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**ARTICLE** *in* CHEMICAL PHYSICS · OCTOBER 2012

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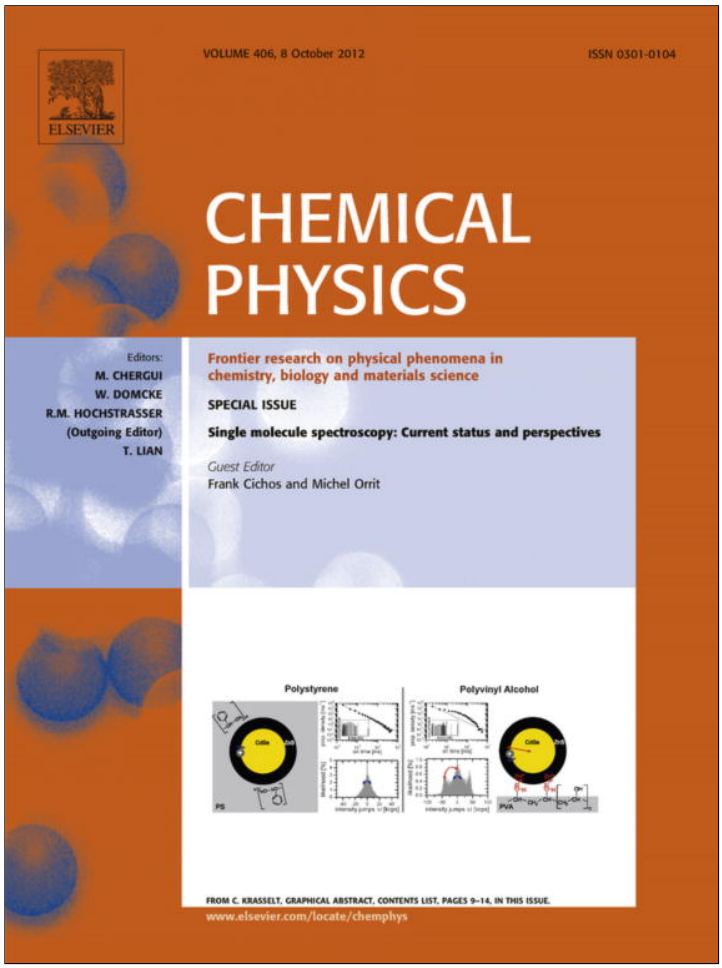


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Chemical Physics 406 (2012) 55–64

Contents lists available at SciVerse ScienceDirect

Chemical Physics

journal homepage: www.elsevier.com/locate/chemphys

# Benchmark theoretical study of the ionization energies, electron affinities and singlet–triplet energy gaps of azulene, phenanthrene, pyrene, chrysene and perylene

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ARTICLE INFO

*Article history:*
Available online 8 August 2012

*Keywords:*
Electron correlation
Relaxation
Focal point analysis
Zero-point vibrations
Chemical accuracy

ABSTRACT

The vertical and adiabatic singlet–triplet energy gaps, electron affinities and ionization energies of azulene, phenanthrene, pyrene, chrysene, and perylene are computed by applying the principles of a focal point analysis onto a series of single-point calculations at the level of Hartree–Fock theory, second-, third-, and fourth-order Møller–Plesset perturbation theory, as well as coupled cluster theory including single, double and perturbative triple excitations, in conjunction with correlation consistent basis sets of improving quality. Results are supplemented with an extrapolation to the limit of an asymptotically complete basis set. According to our best estimates, azulene, phenanthrene, pyrene, chrysene, and perylene exhibit adiabatic singlet–triplet energy gaps of 1.79, 2.92, 2.22, 2.79 and 1.71 eV, respectively. In the same order, the corresponding adiabatic electron affinities (EAs) amount to 0.71, −0.08, −0.40, 0.24, and 0.87 eV, whereas benchmark values equal to 7.43, 8.01, 7.48, 7.66 and 7.15 eV, are found for the adiabatic ionization energies.

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## 1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) have long been subject of extensive theoretical and experimental research activities. In nature, PAHs are found in traces, mainly as product of the burning of organic materials [1]. PAHs are also present in the interstellar medium [2] where they and their ions are known to contribute to major IR absorption bands [3]. Although most of these compounds are dangerous environment pollutants [4] and highly carcinogenic species, they have found wide application in the industry. For instance, azulene is used in the cosmetic industry as a skin conditioning agent [5], phenanthrene is employed for the production of dyes, drugs and pesticides [6] and chrysene is used for the production of UV-filters, paints and sensitizers [6]. Perylene derivatives are common pigments [7], and pyrene enters the making of commercial organic dyes [8].

In continuation of benchmark theoretical studies of the electronic properties of benzene and *n*-acenes [9–12], we aim at investigating at the confines of non-relativistic quantum mechanics the ionization energies, electron affinities, and singlet–triplet energy gaps of azulene, phenanthrene, pyrene, chrysene and perylene, using the well-established principles of a focal point analysis (FPA) [13] in order to reach or approach chemical accuracy (1 kcal/mol, i.e. 0.043 eV) on the computed energy differences. Our main motivation for this work stems from the observation that large discrepancies exist among the reported experimental values. For instance, discrepancies as large as 0.62 eV have been observed when comparing the available experimental data for the electron affinity of perylene [14–16]. Also, the three latest experimental determinations of the EAs of phenanthrene [17–19] exhibit deviations around 0.3 eV. Similarly, recently obtained experimental values for the ionization energy of chrysene [20,21] and perylene [20] exhibit discrepancies around 0.41 eV and 0.2 eV, respectively. Experimental data for the singlet–triplet energy gap of these five compounds are rather scarce [22–26]. To date, no benchmark theoretical study of their electronic properties has been reported yet. Such studies appear to be very much needed for reliable enough insights into the available experimental data. Indeed, the reported theoretical values for the electron affinity, ionization energy and excitation energies of the target systems are the results of calculations employing empirical (Hückel) or semi-empirical Hamiltonians, Density Functional Theory (DFT) [27] or Time Dependent DFT (TDDFT) [28]. Accuracies around 0.1–0.2 eV [29,34] have been claimed when employing DFT in order to evaluate the electron affinities of large PAHs as energy differences in between the neutral and anionic states. However, when dealing with large conjugated systems, it is well known [30,31] that applications of standard exchange–correlation functionals result in much larger

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http://dx.doi.org/10.1016/j.chemphys.2012.08.003

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uncertainties and errors, because of the too fast decay of the electronic potential at large distances resulting from an incomplete compensation of the self-interaction error.

The singlet–triplet energy gap ($E_{ST}$) is a most important electronic property concerning the areas where photo-luminescent processes take place. For instance, singlet–triplet gaps can be used to evaluate the strength of electron–electron correlation in luminescent polymers [32]. The singlet–triplet energy gaps of phenanthrene, pyrene and chrysene have been measured from phosphorescence spectra decades ago, and discussed in a paper by Siebrand [22] (1967) and in the book by Bircks [33]. The singlet–triplet energy gap of chrysene has been determined more recently from photodetachment-photoelectron spectra (PD-PES) at wavelengths of 266 nm and 355 nm [25]. Experimental values for the singlet–triplet energy gap of azulene have been also recently obtained by means of the pulse radiolysis technique [23] and flash kinetic spectrometry [24]. At last, the singlet–triplet energy gap of perylene has been measured [26] by means of the so-called solvent perturbation technique, using chloranil in carbon tetrachloride solution, along with oxygen under high pressure.

