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Earle K. Plyler Prize for Molecular Spectroscopy Dynamics: Photochemistry of Phenol: A Full-Dimensional Semiclassical Simulation¹
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This lecture will present a simulation of the photodissociation of phenol that is made possible by combining four methods in a complementary way: (1) the fourfold way for generating diabatic electronic states, based on diabatic molecular orbitals and configurational uniformity; (2) anchor points reactive potentials for fitting the 33-dimensional diabatic potentials; (3) coherent switches with decay of mixing for multistate dynamics governed by coupled potential energy surfaces, including density matrix coherence and decoherence; (4) army ants tunneling, including electronically nonadiabatic tunneling. By combining all these methods, one can thoroughly sample an ensemble of trajectories with potential energy surfaces and couplings that include multireference dynamic electron correlation. By including army ants tunneling, the trajectory simulation of phenol photodissociation dynamics based on accurate full-dimensional anchor-points reactive potential surfaces and state couplings successfully reproduces the experimentally observed bimodal total kinetic energy release spectra. Analysis of the trajectories uncovers an unexpected dissociation pathway. The new method for including tunneling in full-dimensional molecular dynamics simulations is general, and it can also be used for electronically adiabatic processes.

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