# The infrared spectra of nonplanar polycyclic aromatic hydrocarbons with five- or seven-membered rings

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A B S T R A C T

The infrared (IR) spectra are computed for compact polycyclic aromatic hydrocarbons (PAHs) with one five- or one seven-membered central ring, which have a bowl and saddle shape, respectively. In spite of the large geometric distortion compared with the planar PAHs with only six-membered rings, the IR spectra are surprisingly similar. Species with more than one five-membered ring show larger difference compared with typical PAHs. The C–C modes in the "ball" shaped $C_{60}$ and $C_{70}$ are shifted somewhat from those in typical PAHs. The ions of $C_{60}$ and $C_{70}$ show the typical enhancement of these modes compared with neutrals. Cases where the B3LYP method fail are discussed as is the choice of functional.

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## 1. Introduction

The infrared (IR) emission from the polycyclic aromatic hydrocarbons (PAH) has been observed in numerous sources in our Galaxy and in other galaxies. While the overall features of the PAH emission are similar, the finer details of the observed spectra vary from source to source (see the review by Tielens [1] and references there in). These variations presumably arise from changes in the species and/or the conditions in the emission region. The observed IR emission is the final step in a complicated process. Absorption of visible or ultraviolet light from the nearby stars excites the PAH molecules to higher electronic states, which can either reradiate the energy or internally convert to the ground electronic state and radiate the energy in the IR. There has been work [2,3] on modeling this entire process. The alternative is to assume [4,5] that efficient internal conversion results in highly vibrationally excited ground state PAH molecule and ignore the details of the excitation process. The vibrational energy is therefore set equal a photon energy representative of the exciting star. The energy is radiated in the IR until the molecule reaches the background temperature before another photon is absorbed. This simplified model has had some success [4,5] in modeling PAH IR emission. This suggests that the biggest limitation to completely understanding the observed emission and its variation with source is the completeness of the IR data that any model uses. With this in mind, we have assembled a database [5] containing the IR spectra of more than 600 PAH species and tools to model the emission process.

Our database contains planar or nearly planar PAH molecules. However, the identification of $C_{60}$, $C_{60}^+$, and $C_{70}$ emission [6–9] clearly shows that under some circumstances curved PAH-like species can be formed. Two types of nonplanar PAHs are easy to imagine; the substitution of six-membered rings with five-membered rings that leads to bowl- and ball-like PAHs and the substitution of a six-membered ring by a seven-membered ring that leads to saddle shaped PAHs. We investigated [10] some species with five-membered rings, but they were smaller in size than those believed to exist in space. Some PAHs with five and seven membered rings in the same PAH have been studied [11,12]. While most of these species have spectra that looked like of a typical PAH, Yu and Nyman [12] suggested that a subclass of these species could be responsible for the band at 6.9 μm. Galué studied [13] species derived from $C_{54}H_{18}$ and $C_{96}H_{24}$ with one or more five-membered rings. The addition of multiple 5-membered rings for $C_{54}H_{18}$ resulted in a shift of the 6.3 μm band to shorter wave length. Smaller effects were seen for $C_{96}H_{24}$. Galué suggested that multiple 5-membered rings could be responsible for the shift 6.3 μm observed in some astronomical sources. In this work, we determine the 0 K IR absorption spectra of a series of these nonplanar PAHs containing up to 112 carbon atoms with five- or seven-membered rings and compare their spectra with similar sized planar species.

## 2. Model and methods

The molecules studied in this work are shown in Fig. 1. The series of molecules in the top row have a single five-membered ring in the center that causes the molecule to curve up into a bowl-like

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shape. The molecules in the middle row have multiple five-member rings. The smallest member, $C_{30}H_{10}$, still has a bowl shape, but with more curvature than those in the top row, while the larger two species have closed on themselves to form ball-like structures. The bottom row shows the molecules with a central seven-membered ring. This causes the PAH to pucker, leading to a saddle shape with the two edges bending up and two bending down.

Most of the calculations are performed using the hybrid B3LYP/4-31G approach [14–16], as this level has been shown [17] to yield reliable IR spectra for PAH species. The B3LYP approach can fail to yield reliable IR spectra when there is a very low-lying excited state [18]. As has been discussed previously [10,19], switching to the BP86/4-31G approach [20,21] can commonly yield reliable IR spectra in these cases. Thus we use the BP86/4-31G approach whenever we have concerns about the reliability of the B3LYP/4-31G results.

The failure of the B3LYP/4-31G approach seems to be more common for large PAHs than small PAHs. We therefore reconsider the question of the best fall back functional using the largest molecule with a central five-membered ring. This study is reported in the Appendix A. In this work we tested some functionals that were not calibrated previously [19]. The results of this study yields the same conclusion found previously for different molecules, and this supports our use of the BP86 as the fall back functional.

