Equation of motion coupled cluster methods for electron attachment and ionization potential in polyacenes

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Abstract

Polyacenes have attracted considerable attention due to their various applications in organic optoelectronic materials. This study focuses on linear polyacenes and their electron affinity (EA) and ionization potential (IP) properties. We have employed our recent implementation of EA/IP equation of motion coupled cluster singles and doubles (EA/IP-EOMCCSD) methods which are accurate, computationally efficient and are capable of treating large systems employing reasonable basis sets size. The EA/IP results obtained for naphthalene, anthracene, tetracene, pentacene, hexacene and heptacene are in a good agreement with experiment. Comparison between quality of excitation energies obtained from IP-EOMCCSD and EE-EOMCCSD formalisms were also studied.

Keywords: electron affinity, ionization potential, coupled cluster, naphthalene, anthracene, tetracene, pentacene, hexacene, heptacene, polyacenes

1. Introduction

All carbon materials such as fullerene, carbon nanotubes and graphene can be visualized as extended polycyclic aromatic hydrocarbons (PAHs). [1] Due to their interesting optoelectronic properties, polyacenes have been the focal point of many theoretical and experimental studies in the last few years. Pentacene and tetracene and their derivatives are of particular interest due to their well-defined crystal and thin film forms[2] behaving as p-type organic semiconductor that can be used as electronic devices including low-voltage thin-film transistors, light-emitting diodes and field-effect transistors. In addition, these systems can easily be functionalized or can be used to functionalize other conjugated systems to obtain a variety of electronic devices and light harvesting systems. For example, a pentacene derivative, perfluoropentacene, which contains fluorine atoms in place of hydrogen is an n-type semiconductor whereas, pentacene is p-type semiconductor with the added benefit that the perfluoropentacene molecular size is about the same as pentacene. Furthermore, theoretical calculations indicate that fully replacing H with F atoms has the effect

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of decreasing the HOMO-LUMO energy gap from 2.21 eV (pentacene) to 2.02 eV (perfluoropentacene)[3] demonstrating the ability to engineer the gap-size. Thus, it is clear that an understanding of electron affinities (EAs) and ionization potentials (IPs) is necessary to describe the excited state properties of the "true gap", which may not be the HOMO-LUMO gap as well as to understand interfacial properties where accurate alignment of energetics is required. This is especially important in the design of donor-acceptor interfaces in light harvesting systems where the optical absorption, exciton formation, excitation migration to the donor-acceptor interface, and exciton dissociation processes crucially depend on fine tuning between ionization potential of donor and electron affinity of acceptor.

The accurate determination of the IPs and EAs requires a detailed characterization of the electron correlation effects and the utilization of appropriate basis sets. Several recent studies [4, 5, 6, 7, 8, 9] indicate that the EA/IP extensions of the equation-of-motion coupled cluster (IP/EA-EOMCC) formalism [10, 11] are capable of providing high level of accuracy of calculated ionization potentials and electron affinities. To further estimate the effectiveness of the EA/IP-EOMCC methods in encapsulating essential correlation effects necessary for high-precision characterization of EAs and IPs, in this letter we apply the EA/IP-EOMCC model with singles and doubles (EA/IP-EOMCCSD) to the polyacenes that belong to a class of polycyclic aromatic hydrocarbons which are linear fused benzene rings with the general formula $C_{4n+2}H_{2n+4}$.

Due to their interesting optoelectronic properties, polyacenes have attracted considerable attention as they have been successfully used in various optoelectronic devices such as field effect transistor and components of organic photovoltaics [12, 13, 14] and have been the focal point of many theoretical and experimental studies. In particular, the polyacenes have already been a subject of intensive CC studies in the context of molecular properties and excited-state calculations.[15, 16] The first part of this manuscript covers a brief introduction to IP/EA-EOMCCSD methods followed by computational details, results and discussions, and ending with concluding remarks. Using highly efficient parallel implementations of the EA/IP-EOMCCSD methods [4] we were able to perform simulations using extensive basis sets which enabled us to establish the impact of the basis set choice on the quality of calculated EAs and IPs. We also demonstrate the efficiency of the IP-EOMCCSD formulation in calculating vertical excitation energies corresponding to open-shell doublet states of ionized system. We compare IP-EOMCCSD results with the results obtained with the established EE-EOMCC methods utilizing doublet Restricted Open-Shell Hartree-Fock (ROHF) reference function.

