Theoretical spectral properties of PAHs: towards a detailed model of their photophysics in the ISM

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Abstract. In the framework of density functional theory (DFT) we computed the spectral properties of a total of about 20 polycyclic aromatic hydrocarbons (PAHs) in different charge states. From our complete atlas of PAHs, ranging in size from naphthalene ($C_{10}H_8$) to dicoronylene ($C_{48}H_{20}$), we present here a sample of results concerning both ground–state and excited–state properties. Our theoretical results are in reasonable agreement with the available experimental data. This makes them particularly precious when the latter are not easily obtainable, as is often the case for the highly reactive radicals and ions of such species. In another paper (Mulas et al., same volume) we show that our theoretical results can be reliably used to model the behaviour of these molecules in astrophysical environments.

1. Introduction
Free gas–phase polycyclic aromatic hydrocarbons (PAHs) in different charge and hydrogenation states are commonly thought to be an important component of the interstellar medium [1]. Such molecules have been hypothesized to absorb in the Vis/UV spectral range, producing at least a subset of the diffuse interstellar bands [2, 3] and contributing to the interstellar extinction curve [4], and to efficiently convert the absorbed energy in IR emission in the so–called unidentifed infrared bands [5].

Large PAHs are an intermediate stage between the gas and dust phases of the interstellar matter and they are included in some form in all interstellar dust models [6]. However, despite intensive searches and some promising candidates, no single interstellar PAH has been identified unambiguously to date. In our ongoing effort to produce detailed simulations of the photophysics of *specific* PAHs [7], we are building a database of molecular properties obtained in a uniform way using available quantum–chemical techniques [8, 9], and using them as a basis to run Monte–Carlo models of their behaviour [10, 11].

The most relevant molecular parameters needed to model the photophysics of interstellar PAHs are: a) electron affinities and ionization energies; b) structural parameters and vibrational analysis; c) photo–absorption cross–sections up to the Lyman limit. The set of PAHs for which *all* of these data are simultaneously available is small. We studied a first sample of about 20 different PAHs covering an ample range of structures [8, 9]. Although non–compact PAHs are expected to be less stable than compact ones with the same number of benzenoid rings, we extended our study to non–compact species and radicals. While some studies predict interstellar

PAHs to be on average larger than these species, we began with PAHs containing less than ~ 50 carbon atoms, since computational costs steeply increase for larger species.

In Sect. 2 we describe our computational approach and compare some of our data with available experimental results. In Sect. 3 we discuss their implications in the astrophysical context. Our conclusions are presented in Sect. 4.

2. Computational approach and results

2.1. Ground–state properties

Several works showed that the Density Functional Theory (DFT) [12] can be successfully used to obtain electronic ground–state properties of PAHs. Following well–established theoretical prescriptions [13] we used the hybrid exchange–correlation functional B3LYP and the 4–31G Gaussian basis set as implemented in the NWCHEM computer code [14]. Although basis–set convergence is not expected at this level, this approach is known to provide accurate results for vibrational frequencies, after appropriately scaling them by an empirical factor.

To calculate electron affinities and ionization energies, the use of larger basis sets to expand the molecular orbitals is needed. This is particularly true for anions, which require the inclusion of diffuse functions. Dessent showed the B3LYP/6–31+G* level of theory to yield quite an accurate result for anthracene ($C_{14}H_{10}$) [15]. We extended this same approach to a large sample of PAHs [9]. As shown in Table 1, our results are in good agreement with the available experimental data as well as with previous theoretical calculations. Table 1 lists both the adiabatic and the zero–point energy (ZPE)–corrected electron affinities. We calculated the ZPE corrections in the plain harmonic approximation, without scaling, since appropriate scaling factors for the anions are uncertain [15].

