this fundamental property for two representative PAHs.

Here, we report the results of three different experimental approaches aimed at determining the second ionization energies of corannulene ( $C_{20}H_{10}$ ) and coronene

( $C_{24}H_{12}$ ) (Fig. 1). These two molecules are chosen as prototypes for bowl-shaped (corannulene) and planar (coronene) PAHs. The experimental methods probe the electron-transfer behavior of these hydrocarbons from three different aspects. *i*) Photoionization (PI) methods involve ionization of the neutral molecules to either mono- or dications, *i.e.*,  $PAH \rightarrow PAH^+$  and  $PAH \rightarrow PAH^{2+}$ . *ii*) Charge-stripping (CS) mass spectrometry deals with the electron detachment from mass-selected mono- to dications in high-energy collisions, *i.e.*,  $PAH \rightarrow PAH^{2+}$ . *iii*) Reactivity studies in a selected-ion flow tube (SIFT) apparatus can *inter alia* probe single-electron transfer (SET) from several neutral molecules  $M$  to the dications at thermal energies, *i.e.*,  $M + PAH^{2+} \rightarrow M^+ + PAH^+$ . Further, molecular-orbital calculations are used to estimate the differences due to vertical and adiabatic electron transfer from neutrals to mono- and dications, respectively.

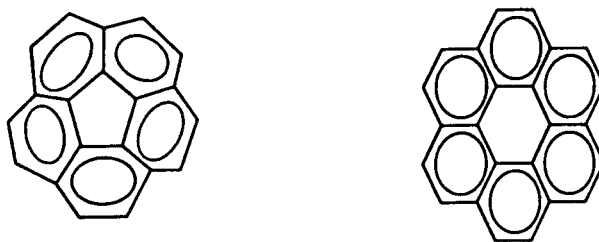


Fig. 1. Structures of corannulene  $C_{20}H_{10}$  and coronene  $C_{24}H_{12}$

**Experimental and Theoretical Details.** – The experiments with molecular dications [7] were performed with three different types of mass spectrometers, which are very briefly described below; for more detailed descriptions, the readers are referred to the original references quoted.

The photoionization experiments used the *CERISES* apparatus [8] for the determination of the first- and second-ionization energies of corannulene and coronene. *CERISES* was installed on the beam line *SA63* of the synchrotron radiation source *SuperACO* at LURE (Orsay, France). This beam line, a normal incidence monochromator, provides with monochromatic light in the range 7–30 eV photon energy. Slits were at all time opened to 1 mm, which gives a resolving power in the range of 500 (*i.e.*, 20 meV at 10 eV). Photon-energy accuracy was verified by recording the ionization potential of Ar, within 2 meV of its nominal value. Measurements corresponding to the first-ionization threshold of the samples were performed after filtering of higher-order light from the grating by means of a LiF window (removing all photons above 11.8 eV).

A small oven, filled with the samples, was adapted to the source in order, first, to obtain sufficient vapor pressure of the neutral samples, and, second, to observe eventual temperature effects on the appearance curves. The neutral species were ionized by monochromatic photons, and ions were extracted by a small extracting field (1 V/cm), through octopolar ion guides, towards a quadrupole mass spectrometer (*Nermag* 350 mm), where mass selection was performed. Detection was achieved by means of multi-channel plate operated in the counting mode.

For charge stripping, a modified *VG-ZAB-HF/AMD 604* four-sector mass spectrometer of *BEBE* configuration (*B* and *E* stand for magnetic and electric sector, resp.) was used [9]. The ions of interest were generated by electron ionization (EI, 70 eV) of the neutral PAHs and accelerated to a kinetic energy of 8 keV. Because of the superior energy resolution of *E*(1), the energy-resolved CS experiments were conducted with *B*(1)-only mass-selected ions [10]. To this end, the mono- and dication signals in CS experiments were recorded at energy resolutions  $E/\Delta E \geq 4999$  by scanning *E*(1), and  $Q_{\min}$  values were determined from the difference between the high-energy onsets of the mono- and the dication peaks<sup>1</sup>). Calibration of the kinetic-energy scale applied charge stripping of the molecular ions of both benzene,  $C_6H_6^+ \rightarrow C_6H_6^{2+}$  with  $Q_{\min}(C_6H_6^+) = 16.2$  eV [6],

<sup>1</sup>) For a representative example of data analysis in CS experiments, see [11].

and toluene,  $C_7H_8 \rightarrow C_7H_8^+$  with  $Q_{\min}(C_7H_8^+) = 15.7$  eV [12]. The values given further below are averages of at least four different experiments, and the indicated errors comprise one standard deviation.