2. Theory

The coupled cluster method [17] is one of the most successful ab initio post-Hartree-Fock methods. In this study we employ the equation-of-motion coupled cluster formalism due to its efficiency in accurately describing excited state processes [18, 19, 20, 21, 22, 23, 24, 25, 26, 27], including the EA and IP. [11, 10, 28, 29, 30, 31, 32] One of the most important advantages of this method is its hierarchical structure (similar to parent CC methods) that provides a direct way to incorporate complicated electron excitations. It should be mentioned that various schemes have been

formulated to approximate EOMCC method. [33, 10, 11, 34, 24, 26, 22, 25, 21]

In the coupled cluster formalism the excited state wavefunction $|\Psi_k\rangle$ is obtained by the action of excitation operator $R(k)$ for the k -state on the correlated ground-state wavefunction in the CC parametrization ($|\Psi_0\rangle = e^T|\Phi\rangle$),

$$|\Psi_k\rangle = R(k)e^T|\Phi\rangle, \quad (1)$$

where $|\Phi\rangle$ is the reference determinant and T the cluster operator, $T = \sum_n T_n$. [17] In the most commonly used CCSD approach, [35] the cluster operator T is approximated by truncating the expansion at the bi-excitation term ($T = T_1 + T_2$), where $T_1 = \sum_i \sum_a t_i^a a^\dagger i$, and $T_2 = \sum_{i<j} \sum_{a<b} t_{ij}^{ab} a^\dagger b^\dagger ji$. The indices $i, j, k, \dots$ ($a, b, c, \dots$) refer to occupied (unoccupied) spin-orbital levels and $a^\dagger$ and i are the creation and annihilation operators, respectively. The unknown CCSD amplitudes t_i^a and t_{ij}^{ab} are obtained by solving the non-linear CCSD equations

$$\langle \Phi_i^a | e^{-T} H e^T | \Phi \rangle = 0 \quad \forall i, a \quad (2)$$

$$\langle \Phi_{ij}^{ab} | e^{-T} H e^T | \Phi \rangle = 0 \quad \forall i, j, a, b \quad (3)$$

where $\langle \Phi_i^a |$ and $\langle \Phi_{ij}^{ab} |$ are singly and doubly excited determinants with respect to the reference determinant ($|\Phi_i^a\rangle = a^\dagger i|\Phi\rangle$ and $|\Phi_{ij}^{ab}\rangle = a^\dagger b^\dagger ji|\Phi\rangle$).

Once the cluster amplitudes are determined from the CCSD equations, the ground-state energy (E_0) can be obtained from the formula

$$E_0 = \langle \Phi | \bar{H} | \Phi \rangle, \quad (4)$$

where $\bar{H}$ is the similarity transformed Hamiltonian defined as $e^{-T} H e^T$.

The excitation operator $R(k)$ in the electron affinity equation of motion coupled clusters singles and doubles (EA-EOMCCSD) method [11] is defined in the following way

$$R(k) = R_1 + R_2 = \sum_a r_i^a(k) a^\dagger + \sum_{a<b} \sum_i r_{ij}^{ab}(k) a^\dagger b^\dagger i. \quad (5)$$

Similarly the $R(k)$ in ionization potential IP-EOMCCSD [10] can be written as,

$$R(k) = \sum_i r_i(k) i + \sum_a \sum_{i<j} r_{ij}^a(k) a^\dagger ji. \quad (6)$$

