INTERSYSTEM CROSSING: A STEP BEYOND STATISTICS

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Traditional statistical models provide only a phenomenological description of intersystem crossing (ISC). They do not capture the dominant energy flow pathways and the state-specific mechanisms responsible for the mixing of zero-order bright state character into dark states. A time-dependent center of gravity metric is sensitive to patterns of bright dark state mixing that deviate from mechanism-free statistical pictures. Doorway-mediated ISC represents the first stage of pulling back the statistical curtain. The center of gravity metric is applied to incoherently excited, time-gated, high-resolution fluorescence excitation spectra of small molecules. It becomes possible to determine the energy of the doorway state relative to the bright state as well as the value of the bright doorway state spin-orbit matrix element. This sort of information was neither available nor dreamt of in the decades when ISC was subjected to intense spectroscopic and theoretical analysis.