On-line database of the spectral properties of polycyclic aromatic hydrocarbons

Giuliano Malloci\textsuperscript{a,b,*}, Christine Joblin\textsuperscript{a}, Giacomo Mulas\textsuperscript{b}

\textsuperscript{a}Centre d’Etude Spatiale des Rayonnements – CNRS et Universitè Paul Sabatier
Toulouse 3 – Observatoire Midi-Pyrénées, 9 Avenue du Colonel Roche, 31028
Toulouse Cedex 4, France

\textsuperscript{b}INAF – Osservatorio Astronomico di Cagliari-Astrochemistry Group, Strada 54,
Localitá Poggio dei Pini, I–09012 Capoterra (CA), Italy

Abstract

We present an on–line database of computed molecular properties for a large sample of polycyclic aromatic hydrocarbons (PAHs) in four charge states: -1, 0, +1, and +2. At present our database includes 40 molecules ranging in size from naphthalene and azulene (C\textsubscript{10}H\textsubscript{8}) up to circumovalene (C\textsubscript{66}H\textsubscript{20}). We performed our calculations in the framework of the density functional theory (DFT) and the time–dependent DFT to obtain the most relevant molecular parameters needed for astrophysical applications. For each molecule in the sample, our database presents in a uniform way the energetic, rotational, vibrational, and electronic properties. It is freely accessible on the web at http://astrochemistry.ca.astro.it/database/ and http://www.cesr.fr/~joblin/database/.

Key words: Astrochemistry, PAHs, Molecular data, DFT, TD–DFT

1 Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a large class of conjugated π–electron systems of great importance in many research areas, such as combustion and environmental chemistry, materials science, and astrochemistry. In the astrophysical context, in particular, PAHs are found in carbonaceous meteorites [1], in interplanetary dust particles [2], and are tentatively identified in the atmospheres of Titan and Jupiter [3] and in the coma of Halley’s comet

* Corresponding author. Tel: +39-070-675-4915; Fax: +39-070-510171
Email address: gmalloci@ca.astro.it (Giuliano Malloci).
[4a–b]. In the study of the interstellar medium (ISM) PAHs have been considered well before any IR observations of interstellar objects were available. Complex molecular aggregates with dimensions of $\sim10$ Å were first proposed to contribute to the interstellar extinction [5]. Large condensed–ring hydrocarbons were later recognised as the “Platt particles”, precursors of small graphite grains [6]. The similarity between the vibration of C–C and C–H bonds in large fused–ring aromatic molecules and on the surface of interstellar carbon particles was then put forward to explain the origin of some emission bands observed in the near and mid–IR in the spectra of many astronomical objects, excited by vis–UV photons [7].

The observed spectra required temperatures unattainable in thermal equilibrium by solid–state particles, suggesting molecule–sized carriers, subject to large temperature fluctuations. From abundance, photo–stability, and spectral constraints PAHs and related species were thus suggested as the most natural carriers of the whole family of these so–called “Aromatic Infrared Bands” (AIBs) observed near 3.3, 6.2, 7.7, 8.6, 11.3, and 12.7 $\mu$m [8a–b]. Following the stochastic absorption of single vis–UV photons, a typical PAH quickly converts most or all of the electronic excitation energy into vibrational energy of low–lying electronic states (typically the ground–state or the first excited state). Due to its low heat capacity [9a–b] the molecule is transiently heated to peak temperatures of the order of $10^3$ K. In a collision–free environment it then loses its energy through the emission of radiation; IR fluorescence, in particular, is the proposed explanation for the observed AIBs [8a–b]. The observations of the AROME balloon–borne experiment [10a–b] already suggested the ubiquitous presence of AIBs in our Galaxy as well as in external galaxies. This is now confirmed by the large wealth of observations made with several space–based missions, such as the Infrared Space Observatory (ISO)\(^1\) and the Spitzer Space Telescope\(^2\), which show that the AIBs dominate the near and medium–IR spectrum of many interstellar and circumstellar objects whose radiation field intensities differ by several orders of magnitude [11a–b].