Inserting Eq. (1) in the non-relativistic Schrödinger equation and left multiplying by e^{-T} yields,

$$\bar{H} R(k) | \Phi \rangle = E_k R(k) | \Phi \rangle. \quad (7)$$

This equation can be recast as,

$$\bar{H}_N R(k) | \Phi \rangle = (E_k - E_0) R(k) | \Phi \rangle, \quad (8)$$

where $\bar{H}_N = \bar{H} - \langle \Phi | \bar{H} | \Phi \rangle$, $\bar{H}_N$ represents similarity transformed Hamiltonian in the normal product form. This allows us to write the above equation in matrix form as

$$\bar{\mathbf{H}}_N \mathbf{R}(\mathbf{k}) = \omega_{\mathbf{k}} \mathbf{R}(\mathbf{k}), \quad (9)$$

where $\omega_k = (E_k - E_0)$ is the energy associated with the EA or IP processes. Here, $\tilde{\mathbf{H}}_N$ is the matrix representation of the $\tilde{H}_N$ operator in the space spanned by excited state determinants generated by the excitation operator $R(k)$ when acting on the reference state. The above matrix equation can be efficiently solved using Davidson based methods [36] to obtain the IP (EA) amplitudes $r_i(k)$ and $r_{ij}^a(k)$ ($r^a(k)$ and $r_i^{ab}(k)$), respectively.

3. Computational Details

The molecular structures for the IP and EA studies for the polyacenes, naphthalene, anthracene, tetracene, pentacene, hexacene and heptacene are shown in Fig. 1. All the EA/IP-EOMCCSD studies were performed using Dunning's correlation consistent aug-cc-pVDZ, aug-cc-pVTZ [37] and Sadlej PVTZ (denoted hereafter by POL1) [38] spherical Gaussian basis sets employing NWChem [39] program package and D_{2h} point group symmetry. The linear polyacene geometries were optimized employing cc-pVTZ basis set and B3LYP level of theory obtained from previous studies. [16, 40] In this study restricted Hartree-Fock (RHF) orbitals were used as reference and the core electrons were excluded from the correlation treatment.

It is worth mentioning that these studies required large basis sets of TZ quality basis set to provide desired level of accuracy [4]. For example, pentacene molecule in aug-cc-pVTZ basis set contains approximately 1300 orbitals. Our implementation of EA/IP-EOM-CCSD is a strong scaling highly parallel method and by using 7040 cores the time to solution of iterative CC method was significantly reduced to 284 seconds per iteration.

4. Results and Discussion

The vertical electron affinities obtained for polyacenes using the EA-EOMCCSD method are summarized in Table 1. From the Table 1 results have the expected trend where starting with naphthalene the EA is negative and increases with increasing acene units where it is positive for all larger polyacenes. POL1 basis set produces correct trends but only qualitatively accurate results as compared with experiment. In addition, the POL1 basis produces slightly smaller EAs as compared to the aug-cc-pVDZ basis for all polyacenes where the differences equal -0.03 eV, -0.01 eV, -0.01 eV, -0.01 eV, -0.02 eV and -0.01 eV for naphthalene, anthracene, tetracene, pentacene, hexacene and heptacene, respectively. Employing a larger aug-cc-pVTZ basis set increases the EAs (with respect to the aug-cc-pVDZ results) by 0.11 eV, 0.15 eV, 0.15 eV and 0.15 eV for naphthalene, anthracene, tetracene and pentacene respectively.

The measurements of EAs for polyacenes have been a subject of intensive studies leading in several cases to inconsistent results. For example, the use of the electron capture detector (ECD) led to the following estimates of EA for naphthalene 0.148 ± 0.006 , [41] 0.134 ± 0.043 , [42] and 0.140 ± 0.050 [43] eV. In contrast, the lowest resonance in the electron transmission spectroscopy (ETS) was located at -0.19 ± 0.03 eV, [44] which was attributed to the adiabatic anionic state. This prediction was further supported by the negative-ion laser photo-electron spectroscopy.[45] Although for larger polyacenes the difference between various experimental predictions are less pronounced. In or-

der to compare theoretical vertical EA results with the experimental adiabatic results both adiabatic and zero-point vibrational energy corrections has to be included.

