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# Steering Complex Photodissociation Dynamics through Initial Vibrational Coherences

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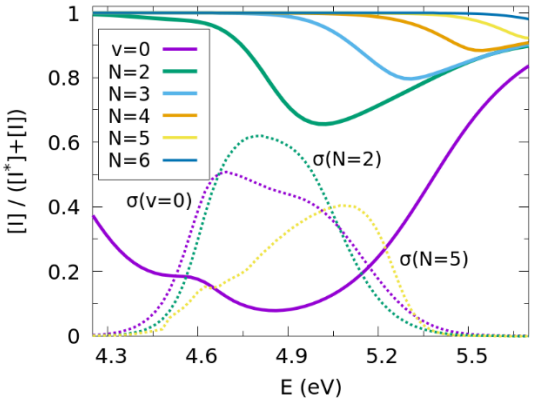
The control of quantum interference is a central concept in coherent control and underpins a wide range of applications in chemistry, from quantum-state preparation to photochemical reaction dynamics and quantum information processing[1]. In chemical physics, a primary objective of quantum control is the manipulation of chemical reactions to enhance yields and, in particular, to improve product selectivity among competing reaction or fragmentation channels. The conventional control scheme involves a two-step process in which a pump pulse initiates the dynamics by preparing a vibronic wave packet in excited electronic states, followed by a control pulse that directs nuclear motion along specific reaction coordinates by modifying phase relationships or inducing transitions between electronic states. In many experimental realizations, the pump and control fields are combined into a single shaped laser pulse, whose complex temporal and spectral structure is optimized using pulse shapers and adaptive learning algorithms[2].

Here we introduce an alternative control strategy, referred to as geometrical optimization[3], in which reaction control is achieved by tailoring the initial molecular wave function. Operationally, this corresponds to reversing the conventional sequence by applying a control pulse prior to photoexcitation. We demonstrate that the coherences imprinted in the initial state are sufficient to determine the reaction outcome even in polyatomic molecules subject to strong nonadiabatic couplings, as illustrated for the A band of $CH_3I$.




*Quantum yield of the I channel in the A band of $CH_3I$, as a function of the number N of vibrational states participating in the initial optimized superposition state*

References:

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