Electron affinities (EAs) and ionization energies (IEs) are also most important electronic properties [34]. Detailed knowledge about EAs and IEs is needed in studies of the toxicity and carcinogenity of PAHs on the ground of computer modeling employing Quantitative Structure–Activity Relationship (QSAR) theories [35]. Indeed, most important descriptors of biological and chemical activity are the energies of the Highest Occupied Molecular Orbital (HOMO) and of the Lowest Unoccupied Molecular Orbital (LUMO), which relate to vertical ionization energies (VIEs) and vertical electron affinities (VEAs), according to Koopmans' theorem [36,37]. EAs are also important in the modeling of rate constants in gas-phase oxidation reactions in diesel combustion [38], and IEs are one of the key features in designing electro-optically active materials [39]. Most of the available experimental data for the electron affinities of the compounds of interest have been obtained by means of Electron Capture Detection (ECD) [18,40,41,19] and Laser Photoelectron Spectroscopy (LPES) [15,25,42–44], whereas experimental data for ionization energies are essentially the results of experiments employing photoionization mass spectrometry (PI) [45], ion/molecule equilibrium constant determination (EQ) [20], photoelectron spectroscopy (PE) [20,46], and laser spectroscopy (LS) [20,47]. On theoretical side, most estimates of IEs and EAs so far are the results of calculations employing DFT [27,48–50]. *Ab initio* multireference configuration interaction approach with single and double excitations, and time-dependent density functional theory along with the Becke–Lee–Yang–Parr functional (TDDFT/BLYP) have also been used for predicting the ionization spectra of PAHs [27,28]. Our group has published detailed studies [51] of the valence one-electron and shake-up ionization spectra of azulene, phenanthrene, pyrene, chrysene, and perylene using the third-order outer-valence Green's function (OVGF [52,53]) and algebraic-diagrammatic construction [ADC(3)] schemes, as well as basis sets of improving quality (6–31G, 6–31G*, cc-pVDZ). Discrepancies around 0.3 to 0.4 eV were observed for the five target compounds when comparing the OVGF/cc-pVDZ values for one-electron binding energies with high resolution experimental (He I UPS) data.

In the present work, vertical electron affinities, ionization energies or electronic excitation energies are determined as energy differences between the total electronic energies of the neutral molecules and of the anions, cations or excited species, respectively, upon the geometries of the initial (neutral) electronic ground state. The corresponding "well-to-well" estimates are obtained by adding to the vertical values the stabilization energies of the anions, cations or excited species due to geometry relaxation from the vertically ionized or excited states. Adiabatic estimates are ultimately inferred by adding zero-point vibrational energy corrections.

Focal point analyses combining size-consistent (size-extensive) approaches such as Møller–Plesset Perturbation theory and Coupled-Cluster theory in conjunction with basis sets of improving quality have been extensively exploited in highly accurate studies [13] of conformational energy differences or torsional barriers, reaction and activation energies, heats of formation, binding energies of π-complexes, ... or static dipole polarizabilities. The FPA approach supplemented by extrapolations to an asymptotically complete basis cc-pV∞Z set has been found in particular to provide exceedingly accurate insights into negative electron affinities [10], corresponding to meta-stable anions with a life time estimated to be around $10^{-14}$ s [54], provided diffuse functions are deliberately removed from the employed correlation consistent cc-pVXZ (X = D, T, Q, ∞) basis sets, in order to enforce a localization of the impinging electron in the molecular region. FPAs exploit the idea of a dual extrapolation towards the highest attainable level in electronic correlation [ideally, the full-CI (configuration interaction) limit [37], in practice coupled cluster theory [55] with single, double and perturbative triple excitations, CCSD(T)], and to the limit of an asymptotically complete basis set (CBS).

## 2. Computational details

All calculations including geometry optimization, vibrational analysis, and single point energy determinations have been carried out using the Gaussian09 [56] program package. Geometry optimization and vibrational analysis have been performed using DFT [57] in conjunction with the Becke three-parameter Lee–Yang–Parr (B3LYP) functional [58] and the cc-pVTZ basis set [59]. The tightest optimization convergence criteria have been enforced at all stages of the calculations, using the Gaussian09 keyword opt = verytight. An ultra-fine pruned integration grid consisting of 99 radial shells per atom and 590 angular points per shell has also been requested for the DFT calculations, resulting in about 7000 points per atom. Single point energy calculations have been performed, in conjunction with various basis sets, upon the optimized B3LYP/cc-pVTZ geometries, at the level of Hartree–Fock (HF) theory [37], Møller–Plesset theory [60] truncated at second-order (MP2) [61], third-order (MP3) [62], and fourth-order with single, double, and quadruple excitations (SDQ-MP4) [63], and at the CCSD and CCSD(T) [55] levels of theory. For the sake of simplicity, the SDQ-MP4 approach will be throughout this study referred to as the MP4 level. The employed basis sets were the Dunning's correlation consistent cc-pVXZ basis sets [59] (X = {D,T,Q}).

Use has been made of the Feller's three-point extrapolation formula [64],

$$E^{HF}(l) = E^{HF}(\infty) + Ae^{-Bl} \tag{1}$$

for evaluating the total HF energy in the limit of an asymptotically complete (cc-pV∞Z) basis set. In the above equation the cardinal number $l$ is 2, 3, 4... when X = D, T, Q... Electron correlation energies at the MP2 level were correspondingly obtained using the Schwarz [65] three-point extrapolation formula:

$$E^{corr}(l) = E^{corr}(\infty) + \frac{B}{(l+\frac{1}{2})^4} + \frac{C}{(l+\frac{1}{2})^6} \tag{2}$$

The total energy obtained at the MP2 level in the limit of the asymptotically complete cc-pV∞Z basis set from a three-point extrapolation employing $l$ = 2, 3, 4 will be referred to as the $S_{MP2}$-QZ result. This value is obtained by adding to the Feller's extrapolated HF energy [$E^{HF}(\infty)$], the result of the Schwartz extrapolation of the MP2 correlation energy [$E^{corr}(\infty)$]. Further extrapolation has been performed toward the CCSD(T) level of theory in the limit of an

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asymptotically CBS using the principles of a FPA, by means of the extrapolation formula:

$$FPA-QZ = S_{MP2} - QZ + (E_{MP4/cc-pVTZ} - E_{MP2/cc-pVTZ}) + (E_{CCSD(T)/cc-pVDZ} - E_{MP4/cc-pVDZ}) \quad (3)$$

The latter formula stems from the observation [9–13] that higher-order correlation contributions are usually much smaller, and converge much faster than the lower-order ones, upon improving the basis set.

