ROTATIONAL SPECTROSCOPY OF VIBRATIONALLY EXCITED STATES OF 3-FLUOROPROPYNE, 4-FLUOROBUTYNE, AND 1-BUTYNE USING IR-FTMW-MW TRIPLE RESONANCE SPECTROSCOPY

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We describe the extension of our pulsed infrared laser / FTMW spectrometer to permit the measurement of rotational transitions in the vibrational excited state that are driven by a resonant microwave field. This IR-FTMW-MW triple-resonance spectroscopy technique uses the Autler-Townes splitting to measure the rotational spectra of levels monitored by FTMW spectroscopy. This technique is used to measure the rotational spectrum of fluoropropyne in the first excited state of the acetylenic C-H stretch. The lineshape of the triple resonance spectrum is discussed with respect to the underlying Autler- Townes effect. We also show that the lineshape contains information about the type of rotational transition driven by the applied microwave field (i.e. either a P/R or Q transition). The rotational spectrum of the excited state is fit to the Watson Hamiltonian. Compared to the pure rotational spectrum, the quality of the fit is worse in the excited state likely reflecting the existence of weak perturbations in the excited state. This technique has also been used to obtain rotational spectra of vibrationally excited states of larger molecules where extensive local perturbations characterize the vibration spectrum. These local perturbations also fragment the excited state rotational spectrum and, usually, lead to weak rotational transitions between the vibrational eigenstates. Measurements of weak rotational transitions from single molecular eigenstates of 4-fluorobutyne and 1-butyne are presented and compared to spectra obtained using infrared-microwave saturation spectroscopy on an electric resonance optothermal spectrometer.