

Vacuum-ultraviolet photoionization of a grandPAH molecule

The interplay of alkyl groups and large polycyclic aromatic hydrocarbons upon photoionization

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ABSTRACT

Context. So-called grandPAH molecules are proposed to be omnipresent in various interstellar regions as they are large enough to be photostable against strong interstellar radiation fields. They are also notoriously difficult to synthesize and sublime. Measuring their gas phase spectra and molecular properties is thus very difficult.

Aims. We report on the experimental photoionization of a defined grandPAH cation ($C_{60}H_{18}(C_{12}H_{25})_4$ m/z 1415 amu). The molecule consists of a large PAH containing 60 sp^2 carbon atoms and four long alkyl groups ($-C_{12}H_{25}$) attached to peripheral positions. The alkyl chains wrap around the aromatic core and stabilize the cation leading to a lowering of the ionization energy.

Methods. The ion yield spectrum of the grandPAH was recorded from 8.1 to 25 eV using an ion trap coupled to vacuum-ultraviolet (VUV) synchrotron radiation. To accurately extrapolate the experimental results toward the unsubstituted grandPAH itself, we perform a series of calculations to quantify this lowering of the ionization energy.

Results. The adiabatic ionization energy of the grandPAH cation was determined as 8.50 ± 0.35 eV. This dual experimental and theoretical methodology can be used to perform other spectroscopic measurements of large, alkylated PAHs to extract properties of the unsubstituted PAH. The implications of these results are discussed in the context of the behavior of large PAHs in interstellar and/or interplanetary dust particles as well as PAH units embedded in insoluble organic material which are found in meteorites.

Key words. astrochemistry – molecular data – molecular processes – methods: laboratory: molecular

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) have attracted interest in astronomy and astrophysics since the 1980s when it was discovered that the infrared emission signatures of composites of soot matched well with those recorded in the Orion nebula (Allamandola et al. 1985; Puget & Leger 1989; Allamandola et al. 1989). Numerous reviews and books are dedicated to their astronomical significance (Tielens 2008, 2013, 2026; Joblin & Tielens 2020; Hrodmarsson et al. 2025a). Later, the term grand-PAH entered the scientific lexicon to describe a group of large PAHs capable of surviving harsh radiation fields in space. Only a few dozen IR spectra of PAHs are required to accurately replicate the IR emission bands observed in such regions (Andrews et al. 2015). These grandPAHs were considered to be fairly large containing 50–70 carbon atoms, but recent experiments have suggested that typical sizes in the NGC 7023 photon-dominated region (PDR) are actually closer to 40–55 (Lemmens et al. 2023). Recently, PAH species as large as containing up to 100 fused aromatic rings are identified in samples from the Ryugu asteroid using atomic force microscopy (Iwata et al. 2026).

Even larger grandPAHs are proposed to be responsible for parts of the IR emission bands from active galactic nuclei (AGN) and other galaxies at high redshift (Cortzen et al. 2019; Rigopoulou et al. 2021; Garcia-Bernete et al. 2022; Kerkeni et al. 2022). In order to compare observations with spectra of PAHs containing more than 50 carbon atoms, theoretical calculations are utilized. Experimental measurements of such colossal PAHs are scarce in the gas phase and have rarely been successfully performed because of their low vapor pressure and propensity to polymerize upon heating (Lewis 1980; Sánchez-Sánchez et al. 2019; Kim et al. 2022). Infrared (IR) spectra of PAHs are known to be sensitive to the PAH size (Peeters et al. 2021) as well as its charged state (Bakes et al. 2001b), but so far, only theoretically calculated IR spectra of large PAHs have been cataloged and made available to the widespread astrophysical and astrochemical communities through the NASA Ames PAH database (Boersma et al. 2014; Bauschlicher et al. 2018).

It is also well known that photoelectric heating due to the photoionization of PAHs by ultraviolet (UV) photons is expected to account for a large fraction of the heating of neutral gas in galaxies (Berné et al. 2022; Hrodmarsson et al. 2025b). Photoelectric heating of PAHs is also used to estimate star formation rates in galaxies (McKinney et al. 2021; Zhang & Ho 2023).

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Furthermore, for large values of the ionization parameter, PAH dications are predicted to become more abundant than PAH monocations in photon-dominated regions such as NGC 7023, protoplanetary disks, high-redshift galaxies, and ultra-luminous infrared galaxies (Berné et al. 2022).

Doubly ionized PAHs are theorized to be an important component of the ISM, in part, due to (i) the relatively large photoionization cross sections of PAH monocations (Leach 1986) and (ii) the overall low ionization energy (IE) of large PAHs. This makes the second ionization energies accessible in the vacuum-ultraviolet (VUV) range (below 200 nm) where the photon flux from the interstellar radiation field is still rather large. Hence, sequential single photon ionization is efficient and competitive with neutralization by stray electrons and/or anions (Berné et al. 2022). Theoretical calculations have since been employed to compute their UV spectra and overall photostability (Mallocci et al. 2007) along with their vibrational signatures (Bakes et al. 2001a,b). In recent years, some vibrational spectra of PAH dications have been measured (Banhatti et al. 2021).

Dications of PAHs may also prompt exotic chemistry in the ISM due to their inherent stability and due to the fact that dications can efficiently transfer charge onto a neutral collision partner (Böhme 2011). For instance, fullerene cations can catalyze reactions like cyanoacetylene forming ionized cyanocyclobutadiene (Milburn et al. 1999).

Evidence of PAHs have also been found on the floor of the Jezero crater, an ancient delta-lake system on Mars (Fornaro et al. 2025). It was suggested that they were formed through endogenous igneous organic processes and preserved by sulfate (SO_4^{2-}) precipitation, implying their presence in their dicationic form.

