APPLICATIONS OF A SINGLE-PULSE BROADBAND FTMW SPECTROMETER: THE DYANMIC ROTATIONAL SPECTRUM OF 4-FLUOROBUT-1-YNE.

BRIAN C. DIAN, KEVIN O. DOUGLASS, GORDON G. BROWN, SCOTT M. GEYER, and BROOKS H. PATE, *Department of Chemistry, University of Virginia, McCormick Rd., P.O. Box 400319, Charlottesville, VA 22904.*.

We perform dynamic rotational spectroscopy on vibrationally excited 4-fluorobut-1-yne using our state-of-the-art, chirped-pulse broadband spectrometer. This new spectrometer allowed us to record 11 GHz of spectrum (7.5-18 GHz) with a single microwave pulse to study the energy-dependence of the isomerization kinetics, dramatically reducing data acquisition times. 4-Fluorobut-1-yne is an asymmetric top found in one of two conformers in a supersonic expansion, with fluorine either *trans* or *gauche* with respect to the ethynyl group. The *trans- gauche* isomerization barrier is approximately 1377 cm^{-1}, and the *trans* form is more stable by 492 cm^{-1}. Infrared laser excitation was used to prepare 4-fluorobut-1-yne in a region of the potential surface where isomerization can occur (3000 cm^{-1}). Using our broadband spectrometer, the rotational spectrum of the infrared excited molecule was recorded from 7.5-18 GHz, covering the $\Delta J = 1 \rightarrow 2$ and $\Delta J = 2 \rightarrow 3$ regions of the spectrum. The overall lineshape of the rotational spectrum was fit with a three-state Bloch model, modified for chemical exchange, yielding an isomerization rate of $k_{iso} = 2.7 \times 10^{10}$ s^{-1}, much slower than the rate predicted by RRKM theory: $k_{iso} = 5.9 \times 10^{11}$ s^{-1}. The single eigenstate rotational spectra recorded with our newly developed spectrometer agree with previously measured single eigenstate rotational spectra, recorded in the acetylenic CH-stretch at 3330 cm^{-1}. Using a combination of double (infrared-microwave) and triple resonance (infrared-microwave-microwave) techniques, single eigenstate rotational spectra were recorded for several IR bands. Infrared excitation of the various CH-stretching bands allows us to observe the isomerization dynamics over a broad energy range (2900-3330 cm^{-1}). Observed changes on the rotational spectrum will be discussed.