

Infrared spectra of isomers of protonated and hydrogenated phenanthridine isolated in solid *para*-hydrogen

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Abstract

Large polycyclic aromatic hydrocarbons (PAH) and polycyclic aromatic nitrogen heterocycles (PANH) have been proposed to be potential carriers responsible for the unidentified infrared (UIR) emission bands in the interstellar medium.¹ The nitrogen atom in PANH induces a blue shift of the CC-stretching mode of the PAH, occurring around 6.3 μm . In addition to PANH, several protonated polycyclic aromatic hydrocarbons (H^+PAH) and the corresponding nitrogen heterocycles (H^+PANH) also exhibit blue shifts.² Therefore, the CC-stretching band of the H^+PANH might agree better with the UIB band at 6.2 μm and H^+PANH might be potential candidates that contribute to the UIR bands.

We report the infrared (IR) spectra of two isomers of protonated phenanthridine ($\text{H}^+\text{C}_{13}\text{H}_9\text{N}$) and seven isomers of mono-hydrogenated phenanthridine ($\text{HC}_{13}\text{H}_9\text{N}$), produced upon electron-bombardment of a mixture of phenanthridine ($\text{C}_{13}\text{H}_9\text{N}$) and *para*-hydrogen (*p*- H_2) during matrix deposition at 3.2 K. IR spectra of protonated species $\text{C}_{13}\text{H}_9\text{NH}^+$ and 4- $\text{H}^+\text{C}_{13}\text{H}_9\text{N}$ were observed. In addition to the hydrogenation on the N atom of $\text{C}_{13}\text{H}_9\text{N}$ to form $\text{C}_{13}\text{H}_9\text{NH}$, mono-hydrogenation at six carbon sites to form 1-, 2-, 3-, 7-, 9-, and 10- $\text{HC}_{13}\text{H}_9\text{N}$, respectively, were also observed. To confirm the spectral identification of hydrogenated phenanthridine, additional experiments on a $\text{C}_{13}\text{H}_9\text{N}/\text{Cl}_2/p\text{-H}_2$ matrix were performed; the matrix was irradiated at 365 nm to generate Cl atoms, followed by IR irradiation to generate H atoms via $\text{Cl} + \text{H}_2$ ($v = 1$) \rightarrow $\text{HCl} + \text{H}$. The H atoms thus generated propagated throughout the matrix and reacted with $\text{C}_{13}\text{H}_9\text{N}$ via quantum tunneling. In these experiments, six hydrogenated phenanthridine species, except the one hydrogenated at the carbon site 3, were clearly observed. Spectral groupings were achieved according to the behaviors of lines upon secondary photolysis at various wavelengths, chosen according to the vertical electronic transitions of various isomers of $\text{HC}_{13}\text{H}_9\text{N}$ predicted with the TD-B3LYP/6-311++G(d,p) method. The spectral assignments were supported via comparison of the experimental results with the vibrational wavenumbers and IR intensities of possible isomers predicted with the B3LYP/6-311++G(d,p) method. All spectra of $\text{H}^+\text{C}_{13}\text{H}_9\text{N}$ and $\text{HC}_{13}\text{H}_9\text{N}$ are new.

For $\text{H}^+\text{C}_{13}\text{H}_9\text{N}$, major observed lines are at 2.95, 6.22 and 12.53 μm ; the CC-stretching band of $\text{C}_{13}\text{H}_9\text{NH}^+$ was observed at 6.22 μm , blue shifted from that of the corresponding PAH, 10- $\text{C}_{14}\text{H}_{11}^+$. For $\text{HC}_{13}\text{H}_9\text{N}$, major lines were observed at 13.43, 13.16, and 13.55 μm for $\text{C}_{13}\text{H}_9\text{NH}$, 9- $\text{HC}_{13}\text{H}_9\text{N}$, and 2- $\text{HC}_{13}\text{H}_9\text{N}$, respectively. Based on the overall spectral pattern, these protonated and hydrogenated species are unlikely to be the carriers of the UIR bands, characterized by emission bands near 3.3, 6.2, 7.7, 8.6, 11.2, and 12.0 μm .

References

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