On new methods for predicting photophysical constants and spectra using the path integral approach: implementations on ORCA

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Abstract: Considering the recent developments in photophysics and photochemistry, particularly on the areas of Solar Cells, OLEDs, artificial photosynthesis and photodynamic therapy, the need for an efficient theoretical method capable of predicting the dynamics of excited states is ever more pressing. Much has been done in solving the time-independent Schrödinger equation, but for relevant predictions on these applications it is necessary to go beyond the static picture. Although there are methods that consider the solutions for the time-dependent Schrödinger equation in more or less approximate ways, the current methods such as the MCTDH[1] and surface hopping[2] are, in general, very costly and applicable only to small systems of about less than 20 atoms. In this work, we propose a new approach where it is possible to obtain these rates in a simpler way. Assuming a harmonic potential energy surface and using the solutions for the path integrals of the harmonic oscillator, it is possible to demonstrate that an analytic solution is obtainable[3]. The theory for the computation of transition rates such as fluorescence, phosphorescence and intersystem crossing was developed and implemented in the free software ORCA in a way that allows for systems of more than 100 atoms with excellent results. In this derivation it is also possible to include temperature and higher order effects such as vibronic coupling and Duschinsky rotations. Also, as the rates are proportional to the observed spectral intensities, the method can be used to predict very accurate absorption and emission spectra with real vibronic resolution. The same theory was also extended to compute the resonant Raman polarizability from the Douglas-Kramers-Heiseberg formula and permits simulation of rRaman spectra including transitions from fundamentals, overtones and combination bands, also including vibronic coupling and mode rotations.

As an example of the capabilities of this new module, named ORCA_ESD (from Excited State Dynamics), we present the absorption and emission spectra for benzene (Fig. 1), as predicted using data from B3LYP/DEF2-TZVP calculations. The module extracts data automatically from the other modules of ORCA and computes the rates in many different levels of approximation. It is important to consider that, in the case of benzene, the S_0-S_1 transition is symmetry-forbidden and all of the intensity observed is due to vibronic coupling. The calculated rate in hexane at 298 K, is 1.63 x10^6 s^{-1} while its best experimental value is 1.76 x10^6 s^{-1}[4].
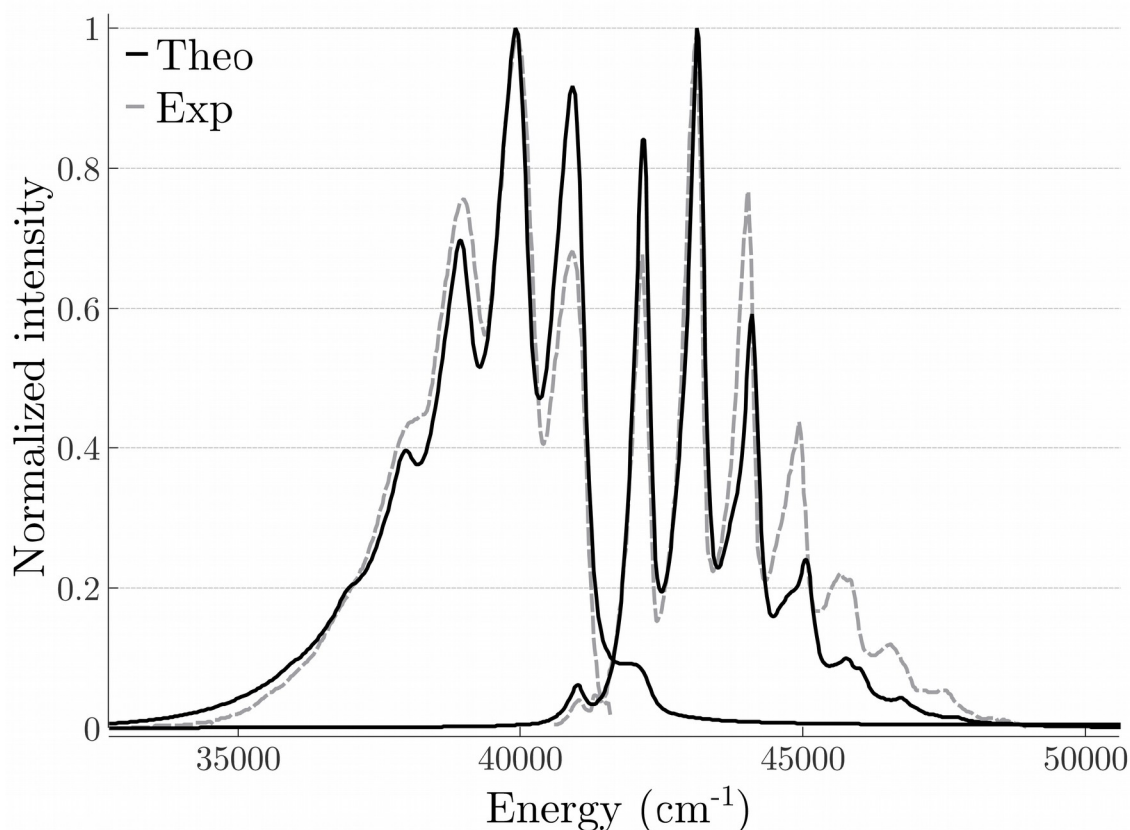
Figure 1. Predicted (in solid black) versus experimental (dashed grey) absorption (right) and emission (left) spectra for the S_0-S_1 transition of benzene in hexane solution at 298 K.

Key-words: excited state dynamics, photophysics, fluorescence, phosphorescence, intersystem crossing.

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