2.2. Excited–state properties

Starting from the optimised ground–state geometries, we used the Time–Dependent DFT [23] to obtain the photo–absorption cross–section of each PAH, in different charge states [8, 9]. Given the lack of quantitative laboratory experiments on the VUV photo–absorption properties of PAHs up to the energy range excitable in the ISM, the use of theoretical quantum–chemistry appears to be the next best alternative [11]. TD–DFT calculations were shown to be a powerful tool to calculate electronic excitation properties for neutral PAHs [24] as well as radical ions up to large species [25, 26]. These calculations were performed using frequency–space implementations of TD–DFT, for which computational costs scale steeply with the number of required transitions, and were limited to the low–energy part of the spectrum. We used the real–time real–space implementation of TD–DFT in the OCTOPUS code [27]. As shown in Fig. 1 from [8], our results are in good agreement with available experimental data [4]. Concerning the low–lying $\pi \to \pi^\star$ transitions occurring in the near–IR, visible and near–UV spectral ranges, Table 2 shows OCTOPUS to yield as accurate results as previously published theoretical ones, compared to available experimental data. Computed vertical excitation energies are precise to within a few tenths of an eV, which is indeed the typical accuracy of TD–DFT [25]. The main drawback of this approach is that one does not obtain independent information for each excited state, such as the symmetry and description of the excited states, but only the direction of its transition dipole moment. Technical details can be found in [8, 9].

3. Discussion

Concerning the calulations of electron affinities, the values obitained lie in the range 0.4–2.0 eV, showing the molecules under study to be able to accept an additional electron in their lowest unoccupied molecular orbital (LUMO). These values can be used for astrophysical modelling purposes, such as in approximate formulae for the ionisation equilibrium of PAHs in interstellar environments (see e. g. [28]).

Table 1. Calculated electron affinities (in eV) of ten PAH in our sample. For comparison, previous theoretical results and available experimental measurements are also listed.

PAH molecule	This work adiabatic	This work ZPE–corrected	Published theoretical adiabatic	Published theoretical ZPE–corrected	Published experimental
Azulene ($C_{10}H_8$)	0.63	0.75[a]/0.72[b]	—	—	0.7900 ± 0.0080 [c]
$C_{13}H_9$ radical	1.25	1.33[a]/1.35[b]	1.29[d]	1.36[d]	1.07 ± 0.10 [e]
Anthracene ($C_{14}H_{10}$)	0.53	0.66[a]/0.64[b]	0.58[d]	0.72[d]	0.5300 ± 0.0050[f]
Tetracene ($C_{18}H_{12}$)	1.08	1.19[a]	1.13[d]	1.24[d]	1.067 ± 0.043[g]
$C_{19}H_{11}$ radical	1.55	1.62[a]	—	—	—
Perylene ($C_{20}H_{12}$)	0.96	1.08[a]	—	—	0.9730 ± 0.0050[h]
Pentacene ($C_{22}H_{14}$)	1.48	1.58[a]	—	—	1.392 ± 0.043[g]
Coronene ($C_{24}H_{12}$)	0.47	0.49[a]	—	—	0.470 ± 0.090[i]
Terrylene ($C_{30}H_{16}$)	1.55	1.66[a]	—	—	—
Quaterrylene ($C_{40}H_{20}$)	1.91	2.00[a]	—	—	—
Dicoronylene ($C_{48}H_{20}$)	1.50	1.60[a]	—	—	—

[a] B3LYP/4–31G value in this work.
[b] B3LYP/6–31+G* value in this work.
[c] Photodetachment photoelectron spectroscopy [16].
[d] B3LYP/DZP++ value from [17].
[e] Laser threshold detachment [18].
[f] Photodetachment photoelectron spectroscopy [19].
[g] Estimated from ion–molecule reaction equilibria [20].
[h] Photodetachment photoelectron spectroscopy [21].
[i] Photodetachment photoelectron spectroscopy [22].

With respect to the excited–state properties caluations, the spectral range covering the near–IR, visible and near–UV, it is obvious that with more than 300 DIBs in this window the accuracy of about 0.3 eV achieved by current TD–DFT methods on the position of the bands cannot be used alone for a firm spectral identification. Still, theoretical spectra in this range are an useful tool both to guide future experiments [26] and to interpret laboratory spectra as they become available [29]. Since there is already an ample literature about low–energy transitions of neutral and cationic PAHs (see e. g. [30, 3]), a thorough description of the low–lying spectral transitions is beyond the scope of this paper.

