"Excited states, photochemistry"

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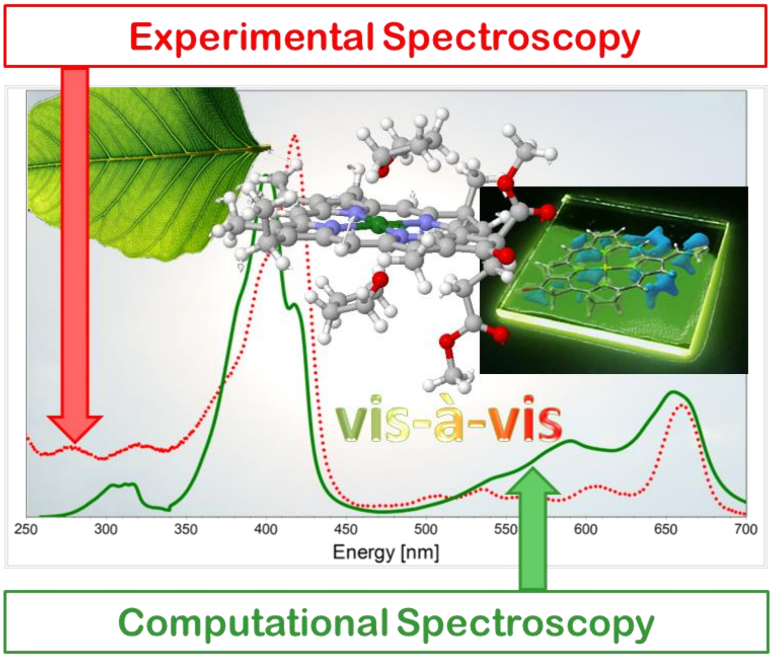
Most of the real-world processes takes place in 'bright' environments, i.e. the molecular system are exposed to solar irradiation, which manifests in photophysical and photochemical processes which are continuously happening not only in the laboratories but in the 'normal' every-day life [1-7]. Thus, the absorption and the emission of light in the UltraViolet-Visible (UV-vis) energy range (200-750 nm, 6.2-1.6 eV) is the most well-known and omnipotent spectroscopic phenomena. As the most natural examples one can mention the existence of colors and the visual abilities of human beings [2]. On the other hand, relatively high energy provided by UV photons leads to destructive processes. In this regard DNA strong absorbtion of UV light is a phenomenon of key biological interest, since a cascade of photochemical events can start from the DNA singlet excited electronic states, leading to the damage of the genetic code, and, eventually, to mutagenesis and carcinogenesis [3,4]. However, these undesired processes can be compensated by the possibility of fast and efficient non-radiative excited state decay channels. Another key issue of current interest are related to the natural and artificial light harvesting systems, such as identification of the most interesting chromophores among a large number of potential candidates for the design of new solar cells [5], or unraveling the many effects contributing to the complex light harvesting processes in natural photosystems [6].



Understanding of optical properties as well as photochemical and photophysical processes is provided through spectroscopic studies, either standard state-to-state one photon absorption and emission (OPA and OPE), their chiroptical couterparts: electronic circular dichroism (ECD) and circularly polarized luminescence (CPL); two-photon processes (TP) as well as pump-probe time-resolved experiments providing insights on excited states dynamics. Moreover, electronic spectra are often used to study the interactions between a molecule and its environment, being the first and key investigations in many different areas of the molecular, biological and nanotechnology sciences. However, spectroscopic results do not provide direct access to molecular structure and dynamics, and interpretation of the indirect information that can be inferred from analysis of the experimental data is seldom straightforward. Typically these complications arise from the fact that spectroscopic properties depend on the subtle interplay of several different effects, whose specific roles are not easy to separate and evaluate. In this context, computational studies can be extremely helpful, essentially at three different levels: (i) supporting and complementing the experimental results to determine structural, electronic and dynamical features of target molecule(s) starting from spectral properties; (ii) dissecting and quantifying the role of different effects in determining the spectroscopic properties of a given molecular / supra-molecular system; (iii) predicting electronic, molecular and spectroscopic properties for novel/modified systems. In such a way computational studies allow the assignment of experimental spectra and their interpretation in terms of basic physical-chemical processes.