PAHs are estimated to account for a substantial fraction of the total interstellar carbon budget [12], and are seen as an intermediate stage between the gas and dust phases of the ISM, i.e., large molecules or very small grains. As such, they are included in some form in all interstellar dust models [13a–c] and are thought to play a role also in the chemistry [14a–c]. They are expected to exist in a wide variety of environments, in a complex statistical equilibrium of different charge and hydrogenation states [15a–d]. We remark that in the astrophysical context and, consequently, in the astrophysical literature, the term “PAHs” does not correspond to the strict definition as given in chemistry textbooks, but should be read more like “PAHs and related species”, including par-

\(^1\) The official ISO web page is http://www.iso.vilspa.esa.es
\(^2\) http://www.spitzer.caltech.edu
tially dehydrogenated species and molecules in which one or more peripheral hydrogen atoms have been substituted by other functional groups. Although several open questions remain opened (their formation mechanisms, their size distribution, their charge and hydrogenation state, etc.) this subject has motivated a large number of observational, experimental, quantum–chemical, and modelling studies [16a–b]. These, in turn, led to the further speculation that PAHs could account for other unidentified spectral features of interstellar origin:

(1) since large neutral PAHs and all ionised PAHs absorb in the visible, they were proposed as plausible candidate carriers of (at least) a subset of diffuse interstellar bands (DIBs) [17a–d], about 300 absorption features observed in the near–UV, visible, and near–IR spectra of reddened stars [18a–b];

(2) mixtures of gaseous PAHs (present as ions, radicals as well as neutral species) could give an important contribution to the 217.5 nm bump and to the far–UV rise of the interstellar extinction curve [19a–b];

(3) PAHs are known to be efficient emitters in the visible through fluorescence and/or phosphorescence mechanisms [20]. On the basis of matrix isolation spectroscopy [21a–d] and gas–phase experiments [22a–b], PAHs and their cations seem to be good candidates to account for the optical emission bands observed in peculiar interstellar objects [23a–b] and related to some DIBs;

(4) small neutral PAHs such as anthracene (C_{14}H_{10}) and pyrene (C_{16}H_{10}), have been tentatively identified in the protoplanetary Red Rectangle nebula [24a–b] and in other ordinary reflection nebulae [25], based on the observation of a blue luminescence (BL), an emission band extending from 360 up to 480 nm;

(5) PAH dications [26a–c] are believed to contribute to the extended red emission (ERE), a broad emission band observed from 540 to about 900 nm in a large number of dusty interstellar environments [27a–b].

1.1 Collecting the spectral properties of PAHs

The knowledge of the molecular parameters for a large sample of PAHs in all their relevant ionisation and hydrogenation states is of fundamental importance for our understanding of the physics and chemistry of the ISM [16a–b].

In the last few years we have started a long–term project to produce an atlas of synthetic spectra of individual PAHs to be compared with astronomical observations both in absorption in the visible [28] and in emission in the IR [29a–e]. To this end we need the previous knowledge of some key molecular parameters for a large number of species, and use them as a basis to run Monte–Carlo sim-
ulations [29a,30a–b] of their photophysics in specific interstellar environments. Such an approach enabled us to perform a cross–check for the identification of small neutral PAHs in the Red Rectangle nebula [24a–b] by comparing our quantitative prediction for the IR emission spectrum of each given molecule and the available ISO data [29c]. In addition, these simulations provide an important preparatory work for the forthcoming Herschel Space Observatory mission in the attempt to identify specific PAHs through their low–frequency vibrational modes involving the whole skeleton of the molecule in a collective vibration [29a–e,31a–b]. Resolving the rotational structure of these so–called “flopping” or “butterfly” modes provides one more crucial identification element for interstellar PAHs [29a–e].

Taking advantage of the great advances realised over the past years in computer performances, we have started a systematic theoretical study of the spectral properties of a large sample of PAHs in different charge states [32a–c]. We used in a uniform way well–known and established quantum–chemical techniques for the study of the electronic ground–state and excited–state properties needed for astrophysical applications (see next Section for technical details).

