

Rovibrational Overtone and Combination Bands of the HCNH⁺ Ion

Miroslava Kassayová¹, Miguel Jiménez-Redondo², János Sarka^{3,4}, Petr Dohnal¹, Juraj Glosík
Paola Caselli² & Pavol Jusko²

¹ Department of Surface and Plasma Science, Faculty of Mathematics and Physics, Charles University, V Holešovičkách 2, Prague, 18000, Czechia

² Max Planck Institute for Extraterrestrial Physics, Gießenbachstraße 1, Garching, 85748, Germany

³ Physikalisches Institut, Universität zu Köln, Zùlpicher Str. 77, Cologne, 50937, Germany

⁴ Institute of Chemistry, Eötvös Loránd University, Pázmány Péter sétány 1/A., Budapest, 1117, Hungary

The HCNH⁺ ion, a linear closed-shell species of considerable relevance in interstellar chemistry, has been the subject of extensive laboratory investigations. While recent studies have concentrated on the hyperfine-resolved pure rotational spectra, the present work focuses on the vibrational spectra in the 6200-6900 cm⁻¹ region, specifically covering overtones and combination bands associated with the principal N-H (ν_1) and C-H (ν_2) stretching modes. Rovibrationally resolved spectra have been obtained for the first overtones $2\nu_1$ and $2\nu_2$, the combination band $\nu_1 + \nu_2$, and another combination band $\nu_2 + \nu_3 + 2\nu_5^0$, where ν_3 corresponds to the C-N stretch and ν_5 to the HNC bending mode. Notably, this last combination band possesses a calculated intensity of merely 0.06 km mol⁻¹, approximately 10⁴ times weaker than the ν_1 fundamental band (482 km mol⁻¹). Such high sensitivity was achieved using a “kick-out” enhanced multi-step laser-induced reaction (LIR) scheme. The endothermic reaction with C₂H₄ was employed; however, the resulting products underwent further reaction with C₂H₄, forming up to C₅H₇⁺ ions, which were subsequently monitored as the spectroscopic signal. The experimental findings are supported by theoretical calculations at the CCSD(T)-F12b/cc-pCVQZ-F12 level.