Vertical singlet–triplet energy gaps, electron affinities and ionization energies are the results of calculations which have been performed on the geometries of the neutrals. Vertical and "well-to-well" energy differences have been estimated at the CCSD(T) level in the limit of an infinitely large cc-pV∞Z basis set, according to the above equation, by adding to the $S_{MP2}$-QZ result almost converged and small high-level correlation corrections, obtained at the MP4/cc-pVTZ and CCSD(T)/cc-pVDZ levels of theory. The outcome of relaxation effects (Geometry Relaxation Energy (GRXE)) has therefore also been most generally evaluated at the CCSD(T)/cc-pV∞Z level by considering the difference in-between the FPA estimates for vertical and "well-to-well" transition energies, except in two particular cases, namely the determination of the electronic affinity and ionization energy of chysene. Rather unfortunately, the coupled cluster iterations upon the anion and cation of this compound indeed failed to properly converge when employing the cc-pVTZ and cc-pVQZ basis sets. In order to supply anyway reliable enough estimates for the missing pieces of information, comparison has been systematically made throughout the study with B3LYP/cc-pVTZ values for GRXEs. The CCSD(T)/cc-pV∞Z and B3LYP/cc-pVTZ estimates of GRXEs were found to be practically equal, within 0.01 eV accuracy, and B3LYP/cc-pVTZ relaxation energies have therefore been used to determine the "well-to-well" electron attachment and ionization energies of chrysene, which correspond to energy differences between minima on the relevant potential energy surface. Adiabatic values were ultimately obtained for all studied electronic transitions by adding B3LYP/cc-pVTZ estimates for zero-point vibrational energy corrections to the FPA estimates of the relevant "well-to-well" transition energies.

## 3. Results and discussion

### 3.1. The electronic ground state

Prior to any other consideration, it was necessary to verify whether a single-reference wavefunction for the electronic neutral ground state is suitable for further many-body calculations on the selected PAHs. This check has been made by using the T1 diagnostics [66] of CCSD theory and energy-based criteria devised by Karton et al. [67] (Table 1). For all studied compounds, the T1 values are lower than 0.0121 at the CCSD/cc-pVDZ level of theory. Also, the percentage of the total atomization energy accounted for by the parenthetical triple excitations %TAE[(T)] is lower than 1.16 % for all studied compounds. According to stringent tests of many-body quantum mechanical theories [67], and since all %TAE[(T)] values are below 2 %, we can safely draw the conclusion that all targets are essentially dominated by dynamical correlation and should be reliably described by single-reference treatments.

In all the FPAs that are reported in the sequel, the HF estimates for the $E_{ST}$s, IEs and EAs are given as HF energy differences (ΔHF results), and the successive improvements in the treatment of electronic correlation are denoted by +MP2,+MP3,+MP4,+CCSD, and +CCSD(T). These improvements correspond to the corrections obtained at the MP2, MP3, MP4, CCSD, and CCSD(T) levels, compared to the HF, MP2, MP3, MP4, and CCSD results, respectively. The CCSD(T)/cc-pVDZ values for the $E_{ST}$, IE and EA are given as ΔCCSD(T) entries.

**Table 1**
T1 diagnostics (CCSD/cc-pVDZ level of theory), and contributions (in %) from perturbative triple (T) excitations to Total Atomization Energies (TAEs, calculations based on the B3LYP/cc-pVTZ geometries for the singlet closed-shell electronic ground state).

| | T1 | %TAE[(T)][a] | %TAE[(T)][b] | %TAE[(T)][c] |
|---|---|---|---|---|
| Azulene | 0.0121 | 0.91 | 0.94 | 1.16 |
| Phenanthrene | 0.0104 | 0.83 | 0.86 | 1.08 |
| Pyrene | 0.0106 | 0.89 | 0.92 | 1.15 |
| Chrysene | 0.0105 | 0.86 | 0.89 | |
| Perylene | 0.0107 | 0.92 | 0.95 | |

[a] Upon a comparison of CCSD/cc-pVDZ, CCSD(T)/cc-pVDZ and CCSD(T)/cc-pV∞Z (FPA_QZ) results for TAEs.
[b] Upon a comparison of CCSD/cc-pVDZ with CCSD(T)/cc-pVDZ results for TAEs.
[c] Upon a comparison of CCSD/cc-pVTZ with CCSD(T)/cc-pVTZ results for TAEs.

### 3.2. Singlet–triplet energy gap

All detailed intermediate results involved in the FPAs of the vertical singlet–triplet energy gaps ($VE_{ST}$) of azulene, phenanthrene, pyrene, chrysene, and perylene are given as main entries in Tables 2–6, along with their "well-to-well" ($WWE_{ST}$) counterparts, which are given in brackets. The corresponding triplet excited states are: $^3B_2$ for azulene and phenanthrene, $^3B_{1u}$ for pyrene and perylene, and $^3B_u$ for chrysene. Upon inspecting these tables, it is clear that the ΔHF values for both the vertical and the "well-to-well" singlet–triplet energy gaps converge rather rapidly to finite values with respect to successive improvements of the basis set. Whatever the level attained in correlation and the size of the basis set, the lowest singlet (closed shell) state of all considered compounds is located below in energy than the first triplet state. The +MP2 corrections are systematically positive and largely dominate the correlation corrections, especially for systems like phenanthrene (Table 3) and perylene (Table 6). On the other hand, the +MP3,+MP4 and +CCSD corrections are all negative. The corrections corresponding to triple perturbative excitations are positive and very small. Convergence of the +MP2 corrections upon improvements of the basis set is smooth for all systems and enables safe extrapolations to the limit of an asymptotically complete (i.e. infinitely large) basis set. In view of the convergence of results

**Table 2**
Focal point analysis of the vertical singlet–triplet gap of azulene. "Well to well" $S_0$–$T_1$ excitation energies ($WWE_{S-T}$) are in parenthesis (all results are given in eV).

| Azulene | | | | |
|---|---|---|---|---|
| No. basis | cc-pVDZ 180 | cc-pVTZ 412 | cc-pVQZ 790 | cc-pV∞Z |
| ΔHF | 1.46 (0.72) | 1.44 (0.73) | 1.43 (0.73) | 1.43[a] (0.73)[a] |
| +MP2 | 1.61 (2.25) | 1.63 (2.35) | 1.64 (2.37) | 1.64[b] (2.39)[b] |
| +MP3 | −0.54 (−0.77) | −0.67 (−0.85) | | |
| +MP4(SDQ) | −0.18 (−0.25) | −0.12 (−0.28) | | |
| +CCSD | −0.18 (−0.30) | | | |
| +CCSD(T) | 0.14 (0.20) | | | |
| ΔCCSD(T) | 2.30 (1.84) | | | |

[a] Obtained using Feller's three-point extrapolation formula.
[b] $S_{MP2}$-QZ result.

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**Table 3**
Focal point analysis of the vertical singlet–triplet gap of phenanthrene. "Well to well" $S_0$–$T_1$ excitation energies ($WWE_{S\text{-}T}$) are in parenthesis (all results are given in eV).

| Phenanthrene | | | | |
|---|---|---|---|---|
| No. basis | cc-pVDZ 246 | cc-pVTZ 560 | cc-pVQZ 1070 | cc-pV∞Z |
| ΔHF | 2.31 (1.63) | 2.28 (1.63) | 2.28 (1.63) | 2.28[a] (1.63)[a] |
| +MP2 | 3.37 (3.49) | 3.48 (3.64) | 3.52 (3.69) | 3.54[b] (3.73)[b] |
| +MP3 | −1.03 (−1.12) | −1.16 (−1.25) | | |
| +MP4(SDQ) | −0.47 (−0.47) | −0.52 (−0.51) | | |
| +CCSD | −0.69 (−0.66) | | | |
| +CCSD(T) | 0.08 (0.13) | | | |
| ΔCCSD(T) | 3.57 (2.99) | | | |

[a] Obtained using Feller's three-point extrapolation formula.
[b] $S_{MP2}$-QZ result.

