SIMULATION OF ACCURATE VIBRATIONALLY RESOLVED ELECTRONIC SPECTRA: THE INTEGRATED TIME-DEPENDENT AND TIME-INDEPENDENT FRAMEWORK

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Two parallel theories including Franck–Condon, Herzberg–Teller and Duschinsky (i.e., mode mixing) effects, allowing different approximations for the description of excited state PES have been developed in order to simulate realistic, asymmetric, electronic spectra line-shapes taking into account the vibrational structure: the so-called sum-over-states or time-independent (TI) method and the alternative time-dependent (TD) approach, which exploits the properties of the Fourier transform.

The integrated TI-TD procedure included within a general purpose QM code [1,2], allows to compute one photon absorption, fluorescence, phosphorescence, electronic circular dichroism, circularly polarized luminescence and resonance Raman spectra. Combining both approaches, which use a single set of starting data, permits to profit from their respective advantages and minimize their respective limits: the time-dependent route automatically includes all vibrational states and, possibly, temperature effects, while the time-independent route allows to identify and assign single vibronic transitions. Interpretation, analysis and assignment of experimental spectra based on integrated TI-TD vibronic computations will be illustrated for challenging cases of medium-sized open-shell systems in the gas and condensed phases with inclusion of leading anharmonic effects.

1. V. Barone, A. Baiardi, M. Biczysko, J. Bloino, C. Cappelli, F. Lipparini Phys. Chem. Chem. Phys, 14, 12404, (2012) 2. A. Baiardi, V. Barone, J. Bloino J. Chem. Theory Comput., 9, 4097–4115 (2013)