

The research project “Control of photo-induced energy transfer in functionalized nano-structures towards the design of nanoscale applications” (COPET) aimed at advancing a combined approach of quantum dynamics methodology and quantum control techniques applicable to photo-induced energy transfer processes in nano-structures consisting of carbon nanohorns, or CNHs, and molecular compounds with several stable equilibrium configurations, or MCCs.

The ultimate objective of such studies has been the design and development of nanoscale devices, such as plastic electronics, solar energy conversion cells, and artificial photosynthetic molecular complexes. For this purpose, we have used the time dependent density functional theory (TDDFT) in order to study the electronic transition density which governs the photo-induced energy and charge transfer process between electronic excited states in functionalized carbon nano-structures (CNSs). The excitonic dynamics has been further investigated with quantum dynamical methods which take into account the coherent excitonic time evolution in interaction with the vibrational degrees of freedom in such systems.

The manipulation of the photo-induced transfer process has been envisioned by switching on demand between the different equilibrium configurations of the molecular compounds used, which often have different physical properties, used for functionalization of the CNHs, by tailored laser pulses (see Figure 1, left). Alternatively, the control of the photo-induced transfer process could be achieved by the introduction of metallic nanoparticles in the proximity of the functionalized CNSs and the resulting near-field effects on the electromagnetic density of states due to the scattered light (see Figure 1, right).

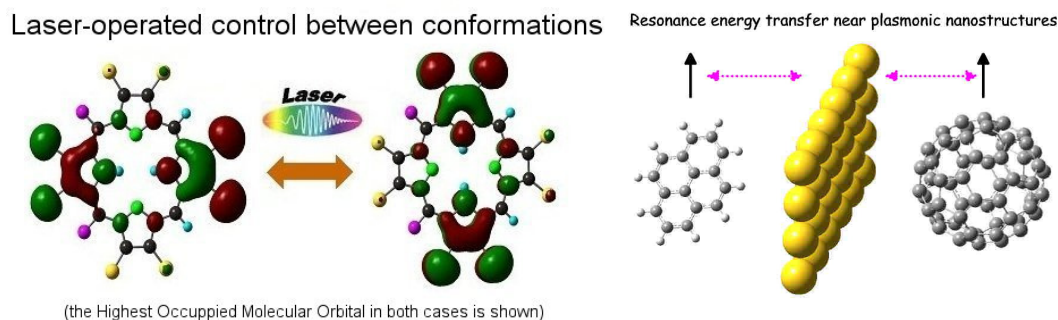


Figure 1: (Left): Laser control of MMC. (Right) Enhancement of energy transfer

The duration of the COPET project was 48 months, from October, 1, 2008 till September, 30, 2012. The work has focussed on the following aspects: (i) The development of methodology for describing the intra- and intermolecular energy transfer dynamics in systems with a large number of degrees of freedom. Such systems include typically a very large (often innumerable) number of states. Nevertheless, one is usually interested in how the energy flows from a relatively small number of initially excited states into the very large number of surrounding states. The energy flow from the configurational space, which includes the initial small number of states, to the rest, large part of configurational space, which consists of the vast majority of the states, can be due to time-dependent or time-independent interactions; (ii) the manipulation of energy transfer between an organic donor and a CNS acceptor, due to near-field effects of the electromagnetic field in the proximity of plasmonic materials; (iii) the investigation of energy and charge transfer properties of heterofullerene-donor dyads by studying the excited states of such systems, as well as their absorption spectra, by TDDFT methods; and (iv) the development of a methodology for taking into account the influence of vibrational degrees of freedom on the energy and charge transfer

process, including the possibility of manipulation of such processes by external electromagnetic fields, as laser pulses.

The main results achieved, with respect to the above directions of work are:

i) A methodology for describing the quantum dynamics of a small space, including a small number of states, coupled to a very large number of states, or even a continuum, by a time (in)dependent interaction has been developed. It has been demonstrated in intramolecular energy transfer due to radiationless transitions in a 24-mode configurational space and on ultrafast strong field molecular dissociation on a diatomic including all ro-vibrational degrees of freedom. These systems have been chosen because recent experimental results are available; therefore, direct comparison of the developed methodology with the experiment is possible. In both cases, the methodology describes the experimental results with excellent agreement.

ii) It is shown that photo-induced intermolecular energy transfer can be greatly enhanced in the ultraviolet frequency range in proximity of plasmonic metamaterials. The rate of the resonance energy transfer for a molecular donor-acceptor system with absorption and emission transition lines in the vacuum ultraviolet near plasma-coated dielectric nano-spheres is calculated by a rigorous first-principle electromagnetic Green's tensor technique. Exemplary donor-acceptor systems based on fullerenes and organic compounds are discussed. The electronic transition spectra of the donor-acceptor molecules are obtained by ab initio calculations.

iii) It is shown that hybrid systems of interest for photo-induced charge transfer consisting of nitrogen- and boron-doped fullerenes as acceptor (A) and pyrene, tetrathiofulvene, and porphyrin molecules as donor (D) compounds linked by a spacer chain are investigated. Our calculations have been carried out employing density functional theory and TDDFT. The near-degeneracy of the acceptor electronic transitions ( $A \rightarrow A^*$ ) to donor transitions ( $D \rightarrow D^*$ ) in the absorption spectrum of these hybrid dyads is indicative that charge transfer processes ( $D \rightarrow A^*$ ) are strongly competing to resonance energy transfer processes in these systems.

iv) A novel methodology has been introduced which allows for quantitatively studying the energy transfer process in small and large systems while the influence of the vibrational degrees of freedom is taken into account within the (un)coupled vibrational harmonic oscillators method. This approach has two important elements: a) it is in principle rigorous for the time interval of interest (though computationally expensive as the duration grows), and b) it can be combined with the methodology developed in i) above.

The scientific innovation, following the successful implementation of the COPET project, will reveal future technologies based on advanced functional nanoarchitectures consisting of carbon nano-structures and MCCs in the areas of opto-electronics, solar energy conversion cells, and artificial photosynthetic systems. By its very nature and goals - multi-configurational molecular compounds, photo-induced transport phenomena, tailored development of nano-structured materials - has a strong applied component, which is highly timely and strongly relevant to the enhancement of scientific excellence in Europe; it is, as such, of great relevance to the wider physics, chemistry, and materials science communities. The results of the COPET project can be utilized for the economic and regional growth and will contribute towards the EU Lisbon goal for knowledge-based activities as a means to economic and social growth.