

## “Predicting chemical reaction rates”

The calculation of rate constants for elementary chemical reactions from first principles provides an important alternative to measuring them experimentally. This is especially true for elementary reactions that cannot be separated from a complex mechanism, that are extremely fast or extremely slow, or that occur under conditions that are difficult to reproduce in the laboratory. In addition, such calculations provide us with insights into the details of a reaction and what factors control it. Under the Born-Oppenheimer approximation, the dynamics of an elementary chemical reaction are determined by the sum of the electronic energy plus the internuclear Coulomb repulsion energy as a function of the nuclear geometry, that is, the potential energy surface (PES). For a given PES, the most practical approach for calculating reliable thermal rate constants is transition state theory with multidimensional semiclassical transmission coefficients. In the conventional formulation of transition state theory (TST), one assumes that the net rate of forward reaction at equilibrium is given by the flux of reaction complexes in the product direction across a coordinate-space hyperplane that divides reactants from products and passes through the saddle point of the PES, whereas in variational transition state theory, the rate constant is obtained from the maximum in the standard-state free energy change for the formation of the system along the reaction path. Because the latter approach finds an approximate dynamical bottleneck to the reaction, it is more accurate. The application of these methods to several relevant reactions will be presented, with

special emphasis on the incorporation of quantum mechanical tunneling and anharmonicity.