Toward reliable line-shapes for the electronic spectra of large molecular systems.

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The subtle interplay of several different effects still makes the interpretation and analysis of experimental spectra in terms of structural and dynamic characteristics a very challenging task. In this context, theoretical studies can be very helpful and this is the reason behind the rapid evolution of computational spectroscopy from a highly specialized research field toward a versatile and widespread tool. However, in the case of electronic spectra (UV–vis, Circular Dichroism, photoelectron, X-ray, etc.), the most popular approach still relies on computation of vertical excitation energies, which are further convoluted to simulate line-shapes. Such a treatment completely neglects the influence of nuclear motions, despite the well recognized notion that proper account of vibrational effects is often mandatory in order to interpret correctly the experimental findings. In this respect, the generation of reliable spectra including the vibronic contributions has become recently feasible even for medium-to-large systems. Here, we present the implementation of an effective procedure rooted into a time-independent model [1,2], integrated in a general-purpose computational chemistry package Gaussian09, offering the possibility to evaluate simply one-photon electronic spectra, using several electronic models, ranging from fully QM descriptions to discrete/continuum QM/MM/PCM [3,4]. Theoretical background, input preparation and data analysis for some specific examples will be presented to illustrate features of such integrated approach.

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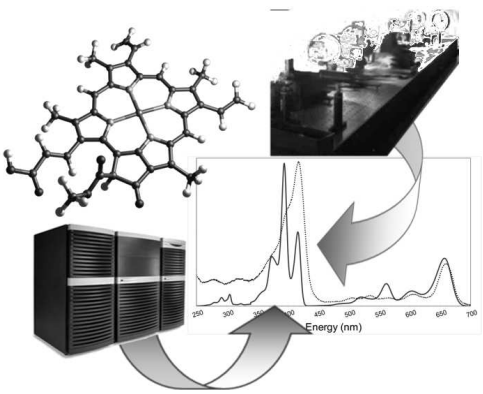
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