Here we present a homogeneous database of the computed molecular properties for a sample of 40 different PAHs. For each molecule in the sample and for its charge states -1, 0, +1 and +2, our spectral database presents in tabular or visual form the energetic, rotational, vibrational, and electronic properties. This database is freely accessible on–line and is suitable for further accumulation of new data. It can be found at the following web–pages:

- [http://astrochemistry.ca.astro.it/database/](http://astrochemistry.ca.astro.it/database/) at the INAF–Osservatorio Astronomico di Cagliari (Italy) and its mirror site at:
- [http://www.cesr.fr/~joblin/database/](http://www.cesr.fr/~joblin/database/) at the Centre d’ Etude Spatiale des Rayonnements of Toulouse (France).

In Sect. 2 we describe the molecular properties available and the theoretical methods we used to obtain them (Sect. 2.1), the sample of different species included until present (Sect. 2.2), and the general structure of the database (Sect. 2.3). Section 3 presents our concluding remarks.

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3 [www.sron.nl/divisions/lea/hifi/directory.html](http://www.sron.nl/divisions/lea/hifi/directory.html)
2 The database

2.1 Molecular properties and theoretical methods

Motivated mainly by basic research in astrophysics, a large number of papers devoted to the experimental [33a–j,34a–j,35a–j,36a–c] and theoretical study [37a–j,38a–j,39a–j] of the spectral properties of PAHs and related species have appeared in the literature over the last decade. Due to the large number of electrons in the molecules considered (416 in the largest one, circumovalene), an \textit{ab initio} study based on the direct solution of the many–electron Schrödinger equation currently has prohibitive computational costs. We here used the density functional theory (DFT) [40] and its time–dependent extension (TD–DFT) [41], which are the methods of choice for the study, respectively, of the ground–state and the excited–state properties of such complex molecules as PAHs.

At present, the computed molecular properties of individual PAHs that can be found in our database are:

1. harmonic vibrational frequencies and integrated IR absorption cross–sections;
2. rotational constants at the optimised ground–state geometry;
3. electron affinities;
4. first and second ionisation energies;
5. permanent dipole moments;
6. vis–UV photo–absorption cross–sections up to \( \sim 30 \) eV;
7. static dipole polarisabilities;

These are the most relevant molecular parameters needed for astrophysical purposes. The set of PAHs for which \textit{all} of the above data are simultaneously available from laboratory experiments is relatively small. Thanks to the ever increasing computational power available, the use of quantum–chemical tools is the next best alternative and can be furthermore useful as a guide for future experimental work.

All calculations for the electronic ground–state have been performed using the Density Functional Theory module of the Gaussian–based code \textsc{nwchem} [42]. In particular, we employed the widely used hybrid B3LYP functional, a combination of the Becke’s three parameters exchange functional [43] and the Lee–Yang–Parr gradient–corrected correlation functional [44]. We first optimised the ground–state geometries using the relatively inexpensive 4–31G basis set, followed by the full vibrational analyses (item 1) to confirm the geometries obtained to be global minima on the potential energy surface. The combination B3LYP/4–31G was shown to give good results in the study of the vibrational properties of PAHs, scaling all frequencies by the same empirical
scale–factor [37i,37j]. We thus adopted the same uniform scaling procedure derived by these authors for all of the PAHs under study in their -1, 0, +1 and +2 charge states. Since for open–shell systems analytical second derivatives are not yet implemented in the version of NWChem that we used (version 4.7), we performed the vibrational analyses for all the anions, cations, and dications triplets, using the Gaussian03 quantum chemistry package [45].

We then started from the optimal geometries and the corresponding self consistent field solution obtained in the previous step to refine the optimisation with the larger 6–31+G* basis–set, a valence double zeta basis set augmented with d polarisation functions and s and p diffuse functions to each carbon atom [46]. The rotational constants (item 2) have been derived from the optimised B3LYP/6–31+G* geometries. Although basis set convergence is not yet expected at this level, in view of the large systems under study some compromise between accuracy and computational costs had to be made.

