Quantum chemical methods
for modelling of vibrational-electronic transitions
in systems with hundreds of atoms

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Vibrational-electronic (vibronic) transitions are involved in a number of key phenomena including electron transfer, energy transfer, light absorption and photoluminescence. One of the complicating factors in the detailed modelling of these processes is the huge density of vibronic states that imposes severe constraints on the applicability of state resolved vibronic structure methods.

We have developed recently a unifying framework for the time-dependent and time-independent treatment of such processes, which combines the efficiency of time-dependent approaches in obtaining vibronic spectral profiles with the possibility to conveniently extract state resolved information [1]. Besides sum rules for rigorous prescreening of Franck-Condon and Herzberg-Teller integrals in the harmonic approximation at finite temperature [2,3], we employ also time-independent cumulant expansions that provide access to vibrational-electronic spectra at low resolution [4]. This scheme has been implemented in the vibronic structure program hotFCHT [1,5].

In this presentation, the underlying methodological framework will be outlined and its application to various types of spectroscopy will be presented.