DETERMINATION OF THE CONFORMATIONAL ISOMERIZATION RATE OF 4-FLUOROBUT-1-YNE USING DYNAMICAL ROTATIONAL SPECTROSCOPY

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The conformational isomerization rate of 4-fluorobut-1-yne has been measured at an energy of 3330 cm^{-1} above the zero point energy through the rotational spectroscopy of single vibrationally-excited eigenstates. 4-Fluorobut-1-yne exist as two conformers ($trans$ and $gauche$) with a barrier to isomerization from of 1400 cm^{-1}. Using infrared-microwave double-resonance and infrared-microwave-microwave triple-resonance spectroscopy the rotational spectra of several different eigenstates were obtained for J=2 and J=3. Each of the conformers has characteristic rotational frequencies, known from ground-state microwave spectroscopy. When the molecule is excited above the barrier to isomerization both conformers contribute to the rotational spectra and the isomerization rate is determined from the overall line shape of the dynamic rotational spectra. Peculiarities of the line shape due to the large difference (factor of 10) in the dipole moment, μ_a, of the two conformers will be discussed. From these rotational spectra we measure a conformational isomerization rate of 2.2×10^{10} s^{-1}. This rate is significantly slower than the rate calculated using RRKM theory, 7×10^{11} s^{-1} and orders of magnitude faster than the upper limit given by the measured intramolecular vibrational energy redistribution rate: 7.1×10^{8} s^{-1}.