Modeling of Fluence-Dependent Hole-Burned Spectra and Hole-Growth Kinetics Using Multiple Two-Level Systems

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Numerical formalism is presented that perfectly describes low-temperature hole-burned spectra and spectral hole-growth dynamics of aluminum phthalocyanine tetrasulphonate embedded in hyperquenched glassy water films over more than seven orders of fluence magnitude (0.4 μJ/cm^2 to 5.9 J/cm^2). Frequency change during hole-burning is traditionally explained with the help of an extrinsic two-level-system (TLS$_{ex}$) centered on impurity molecule. The analysis presented shows that a single chromophore in an amorphous medium couples with multiple independent TLS$_{ext}$, which all pertain perfect photo-memory, thus allowing a full return to the "preburn" initial state (Figure 1). We show that the experimentally observed narrow photoproduct peak at higher energies, in close vicinity of the zero-phonon hole, reflects a dynamical feature of holeburning process populating "terminal" states (states that with sufficiently high probability do not interact with the laser excitation). For a single chromophore, multiple possibilities exist to create photoproduct when in interaction with the burning laser. Until terminal state is reached, chromophore can interact with burning laser-light multiple times. Due to phonon-assisted absorption, terminal states are typically at higher energies than the zero phonon hole in agreement with many experimental observations. For review of earlier work, please see[1] and references therein.

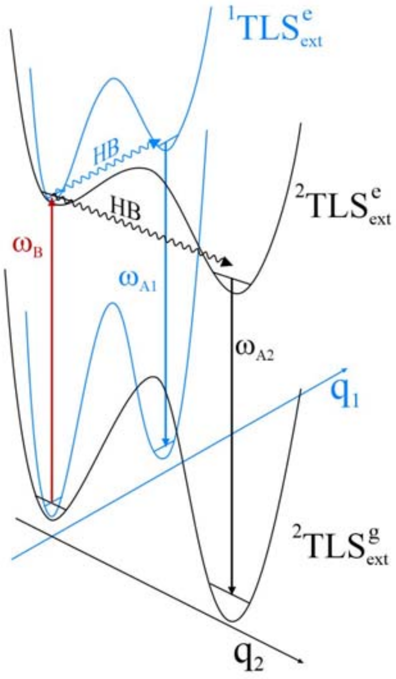

Figure 1. The n-TLS system (where n=2). An n-TLS realizes on the same chromophore and its surrounding solvent shell; there are n independent and different reaction coordinates, q_n. Chromophore is excited with the laser at ω_B. In the excited state, the system can tunnel along n different reaction coordinates and end up in n different stable configurations with different transition frequencies, ω_{An}.

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References

1. T. Reinot, V. Zazubovich, J.M. Hayes, and G.J. Small, J. Phys. Chem. B, 2001, **105**, 5083-5098.