

Vibrational relaxation and decoherence of photolyzed carbon monoxide in a hemoprotein: dynamical simulations and non-linear optical response signals for the detection of coherence decay

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We theoretically investigate dissipative processes in non-equilibrium systems by means of mixed quantum-classical models and present possible detection schemes by ultrafast non-linear spectroscopic set-ups.

Inspired by experimental findings, we follow as an example the relaxation dynamics of the excited vibrational mode of a CO molecule after photolysis from the hemoprotein FixL [1].

The simulations are based on a vibrational surface hopping approach treating the vibrational states of CO quantum mechanically, while all remaining degrees of freedom are described by classical molecular dynamics. This approach allows to directly simulate vibrational relaxation. The CO vibrational states form the 'surfaces' for the classical trajectories of protein and solvent atoms. In return, environmentally induced non-adiabatic couplings between these states cause transitions describing the vibrational relaxation from first principles, yielding a detailed atomistic picture of the energy relaxation pathways, taking the molecular structure and dynamics of the protein and its solvent fully into account [2].

In the process considered, the ultrafast dissociation leads to a non-equilibrium quantum state of the CO vibrational mode with possible coherences. In very general terms, such a nonequilibrium state interacting with a set of laser pulses in a four-wave-mixing setup leads to signal emission in directions opposite to the ones usually considered. When combined with a pump mechanism which sets a time origin for the nonequilibrium state creation, such as the UV pulse leading to the ultrafast dissociation of CO from FixL, this particular optical response can be utilized to directly follow decoherence processes in real time. By varying the time delays within the probe sequence, signals in these unconventional directions can also be used to detect two-dimensional spectra determined by the dynamics of up to three-quantum coherences, revealing anharmonicities and environmental influences [3].

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References:

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