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Toward an Accurate Model for the Line Shape Analysis of 2D Correlation Spectra[1] MOHAMMADHASAN DINPAJOOH, DMITRY MATYUSHOV, Arizona State Univ — Bilinear (linear plus quadratic) coupling of a dipolar polarizable chromophore to a Gaussian thermal bath (Q-model[2]) is applied to study the effect of non-Gaussian statistics of the transition frequency on time-resolved linear and nonlinear correlation (2D) spectra. Exact lineshape functions of time-resolved fluorescence spectra and broadening functions of 2D correlation spectra (2DCS) are derived based on the summation of an infinite cumulant series of the transition frequency, in contrast to the two-cumulant approximation of the Gaussian models. The formal theory is supported by molecular dynamics simulations of a dipolar polarizable chromophore dissolved in a modified TIP4P water. We show that the Q-model, unlike the Gaussian model, can capture the asymmetry of 2DCS and bending of the center line in 2DCS reported experimentally. The theory provides a consistent formalism of the line shape analysis in cases when Gaussian models do not apply.

[1]NSF CHE–1213288, TG-MCB080116N
[2]D. V. Matyushov and G. A. Voth, J. Chem. Phys., **113**, 5413 (2000)

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