It is worth noting that astronomical PAHs contain aliphatic substituents (Yang et al. 2017a,b) and PAHs with aliphatic side chains are suggested as important components of interstellar dust (Dartois et al. 2005). Alkylated PAHs are of significant interest in astrochemistry in general since methylated forms of pyrene and fluoranthene are detected in various asteroid samples (Sabbah et al. 2024; Naraoka et al. 2023; Aponte et al. 2023).

For very large PAHs, few experimental measurements on isolated gas phase monomers are currently known. The synthesis and isolation of large PAHs are very demanding although significant advancements have been reported in the past decade (Simpson et al. 2002; Narita et al. 2015; Li et al. 2016; Xu et al. 2020). Experimental techniques capable of measuring the properties of such large PAHs or other less polar or non-polar species such as fullerenes have been developed such as atmospheric pressure chemical photoionization (APCI) (Palotás et al. 2019, 2021) or atmospheric pressure photoionization (APPI) sources (Kaupila et al. 2017).

APCI methods are useful when samples come in very small amounts and possess low ionization efficiency or low solubility. In cases of PAHs, however, APCIs tend to produce protonated species which are difficult or even impossible to detangle from the cationic species. APPI sources, however, are appropriate when the molecule under investigation is easily solvated. An appealing way of chemically modifying PAHs meant for such experiments relies on attaching alkyl chains to the PAH. The solubilization effect of long alkyl groups comes from an increased entropy and the suppression of aggregation whereby the alkyl groups wrap the aromatic core. Chlorination of PAHs also leads to a similar suppression, but rests upon ring puckering due to steric hindrance between chloro substituents (Tan et al. 2013).

Here, we consider a structurally defined alkylated grandPAH (Figure 1), previously referred to as a soluble C_{60} graphene

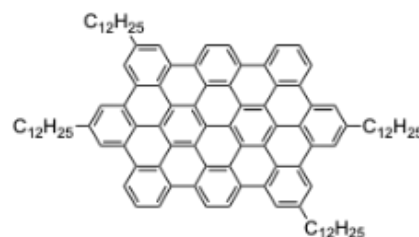


Fig. 1. Chemical structure of the grandPAH molecule investigated. Chemical formula: $\text{C}_{60}\text{H}_{18}(\text{C}_{12}\text{H}_{25})_4$, nominal mass = 1415 amu.

segment (Iyer et al. 1998), which serves as a benchmark for measurements of the single photon ionization energy of very large PAH cations. The interstellar PAH family is dominated by compact PAHs with long straight edges with few corners whose C:H ratios are likely larger than 2.5 (Tielens 2026), i.e., similar to the C_{60} graphene segment. To extract the ionization energy of the unsubstituted grandPAH we performed theoretical calculations that quantify the effects of the alkyl groups on ionization energy of the gas phase grandPAH. In parallel, a second set of calculations has been performed which highlights the most appropriate calculations of the first and second photoionization energies (Giuliani & Hrodmarsson 2026).

2. Methods

2.1. Experimental

Measurements were performed at the DESIRS beamline of the Synchrotron SOLEIL facility in St. Aubin, France (Nahon et al. 2012). PAH cations were produced with an APPI source (Kaupila et al. 2017) and collected in a Thermo Scientific™ LTQ XLTM linear ion trap (Milosavljević et al. 2012). Subsequently, they were irradiated with VUV synchrotron light. This source has been employed previously to measure the VUV photoabsorption and photoionization of smaller PAH cations (Zhen et al. 2015; Wenzel et al. 2020; Joblin et al. 2020). The grandPAH used in this work was prepared following a reported procedure (Iyer et al. 1998; Yao et al. 2019). ortho-Dichlorobenzene (o-DCB) served as solvent for the grandPAH in a concentration of 10^{-6} mol/L. The solution was then injected into the instrument via a syringe with a flow rate of 10 $\mu\text{L}/\text{min}$. UV radiation from a Kr lamp was used to provide a soft ionization palate for the grandPAH (Giuliani et al. 2012).

Three sets of measurements were performed covering different energy ranges, namely 8–16 eV, 15–21 eV, and 20–25 eV where the first two were measured with 0.2 eV step sizes, and the last one in 0.5 eV energy steps. A gas filter filled with Ar was employed to suppress higher harmonics from the undulator by several orders of magnitude up to 16 eV (Marcouille 2007). Above 16 eV, the transmission of higher harmonics by the higher (>1) orders of the monochromator’s grating was considered negligible. The photon flux was measured with an IRD AXUV100 calibrated Si photodiode to normalize the ion yields. Experimental errors on the average mass spectra are obtained by taking the standard error of the sample mean. We estimate an experimental error of 15% on the flux measurement. First-order linear error propagation is used to obtain the final error on the spectra.

2.2. Theoretical

SCC-DFTB3 calculations were carried out with DFTB+(v23.1) (Hourahine et al. 2020) using an electronic temperature of 300 K to improve self-consistent charge convergence. DFT-D4 corrections non-additive triple-dipole contributions

(Caldeweyher et al. 2019), were added to the DFTB3 calculation using the following parameters: Dispersion = DFTD4 $s_6 = 1.0$ $s_8 = 0.6635015$ $s_9 = 1.0$ $a_1 = 0.5523240$ $a_2 = 4.3537076$. The version 3.0.2 of CREST (Grimme 2019; Pracht et al. 2020, 2024) was used. XTB-GFN2 (Bannwarth et al. 2019) calculations were carried out with the xTB (Bannwarth et al. 2020) code version 6.6.1. All the DFT calculations were performed based on the 6.1.0 version of ORCA (Neese 2003; Neese et al. 2020; Neese 2023, 2025). The composite R2SCAN-3c method was chosen owing to its demonstrated capability to treat non-covalent interactions. The computational resources provided by the GRADES group at SOLEIL were accessed through the DARTS framework (Farhi 2023). The Extended Transition State with Natural Orbitals for Chemical Valence (ETS-NOCV/EDA-NOCV) feature of ORCA has been applied (Sabando et al. 2025) to compute the effect of alkyl substitution on a PAH core, labeled as segment 1 and segment 2, respectively. The multiplicity of the alkyl moiety question was set to $M=2$ with spin flip and that of the PAH segment was adjusted to match the multiplicity of the system. All the calculations were performed with the TightSCF keyword. Molecular structures, molecular orbitals and electron densities were plotted with ChimeraX version 1.8 (2024-06-10) (Goddard et al. 2018; Pettersen et al. 2021; Meng et al. 2023), which was also used to calculate and display the density differences (see Appendices A & B).

