

Vibronic transitions in large molecular systems: thermal time-correlation function and rigorous prescreening of Herzberg-Teller terms

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Franck-Condon (FC) factors are crucial ingredients for the detailed quantum mechanical understanding of photophysical processes. For the description of weak or even FC-forbidden transitions, however, one is forced to go beyond this level of approximation and has to account for vibronic coupling effects [1]. The Herzberg-Teller (HT) approach is perhaps the most obvious extensions of the FC approximation (see *e.g.* Ref. [2] and references therein) and requires the calculation of additional integrals involving the vibrational wavefunctions of the different electronic states. Various methods to compute these multi-dimensional HT integrals efficiently have been reported in the past (see *e.g.* Ref. [2,3]). The problem in large molecular systems is, however, the sheer number of HT integrals which increases steeply with increasing system size, temperature and energy window whereas usually only a tiny fraction of these HT integrals contributes significantly to a given photophysical quantity of interest. In this work, the methodologies reported previously [4,5] for rigorous prescreening of multi-dimensional FC factors at 0 K and finite temperature are extended to treat HT transitions. Sum rules for Boltzmann weighted HT integrals, including the interference contributions of the vibrational normal modes, are obtained from our HT generating function and employed to determine contributions of entire batches of HT integrals to the integrated HT profile. In advance, our sum rules provide rigorous upper and lower bounds on the total contribution of the selected integrals to the HT or FCHT profile. As opposed to previous restriction schemes, detailed error control is possible, which is crucial for the calculation of HT profiles of large molecular systems. Our HT generating function method can straightforwardly be extended to go beyond the linear HT approximation and to incorporate terms involving the linear momentum operator. It is also directly applicable to the computation of the time-correlation function (TCF) by the method suggested in Ref. [5].

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