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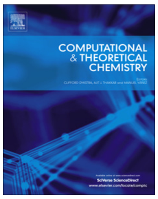

Environmental and dynamical effects on the optical properties of molecular systems by time-independent and time-dependent approaches: Coumarin derivatives as test cases

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ABSTRACT

The main building blocks of a virtual spectrometer aimed at the vis-à-vis comparison between computed and experimental electronic spectra of large-size molecules in condensed phases are shortly analyzed with special attention to stereo-electronic, dynamic and environmental effects. The combined use of time-dependent and time-independent models allows to deal effectively with both high- and low-resolution spectra involving several electronic states at finite temperatures and in different environments ranging from isotropic solutions to surfaces and interiors of nanoparticles. The most salient features of virtual spectrometer are next illustrated by studying absorption and emission spectra of several coumarin derivatives in different environments.

1. Introduction

The accurate simulation of spectroscopic processes is becoming increasingly important as an invaluable tool to assist and sometimes guide experiments [1–4]. In particular, the study of electronic excited states is at the frontier of contemporary investigations and goes beyond conventional molecular sciences to include multidisciplinary research fields, like life- and material-science [5–15], not to speak, very recently of cultural heritage aspects [16,17]. In the last years the study of medium and large-size molecules has been revolutionized by the development of methods based on the density functional theory (DFT) and its time-dependent extension (TD-DFT) [18,19] which are nowadays providing remarkably accurate results at least for low-lying valence excited states and is constantly increasing the range of possible applications thanks to ongoing efforts to solve some well-known shortcomings (e.g., charge transfer states, double excitations, etc.) [20,21]. In particular, the development of effective analytic gradients [22,23] and, very recently, of analytic Hessians [24,25], is allowing a full characterization of excited electronic states.

In this framework, moving from the standard practice of extracting numerical data from experiment to be compared with quantum mechanical (QM) results toward the direct comparison between recorded and computed spectra would strongly reduce any arbitrariness and allow a proper account of the information hidden behind both positions and shapes of spectral bands [15,26]. In particular, the convolution of vertical (or adiabatic) excitation energies by phenomenological (mostly symmetrical) distribution functions completely neglects the vibrational structure present in experimental spectra, leading to a number of difficulties: for instance, it cannot be used for the interpretation of high-resolution data showing a detailed vibrational structure and is also limited for low-resolution spectra, whose asymmetric peaks and often also relative intensities cannot be reproduced by a single distribution function. This problem has been widely studied, and two different approaches have been explored following time-independent (TI) [27–29] or time-dependent (TD) [30,31] routes. The first general approach is based on a sum-over-states formalism, where the spectrum is obtained as the ensemble of all transitions between the vibrational initial and final states treated independently from one another. Very effective numerical procedures have been introduced over the years for including Franck–Condon, Herzberg–Teller, Duschinsky and anharmonic effects also for medium- and large-size systems. This is the method of choice when high-resolution spectra allowing band identifications are

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sought, but has difficulties in obtaining fully converged results especially when temperature effects are of interest. In such circumstances a time dependent route becomes more effective since it exploits the properties of the Fourier transform leading to fully converged spectra including also temperature effects, without additional computational cost. The recent development of a general code including both TI and TD models [28,29,31] based on the same general data and algorithms is allowing the combined use of both approaches and the consequent availability of both high-resolved and fully converged spectra at finite temperatures [15]. However, the problem of large amplitude motions cannot be effectively dealt with these kinds of methods and requires either full quantum dynamic approaches (which start to become feasible thanks to the development of multi configuration time dependent Hartree, MCTDH, models [32,33]) or cheaper reduced dimensionality stochastic models based on the Smoluchowski equation [34,35]. An example of the latter approach will be sketched in the following.

From another point of view, all the above applications require also a realistic description of the complex environment around the chromophore, due to its non-negligible tuning effects often determining the spectroscopic outcome. Since the computational resources required for treating large systems are still beyond what is achievable by full QM computations, a reasonable compromise between accuracy and computational effort can be achieved by resorting to multi-scale or focused models, where the system is separated in multiple layers and the target structure is treated with a higher level of theory while the rest is described with less accurate but computationally less demanding approaches [36–42,35,43–46,7,47–50]. In general, environmental models can be separated in two large categories: explicit and implicit models. The former maintain an atomistic (albeit simplified) representation of the environment, thus are able to describe specific system-environment interactions (e.g., hydrogen bonds) and provide a more realistic picture. The drawback is that explicit models require a large number of atoms/molecules belonging to the environment to properly take into account long-range interactions (e.g. solvent bulk effects) and, consequently, require the consideration of a large number of configurations in order to achieve a statistical average of a given property. Implicit models, on the other hand, replace the atomistic representation of the environment with a continuum, polarizable medium [51–55]. The advantage here is a lower computational cost since long-range bulk effects and statistical averaging are naturally accounted for. The drawback is that specific system-environment interactions cannot be properly described. The best of the two worlds can be obtained by a judicious combination of the two approaches, which would limit the number of explicit atoms/molecules belonging to the environment to the nearest-neighbors of the chromophore (e.g. the first few solvation shells) to account for specific interactions, while including long-range effects through a continuum model. In this way, the number of explicit configurations (and corresponding QM calculations) necessary for statistical averages can be greatly reduced. A system-bath separation can be followed also concerning spectra computations using classical mechanics to take into account the broadening issuing from bath motions (essentially through averaging of the results computed by several snapshots obtained by molecular dynamics simulations) [56,57] and the above-described quantum TI or TD approaches for describing true vibronic effects issuing from the internal motions of a representative structure of the system possibly perturbed by an average field describing the effect of the bath.

