Vibrational Funnels for Energy Transfer during Internal Conversion in Organic Chromophores

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Photoinduced electronic energy transfer in large multichromophoric molecular systems is naturally accompanied by intramolecular vibrational energy redistributions[1]. Ab initio molecular dynamics (AIMD) simulations analysed in terms of vibrational normal modes, is a widely used technique that facilitates understanding of complex structural motions and coupling between electronic and nuclear degrees of freedom[2]. Usually, only a subset of vibrations is directly involved in the process of interest. Herein, different complementary criteria are analyzed to systematically identify the subset of vibrational normal modes that actively participate on the internal conversion process of different multichromophoric conjugated molecules: chlorophylls[3], donor-acceptors[4], and dendrimers[5]. Energy transfer coordinates are analyzed in terms of state-specific normal modes defined according to the different potential energy surfaces (PESs) involved. On one hand, we identify those vibrations that contribute the most to the direction of the main driving force on the nuclei during electronic transitions, represented by the non-adiabatic derivative coupling vector between donor and acceptor electronic states. On the other hand, we monitor normal mode transient accumulations of excess energy and their intramolecular energy redistribution fluxes. We observe that the subset of active modes varies according to the PES on which they belong and these modes experience the most significant rearrangements and mixing. Besides, we apply normal mode constraints[6] in AIMD simulations as implemented in the non-adiabatic excited state molecular dynamics (NEXMD) code[7]. In this way, we directly measure the impact of normal mode constraints on the photoinduced energy transfer. Our results show that the electronic relaxation can be significantly slowed down by freezing a well-selected small subset of active normal modes characterized by their contributions in the direction of energy transfer. The application of these constraints reduces the non-adiabatic coupling between electronic excited states during the entire dynamical simulations. Furthermore, we validate reduced dimensionality models by freezing all the vibrations except a few active modes. Altogether, our analysis can be broadely used to underpin the role vibrational motion in a studied process and to formulate reduced models that describe essential physical phenomena.

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