SIMPLIFIED CARTESIAN BASIS MODEL FOR INTRAPOLYAD EMISSION INTENSITIES IN THE $\tilde{A} \rightarrow \tilde{X}$ BENT-TO-LINEAR TRANSITION OF ACETYLENE

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The acetylene emission spectrum from the trans-bent electronically excited $\tilde{A}$ state to the linear ground electronic $\tilde{X}$ state has attracted considerable attention because it grants Franck-Condon access to local bending vibrational levels of the $\tilde{X}$ state with large-amplitude motion along the acetylene $\equiv$ vinylidene isomerization coordinate. For emission from the ground vibrational level of the $\tilde{A}$ state, there is a simplifying set of Franck-Condon propensity rules that gives rise to only one zero-order bright state per conserved vibrational polyad of the $\tilde{X}$ state. Unfortunately, when the upper level involves excitation in the highly admixed ungerade bending modes, $\nu_3^t$ and $\nu_6^t$, the simplifying Franck-Condon propensity rule breaks down—so long as the usual polar basis (with $v$ and $l$ quantum numbers) is used to describe the degenerate bending vibrations of the $\tilde{X}$ state—and the intrapolyad intensities result from complicated interference patterns between many zero-order bright states. We show that when the degenerate bending levels are instead treated in the Cartesian two-dimensional harmonic oscillator basis (with $v_x$ and $v_y$ quantum numbers), the propensity for only one zero-order bright state (in the Cartesian basis) is restored, and the intrapolyad intensities are simple to model, so long as corrections are made for anharmonic interactions. As a result of trans $\leftrightarrow$ cis isomerization in the $\tilde{A}$ state, intrapolyad emission patterns from overtones of $\nu_3^t$ and $\nu_6^t$ evolve as quanta of trans bend ($v_3^t$) are added, so the emission intensities are not only relevant to the ground-state acetylene $\leftrightarrow$ vinylidene isomerization—they are also a direct reporter of isomerization in the electronically-excited state.