**Table 4**
Focal point analysis of the vertical singlet–triplet gap of pyrene. "Well to well" $S_0$–$T_1$ excitation energies ($WWE_{S\text{-}T}$) are in parenthesis (all results are given in eV).

| Pyrene | | | | |
|---|---|---|---|---|
| No. basis | cc-pVDZ 274 | cc-pVTZ 620 | cc-pVQZ 1180 | cc-pV∞Z |
| ΔHF | 2.08 (1.41) | 2.06 (1.43) | 2.06 (1.43) | 2.06[a] (1.43)[a] |
| +MP2 | 1.45 (1.80) | 1.49 (1.89) | 1.52 (1.92) | 1.53[b] (1.94)[b] |
| +MP3 | −0.39 (−0.55) | −0.44 (−0.62) | | |
| +MP4(SDQ) | −0.21 (−0.23) | −0.23 (−0.26) | | |
| +CCSD | −0.23 (−0.23) | | | |
| +CCSD(T) | 0.00 (0.07) | | | |
| ΔCCSD(T) | 2.71 (2.27) | | | |

[a] Obtained using Feller's three-point extrapolation formula.
[b] SMP2-QZ result.

**Table 5**
Focal point analysis of the vertical singlet–triplet gap of chrysene. "Well to well" $S_0T_1$ excitation energies ($WWE_{S\text{-}T}$) are in parenthesis (all results are given in eV).

| Chrysene | | | | |
|---|---|---|---|---|
| No. basis | cc-pVDZ 321 | cc-pVTZ 705 | cc-pVQZ 1350 | cc-pV∞Z |
| ΔHF | 2.58 (1.65) | 2.55 (1.66) | 2.55 (1.66) | 2.55[a] (1.67)[a] |
| +MP2 | 1.80 (3.65) | 1.85 (3.83) | 1.88 (3.87) | 1.90[b] (3.91)[b] |
| +MP3 | −0.59 (−1.27) | −0.66 (−1.41) | | |
| +MP4(SDQ) | −0.25 (−0.54) | −0.28 (−0.59) | | |
| +CCSD | −0.29 (−0.75) | | | |
| +CCSD(T) | 0.02 (0.10) | | | |
| ΔCCSD(T) | 3.27 (2.86) | | | |

[a] Obtained using Feller's three-point extrapolation formula.
[b] $S_{MP2}$-QZ result.

**Table 6**
Focal point analysis of the vertical singlet–triplet gap of perylene. "Well to well" $S_0$–$T_1$ excitation energies ($WWE_{S\text{-}T}$) are in parenthesis (all results are given in eV).

| Perylene | | | | |
|---|---|---|---|---|
| No. basis | cc-pVDZ 340 | cc-pVTZ 768 | cc-pVQZ 1460 | cc-pV∞Z |
| ΔHF | 1.21 (0.59) | 1.18 (0.59) | 1.17 (0.58) | 1.17[a] (0.58)[a] |
| +MP2 | 2.66 (2.95) | 2.75 (3.06) | 2.78 (3.10) | 2.80[b] (3.13)[b] |
| +MP3 | −0.77 (−0.89) | −0.86 (−1.00) | | |
| +MP4(SDQ) | −0.38 (−0.40) | −0.42 (−0.44) | | |
| +CCSD | −0.56 (−0.55) | | | |
| +CCSD(T) | 0.03 (0.09) | | | |
| ΔCCSD(T) | 2.19 (1.79) | | | |

[a] Obtained using Feller's three-point extrapolation formula.
[b] $S_{MP2}$-QZ result.

upon improving the basis set and upon increasing the level attained in correlation, and experience acquired with comparable FPAs [9–12] upon *n*-acenes, highly reliable estimates for the vertical ($VE_{ST}$) and "well-to-well" ($WWE_{ST}$) singlet–triplet gap can be obtained for azulene, pyrene and chrysene, within an estimated accuracy of a few hundredths eV, upon extrapolating the CCSD(T) results to the limit of an asymptotically complete cc-pV∞Z basis set, using Eqs. (1)–(3). Adiabatic singlet–triplet energy gaps ($AE_{ST}$) have been correspondingly determined by adding to the $WWE_{ST}$ values obtained in this limit the B3LYP/cc-pVTZ estimates for zero-point vibrational energy (ZPVE) (Table 7). Geometry relaxation energies (GRXE) are displayed as third entry in Table 7. These latter contributions have been estimated in the limit of a CCSD(T)/cc-pV∞Z treatment as the energy differences in between the vertical and "well-to-well" singlet–triplet energy gaps. The reader is referred further to Table 7 for a comparison of our best FPA-QZ estimates with experimental results. The best agreement between experiment and theory is observed with azulene, with a discrepancy of 0.046 eV only. The experimental result for azulene has been obtained by means of the pulse radiolysis technique [24] applied on non-polar benzene solutions of anthracene ($6–8 * 10^{-2}$ mol $L^{-1}$) containing azulene ($4–10 * 10^{-4}$ mol $L^{-1}$). Differences between our best adiabatic estimates and experimental data for the other compounds are 0.24 eV (phenanthrene), 0.12 eV (pyrene), 0.12 eV (chrysene), and 0.16 eV (perylene). These rather large differences between theory and experiment are certainly due to the fact that experimental values were obtained from measurements in polar solutions and glassy matrices, which may give rise to complications associated with intermolecular interactions. Indeed, the experimental values for the singlet–triplet energy gaps of phenanthrene and pyrene are the results of measurements in a mixture of ether, isopentane, and alcohol at 77 K where it forms a glass. Similarly, the experimental data [26] for perylene have been obtained from measurements employing the solvent perturbation technique, using chloranil in carbon tetrachloride solution along with oxygen under high pressure at room temperature. The oxygen forms a contact charge-transfer complex with the hydrocarbon and the absorption spectrum corresponds therefore to the superposition of the $S_0 \rightarrow T_1$ transition, on the charge-transfer band. At last, note that the experimental value for chrysene was determined from Photodetachment-Photoelectron Spectroscopy (PD-PES) spectra at wavelengths of 266 nm and 355 nm [25] and is subject therefore to geometrical complications arising from the removal of an electron from the *anion*.

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**Table 7**
Calculated and experimental singlet–triplet energy gaps, along with the zero-point vibrational energy (ΔZPE) and geometry relaxation (GRXE) contributions. All results are given in eV.

| | VES-T CCSD(T)/ cc-pV∞Z[a] | WWES-T CCSD(T)/ cc-pV∞Z[a] | GRXE CCSD(T)/ cc-pV∞Z | ΔZPE B3LYP/ cc-pVTZ | AES-T CCSD(T)/ cc-pV∞Z[b] | Experimental |
|---|---|---|---|---|---|---|
| Azulene | 2.24 | 1.89 | −0.35 | −0.11 | 1.79 | 1.739 ± 0.009[c]<br>1.677[d] |
| Phenanthrene | 3.54 | 3.06 | −0.48 | −0.14 | 2.92 | 2.68[e] |
| Pyrene | 2.70 | 2.34 | −0.36 | −0.12 | 2.22 | 2.10[e] |
| Chrysene | 3.24 | 2.93 | −0.31 | −0.14 | 2.79 | 2.64 ± 0.01[f] |
| Perylene | 2.14 | 1.81 | −0.34 | −0.10 | 1.71 | 1.55[g] |

[a] FPA-QZ estimate (see text for details).
[b] Upon adding ΔZPE corrections to $WWE_{S\text{-}T}$ CCSD(T)/cc-pV∞Z data.
[c] Obtained by means of the Pulse Radiolysis Technique, for details see Ref. [24].
[d] Obtained from the measurements of the rates of energy transfer by means of the flash kinetic spectrometry, for details see Ref. [23].
[e] Measurement has been carried out in a mixture of ether, isopentane, and alcohol at 77 K where it forms a glass, or in another related solvent (EPA+), for details see Ref. [22], and references therein.
[f] Determined from PD-PES spectra, for detail see Ref. [25].
[g] measured using so-called solvent perturbation technique using oxygen under high pressure, for details see text and Ref. [26].

