VIBRATIONAL ENERGY REDISTRIBUTION (IVR): NEW MODELS AND COMPUTATIONAL APPROACHES

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A deterministic model for IVR, which incorporates arbitrarily high order resonances via a scaling and factorization law for the vibrational matrix elements, is discussed. We also derive from this a "statistical vibrational triangle rule model," which takes into account the changes in dynamics during the progression from regular to chaotic spectra. In many practical cases under experimental study, highly vibrationally excited molecules fall into this intermediate regime. The models make a variety of simple predictions about the dilution factor, IVR rate, fraction of occupied phase space (Heller's F) as a function of energy, state density, molecular anharmonicity, and various other parameters. These are compared to both ultrafast and high-resolution IVR experimental data.

To evaluate IVR spectra or survival probabilities from these models, large scale computations on semi-sparse matrices of dimension 10,000-100,000 are required. These present a formidable challenge even for supercomputers using standard algorithms, such as Lanczos eigenvector calculations. We discuss symplectic propagators and the "matrix fluctuation-dissipation" (or MFD) theorem. These allow efficient computation of exact spectra, survival probabilities, and rates without full knowledge of the eigenfunctions.