We henceforth concentrate our discussion on the UV range since our most important new results are the electronic absorption properties of small to medium–sized PAHs in this spectral domain. In the past, several authors noted that if neutral PAHs were to be responsible for the AIBs, their UV spectroscopic signatures ought to be detectable on the interstellar extinction curve (see e. g. the discussion in [31]). This was not taken as a serious drawback of the PAH hypothesis, since PAHs were expected to be mostly ionised in the diffuse ISM and their cations were assumed to have no sharp features in the near–UV [32]. Several works [33, 26] subsequently cast some doubt on the general validity of the above assumption. Our results further show that any singly charged PAH ions *generally* appear to display almost as strong near–UV bands as their parent neutrals and, therefore, ought to be just as detectable if they were to account for
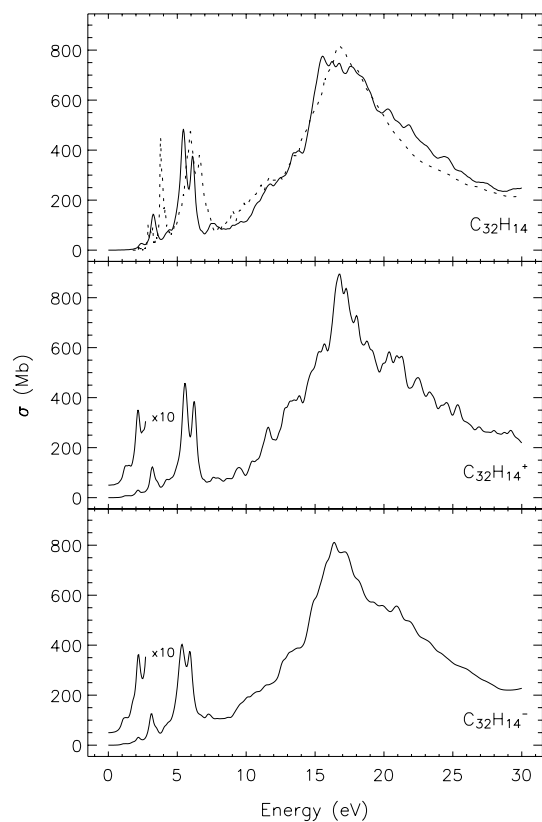
Figure 1. Comparison between the the computed photoabsorption cross–sections of ovalene ($C_{32}H_{14}$) in neutral (top panel), cationic (middle panel) and anionic (bottom panel) charge states. The top panel also shows the comparison between the calculated (solid line) and experimental (dotted line, from [4]) gas–phase absorption spectra.
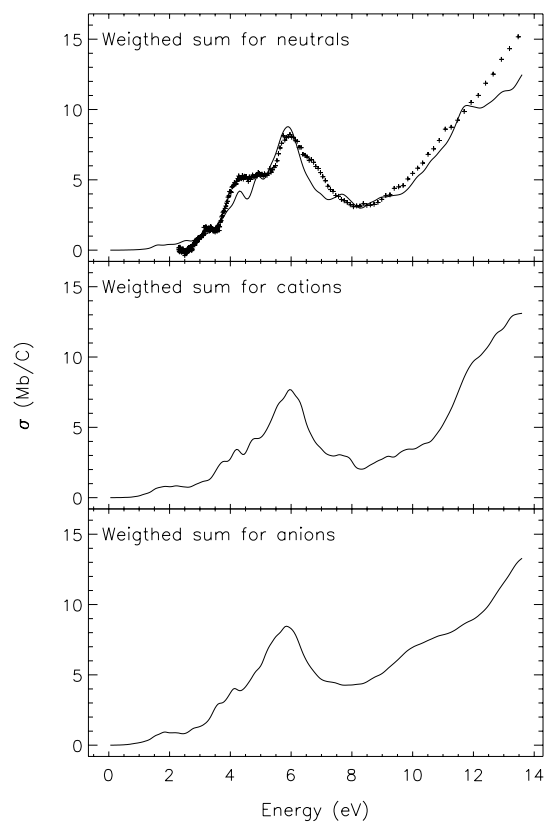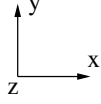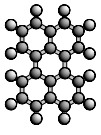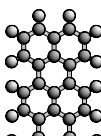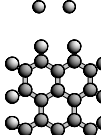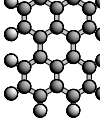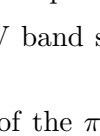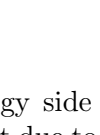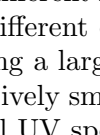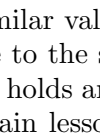
Figure 2. Comparison between the weighted sum of our computed spectra for both PAH neutrals (top panel), the corresponding cations (middle) and anions (bottom). Statistical weights are assumed to be proportional to the inverse of the total number of carbon atoms N_C of each molecule. In the upper panel we also reproduce (crosses) the experimental result obtained by [4] for a natural mixture of neutral PAHs with average $N_C = 24$, very close to our sample of molecules.