3. GrandPAH conformers

For the grandPAH molecule (Figure 1), the flexible dodecyl alkyl chains can adopt multiple conformers that influence the electron densities of the PAH skeleton. Alkanes absorb on graphene (Kamiya & Okada 2013; Liu et al. 2019; Kartashynska 2024) and it is known that alkyl arms interact with the aromatic core and fold over it via CH- π interactions. Prior to presenting the experimental results we, first, quantify the ionization energy decrease of the PAH which is caused by the alkyl substitution.

Conformers were sampled from four different ensemble structures, or aggregates, which were separated by how the conformers either fold all arms on one side (4-0), three arms on one side and one on the other (3-1) or two arms on each side (2-2). The 2-2 aggregates were further split into 2-2a and 2-2b where the alkyl groups on one side fold on the opposite or same face, respectively.

CREST analysis (Grimme 2019; Pracht et al. 2020, 2024) for each of the conformers was performed using the non-covalent interaction mode (-nci option). The atoms of the aromatic core were kept fixed to reduce computation time. The resulting aggregates which were used to calculate the averaged properties of the grandPAH were then optimized without constraints at the GFN2-xTB level. The most stable conformations of the different aggregates are presented in Figure 2.

The optimized aggregates were then concatenated into a single trajectory which was subsequently submitted to a CREGEN ensemble sorting. At the xTB-GFN2 level, the most stable conformers are all 2-2a (Table A.1). The difference between 2-2a and 2-2b is further illustrated in Figure 3. 2-2a and 2-2b conformers amount to 87% and 6.9% of the population at room temperature and correspond to structures 1-24 and 26-57 in Table A.1. In 2-2a, all the alkyl chains adopt a parallel (flat-on) orientation on the aromatic core in agreement with previous work (Kartashynska 2024). In 2-2b, one of the alkyl chains is oriented in a perpendicular (edge-on) manner on the core.

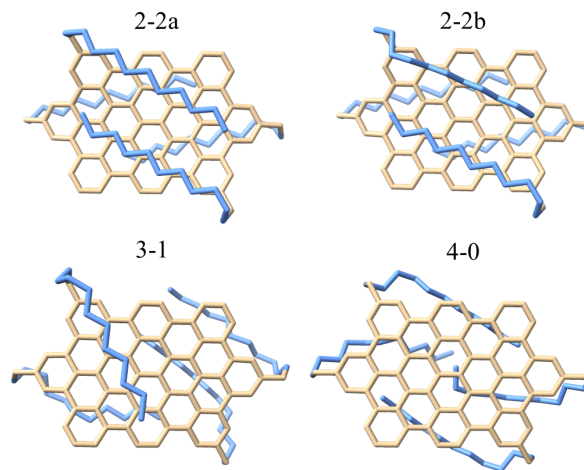


Fig. 2. Most stable conformations of each of the four aggregates of the grandPAH. Alkyl chains are shown in blue.

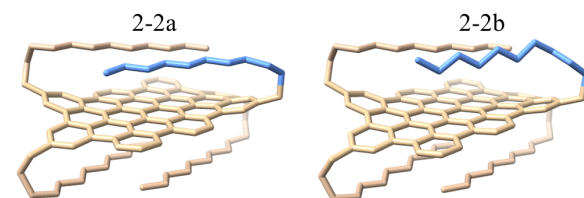


Fig. 3. Representation of the structural difference between the 2-2a and 2-2b aggregates of the grandPAH.

4. Experimental and computed ionization energies

Figure 4 presents the accumulated mass spectra recorded between 8 and 25 eV of the grandPAH. Because of the large number of carbon atoms, the most intense peak in the mass spectrum does not belong to the 1415 amu isotope, but to that of 1416 amu. Above m/z 1417, no ions were retained in the ion trap to simplify the data treatment. The dication signals for the three principal isotopologues were observed at m/z 707.5, 708, and 708.5.

A minor peak is observed at m/z 1414 (and m/z 707 for the dication), signifying H loss. As the signal intensity of the H loss scales relative to the parent in both the singly and doubly ionized masses, we can assume that the H-loss was collision induced in the ion trap, rather than due to the ionization of the molecule by the Kr lamp.

To identify the second ionization threshold, a Wannier type threshold law (Wannier 1953) was used to fit the experimental data. The fitting function we used is the following:

$$if E \leq AE, Y = b, \quad (1)$$

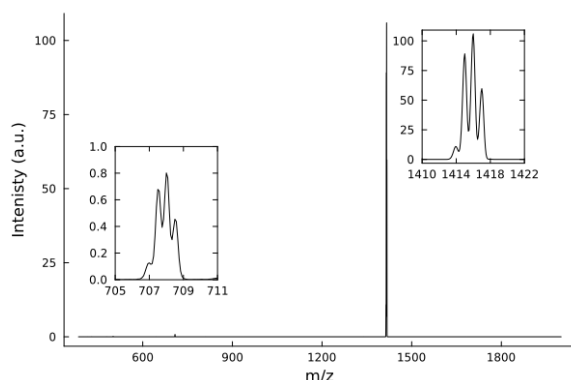
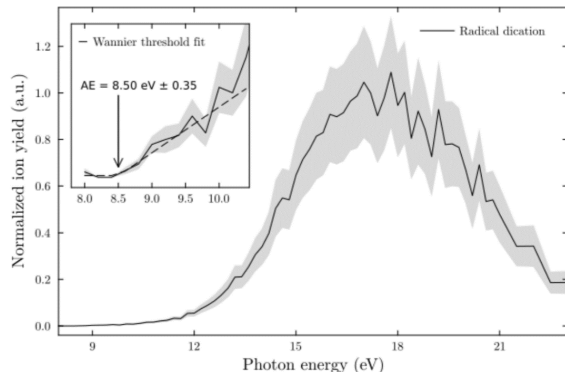
$$if E > AE, Y = b + a(E - AE)^c, \quad (2)$$