In Table 2 pseudo adiabatic electron affinity results obtained by including zero-point vibrational energy (Δ ZPE) and energetics associated with geometry relaxation corrections (or adiabatic energy corrections - Δ ADIAB) are shown. The Δ ZPE was computed by taking the ZPE differences between the neutral and anionic states at the B3LYP level of theory. Both Δ ZPE and geometry relaxation corrections (Δ ADIAB) were taken from studies done by Hajgató *et. al.* [46] (Tables XI and X). The addition of the B3LYP Δ ZPEs and Δ ADIABs corrections to the vertical electron affinities produces pseudo ADIAB EAs equal to -0.23 eV, 0.49 eV, 1.01 eV and 1.38 eV for naphthalene, anthracene, tetracene and pentacene respectively (see Table 2). For naphthalene the inclusion of these two effects leads to pseudo ADIAB EA that is in a very good agreement with the ETS value of -0.19 ± 0.03 eV. [44] For anthracene the pseudo adiabatic EA-EOMCCSD value of 0.49 eV is in a very good agreement with the ECD and with photodetachment photoelectron spectroscopy experimental values of 0.46 [47] and 0.53 ± 0.005 [48] eV, respectively. The pseudo adiabatic EA-EOMCCSD value (1.01 eV) for tetracene is in very good agreement with ion-molecule electron transfer equilibrium (1.063 ± 0.043 eV [49]) and photoelectron spectroscopy (1.058 ± 0.005 eV [50]) experiments. For pentacene, we have almost perfect agreement between pseudo adiabatic EA-EOMCCSD result (1.38 eV) and ion-molecule electron transfer equilibrium experiment (1.392 ± 0.043 eV [49]).

For completeness, we include a comparison of our EA-EOMCCSD simulations to Focal Point Analysis (FPA), FPA-QZ and FPA-5Z results of Hajgató, *et. al.* [46] (see again Table 1). The FPA-QZ results correspond -0.60 eV, 0.21 eV, 0.77 eV, 1.17 eV and 1.44 eV for naphthalene, anthracene, tetracene, pentacene, hexacene and heptacene, respectively (see Table 1). Similar results obtained with the FPA-5Z approach are -0.49 eV, 0.28 eV, 0.82 eV, 1.21 eV and 1.47 eV. The discrepancies between the FPA-5Z and EA-EOMCCSD in aug-cc-pVTZ basis are 0.03 eV, 0.04 eV, 0.02 eV and 0.01 eV for naphthalene, anthracene, tetracene and pentacene respectively. Employing the smaller aug-cc-pVDZ basis for hexacene produces a deviation of 0.11 eV from the FPA-5Z result. In analogy to the EA results, increasing the basis set size improves the FPA results.

The ionization potential results obtained for linear polyacenes using IP-EOMCCSD method is given in Table 3 and Fig. 2, which shows errors, with respect to the experimentally inferred data, for the first three IP-EOMCCSD ionization potentials obtained using aug-cc-pVTZ basis set. From Table 3 one can notice that for naphthalene by increasing the correlated-consistent basis set size from aug-cc-pVDZ to aug-cc-pVTZ IP increased by 0.13 eV to 8.19 eV, which deviates only by 0.04 eV as compared to the experimental value of 8.15 eV. The ionization potential obtained for naphthalene for A_u symmetry is 8.04 eV, 8.06 eV and 8.19 eV in POL1, aug-cc-pVDZ, and aug-cc-pVTZ basis sets, respectively. Using the aug-cc-pVTZ basis set IPs are closer to experimental results for all polyacenes. The deviation from experiments is -0.04 eV, 0.05 eV, 0.15 eV, and 0.22 eV for naphthalene, anthracene, tetracene and pentacene respectively. Similar to the EA results, increasing the basis set quality and size from POL1 to aug-cc-pVTZ systematically improves the IP results as compared to experiment that in addition, are in very good agreement with experiment. The errors shown in Fig.2 suggest that in order to reduce discrepancies between experimental and

IP-EOMCCSD first ionization potentials one may go beyond aug-cc-pVTZ basis set quality. The IP and EA obtained from IP/EA-EOMCCSD in aug-cc-pVTZ basis set is summarized in Figure 3.

