Nonlinear Optics from real-time TDDFT

First-Principles Description of Nonlinear Optical Properties of Light-Absorbing Materials

***C. Cocchi**, Institut für Physik, Humboldt-Universität zu Berlin*

In Short

- *Ab initio* study of nonlinear optical properties of light-absorbing materials by real-time time-dependent density-functional theory
- Assessing the role of triplet channels, exchange-correlation functionals, and incident laser fields in optical nonlinearities
- Real-time study of excitations at the interface between light-absorbing molecules and inorganic surfaces

Among the materials for the next generation of optoelectronic devices, inorganic-organic interfaces are of particular importance. Combining inorganic semiconductors, conjugated organic molecules, and metal nanostructures into hybrid materials will lead to novel features that can potentially give rise to a new class of devices. To achieve this goal, a thorough characterization of the intrinsic electronic and optical properties of these systems is essential. First-principles theory plays a decisive role in this context and in particular density-functional theory (DFT) and its time-dependent extension (TDDFT) are among the most popular and powerful approaches for this purpose. Although they have been successfully exploited to describe the linear response of any kind of systems, nonlinear optical (NLO) properties are still largely unexplored from an *ab initio* perspective. However, these effects crucially drive the optical behavior of materials when interacting with intense lasers sources. (Reverse) saturable absorption, excited-state absorption, and optical limiting, are only some of the many phenomena that can occur when a light-absorbing element is irradiated with a strong beam. The final goal of this project is to provide an accurate first-principles description of NLO properties of light-absorbing elements of hybrid inorganic-organic interfaces, shedding light on the fundamental processes ruling them. For this purpose, it is necessary to assess the methodology that enables an accurate description of the key phenomena in both types of materials involved, as well as novel features emerging when they are combined.

We have recently exploited real-time TDDFT (RT-TDDFT) in the Yabana-Bertsch scheme for the time-propagation 1, to study optical power limiting in a prototypical macrocyclic molecule 2. Optical limiting consists in the strong attenuation of the intensity of a laser source when passing through a material. This effect has important technological implications for the production of filters protecting from intense radiation light-sensitive elements, including the human eye. Conceptually, it is based on reverse saturable absorption, a third-order optical nonlinearity consisting in the activation of excitations that are dipole-forbidden in the linear regime, upon exposure of the sample to an intense laser source. For this investigation we chose a free-base phthalocyanine (Fig. 1a), a macrocyclic molecule characterized by a complex optical spectrum in the linear regime. Most relevantly, it has an extended transparent band in the visible region, around the frequency of the green light (532 nm = 2.33 eV). When the molecule is impinged by light of strong intensity, the absorption in this region grows significantly (see Fig. 1) as a consequence of the reverse saturable absorption, which is responsible for optical limiting.

This behavior is further demonstrated by plotting the output fluence with respect to the input one (Fig. 2). At very low intensities the system behaves as in the linear regime. As the fluence of the incident laser starts to increase, the output fluence deviates remarkably from linearity. The threshold between the linear and the nonlinear regime is given by the so-called saturation fluence (F_{sat}), which is a material-dependent parameter. Above this value, the increase of the output fluence with respect to the input one slows down significantly, up to reaching a plateau at extremely high intensities of the impinging field. The very good agreement with the experimental data 3 confirms the high potential of this approach for describing optical limiting and, more in general, third-order optical nonlinearities ruled by reverse sat-

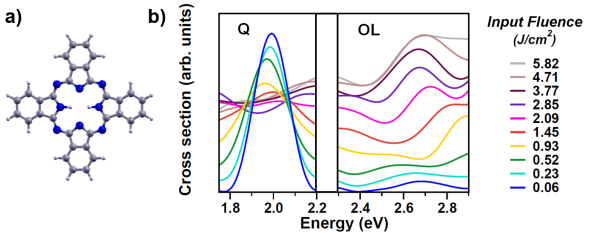

***Figure 1:** a) Ball-and-stick representation of a free-base phthalocyanine (Pc), with C atoms in grey, N atoms in blue, and H atoms in white. b) Absorption cross section of Pc in the visible region at increasing values of the input fluence specified on the right. The so-called Q-band at lower energies and the optical limiting (OL) region around the frequency of the green laser are shown. Adapted from Ref. 2.*