We thus computed the adiabatic and vertical values of both the electron affinity (item 3) and the first and second ionisation energy (item 4). Adiabatic values are evaluated as the difference between the total energies of the neutral and the corresponding ion minima, respectively; these quantities, therefore, take into account the structural relaxation of the molecule following the ionisation process. The vertical values, computed at the optimised geometry of the neutral molecule, neglect structural relaxation but include wavefunctions relaxation due to the addition of one electron (anion) or the removal of one (cation) or two (dication) electrons. All neutral and singly–ionised species were computed as singlet and doublet, respectively, while for dications we computed both their singlet and triplet ground states. This enabled us to predict the relative energies of electronic states having different multiplicities. For almost all of the molecules under study (34 out of a total of 40), our calculations predict the dication overall ground–state to be the singlet [32c]. Whenever available, we list the experimental electron affinities and single ionisation energies as reported in the NIST Chemistry WebBook [47]. As to the second ionisation energies we report the values obtained in the only available experimental measurements of the second ionization energies of the PAHs we considered [26c,34j,36b]. For polar species we list also the corresponding permanent dipole moments (item 5), which might be relevant for the astronomical search of PAHs in the microwave region through their pure rotational spectrum [35j].

Concerning item 6 in the above list, we already presented a collection of individual vis–UV photo–absorption spectra computed in a uniform way for a large sample of anionic, neutral, cationic, and dicationic PAHs [32a–c]. We used a real–time real–space implementation of the Time–Dependent Density Functional Theory (TD–DFT) [48] as given in the Octopus computer code [49]. Our results are in good agreement with the only available measurements.
of photo–absorption cross–sections of neutral PAHs from the visible to the vacuum–UV spectral domain [19a–b]. While experimental spectra in the far–UV are needed for a similar direct validation for PAH ions, our theoretical data for neutral species reproduce the overall far–UV behaviour, including the broad absorption peak dominated by $\sigma^* \leftarrow \sigma$ transitions, which matches well both in position and width. The computed vertical excitations of $\pi \rightarrow \pi^*$ character falling in the low–energy range are expected to be precise to within a few tenths of an eV, which are the typical accuracies of TD–DFT calculations using the currently available exchange–correlation functionals [38c,39b]. With respect to other theoretical studies of the electronic excitations of PAHs, the main step forward achieved by our work is represented by the spectral range covered, that extends up to $\sim 30$ eV. This piece of information has proven to be particularly useful for astrophysical modelling when laboratory data are missing [29c,29d,29e]. On the other hand, the main drawback is that we do not obtain independent information for each excited electronic state, such as its symmetry and its description in terms of promotion of electrons in a one–electron picture. With the OCTOPUS code we also obtain the static dipole polarisabilities (item 7), whose knowledge is important in the study of chemical reactivity.

More technical details about the calculations we performed with both the OCTOPUS and NWChem codes, as well as on the expected accuracy achieved, can be found elsewhere [32a–c].

### 2.2 The sample of molecules

A wide range of PAHs and related species are thought to exist in the ISM [16b]. The total of 40 molecules selected in this work, ranging in size from naphthalene and azulene ($C_{10}H_8$) to circumovalene ($C_{66}H_{20}$), cover an ample range of structures inside the two large classes of pericondensed and catacondensed species. Although non–compact PAHs are expected to be less stable than compact ones with the same number of benzenoid rings, we extended the present study to both classes, including also large oligoacenes such as pentacene ($C_{22}H_{14}$) and hexacene ($C_{26}H_{16}$). In addition we included some PAHs with five–membered rings, namely fluorene ($C_{13}H_{10}$), fluoranthene ($C_{16}H_{10}$) and corannulene ($C_{20}H_{10}$). Whenever possible, the known symmetry of the molecular geometry was assumed during calculations, e.g., $C_{2v}$ for phenanthrene ($C_{14}H_{10}$), $C_{2h}$ for chrysene ($C_{18}H_{12}$), $D_{2h}$ for triphenylene ($C_{18}H_{12}$), $D_{2h}$ for ovalene ($C_{32}H_{14}$), $D_{6h}$ for coronene ($C_{24}H_{12}$), hexabenzocoronene ($C_{42}H_{18}$) and circumcoronene ($C_{54}H_{18}$) and so forth. In the case of some of the molecules with a more than 2–fold symmetry axis, symmetry breaking was observed upon single and double ionization, as expected from Jahn–Teller distortion [38b]. More specifically, we obtained a symme-
try reduction from $D_{6h}$ to $D_{2h}$ point group for coronene, hexabenzoronene, and circumcoronene, from $D_{3h}$ to $C_{2v}$ for triphenylene and from $C_{5v}$ to $C_s$ for corannulene.