where Y stands for the experimentally measured cross section and AE is the appearance energy. Figure 5 presents the dication yield with the second ionization onset magnified where $E = AE$. This allows one to determine the ionization energy as 8.50 ± 0.35 eV (as obtained by the standard error of the least square fit). The ion yield also displays a plasmon resonance typical of PAHs around 17 eV (Bull et al. 2023; Roy Chowdhury et al. 2024; Hrodmarsson et al. 2025b).

Based on recent computational benchmarking of the most appropriate methods to calculate the first and second ionization energies of PAHs (Giuliani & Hrodmarsson 2026),

Table 1. Theoretical adiabatic IEs (in eV) of the main conformations of the grandPAH as well as of the PAH core and experimental second IE energy.

Species	Conformer	Method	IE ₁	IE ₂	IE _d
grandPAH		Experiment		8.50 ± 0.35	
grandPAH	2-2a	DFTB3/D4	6.34	8.67	15.01
		R2SCAN-3C	5.92	8.28	14.19
	2-2b	DFTB3/D4	6.35	8.69	15.03
		R2SCAN-3C	5.89	8.31	14.19
	3-1	DFTB3/D4	6.34	8.67	15.01
		R2SCAN-3C	5.90	8.27	14.17
PAH core	4-0	DFTB3/D4	6.35	8.70	15.05
		R2SCAN-3C	5.88	8.26	14.14
	0-0	DFTB3/D4	6.55	9.12	15.67
		R2SCAN-3C	6.08	8.71	14.80

**Fig. 4.** Integrated mass spectra of the grandPAH recorded by irradiating with photons from 8 to 25 eV.**Fig. 5.** Dication yield as a function of photon energy, along with a zoom of the dication signal onset. The shaded area indicates the signal uncertainty.

calculations at the DFTB3 level of theory with D4-dispersion correction were chosen¹. The ionization energies were also calculated using the R2SCAN-3C method. This method is efficient in treating non-covalent interactions and has offered excellent results in the calculations of the second ionization energy.

The ionization energies were calculated using DFTB3-D4 and R2SCAN-3c. The results are presented in Table 1. For the 2-2a and 2-2b conformations, the calculated ionization energies agree within 10 meV with DFTB3/D4 and 30 meV with R2SCAN-3C. The second ionization energies agree with the experimental value within the experimental accuracy. However, the conformations cannot be distinguished by their ionization energy values.

¹ These benchmarking calculations should not be confused with the experimental benchmarking described in this paper.

The ionization energies of the unsubstituted grandPAH have also been calculated. Attaching the alkyl arms to the PAH core changes the first ionization energy from 6.55 eV for the core to 6.34 eV for the 2-2 conformer, i.e., by 210 meV at the DFTB3-D4 level. The second ionization energy is lowered by 450 meV from 9.12 eV for the unsubstituted PAH core, to 8.67 eV for the most stable one.

5. Effects of alkyl chains on the electronic structure and ionization energies

To quantify the lowering of the ionization energies of the unsubstituted PAH, the gradual derivatization of the core with increasing number of alkyl substituents is considered. Thus, the vertical ionization energies of the singly (core-(C₁₂H₂₅)), doubly (core-(C₁₂H₂₅)₂) and triply alkylated (C₁₂H₂₅)₃) conformers in addition to the most stable 2-2a conformer (C₁₂H₂₅)₄) were calculated. The doubly alkylated ensemble structures were found in a 2-0 aggregate and the triply alkylated in 2-1. The R2SCAN-3C method results are presented in Table 2. Here, the alkyl chains are sitting flat on the PAH. The ΔE columns give the change in ionization energies upon addition of a supplementary alkyl chain. It should be noted that the values in Table 2 correspond to vertical ionization energies, rather than adiabatic ionization energies in Table 1. We stress that the differences between the values are small which indicates the geometry does not significantly change upon ionization.

The attachment of a single chain to the PAH core reduces the first ionization energy by 60 meV. This is a modest change which appears to saturate with increasing number of substituted alkyl chains. Attaching a second chain folded on the same side of the plane, reduces the first ionization energy by an additional 50 meV, and attaching a third and fourth results in a reduction of 30 meV. These figures are in agreement with the magnitude of CH- π interaction, which is of the order of 1 kcal/mol (43 meV) (Tsuzuki & Fujii 2008).

The successive alkyl-substitution produces larger effects on the second ionization energy. The first alkyl chain lowers IE by 150 meV and the second, third, and fourth by 110 meV, 100 meV and 80 meV, respectively. The double ionization energies disclose an even higher impact of the derivatization ranging from 210 meV for the first substitution to 110 meV for the fourth one, exactly equaling the combined differences from the first and second ionization energies.

In parallel, the highest occupied molecular orbital (HOMO) of the neutral molecules and the singly occupied molecular orbital (SOMO) of the cations are also provided along with their energies in Figure A.1. As expected, the HOMO and the SOMO appear almost identical as they only involve the PAH moiety and

Table 2. Theoretical vertical ionization energies (in eV) for the gradual derivatization of the PAH core with 1, 2, 3 and 4 alkyl chains, using the R2SCAN-3C method.

