EIGENSTATE RESOLVED INFRARED AND INFRARED-INFRARED DOUBLE RESONANCE STUDY OF BENZENE VIBRATIONAL RELAXATION IN THE C-H STRETCH FIRST OVERTONE REGION

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The eigenstate resolved, infrared spectrum of benzene, C_6H_6, was recorded in the region of the first C-H stretching overtone (6000 cm^{-1}). The spectrum was observed using a molecular beam laser spectrometer with optothermal detection. The Benzene overtone spectrum has long been one of the most important model systems for studies of Intramolecular Vibrational energy Relaxation (IVR), and has been the subject of numerous experimental and theoretical investigations. The best previous investigation of the first CH overtone region gave an effective resolution of 4 cm^{-1} due to the convolution of laser linewidth and rotational structure. By using our spectrometer, with an instrumental resolution of ~ 5 MHz ($\sim 2 \times 10^4$ times higher than the previous study), we have observed an extremely dense spectrum, with a density of thousands of lines per cm^{-1}. Given the density of the spectrum, combined with the highly 'degenerate' rotational structure expected for a perpendicular transition in a planar symmetric top, rotational assignment by combination differences appeared unpromising. In order to make progress with the analysis of the spectrum, we have exploited near coincidences of the Q(2,0) and Q(3,0) transitions of the benzene ν_{14} fundamental with the R_{30} line of the $^{13}CO_2$ laser. This allowed us to use mid–IR/near-IR double resonance to observe the spectrum of a single lower rotational state by modulation of the CO_2 radiation (which crossed the molecular beam before the near–IR radiation), while scanning the near-IR laser. To date, we have observed the spectrum near the strongest transition (6006 cm^{-1}) observed in the previous study. We observe three 'clumps' of lines whose centers are separated by the expected P,Q, and R transitions from the J=2 lower state. The clumps have full width of ~ 0.5 cm^{-1}, implying an IVR lifetime for this 'feature state' of ~ 10 ps. The clumps, however, reveal sub–structure, which implies the presence of dynamical bottle–necks to IVR on even longer timescales. Analysis of the data is in progress.

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