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Nonlinear Response Functions in Model Dissipative Anharmonic Systems MOHAMMAD SAHRAPOUR, NANCY MAKRI, University of Illinois at Urbana-Champaign — We report the results of simulations of third order response functions ($R^{(3)}(\tau_3, 0, \tau_1) = \mathrm{Tr}\left\{\hat{\alpha}(\tau_3)[\hat{\alpha}, [\hat{\alpha}(\tau_1), \rho_0]]\right\}$ where $\hat{\alpha}$ is the polarizability) for harmonic, Morse, and anharmonic model systems in a linearly dissipative environment. These simulations are carried out via the iterative path integral methodology developed earlier in our group which delivers efficient, numerically exact long time quantum dynamics. We find that even minor anharmonicity in the potential qualitatively changes the response function; rotating the pattern seen by 45^o in the $\tau_1 - \tau_3$ plane. We also observe that modulations in the τ_3 direction increase in frequency as we go to a more anharmonic potential. As the temperature is increased, these modulations also appear in the τ_1 direction. It is also found that asymmetry in the potential, at least at temperatures considered here, does not have a significant effect. Finally, in all three systems we notice that decay in the τ_3 direction is faster than in the τ_1 direction. The observed sensitivity of the response function to anharmonicities in the potential can be exploited to construct more accurate molecular potentials once the appropriate non-linear spectroscopic experiments have been performed.

Mohammad Sahrapour
University of Illinois at Urbana-Champaign

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