CYANOPOLYYNE CATIONS AS CARRIERS OF A SET OF DIFFUSE INTERSTELLAR BANDS

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It is proposed that a set of diffuse interstellar bands (DIBs) can be attributed to the $\tilde{B}^2\Pi - \tilde{X}^2\Pi$ electronic transitions of the cyanopolyyne cations, $HC_{2n+1}N^+$, based on comparisons with laboratory observations in Ne matrices by Forney et al.¹ For HC_7N^+ the DIB λ 6614 is assigned as the 0_0^0 origin band, and $\lambda\lambda$ 6426, 6196, 5982, and 5850 to transitions to upper-state fundamental vibrations. The three-peaked structure of λ 6614 under high resolution^{2,3} is assigned as P and R branches of the two subbands ${}^2\Pi_{1/2} - {}^2\Pi_{1/2}$ and ${}^2\Pi_{3/2} - {}^2\Pi_{3/2}$, with the central pair of branches overlapping. The 0_0^0 band of HC_9N^+ is assigned to λ 7562, with vibrational bands at $\lambda\lambda$ 7358, 6919, and 6521, while the 0_0^0 band of $HC_{11}N^+$ is assigned to λ 8531, with vibrational bands too weak to identify. These are all relatively sharp DIBs, with full widths at half maximum (FWHMs) in the range 1.7–3.1 cm⁻¹. Assignments are less satisfactory for shorter members of the series. The 0_0^0 bands of HC_5N^+ and HC_3N^+ may be $\lambda\lambda$ 5797 and 5110, respectively, but the former seems to have a rather narrow PR separation under high resolution, although its FWHM of 2.9 cm⁻¹ lies in the above range, while the latter is much broader (FWHM = 45 cm⁻¹) than higher members of the series. The first member of the series, HCN⁺, does not have a ... $\pi^3\pi^4 \leftarrow ... \pi^4\pi^3$ electronic transition of this type.

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