The selected-ion flow-tube mass spectrometer consists of an ion source, a first quadrupole mass filter (Q1) for mass selection of the precursor ions, an ion flow-tube for carrying out reactivity studies, and a second quadrupole mass filter (Q2) for product analysis [13]. In the ion source of the SIFT, corannulene and coronene were subjected to electron ionization at 60 and 50 eV, resp. The dications formed were filtered with Q1 and injected into the flow tube through a *Venturi*-type interface. He was used as the SIFT buffer gas at 0.35 Torr and a flow tube temp. of  $296 \pm 2$  K. The selected ions entering the flow tube were allowed to thermalize by collisions with He (*ca.*  $4 \cdot 10^8$  collisions) prior to reaching the reaction region further downstream at the point of addition of the reagent gas. Reactant and product ions were monitored still further downstream by sampling the reacting mixture and analyzing the ions with Q2 as a function of the added reagent gas. Ions were counted with a channeltron electron multiplier.

Commercial coronene samples (*Acros*, *Aldrich*) were used without further purification. Corannulene was prepared by a three-step synthesis reported in [14].

In the theoretical study, a compromise between accuracy and the computing-time expenditure has to be found due to the large size of the systems under consideration. The B3LYP method implemented in Gaussian98 [15] was used with the corresponding 6-311G(d,p) basis sets. Full geometry optimizations as well as frequency analyses were performed at this level of theory. To evaluate the performance of this approach, reference computations for some smaller PAHs were also made (only benzene and naphthalene were included here).

**Experimental Results.** – At first, let us describe the experimental findings about the ionization energies<sup>2)</sup> of corannulene and coronene obtained by three different mass spectrometric techniques.

*Photoionization MS.* The first-ionization energies of corannulene ( $C_{20}H_{10}$ ) and coronene ( $C_{24}H_{12}$ ) can be derived in a straightforward manner from the appearance curves of the corresponding monocation peaks as a function of photon energy. Both curves show reasonably sharp onsets, and  $IE(C_{20}H_{10}) = 7.83 \pm 0.02$  eV and  $IE(C_{24}H_{12}) = 7.26 \pm 0.05$  eV were obtained accordingly from the first apparent rise of the PI signals from the noise level. Both values are further consistent with previous studies: the ionization energy of corannulene has been determined as  $IE(C_{20}H_{10}) = 7.7$  eV by bracketing techniques [16] and that of coronene as  $IE(C_{24}H_{12}) = 7.20 \pm 0.02$  eV by photoionization [6]. Considering the lower error limit of the previous measurement, we use  $IE(C_{24}H_{12}) = 7.21 \pm 0.02$  eV as a weighted average. The determination of second-ionization energies by photoionization is more difficult, because unlike monocations, the dication signals do not show sharp onsets, but rather rise gradually. Therefore, the values bear larger errors and should only be regarded as upper limits in a strict sense. The best estimates for the dication thresholds are  $20.1 \pm 0.2$  eV for corannulene and  $18.5 \pm 0.2$  eV for coronene; again, the agreement with the previous value of  $18.7 \pm 0.2$  eV for coronene is reasonable [6]. Further, measurements were conducted at different temperatures of the oven containing the PAH samples, because there might exist an effect of the neutral's internal energy on the apparent onsets of the dication

<sup>2)</sup> Note the following definitions of the terms used.  $IE_a(\text{PAH})$  and  $IE_a(\text{PAH}^+)$  stand for the adiabatic ionization energies of the neutral and monocationic PAHs; thus, these properties correspond to the (adiabatic) first- and second-ionization energies of the neutral species. Accordingly,  $IE_v(\text{PAH})$  and  $IE_v(\text{PAH}^+)$  represent the vertical ionizations of the respective precursors to the next charge states.  ${}^2IE_v(\text{PAH})$  stands for the double ionization of a neutral to a dication as potentially occurring upon photoionization; the corresponding adiabatic property  ${}^2IE_a(\text{PAH})$  is equal to  $IE_a(\text{PAH}) + IE_a(\text{PAH}^+)$  as well as to the sum of the (adiabatic) first and second  $IE$ s of the neutral. For all these properties, the associated terms  $\Delta IE_{v/a}$  express the differences between vertical and adiabatic electron-transfer processes.

signals. However, within the experimental uncertainty of  $\pm 0.2$  eV, no dependencies of the measured thresholds of the mono- and dications from the oven temperatures were found for either corannulene or coronene.