Species	IE ₁		IE ₂		IE _d	
	ΔE		ΔE		ΔE	
PAH core	6.11		8.75		14.93	
Core-C ₁₂ H ₂₅	6.05	-0.06	8.60	-0.15	14.72	-0.21
Core-(C ₁₂ H ₂₅) ₂	6.01	-0.05	8.49	-0.11	14.57	-0.15
Core-(C ₁₂ H ₂₅) ₃	5.98	-0.03	8.39	-0.10	14.45	-0.14
grandPAH	5.95	-0.03	8.31	-0.08	14.34	-0.11

do not delocalize to the alkyl chains. The electron density differences ($\Delta\rho$) for the first ionization ($\rho_{cation}-\rho_{neutral}$), the second ionization ($\rho_{dication}-\rho_{cation}$) and the double ionization ($\rho_{dication}-\rho_{neutral}$) are also presented in Figure A.2. There, the density of the final state is calculated at the geometry of the initial state, i.e., we assume vertical ionization. As expected, all the different $\Delta\rho$ values indicate that the density is lost on the aromatic PAH core and involves π orbitals. A small reorganization of the density is observed in the plane along C-H and C-C bonds. The electron density differences clearly document the stabilization of the cations by the shift of electron density from the alkyl arm to the aromatic PAH core.

Some deeper insights can be gained through an Extended Transition State – Energy Decomposition Analysis (ETS/EDA). The results of this analysis is presented in Appendix B.

6. Discussion

Apart from the collision-induced H-loss, no obvious fragmentation patterns of the parent molecule or the dication could be discerned in the mass spectra. Efficient internal vibrational relaxation appears absolutely plausible in view of the nature of the grandPAH (Stockett et al. 2019a,b). The same goes for recurrent fluorescence which is known as an efficient cooling mechanisms in PAHs like perylene (Stockett et al. 2020) and especially 1-cyanonaphthalene (Navarro Navarrete et al. 2023; Stockett et al. 2023). The tendency of increasing ionization vs fragmentation yields with increasing molecular size has already been observed in smaller PAH cations (Wenzel et al. 2020; Zhen et al. 2016, 2015). This can be rationalized by the greater number of vibrational degrees of freedom which efficiently dissipate the excess energy and prevent fragmentation to the benefit of photoionization whose quantum yield reaches unity.

These measurements demonstrate that the APPI technique can be used on samples of alkylated large PAHs to obtain ionization energies of the unsubstituted PAHs. This is quite unprecedented as previously, gas phase experiments on large PAHs are prohibited by their low vapor pressures and tendencies to polymerize when heated to high temperatures (Lewis 1980; Sánchez-Sánchez et al. 2019; Kim et al. 2022). The APPI source thus offers an attractive method to measure the physical and chemical properties of large isolated PAHs in the gas phase.

However, the alkylation of the large PAH is no mere ‘sand-box’ activity. There is also a strong astrobiological relevance to large, alkylated PAHs, in addition to models of the ionization properties of very large PAHs relevant to the diffuse ISM. Below we will discuss the results in the context of models of photoelectric heating due to PAHs in the ISM, large PAHs in meteorites, and their astrobiological role in the quest for the origin of life.

6.1. Ionization of large PAHs in the interstellar medium

Regarding the contribution of PAHs to the photoelectric heating of the ISM, we compare our results with the modeling work of

Table 3. Comparisons of the numerical values for the adiabatic ionization energies of neutral PAHs and cationic PAHs⁺ in eV derived from the models of BT.

	Disk	Sphere	This work
PAH ($N_C = 60$)	6.02	5.82	6.08 (PAH) 5.95 (grandPAH)
PAH ($N_C = 108$)	5.61	5.57	
PAH ⁺ ($N_C = 60$)	9.26	8.65	8.50 $\pm$ 0.35 8.71 (PAH ⁺) 8.31 (grandPAH ⁺)
PAH ⁺ ($N_C = 108$)	8.02	7.90	

Bakes & Tielens (1994) (BT) which has been extensively used for the ionization properties of PAHs containing up to 96 carbon atoms (Andrews et al. 2016). They provide ionization energies of both flat graphite sheets and spherical carbons like fullerenes. This can be revealing since the grandPAH used in this work in a way reflects a flat sheet covered by alkylated arms, acquiring some 3D character ultimately resembling a small nanoparticle. Simultaneously, our theoretical work reveals the ionization energies of the unsubstituted PAH. Thus, we can compare our results with those of BT both in terms of a disk (PAH) and a sphere (functionalized PAH). The results of the first and second ionization energies from BT are shown in Table 3.

BT adopted a work function for an infinite graphite sheet of 4.4 eV which was used to model the ionization energies of carbon disks and spheres as a function of the number of carbon atoms. The ionization energies of their neutral PAHs from the disk model for 60 and 108 carbon atoms are ca. 0.5 eV smaller than those predicted by Bourgalais et al. (2023) and both of the sphere and disk models overestimate the value computed for the grandPAH in the present work. Their values for the ionization energies of a 60 carbon atom sphere (5.82 eV and 8.65 eV, respectively) were also around 1.8 eV below the true values for the C₆₀ fullerene, namely 7.60 eV (Hrodmarsson et al. 2024) and 10.5 eV (Douix et al. 2017), respectively.

For the first ionization energies BT predict a decrease of 0.20 eV from a disk to a sphere for 60 carbon atoms. This corresponds to a much smaller decrease in the first ionization energy from the aromatic PAH to the folded grandPAH (pseudo-sphere), or 13 meV. In BT, this difference reduces to 0.04 eV for 108 carbon atoms. The experimentally derived second ionization energy of the grandPAH and our calculated values agree slightly better with that predicted by the $N_C = 60$ sphere of BT. However, the computationally derived ionization energy of the PAH cation (8.71 eV) does not match that predicted for the $N_C = 60$ disk. The $N_C = 108$ predictions are not comparable with the present calculations and experiment neither. It is thus evident that the present results cannot be replicated by the BT model used to describe the photoelectric heating associated with small interstellar carbon grains whose size is approximately that of a single large PAH.