**Table 8**
Focal point analysis of the vertical electron affinity of azulene. "Well to well" electron affinities (WWEA) are in parenthesis (all results are given in eV).

| Azulene | | | | |
|---|---|---|---|---|
| No. basis | cc-pVDZ 180 | cc-pVTZ 412 | cc-pVQZ 790 | cc-pV∞Z |
| ΔHF | −0.19 (0.05) | −0.07 (0.14) | 0.00 (0.20) | 0.04[a] (0.24)[a] |
| +MP2 | −0.77 (−0.73) | −0.56 (−0.56) | −0.49 (−0.50) | −0.44[b] (−0.45)[b] |
| +MP3 | 0.43 (0.44) | 0.43 (0.44) | | |
| +MP4(SDQ) | 0.22 (0.22) | 0.25 (0.24) | | |
| +CCSD | 0.23 (0.21) | | | |
| +CCSD(T) | -0.11 (-0.11) | | | |
| ΔCCSD(T) | -0.19 (0.08) | | | |

[a] Obtained using Feller's three-point extrapolation formula.
[b] $S_{MP2}$-QZ result.

**Table 9**
Focal point analysis of the vertical electron affinity of phenanthrene. "Well to well" electron affinities (WWEA) are in parenthesis (all results are given in eV).

| Phenanthrene | | | | |
|---|---|---|---|---|
| No. basis | cc-pVDZ 246 | cc-pVTZ 560 | cc-pVQZ 1070 | cc-pV∞Z |
| ΔHF | −1.37 (−1.13) | −1.25 (−1.06) | −1.19 (−1.01) | −1.15[a] (−0.97)[a] |
| +MP2 | −0.49 (−0.53) | −0.27 (−0.35) | −0.19 (−0.29) | −0.14[b] (−0.24)[b] |
| +MP3 | 0.36 (0.40) | 0.36 (0.41) | | |
| +MP4(SDQ) | 0.25 (0.26) | 0.26 (0.27) | | |
| +CCSD | 0.24 (0.26) | | | |
| +CCSD(T) | 0.00 (0.01) | | | |
| ΔCCSD(T) | −1.02 (−0.73) | | | |

[a] Obtained using Feller's three-point extrapolation formula.
[b] $S_{MP2}$-QZ result.

**Table 10**
Focal point analysis of the vertical electron affinity of pyrene. "Well to well" electron affinities (WWEA) are in parenthesis (all results are given in eV).

| Pyrene | | | | |
|---|---|---|---|---|
| No. basis | cc-pVDZ 274 | cc-pVTZ 620 | cc-pVQZ 1180 | cc-pV∞Z |
| ΔHF | −0.79 (−0.65) | −0.70 (−0.61) | −0.66 (−0.56) | −0.63[a] (−0.53)[a] |
| +MP2 | −0.05 (−0.03) | 0.19 (0.17) | 0.27 (0.24) | 0.32[b] (0.29)[b] |
| +MP3 | 0.01 (0.20) | 0.16 (0.18) | | |
| +MP4(SDQ) | 0.32 (0.17) | 0.16 (0.17) | | |
| +CCSD | 0.10 (0.11) | | | |
| +CCSD(T) | 0.00 (0.02) | | | |
| ΔCCSD(T) | −0.41 (−0.19) | | | |

[a] Obtained using Feller's three-point extrapolation formula.
[b] $S_{MP2}$-QZ result.

**Table 11**
Focal point analysis of the vertical electron affinity of chrysene. "Well to well" electron affinities (WWEA) are in parenthesis (all results are given in eV).

| Chrysene | | | | |
|---|---|---|---|---|
| No. basis | cc-pVDZ 321 | cc-pVTZ 705 | cc-pVQZ 1350 | cc-pV∞Z |
| ΔHF | −1.13 (−0.78) | −1.03 (−0.73) | −0.97 (−0.68) | −0.94[a] (−0.65)[a] |
| +MP2 | 0.25 (−1.31) | 0.51 (−1.17) | 0.59 (−1.11) | 0.64[b] (−1.07)[b] |
| +MP3 | 0.09 (0.66) | 0.06 (0.70) | | |
| +MP4(SDQ) | 0.12 (0.39) | 0.13 (0.42) | | |
| +CCSD | 0.04 (−)[c] | | | |
| +CCSD(T) | 0.03 (−)[c] | | | |
| ΔCCSD(T) | −0.59 (−)[c] | | | |

[a] Obtained using Feller's three-point extrapolation formula.
[b] $S_{MP2}$-QZ result.
[c] Unconverged.

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**Table 12**
Focal point analysis of the vertical electron affinity of perylene. "Well to well" electron affinities (WWEA) are in parenthesis (all results are given in eV).

| Perylene | | | | |
|---|---|---|---|---|
| No. basis | cc-pVDZ 340 | cc-pVTZ 768 | cc-pVQZ 1460 | cc-pV∞Z |
| ΔHF | −0.05 (0.07) | 0.04 (0.12) | 0.09 (0.17) | 0.13[a] (0.20)[a] |
| +MP2 | −1.32 (−1.33) | −1.11 (−1.16) | −1.03 (−1.09) | −0.98[b] (−1.05)[b] |
| +MP3 | 0.60 (0.62) | 0.63 (0.65) | | |
| +MP4(SDQ) | 0.36 (0.37) | 0.39 (0.40) | | |
| +CCSD | 0.47 (0.50) | | | |
| +CCSD(T) | −0.01 (0.01) | | | |
| ΔCCSD(T) | 0.06 (0.24) | | | |

[a] Obtained using Feller's three-point extrapolation formula.
[b] $S_{MP2}$-QZ result.

### 3.3. Electron affinities

The anions of azulene, phenanthrene, pyrene, chrysene, and perylene anions possess a $^2B_1$, $^2A_2$, $^2A_u$, $^2B_g$, and $^2B_{1g}$ electronic ground state, respectively. The results of the focal point analysis of the vertical electron affinities (VEAs) and corresponding "well-to-well" values of these five compounds are given in Tables 8–12. Again, ΔHF results converge smoothly to a finite value with respect to successive improvements of the basis set. In the case of azulene (Table 8), phenanthrene (Table 9) and perylene (Table 12), the +MP2 corrections are negative while higher order corrections up to the CCSD(T) level are positive. For these three compounds the +MP2 corrections tend to decrease in absolute value when going to the limit of an asymptotically complete basis set. For chrysene (Table 11) the "well-to-well" +MP2 corrections are also all negative, whereas the vertical +MP2 corrections are all positive. For pyrene (Table 10), the +MP2 correction reverses from a negative to a positive value as the basis set improves. Starting from the MP3 level, the correlation energy systematically increases the VEA and adiabatic electron affinity (AEA) upon including higher order correlation terms. For pyrene and chrysene (Tables 10 and 11), the influence of the high-order correlation energy terms on our theoretical estimates of the electron affinity is particularly noticeable. The actual electron affinity of those two PAHs is positive, due to the contributions of higher order electron correlation corrections and the contributions of the ΔZPE, which are all positive. According to the FPAs and extrapolations of results to the CCSD(T)/cc-pV∞Z level, our best estimates for the VEAs of azulene, phenanthrene, pyrene, chrysene, and perylene are 0.4036 eV, −0.4246 eV, 0.1241 eV, −0.0451 eV, and 0.6288 eV, respectively. The vertical electron affinity of chrysene at the HF level is negative and it remains negative even after incorporating correlation corrections up to the CCSD(T) level, in the limit of an asymptotically complete cc-pV∞Z basis set.

