

COHERENT MANIPULATION OF ROVIBRONIC BRANCH INTENSITIES: APPLICATION TO THE TROPOLONE $\pi^* \leftarrow \pi$ TRANSITION

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High-Resolution Degenerate Four-Wave Mixing (DFWM) spectroscopy has been employed to dissect and interpret the room-temperature band contours exhibited in the 370nm origin region of the tropolone $\tilde{A}^1B_2 \leftarrow \tilde{X}^1A_1$ ($\pi^* \leftarrow \pi$) absorption system. In particular, judicious selection of polarization state for the incident electromagnetic fields combined with polarization-resolved detection of the emerging signal wave has been found to facilitate dramatically the discrimination and assignment of overlapping rotational structure. This novel approach has enabled selective suppression of high- J ($J \geq 10$) intensity attributable to $P(J)$, $Q(J)$, and/or $R(J)$ branches comprising the $0^+ \leftrightarrow 0^+$ and $0^- \leftrightarrow 0^-$ tunneling doublet, thereby alleviating much of the congestion normally associated with the electronic transitions of such large polyatomic species. The nature and limitations of these spectral simplification procedures will be discussed in the framework of a tensor-based analysis of weak-field DFWM response, with special emphasis placed on the utility of exploiting such schemes for the elucidation of molecular structure and dynamics. Refined rotational constants, transition moment character, and population decay rates have been deduced for the tropolone \tilde{A}^1B_2 potential energy surface through least-squares regression of observed rovibronic features.