There are no experimental results for heptacene but to allow for comparison with future experimental studies an IP value of 5.89 eV was obtained using aug-cc-pVDZ basis set. Comparing to the trends of the other polyacenes in this study it can be hypothesized that by going to larger basis sets will lead to increase in IP values for the three lowest ionization potentials.

It is also instructive to compare ionization potentials calculated with the IP-EOMCC with the ionization energies obtained as direct differences between CCSD singlet state energies of neutral systems and doublet state energies obtained with the CCSD and EE-EOMCCSD methods for ionized systems. In a similar way, doublet excitation energies calculated for the ionized species can also be studied.

The results of this study are shown in Table 4 (comparison of ionization potentials) and Table 6 (comparison of doublet excitation energies). In all cases considered in Tables 4 and 5 (naphthalene, anthracene, and tetracene molecules) the IP obtained as a difference between CCSD (singlet state) and CCSD/EOMCCSD (doublet states) energies (EE-EOMCCSD) are in a good agreement with the ionization potentials obtained with the IP-EOMCCSD approach. It is worth mentioning that the IP-EOMCCSD formulation is numerically more efficient than the EE-EOMCCSD approach. The effectiveness of the IP-EOMCCSD approach in calculating doublet excitation energies of cations is shown in Table 4. Again, the IP-EOMCCSD excitation energies are in qualitative agreement with the EE-EOMCCSD results obtained using doublet reference function. In order to estimate the effect of triple excitations for doublet excited states the completely renormalized equation of motion coupled cluster method with singles, doubles and noniterative triples correction, CR-EOMCCSD(T) method [51] was employed. The IP-EOMCCSD/EE-EOMCCSD excitation energies were consistently 0.2-0.4 eV above the CR-EOMCCSD(T) results, which is a good motivation for developing non-iterative IP-EOMCC corrections accounting for the effect of triple excitations. As in the IP-EOMCCSD vs EE-EOMCCSD case the (T) type correction for the IP-EOMCCSD approach is cheaper than the analogous CR-EOMCCSD(T) correction.

5. Conclusions

In this manuscript we have calculated the vertical EA and IP in naphthalene, anthracene, tetracene, pentacene, hexacene and heptacene employing our recently developed EA/IP-EOMCCSD parallel implementation. [4] We have compared our results with the available computational studies and experimental results. Highly efficient implementation of the EA/IP-EOMCCSD formalisms enabled calculations with large aug-cc-pVTZ basis set, which for the pentacene molecule contains over 1300 basis functions.

As in the case of all calculations using approximate CC methods, there are two main sources of errors: (1) the quality of basis set and (2) the level of excitation level used to define given CC approximation. A good agreement of the pseudo-adiabatic EAs in aug-cc-pVTZ basis set with the experimental values may indicate that for relatively large

basis sets the effect of missing correlations related to the excitations not included in the EA-EOMCCSD formalism (i.e., triples, quadruples, etc.) is rather small for systems considered here. In particular, for the challenging case of the naphthalene molecule we found that the pseudo-adiabatic EA-EOMCCSD/aug-cc-pVTZ prediction is in perfect agreement with the location of lowest resonance in the electron transmission spectroscopy experiment. We have also demonstrated that the IP-EOMCCSD results obtained with the aug-cc-pVTZ are in very good agreement with the experimental results. The use of smaller aug-cc-pVDZ and POL1 basis sets leads to less accurate IPs compared to experimental values. However, it is interesting to notice that energy separations between states in N-1 particle spaces seems to be less sensitive to the basis set choice.