AEAs are calculated by adding to the "well-to-well" electron affinities (WWEA) the ΔZPE correction calculated at the B3LYP/cc-pVTZ level of theory. In the case of chrysene, the WWEA could not be obtained at the CCSD(T)/cc-pV∞Z level, because the coupled cluster iterations failed to converge to the correct state when employing the cc-pVTZ and cc-pVQZ basis sets, and structural relaxation energies had therefore to be supplied at the B3LYP/cc-pVTZ and CCSD(T)/cc-pVDZ levels of theory. From a comparison (Table 13) of GRXEs obtained for the electron affinities of all other compounds at these two levels as well as the CCSD(T)/cc-pV∞Z level of theory, we expect that the error arising from this restriction in our treatment should not exceed 0.01 eV. Adiabatic estimates, together with the corresponding vertical and 'well-to-well" estimates, GRXE, ΔZPE corrections and experimentally obtained values are given in Table 13. Our best estimates for the AEAs

**Table 13**
Calculated and experimental electron affinities, along with the zero-point vibrational energy (ΔZPE) and geometry relaxation (GRXE) contributions. All results are given in eV.

| | VEA CCSD(T)/ cc-pV∞Z[a] | WWEA CCSD(T)/ cc-pV∞Z[a] | GRXE CCSD(T)/ cc-pV∞Z | GRXE B3LYP/ cc-pVTZ | ΔZPE B3LYP/ cc-pVTZ | AEA CCSD(T)/ cc-pV∞Z[b] | Experimental |
|---|---|---|---|---|---|---|---|
| Azulene | 0.40 | 0.58 | 0.17 | 0.15 | 0.13 | 0.71 | 0.80 ± 0.10[f]<br>0.690 ± 0.040[g]<br>0.790 ± 0.008[h] |
| Phenanthrene | -0.42 | -0.26 | 0.17 | 0.16 | 0.18 | -0.08 | −0.01 ± 0.04[i]<br><0.269 ± 0.035[j] |
| Pyrene | 0.12 | 0.24 | 0.12 | 0.11 | 0.16 | 0.40 | 0.39[k]<br>0.406 ± 0.010[l] |
| Chrysene | -0.05 | –[c] | 0.11[d] | 0.11 | 0.18 | 0.24[e] | 0.32 ± 0.01[m]<br>0.3970 ± 0.0080[n] |
| Perylene | 0.63 | 0.72 | 0.09 | 0.09 | 0.15 | 0.87 | 0.973 ± 0.005[o]<br>0.993 ± 0.043[p] |

[a] FPA-QZ estimate (see text for details).
[b] Upon adding ΔZPE corrections to WWEA CCSD(T)/cc-pV∞Z data.
[c] Unconverged.
[d] CCSD(T)/cc-pVDZ result.
[e] Using the B3LYP/cc-PVTZ estimate for the GRXE.
[f] Obtained by means of Laser Photoelectron Spectroscopy (LPES), for details see Ref. [42].
[g] Obtained with the Electron Capture Detection (ECD), for details see Ref. [40].
[h] Obtained by means of LPES, for details see Ref. [43].
[i] by an extrapolation method using the water cluster data, for details see Ref. [17].
[j] obtained using ECD, for details see Ref. [18].
[k] obtained using ECD, for details see Ref. [41].
[l] obtained by means of LPES, for details see Ref. [44].
[m] obtained by means of LPES, for details see Ref. [25].
[n] Obtained using ECD, for details see Ref. [19].
[o] Obtained by means of LPES, for details see Ref. [15].
[p] Obtained by means of ion/molecule reaction equilibrium method, for details see Ref. [16].

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**Table 14**
Focal point analysis of the vertical ionization energy of azulene. "Well to well" ionization energies (WWIE) are in parenthesis (all results are given in eV).

| Azulene | | | | |
|---|---|---|---|---|
| No. basis | cc-pVDZ 180 | cc-pVTZ 412 | cc-pVQZ 790 | cc-pV∞Z |
| ΔHF | 5.62 (5.45) | 5.63 (5.47) | 5.65 (5.49) | 5.66[a] (5.50)[a] |
| +MP2 | 2.64 (2.64) | 2.97 (2.98) | 3.07 (3.08) | 3.13[b] (3.14)[b] |
| +MP3 | −0.72 (−0.72) | −0.83 (−0.84) | | |
| +MP4(SDQ) | −0.22 (−0.22) | −0.26 (−0.26) | | |
| +CCSD | −0.26 (−0.25) | | | |
| +CCSD(T) | 0.14 (0.15) | | | |
| ΔCCSD(T) | 7.22 (7.05) | | | |

[a] Obtained using Feller's three-point extrapolation formula.
[b] $S_{MP2}$-QZ result.

**Table 15**
Focal point analysis of the vertical ionization energy of phenanthrene. "Well to well" ionization energies (WWIE) are in parenthesis (all results are given in eV).

| Phenanthrene | | | | |
|---|---|---|---|---|
| No. basis | cc-pVDZ 246 | cc-pVTZ 560 | cc-pVQZ 1070 | cc-pV∞Z |
| ΔHF | 6.54 (6.36) | 6.53 (6.36) | 6.54 (6.37) | 6.55[a] (6.38)[a] |
| +MP2 | 2.46 (2.50) | 2.80 (2.84) | 2.89 (2.94) | 2.96[b] (3.01)[b] |
| +MP3 | −0.64 (−0.66) | −0.76 (−0.78) | | |
| +MP4(SDQ) | −0.26 (−0.25) | −0.30 (−0.30) | | |
| +CCSD | −0.34 (−0.34) | | | |
| +CCSD(T) | 0.03 (0.03) | | | |
| ΔCCSD(T) | 7.79 (7.64) | | | |

[a] Obtained using Feller's three-point extrapolation formula.
[b] SMP2-QZ result.

obtained by means of the FPA are 0.7075 eV, −0.0795 eV, 0.3999 eV, 0.2446, and 0.8709 eV for azulene, phenanthrene, pyrene, chrysene and perylene, respectively. These compare very favorably, within an average accuracy of 0.05 eV (1.25 kcal/mol), with the most recent experimental values that were reported for the electron affinities of these five compounds: 0.690 ± 0.040 eV [43], −0.01 ± 0.04 eV [17], 0.406 ± 0.010 eV [44], 0.32 ± 0.01 eV [25], and 0.973 ± 0.005 eV [16], respectively. A discrepancy of 0.07 eV is noticed for phenanthrene. Note that in this case, the experimental value has been obtained from an extrapolation to vacuum of data obtained for water clusters [17], and should be apprehended therefore with the greatest care. Besides, for molecules with very low electron affinities (<0.1 eV), as is the case of phenanthrene, electron scattering is a most difficult problem [68]. In such situations, the experimental values which are obtained by means of Electron Capture Detection (ECD) must be regarded as upper limits of the true adiabatic EAs. This observation is in line with a recent determination of the EA of phenanthrene using the ECD approach, giving an upper limit of 0.269 ± 0.035 [18], thus 0.35 eV above our benchmark value for the adiabatic EA. The rather large disagreements (0.0754 eV and 0.1021 eV)