6.2. PAHs in astrobiology and the origins of life

Before discussing the incorporation of PAHs into meteorites, one should note that PAH formation is observed during the processing of interstellar C_2H_2 ice analogs. Such experiments mimic conditions within envelopes of evolved stars (C-rich AGB stars) and to some extent diffuse and translucent clouds. An important distinction between the diffuse and translucent cloud stage, however, is that in translucent clouds H-atom addition reactions start to dominate over UV irradiation which can make saturated alkane chains but not hydrogenate already formed PAHs. In this veil, C_2H_2 ices irradiated by UV photons exhibit the formation of PAHs branched by unsaturated carbon chains (Samarth et al. 2026). These organic residues form very early on during the irradiation process and remain qualitatively unchanged upon further UV exposure, indicating a significantly decreased propensity to dissociate upon UV processing with increasing size. Moreover, if the irradiated C_2H_2 ice is subsequently exposed to H atoms, various saturated hydrocarbons are observed (Fedoseev et al. 2025). This suggests that the grandPAH molecule studied here could be formed in the translucent cloud stage to be eventually incorporated into meteorites during the early formation of the Solar System.

PAHs are, namely, exceedingly abundant in meteorites and recently PAHs containing upward of 100 aromatic rings are detected in the Ryugu asteroid (Iwata et al. 2026). In addition, there are striking similarities in the aliphatic C–H stretch IR spectra originating from the diffuse ISM dust and insoluble organic material (IOM) (Ehrenfreund et al. 1992). IOM in carbonaceous chondrites often comprises individual PAH units interlinked with other functional groups, such as alkyl chains. Following this point, it is well established that chondritic IOM shares some fundamental physico-chemical properties with so-called allomelanin-type materials (d’Ischia et al. 2021).

Melanins are natural pigments found in most organisms comprising monomers and/or polymers of functionalized PAHs. Their production appears to be a universal and enigmatic form of adaption of living organisms to terrestrial conditions. They are found in almost every known large taxon suggesting an evolutionary importance of melanogenesis (d’Ischia et al. 2021). Non-nitrogenated melanins are typically found in the lowest evolutionary levels of organisms such as fungi and bacteria and are believed to be the closest to their prebiotic precursors. These are broadly classified as allomelanins.

There are multiple chemical and physical properties that are common to this class of molecules which are all associated with the unusual chemical complexity at the level of the conjugated π system. Examples include a dark or black color due to broad and featureless UV/Vis absorption spectra (Manini et al. 2020), an intrinsic paramagnetic character that is responsible for broad and stable EPR signals (d’Ischia et al. 2020), semiconductor type conductivity (Pezzella et al. 2015), efficient non-radiative excited state deactivation, and a strong binding of metals. As such, these conjugated π system properties are also shared by PAHs. The occurrence of allomelanins in several bacteria and fungi that appeared on Earth before plants and higher organisms are thus indicative of diverse biological roles their precursors played in astrobiology (Meredith & Sarna 2006; Gessler et al. 2014). These include protection from harsh UV radiation, free electron scavengers, heavy metals, oxidative stress, and an overall contribution to their survival in adverse environments (Pavan et al. 2020).

This work has quantified how sequential alkylation of large PAHs influences its conjugated π system. This leads to

a lowering of the ionization energies further explicating the exact physico-chemical processes by which biomolecules in the nascent Solar System (and in the protosolar nebula from which the Solar System formed) could be protected from destructive radiation. Upon ionization, the electron density is solely lost from the aromatic π system which is followed by a smaller redistribution of the electron density in the plane along C–H and C–C bonds. Collectively, these effects document the stabilization of the cations by slightly drawing electron densities from the alkyl groups and protecting them from dissociation. Hence, the formation of stable alkyl-PAH moieties following dust formation during the translucent molecular cloud stage could act as a local stabilizing or protecting formation site for other prebiotic molecules (d’Ischia et al. 2021).

7. Conclusions

In this work we have performed the first experimental photoionization measurements of an isolated grandPAH molecule. The molecule consists of a large aromatic PAH core with 60 carbon atoms with four large alkyl ($C_{12}H_{25}$) groups attached which make the molecule soluble in organic solvents and render it suitable for atmospheric pressure ionization techniques.

Accompanying the experimental results are a series of calculations on the first, second, and double ionization energies of its multiple conformers. The calculation results matched the experimental ones within a 100 meV margin, which equals the accuracy of the method. The computed range for the second ionization energy agrees well with the experimental value of 8.50 ± 0.35 eV. The calculated first ionization energies of the aromatic PAH core are higher than those obtained for the conformers of the grandPAH molecule by 170 meV. The systematic decrease in ionization energies with increasing alkane chain attachment demonstrates the impact of CH- π interactions, which involve hydrogen atoms from the alkyl groups and the π electron system of the PAH complex.

It is found that alkyl substitution primarily lowers the ionization energies of the PAH both through ground state electron donation and final state stabilization of the charged species. Hence, the dominant mechanism is a reduction of steric repulsion between the PAH π system and the alkyl σ framework upon ionization, complemented by inductive polarization of the alkyl chains. This effect becomes increasingly important for higher charge states.

Overall, it appears that using the APPI technique can be used to perform gas phase measurements on large PAH molecules. The calculations quantify the sequential lowering of the ionization energies by the attached alkyl groups. Hence, this methodology can be expanded to other large, alkylated PAHs to obtain the ionization energies of the unfunctionalized PAH. Thus, it has the capacity to provide better experimental constraints to the ionization energies of large PAHs in ISM models.

