MOLECULAR ROTATION IN THE PRESENCE OF INTRAMOLECULAR VIBRATIONAL REDISTRIBUTION: MOTIONAL NARROWING OF TRIFLUOROPROPYNE AT 6550 cm^{-1}.

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We present the basic principles of dynamic rotational spectroscopy for the highly vibrationally excited symmetric top molecule trifluoropropyne (TFP, CF_3CCH). Single molecular eigenstate rotational spectra of TFP were recorded in the region of the first overtone of the ν_1 acetylenic stretching mode at 6550 cm^{-1} by infrared-pulsed microwave-Fourier transform microwave (IR pMW-FTMW) triple resonance spectroscopy. The average rotational constant (B) of the highly vibrationally mixed quantum states at 6550 cm^{-1} is 2909.33 MHz, a value that is 40 MHz larger than the rotational constant expected for the unperturbed C-H stretch overtone (2869.39 MHz). The average rotational constant and rotational line shape of the molecular eigenstate rotational spectra are compared to the distribution of rotational constants expected for the ensemble of normal-mode vibrational states at 6550 cm^{-1} that can interact by intramolecular vibrational energy redistribution (IVR). The normal-mode population distribution at 6550 cm^{-1} can be described using a Boltzmann distribution with a microcanonical temperature of 1200 K. At this energy the rotational constant distribution in the normal-mode basis set is peaked at 2910 MHz with a width of approximately 230 MHz FWHM. The experimentally measured dynamic rotational spectra are centered at the normal-mode distribution peak however, the spectral width is significantly narrower (40 MHz FWHM) than the normal-mode ensemble width. This reduction of the width, along with the Lorentzian shape of the ensemble eigenstate rotational spectrum when compared to the Gaussian shape of the calculated ensemble distribution, illustrates the narrowing of the spectrum due to IVR exchange. The IVR exchange rate was determined to be 120 ps, 5-10 times faster than the rate at which energy is redistributed from the v=2 level of the acetylenic stretch.