Identifying specific interstellar polycyclic aromatic hydrocarbons

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Abstract. Interstellar Polycyclic Aromatic Hydrocarbons (PAHs) have been thought to be ubiquitous for more than twenty years, yet no single species in this class has been identified in the Interstellar Medium (ISM) to date. The unprecedented sensitivity and resolution of present Infrared Space Observatory (ISO) and forthcoming Herschel observations in the far infrared spectral range will offer a unique way out of this embarrassing impasse.

1. Introduction

The hypothesis of the ubiquitous presence of free gas–phase polycyclic aromatic hydrocarbons (PAHs) in the interstellar medium (ISM) was first set forth about 20 years ago by [1]. This class of molecules was suggested as the most natural interpretation for the so–called “Aromatic Infrared Bands” (AIBs), a set of emission bands observed in the near–IR in many dusty environments excited by UV photons [2]. Such bands are the spectral fingerprint of the excitation of vibrations in aromatic C–C and C–H bonds [3] and are relatively insensitive to the specific chemical species containing them. Later on, PAH cations were also proposed to account for a subset of the “Diffuse Interstellar Bands” (DIBs) [4], more than 300 unidentified absorption features observed in the near-UV, visible and near-IR in the spectra of reddened stars [5].

In general, PAHs are believed to play an important role in the physics and chemistry of the ISM, with properties which lie in between the gas and dust phases, behaving at the same time as very small solid particles and very large molecules. This motivated many observational, experimental and theoretical efforts in the last two decades, which confirmed aromatic species to be very promising candidates to explain AIBs and some of the DIBs, locking a substantial fraction of the total interstellar carbon budget. However, despite the impressive number of studies related to this subject, the ISO identification of the basic aromatic unit benzene [6], which showed the interstellar PAHs chemistry to be feasible [7], and the tentative identification of neutral anthracene and pyrene in the Red Rectangle [8], no definitive spectral identification in astronomic observations of any specific individual member in this class exists to date.

“Classical” AIBs do not permit an unambiguous identification of any single molecular species, because vibrational transitions in the near and medium IR, are a common, shared feature of the whole class of PAHs [9]. These vibrational modes just probe specific functional groups and not the overall structure of the whole molecule. Indeed, the emission in these bands is usually explained assuming a whole population of different PAH molecules to contribute to them [10].
On the other hand, each specific PAH ought to show a unique spectral fingerprint in the far infrared region, which contains the low–frequency vibrational modes associated with collective oscillations of the whole carbon skeleton of the molecule [9, 11, 12, 13]. Moreover, far–IR bands, in the PAH hypothesis, are expected to be emitted preferentially when the excitation energy of the molecule is relatively low [12]; this would result in slower internal vibrational redistribution of energy and thus smaller lifetime broadening, implying that their rotational envelopes, or even their fully resolved rotational structure, might be still discernible, as hinted by the gas phase laboratory measurements of [11]. Indeed the expected resolution of the far–IR spectrograph on board of the ESA Herschel mission would be able to resolve such rotational envelopes, if present, providing one more crucial identification element for interstellar PAHs.

The far–IR spectrum emitted by a given interstellar PAH will depend essentially just on its molecular properties and on the exciting radiation field, and can be modelled in detail if all these “ingredients” are known [12, 13, 14]. The stumbling block in performing such a calculation in a systematic way for a large sample of specific PAHs and radiation fields is indeed in the lack of said “ingredients”: there are precious few species for which both the complete vibrational analysis and the photoabsorption spectrum up to the Lyman limit are known, to date. We here demonstrate that state–of–the–art quantum chemistry techniques can provide a fairly accurate estimate of such ingredients, which in turn yields similarly accurate predicted infrared spectra.

In the following Sect. 2 we briefly summarise our modelling procedure and assess its expected accuracy. The results obtained are discussed in Sect. 3.

2. Validation of the modelling procedure

In previous papers [13, 14], we demonstrated the use of a Monte–Carlo model to simulate the detailed photophysics of a specific PAH, namely neutral and cationic ovalene (C_{32}H_{14}), embedded in a given radiation field (RF). A similar approach for neutral coronene (C_{24}H_{12}) were previously used by [12]. In both cases, published laboratory measurements of the vis/UV photo–absorption spectra were used, while the vibrational properties were obtained using the Density Functional Theory (DFT).