As long as the structural differences between neutrals, mono-, and dications are not enormous (see below), the onsets of the photoionization signals can further be assumed to correspond closely to adiabatic ionization energies, thus,  $IE_a(\text{C}_{20}\text{H}_{10}) = 7.83 \pm 0.02$  eV and  $IE_a(\text{C}_{24}\text{H}_{12}) = 7.21 \pm 0.02$  eV for the neutrals, and  $IE_a(\text{C}_{20}\text{H}_{10}^+) = 12.3 \pm 0.2$  eV and  $IE_a(\text{C}_{24}\text{H}_{12}^+) = 11.3 \pm 0.2$  eV for the monocations, respectively.

*Sector MS.* Both, mass-selected corannulene and coronene monocations afford good dication yields in keV collisions. Energy-resolved charge-stripping experiments give averaged  $Q_{\min}$  values of  $Q_{\min}(\text{C}_{20}\text{H}_{10}^+) = 13.8 \pm 0.3$  eV and  $Q_{\min}(\text{C}_{24}\text{H}_{12}^+) = 12.8 \pm 0.3$  eV. To a first approximation [6][7], the  $Q_{\min}$  values correspond to the vertical ionization energies  $IE_v$  of the corresponding monocations, thus suggesting  $IE_v(\text{C}_{20}\text{H}_{10}^+) = 13.8 \pm 0.3$  eV and  $IE_v(\text{C}_{24}\text{H}_{12}^+) = 12.8 \pm 0.3$  eV. Note that these values are significantly above the adiabatic  $IE$ s indicating either quite unfavorable *Franck-Condon* effects for the mono- to dication transitions and/or systematic errors (see below).

*SIFT MS.* In the flow-tube studies, mass-selected corannulene and coronene dications were reacted with various neutral molecules M. It is important to point out that the experimental conditions safely ensure complete thermalization of the dication precursors. In the present context, occurrence of single-electron transfer (SET) from the neutrals to the PAH dications according to *Reaction 1* is of particular interest.



*Table 1* summarizes the reactions studied in the order of increasing  $IE$ s of the neutral reagents. With ethene and  $\text{NH}_3$  as neutral reagents ( $IE$ s = 10.51 and 10.16 eV, resp.), corannulene dication exclusively undergoes association to the corresponding doubly charged adduct ions. Charge transfer according to *Reaction 1* is first observed for hexafluorobenzene, which has an  $IE$  of 9.91 eV [17]<sup>3</sup>). In fact, association of corannulene dication with  $\text{C}_6\text{F}_6$  to afford  $\text{C}_{20}\text{H}_{10}\text{C}_6\text{F}_6^{2+}$  cannot compete with the electron-transfer process. Conversely, association occurs exclusively in the reaction of the coronene dication with  $\text{C}_6\text{F}_6$ . In the case of NO ( $IE = 9.264$  eV [17]), electron transfer is efficient for both  $\text{PAH}^{2+}$  dications, though association can compete to some extent. Although the  $IE$  of benzene is slightly lower than that of NO ( $IE = 9.246$  vs. 9.264 eV [17]), association prevails for the arene, probably due to the better electrostatic interaction in the case of the polarizable benzene molecule compared to NO and the larger number of rovibrational degrees of freedom of benzene. Among the neutral reactants under study, distinct chemical reactivity in terms of the obvious formation of new chemical bonds is only observed for strong oxidizing agents such as  $\text{NO}_2$  ( $IE = 9.75$  eV [17]) and molecular chlorine ( $IE = 11.48$  eV [17]) with corannulene dication.

