Classical Molecular Dynamics in a Quantum Spirit

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In gas phase chemistry, fully quantum mechanical dynamics remains a challenge for systems greater than 4 or 5 atoms, especially at higher energies. Ring polymer molecular dynamics (RPMD) can handle larger systems with nearly quantum accuracy but can be problematic for computation of state-specific quantities and can be difficult to converge for complex forming reactions. On the other hand, Quasi-classical trajectory (QCT) based methods, where quantum effects are accurately included, may offer a promising alternative.
Classical dynamics is intuitive and becomes more computationally efficient at higher energies. A general QCT-based method for state-resolved rate constants and cross sections including quantum zero-point effects is presented. The method is applied to gas phase reactions of astrophysical interest, energy transfer collisions, and combustion reactions. Results are compared to recent measurements and benchmark RPMD and quantum calculations. Where standard QCT methods are shown to fail, quantum zero-point effects can be accurately included through analysis of the classical action and properly normalized weighting of classical trajectories. These results suggest simulation of detailed, state-resolved gas-phase and gas-surface chemistry may be possible with suitably modified QCT-based methods.