

Abstract

This theoretical work is concerned with tunneling processes in hydrogen atom transfer reactions (HAT) of three and polyatomic molecules. Especially, molecules with intramolecular hydrogen bonds are considered. In particular, the state-specific tunneling splittings of vibrational levels is addressed. A theoretical description of tunneling requires the solution of the multidimensional Schrödinger equation.

One objective of this work was the extension and comparison of semiclassical methods with quantum mechanical exact results. In semiclassical mechanics the propagation of a wave packet is described by an ensemble of classical trajectories. Two different methods were investigated. The first method allows for the inclusion of tunneling into simulations based on classical trajectories. It invokes trajectories that are propagated in the forbidden region (i.e., “under the barrier”), the equations of motion of which were introduced by Takatsuka *et al.* [Phys. Rep. **322**, 347 (1999)]. Thus, the new method is distinguished from previous ones, that treat tunneling to occur on predefined paths, e.g., straight lines. The performance of the new method was demonstrated for generic symmetric mode coupling potential energy surfaces and a model of the HO_2^- anion. The second method is a combination of semiclassical propagation by means of the Herman-Kluk propagator with harmonic inversion of cross-correlation functions by filter diagonalization [V. A. Mandelshtam, M. Ovchinnikov, J. Chem. Phys. **108**, 9206 (1998)]. This method was formerly considered as a hybrid quantum semiclassical approach. However, the investigation in this work suggests, that essentially it is a pure semiclassical method. Application of the method to one and two dimensional systems are given.

The second objective of this work was a pure quantum description of tunneling in HAT for polyatomic molecules. An efficient representation of the multidimensional Hamiltonian was derived that relies on so-called reaction plane coordinates, originally introduced by Takada and Nakamura [J. Chem. Phys. **102**, 3977 (1995)], which are collective coordinates that describe the contortion of the molecule. This approach was combined with the multi-configuration time-dependent Hartree (MCTDH) method, yielding an efficient means for solving the multidimensional Schrödinger equation.

As an example, the new approach was applied to the tautomerization of tropolone. A particular mode near 360 cm^{-1} , the reaction mode, was identified, that promotes tunneling considerably. Moreover, the IR spectrum was simulated by means of a 12D model. The results were discussed in view of experimental results, suggesting a new assignment of important features of the spectrum.