CONFORMATIONAL ISOMERIZATION KINETICS OF 4-BROMOBUT1-YNE FROM HIGH-RESOLUTION INFRARED SPECTROSCOPY AND DYNAMICAL ROTATIONAL SPECTROSCOPY

FRANCES S. REES, JOHN C. KESKE and BROOKS H. PATE, *Department of Chemistry, University of Virginia, McCormick Rd., Charlottesville, VA 22901*; R.D. SUENRAM, *National Institute of Standards and Technology, Optical Technology Division, Gaithersburg, MD, 20899-8441*.

The rate of conformational isomerization between the more stable trans and less stable gauche conformers of 4-bromobut-1-yne is measured by dynamical rotational spectroscopy. The high-resolution, molecular-beam infrared spectrum of the acetylenic C-H stretch of the trans conformer of 4-bromobut-1-yne is rotationally assigned using microwave-infrared double-resonance spectroscopy in an electric resonance optothermal spectrometer. The vibrational spectrum of the gauche conformer is not observed. The existence of intramolecular vibrational energy redistribution (IVR) is indicated by the extensive local perturbations to the spectrum that fragment the vibrational spectrum. The time scale for IVR following coherent preparation of the acetylenic C-H stretch of the trans conformer is about 2 ns (for both isotopes). The isomerization rate at 3330 cm^{-1} is measured through the single-eigenstate rotational spectrum. This spectrum is obtained using a saturation spectroscopy infrared-microwave double-resonance technique. From a line shape analysis of the spectrum, the time scale for isomerization is determined to be 120 ps. This measurement shows that the isomerization process is highly mode-specific with a strong reduction in the rate for coherent excitation of the acetylenic C-H stretch of the trans conformer. This result is compared to isomerization rate measurements on other halobutynes.