**Table 16**
Focal point analysis of the vertical ionization energy of pyrene. "Well to well" ionization energies (WWIE) are in parenthesis (all results are given in eV).

| Pyrene | | | | |
|---|---|---|---|---|
| No. Basis | cc-pVDZ 274 | cc-pVTZ 620 | cc-pVQZ 1180 | cc-pV∞Z |
| ΔHF | 6.01 (5.88) | 6.00 (5.89) | 6.02 (5.90) | 6.03[a] (5.92)[a] |
| +MP2 | 1.98 (2.03) | 2.28 (2.33) | 2.36 (2.42) | 2.42[b] (2.48)[b] |
| +MP3 | −0.46 (−0.47) | −0.61 (−0.57) | | |
| +MP4(SDQ) | −0.15 (−0.16) | −0.12 (−0.19) | | |
| +CCSD | −0.18 (−0.19) | | | |
| +CCSD(T) | 0.03 (0.03) | | | |
| ΔCCSD(T) | 7.23 (7.13) | | | |

[a] Obtained using Feller's three-point extrapolation formula.
[b] $S_{MP2}$-QZ result.

**Table 17**
Focal point analysis of the vertical ionization energy of chrysene. "Well to well" ionization energies (WWIE) are in parenthesis (all results are given in eV).

| Chrysene | | | | |
|---|---|---|---|---|
| No. basis | cc-pVDZ 321 | cc-pVTZ 705 | cc-pVQZ 1350 | cc-pV∞Z |
| ΔHF | 6.39 (6.00) | 6.38 (5.99) | 6.40 (6.01) | 6.41[a] (6.02)[a] |
| +MP2 | 1.56 (3.33) | 1.82 (3.72) | 1.90 (3.83) | 1.96[b] (3.91)[b] |
| +MP3 | −0.33 (−0.95) | −0.41 (−1.11) | | |
| +MP4(SDQ) | −0.09 (−0.39) | −0.11 (−0.45) | | |
| +CCSD | −0.14 (−)[c] | | | |
| +CCSD(T) | 0.02 (−)[c] | | | |
| ΔCCSD(T) | 7.40 (−)[c] | | | |

[a] Obtained using Feller's three-point extrapolation formula.
[b] $S_{MP2}$-QZ result.
[c] Unconverged.

**Table 18**
Focal point analysis of the vertical ionization energy of perylene. "Well to well" ionization energies (WWIE) are in parenthesis (all results are given in eV).

| Perylene | | | | |
|---|---|---|---|---|
| No. basis | cc-pVDZ 340 | cc-pVTZ 768 | cc-pVQZ 1460 | cc-pV∞Z |
| ΔHF | 5.29 (5.18) | 5.28 (5.17) | 5.29 (5.18) | 5.31[a] (5.19)[a] |
| +MP2 | 3.44 (3.48) | 3.82 (3.87) | 3.94 (3.99) | 4.01[b] (4.07)[b] |
| +MP3 | -0.94 (-0.95) | -1.11 (-1.12) | | |
| +MP4(SDQ) | -0.38 (-0.39) | -0.44 (-0.45) | | |
| +CCSD | -0.61 (-0.62) | | | |
| +CCSD(T) | 0.04 (0.04) | | | |
| ΔCCSD(T) | 6.83 (6.75) | | | |

[a] obtained using Feller's three-point extrapolation formula.
[b] $S_{MP2}$-QZ result.

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**Table 19**
Calculated and experimental ionization energies, along with the zero-point vibrational energy (ΔZPE) and geometry relaxation (GRXE) contributions. All results are given in eV.

| | VIE CCSD(T)/ cc-pV∞Z[a] | WWIE CCSD(T)/ cc-pV∞Z[a] | GRXE CCSD(T)/ cc-pV∞Z | GRXE B3LYP/ cc-pVTZ | ΔZPE B3LYP/ cc-pVTZ | AIE CCSD(T)/ cc-pV∞Z[b] | Experimental |
|---|---|---|---|---|---|---|---|
| Azulene | 7.58 | 7.44 | −0.14 | −0.13 | −0.01 | 7.43 | 7.38 ± 0.03[e]<br>7.32 ± 0.05[f]<br>7.43 ± 0.04[g] |
| Phenanthrene | 8.13 | 8.01 | −0.13 | −0.11 | 0.00 | 8.01 | 7.903[h]<br>7.87 ± 0.02[i]<br>7.8914 ± 0.0006[j] |
| Pyrene | 7.57 | 7.49 | −0.09 | −0.08 | −0.01 | 7.48 | 7.4256 ± 0.0006[j]<br>7.4[k]<br>7.50 ± 0.05[l] |
| Chrysene | 7.73 | –[c] | –[c] | −0.08 | 0.00 | 7.65[d] | 7.60 ± 0.03[m]<br>8.0 ± 0.2[n]<br>7.59 ± 0.05[l] |
| Perylene | 7.20 | 7.12 | −0.08 | −0.07 | 0.03 | 7.15 | 6.960 ± 0.001[o]<br>6.90 ± 0.01[m]<br>7.00 ± 0.01[m] |

[a] FPA-QZ estimate (see text for details).
[b] Upon adding DZPE corrections to WWIE CCSD(T)/cc-pV1Z data.
[c] Unconverged.
[d] Using the B3LYP/cc-PVTZ estimate for the GRXE.
[e] Determined by means of photo-ionization mass spectrometry, for details see Ref. [45].
[f] Determined by means of ion/molecule equilibrium constant determination, for details see Ref. [20].
[g] Obtained by means of photoelectron spectroscopy, for details see Ref. [69].
[h] Obtained by means of photoelectron spectroscopy, for details see Ref. [46].
[i] Obtained from the time-resolve photo-ionization efficiently curve, for details see Ref. [70].
[j] Obtained by means of two laser resonant photo-ionization mass spectroscopy, for details see [47].
[k] Obtained by means of photoelectron spectroscopy, for details see Ref. [71].
[l] Determined using gas-phase ion-equilibrium measurements, for details see Ref. [21].
[m] Obtained by means of photoelectron spectroscopy, for details see Ref. [20].
[n] Obtained by means of electron impact techniques, for details see Ref. [20].
[o] Obtained by means of laser spectroscopy, for details see Ref. [20].

between theory and LPES data in the case of chrysene and perylene are also worth some further examination. The experimental EA of these two compounds were simply directly inferred from the laser photoelectron detachment energies of the *anions* [15,25]. Very obviously, however, these may not exactly compare with the adiabatic electron affinities of the *neutrals*, due to the different geometry implications of the transitions of interest, especially if one considers that the experimentally studied photodetachment processes are vertical transitions.

