ROTATIONALLY RESOLVED VIBRATIONAL OVERTONE SPECTRA OF JET-COOLED METHANOL

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Infrared-optical double resonance excitation permits the measurement of fully rotationally resolved vibrational overtone spectra of jet-cooled methanol up to the $6\nu_{OH}$ level. These weak transitions to high vibrational levels are detected using the technique of IR assisted photofragment spectroscopy (IRLAPS). The elimination of spectral congestion reveals splittings of the zeroth-order rovibrational levels that reflect vibrational coupling to dark background levels. Analysis of the overtone spectra as a function of the number of OH stretch quanta indicates the presence of a strong coupling between zeroth-order states with nν_{OH} and those with (n-1)ν_{OH} + $\nu_{CHasym.st.}$. This coupling is most clearly manifest at the $5\nu_{OH}$ level where the OH stretch frequency is anharmonically shifted close to that of the CH asymmetric stretch frequency. Finer spectral splittings reflect the coupling of the mixed OH-CH stretch states with the rest of the vibrational bath. The most recent results using this technique for CH_3OH and its partially deuterated analogs will be discussed.