



Isomers of Hydrogenated Polycyclic Aromatic Hydrocarbons Explain the Presence of Infrared Bands in the $3\ \mu\text{m}$ Region

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Abstract

A large number of hydrogenated coronene, circumcoronene, and circumcircumcoronene isomers have been investigated by means of density functional theory calculations. The computation of their IR spectra puts forward significant differences between the different isomers in the $3\ \mu\text{m}$ region and shows that hydrogenated polycyclic aromatic hydrocarbons can account for the aromatic infrared bands resulting from the absorption of light by the interstellar medium. In particular, the intense $3.3\ \mu\text{m}$ band, as well as the weak features observed at 3.40 , 3.46 , 3.51 , and $3.56\ \mu\text{m}$ are reasonably reproduced by the present calculations. The latter two are only observed when hydrogenation takes place in tertiary carbon atoms, showing that the frequencies at which these IR bands appear are a consequence of their position and chemical environment within the molecule.

Unified Astronomy Thesaurus concepts: Polycyclic aromatic hydrocarbons (1280); Interstellar molecules (849); Infrared sources (793); Cosmochemistry (331); Molecular spectroscopy (2095); Line positions (2085); Spectral line identification (2073)

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a family of carbonaceous molecules with enhanced chemical stability that have been proposed to be at the origin of the so-called aromatic infrared bands (AIBs), a series of infrared (IR) features found in the region of $3\text{--}20\ \mu\text{m}$ ($3300\text{--}500\ \text{cm}^{-1}$) associated with a variety of astronomical environments, such as planetary nebulae and protoplanetary nebulae (Leger & Puget 1984; Allamandola et al. 1985; Tielens 2008, 2013). AIBs, which are thought to arise from radiative cooling of isolated PAHs upon excitation by ultraviolet radiation (Allamandola et al. 1989), are most likely due to vibrational modes of these molecules.

In space, PAHs can undergo different reactions such as ionization, fragmentation, or hydrogenation/dehydrogenation (Tielens 2008; Bierbaum et al. 2011; Montillaud et al. 2013; Gatchell et al. 2015; Zhen et al. 2015, 2016; Rapacioli et al. 2018). The comprehension of such processes is crucial to understand the evolution and population of these species in the interstellar medium (ISM) and its contribution to the global evolution of carbon, from small carbon molecules to carbonaceous grains (Henning & Salama 1998; Cherchneff et al. 2011; Contreras & Salama 2013). It is expected that different PAHs of variable size, structure, charge, and degree of hydrogenation might contribute to AIBs.

One of the most studied AIBs is the one observed at $3.3\ \mu\text{m}$ ($3030\ \text{cm}^{-1}$), which is associated with the C–H stretching vibrational modes of pristine PAHs (Giard et al. 1989). This main band is accompanied by a set of weak features at 3.40 , 3.46 , 3.51 , and $3.56\ \mu\text{m}$ (with different relative intensities depending on the observational source) whose assignment is still controversial (Joblin et al. 1996; Sloan et al. 1997; Li & Draine 2012). One of the hypotheses is that they originated from C–H stretching vibrational modes of hydrogenated PAHs (Bernstein et al. 1996; Wagner et al. 2000; Pauzat & Ellinger 2001; Sandford et al. 2013; Steglich et al. 2013).

Hydrogenated PAHs are PAHs with an excess of hydrogen atoms that convert the sp^2 aromatic carbon atoms into sp^3 aliphatic ones. In particular, hydrogenated PAHs have attracted attention due to the possibility that they behave as catalysts for H_2 formation (Le Page et al. 2009; Boschman et al. 2012; Mennella et al. 2012; Thrower et al. 2012; Skov et al. 2014).

Over the last decades, several experimental and theoretical studies on hydrogenated PAHs have been carried out. For instance, it was shown (Rauls & Hornekær 2008) that neutral coronene can be hydrogenated following an almost barrierless process where hydrogenation in edge and center coronene positions starts before all outer edge positions become hydrogenated. This was recently corroborated by temperature programmed desorption experiments in combination with theoretical calculations proposing a sequence to hydrogenate neutral coronene molecules until full coverage (Jensen et al. 2019). As considering all possible isomers is impossible even for smaller PAHs, these studies are based on obtaining sequential hydrogenation patterns that result from high-level calculations of selected isomers by using reasonable chemical rules. Similar studies have been performed for the hydrogenation of coronene cations until full coverage (Cazaux et al. 2016, 2019), showing a preference for the addition of an odd number of H atoms in contrast to what occurs for neutral coronene. The presence of ionized PAHs depends on the far-ultraviolet (FUV) flux and PAH cations are more probable at the surface of photodissociation regions (PDRs).

In addition, low-temperature high-resolution gas-phase IR spectra of a few hydrogenated derivatives of naphthalene, anthracene, phenanthrene, and pyrene have been obtained experimentally and matched to theoretical spectra (Mackie et al. 2018; Maltseva et al. 2018) showing that to accurately describe the IR spectrum it is necessary to include anharmonicity and Fermi resonances especially at the $3\ \mu\text{m}$ region due to the importance of combination bands, overtones, and

resonances (Mackie et al. 2015, 2016; Maltseva et al. 2015). However, these studies are restricted to date to a few small PAHs due to the huge computational cost of this methodology. Other studies have shown that hydrogenated PAHs are stable under very different conditions and can be formed in the ISM (Mennella et al. 2012; Thrower et al. 2012; Klærke et al. 2013).

