

# Divide-and-Conquer Semiclassical Dynamics: A Viable Route for Spectroscopic Calculations of High Dimensional Molecular Systems

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The accurate prediction of vibrational spectra has become a very challenging task for theoretical methods. The most relevant stumbling block is represented by the necessity to employ quantum methods, since very often quantum effects, like zero point energy, quantum anharmonicities, and overtones, are not negligible to gain insights into the physics of a molecular system. Unfortunately, quantum mechanical methods are usually affected by the so-called curse of dimensionality problem, which limits their applicability to small and medium sized molecules. A viable alternative is represented by the Semiclassical theory, which is obtained by stationary-phase approximating to the second order of the Feynman Path-Integral representation of the Quantum time evolution operator, and allows to calculate spectral densities.<sup>[1]</sup> In particular, the Coherent State Representation was shown to be very valid in molecular applications.<sup>[2,3,4,5]</sup> However, even in this case the curse of dimensionality occurs and the method runs out of steam when the system dimensionality increases to 25-30 degrees of freedom or more. Here, we present a method, called Divide-and-Conquer, able to overcome this issue, and to reproduce spectra of high-dimensional molecular systems, while retaining the typical semiclassical accuracy (20-30 cm<sup>-1</sup>).<sup>[6,7]</sup> The method is tested on simple molecules. Then, it is used to calculate spectra of a C<sub>60</sub> model, which is made by 174 degrees of freedom, and of variously sized-water clusters characterized by strong hydrogen-bonding that red shifts the involved OH stretches.<sup>[8]</sup> Finally, the method is also combined with ab-initio molecular dynamics to abandon the necessity to employ pre-fitted Potential Energy Surfaces, and applied to study supramolecular systems as the protonated glycine dimer and hydrogen-tagged protonated glycine.<sup>[9]</sup>

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