PAHs and the Universe
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SPECTROSCOPY OF PROTONATED AND DEPROTONATED PAHS

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Abstract. The spectroscopic properties of protonated and deprotonated PAHs are investigated through Density Functional Theory (DFT) calculations, with reference to their potential astrophysical significance. Attention is focussed on electronic and rotational spectra.

1 Introduction

Evidence for polycyclic aromatic hydrocarbons (PAHs) in the interstellar medium (ISM) is drawn almost exclusively from their infrared emission spectra – the so-called "unidentified" infrared (UIR) emission bands (see Tielens 2008, and references therein). However, it has proved to be very difficult to identify an individual PAH from these spectra as the features are indicative of molecular groups rather than particular molecules; observation of far-IR spectra may alleviate this problem as discussed by Joblin *et al.* elsewhere in this volume. The spectra show significant variation between and within objects so if knowledge of the underlying mix of molecules were available then profile modelling could be very productive and act as a probe of astronomical conditions. In contrast to infrared spectra, electronic and rotational spectra are very dependent on the specific molecule with major differences present even between isomers. For this reason it is of interest to undertake a theoretical investigation of the electronic and rotational spectroscopic properties of PAHs, in part as a guide for laboratory experiments. We present here predicted electronic spectra of protonated and deprotonated PAHs, which are generally closed-shell molecules and have positive and negative charge, respectively (see Fig. 1). The research seeks to contribute to the long-standing problem of the diffuse interstellar bands (DIBs) in the optical region (see Snow & Destree and Cox, this volume), for which PAHs are attractive candidates. We also explore the possibility of detection of specific PAHs through rotational spectroscopy.

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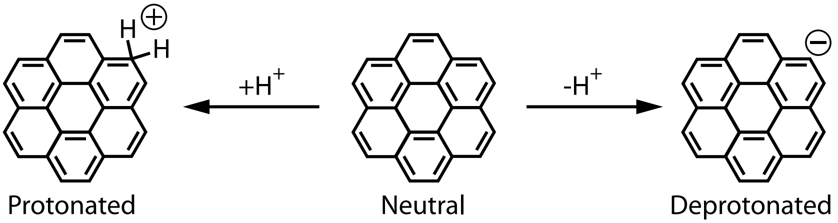

Fig. 1. Illustration of the relation between neutral coronene ($C_{24}H_{12}$) and its protonated and deprotonated forms. All three molecules have closed-shell electronic structures. In each case the full aromaticity of the structure is maintained

2 Theoretical methods

We employ Density Functional Theory (DFT) to calculate molecular structures and energetic properties, and its time-dependent form (TD-DFT) for predictions of approximate electronic absorption spectra. Geometry optimisations and TD-DFT calculations were conducted using the B3LYP functional with a 6-31G* basis set for protonated PAHs and a 6-31+G** basis (Hehre *et al.* 1972; Hariharan *et al.* 1973) for deprotonated (anionic) PAHs. The latter basis set is not a standard part of the Q-Chem package used in this work (Shao *et al.* 2006).

3 Protonated PAHs ($HPAH^+$)

3.1 Electronic spectroscopy of protonated PAHs

Alongside research on PAHs in connection with the UIR bands, there is long-standing interest in their possible rôle in relation to the DIB band problem (see Herbig 1995 and Sarre 2006, and references therein). The potential significance of protonated PAHs, denoted here $HPAH^+$, in connection with this problem was first highlighted by Le Page *et al.* (1997) and both this aspect and the chemistry of $HPAH^+$ molecules have been discussed in subsequent papers (Snow *et al.* 1998; Le Page *et al.* 2003). Although small-to-medium sized neutral PAHs generally absorb in the UV or near-UV part of the spectrum, and in principle would be detectable in absorption in the spectra of background stars, no such evidence has yet been found. Larger neutral PAHs such as hexa-peri-hexabenzocoronene ($C_{42}H_{18}$) with absorption bands in the 4000–4500 Å range, would appear to be promising candidates, but to date no correspondence with DIBs has been found (Kokkin *et al.* 2008). Consequently attention has also been paid to ionic forms of PAHs and, partly because of ease of production in the laboratory, to radical cations which generally absorb in the visible spectral region. However, being open-shell molecules, they are expected to be reactive and so alternative ionic forms including