In spite of the abundant literature, little attention has been paid to the fact that hydrogenation of PAHs can lead to multiple stable isomeric forms that could also be responsible for the observed AIBs. This is not of minor importance, as, e.g., there are more than 3 million possibilities to place four hydrogen atoms on a circumcircumcoronene ($C_{96}H_{24}$) and the number of possibilities grows exponentially with the size of the PAH and the number of additional hydrogen atoms. Considering that the size of the most stable hydrogenated PAHs is expected to be large due to their higher photostability (Le Page et al. 2003; Boschman et al. 2012; Montillaud et al. 2013) and that hydrogenation is expected to lead to a broad distribution, i.e., hydrogenated species with a different number of additional hydrogen atoms might coexist (Duley 2006; Rapacioli et al. 2018), the number of hydrogenated PAH structures available at ISM conditions can be very large. In this sense, theoretical models that allow for a rapid prediction of the relative stability of all potentially accessible isomers are crucial to identify the most stable structures for each hydrogenation state among the huge amount of possible ones. These stable structures can then be the target of elaborate quantum chemistry calculations in order to predict their electronic properties and IR spectra, thus minimizing the risk of performing expensive calculations for the wrong species.

In this work we have performed systematic theoretical calculations of the relative stability of a large number of isomers of hydrogenated PAHs by using an extension of a previously proposed theoretical model that allows one to consider millions of possible structures and to identify the most stable ones. For the most stable isomers, we have evaluated the corresponding IR spectra. We show that the bands found in the $3\ \mu\text{m}$ region of the IR spectra resulting from astronomical objects can be explained in general by considering the contribution from several isomers of hydrogenated PAHs of comparable stability. This is a consequence of the fact that the position and environment of additional hydrogen atoms determines the wavelength at which the IR bands associated with the C–H stretching modes appear.

For a better identification of the degree of hydrogenation of the structures discussed in this work, from now on, we will use the notation of C_xH_{y+z} , where C_xH_y is the empirical formula of the pristine PAH and z is the number of additional hydrogen atoms.

2. Methods

To screen the relative stability of a large number of hydrogenated isomers of coronene ($C_{24}H_{12}$), circumcoronene ($C_{54}H_{18}$), and circumcircumcoronene ($C_{96}H_{24}$), we have used an extension to PAHs of the eXofullerene Stabilization Index (XSI) model. The model developed in our group (Wang et al. 2017; Pla et al. 2018) and implemented in the FullFun code (Wang et al. 2018) was used in the past to identify the most stable structures of different exohedral fullerenes. Here we have evaluated the XSI for the above PAHs for an even number of additional hydrogen atoms from 2 to 12. A step-wise addition procedure was used to generate the structures with a number of

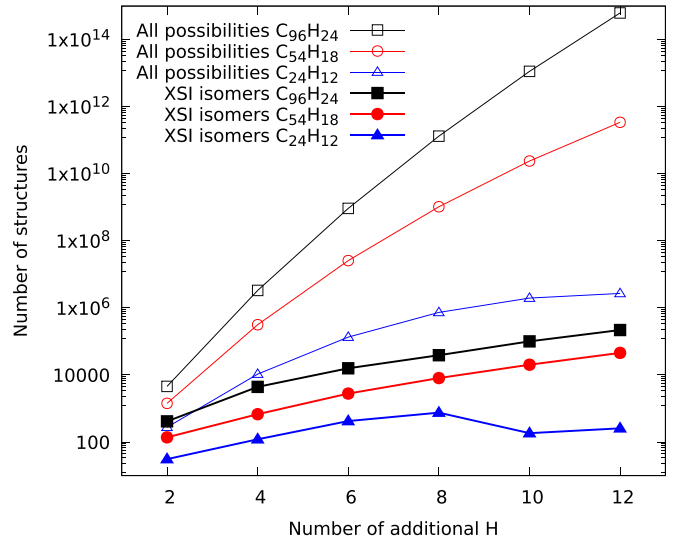


Figure 1. Number of structures obtained with the XSI and number of all possible structures as a function of the number of additional hydrogen atoms.

additional hydrogen atoms larger than 2 using a cutoff of $0.5 |\beta|$, where β is the resonance integral in the Hückel Molecular Orbital approach. Figure 1 shows a plot of the total number of possible structures (without symmetry considerations) and those considered in our XSI approach for coronene, circumcoronene, and circumcircumcoronene as a function of the degree of hydrogenation. It can be seen that in spite of the energy cutoff used to generate the hydrogenated structures, the number of isomers to which the XSI approach has been applied is still huge.

