Rovibrational eigenenergy structure of the [H,C,N] molecular system

G. Ch. Mellau[a]

[a] Physikalisch-Chemisches Institut, Justus-Liebig-Universität Giessen, Heinrich-Buff-Ring 58,
D-35392 Giessen, Germany, E-mail: georg@mellau.de

The isomerization reaction HCN↔CNH is one of the simplest models of a chemical reaction and one of the prototypical model systems used for the study of unimolecular reactions. Regarding this isomerization reaction one of the key questions is how the isomerization manifests itself in the vibration-rotation eigenenergy spectrum of the [H,C,N] molecular system. The spectroscopic signature describes how the wave functions of the two isomers H-CN and CN-H located in two different minima merge step by step to a single delocalized wave function [1] corresponding to a single “combined” $H_{0.5}$-CN-$H_{0.5}$ molecule. The analysis of high resolution infarred emission spectra and of the complete ab initio eigenergy list of the [H,C,N] molecular system published recently in a series of seven papers [2-4] are the first step in elucidating the physics behind the HCN↔HNC isomerization. Even if this is not apparent at first sight, these papers contain some milestones of molecular physics: The first full quantum mechanical experimental description of a polyatomic molecule up to highly excited energies (based on the complete eigenvalue list of all compatible observables), the first practically error-free partition function at room temperature for a polyatomic molecule (which differs significantly from the value known in literature) or the first quantitative description for the vibrational onset of the isomerization.

HCP is the single molecule that has been successfully examined for spectroscopic signatures of the HAB↔ABH isomerization [5]. The most important result of those studies is the coexistence of the normal mode bending vibrations localized in the HCP potential well with a new reaction-mode vibration mode closely following the reaction path. For the [H,C,N] system two fundamental questions arise. Is the structure of vibrational states similar to the one found for HCP? What is the effect of the high rotational excitation on the isomerization states?

The theoretical studies published so far consider the problem of the isomerization states mostly in rotationless states. The picture we get using only these states is incomplete and the description of the isomerization based only on these states is not complete. To understand the eigenenergy structure it is necessary to use data from *ab initio* calculations. In fact all eigenvalues up to the isomerization barrier have already been calculated [6]. For the [H,C,N] molecular system only parity and total angular momentum are exact quantum numbers and the eigenenergies have to be labeled with vibrational quantum numbers in a complicated assignment procedure. The assignment of all *ab initio* rovibrational eigenenergies [3,4] is now complete up to 3000 cm^{-1} above the isomerization barrier, results from this analysis are presented in this work.

[1] J. M. Bowman, *Science* **2000**, *290*, 724-725.
[2] G. Ch. Mellau, *J. Chem. Phys.* **2010**, *133*, 7164303.
[3] G. Ch. Mellau, *J. Chem. Phys.* **2011**, *134*, 194302.
[4] G. Ch. Mellau, *J. Chem. Phys.* **2011**, *134*, 234303.
[5] H. Ishikawa, R. W. Field, S. C. Farantos, M. Joyeux, J. Koput, C. Beck, and R. Schinke, *Ann. Rev. Phys. Chem.* **1999**, *50*, 443-484.
[6] G. J. Harris, J. Tennyson, B. M. Kaminsky, Y. V. Pavlenko, and H. R. A. Jones, *MNRAS* **2006**, *367*, 400-406.