This work also contributes directly to our understanding of PAHs in astrobiology and origins of life research. The results reflect a key element in describing the presence of PAHs in different environments and how they interact with their nearest molecular environments, whether in diffuse gaseous media or on dust grain surfaces in space or in our terrestrial environment. This effect is similar to the one expected of PAH moieties in IOM and allomelanins. There they can act as a protective binding site against harsh irradiation for other prebiotic molecules in their nearest vicinity.

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Appendix A: CREST analysis

Here, in Table A.1 we show the numerical results of the CREST analysis of the conformers of the grandPAH molecule. These are further visualized by showing the HOMO and the SOMO of the cations as well as the electron density differences between the neutral, cation, and dication in Figures A.1 and A.2.

Appendix B: Extended transition state – energy decomposition analysis

Some deeper insights can be gained through an Extended Transition State – Energy Decomposition Analysis (ETS/EDA). Although it was originally developed to analyze chemical bonding by decomposing the interaction energy between predefined moieties, its formal structure allows an analysis of electronic state changes. This differential ETS/EDA approach provides an interpretation of how each single alkyl substitution modulates ionization energies by quantifying how steric repulsion, orbital polarization, and dispersion change upon electron removal. In this way, ETS/EDA serves as a state-to-state energy partitioning tool, offering mechanistic insight into substituent effects on ionization energies beyond a simple total-energy comparison.

In the ETS/EDA framework the interaction energy is decomposed into the following components

$$\Delta E_{int} = \Delta E_{orb} + \Delta E_{elstat} + \Delta E_{Pauli} + \Delta E_{disp}. \quad (B.1)$$

Here, ΔE_{orb} represents the stabilizing orbital interaction due to polarization, charge transfer, donor–acceptor interactions or changes in covalent mixing. ΔE_{elstat} is the Coulomb electrostatic interactions between the charge density of the static moieties. ΔE_{disp} stands for the variation in dispersion correction upon the interaction. Finally, ΔE_{Pauli} is the combined Pauli repulsion and the exchange-correlation contributions, namely, $\Delta E_{Pauli} = \Delta \tilde{E}_{Pauli} + \Delta E^0(XC)$. This combined quantity is more physically

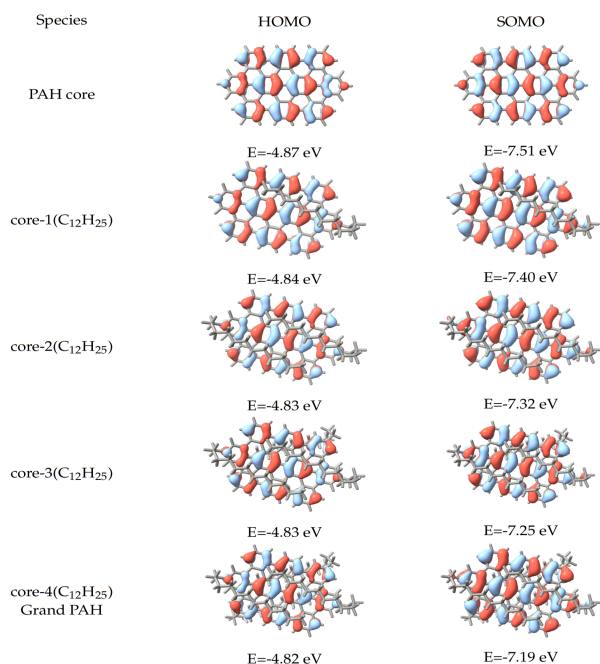


Fig. A.1: Main HOMOs of the neutral and SOMO of the cation for the gradual derivatization of the PAH core.

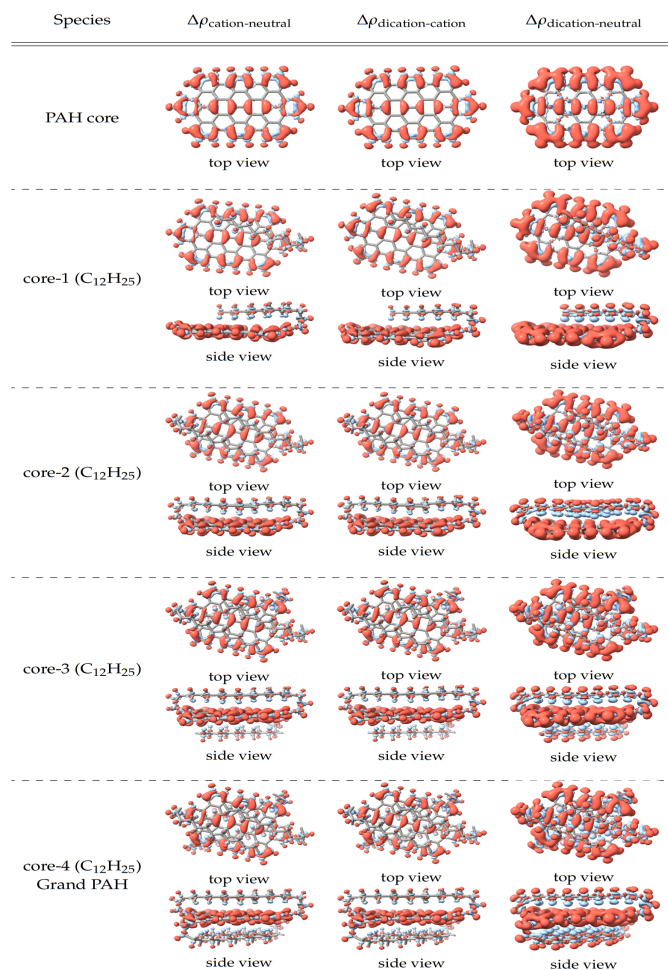


Fig. A.2: Density differences for the PAH core and the gradual alkyl substitutions corresponding to the first ($\Delta\rho_{cation-neutral}$), second ($\Delta\rho_{dication-cation}$), and double ionizations ($\Delta\rho_{dication-neutral}$). Isosurface plotted at $5 \times 10^{-4} e/a_0^3$.

meaningful and less sensitive to the choice of the functional than individual terms (Sabando et al. 2025; Mitoraj et al. 2009). ΔE_{Pauli} and ΔE_{elstat} have been combined into ΔE_{steric} following (Ziegler & Rauk 1979a,b) to provide a simple chemical interpretation. Generally, ΔE_{steric} expresses interaction between two moieties.