We have benchmarked the XSI results against Density Functional Theory (DFT) calculations to show that the XSI model can reproduce the stability of hydrogenated PAHs. For that, we have evaluated the relative energies of several isomers by performing full geometry optimizations at the M06-2X/6-31G(d,p) level of theory (Zhao & Truhlar 2008) using the Gaussian09 software package (Frisch et al. 2009). The results for $C_{24}H_{12+4}$, $C_{54}H_{18+6}$, and $C_{96}H_{24+8}$ are shown in Figure 2 where two panels are depicted for each case. The left one is a general benchmarking where 20 isomers were selected randomly over the whole set generated by XSI. The right panel shows an inset of the low-energy region (0–1 eV) considering all isomers lying in this energy range. As can be observed, the correlation between XSI and DFT relative energies is good independently of the size of the system. Although in some particular cases the DFT energetic order cannot be exactly reproduced, as expected from a low-level computational method, XSI succeeds in identifying the most stable structures among a large number of possible isomers.

For each PAH and degree of hydrogenation, the most stable isomers in a range of $0.5 |\beta|$ were selected for further analysis. DFT calculations were carried out to optimize structures as stated above. Frequencies were also obtained at the same M06-2X/6-31G(d,p) level of theory to ensure that the calculated points correspond to a minimum in the potential energy surface and to obtain the IR spectra presented in this work. Due to the large number of isomers considered and the large size of some of them, theoretical IR spectra were calculated within the harmonic approximation. A scaling factor of 0.95 was applied to all spectra to better fit experimental data. This scaling factor is similar to that used in previous works that have made use of

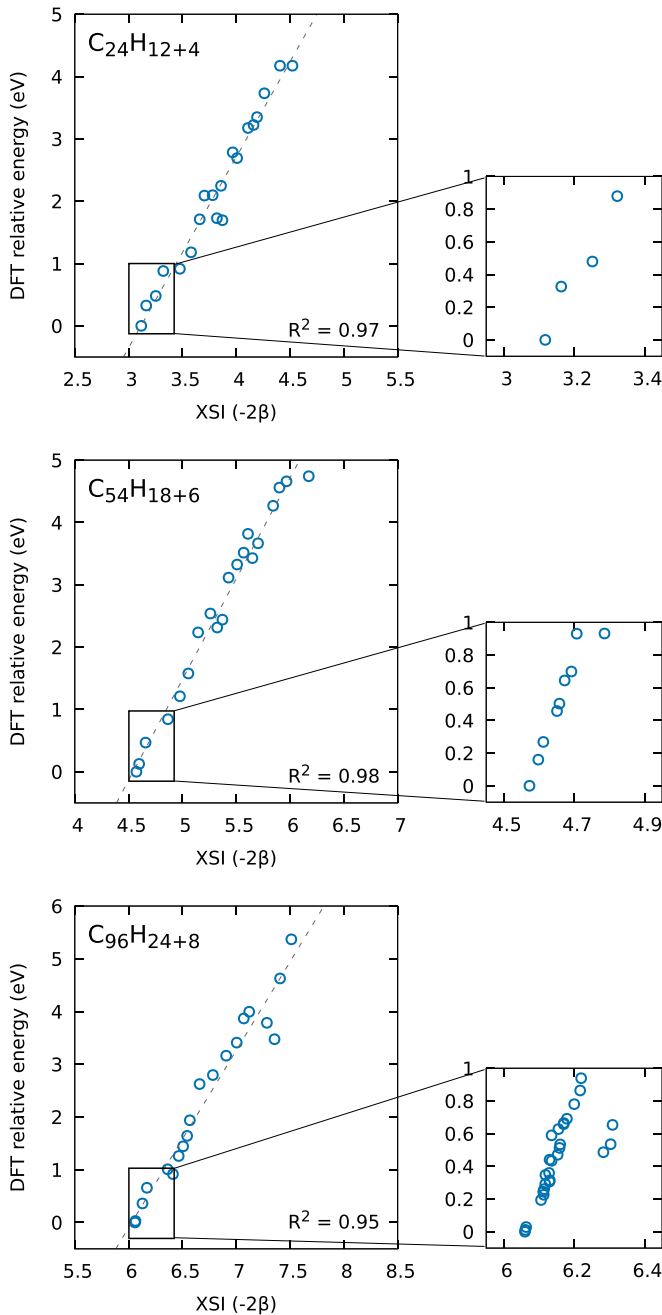


Figure 2. Correlation between XSI and M06-2X/6-31G(d,p) relative energies of C₂₄H₁₂₊₄, C₅₄H₁₈₊₆, and C₉₆H₂₄₊₈ for 20 randomly chosen isomers and for all isomers lying in the low-energy range (0–1 eV).

the same functional and similar basis sets (Laury et al. 2011, 2012). The latter works have shown that lower scaling factors (i.e., deviating more from 1.0) should be used for the higher frequencies, in agreement with the NASA Ames PAH IR spectroscopic database that recently incorporated the use of three scaling factors for three different ranges of frequencies (Bauschlicher et al. 2018). The vertical spectral lines that result from the theoretical calculations were convoluted using an FWHM of 7 cm⁻¹. To simplify the analysis, we only studied the most stable conformer for each isomer, which corresponds to an alternated distribution of the additional hydrogen atoms.

