DETERMINING THE IVR RATE FROM CORIOLIS COUPLING IN PHENYLACETYLENE USING DYNAMIC ROTATIONAL SPECTROSCOPY

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We present the basic principles of dynamic rotational spectroscopy for the vibrationally excited asymmetric top molecule phenylacetylene (PA). The dynamic rotational spectra were recorded using various infrared-pulsed microwave-Fourier transform microwave (IR-pMW-FTMW) triple resonance spectroscopies. Preparation of the molecules by infrared excitation of the acetylenic C-H stretch excites the molecule into an energy regime where intramolecular vibrational redistribution (IVR) can occur. The resulting excited state spectra are shifted by approximately 50 MHz to higher frequency from the pure rotational ground state transitions and are spread over several quantum states, characteristic of rotational spectra in the presence of IVR. The excited state spectra are perturbed by parallel Coriolis coupling effects, evident by the K-mixing in the rotational spectrum. The single eigenstate rotational spectra recorded in the region of the K=2 asymmetry doublets in both the J = 5-4 and J = 6-5 excited state rotational levels show evidence for coalescence, suggesting that the coriolis mixing is sufficiently fast to compete with asymmetry splitting. These single eigenstate spectra were used to determine the strength of the Coriolis coupling using a two-state Bloch model.