QUANTUM TUNNELING IN THE MIDRANGE VIBRATIONAL FUNDAMENTALS OF TROPOLONE

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The FTIR spectrum of tropolone(OH) vapor in the 1175 - 1700 cm^{-1} region is reported at 0.0025 and 0.10 cm^{-1} spectral resolutions. Estimates for the spectral doublet component separations for 11 fundamentals are based on the measurement of sharp Q branch peaks. The three highest of six a_1 modes show splittings $\Delta_v \approx \Delta_0$ (the known ZP splitting value), and four of the five observed b_2 modes show splittings $\Delta_v \approx$ 0.90 Δ_0. The remaining four splittings fall 4 to 14 % from Δ_0, including Δ_8 (nominal COH bending) = 1.10 Δ_0. The data show that significant anharmonic behavior accompanies the mild perturbations of midrange vibrational excitations on the ZP tunneling mechanism. The results suggest the onset of fast IVR processes that can delocalize and smooth the imprint of the vibrational excitation energy on the ZP PES topography before the tautomerization process can occur. Further, the results suggest dynamical characteristics of the b_2 modes include a damping effect on the tunneling process.