We have also demonstrated that the numerically more efficient IP-EOMCCSD formalism is capable of providing the EOMCCSD quality of excitation energies for doublet states of ionized systems considered in this manuscript. This letter also shows that despite the relatively high computational cost of these methods it is now possible due to successful parallelization can be applied to chemically interesting systems at coupled cluster quality of theory where correlation plays an important role.

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Table 1: The vertical electron affinity (in eV) for polyacenes (N=2-7) using EA-EOMCCSD. All core electrons were excluded from the correlation treatment. In brackets the symmetry labels of electronic states are given. The FPA-QZ and FPA-5Z results were taken from Ref. [46].

Polyacene	EA-EOMCCSD/Basis	(eV)	Other studies	(eV)
Naphthalene	aug-cc-pVDZ	-0.63(A_g)	FPA-QZ	-0.60
	POL1	-0.66(A_g)	FPA-5Z	-0.49
	aug-cc-pVTZ	-0.52(A_g)		
Anthracene	aug-cc-pVDZ	0.09(B_{1u})	FPZ-QZ	0.21
	POL1	0.08(B_{1u})	FPA-5Z	0.28
	aug-cc-pVTZ	0.24(B_{1u})		
Tetracene	aug-cc-pVDZ	0.65(B_{3g})	FPZ-QZ	0.77
	POL1	0.64(B_{3g})	FPA-5Z	0.82
	aug-cc-pVTZ	0.80(B_{3g})		
Pentacene	aug-cc-pVDZ	1.05(B_{1u})	FPA-QZ	1.17
	POL1	1.04(B_{1u})	FPA-5Z	1.21
	aug-cc-pVTZ	1.20(B_{1u})		
Hexacene	aug-cc-pVDZ	1.36(B_{3g})	FPA-QZ	1.44
	POL1	1.34(B_{3g})	FPA-5Z	1.47
Heptacene	aug-cc-pVDZ	1.59(B_{1u})		
	POL1	1.58(B_{1u})		

Table 2: Comparison of (pseudo) adiabatic electron affinity with experimentally available adiabatic electron affinity results. The Δ ZPE and Δ ADIAB, refers to zero-point vibrational energies and geometry relaxation corrections taken from Ref.[46]. All results are reported in eV. Vertical electron affinities (EAs) were obtained with the aug-cc-pVTZ basis set.

Polyacene	EA	Δ ZPE ^[46]	Δ ADIAB ^[46]	Pseudo ADIAB EA	Expt.
Naphthalene	-0.52	0.160	0.131	-0.23	0.148±0.006 [41], 0.134±0.043 [42] 0.140±0.05 [43], -0.19±0.03 [44]
Anthracene	0.24	0.144	0.102	0.49	0.46 [47], 0.556±0.008 [41] 0.66±0.08 [52], 0.530±0.005 [48]
Tetracene	0.80	0.127	0.082	1.01	0.88±0.04 [53], 1.063±0.043 [49] 1.058±0.005 [50]
Pentacene	1.20	0.115	0.067	1.38	1.392±0.043 [49]

Table 3: The vertical ionization potential (in eV) for polyacenes (N=2-7) using the IP-EOMCCSD approach. The experimental results (^a) are taken from references [54]. All core electrons were kept frozen in the CC calculations. In brackets the symmetry labels of electronic states are given.

