PAH clusters as interstellar very small grains

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Abstract. PAH clusters are one candidate species for the interstellar "very small grains" or "VSGs", i.e., dust grains small enough to be stochastically heated and contribute to the aromatic infrared emission bands (AIBs). This possibility motivated laboratory experiments on the infrared spectroscopy of PAH clusters using matrix isolation spectroscopy. The spectral shifts due to PAH clustering in argon matrices provide clues for the AIB contribution from PAH clusters in the interstellar medium. Here we review results from a number of small PAH species, extrapolation to the much larger PAHs believed to be present in the interstellar medium, and the implications for a PAH cluster contribution to the VSG population.

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1. Introduction

Polycyclic aromatic hydrocarbons (or PAHs) have long been considered to be the principal carrier of the interstellar aromatic infrared emission bands (AIBs) seen throughout the Galaxy and are believed to have a major role in the evolution of the interstellar medium and star formation (Tielens 2008, 2013).

The contribution of PAH van der Waals clusters to the AIBs has been uncertain due to a lack of experimental data. Léger and Puget (1984) suggested that a $\sim$5 Å "sphere" of graphite would have AIB emission similar to planar large PAH molecules. An alternative theory is that the PAH clusters are instead responsible for the broad emission plateaus that seem to underly the much narrower AIBs (Bregman *et al.* 1989; Allamandola *et al.* 1989). This model is supported by observations suggesting that the degree of clustering produces variability of the plateau emission relative to the AIBs (Bregman *et al.* 1989).

Rapacioli *et al.* (2005) used a blind signal separation analysis of IR emission spectra of photodissociation regions to identify several broad component populations of AIB emitting molecules. One component of emitters had a modestly redshifted 11.2 μm band compared to neutral PAHs and was identified with very small grains (in this context, dust grains small enough to be stochastically heated and contribute to the AIBs, e.g., Puget & Léger (1989)). Based upon spatial maps of the component spectra, these very small grains appeared to be evolving into the PAH molecular component of the AIB emitters (Rapacioli *et al.* 2005; Berné *et al.* 2007) and may contain up to 80% of the carbon within the AIB carriers in some regions (Pilleri *et al.* 2012).

2. Laboratory experiments

To address the contribution of PAH clusters to the AIBs, we conducted laboratory experiments using IR matrix isolation spectroscopy to investigate the effects of cluster formation on the IR spectra of PAHs (Roser & Allamandola 2010; Roser *et al.* 2014; Roser & Ricca 2015). We co-deposited a selected PAH molecule (sublimed using external

heating) and argon matrix onto a CsI window held at a constant 5 K by a closed-cycle cryostat. An FTIR spectrometer then measured IR transmission spectra of the deposits.

To avoid temperature processing of the deposited ices to drive PAH clustering (cf. Witteborn *et al.* (1989)), we instead studied an ensemble of newly deposited PAH/argon ice mixtures. Most PAH molecules are well-isolated from one another in the low concentration (typically Ar/PAH = 1000–2000) deposits. At higher PAH concentrations there are more random associations of PAH molecules embedded within the ice matrix and cluster features in the spectra are more evident (see Roser *et al.* (2014) for further details).

Theoretical calculations of the IR absorption spectrum of small PAH clusters, generally dimer to tetramer in size, were used to investigate the cluster structures potentially forming in the experiments (Roser *et al.* 2014; Roser & Ricca 2015).

3. Results and Conclusions

Laboratory experiments and associated theoretical calculations identified spectral shifts of the C–H out-of-plane (CH_{oop}) bending modes due to clustering as diagnostic of the preferred cluster structures formed in the matrix. Linear or bent-linear PAHs (naphthalene, anthracene, phenanthrene, and chrysene) produced CH_{oop} cluster features that were blueshifted relative to the monomer CH_{oop} positions, indicating a preference for tee-oriented clusters. We observed redshifted CH_{oop} cluster features for the compact PAHs pyrene and benzo[*ghi*]perylene, which are indicative of parallel-oriented clusters.

Although the exact structures of the interstellar PAHs are not known, we anticipate that compact PAHs are generally more stable and therefore more likely to be present in the interstellar medium. We therefore predicted that clusters of the interstellar PAHs will have redshifted CH_{oop} bands relative to their monomers (Roser & Ricca 2015). Assuming that these cluster bands have an observed redshift similar to the observed 1–4 cm^{-1} for pyrene and benzo[*ghi*]perylene, our results better support the model of PAH clusters as a very small grains component as identified by Rapacioli *et al.* (2005). PAH clusters may still contribute to the underlying plateaus, but cluster redshifts of ∼10 cm^{-1} alone do not explain a CH_{oop} region plateau of some 200–300 cm^{-1} in width (Hony *et al.* 2001).

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