Control by decoherence: weak field control of an excited state objective

Ronnie Kosloff and Gil Katz

Fritz Haber Research Center for Molecular Dynamics,
Hebrew University of Jerusalem, Jerusalem, 91904, Israel

Mark A. Ratner

Department of Chemistry, Northwestern University
Evanston, Illinois 60208-3113

Abstract. Coherent control employing a broad band excitation is applied to a branching reaction in the excited state. In weak field for an isolated molecule a control objective is only frequency dependent. This means that phase control of the pulse cannot improve the objective beyond the best frequency selection. Once the molecule is put in a dissipative environment a new time scale emerges. I will demonstrate that the dissipation allows to achieve coherent control of branching ratios in the excited state. The model studied contains a nuclear coordinate and three electronic states: the ground and two coupled diabatic excited states. The influence of the environment is modeled by the stochastic surrogate Hamiltonian. This is a consistent fully quantum system bath description of the dynamics. A stochastic layer allows the system to reach thermal equilibrium. The excitation is generated by a Gaussian pulse where the phase control introduced a chirp to the pulse. For sufficient relaxation we find significant control in weak field depending on the chirp rate. The observed control is rationalized by a timing argument caused by a focused wavepacket. The initial non adiabatic crossing is enhanced by the chirp. This is followed by energy relaxation which stabilizes the state by having an energy lower than the crossing point.

(i) Gil Katz, David Gelman, Mark A. Ratner, and Ronnie Kosloff, *Stochastic surrogate Hamiltonian*, J. Chem. Phys., **129**, 034108 (2008).

(ii) Gil Katz, Mark Ratner and Ronnie Kosloff, *Control by decoherence: weak field control of an excited state objective*, New J. Phys., **12**, 015003 (2010).