3. Results and Discussion

Figure 3 shows the DFT relative energies of the most stable hydrogenated isomers of coronene, circumcoronene, and circumcircumcoronene with a number of additional H atoms from 2 to 12. All the isomers depicted lie in a range from 0 to 1 eV. It can be observed that the number of isomers in this energy range increases with the size of the PAH. So there is a large number of candidates that can contribute to the IR spectrum obtained from astronomical objects.

To show the diversity of structures found in the lower energy region, the isomers of C₂₄H₁₂₊₆ are represented in the bottom of Figure 3. These isomers are representative of what is found for other degrees of hydrogenation and PAHs. In some cases, it can be observed that additional H atoms appear together in contiguous carbon atoms whereas in other cases appear in two or more groups. It is worth noticing that with our methodology we find the same structures (e.g., isomers b and d of Figure 3) as those predicted in earlier work based on a hydrogenation sequence (Jensen et al. 2019), but we also find other stable structures. In particular, structures in which H atoms are located in different parts of the coronene, such as structure a of Figure 3, which is predicted to be the most stable one, were not considered in previous studies. We can also distinguish between two different types of carbon atoms: (i) carbon atoms that are at the edge and have only two neighboring carbon atoms and one hydrogen atom (denoted hereafter as secondary), and (ii) carbon atoms with three neighboring carbon atoms that are essentially located at the central part of the PAH but can also be located at the edge (denoted as tertiary). Given the variety of structures obtained, it is expected that different isomers may give rise to different IR spectral features. We have focused on the 3 μm region of the IR spectrum as it is the region where the most noticeable changes are observed upon hydrogenation (Sandford et al. 2013).

Figure 4(a) shows the theoretical harmonic IR spectra in the 3 μm region of the most stable isomer of C₂₄H₁₂₊₂, C₅₄H₁₈₊₂, and C₉₆H₂₄₊₂. The feature appearing at 3.3 μm, which has two components, corresponds to the aromatic C–H stretching. The splitting in two components is due to the solo and duo vibrations, that is, to the cases in which there is one or two aromatic H atoms in contiguous secondary C atoms surrounded by tertiary C atoms, respectively. (Maltseva et al. 2016). The aliphatic C–H stretching bands appear at longer wavelengths when hydrogenation takes place. The two bands around 3.40 and 3.46 μm are due to antisymmetric and symmetric vibrations of the C–H bonds occupying a secondary position, respectively. However, when more H atoms are added, some isomers can present additional bands (see Figure 4(b)). In this case, bands located around 3.51 μm are due to the stretching of the C–H bond that results from hydrogenation at a tertiary position. It can also be observed that whereas the aromatic and two-hydrogen aliphatic bands have a well defined frequency that almost does not vary with the size of the system, the one-hydrogen aliphatic bands present a small blueshift as the size increases.

Analyzing carefully the spectrum of other isomers we have been able to derive some general trends. Figure 5 shows the IR spectra of the C₂₄H₁₂₊₆ isomers shown in Figure 3. The spectra present aliphatic C–H stretching bands at 3.40 and 3.46 μm but some isomers also present low intensity bands at longer wavelengths. These bands correspond to hydrogenation in tertiary positions. The bands observed around 3.56 μm for

