

## A PHASE DIAGRAM FOR ENERGY FLOW-LIMITED REACTIVITY

CHENGHAO ZHANG, *Department of Physics, University of Illinois at Urbana-Champaign, Urbana, IL, USA*; EDWIN SIBERT, *Department of Chemistry, University of Wisconsin–Madison, Madison, WI, USA*; MARTIN GRUEBELE, *Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, IL, USA*.

Intramolecular vibrational redistribution is often assumed in Rice–Ramsperger–Kassel–Marcus and other rate calculations. In contrast, experimental spectroscopy, computational results, and models based on Anderson localization have shown that ergodicity is achieved rather slowly during molecular energy flow and the statistical assumption might easily fail due to quantum localization.

Here, we develop a simple model for the interplay of IVR and energy transfer and simulate the model with near-exact quantum dynamics for 10-degree of freedom system. We find that there is a rather sharp “phase transition” as a function of molecular anharmonicity “ $a$ ” between a region of facile energy transfer and a region limited by IVR with incomplete accessibility of the state space. The very narrow transition range of the order parameter “ $a$ ” happens to lie right in the middle of the range expected for molecular vibrations, thus demonstrating that reactive energy transfer dynamics occurs not far from the localization boundary, with implications for controllability of reactions.

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