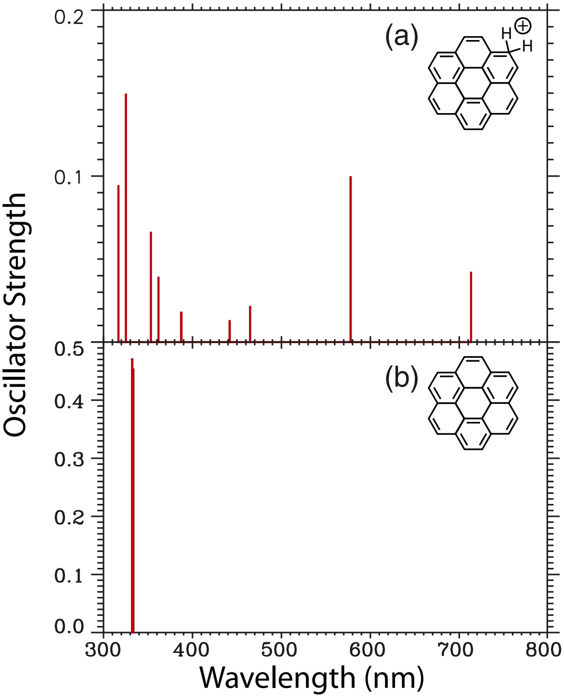

Fig. 2. Calculated electronic transitions of (a) protonated coronene and (b) coronene.

protonated PAHs are worthy of consideration. At present laboratory recording of electronic spectra of $HPAH^+$ molecules at high-resolution is in its infancy but developing, as outlined in this Symposium. For large systems the only current theoretical method that lends itself to predicting electronic spectra is TD-DFT and the precision is low, being in the region of ± 0.3 eV. However, the results can still be very useful in identifying potential candidates. The calculated electronic absorption spectrum of *e.g.* protonated coronene differs markedly from its corresponding neutral parent molecule as seen in Figure 2. Although the protonated molecule has transitions in the near-UV, as is the case for the neutral molecule, it also has strong transitions in the visible part of the spectrum. Although the effect of protonation on the absorption spectrum of benzene has been known for many years, extension to polycyclic aromatic hydrocarbons is new. The precision of TD-DFT calculations is far too low to discuss any meaningful attribution of DIBs to specific molecules, but the semi-quantitative result is significant. In particular it may assist in planning laboratory experiments in the condensed (inert gas matrix) or, preferably, gas phase. The dissociation energies of protonated PAHs are lower than their neutral counterparts which does raise some question as to their photostability, although for large protonated PAHs fragmentation is expected to be reduced due to the very high density of states.

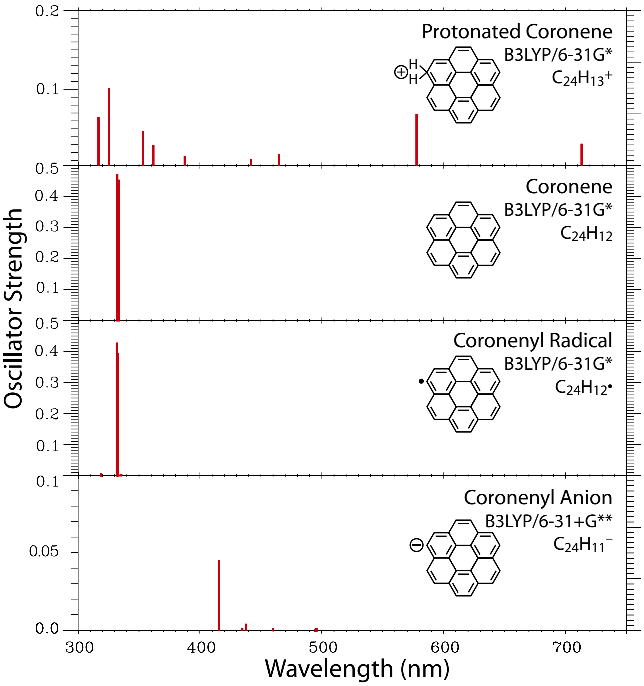

Fig. 3. Calculated transitions of protonated, neutral, radical and deprotonated coronene.

4 Deprotonated PAHs (PAH^-_{n-1})

As far as we are aware, deprotonated PAHs have not been considered explicitly in an astrophysical context. The analogous deprotonated polyacetylenes such as C_6H^- are the subject of intense current activity as recorded through their laboratory rotational spectra and corresponding studies by radioastronomy (McCarthy *et al.* 2006). PAH anions have been discussed in connection with interstellar chemistry and as possible contributors to the UIR bands, but generally in terms of the radical anion form (Bakes & Tielens 1998). The electron affinities of closed-shell neutral PAHs (Malloci *et al.* 2005) are a factor of 2–3 lower than those of the neutral radicals of interest here. We have computed using DFT the electron affinities of a number of radicals (values in eV, for the most stable isomer) as follows: pyrenyl (1.57), coronenyl (1.68) and ovalenyl (2.00). While these electron affinities are lower than for the polyacetylenic radicals they are still reasonably high and deprotonated anions should form readily through radiative electron attachment to the radical. Given the special nature of anions a different basis (6-31+G**) was employed. In all cases it is found that the negative charge is very localized at the site of proton removal.

