VIBRATIONAL ENERGY REDISTRIBUTION – MATRIX ELEMENT FACTORIZATION AND CUMULANT EXPANSION

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Intramolecular vibrational energy redistribution (IVR) is an important phenomenon in highly excited molecules. We model IVR by means of a novel cumulant expansion to estimate the off-diagonal matrix elements of the vibrational Hamiltonian ignoring rotational contributions. Such a model is characterized by only a few parameters, such as the vibrational frequency and cubic anharmonicity, and is based on scaling and factorization properties of high order matrix elements. A cumulant expansion of potential constants accounts for both kinetic and spatial localization effects in the potential energy surface. Large amplitude motions, such as the internal rotation in methanol, have recently been incorporated into the model. Thus IVR of virtually any medium sized organic molecule can be described by this model.