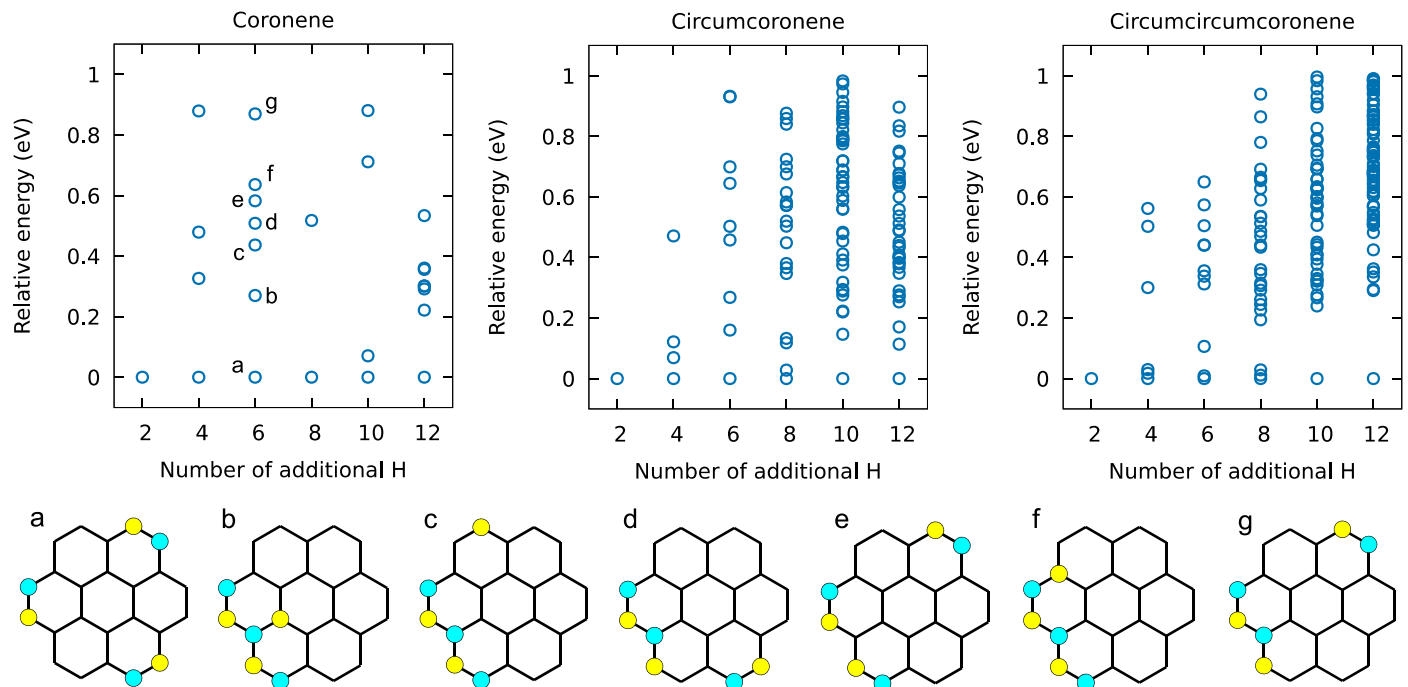


Figure 3. Relative energies (eV) at the DFT level of all isomers selected by the XSI model for coronene, circumcoronene, and circumcircumcoronene for an additional number of hydrogen atoms from 2 to 12. Some isomers are depicted schematically. Additional H atoms are represented as blue and yellow circles indicating that they are pointing out up or down from the PAH plane.

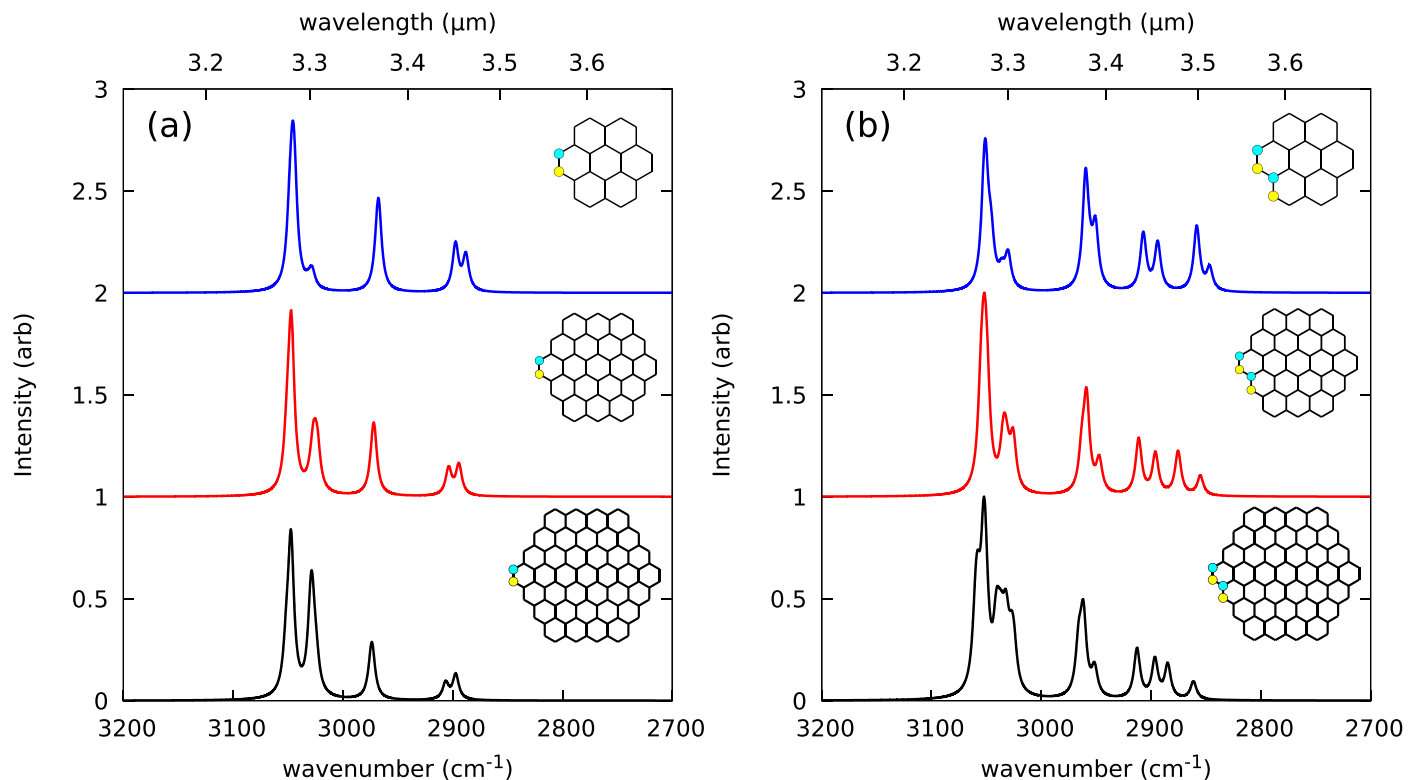


Figure 4. Convolved theoretical harmonic spectra of (a) the most stable isomer of $C_{24}H_{12+2}$ (top), $C_{54}H_{18+2}$ (center), and $C_{96}H_{24+2}$ (bottom) and (b) the fourth most stable isomer of $C_{24}H_{12+4}$ (top), $C_{54}H_{18+4}$ (center), and $C_{96}H_{24+4}$ (bottom). Isomers are schematically depicted as an inset.

