MOLECULAR ROTATION IN THE PRESENCE OF CONFORMATIONAL ISOMERIZATION DYNAMICS: THE DYNAMIC ROTATIONAL SPECTRUM OF PENT-1-EN-4-YNE AT 3330 cm^{-1}

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We present the basic principles of dynamic rotational spectroscopy for the vibrationally excited asymmetric top molecule pent-1-en-4-yne. Pent-1-en-4-yne is found in one of two stable conformations (cis and skew) in a supersonic expansion with the cis conformer being more stable. Using a combination of infrared-Fourier transform microwave (IR-FTMW) double resonance and high-resolution single photon infrared spectroscopies, single eigenstate rotational spectra were recorded above the barrier to isomerization. Preparation of the molecules by infrared excitation of the acetylenic C-H stretch of the cis conformer excites the molecule into an energy regime where intramolecular vibrational redistribution (IVR) and isomerization can occur. The single eigenstate rotational spectra recorded in the region of the J = 1-2 and J = 3-2 ground state rotational transitions are severely fractionated, spread over several gigahertz and peaked between the ground state pure rotational transitions of each conformer for a given ΔJ. These dynamic rotational spectra are characteristic of molecular rotation in the presence of isomerization and exhibit coalescence of the rotational spectrum similar to motional narrowing found in NMR spectroscopy. The coalescence spectra are compared to a two-state Bloch model to recover the isomerization rate information embedded within the lineshape of the dynamic rotational spectra.