In addition to the choice of functional, the size of the basis set can affect the results. The choice of the 4-31G basis set was originally made as a compromise between computer time and accuracy of the IR spectra. The improvements in the computational methods and the increases in computer power since our first PAH studies, mean that it is now possible to compute the IR spectra using larger basis sets than 4-31G. However, the 4-31G basis set is still our preferred choice because it is consistent with that used in our PAH database [5]; that is, we feel that it is important to keep the level of theory as constant as possible, since this data is being used to model the observed IR emission. In this work we consider nonplanar molecules where the bonding is strained compare to that in typical PAHs, therefore in addition to testing different functionals, we also performed some calibration calculations using the larger 6-31G* basis set.
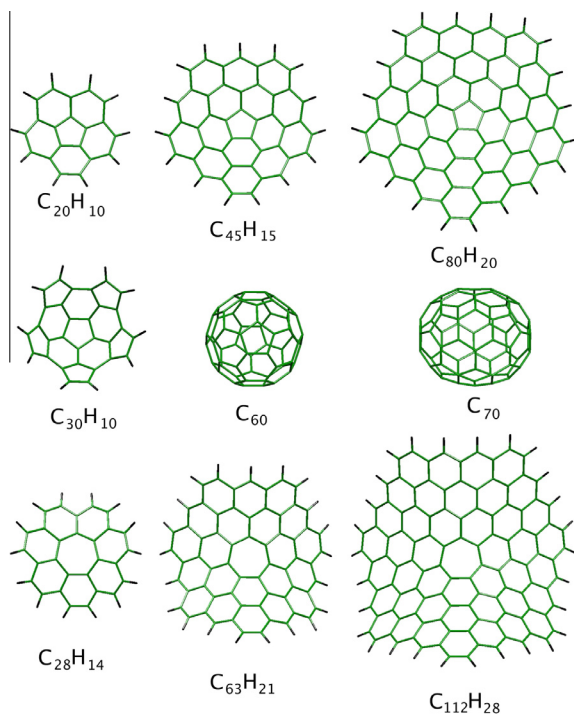
We use the same basis sets for the cations, neutrals, and anions. If the extra charge were localized in the anions, the lack of diffuse functions could lead to significant errors in the computed IR spectra. However, the charge is rather delocalized over the PAH and tests show [11] that the addition of diffuse functions to $C_{24}H_{12}$ makes only a small difference in the IR spectra and the size of this basis set effect decreases rapidly with increasing PAH size. Thus the small 4-31G basis set can be applied to all three charge states for the size of the molecules studied in this work.

We have shown previously [17,19] that a single scale factor for the B3LYP/4-31G approach brings the computed harmonic frequencies into good agreement with experiment. In previous work, we also used a single scale factor for the BP86/4-31G approach because using two scale factors (one of the C–H and a second for all other bands) made virtually no reduction in the errors. However, the BP86/4-31G approach showed systematic difference with the B3LYP in the 10–15 μm region. Therefore in this work we use three scale factors for the BP86/4-31G approach: one of the C–H stretch, a second for 6–9 μm, and a third for all wave lengths longer than 9 μm. In addition, we minimize the sixth power of the difference between theory and experiment. This slightly increases the average absolute error, but significantly reduces the maximum error. This procedure reduces the difference between the B3LYP and BP86 approaches in the 10–15 μm region and hardly affects the rest of the spectra. The scale factors deduced for PAH molecules might not be appropriate for the in ball shaped molecules due to their strained structure. Therefore, in this work we determine scale factors for the B3LYP and BP86 approaches for both the 4-31G and 6-31G* basis sets for $C_{60}$ and compare them with those determined for the unstrained, planar naphthalene.

The ions of many of the species studied in this work will undergo a Jahn–Teller distortion. If the distortion leads to deep minima, the harmonic frequencies for the distorted structure should be as reliable as for species without a Jahn–Teller splitting. This is not the case for most PAH species where the distortion is very small, probably due to the stiff multi-ring structure. For example, the Jahn–Teller stabilization for $C_{80}H_{20}^+$ is 150 cm$^{-1}$. This is very similar to the 140 cm$^{-1}$ found previously [22] for $C_{96}H_{24}^+$. In such cases dynamic Jahn–Teller effects could be important. However, as discussed previously [8,23,22,24], theory using the harmonic
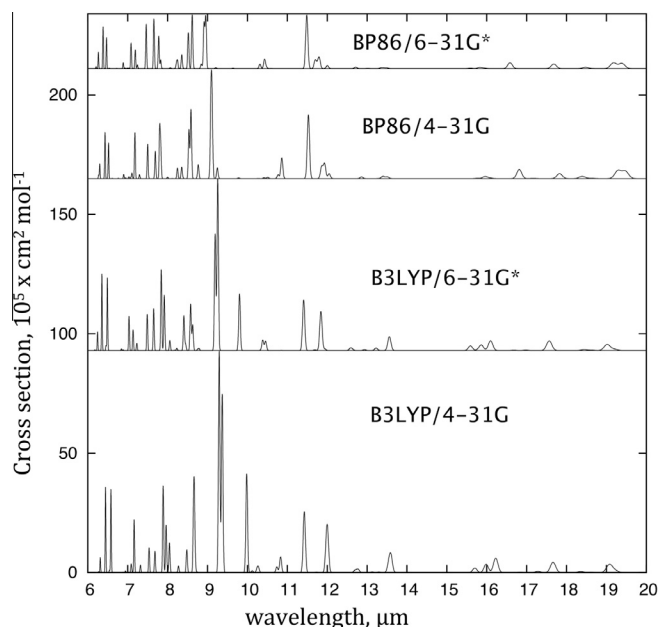


Fig. 1. The molecules studied in this work.



Fig. 2. Spectra $C_{20}H_{10}^+$ as a function of level of theory. The spectra have been shifted in $y$ for clarity.