

# Infrared spectra of protonated and hydrogenated corannulene (C<sub>20</sub>H<sub>10</sub>) and sumanene (C<sub>21</sub>H<sub>12</sub>) using matrix isolation in solid para-hydrogen - implications for the UIR bands

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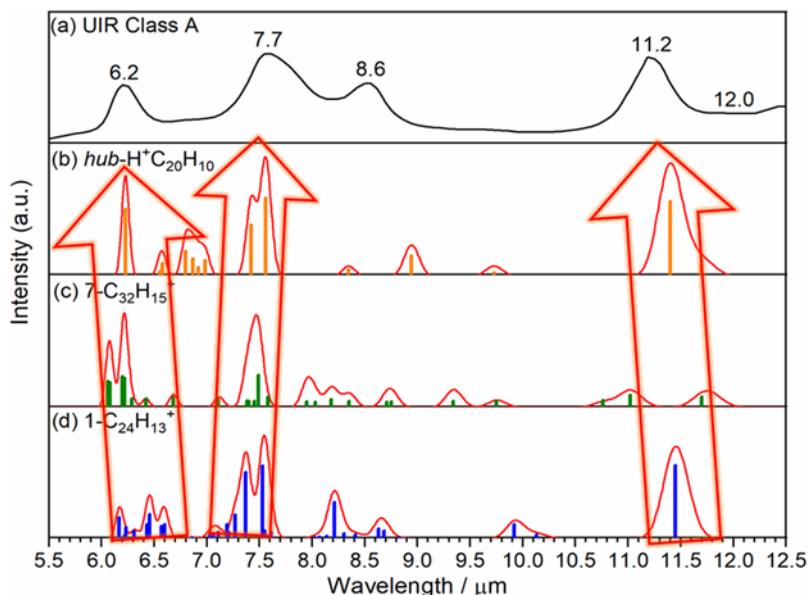
**Abstract.** Polycyclic aromatic hydrocarbons (PAH) and their derivatives, including protonated and cationic species, are suspected to be carriers of the unidentified infrared (UIR) emission bands observed from the galactic and extragalactic sources. We investigated the infrared (IR) spectra of protonated nonplanar PAHs: corannulene (C<sub>20</sub>H<sub>10</sub>) and sumanene (C<sub>21</sub>H<sub>12</sub>), that are regarded as a fragments of a fullerene, C<sub>60</sub>. The protonated corannulene H+C<sub>20</sub>H<sub>10</sub> and sumanene H+C<sub>21</sub>H<sub>12</sub> were produced in separate experiments by bombarding a mixture of corannulene/sumanene and para-hydrogen (p-H<sub>2</sub>) with electrons during deposition at 3.2 K. During maintenance of the electron-bombarded matrix in darkness the intensities of IR lines of protonated corannulene decreased because of neutralization by electrons that were slowly released from the trapped sites whereas the hydrogenated species were produced. The observed lines were classified into several groups according to their responses to darkness and secondary irradiation at 365 nm/385 nm LEDs. Spectral assignments were derived based on a comparison of the observed spectra with those predicted with the B3PW91/6-311+ +G(2d,2p) method. The observed IR spectrum of hub-H+C<sub>20</sub>H<sub>10</sub>, the most stable protonated isomer, resembles several bands of the Class-A UIR bands.

**Keywords.** astrochemistry, ISM: clouds, infrared: ISM, techniques: spectroscopic

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## 1. Introduction

Polycyclic aromatic hydrocarbons (PAH) are of significant importance in both terrestrial and extra-terrestrial environments. PAH gained attention in the interstellar chemistry as they are attributed to be the potential emitters of the Unidentified IR



**Figure 1.** Comparison of UIR bands with experimental infrared spectra of H+PAH in solid *p*-H<sub>2</sub>. (a) UIR Class A spectrum observed from the Iris nebula, NGC 7023, (b) *hub*-H+C<sub>20</sub>H<sub>10</sub>, (c) protonated ovalene (7-C<sub>32</sub>H<sub>15</sub><sup>+</sup>) and (d) protonated coronene (1-C<sub>24</sub>H<sub>13</sub><sup>+</sup>). Experimental spectra are presented with sticks of which the heights represent integrated intensities. Solid lines represent spectra convoluted with Gaussian profiles of fwhm 30 cm<sup>-1</sup>.

(UIR) emission bands. However, the exact forms of PAHs that could be responsible for the UIR band still remains a major challenge. Since proton sources such as H<sup>+</sup> and H<sub>3</sub><sup>+</sup> are abundant in interstellar medium (ISM), the proton transfer reactions to produce protonated species are likely to occur. Because the proton affinities of PAH are high, protonated PAH are postulated to be present in the ISM (Pathak & Sarre (2008)).

Corannulene (C<sub>20</sub>H<sub>10</sub>) and sumanene (C<sub>21</sub>H<sub>12</sub>) are fragments of Bucky ball C<sub>60</sub> and have a bowl-like structure. They were proposed to be intermediates in the formation of fullerenes in outer space (Rouillé & Jäger (2008)). Protonated corannulene (H+C<sub>20</sub>H<sub>10</sub>) and sumanene (H+C<sub>21</sub>H<sub>12</sub>) hence could be of astrophysical significance and it is imperative to investigate the infrared spectra of H+C<sub>20</sub>H<sub>10</sub> and H+C<sub>21</sub>H<sub>12</sub> in the laboratory.

## 2. Experiment

Our recent technique of using electron bombardment on a *p*-H<sub>2</sub> matrix to produce protonated/hydrogenated species cleanly and efficiently can provide direct IR absorption spectra covering a wide spectral range with narrow lines (Wu *et al.* (2004)). The experiments were carried out with a closed-cycle helium refrigerator, capable of cooling to 3.2 K, which was coupled with a FTIR having an HgCdTe detector to cover the spectral range 500-4000 cm<sup>-1</sup>. Protonated corannulene (H+C<sub>20</sub>H<sub>10</sub>) and their neutral counterparts were produced upon electron bombardment of the matrix during deposition of C<sub>20</sub>H<sub>10</sub> mixed in *p*-H<sub>2</sub> over a period of 10 h. The matrix was then maintained in darkness for 30 h followed by secondary photolysis using light at various wavelengths from several light-emitting diodes.

### 3. Results and Conclusion

When the matrix after deposition along with electron bombardment was maintained in darkness, the protonated species became diminished, whereas its neutral counterparts were produced. Infrared absorption features, grouped according to the behavior after maintaining the matrix in darkness and upon secondary photolysis were assigned to several conformers of protonated (or hydrogenated) isomers of  $C_{20}H_{10}$  by comparison with the quantum-chemically calculated IR spectra. Two protonated species of  $C_{20}H_{10}$  (with proton at the hub and rim sites) Sundararajan *et al.* (2018) and their respective neutral counterparts are unambiguously identified. The hub-H+ $C_{20}H_{10}$  had close resemblance with many bands in the astronomical UIR emission features with an average red-shift of  $0.23 \mu\text{m}$  as shown in Figure 1. In addition, an alternate method to produce hydrogenated PAHs by UV and IR irradiation of  $C_{20}H_{10}/Cl_2/p\text{-}H_2$  also produced the most stable rim and the second most favorable hub isomer. (Sundararajan *et al.* (2019)).

Similarly, sumanene ( $C_{21}H_{12}$ ) was also investigated using this technique to produce protonated and hydrogenated  $C_{21}H_{12}$ .

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