Formation of Polycyclic Aromatic Hydrocarbons exhibiting (5,7)-member ring defects in Planetary Nebulae

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Abstract:

Polycyclic aromatic hydrocarbons (PAHs) are nowadays widely accepted as one of the carriers of the ubiquitous aromatic infrared (IR) bands. The IR spectra of many planetary nebulae (PNe) are dominated by mid-IR emission features, attributed to the IR fluorescence of PAHs. Recent observations of PNe show the simultaneous presence of mid-IR features attributed to neutral fullerene molecules (i.e. C₆₀) and PAHs (García-Hernández et al. 2010, ApJ, 724, 39). In general, PNe show evidence of mixed chemistry with emission from PAHs, silicate dust, fullerenes and contributions from other molecular components. The still unidentified IR features seen in PNe require further laboratory and



observational investigations.

We present a theoretical study of the IR spectra of PAHs containing (5,7)-member ring defects. Using density functional theory, we investigate the effects such defects have on the IR spectra of pyrene ($C_{16}H_{10}$) and coronene ($C_{24}H_{12}$). In addition, we explore parts of the potential energy surface of the neutral species and discuss alternative formation pathways, especially in the environment of PNe.

The molecules:

Coronene and pyrene can be seen as limiting or prototypical cases in various respects. They are among the smallest hydrocarbons that can exhibit (5,7)-ring defects. Previous work (Yu et al. 2012, ApJ, 751, 3) has raised the suspicion that effects of such defects might be more intriguing with decreasing size of the PAHs. Our investigations represent the limiting cases with respect to the size of the PAHs. We show investigations on the minimal energy pathway between the ground and (5,7)-member ring defected states. Doing so, it turns out that while coronene proceeds via a Stone-Wales transition from its ground to its defected state, pyrene does not; and while pyrene exhibits a Stone-Wales defect, coronene does not. The latter is the underlying reason for another respect in which the two studied molecules can be regarded as limiting and prototypical. Whereas pyrene retains some of its symmetry due to the symmetry exhibited by the Stone-Wales defect itself, coronene loses much more of its symmetry. To study these small systems is thought to be an important step towards a substantial understanding of the role of (5,7)-ring defects for the IR spectra of PAHs.



The modeling:

The geometry optimizations and harmonic frequency calculations were mostly performed using the B3LYP density functional theory. An exploration of parts of the potential energy surface of the neutral species to investigate their thermodynamic stability was done using the G4(MP2) extrapolation method in order to obtain accurate energies for local minima and transition states.

We get exactly the same IR spectra for the unmodified coronene and pyrene as the NASA Ames PAH IR Spectroscopic Database (Bauschlicher et al. 2010, ApJS, 189, 341). By this we believe that all our computed spectra are reliable.



Figure 1: Possible formation pathways of the (5,7)–member ring defects depicted for (a)-(e) pyrene and (f)-(h) coronene. (a)-(e): Transition of pyrene to 7755-pyrene via a minimal energy pathway on the potential energy surface of $C_{16}H_{10}$. (f)-(g): Stone-Wales transition connecting coronene and 755-coronene as the minimal energy pathway on the potential energy surface of $C_{24}H_{12}$. Several of the aromatic hexagons are replaced by an adequate amount of pentagons and heptagons, see the examples for 7755-pyrene (e) and 755-coronene (h).

Figure 2: A comparison between the IR spectra of pyrene (green) and pyrene exhibiting the (5,7)-ring defect (blue). The changes in intensity and shifts in positions of the lines in the spectrum are clearly visible. In grey we show the transmission curve of the atmosphere, calculated with the code LNFL/LBLRTM (Clough et al. 2005, JQSRT, 91, 233) for airmass = 1 and a years averaged atmospheric profile scaled to 3mm PWV (precipitable water vapor), a typical PWV value for Paranal.



Results:

In figure 2 and 3 we show the resulting spectra of our calculations for pyrene and coronene. As a result of the transformations in the molecule, both of them lose their typical spectroscopic signature. There is a clear difference in the spectrum of the unmodified molecule and the one exhibiting the (5,7)–member ring defect. The formation of these (5,7)-ring defects in PAHs may be well supported in PNe. The environment strongly enables the transition from the ground state to the defect state. Therefore the knowledge of the IR spectra of these molecules will support the investigations in understanding the unidentified IR emission bands in PNe.

Figure 3: A comparison between the IR spectra of coronene (green) and coronene exhibiting the (5,7)-ring defect (blue). Same as for pyrene, the lines change in intensity and position within the spectrum. In grey again the transmission curve of our atmosphere, to get an idea about the observability and detectability. For both coronene and pyrene we can see further features at longer wavelengths.

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