HIGHLY EXCITED BENDING VIBRATIONAL STATES OF HNC AND HCN

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The isomerization reaction HCN $\rightleftharpoons$ HNC is a model system for the study of unimolecular reactions. To support the theoretical studies, the experimental characterization of highly excited bending vibrational states that could trigger the isomerization reaction is of special interest. In an emission experiment HNC can be produced by by heating the HCN gas. As higher the gas temperature as more the HCN $\rightleftharpoons$ HNC equilibrium will shift towards HNC. Using a hot gas infrared emission experiment I recorded emission spectra of HCN and HNC [1-3] which are extremely rich in transitions in comparison with even very long path absorption measurements. In these experiments I found out that HCN and HNC decompose at the quartz or ceramic cell surface at temperatures just above 1100 K. Over some years I have done many unsuccessful attempts to passivate the cell surface and increase the emission cell temperature. Recently I have been successful in recording a HCN/HNC spectrum in the ν_2 bending wavenumber region at 1580 K. I will present the analysis of transitions between highly excited bending vibrational states of HNC and show what we can learn from this new spectroscopic data regarding the HCN $\rightleftharpoons$ HNC isomerization reaction. The transitions between the highest HCN and HNC excited states correspond to very weak lines in a very dense, high signal to noise ratio emission spectrum. I developed over the past years the SyMath^{TM} spectroscopic analysis program [1,4] for the assignment of very dense spectra using the computer algebra system Mathematica^{TM}. SyMath^{TM} combines line position analysis (least square fit of the parameters of the Hamiltonian to the line positions) with intensity analysis (least square fit of the Doppler line shapes to the spectrum data points) and allows to simplify the spectrum from the already detected and analyzed bands. I will present the basic ideas behind this new generation of software system [5] designed for physical and chemical applications and show how I analysed the HNC spectrum using SyMath^{TM} .

[1] G. Ch. Mellau, B. P. Winnewisser and M. Winnewisser, *J. Mol. Spectrosc.* **in press**.
[2] A. Maki and G. Ch. Mellau,*J. Mol. Spectrosc.* **206**, 47-52 (2001).
[3] A. G. Maki, G. Ch. Mellau, S. Klee, M. Winnewisser, and W. Quapp, *J. Mol. Spectrosc.* **202**, 67-82 (2000).
[4] http://www.symath.com, [5] http://www.georg.mellau.de/; teaching/physical-informatics