APPLICATIONS OF A SINGLE-PULSE BROADBAND FTMW SPECTROMETER: VARIATIONS IN THE DYANMIC ROTATIONAL SPECTRUM OF CYCLOPROPANECARBOXALDEHYDE AS A FUNCTION OF EXCITATION ENERGY

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Using our state-of-the-art chirped-pulse broadband rotational spectrometer, we examine the isomerization dynamics of vibrationally excited cyclopropanecarboxaldehyde (CPCA). CPCA is found in one of two conformational minima, either the *cis* or *trans* form, both of which are populated in a supersonic expansion. The ground state microwave spectrum, dipole moments and torsional potential constants have been previously measured by Volltraurer and Schwendeman [a] and serve as a basis for this work. The barrier to *cis*→ *trans* interconversion, was found to be 1540 +/- 144 cm^{-1}, where the *cis* form is more stable by 10 +/- 30 cm^{-1}. Using a combination of double (infrared-microwave) and triple (infrared-microwave-microwave) resonance techniques, we have recorded the rotational spectrum of vibrationally excited CPCA in a number of CH-stretching modes from 2700-3100 cm^{-1}. Our single-pulse, broadband rotational spectrometer measured the ΔJ = 1→2 region of the rotational spectrum from 10-18 GHz, allowing us to record single eigenstate rotational spectra in a matter of minutes. The overall lineshape of the vibrationally excited rotational spectrum is fit to a three-state Bloch model modified for chemical exchange. The lineshape of the excited state rotational spectra is used to determine the *cis-trans* isomerization rate, and the overall lineshape of the rotational spectrum is dependent upon which infrared band is used to prepare the molecule. The dynamical consequences of the rotational lineshape will be discussed.

[a] H. N. Volltrauer, R. H. Schwendeman, J. Chem. Phys. 54, 260 (1971).