Unfortunately, complete optical absorption spectra of neutral and cationic PAHs ranging from the visible to the Lyman limit have been measured only for very few species. However, we recently calculated ab initio vis/UV absorption spectra of a sample of 20 PAHs and their respective cations, using the Time–Dependent DFT implementation in the OCTOPUS computer code [15], and showed them to be in good agreement with experimental data when available [16], which validated their use as a quite decent surrogate [17].

Encouraged by the above results, we decided to explicitely validate the use of our calculated absorption spectra as “ingredients” for our Monte–Carlo simulations, assessing the additional error this introduces when compared with using laboratory data. For the other “ingredient”, the complete vibrational analysis, we calculated the harmonic frequencies at the B3LYP/4-31G level of theory [9, 19] using the NWChem computer program [18]. Figure 1 shows the comparison between ab initio [17] and laboratory [16] photo–absorption cross sections for the anthracene and ovalene molecules, and the impact of their differences on the estimated absorption rates in three vis/UV RFs. We considered the average ISRF 5 Kpc away from the galactic centre and the RFs of the photodissociation region of the Red Rectangle reflection nebula and of the planetary nebula IRAS 21282+5050 [13, 14]. For both molecules the agreement between synthetic and laboratory spectra is reasonably good, with typical differences of ~0.3 eV between calculated and measured energies of the absorption bands. In some cases these relatively small differences are widely amplified in the low–energy part of the photon absorption rates for the Red Rectangle and, to a lesser extent, for the average ISRF, because these RFs are very steep, e. g. the photon flux changes about an order of magnitude between ~4.8 and ~5.2 eV.

Table 1 summarises the integrated photon absorption rates $R$ and the average energy $\bar{E}$
Figure 1. The top panel shows the comparison between the laboratory (dotted line) and the theoretical absorption cross-section (continuous line) for anthracene (left panel) and ovalene (right panel) from [17], expressed in megabarns ($1 \text{ Mb} = 10^{-18}\text{cm}^2$). The three panels below show the comparison between the resulting photon absorption rates in the three RFs considered.
Table 1. Comparison between the photon absorption rates $R$ (in s$^{-1}$) and the average absorbed energy $E$ (in eV) computed using theoretical [17] and laboratory [16] cross sections for anthracene (C$_{14}$H$_{10}$), pyrene (C$_{16}$H$_{10}$), coronene (C$_{24}$H$_{12}$) and ovalene (C$_{32}$H$_{14}$) in the three RFs considered.

| Radiation field | Average ISRF | Red Rectangle | IRAS 21282+5050 |
|-----------------|--------------|---------------|-----------------|
|                 | $R$ (s$^{-1}$) | $E$ (eV)     | $R$ (s$^{-1}$) | $E$ (eV) |
| Anthracene (C$_{14}$H$_{10}$) |             |              |                |          |
| lab             | 6.0 $\cdot 10^{-8}$ | 7.6         | 6.2 $\cdot 10^{-6}$ | 5.3   | 5.9 $\cdot 10^{-3}$ | 8.9 |
| th              | 6.3 $\cdot 10^{-8}$ | 6.8         | 1.1 $\cdot 10^{-5}$ | 4.4   | 5.3 $\cdot 10^{-3}$ | 8.7 |
| Pyrene (C$_{16}$H$_{10}$)   |             |              |                |          |
| lab             | 5.6 $\cdot 10^{-8}$ | 7.4         | 6.8 $\cdot 10^{-6}$ | 5.4   | 5.1 $\cdot 10^{-3}$ | 8.9 |
| th              | 7.7 $\cdot 10^{-8}$ | 6.6         | 1.4 $\cdot 10^{-5}$ | 4.5   | 5.8 $\cdot 10^{-3}$ | 8.8 |
| Coronene (C$_{24}$H$_{12}$) |             |              |                |          |
| lab             | 1.4 $\cdot 10^{-7}$ | 6.8         | 2.2 $\cdot 10^{-5}$ | 4.9   | 1.1 $\cdot 10^{-2}$ | 8.6 |
| th              | 1.3 $\cdot 10^{-7}$ | 6.1         | 2.4 $\cdot 10^{-5}$ | 4.4   | 8.6 $\cdot 10^{-3}$ | 8.5 |
| Ovalene (C$_{32}$H$_{14}$) |             |              |                |          |
| lab             | 2.4 $\cdot 10^{-7}$ | 5.6         | 5.6 $\cdot 10^{-5}$ | 4.0   | 1.3 $\cdot 10^{-2}$ | 8.2 |
| th              | 2.8 $\cdot 10^{-7}$ | 4.6         | 6.3 $\cdot 10^{-5}$ | 3.5   | 1.1 $\cdot 10^{-2}$ | 8.2 |