The overall rate constants vary substantially and in particular do not correlate with the neutrals'  $IE$ s. For example, the rate constants for ammonia and benzene are of

<sup>3</sup>) For a compilation of ionization energies, also see: <http://webbook.nist.gov/chemistry/>

Table 1. Branching Ratios and Observed Rate Constants  $k_{\text{obs}}$  of the Reactions of Corannulene  $\text{C}_{20}\text{H}_{10}^{2+}$  and Coronene  $\text{C}_{24}\text{H}_{12}^{2+}$  Dications, Respectively, with  $\text{C}_6\text{D}_6$ ,  $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{C}_6\text{F}_6$ ,  $\text{NH}_3$ ,  $\text{C}_2\text{H}_4$ , and  $\text{Cl}_2$  in He Buffer Gas at 0.35 Torr and 298 K

	$IE$ [eV] <sup>a)</sup>	$\text{C}_{20}\text{H}_{10}^{2+}$		$\text{C}_{24}\text{H}_{12}^{2+}$	
$\text{C}_6\text{D}_6$	9.25	$\text{C}_{20}\text{H}_{10}^{2+} + \text{C}_6\text{D}_6 \rightarrow \text{C}_{20}\text{H}_{10}^+ + \text{C}_6\text{D}_6^+$	0.30	$\text{C}_{24}\text{H}_{12}^{2+} + \text{C}_6\text{D}_6 \rightarrow \text{C}_{24}\text{H}_{12}^+ + \text{C}_6\text{D}_6^+$	0.30
		$\rightarrow \text{C}_{20}\text{H}_{10}\text{C}_6\text{D}_6^{2+}$	0.70	$\rightarrow \text{C}_{24}\text{H}_{12}\text{C}_6\text{D}_6^{2+}$	0.70
		$k_{\text{obs}} = 1.7 \cdot 10^{-9} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$		$k_{\text{obs}} = 1.6 \cdot 10^{-9} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$	
$\text{NO}$	9.26	$\text{C}_{20}\text{H}_{10}^{2+} + \text{NO} \rightarrow \text{C}_{20}\text{H}_{10}^+ + \text{NO}$	0.85	$\text{C}_{24}\text{H}_{12}^{2+} + \text{NO} \rightarrow \text{C}_{24}\text{H}_{12}^+ + \text{NO}^+$	0.70
		$\rightarrow \text{C}_{20}\text{H}_{10}\text{NO}^{2+}$	0.15	$\rightarrow \text{C}_{24}\text{H}_{12}\text{NO}^{2+}$	0.30
		$k_{\text{obs}} = 2.3 \cdot 10^{-10} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$		$k_{\text{obs}} = 1.3 \cdot 10^{-10} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$	
$\text{NO}_2$	9.75	$\text{C}_{20}\text{H}_{10}^{2+} + \text{NO}_2 \rightarrow \text{C}_{20}\text{H}_{10}\text{O}^+ + \text{NO}^+$	0.60	$\text{C}_{24}\text{H}_{12}^{2+} + \text{NO}_2 \rightarrow \text{C}_{24}\text{H}_{12}\text{O}^+ + \text{NO}^+$	0.60
		$\rightarrow \text{C}_{20}\text{H}_{10}\text{O}^{2+} + \text{NO}$	0.40	$\rightarrow \text{C}_{24}\text{H}_{12}\text{O}^{2+} + \text{NO}$	0.25
				$\rightarrow \text{C}_{24}\text{H}_{12}^+ + \text{NO}_2^+$	0.10
				$\rightarrow \text{C}_{24}\text{H}_{12}\text{NO}_2^{2+}$	0.05
		$k_{\text{obs}} = 9.2 \cdot 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$		$k_{\text{obs}} = 6.3 \cdot 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$	
$\text{C}_6\text{F}_6$	9.91	$\text{C}_{20}\text{H}_{10}^{2+} + \text{C}_6\text{F}_6 \rightarrow \text{C}_{20}\text{H}_{10}^+ + \text{C}_6\text{F}_6^+$	1.00	$\text{C}_{24}\text{H}_{12}^{2+} + \text{C}_6\text{F}_6 \rightarrow \text{C}_{24}\text{H}_{12}\text{C}_6\text{F}_6^{2+}$	1.00
		$k_{\text{obs}} = 2.4 \cdot 10^{-10} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$		$k_{\text{obs}} = 1.1 \cdot 10^{-10} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$	
$\text{NH}_3$	10.16	$\text{C}_{20}\text{H}_{10}^{2+} + \text{NH}_3 \rightarrow \text{C}_{20}\text{H}_{10}\text{NH}_3^{2+}$	1.00	$\text{C}_{24}\text{H}_{12}^{2+} + \text{NH}_3 \rightarrow \text{C}_{24}\text{H}_{12}\text{NH}_3^{2+}$	1.00
		$k_{\text{obs}} = 1.9 \cdot 10^{-9} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$		$k_{\text{obs}} = 1.4 \cdot 10^{-9} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$	
$\text{C}_2\text{H}_4$	10.51	$\text{C}_{20}\text{H}_{10}^{2+} + \text{C}_2\text{H}_4 \rightarrow \text{C}_{20}\text{H}_{10}\text{C}_2\text{H}_4^{2+}$	1.00		
		$k_{\text{obs}} = 1.8 \cdot 10^{-10} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$			
$\text{Cl}_2$	11.48	$\text{C}_{20}\text{H}_{10}^{2+} + \text{Cl}_2 \rightarrow \text{C}_{20}\text{H}_{10}\text{Cl}_2^{2+} + \text{Cl}$	1.00		
		$k_{\text{obs}} = 6.2 \cdot 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$			

