Finite-temperature, anharmonicity, and Duschinsky effects on two-dimensional electronic spectra from ab initio thermo-field Gaussian wavepacket dynamics

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Accurate description of finite-temperature vibrational dynamics is indispensable in the computation of two-dimensional electronic spectra. Such simulations are often based on the density matrix evolution, statistical averaging of initial vibrational states, or approximate classical or semiclassical limits. While many practical approaches exist, they are often of limited accuracy and difficult to interpret. Here, we use the concept of thermo-field dynamics [1, 2] to derive an exact finite-temperature expression that lends itself to an intuitive wavepacket-based interpretation [3]. Furthermore, an efficient method for computing finite-temperature two-dimensional spectra is obtained by combining the exact thermo-field dynamics approach with the thawed Gaussian approximation for the wavepacket dynamics, which is exact for any displaced, distorted, and Duschinsky-rotated harmonic potential but also accounts partially for anharmonicity effects in general potentials [4]. Using this new method, we directly relate a symmetry breaking of the two-dimensional signal to the deviation from the conventional Brownian oscillator picture.

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