The quantum dynamics experienced by a single molecular eigenstate excited by incoherent light

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Abstract

Contrary to conventional wisdom that all dynamics is a result of interference (or "dephasing") between many (at least 2) energy eigenstates, we show that when a continuum of states is present, even a single molecular eigenstate undergoes "steady-state" quantum dynamics. Moreover, this type of dynamics can be initiated by incoherent (e.g., solar) light sources. Continua are invariably involved in molecular systems due to a variety of sources such as the ever present bath modes; spontaneously emitted photons; the detachment of electrons; or the dissociation of chemical bonds. Contrary to a single bound energy-eigenfunction which is a real ("standing-waves") function that carries no flux, hence has no dynamics, a single (complex) continuum energy-eigenfunction carries "steady-state" flux given by the group velocity of the energetically narrow wave packet it represents. When this energy eigenfunction is a multi-mode resonance embedded in a continuum via a chain of intramolecular couplings, this dynamics may be initiated by any (light) source, and is controlled, contrary to coherent wave packet dynamics, by the position of the resonance rather than its width.