AIBs. On the other hand, it is known that PAH mixtures might not exhibit sharp features in the near–UV because their bands would blend in a broad peak contributing to the well–known extinction bump at 2175 Å and to the far–UV rise [4].

To address this point, we performed a weighted sum of the single spectra we computed, assuming statistical weights to be simply inversely proportional to the total number of carbon atoms N_C of each molecule, i. e. we just made a straight average of the cross–sections normalized per carbon atom. Figure 2 displays the overall expected spectra for our mixture of 20 different neutral, cationic and anionic PAHs. An inspection of the upper panel, corresponding to neutrals, shows that, despite the relatively small number of different species considered, together with the simplistic assumption of statistical weights of the form $1/N_C$, our results agree surprisingly well with the general trend observed for a natural mixture of PAHs and derivatives with $N_C = 24$

Table 2. Singlet $\pi^\star \rightarrow \pi$ excitations of a subset of PAHs in our sample. Excitation energies (in eV) and oscillator strengths (in parentheses) are compared to published experimental and TD–DFT results. The direction of the transition dipole for each band is given according to the molecular geometries sketched.

Dipole orientation	This work	Published theoretical	Published experimental	
	Perylene cation ($C_{20}H_{12}^+$)			
x	1.89(0.034)	1.92(0.029)[a]	/	
y	2.38(0.326)	2.44(0.348)[a]	2.36(/)[a]	
	Perylene anion ($C_{20}H_{12}^-$)			
x	1.66 (0.035)	1.64 (0.035)[a]	—	
y	2.32 (0.381)	2.26 (0.333)[a]	2.23 (/)[a]	
	Terrylene cation ($C_{30}H_{16}^+$)			
x	1.82 (0.019)	1.83 (0.014)[a]	/	
y	1.88 (0.667)	1.93 (0.706)[a]	1.80(/)[a]	
	Terrylene anion ($C_{30}H_{16}^-$)			
x	1.61 (0.035)	1.59 (0.029)[a]	—	
y	1.79 (0.665)	1.76 (0.605)[a]	1.67 (/)[a]	
	Quaterrylene cation ($C_{40}H_{20}^+$)			
y	1.58 (1.044)	1.62 (1.028)[a]	1.48(/)[a]	
x	1.79 (0.021)	1.81 (0.018)[a]	/	
	Quaterrylene anion ($C_{40}H_{20}^-$)			
y	1.51 (1.074)	1.50 (0.972)[a]	1.41 (/)[a]	
x	1.52 (0.029)	1.56 (0.025)[a]	—	

[a] TD–DFT calculations (BLYP/6–31G*) and Neon matrix isolation spectroscopy data [29].

[4]. The effect of coadding single spectra is to wash out near–UV band structures and, at the same time, to produce two distinct features:

- a collective broad absorption peak, resulting from the sum of the $\pi^\star \rightarrow \pi$ transitions, at 6 eV, which ought to contribute to the short–wavelength side (about 207 nm) of the UV extinction bump, and
- a smooth far–UV rise.

The coadding leaves some discernible structure on the low–energy side of the main peak, in particular two peaks which appear at 4.2 and 4.8 eV. They are not due to a single molecule, but instead to a casual near coincidence of relatively strong bands in different molecules. A different sample of molecules would display similar near coincidences at different energies, therefore we expect such structure to be more and more washed out considering a larger and larger sample, and conversely to be only visible in a sample dominated by a relatively small number of species.

There is to date no available experimental study on the overall UV spectrum of mixtures of PAH ions; however, the good agreement we obtained for neutrals between the weighted sum of our synthetic spectra and the data from [4] leads us to infer a similar validity for the weighted sum of synthetic spectra of cations and anions. As expected, due to the similarity of their UV spectra to those of their parent neutrals, the discussion above still holds and can be transported unchanged to ions. From the astrophysical point of view, the main lesson to be learned from Fig. 2 seems to be that if *any* PAHs of small to medium size, be they neutral or ionised, are to

account for the far–UV rise of the interstellar extinction curve they *must* also contribute to the short–wavelength side of the extinction bump at 2175 Å.

4. Conclusions

Detailed information about ground and excited–state properties of PAHs enable one to model in a quantitative way the overall photophysics and ionisation balance of *specific* PAHs in many interstellar environments. The individual data we have obtained for an increasingly large sample of PAHs will enable the astrophysical community to significantly improve on such models.

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