MAR15-2014-020142

Abstract for an Invited Paper
for the MAR15 Meeting of
the American Physical Society

Multistate trajectory and statistical theories of spin-forbidden kinetics

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Rate coefficients for several spin-forbidden reactions relevant to combustion are calculated using multistate trajectory and statistical theories. The two approaches are compared, and the appropriateness of treating singlet/triplet crossing seams as "nonadiabatic transition states" for spin-forbidden reactions is discussed. We show that the spin-forbidden reaction coordinate is coupled to the remaining nuclear degrees of freedom, leading to multidimensional effects not typically included in statistical treatments. We identify: static multidimensional effects due to the geometry-dependence of the shape of the crossing seam and spin-orbit coupling, dynamical multidimensional effects where the electronic transition probability depends on the distribution of the total internal energy of the system, and nonlocal multidimensional effects due to the instantaneous value of the electronic phase at multiple seam crossings. A semiclassical model based on short-time full-dimensional trajectories that includes all three multidimensional effects as well as a model for electronic decoherence is presented. The results of this new multidimensional nonadiabatic statistical theory are compared with the results of one-dimensional Landau-Zener and weak coupling models for several reactions.