Polyacene	Basis	Vertical IP (eV)	Vertical IP (eV)	Vertical IP (eV)
Naphthalene	aug-cc-pVDZ	8.06(<i>A_u</i>)	8.71(<i>B_{1u}</i>)	10.09(<i>B_{2g}</i>)
	POL1	8.04(<i>A_u</i>)	8.69(<i>B_{1u}</i>)	10.08(<i>B_{2g}</i>)
	aug-cc-pVTZ	8.19(<i>A_u</i>)	8.84(<i>B_{1u}</i>)	10.22(<i>B_{2g}</i>)
	Expt. ^a	8.15(<i>A_u</i>)	8.88(<i>B_{1u}</i>)	10.08(<i>B_{2g}</i>)
Anthracene	aug-cc-pVDZ	7.28(<i>B_{2g}</i>)	8.41(<i>B_{3g}</i>)	9.23(<i>A_u</i>)
	POL1	7.27(<i>B_{2g}</i>)	8.39(<i>B_{3g}</i>)	9.21(<i>A_u</i>)
	aug-cc-pVTZ	7.42(<i>B_{2g}</i>)	8.55(<i>B_{3g}</i>)	9.36(<i>A_u</i>)
	Expt. ^a	7.47(<i>B_{2g}</i>)	8.57(<i>B_{3g}</i>)	9.23(<i>A_u</i>)
Tetracene	aug-cc-pVDZ	6.76(<i>A_u</i>)	8.23(<i>B_{1u}</i>)	8.51(<i>B_{2g}</i>)
	POL1	6.75(<i>A_u</i>)	8.21(<i>B_{1u}</i>)	8.49(<i>B_{2g}</i>)
	aug-cc-pVTZ	6.89(<i>A_u</i>)	8.36(<i>B_{1u}</i>)	8.64(<i>B_{2g}</i>)
	Expt. ^a	7.04(<i>A_u</i>)	8.44(<i>B_{1u}</i>)	8.63(<i>B_{2g}</i>)
Pentacene	aug-cc-pVDZ	6.38(<i>B_{2g}</i>)	7.94(<i>A_u</i>)	8.10(<i>B_{3g}</i>)
	POL1	6.37(<i>B_{2g}</i>)	7.93(<i>A_u</i>)	8.08(<i>B_{3g}</i>)
	aug-cc-pVTZ	6.52(<i>B_{2g}</i>)	8.08(<i>A_u</i>)	8.24(<i>B_{3g}</i>)
	Expt. ^a	6.74(<i>B_{2g}</i>)	8.03(<i>A_u</i>)	8.40(<i>B_{3g}</i>)
Hexacene	aug-cc-pVDZ	6.11(<i>A_u</i>)	7.50(<i>B_{2g}</i>)	8.02(<i>B_{1u}</i>)
	POL1	6.09(<i>A_u</i>)	7.48(<i>B_{2g}</i>)	7.99(<i>B_{1u}</i>)
	Expt. ^a	6.44(<i>A_u</i>)	7.55(<i>B_{2g}</i>)	8.14(<i>B_{1u}</i>)
Heptacene	aug-cc-pVDZ	5.89(<i>B_{2g}</i>)	7.14(<i>A_u</i>)	7.95(<i>B_{3g}</i>)
	POL1	5.88(<i>B_{2g}</i>)	7.13(<i>A_u</i>)	7.93(<i>B_{3g}</i>)

Table 4: Comparison between the vertical ionization potential (in eV) for polyacenes (N=2-7) obtained using IP-EOMCCSD and CCSD/EE-EOMCCSD. All core electrons were excluded from the CC calculations. For the sake of brevity, acronyms ADZ and ATZ refer to the aug-cc-pVDZ and aug-cc-pVTZ basis sets, respectively. The CCSD IP is obtained as the difference of CCSD energies of polyacene and its cation. While the other two EE-EOMCCSD energies are obtained by adding the vertical excitation energies to the CCSD energy difference. In all the three systems investigated the first IP is almost the same in aug-cc-pVTZ basis set obtained in both approaches.

N	CCSD	IP-EOM	EE-EOM	IP-EOM	EE-EOM	IP-EOM
Basis						
N=2						
ADZ	8.12(A_u)	8.06(A_u)	8.12+0.72=8.84(B_{1u})	8.71(B_{1u})	8.12+1.95=10.07(B_{2g})	10.09(B_{2g})
ATZ	8.20(A_u)	8.19(A_u)	8.20+0.73=8.93(B_{1u})	8.84(B_{1u})	8.20+1.94=10.14(B_{2g})	10.22(B_{2g})
N=3						
ADZ	7.35(B_{2g})	7.28(B_{2g})	7.35+1.22=8.57(B_{3g})	8.41(B_{3g})	7.35+1.89=9.24 (A_u)	9.23 (A_u)
ATZ	7.42(B_{2g})	7.42(B_{2g})	7.42+1.22=8.64(B_{3g})	8.55(B_{3g})	7.42+1.88=9.30 (A_u)	9.36 (A_u)
N=4						
ADZ	6.82(A_u)	6.76(A_u)	6.82+1.57=8.39(B_{1u})	8.23(B_{1u})	6.82+1.69=8.51 (B_{2g})	8.51 (B_{2g})
ATZ	6.89(A_u)	6.89(A_u)	6.89+1.57=8.46(B_{1u})	8.36(B_{1u})	6.89+1.69=8.58 (B_{2g})	8.64 (B_{2g})