<sup>a)</sup> Taken from [17].

similar magnitudes while the  $IE$ s of the neutrals differ by almost 1 eV. It appears more plausible to correlate the rate constants with the stabilities of the corresponding electrostatic complexes. Thus, fast reactions dominated by adduct formation occur for the dipolar ammonia as well as the polarizable benzene molecule, whereas the small, less polarizable neutrals  $\text{NO}_2$ ,  $\text{C}_2\text{H}_4$ , and  $\text{Cl}_2$  react much more slowly. Exceptions to this rule of thumb are the relatively fast rate for  $\text{NO}$  and the slow reaction of  $\text{C}_6\text{F}_6$ . The former exception can be rationalized in terms of the effectively competing SET channel that is unavailable to the other neutrals except benzene. The inefficiency of the addition reaction of hexafluorobenzene with the two PAH dications can be attributed to the weak binding properties of this perfluorinated molecule. Thus, the electron-withdrawing F substituents disfavor coordination of cationic species to the aromatic ring while the F-atoms themselves are also poor coordinators. This qualitative argument is supported by the huge difference in the binding energies of gold cation to benzene and its hexafluoro derivative, *i.e.*,  $D_0(\text{Au}^+ - \text{C}_6\text{H}_6) = 3.0 \text{ eV}$  [18] *vs.*  $D_0(\text{Au}^+ - \text{C}_6\text{F}_6) = 1.3 \text{ eV}$  [19].

Summarizing the SIFT data in terms of brackets for the occurrence of *Reaction 1* yields thresholds of  $10.1 \pm 0.2 \text{ eV}$  for the corannulene dication and  $9.5 \pm 0.3 \text{ eV}$  for the coronene dication, respectively. It is important to note that these thresholds are not direct measures of the  $IE$ s of the monocations of the corresponding PAHs because formation of two monocations in a dication/neutral reaction is associated with a considerable *Coulomb* barrier [7]. For the same reason, however, these figures provide

solid lower limits for the monocation *IEs*, specifically,  $IE(\text{C}_{20}\text{H}_{10}^+) > 10.1 \pm 0.2$  eV and  $IE(\text{C}_{24}\text{H}_{12}^+) > 9.5 \pm 0.3$  eV.

**Theoretical Results.** – Given the size of the systems under study, some compromise in the level of theory applicable needs to be made. Thus, the B3LYP/6-311G(d,p) approach chosen is certainly inappropriate to predict absolute *IEs* within chemical accuracy ( $< 0.1$  eV). For example, a detailed examination by *Pople* and co-workers on the performance of B3LYP for the computation of first *IEs* gave a mean error of  $\pm 0.18$  eV for a set of 83 reference compounds [20]. Of particular interest in the present context is that the *IEs* of all closed-shell hydrocarbons examined by *Pople* and co-workers are underestimated by *ca.* 0.2 eV with B3LYP. While this effect is in part associated with incompleteness of the basis sets, *DiLabio et al.* have attributed this particular overestimation of the cation stabilities to unbalanced treatments of closed- and open-shell hydrocarbons with B3LYP [21]. Hence, the major relevance of the present theoretical studies is the prediction of the relative energetics of the various states and the differences between vertical and adiabatic electron-transfer processes ( $\Delta IE_{\text{v/a}}$ ) in particular.

