Abstract

Molecular dynamics, using both classical and quantum mechanical approaches, is used to investigate the general behavior of a set of systems within the conceptual framework of unimolecular reactions. Special focus is given to quantum effects on ergodicity, vibrational energy transfer, and dissociation processes. The systems investigated include the vibrations of NO_2 in its electronic adiabatic ground state, the famous two-dimensional systems of Henon-Heiles and Barbanis, collisional energy transfer of CF_3Br, and the dissociation properties of a collinear representation of a water cluster. Also a simple phenomenological model allowing a non-rapid energy exchange within a molecule is developed to exemplify how nonergodicity on short timescales may affect unimolecular reaction rate coefficients. Of particular interest in this study is the quantum mechanical promotion of nonergodic effects, how ergodicity should manifest itself in the quantum mechanical energy eigenfunctions, and how the ergodic properties in general affects dissociation in a system. A spectral filtering method to obtain pre-selected eigenfunctions of a system is evaluated and exemplified with the NO_2 system, and the so obtained eigenstates are investigated with respect to their ergodic character. Concerning collisional induced dissociation and the vibrational excitation, we find that classical mechanics and quantum mechanics often agree to an amazing extent, but that this is independent on how the classical trajectories are initialized and how the question of vibrational zero point energy is handled. It is also pointed out how mixed quantum classical methods via a mean-field approach may generate unphysical effects.