some isomers (see the green arrows in Figure 5) are due to the C–H stretching of H atoms in tertiary positions, which have only one hydrogenated neighboring C atom. In the second spectrum from the top in Figure 5 we can observe that there are two bands associated with H atoms in tertiary positions. The

difference between the two is that one has one hydrogenated neighboring C atom (green arrow) whereas the other has two (orange arrow). The latter results in a band around $3.51 \mu m$ as was observed for hydrogenated PAHs presented in Figure 4(b) and that can be identified in the spectra of other isomers of

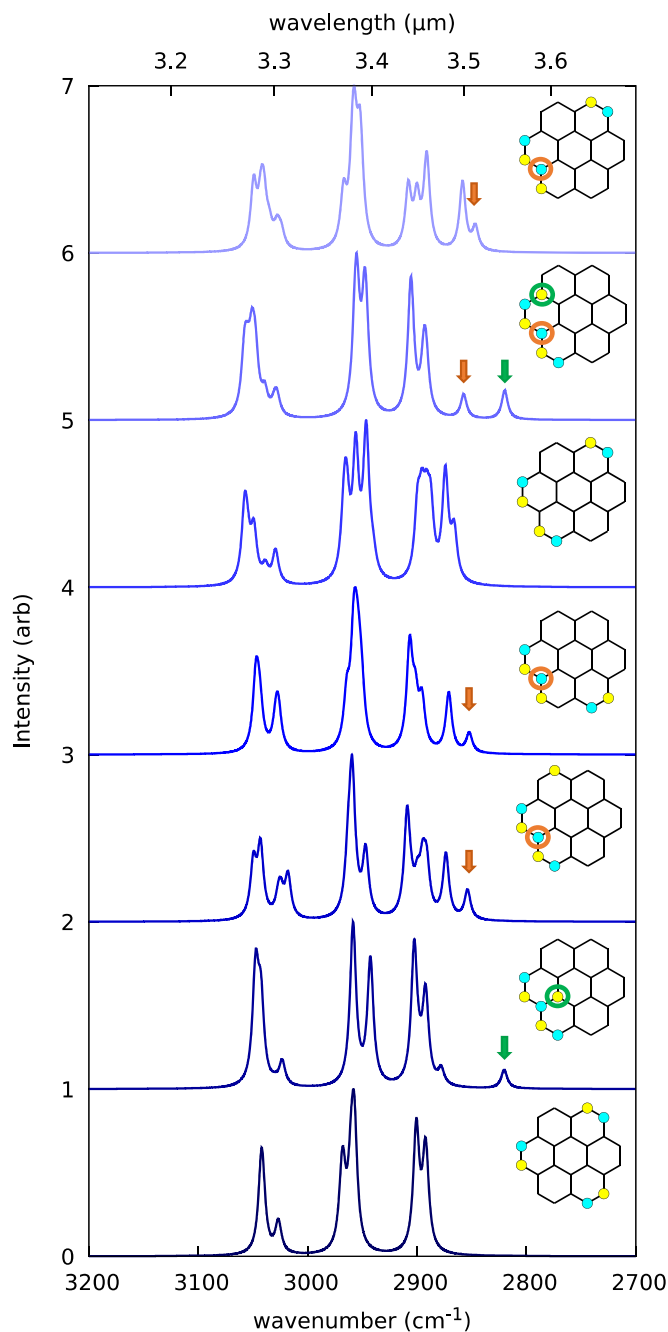


Figure 5. Convolved theoretical harmonic spectra of the most stable isomers of $C_{24}H_{12+6}$. Isomers are schematically depicted as an inset. Bands located around 3.51 and $3.56 \mu m$ are indicated by orange and green arrows, respectively. The corresponding H atoms that mostly contribute to those bands are identified with the same colors.

Figure 5. Thus, results reveal that when tertiary positions become hydrogenated, bands at longer wavelengths appear and their position depends on the neighboring atom’s environment, with the C–H bonds that have less hydrogenated neighboring C atoms being the ones that appear at longer wavelengths. This is consistent with previous results (Steglich et al. 2013) showing that fully hydrogenated coronene $C_{24}H_{12+24}$ presents an intense band at $3.51 \mu m$ corresponding to the tertiary CH stretches.

Figures 6 and 7 show results for four stable isomers of $C_{54}H_{18+12}$ and $C_{96}H_{24+10}$, where the same conclusions can be

drawn: bands that result from hydrogenation in tertiary positions give rise to spectral features around 3.51 and $3.56 \mu m$ if these H atoms are surrounded by one or two additional hydrogenated C atoms, respectively. For instance, the band observed around $3.51 \mu m$ for three different isomers of $C_{96}H_{24+10}$ depicted in Figure 7 shows that the position of this band is not exactly constant for the different isomers but that it appears around the same frequency range. Trends observed are general for the other hydrogenated PAHs. It is also worth noting that the absence of bands at 3.51 and $3.56 \mu m$ is characteristic of hydrogenated PAHs in which extra H atoms are located by pairs in different parts of the PAH (isomers a and e of Figure 5 and the lower spectrum in Figures 6 and 7, which include the most stable hydrogenated PAHs predicted at the DFT level).

