A time averaged semiclassical approach to IR spectroscopy

Semiclassical vibrational spectroscopy is based on the evolution of classical trajectories and is able to reproduce quantum effects with good accuracy at the cost of a reasonable computational effort. [1-5] Nevertheless, semiclassical vibrational power spectra do not simulate all the features of the experimental IR spectra, since intensities in power spectra are not directly related to IR absorptions. Therefore, we developed a new semiclassical approach to the calculation of molecular IR spectra, by employing the time average technique upon symmetrization of the quantum dipole-dipole autocorrelation function. [6,7] We tested the accuracy of this new method on a few simple analytical systems and small molecules in the gas phase. In particular, spectra in the limit of infinite or zero temperature were investigated. Overall the method features excellent accuracy in calculating absorption intensities and provides estimates for the frequencies of vibrations in agreement with the corresponding power spectra.

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