In the following, after a short review of the theoretical background, the possibilities of our integrated approach (referred to as virtual spectrometer) will be illustrated using as test systems some coumarin derivatives (see Fig. 1), also known as benzopyrons, which are well known naturally occurring compounds that have found widespread application in different fields of scientific research as well as technological developments, like, e.g. solar cell technology [58,59], medicine [60–62] or high-resolution cell imaging applications [63].

2. Methodology

2.1. Vibronic time-independent and time-dependent quantum models

Computation of vibronic spectra within time-independent and time-dependent quantum mechanical approaches are described in more detail in Ref. [27,30] and references therein. Here, we mainly refer to the integrated procedure set within the Born–Oppenheimer and harmonic approximations (along with Eckart conditions), which is described in detail in Refs. [28,29,31]. This approach can be applied to one-photon absorption and emission (OPA/OPE) spectra, and has been also extended to electronic circular dichroism (ECD), circularly polarized luminescence (CPL) and Resonance-Raman spectra [64].

We recall the sum-over-states expression for a one-photon vibronic spectrum, adopting the general formulation proposed previously [28]:

$$I = \alpha\omega^{\beta}\sum_{i}\sum_{f}\rho\left[d_{IF}^{\mathrm{A}}\cdot {d_{IF}^{\mathrm{B}}}^{*}\right]\delta(\epsilon_F-\epsilon_I\pm\nu_0) \tag{1}$$

where δ is the Dirac function d_{IF}^{A} and d_{IF}^{B} are transition dipole moment integrals between the initial and final vibronic states, and the sign +/− holds for emission/absorption, respectively. One-photon absorption (OPA) and one-photon emission (OPE) spectra can be easily expressed within this formulation by defining the intensity (I) and parameters α, β as well as the transition dipole moments d_{IF}^{A} and d_{IF}^{B} with the values given in the list below:

$$\mathrm{OPA}: I=\epsilon(\omega),\quad \alpha=\frac{10\pi N_a}{3\epsilon_0\ln(10)\hbar c},\quad \beta=1,\quad d_{IF}^{\mathrm{A}}=d_{IF}^{\mathrm{B}}=\mu_{IF}$$

$$\mathrm{OPE}: I=I_{em}/N,\quad \alpha=\frac{2N_a}{3\epsilon_0 c^3},\qquad \beta=4\quad d_{IF}^{\mathrm{A}}=d_{IF}^{\mathrm{B}}=\mu_{IF}$$

where $\epsilon(\omega)$ is the molar absorption coefficient for a given angular frequency ω, I_{em}/N is the energy emitted by one mole per second, N_a is the Avogadro constant, c the speed of light, ϵ_0 the vacuum permittivity; $\boldsymbol{\mu}_{IF}$ is the electric transition dipole moment between the vibronic states I and F. However, analytical expressions for the electric dipole transition moment are not known, thus a Taylor expansion of the transition dipole moment with respect to the normal modes $\mathbf{Q}$ around the equilibrium geometry of one of the electronic states is usually employed:

$$\mathbf{d}_{IF}^{x}(\mathbf{Q})\approx\mathbf{d}_{IF}^{x}(\mathbf{Q}_{eq})+\sum_{i=1}^{N}\frac{\partial\mathbf{d}_{IF}^{x}}{\partial Q_i}\mathbf{Q}_i+\ldots \tag{2}$$

The zeroth order term corresponds to the well-known Franck–Condon (FC) approximation [65,66], which assumes that the electronic transition happens in such a short time that the nuclei remain in their equilibrium position. This approximation is satisfactory for fully-allowed transitions and when the potential energy surfaces of the ground and excited states are similar. However, when those conditions are not met, the inclusion of the linear terms in the Taylor series (first order in Eq. 2), namely the Herzberg–Teller (HT) approximation [67], is mandatory.

Finally, the calculation of the matrix elements of the electric dipole moment operator requires a relation between the normal modes of the lower and higher states, which as a general rule, are different. The standard approach refers to the linear transformation between the two sets of normal modes proposed by Duschinsky [68],