4. Astrophysical Implications

Hydrogenated PAH molecules have been experimentally and theoretically studied in their neutral and cationic forms (Thrower et al. 2012; Klärke et al. 2013; Cazaux et al. 2016, 2019; Jensen et al. 2019; Campisi et al. 2020). It has been demonstrated that specific isomeric forms are more abundant than others but that hydrogenation on the different positions (secondary and tertiary) occurs. For example, in the case of neutral coronene, the preferred isomeric forms of 2, 4, and 6 H atoms of the main and alternative sequences of hydrogenation (Jensen et al. 2019) are among the most stable isomers shown in Figure 3. The structures with six additional H atoms previously found (isomers b and d) but also others found in this work (isomers c, f, and g) of Figure 3 are already hydrogenated in tertiary positions, therefore showing that even for low degrees of hydrogenation, tertiary positions are hydrogenated.

The conditions in some regions of the ISM, for instance at the surface of PDRs, cause hydrogenated PAHs to become ionized, showing stable structures that are different from those of their neutral counterparts (Cazaux et al. 2019). In addition, it has been shown that H atoms attached to cationic PAHs can roam over the peripheral carbon atoms producing a “scrambling” of the different isomers upon absorption of interstellar FUV photons (Wiersma et al. 2020). Thus, although not all possible isomers are going to contribute equally to spectral features in the ISM, it is still under study which are the different isomers that contribute depending on the reactions that can take place under the particular conditions of the ISM. If “scrambling” of H atoms inside PAHs is a feasible process, it can be expected that the most stable isomers may have strong contributions to the observed AIBs. Thus, their identification would be crucial for a correct interpretation of the astronomical IR spectra.

The IR features obtained from astronomical observations are key to identifying molecular species in space. From our study we have rationalized the differences in the $3 \mu m$ region of the spectrum of the different isomers of hydrogenated PAHs showing that hydrogenation in tertiary positions gives rise to spectral features around 3.51 and $3.56 \mu m$ depending on the number of surrounding H atoms and that these positions are practically independent of the size of the PAH. Thus, a rough prediction of the IR spectra in the $3 \mu m$ region can be made just by looking at the molecular structure. These longer wavelength IR bands, although not very intense, are likely to increase their relative intensity when the effect of anharmonicity and Fermi

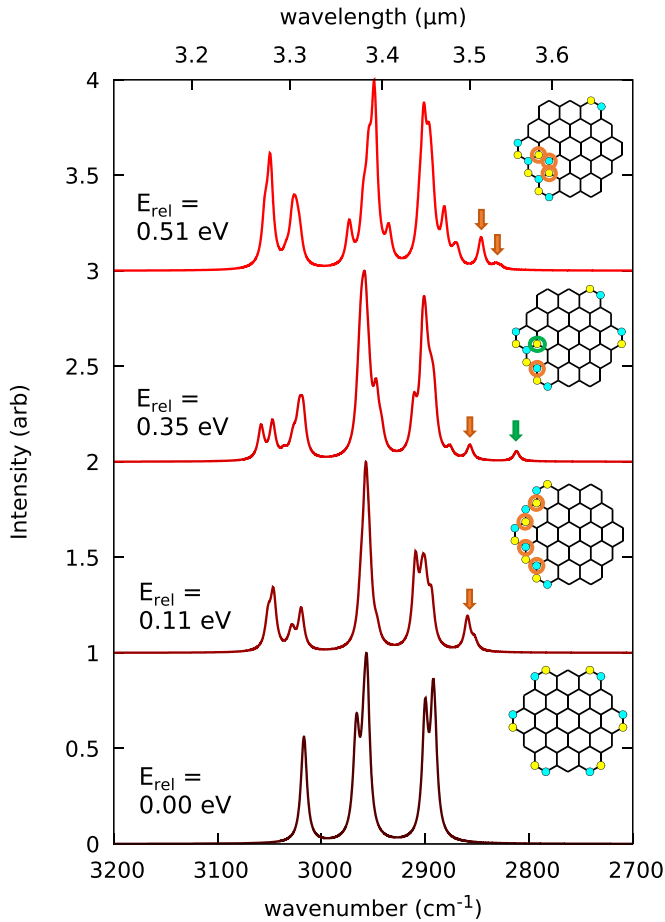


Figure 6. Convolved theoretical harmonic spectra of four stable isomers of $C_{54}H_{18+12}$. Isomers are schematically depicted as an inset. Bands located around 3.51 and $3.56 \mu\text{m}$ are indicated by orange and green arrows, respectively. The corresponding H atoms that mostly contribute to those bands are identified with the same colors. Energy differences (E_{rel}) correspond to the DFT values.

