EIGENSTATE RESOLVED DOUBLE RESONANCE STUDY OF BENZENE INTRAMOLECULAR VIBRATIONAL ENERGY REDISTRIBUTION IN THE C-H STRETCH FIRST OVERTONE REGION: A GOOD CANDIDATE FOR A SUCCESSFUL TIER MODEL ANALYSIS.

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The mid-resolution ($\sim$ 1 cm^{-1}) infrared spectrum of benzene C_6H_6 in the region of the first C-H stretching overtone (around 6000 cm^{-1}) contains at least 30 distinct bands spread over a range of 300 cm^{-1} [R.H. Page *et al.*, *JCP* **88**, 4621 (1988)]. By using a build-up cavity coupled molecular beam spectrometer, with a resolution of $\sim$ 5 MHz, we have been able to resolve the eigenstates of the most intense band at $\sim$ 6005 cm^{-1} [A. Callegari *et al.*, *JCP* **106**, 432 (1997)]. V-type double resonance has been used for rotational state selection by exploiting a near coincidence of the $^rQ_0(2)$ transition of the ν_{14} fundamental with the R_{30} line of the $^{13}CO_2$ laser [M-L. Junttila *et al.*, *J. Mol. Spec* **147**, 513 (1991)]. Recent improvements in the spectrometer have allowed us to resolve the second most intense band located at $\sim$ 6000 cm^{-1} with the same signal to noise. Upon close inspection the two bands show little resemblance in terms of line positions and intensities, yet their statistical properties are practically identical as far as lifetime ($\sim$ 25 ps), density of states ($\sim$ 100/cm^{-1}), strength of the couplings and level spacings distribution are concerned. In both cases three clumps of 40 to 90 lines each are clearly recognizable, corresponding to the P, Q and R transitions that originate from the J=2 lower state. Also within each band the three clumps (corresponding to different final J states) show striking similarities in terms of line positions and intensities. This, in turn, means that rotational motion at these low J's doesn't significantly change the relative position of the bright state w.r.t. the bath states nor the strength of their coupling.

The similar behavior of the two bands is consistent with a tier model where the coupling to the bath states is mediated by strong low-order resonances with intermediate distant states, as opposed to a model where weak high order couplings to nearby states are directly involved.

Sequential double resonance transitions from the upper ν_{14} state have also been measured, but the complicated K structure observed has so far kept us from definite assignments.

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