The B3LYP/6-311G(d,p) level of theory is employed to assess the energetics of the neutral, the mono-, and dicationic species of interest (*Table 2*). For an evaluation of the accuracy of the computational predictions, benzene and naphthalene are additionally studied as reference molecules. Compared to experiment, the adiabatic first *IEs* of the four hydrocarbons are slightly underestimated with B3LYP (mean deviation  $-0.25$  eV). While the detailed evaluation of the second *IEs* is postponed to the discussion, a similar trend is indicated by comparing the computed double-ionization energies  ${}^2IEs$  of the neutrals to the dications with the photoionization thresholds given in *Table 2*. Using the computed dication ground-states for comparison with the photoionization thresholds, a mean deviation of  $-0.8$  eV is derived. Roughly, these values imply an underestimation of the *IEs* by 2–3% with the B3LYP/6-311G(d,p) approach for mono- and dications.

As far as the dication states are concerned, the B3LYP computations predict triplet ground states for benzene, corannulene, and coronene, while the naphthalene dication appears to have a singlet ground state (see also [22]). As a note of caution, we add, however, that the performance of density-functional methods with respect to the accurate energetic ordering of electronic states having different multiplicities is somewhat limited [23]. Irrespective of the actual ground-state assignment, it should be noted that, except for benzene, the dication state-splittings are more or less within the accuracies of the experimental methods discussed here.

Most important in the present context, however, is the point that the differences between vertical and adiabatic ionization energies are not especially large. Maximal values occur for formation of benzene dication in the (excited) singlet state. The differences  $\Delta IE_{\text{v/a}}$  are particularly small for the respective dication ground states, *i.e.*, *ca.* 0.1 eV for first and second *IEs* and ranging from 0.1 to 0.5 eV for double ionization. Therefore, differences in *Franck-Condon* factors [24] can certainly not be applied to rationalize the spread of the experimental data discussed above.

Among the theoretical results, one interesting aspect deserves comment. For a continuous change of electronic and geometric properties as a function of charge, it is

Table 2. *Adiabatic and Vertical Ionization Energies (in eV) of Benzene, Naphthalene, Corannulene, and Coronene Computed at the B3LYP/6-311G(d,p) Level of Theory (dication ground states in bold)*

	Ion state	$IE_a^a)$	$IE_v^b)$	$\Delta IE_{v/a}$	$IE_1 + IE_2^c)$	$\Delta \Delta IE^d)$	Exper.
First <i>IEs</i>							
$C_6H_6$	doublet	9.03	9.18	0.15			9.22 <sup>e)</sup>
$C_{10}H_8$	doublet	7.82	7.92	0.10			8.15 <sup>e)</sup>
$C_{20}H_{10}$	doublet	7.58	7.71	0.13			7.83 <sup>h)</sup> /7.7 <sup>g)</sup>
$C_{24}H_{12}$	doublet	6.98	7.03	0.05			7.20 <sup>e)</sup> /7.26 <sup>f)</sup>
Second <i>IEs</i>							
$C_6H_6$	singlet	15.36	16.10	0.74			
	<b>triplet</b>	<b>15.28</b>	<b>15.47</b>	<b>0.19</b>			16.2 <sup>h)</sup>
$C_{10}H_8$	<b>singlet</b>	<b>13.22</b>	<b>13.31</b>	<b>0.09</b>			
	triplet	13.66	13.79	0.13			14.6 <sup>h)</sup>
$C_{20}H_{10}$	singlet	12.01	12.21	0.20			
	<b>triplet</b>	<b>11.66</b>	<b>11.76</b>	<b>0.10</b>			13.8 <sup>i)</sup>
$C_{24}H_{12}$	singlet	10.90	10.98	0.08			
	<b>triplet</b>	<b>10.79</b>	<b>10.86</b>	<b>0.07</b>			12.8 <sup>i)</sup>
Double <i>IEs</i>							
$C_6H_6$	singlet	24.39	25.55	1.16	25.28	0.27	
	<b>triplet</b>	<b>24.31</b>	<b>24.50</b>	<b>0.19</b>	<b>24.65</b>	<b>-0.15</b>	25.3 <sup>e)</sup>
$C_{10}H_8$	<b>singlet</b>	<b>21.04</b>	<b>21.41</b>	<b>0.37</b>	<b>21.23</b>	<b>0.18</b>	
	triplet	21.48	21.61	0.13	21.71	-0.10	21.5 <sup>e)</sup>
$C_{20}H_{10}$	singlet	19.59	20.14	0.55	19.92	0.22	
	<b>triplet</b>	<b>19.24</b>	<b>19.71</b>	<b>0.47</b>	<b>19.47</b>	<b>0.24</b>	20.1 <sup>f)</sup>
$C_{24}H_{12}$	singlet	17.88	18.13	0.25	18.01	0.12	
	<b>triplet</b>	<b>17.77</b>	<b>17.83</b>	<b>0.06</b>	<b>17.89</b>	<b>-0.06</b>	18.7 <sup>e)</sup> /28.5 <sup>f)</sup>