### 3.4. Ionization energies

The cations of azulene, phenanthrene, pyrene, chrysene, and perylene were found to possess a $^2A_2$, $^2B_1$, $^2B_{1g}$, $^2A_u$, $^2A_u$ electronic state, respectively. Details of the Focal Point Analyses of the associated vertical and well-to-well ionization energies are supplied in Tables 14–18, respectively. Again, the ΔHF results and the +MP2 corrections converge smoothly with the cardinal number (X) characterizing the cc-pVXZ basis set, and can thus be extrapolated reliably to an asymptotically complete cc-pV∞Z basis set. The estimates obtained on the ground of the FPAs (Eq. (3)) by extrapolation of results obtained at the CCSD(T) level to the limit of an asymptotically complete cc-pV∞Z basis set are supplied in Table 19. Upon inspecting Tables 14–18, it appears that the +MP2 contributions are systematically positive, and that they largely dominate the correlation corrections. Also, these contributions tend to increase upon improving the basis set. For all compounds of interest, corrections at the +MP3,+MP4, and +CCSD levels are on the contrary always negative, and tend therefore to compensate the +MP2 contribution. Estimates of VIEs obtained by means of the FPA amount to 7.5836 eV, 8.1348 eV, 7.5722 eV, 7.7416 eV, and 7.1991 eV for azulene, phenanthrene, pyrene, chrysene and perylene, respectively.

The adiabatic ionization energies (AIE) have been obtained by adding to the FPA estimates of WWIEs the B3LYP/cc-pVTZ estimates for zero-point vibrational energy correction. Estimates of the adiabatic and vertical IE at the CCSD(T)/cc-pV∞Z level, "well-to-well" values, GREXs and ΔZPE corrections are provided in Table 19, where they can be compared with the experimentally obtained results. Our best FPA estimates of the adiabatic ionization energies of azulene, phenanthrene, pyrene, chrysene and perylene are equal to 7.4283 eV, 8.0129 eV, 7.4755 eV, 7.6527 eV, and 7.1487 eV, respectively. The experimental IE values were obtained from measurements employing gas-phase ion-equilibrium constant determination [21], photo-ionization mass spectrometry [45], photoelectron spectroscopy [20,46] and laser spectroscopy [20,47]. The experimentally obtained ionization energies amount to 7.38 ± 0.03 eV [20] for azulene, 7.903 eV [46] for phenanthrene, 7.4256 ± 0.0006 eV [47] for pyrene, 7.60 ± 0.03 eV [20] for chrysene and 6.960 ± 0.001 eV [20] for perylene. Discrepancies between our best FPA estimates for adiabatic ionization energies and experimental values are thus 0.0438 eV for azulene, 0.0499 eV for pyrene, and 0.0517 eV for chrysene. Discrepancies deceptively increase to 0.107 eV in the case of phenanthrene and even to 0.199 eV in the case of perylene. These larger discrepancies may be indicative of stronger correlation effects, which a CCSD(T) treatment may fail to apprehend within chemical accuracy. Indeed, details of the focal point analysis of the vertical and well-to-well ionization energy of perylene (Table 18) clearly demonstrate the very strongly correlated nature of this compound. Indeed, the individual +MP2,+MP3,+MP4 and +CCSD corrections are in absolute values much larger than usual, and their convergence with the basis set appears also to be much slower.

For chrysene, because of convergency problem in the coupled cluster iterations for the cation, the GREX contribution to "well-to-well" ionization energy could only be determined on the

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grounds of B3LYP/cc-pVTZ calculations (Table 19). Comparison of B3LYP/cc-pVTZ and CCSD(T)/cc-pV∞Z estimates for the GRXEs associated with the ionization energies of all other target PAHs indicate that the error made in estimating the GREX for the ionization energy of chrysene at the B3LYP/cc-pVTZ level is around 0.01 eV.

## 4. Conclusions

The vertical, well-to-well and adiabatic singlet–triplet energy gaps, electron affinities and ionization energies of azulene, phenanthrene, pyrene, chrysene and perylene have been quantitatively evaluated, at benchmark theoretical levels within the limits of non-relativistic quantum mechanics. The principles of a Focal Point Analysis have been systematically applied on energy differences calculated at the level of Hartree–Fock [HF] theory, second- [MP2], third- [MP3], and fourth-order [SDQ-MP4] Møller-Plesset perturbation theory, as well as coupled cluster theory including single, double and perturbative triple excitations [CCSD(T)], in conjunction with correlation consistent cc-pVXZ basis sets of improving quality (X = D, T, Q), in order to evaluate vertical and well-to-well transition energies at the CCSD(T) level in the limit of an asymptotically complete (X = ∞) basis set. Adiabatic transition energies were ultimately obtained by adding to the well-to-well CCSD(T)/cc-pV∞Z energy differences B3LYP/cc-pVTZ estimates for the zero-point vibrational corrections.

Our best estimates for the vertical singlet–triplet energy gaps of azulene, phenanthrene, pyrene, chrysene, perylene amount to 2.24 eV, 3.54 eV, 2.70 eV, 3.24 eV, 2.14 eV, respectively. The best adiabatic estimates obtained by adding the zero-point vibration energies and geometry relaxation energy contribution to the vertical estimates, are, in the same order, 1.79 eV, 2.92 eV, 2.22 eV, 2.79 eV, 1.71 eV. In view of the complexity and strongly correlated nature of the selected molecular targets, these results support favorably the comparison with experiment, with discrepancies ranging from 0.046 eV (azulene) up to 0.24 eV (phenanthrene). We noted that most experimental data are the results of measurements which have been performed in solid matrices or solvents, and are thus subject to complications arising from the molecular environment (intermolecular forces and polarization effects, packing effects).

Our best estimates for the vertical electron affinities of azulene, phenanthrene, pyrene, chrysene and perylene amount to 0.40 eV, −0.42 eV, 0.12 eV, −0.05 eV, and 0.63 eV, respectively. Upon taking into account geometry relaxation effects and zero point vibrational energy, we obtain adiabatic electron affinities that are equal to 0.71 eV, −0.08 eV, 0.40 eV, 0.24 eV, and 0.87 eV, respectively. Our theoretical results sustain again most favorably the comparison with experiment, with discrepancies ranging from only 0.006 eV and 0.017 eV for pyrene and azulene, up to 0.075 and 0.1 eV in the case of chrysene and perylene, respectively. We noted that the latter two experimental values were obtained using laser photodetachment electron spectroscopy, and are therefore subject to geometrical complications arising with the sudden (vertical) removal of an electron from the anion.

Our best FPA estimates for the vertical ionization energies of azulene, phenanthrene, pyrene, chrysene and perylene amount to 7.58 eV, 8.13 eV, 7.57 eV, 7.73 eV, and 7.20 eV, respectively. Adiabatic estimates obtained upon incorporating geometry relaxation energies and zero point vibrational contributions are, in the same order, equal to 7.43 eV, 8.01 eV, 7.48 eV, 7.65 eV, and 7.15 eV, respectively. Discrepancies between theory and experiment range from 0.04 eV, 0.05 eV and 0.05 eV, for azulene, pyrene and chrysene, up to 0.11 and 0.19 eV for phenanthrene and perylene. The latter very large discrepancy is probably ascribable to the more strongly correlated nature of perylene, which a single-reference CCSD(T) treatment may fail to apprehend within chemical accuracy. Also, one should examine more closely the outcome of steric hindrances and vibronic coupling interactions within the bay regions of compounds like phenanthrene and chrysene.

## Acknowledgements

All calculations presented in this work have been performed upon the infrastructure of the VSC Flemish Supercomputer Center, funded by the Hercules foundation and the Flemish Government department EWI. This work has been supported by the FWO-Vlaanderen, the Flemish branch of the Belgian National Science Foundation, and by the BijzonderOnderzoeksFonds (BOF: special research fund) at Hasselt University. M. S. D and B. H. especially acknowledge financial support from a Research Program of the Research Foundation – Flanders (FWO_Vlaanderen; project number G.0350.09 N, entitled “From orbital imaging to quantum similarity in momentum space”).

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