Optical Limiting from first principles

Ab initio description of optical nonlinearities induced by impulsive broadband radiation (INPULS)

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In Short

- Identify the driving mechanisms of optical limiting using real-time time-dependent density functional theory (RT-TDDFT).

- Assess the role of electron-vibrational couplings in optical nonlinearities using RT-TDDFT coupled with Ehrenfest dynamics.

- Describe the interactions with the environment in optical nonlinearities of conjugated molecules.

Thanks to their large polarizability, carbon-conjugated molecules host a plethora of exciting nonlinear optical properties. Among them, optical limiting (OL) is regarded with a particular interest in several application fields as it consists of the activation by strong field intensities of light absorption channels that are unavailable in the linear regime. Materials hosting this process can be used as protection elements against intense radiation. The theoretical description of OL is still largely based on empirical models, despite the popularity gained by first-principles methods in the last few decades. In particular, real-time time-dependent density functional theory (RT-TDDFT) has established itself as a reliable and predictive method to access the spectroscopic response of molecules and extended systems, especially upon the effect of (intense) electromagnetic irradiation even produced by ultrashort pulses [1, 2]. Furthermore, this method is prone to be coupled to the Ehrenfest scheme for molecular dynamics, thus enabling the inclusion of electron-vibrational couplings in the response of the systems [1].

The first attempt to use RT-TDDFT to describe OL was proposed by the applicant in 2014 [3]. Taking a free-base phthalocyanine as a test system, the Yabana-Bertsch scheme [4] to trigger the wave-function propagation RT-TDDFT was applied to access the nonlinear response of the system under an instantaneous broadband perturbation. The results of this study, summarized in Fig. 1, indicate the activation of a dark band (labeled OL) upon increasing input fluence. Concomitantly, the optically active Q-band in the linear regime loses oscillator strength.

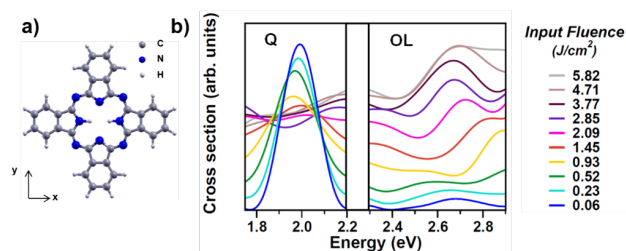The method proposed in Ref. 3 was later scrutinized in comparison with an analytical model [5] to

Figure 1: a) Ball-and-stick representation of a free-base phthalo-cyanine (Pc). b) Absorption cross-section of the Pc in the visible region at increasing values of the input fluence. The so-called Q-band and the optical limiting (OL) region around the frequency of the green light are shown. Taken from Ref. 3.
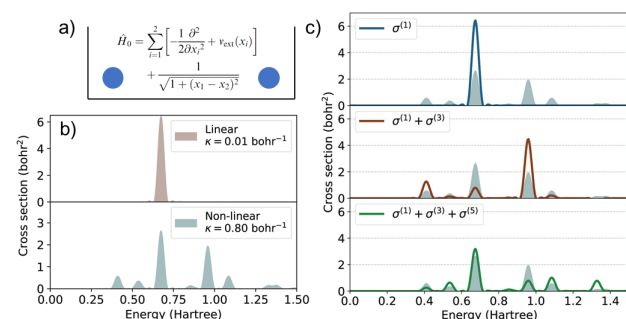

Figure 2: a) Sketch of the model system with two interacting particles (blue spheres) in a one-dimensional box. The Hamiltonian of such a system is reported in the background. b) Absorption cross-section of a quaterthiophene molecule computed from RT-TDDFT in the linear regime (top panel) and in the nonlinear one (middle panel). The grey shaded area marks the OL window for which the linear and nonlinear cross sections are overlaid on the bottom panel. d) Decomposition of the absorption cross-section shown in panel b) into the perturbative contributions of increasing (odd) order. Even-order contributions vanish due to inversion symmetry. Elaborated from Ref. 5.

identify contributions stemming from different perturbative orders that are automatically embedded in RT-TDDFT response (see Fig. 2). This analysis stimulated the idea of performing a systematic comparison with other RT-TDDT schemes such as pump-probe simulations which enable one to target specific excitations with resonance pulses. In the case of ethylene illustrated in Fig. 3, the laser stimulates the lowest energy transition between the frontier orbitals around 7.6 eV. At later times when the pulse is switched off, the signature of excited-state absorption is visible in the spectrum (Fig. 3a) around 2 eV. The population of the first and second excitations, S_1 and S_2, under the action of a train of pulses in resonance with their energies can be monitored in these simulations (see Fig. 3b), confirming
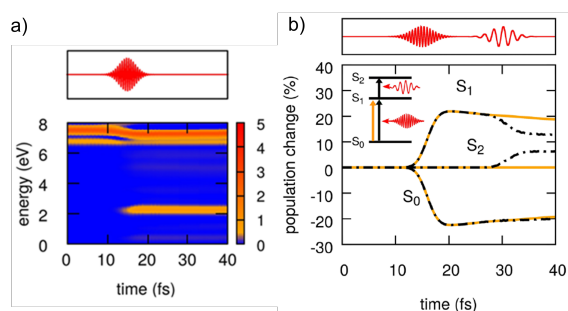
the nature of the involved physical mechanism.

Figure 3: *a) Transient absorption spectrum of ethylene resonantly excited at 7.6 eV. The color scale indicates the total absorption cross-section. b) Variations of the populations of S_0 (ground-state), as well as of the first and second excited states, S_1, and S_2 of ethylene upon the application of a train of pulses in resonance with their energy differences: E_{S0} - E_{S0} = 7.6 eV and E_{S2} - E_{S1} = 2.1 eV. Taken form Ref. 1.*

On top of these pump-probe simulations with resonant, ultrafast pulses, RT-TDDFT enables the study of coupled electron-nuclear dynamics in the framework of the Ehrenfest scheme. With the project IN-PULS, recently funded by the DFG, these calculations will be performed to analyze the role of vibrations in optical nonlinearities. Finally, for realistic comparisons with experiments, we want to include in the simulations the interactions with a polarizable environment. The interface of RT-TDDFT with the polarizable continuum model (PCM) 6 is the strategy employed in the final stage of the project INPULS.

The calculations proposed herein will be carried out with the software `octopus` 7 implementing RT-TDDFT on numerical spatial grids with the aid of pseudopotentials. We will focus on four groups of prototypical organic molecules: n-thiophene (n=2,4,6,8) oligomers; hydrogenated and fluorinated n-acene (n=2,3,4,5,6) oligomers; free-base and Mg-porphyrin and free-base and Mg-phtalocyanine, which are relevant for their optical response even in the nonlinear regime. In the first year, We will apply the "kick" approach developed in Ref. 3 to access their absorption cross-section under the action of instantaneous broadband perturbations of increasing intensity. Subsequently, we will impinge the systems with ultrashort and narrow-band pulses to target specific excitations and thus understand the origin of the peaks in the nonlinear optical spectra. In the following years, we will specifically address the role of electron-vibrational couplings by performing RT-TDDFT simulations in conjunction with Ehrenfest dynamics. Finally, we will include in the simulations the PCM in order to assess and quantify the influence of the environment on the nonlinear response of the considered classes of molecules. Direct comparison with experiments performed by an external project partner is envisioned as a quantitative point of reference for our results. The inclusion of the developed method into an automated workflow will enable its dissemination also beyond the theorists' community.

WWW

`https://uol.de/en/est`

More Information

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Project Partners

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DFG Subject Area

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