The ETS/EDA terms have been computed in ORCA (Sabando et al. 2025) for the neutral molecule and for the radical cation at the geometry of the neutral. Similar calculations have been made for the second ionization between the cation and the dication at the cation geometry and for the double ionization energy through the comparison of the neutral and the dication and the neutral geometry. The results are presented in Table B.1.

The magnitude of the stabilization increases with the charge of the PAH. As an example, in the singly substituted molecule the interaction energy change is 0.086 eV upon first ionization, 0.206 eV upon second ionization, and 0.304 eV for the double ionization process. These figures are consistent with the experimental observations. The attachment of a single (C₁₂H₂₅) chain lowers the first ionization energy by 60 meV, the second IE by 150 meV and the double IE by 210 meV (as seen in Table 2). This compares well with the -86 meV, -206 meV and -304 meV changes in interaction energy. This trend is preserved across

the series and mirrors the progressively larger lowering of the second and double ionization energies compared to the first.

Across all substituted molecules and charge increments, the largest stabilizing contributions arise from the reduction of the orbital energy and the steric repulsion. When the π -electron density is reduced upon ionization, the overlap with the σ -electron density of the alkyl chains is also reduced. Therefore, upon ionization, both $\Delta E_{\text{orbital}}$ and ΔE_{steric} decrease by for the first ionization (31–86 meV) and by a comparable value for the second ionization. The higher value obtained for the dication explains why the double ionization energy is more strongly affected by alkyl substitution than the first and second ionization energies.

The orbital interaction term provides a consistent additional stabilization upon ionization (0.04–0.05 eV for IE_1 and up to 0.17 eV for IE_2). This contribution reflects inductive polarization of the alkyl σ framework in response to the positively charged PAH core rather than explicit charge transfer. Notably, the orbital contribution scales with the charge state of the PAH but exhibits only weak dependence upon the number of alkyl chains. This suggests that once polarization channels are established, additional chains contribute only marginally. Furthermore, it supports a picture dominated by non-covalent induction rather than electron donation. In contrast, the electrostatic term becomes less favorable upon ionization, contributing positively to ΔE . This destabilizing effect partially compensates the Pauli and orbital stabilization. Such behavior is typical for static electrostatic interactions which do not account for density relaxation and must therefore be interpreted in conjunction with the orbital term. The dispersion contribution is negligible in all cases and does not change appreciably upon ionization confirming that dispersion does not play a significant role in the observed ionization-energy shifts.

In summary, the ETS/EDA results quantitatively rationalize the trends observed for the vertical ionization energies. The modest reduction of IE_1 (0.03–0.06 eV) arises from a balance between the molecule and inductive stabilization on the one hand, and unfavorable electrostatics on the other.

Table A.1: Lowest energy conformers from CREST analysis along with the structure conformations.

Conform.		E_{rel} (kcal)	$E_{\text{tot}} (E_h)$ xTB-GFN2	$E_{\text{tot}} (E_h)$ R2SCAN-3C
1	2-2a	0	-292.03440	-113907.89
2	2-2a	1.503	-292.03201	
3	2-2a	2.309	-292.03072	
4	2-2a	2.380	-292.03061	
5	2-2a	2.587	-292.03028	
6	2-2a	3.035	-292.02957	
7	2-2a	3.051	-292.02954	
8	2-2a	3.734	-292.02845	
9	2-2a	3.790	-292.02836	
10	2-2a	4.209	-292.02770	
...	...	...	...	
25	4-0	9.449	-292.01935	-113907.51
26	2-2b	9.599	-292.01911	-113907.49
27	2-2b	9.646	-292.01903	
28	2-2b	9.866	-292.01868	
29	2-2b	9.969	-292.01852	
30	2-2b	10.126	-292.01827	
...	...	...	...	
58	3-1	11.661	-292.01582	-113906.96
59	3-1	11.666	-292.01581	
...	...	...	...	

Table B.1: Comparison of the variation of ETS/EDA between the vertical first, second, and double ionizations. All energies are in eV.

Species	Energy terms	$\Delta E_{\text{cat-ne}}$	$\Delta E_{\text{di-cat}}$	$\Delta E_{\text{din-ne}}$
Core- ($\text{C}_{12}\text{H}_{25}$)	Interaction	-0.086	-0.206	-0.304
	Orbital energy	-0.049	-0.174	-0.184
	Steric	-0.039	-0.033	-0.123
	Dispersion	0.002	0.001	0.003
Core- ($\text{C}_{12}\text{H}_{25}$) ₂	Interaction	-0.081	-0.187	-0.265
	Orbital energy	-0.045	-0.156	-0.199
	Steric	-0.037	-0.032	-0.068
	Dispersion	0.001	0.001	0.002
Core- ($\text{C}_{12}\text{H}_{25}$) ₃	Interaction	-0.082	-0.131	-0.209
	Orbital energy	-0.048	-0.096	-0.145
	Steric	-0.035	-0.036	-0.066
	Dispersion	0.001	0.001	0.002
grandPAH	Interaction	-0.075	-0.113	-0.182
	Orbital energy	-0.045	-0.082	-0.128
	Steric	-0.031	-0.031	-0.054
	Dispersion	0.001	0.001	0.002