The overall agreement is excellent in the case of the PN IRAS 21282+5050, whose RF is rather flat. The largest differences, for opposite reasons, can be seen for the Red Rectangle, but mostly for the two smallest molecules, namely anthracene and pyrene. Even in these worst cases, $R$ values still appear accurate to better than a factor of two, while $E$ is accurate to better than $\sim 20\%$. These two errors are systematically in opposite directions, since they both stem from the relatively small differences in the absorption band theoretical positions at low energies and the steepness of the RFs. Hence the energy absorption rate, i.e. the energy absorbed per unit time by a single molecule embedded in a given RF, obviously given by $R \cdot E$, is more accurate than $R$. In any standard PAH model the energy absorption rate $R \cdot E$ of a molecule equals by and large the total power it radiates in all of its vibrational bands, while $E$ governs their relative intensities.

Figure 2 compares the calculated IR emission spectra resulting from synthetic and laboratory absorption cross sections for ovalene. As expected from the remarks above, the agreement is quantitatively very good, the worst error being of the order of $\sim 20\%$ in the Red Rectangle. We remark that the discriminating capabilities of the calculated spectra are even better: the intensity ratios between the bands longwards of $\sim 20$ µm appear unaffected, to within a few percent, by the difference between the ab initio and experimental photoabsorption spectra. We conclude that in all cases the use of our ab initio photoabsorption spectra in modelling the photophysics of PAHs paves the path for building a large, systematic database of PAH IR emission spectra with little sacrifice in terms of diagnostic power.

As a matter of fact, the most important source of inaccuracy in our synthetic far–IR spectra results to be currently in the vibrational analysis. The frequencies of the vibrational modes calculated at the B3LYP/4–31G level of DFT are known to be within $\sim 3\%$ of available experimental data, when appropriately scaled. This may be not accurate enough for a secure identification, given the multitude of unidentified far–IR bands which appear to be present in
ISO LWS data and the correspondingly larger number expected to show up in the forthcoming, much more sensitive Herschel data. The accuracy of the \textit{ab initio} intensities is worse, the errors being of the order of $\sim$30\% on the average and as large as a factor of $\sim$3 for some bands. The use of significantly larger basis sets improves the accuracy of calculated intensities \cite{20} at the price of a much larger computational cost (about 5 to 10 times longer DFT calculations).

Figure 3 compares the calculated IR emission spectrum resulting from our vibrational analysis at the B3LYP/4–31G versus the one at the B3LYP/cc–pVDZ level of theory obtained by \cite{20}. The uncertainties in the vibrational analyses used are clearly seen to propagate unchanged through the Monte–Carlo simulations of the photophysics into the synthetic IR emission spectra.

3. Conclusion
Our completely synthetic far–IR spectra can be used, within their acknowledged uncertainties, as a very strong constraint for PAH identification on ISO–LWS and, in the future, on Herschel data. This constraint will obviously be much stronger, even if still not final, if multiple bands, with the expected intensity ratios, can be identified for a single molecule. Targeted laboratory experiments, based on such tentative identifications, will then be needed to produce a much more accurate refinement of the predicted IR emission spectra, and thus discriminate remaining ambiguities and say the final word.

Figure 2. Comparison between two sets of model runs for the ovalene molecule (C$_{32}$H$_{14}$). From top to bottom, different boxes show the expected IR emission spectra in different exciting RFs. For each RF, the left and right panel show the results of the model run using theoretical \cite{17} and laboratory absorption spectra \cite{16}, respectively. In each plot, the far–IR part of the spectrum is also overplotted magnified ten times and shifted up for clarity.
Figure 3. Comparison between two sets of model runs for the coronene molecule (C$_{24}$H$_{12}$) in the average ISRF, both using our calculated absorption spectrum [17]. The left and right panel show the results of the model run using the vibrational analysis at the B3LYP/4–31G and B3LYP/cc–pVDZ [20] levels, respectively. In each plot, the far–IR part of the spectrum is also overplotted magnified ten times and shifted up for clarity. Ticks mark the bands which are “forbidden” in electric dipole approximation but are expected to be emitted in the ISM.

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