<sup>a)</sup> Computed adiabatic values including zero point energies. <sup>b)</sup> Computed vertical values assuming the adiabatic zero-point energies. <sup>c)</sup> Sum of the vertical first- and second-ionization energies; only defined for the last four rows. <sup>d)</sup> Difference  $\Delta \Delta IE = {}^2IE_v - (IE_1 + IE_2)$ ; this quantity is only defined for the last four rows. <sup>e)</sup> Photoionization thresholds taken from [6]. <sup>f)</sup> Photoionization thresholds, this work. <sup>g)</sup> Ion/molecule bracketing, see [16]. <sup>h)</sup> Charge stripping data taken from [6]. <sup>i)</sup> Charge-stripping data, this work.

expected that stepwise (vertical) ionization  $PAH \rightarrow PAH^+ \rightarrow PAH^{2+}$  with intermediate relaxation of the monocation is less energy-demanding than direct (vertical) double ionization  $PAH \rightarrow PAH^{2+}$ . Hence,  $\Delta \Delta IE_v = {}^2IE_v(PAH) - [IE_v(PAH) + IE_v(PAH^+)]$  is expected to be positive. While this trend is indeed observed for all singlet dications under study, the transitions from the singlet neutrals to the triplet dications give the opposite sign for benzene, naphthalene, and coronene. Qualitatively, this finding implies that the structures of the triplet dication states show a better match with the neutral ground states than with the monocation intermediates. The bent corannulene molecule appears as an exception in this respect, as  $\Delta \Delta IE_v$  is positive for both the singlet and triplet dications.

**Discussion.** – Before explicitly evaluating the absolute values of the second *IEs*, it is worthwhile noting that all methods agree reasonably that coronene is significantly easier to ionize than corannulene. Thus, both photoionization as well as charge stripping yield differences of *ca.* 1.0 eV, a lower limit of 0.6 eV is implied by the SIFT

study, and the calculations predict a difference of 0.87 eV between the adiabatic ionizations of these PAHs monocations to their triplet ground-state dications.

Having made these introductory remarks, let us use the theoretical data to analyze the mass spectrometric results in some more detail. As  $\Delta IE_{v/a}$  is comparable in magnitude to the experimental error, we may safely assume that the onsets of the PI signals of the mono- and dications correspond to the adiabatic *IEs* of corannulene and coronene, respectively. Thus, the best estimates of ionization energies are  $IE(C_{20}H_{10}) = 7.83 \pm 0.02$  eV and  $IE(C_{24}H_{12}) = 7.21 \pm 0.02$  eV for the neutral molecules, and  $IE(C_{20}H_{10}^+) = 12.3 \pm 0.2$  eV and  $IE(C_{24}H_{12}^+) = 11.3 \pm 0.2$  eV for the monocations. The monocation *IEs* are in obvious disagreement with the charge stripping data, *i.e.*,  $Q_{\min}(C_{20}H_{10}^+) = 13.8 \pm 0.3$  eV and  $Q_{\min}(C_{24}H_{12}^+) = 12.8 \pm 0.3$  eV; the corrections due to  $\Delta IE_{v/a}$  are minor (0.1 eV) and cannot account for the differences of *ca.* 1.5 eV in both cases. Note, however, that the relative difference agrees well. Thus, if we use coronene as the calibrant in charge stripping of corannulene,  $Q_{\min}(C_{20}H_{10}^+) = 12.2 \pm 0.3$  eV is obtained, which agrees very well with  $IE(C_{20}H_{10}^+) = 12.3 \pm 0.2$  eV derived above. Obviously, a yet unknown effect is operative in the calibration procedure of the charge-stripping experiments in which the transitions of benzene and toluene monocations to the corresponding dications were used as references. Among others [25], possible reasons could be associated with the large differences in mass or size of the small PAHs  $C_6H_6$  and  $C_7H_8$  used as references compared to  $C_{20}H_{10}$  and  $C_{24}H_{12}$ , respectively. With regard to the extensive CS studies of *Beynon* and co-workers in the 1980s, a mere mass effect appears unlikely, however. For example, along the series Mg–Ba, the  $Q_{\min}$  values of the monocations were found to agree with spectroscopic data [26]. In contrast, size dependencies in the efficiency of energy transfer are well known in KeV collisions; the conversion of translational into internal energy is particular relevant [27]. Thus, rovibrational modes of the corannulene and coronene monocations could adsorb a certain amount of collision energy prior to ionization to the corresponding dications, thereby shifting the  $Q_{\min}$  values to higher energies. In comparison, the energy depositions in the benzene and toluene ions used as references in the CS experiments are significantly smaller. Operation of such effects could well explain the fact that the absolute  $Q_{\min}$  values of corannulene and coronene are too large compared to the ionization energies derived from the photoionization data while the relative data agree. With regard to the arguments put forward in [6], it is to be stressed once more that the above explanation does not refer to *Franck-Condon* effects in vertical ionization.