These lectures and exercises are intended to give a general overview about computational approaches for modelling excited electronic states, while only essential aspects of the underlying theoretical models will be discussed. I will particularly concentrate on computational approaches related to the simulation and interpretation of state-to-state electronic spectra: one photon absorption and emission, as well as their chiroptical counterparts.

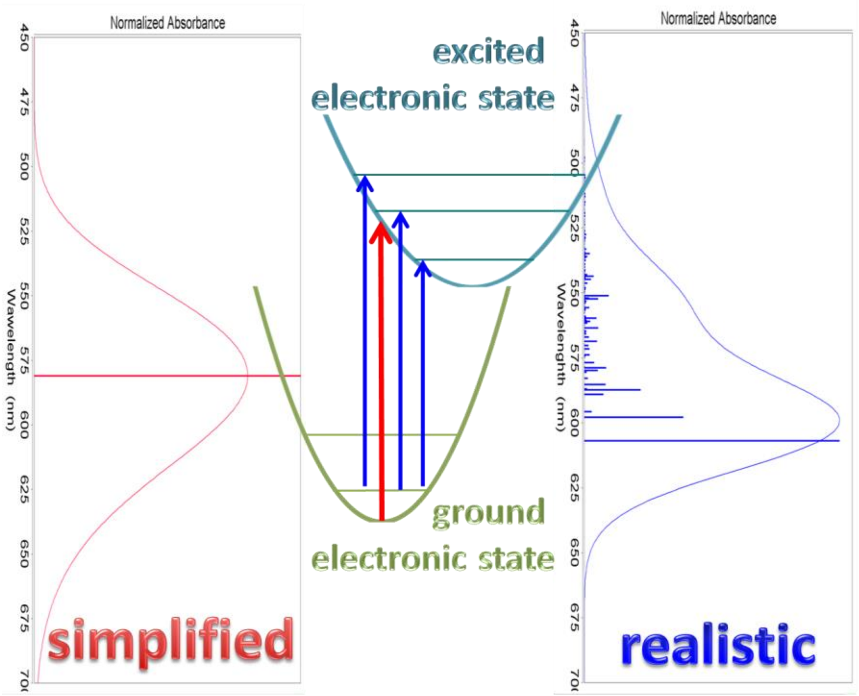


Figure 1. Simulation of electronic spectra: simplified model with only vertical electronic transition vs realistic model where transitions between vibrational levels of the two electronic states are taken into account.

Currently, most computations are limited to excitation energy and electronic transition moments, which are in turn convoluted to simulate the natural broadening in real conditions. In doing so, the experimental asymmetry of the band-shape, due to the vibronic structure is lost, leading to an incorrect estimate of the absorption and emission maxima and their relative intensities (Fig.1). Moving from the common practice of extracting numerical data from experiment to be compared with quantum mechanical (QM) results toward a direct *vis-`a-vis* comparison of experimental and simulated spectra strongly reduce any arbitrariness in the analysis of complex experimental outcomes and allow a proper account of the information connected to both position and shape of spectral bands. Simulation of vibrationally-resolved electronic spectra [3-12], including environment and temperature effects, can be routinely done nowadays even for medium-to-large systems. Moreover, multiple electronic states can be taken into account, making possible the full characterization of the photophysical properties of natural compounds, with all analysis further facilitated thanks to user-friendly graphical tools [13].

