

Conical intersection in a highly fluorescent molecule unraveled by coherent wavepacket evolution analysis

Johanna Brazard¹, Laurie A. Bizimana¹, William P. Carbery¹, Tobias Gellen¹, Daniel B. Turner¹

¹ Department of Chemistry, New York University, 100 Washington Square East, New York, New York 10003, United States

E-mail: johanna.brazard@ipcms.unistra.fr

Conical intersections are molecular configurations at which Born-Oppenheimer approximation is not valid anymore and thus potential-energy surfaces touch.¹ Despite their importance and predicted ubiquity,² conical intersections have been experimentally detected in only a few molecules. The spectroscopic signatures of a conical intersection are: negligible fluorescence, high photoactivity, or femtosecond electronic kinetics.³ Those studies established a “photochemistry paradigm” wherein it was established that the coherent movement of a wavepacket from one electronic surface to another signifies passage through a conical intersection.⁴

We studied the ultrafast photophysics of a highly fluorescent oxazine molecule, cresyl violet perchlorate (CV), by transient absorption and two-dimensional electronic spectroscopy (2DES) using sub-8 fs pulses.^{5,6} The signature of a conical intersection, in a mode at 593 cm^{-1} , was unraveled by applying coherent wavepacket evolution analysis to the transient absorption data of CV (Fig. 1). This strongly Raman-active mode is associated with an in-plane vibrational mode of the aromatic oxazine ring.

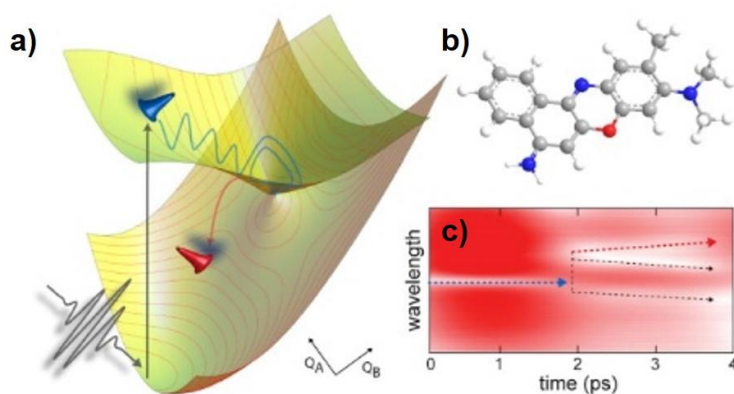


Figure 1. a) Schematic representation of the coherent wavepacket evolution through a conical intersection. Initial excitation (grey) results in an oscillating wavepacket (blue) on the excited adiabatic potential-energy surface which crosses through a conical intersection onto the ground adiabatic potential energy surface (red). b) Molecular structure of cresyl violet perchlorate (CV). c) Coherent wavepacket evolution signal for CV with Fourier shift. The initial node at the fluorescence maximum (615 nm) disappears at 1.7 ps and three nodes appear (596, 610 nm, and 621 nm).

2D ES reveals how the dynamics vary as a function of excitation frequency. The topological features of the ground and excited potential energy surfaces of CV were probed by 2DES. We show that both potential energy surfaces are harmonic and with a uniform width.

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