Having established the *IEs*, we can now analyze the ion/molecule reactions examined with the SIFT apparatus in more detail. Single-electron transfer in a reaction of a dication with a neutral species according to *Reaction 1* is associated with considerable barrier due to *Coulomb* repulsion of the two monocationic products formed. In the experiment, charge separation is first observed to occur with hexafluorobenzene ( $IE = 9.91$  eV) in the case of corannulene and with  $NO_2$  ( $IE = 9.75$  eV) in the case of coronene. The magnitude of the *Coulombic* barrier can be estimated according to a model developed for single-electron transfer reactions of fullerene dications [28]<sup>4</sup>). These barriers amount to 2.2 and 1.9 eV assuming that the electron transfer occurs at contact upon an edge-on (rather than face-on) approach at

<sup>4</sup>) For more general discussions and leading references, see [29].



intercharge separations equal to the diameters of the C-skeletons, which are computed to be 6.48 and 7.49 Å for corannulene and coronene, respectively. Within this approximation, the ionization energies can be estimated to be  $IE(C_{20}H_{10}^+) = 12.3 \pm 0.2$  eV and  $IE(C_{24}H_{12}^+) = 11.4 \pm 0.2$  eV with no uncertainty being assigned to the model calculation. These values are in remarkable agreement with the values derived from photoionization.

**Conclusion.** – Three different experimental techniques in conjunction with *ab initio* theory are used to study the mono- and dications of the prototype PAH molecules corannulene and coronene. All experiments as well as theory agree upon the fact that ionization of corannulene is more energy-demanding than that of coronene. Photoionization thresholds give  $IE(C_{20}H_{10}) = 7.83 \pm 0.02$  eV,  $IE(C_{24}H_{12}) = 7.21 \pm 0.02$  eV,  $IE(C_{20}H_{10}^+) = 12.3 \pm 0.2$  eV, and  $IE(C_{24}H_{12}^+) = 11.3 \pm 0.2$  eV as best estimates of the adiabatic properties. While charge-stripping experiments agree upon the relative *IE*s of the two PAHs, the measured  $Q_{\min}$  values are substantially overestimated in comparison to the photoionization thresholds. B3LYP Calculations reveal that neither differences between vertical and adiabatic transitions nor formation of the dications in different electronic states can explain this discrepancy. Instead, it is suggested that the CS stripping are shifted to higher energies due to dissipation of some translational energy into the rovibrational manifold of the larger PAH molecules. The proposed effect of molecular size upon the calibration of energy-resolved CS experiments remains to be analyzed further; the impulse-collision transfer (ICT) theory seems to provide a starting point in this respect [27b]. Charge separations in ion/molecule reactions using a SIFT apparatus are in good agreement with the PI studies, if the *Coulomb* repulsion of the monocationic fragments formed is taken into account. As far as the existence of multiply charged PAHs ions in interstellar media is concerned, the sizable *Coulomb* barriers apparent in the reactivity studies in the SIFT apparatus further imply considerable kinetic stabilizations of PAH<sup>2+</sup> dications with respect to SET in the presence of the most abundant interstellar neutral molecules.

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