HIGH RESOLUTION MOLECULAR BEAM SPECTROSCOPY OF THE HCN DIMER IN THE 1.5 μm REGION. REINVESTIGATION OF THE $\nu_1 + \nu_2$ BAND AND COMPARISON WITH THEORY.

A. CALLEGARI, H. K. SRIVASTAVA, P. ENGELS[a], K. K. LEHMANN and G. SCOLES, *Department of Chemistry, Princeton University, Princeton NJ, 08544-1009*; A. HEYL and P. BOTSCHWINA, *Institut für Physikalische Chemie der Universität Göttingen, Tammannstr. 6, D-37077 Göttingen.*

The 1.5 μm spectrum of the $\nu_1 + \nu_2$ combination band of the HCN dimer has been reinvestigated with improved sensitivity in a molecular beam spectrometer. The ν_1 and ν_2 modes are nominally the free CH stretch and the hydrogen bound CH stretch respectively. The improved signal to noise has allowed us to increase the number of observed rotational states to J=24. The observed linewidths range from 12 to 60 MHz, the largest values corresponding to mixing with a perturbing state that becomes resonant around J=10. Contrary to expectations, the lifetime of the upper state far from the perturbation is at least two times longer than the one observed by Jucks and Miller [JCP 88, 6059, (1988)] for the ν_2 fundamental. This shows that changing the vibrational state of the outer CH stretch, whose lifetime is two orders of magnitude longer than that of the ν_2 fundamental, makes it possible to control the lifetime of the hydrogen bond breaking.

The transition strength is measured to be about 14 times smaller than that of the $2\nu_1$ overtone, about six times larger than expected based on a simple dipole-induced dipole model for the coupling between ν_1 and ν_2. Five-dimensional potential energy and electric dipole moment functions have been constructed for the stretching vibrations on the basis of large-scale CEPA-1 and CCSD(T) calculations. The absolute IR intensity of the $\nu_1 + \nu_2$ band is predicted to be 0.06 km mol^{-1}, a factor of 24 smaller than that of the $2\nu_1$ band (i.e. within a factor two of the experimental value). The origin of the $2\nu_2$ band is predicted at 6370 cm^{-1} and its intensity is calculated to be 0.12 km mol^{-1}. This band has not been experimentally observed so far.

[a] Visiting from the University of Bonn, Institut für Angewandte Physik, Wegelerstr. 8, 53115 Bonn, Germany