Although some studies show interstellar PAHs to be on average larger than the species we considered [12], we restricted ourselves to molecules containing up to a maximum of 66 carbon atoms, since computational costs steeply scale with dimensions (e.g., about 3000 CPU hours on an IBM SP5 for the circumovalene ions, which were the most expensive species considered).

2.3 General structure of the database

The main pages http://astrochemistry.ca.astro.it/database/ and http://www.cesr.fr/~joblin/database/ contain the full list of molecules considered; they are ordered by increasing masses. Direct links to the official web pages of the packages and computing resources used are given. A separate page can then be accessed for each given species. The latter includes a graphical representation of the selected molecule and the links to the following pages:

(i) The corresponding NIST web page (if available).
(ii) The html table of the harmonic vibrational analyses for each of the four charge states considered (item 1 in the list of the previous section); a pdf version of the table can also be downloaded.
(iii) The table of the general parameters of the molecule (items 2 to 6) with the addition of its symmetry properties (symmetry properties, irreducible representations $\Gamma_{3N}$ and $\Gamma_{\text{vib}}$, and IR–active modes).
(iv) The plots of the vis–UV photo–absorption cross–sections (item 7) for each charge–state; all of the spectra can also be downloaded in ascii format.
(v) A list with some of the more representative papers related to the given molecule; more than 500 references are currently included, each of them pointing to the official web page of the journal (when available).

As to the last point, in particular, many references are likely to have been missed in our bibliographic search. We will be thankful to anyone who will send us more relevant references.

2.4 Related links

There are several other internet resources reporting relevant data and bibliographic references on the spectral properties of PAHs. Among them, we refer the reader to the official web page of the Astrochemistry Laboratory at NASA
Ames Research Center http://www.astrochemistry.org/ and the Polycyclic Aromatic Hydrocarbon Structure Index http://ois.nist.gov/pah/ and the Chemistry WebBook http://webbook.nist.gov/chemistry/ of the National Institute of Standards and Technology. Up to date references and direct links to personal web pages can also be found in the web-page http://www.astrochymist.org/, which is devoted to the field of astrochemistry in general.

3 Future perspectives

In the near future we will extend our database towards two main directions. We will include larger PAHs and, at the same time, we will study some derivatives of the molecules already considered. In particular, we plan to study de–hydrogenated [50,51] or super–hydrogenated species [52], and species including heteroatoms such as oxygen [53], nitrogen [54a–c] or organometallic compounds [36c,38e]. Better levels of theory (e.g., larger bases and/or newly developed exchange–correlation functionals) will be employed for the calculation of some of the molecular properties considered. In addition, we plan to compute other poorly known molecular parameters, such as the anharmonic correction to vibrational terms and rotational constants [55a–b] and the vibronic structure of electronic absorption and emission spectra [56a–b]. On a parallel track, all of these data will be used to produce synthetic spectra to compare with actual astronomical observations. Of course, external contributions to be included in the database, either experimental or theoretical results, are also very welcome. We therefore invite anybody interested in having their results made available on our database to submit their contributions following the contact links in the on–line web–pages; the appropriate citation to the owner of the data will be reported.

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