Probing coherence in ultrafast molecular processes: a theoretical perspective

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Revealing possible long-living quantum coherence in ultrafast processes allows detecting genuine quantum mechanical effects in complex systems, such as materials [1] and biomolecules [2]. To investigate such effects from a quantum chemistry perspective, we are developing methods to simulate the time evolution of molecular systems based on ab initio calculations that include the effect of an external medium (e.g., a solvent, plasmonic nanoparticles) on the molecule [3], as well as of dephasing of the electronic wave function, determining loss of coherence. The latter has been accomplished by means of the stochastic Schrödinger equation [4]. To test the approach, we have simulated [5] femtosecond pulse-shaping ultrafast spectroscopy of terrylenediimide [6], finding that the experimental results could be reproduced. Then, we have investigated the absorption of light pulses for a more complex system (a molecular chromophore close to a spherical silver nanoparticle), and we found that including dephasing is essential to provide a qualitatively correct picture of metal-enhanced molecular absorption, that depends on the interplay of light pulse duration, plasmon lifetime and electronic coherence [7]. Funding from EU grant ERC-CoG-2015 No. 681285 is gratefully acknowledged.

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