

PROBING THE CONFORMATIONAL ISOMERIZATION PROCESS IN 4-CHLOROBUT-1-YNE THROUGH SINGLE EIGENSTATE ROTATIONAL SPECTROSCOPY

JOHN KESKE and B. H. PATE, *Department of Chemistry, University of Virginia, McCormick Rd., Charlottesville, VA 22901.*

4-Chlorobut-1-yne exists in two stable conformations, trans and gauche. Ab initio calculations predict that the trans conformer is more stable by about 500 cm^{-1} and the barrier to direct isomerization is about 1500 cm^{-1} . We have investigated the isomerization dynamics of chlorobutyne at 3330 cm^{-1} by measuring the rotational spectrum of single quantum states prepared through excitation of eigenstates of the acetylenic C-H stretch. Because the IVR rate is slow for this band, we are able to saturate the strongest transitions in the spectrum with the available laser power (15 mW). The rotational spectra of these directly prepared states have been measured through infrared-microwave saturation spectroscopy. However, we see little evidence of mixing between the trans and gauche conformers for these states. Using an infrared-microwave-microwave triple resonance technique we are able to measure the rotational spectrum of eigenstates that have larger contributions of the above-barrier free rotor states. These eigenstates show more extensive mixing of the conformers.