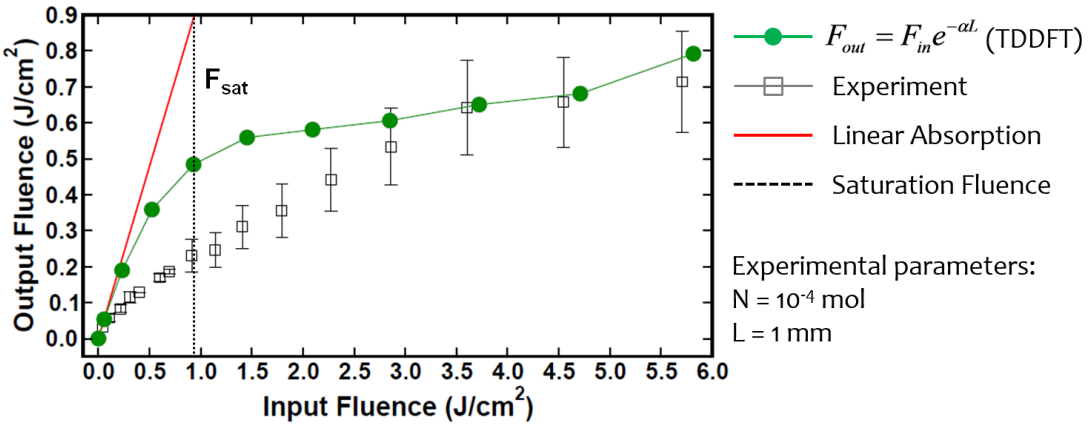

Figure 2: *Optical limiting curve of a Pc molecule, from Ref. 2. Green filled dots are the result from RT-TDDFT, obtained by systematically increasing the initial kick to trigger the time propagation. The curve is obtained by inserting the specified experimental parameters. Grey empty squares are experimental data from Ref. 3. The solid red and dashed black lines indicate the ideal linear absorption regime and the values of the saturation fluence F_{SAT}, respectively.*

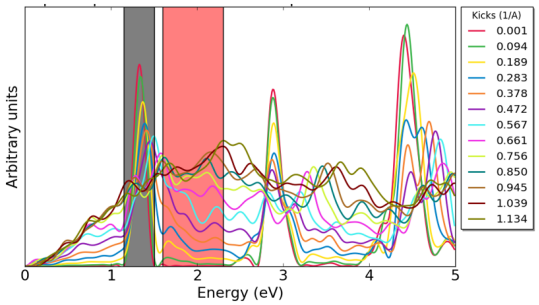

Figure 3: *Triplet spectra of a Pc molecule at increasing intensity of the incident field, expressed by the applied momentum (kick). The region around the first peak is shaded in black, while the transparent window between the first and second peak is highlighted in red.*

urable absorption and analogous mechanisms.

In the first quarter of this project, we have extended our analysis to the role of the triplet excitations. Although triplet excitations, being spin forbidden, cannot be directly probed in light absorption measurements, our theoretical framework gives us access to these channels and to their dipole character. The triplet spectra computed at increasing intensity of the incident beam (Fig. 3) exhibit analogous behavior to the singlet ones presented in Ref. 2: The first peak is increasingly quenched with the field intensity, while the non-absorbing window between the first and second peak is no longer so when strong fields are applied. Further investigation is on going to further assess the role of intersystem crossing in optical limiting.

In the continuation of this project we will extend our analysis on other classes of light-absorbing molecules that are particularly relevant in hybrid interfaces. The current work of in-depth analysis of the most relevant mechanisms at the basis of the linear and nonlinear optical response are aimed at providing the necessary background to understand these phenomena also in complex inorganic/organic materials.

Calculations will be carried out with OCTOPUS 4 and NWCHEM, open-source codes that offer an efficient implementation of RT-TDDFT. Both packages have aptimized parallelism schemes that are particularly suitable for running on supercomputing architectures 5 6.

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More Information

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Project Partners

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