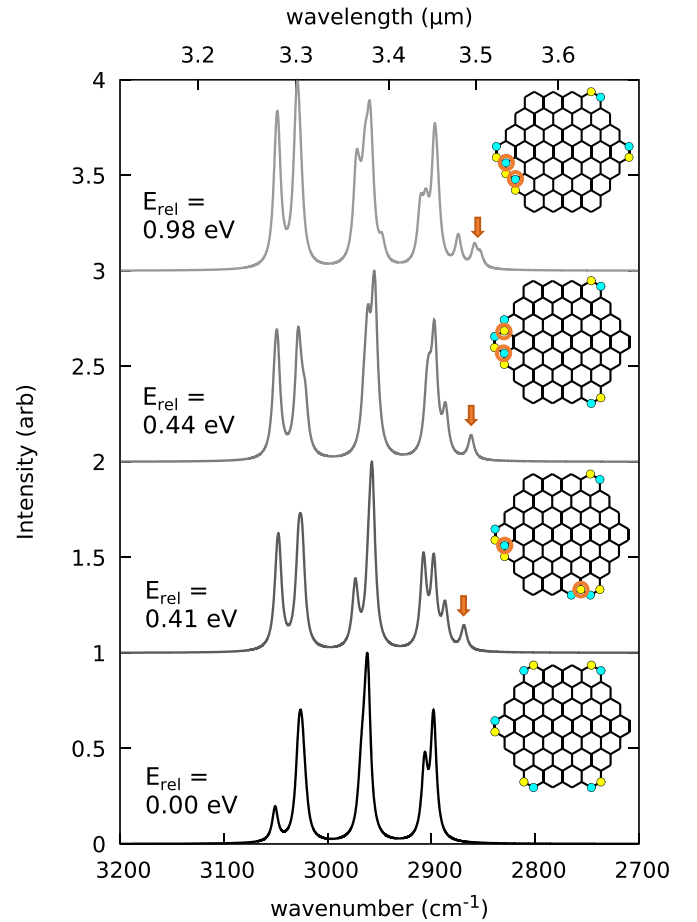


Figure 7. Convolved theoretical harmonic spectra of four stable isomers of $C_{96}H_{24+10}$. Isomers are schematically depicted as an inset. Bands located around 3.51 and $3.56 \mu\text{m}$ are indicated by orange and green arrows, respectively. The corresponding H atoms that mostly contribute to those bands are identified with the same colors. Energy differences (E_{rel}) correspond to the DFT values.

5. Conclusion

resonances is included. As illustration, it was shown that some features in this region are not systematically predicted in the harmonic approximation (Maltseva et al. 2018) and that for relatively higher degrees of hydrogenation, a larger number of features appears when including anharmonicity and Fermi resonances (Mackie et al. 2018). Thus, one may expect that besides the bands obtained in the harmonic approximation, more combination bands and overtones will show up. We have demonstrated that the presence of bands at longer wavelengths not only can be the consequence of including anharmonicity but also of the presence of different isomers of hydrogenated PAHs.

Our study shows that hydrogenated PAHs are good candidates to explain all the features observed in the $3 \mu\text{m}$ region of the IR spectrum in astronomical environments. However, we cannot discard that other molecules containing C–H bonds and with a potentially large number of isomeric forms can also contribute in the same region of the spectrum. For instance, the secondary and tertiary C–H stretching bands of diamonoid molecules can also contribute to the 3.46 and $3.51 \mu\text{m}$ bands (Allamandola et al. 1992; Pirali et al. 2007).

Previous studies have shown that hydrogenated PAHs can be responsible for some of the small features found in the $3 \mu\text{m}$ region of the IR spectrum. In particular, the bands found at 3.40 , 3.46 , and $3.51 \mu\text{m}$ (Mackie et al. 2018). However, only the IR spectrum of a few hydrogenated PAHs among all possible isomeric forms have been experimentally measured with high resolution. In this study, we have used a new methodological approach to consider a large number of isomers of hydrogenated PAHs and to select the most relevant ones based only on energetic criteria. We have shown that the predicted structures lead to additional bands not observed from isomers considered in previous studies.

The computation of theoretical harmonic spectra for some of the most stable structures has evidenced that hydrogenated PAHs can account for all of the AIBs observed in the $3 \mu\text{m}$ region of the IR spectrum resulting from astronomical environments, that is, the intense $3.3 \mu\text{m}$ band associated with aromatic C–H stretching vibrations and the small features at 3.40 , 3.46 , 3.51 , and $3.56 \mu\text{m}$ related to the aliphatic C–H stretching vibrations. The bands that appear at longer wavelengths (3.51 and $3.56 \mu\text{m}$) are explained by considering isomers that contain some additional hydrogen atoms in tertiary positions and that are not totally surrounded by hydrogenated

carbon atoms. The tertiary positions, which are found to be hydrogenated even for not very high degrees of hydrogenation at lower energies, are even more abundant for isomers at higher energies. It will be interesting to experimentally measure the spectra of other isomers with H atoms in tertiary positions or to obtain more sophisticated theoretical spectra. We think that this work could help in the identification of the different isomers that can be behind the AIBs. In particular, our results could be relevant to interpret IR astronomical spectra that will be obtained by the James Webb Space Telescope in the near future.

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