Detection of conical intersection from the vibrational coherences

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Vibrational coherences can be considered as a tool to detect the Conical Intersection (CI), because the wavepacket motion is affected by the surface crossing. Here, we identify the spectroscopic signatures associated with CI by analyzing the coherent wavepacket motions extracted from the linear absorption (1D) and two-dimensional electronic spectra (2DES).

Conical Intersections (CIs) play a crucial role in photochemistry, photophysics and chemical reaction dynamics [1]. CI is believed to be ubiquitous in organic and bio-organic chromophores, and that it plays a major part in charge and energy transfer mechanisms. Despite extensive experimental and theoretical studies, spectroscopic signatures of the CI are still missing. Vibrational coherence can be considered as a tool to detect the CI, because the wavepacket motion is believed to be affected by the surface crossing. Recent studies using time-resolved optical spectroscopy have been focused on following the evolution of the vibrational wavepacket after passing through the CI [2,3]. Although it allows to uncover the nuclear coherences associated with CI, it is unclear how these vibrational signatures can be used as evidence for the presence of CI in a system.

The aim of this study is to identify the spectroscopic signatures of the CI by analyzing the coherent wavepacket in the electronic ground and excited state. The coherent wavepacket motions were extracted from the 1D and 2DES. To perform our analysis two quantum mechanical models of the *cis-trans* photoisomerization were considered: a model where the CI is explicitly included and a model where the CI is absent (see Figure 1). A comparison between the two models allows us to identify the signatures of the CI.
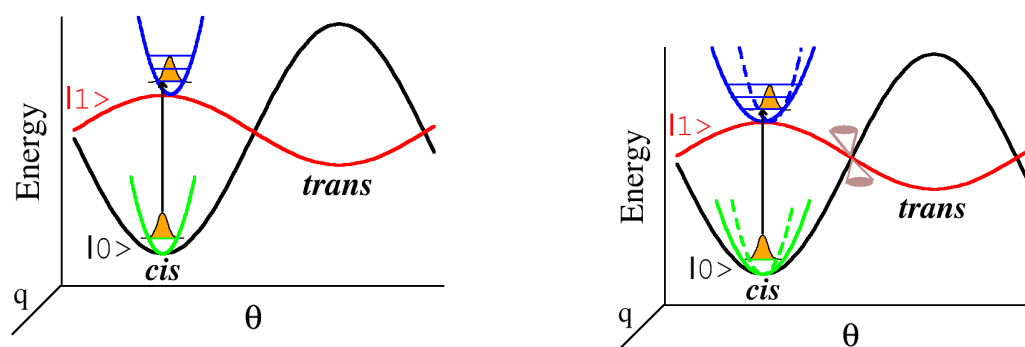

Figure 1: Schematic potential energy surface for the model without CI (left) and with CI (right). Note the distortion in the CI model due to the anharmonic nature of the adiabatic potential. The model includes two electronic states |0> denotes the electronic ground state, and |1> excited electronic states, and two nuclear degrees of freedom, the torsional mode θ and a coupling mode q.

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