Table 5: Difference in vertical ionization potentials (in eV) for polyacenes (N=2-7) obtained using IP-EOMCCSD, EE-EOMCCSD and CR-EOMCCSD(T). All core electrons were excluded from the correlation treatment. The ADZ and ATZ acronyms refer to the aug-cc-pVDZ and aug-cc-pVTZ basis sets, respectively.

Polyacene	Method	Basis	IP1-IP2	IP1-IP3
Naphthalene	EE-EOMCCSD	ADZ	$0.72(A_u-B_{1u})$	$1.95(A_u-B_{2g})$
	CR-EOMCCSD(T)	ADZ	$0.41(A_u-B_{1u})$	$1.63(A_u-B_{2g})$
	IP-EOMCCSD	ADZ	$0.65(A_u-B_{1u})$	$2.04(A_u-B_{2g})$
	EE-EOMCCSD	ATZ	$0.73(A_u-B_{1u})$	$1.94(A_u-B_{2g})$
	CR-EOMCCSD(T)	ATZ	$0.37(A_u-B_{1u})$	$1.57(A_u-B_{2g})$
	IP-EOMCCSD	ATZ	$0.65(A_u-B_{1u})$	$2.03(A_u-B_{2g})$
Anthracene	EE-EOMCCSD	ADZ	$1.22(B_{2g}-B_{3g})$	$1.89(B_{2g}-A_u)$
	CR-EOMCCSD(T)	ADZ	$0.91(B_{2g}-B_{3g})$	$1.56(B_{2g}-A_u)$
	IP-EOMCCSD	ADZ	$1.13(B_{2g}-B_{3g})$	$1.94(B_{2g}-A_u)$
	EE-EOMCCSD	ATZ	$1.22(B_{2g}-B_{3g})$	$1.88(B_{2g}-A_u)$
	CR-EOMCCSD(T)	ATZ	$0.87(B_{2g}-B_{3g})$	$1.52(B_{2g}-A_u)$
	IP-EOMCCSD	ATZ	$1.13(B_{2g}-B_{3g})$	$1.94(B_{2g}-A_u)$
Tetracene	EE-EOMCCSD	ADZ	$1.57(A_u-B_{1u})$	$1.69(A_u-B_{2g})$
	CR-EOMCCSD(T)	ADZ	$1.27(A_u-B_{1u})$	$1.38(A_u-B_{2g})$
	IP-EOMCCSD	ADZ	$1.47(A_u-B_{1u})$	$1.75(A_u-B_{2g})$
	EE-EOMCCSD	ATZ	$1.57(A_u-B_{1u})$	$1.69(A_u-B_{2g})$
	CR-EOMCCSD(T)	ATZ	$1.23(A_u-B_{1u})$	$1.34(A_u-B_{2g})$
	IP-EOMCCSD	ATZ	$1.47(A_u-B_{1u})$	$1.75(A_u-B_{2g})$

Figure 1: Geometries of polyacenes considered in the present studies.

Figure 2: Errors (in eV) of the first three ionization potentials obtained with the IP-EOMCCSD approach using aug-cc-pVTZ (all core electrons were kept frozen in the course of calculations) with respect to experimental data (see text for details).

Figure 3: The IP and EA obtained from IP/EA-EOMCCSD in aug-cc-pVTZ basis set is shown below.

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