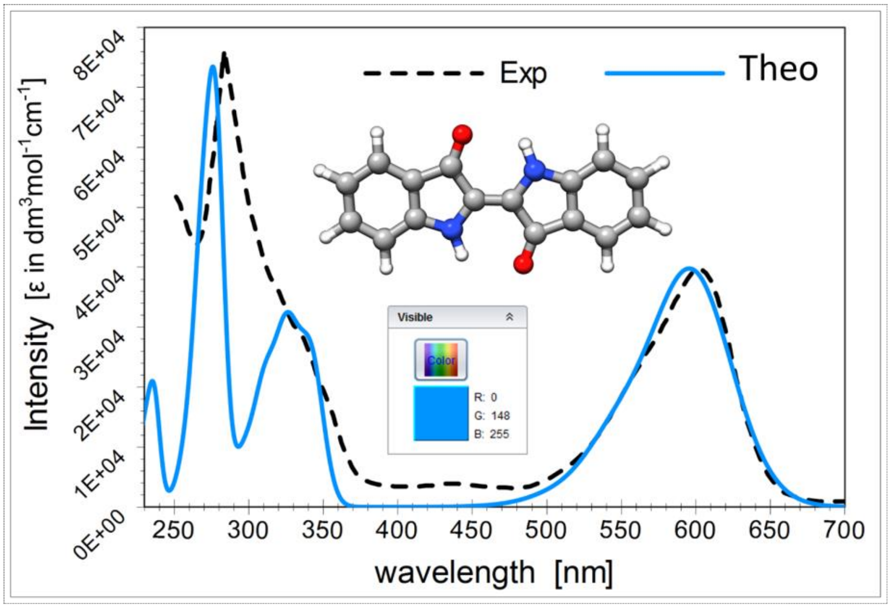


Figure 2. Simulated and experimental spectra of indigo, along with color prediction.

I. Unified and general theoretical model

Presented theoretical model [3-12] is developed for systems and phenomena localized on a limited space region, but possibly tuned by the more distant environment. Furthermore, it is assumed that the Born-Oppenheimer approximation is satisfied and that quantization of molecular rotation can be neglected. Under such circumstances the physical-chemical properties of a molecular system are governed by a potential energy surfaces (PESs) and by the corresponding property surfaces (PSs) for each electronic state, together with the needed transition moments.

Electronic spectra involve transitions between vibrational energy levels of two different electronic states, the upper state being neutral or ionic, and deriving from valence or core electron excitation. Electronic spectra line shapes, based on the underlying vibrational pattern, can be simulated by assuming that the electronic transition takes place in such a short time that the position of the nuclei remains almost unchanged. Then, the vibrational pattern of electronic spectra can be obtained from the computation of the overlap integrals, also known as Franck-Condon (FC) integrals, between the vibrational wavefunctions of the electronic states involved in the transition. In this frame, the theoretical models are defined according to the description of the PES for the electronic states involved and the approximation used for the evaluation of the transition dipole moment. This general procedure relies (so far) on the harmonic approximation, however anharmonic effects on excited electronic state frequencies can be taken into account by applying mode-specific anharmonic corrections. Finally, the issue of the infinite number of vibronic transitions can been overcome by the development of pre-screening black-box procedures and time-dependent path-integral models. The latter are characterized by an automatic inclusion of all vibrational states, while the former procedures allow to identify and assign single vibronic transitions; both approaches can be effectively combined in order to take into account their respective advantages.

II. Computational strategy: accuracy and feasibility

In many practical cases, a detailed analysis of the experimental electronic spectra is quite difficult due, for example, to the often non-trivial identification of the electronic band origin, multi-mode effects, possible overlaps of several electronic transitions and non-adiabatic and/or anharmonic effects. Although such complications are challenging also for the theoretical approaches, examples clearly show how theoretical simulations can provide a valuable tool with remarkable interpretative potential. When choosing the most proper model for a specific system, it should be realized that it is in general unknown *a priori* whether non-adiabatic effects exist in the region of the coordinate space relevant for the spectral features. In this respect, a particular care need to be taken while applying approaches, like the vertical ones, which may be operated with a minimal exploration of the final state PES. On the other side, more extended examinations of PES, such as those necessary to locate the excited state minima can bring to light issues that may otherwise remain unobserved. After that, for cases where relevant non-adiabatic effects exist, a proper modeling of the spectroscopy of the system under investigation cannot be done without a multi-electronic state treatment. On the other hand a disagreement between simulations and experiment may indicate existence of significant non-adiabatic couplings and can be used as a 'finger-print' of such effects. However, one should be aware that the disagreement between experimental and simulated spectra should not be attributed to non-adiabatic effects prior to exploring in detail the possible features of ``single-state'' vibronic models (e.g. full dimensionality). Beyond the possible non-adiabatic interactions, anharmonicity stands as an additional general factor to be taken into account in the spectroscopy of real systems. While a general route to its full treatment is out of reach for sizeable systems, it can be accounted for in a simplified manner in semi-rigid systems with nearly ``diagonal'' normal modes of the reference state leading, nonetheless, to significant improvement of the simulated spectra accuracy.

All the above mentioned issues will be illustrated with examples showing the advantages of modern computational spectroscopy approaches with respect to traditional models. Applications will be selected to highlight their flexibility, expected accuracy and interpretative capability, and to provide some guidelines for the choice of the most suitable models for a given problem, taking into proper account their computational feasibility.

References:

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