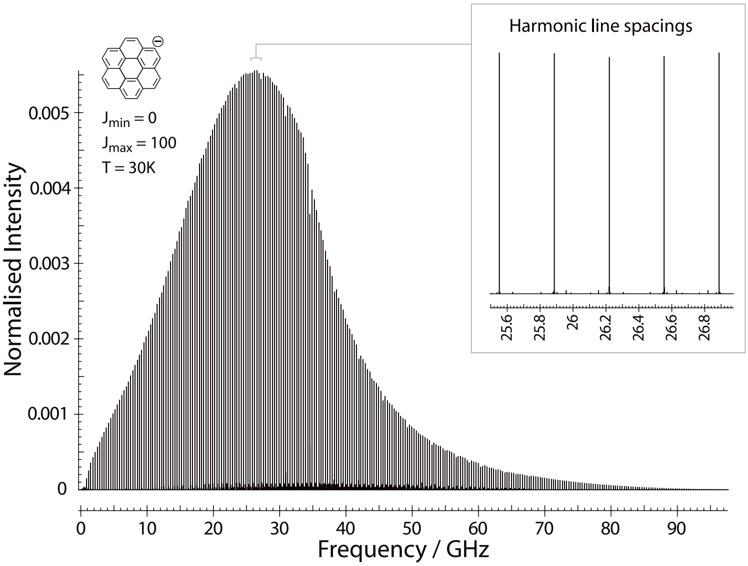

Fig. 4. Computed pure rotational spectrum of the coronenyl anion for J values up to 100 and at 30 K. The inset shows a ~1 GHz region of very nearly equally (harmonically) spaced lines.

4.1 Electronic spectroscopy of deprotonated PAHs

An example of a calculated electronic spectrum, for deprotonated coronene, is given in Figure 3 (lowest panel) where it is compared with corresponding spectra of the protonated, closed-shell neutral and neutral radical forms. These are all over-simplifications given that no vibrational band structure is included. The deprotonated coronene molecule exhibits just one significant band in the 300–750 nm region. The astronomical importance of this spectrum is uncertain because in diffuse and translucent clouds it is probable that photodetachment of the electron would destroy the anion; the calculated band at *e.g.* ~420 nm corresponds to a photon energy of ~3 eV which is well above the ionization energy of ~1.7 eV and so autodetachment would occur on photoexcitation. However, in denser regions this restriction is lifted. The possibilities of detection of such species by radioastronomy is now considered.

4.2 Rotational spectroscopy of deprotonated PAHs

The wealth of information gleaned about dense clouds through radioastronomy is reliant on the detected molecules possessing permanent electric dipole moments.

PAHs are very likely present in some form but as the simplest neutral systems are not polar no detection is possible through their rotational spectra. One modification, and one subjected to a radioastronomical search, is corannulene which has a significant dipole moment as it is non-planar (Pilleri *et al.* 2009). PAHs containing heteroatoms may also offer some opportunities. For PAH ions it is likely that protonated forms are present but these molecules are asymmetric tops and so the spectra are extremely complex with huge line-dilution. An alternative that might allow progress is the class of deprotonated PAHs. The removal of one peripheral hydrogen nucleus does affect slightly the centre-of-mass of an otherwise symmetrical PAH, but does not introduce asymmetry to the extent caused by off-plane hydrogens in protonated versions. Deprotonated PAHs are therefore very nearly symmetric top molecules but, crucially, possess large electric dipole moments which fall in the 10–14 Debye range for the coronenyl, ovalenyl, circumpyrenyl and cirumcoronenyl anions. Figure 4 shows a spectrum computed using the pgopher package (Western 2009) where at 30 K there are a large number of apparently barely resolved lines. However, the molecules are very nearly symmetric tops and so the main pattern is a series of equally spaced lines as the finer (K) structure is unresolved (see inset). While the capacity to calculate accurate predicted line positions for deprotonated PAHs is certainly beyond any current theoretical method, identification of harmonically related frequencies has played a significant role in identifying linear molecules in astronomical environments, including C_6H^-, and these could be sought in radio data.

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