

Barrier evasion and roaming in the dynamics of elementary chemical reactions

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For chemical reactions where the reactant and product domains of configuration space are separated by a barrier, the rate coefficient commonly is calculated using transition state theory (TST), an approximate statistical method. The TST rate coefficient expression is based on the properties of limited ranges of the potential energy surface (PES) of the reaction: those of the narrow region near the reactants as well as at the saddle point separating reactants from products (the energy difference of the two structures, their vibrational frequencies and rotational constants). In many chemical reactions such an approach is not satisfactory, because the details of the dynamics and the rate coefficient are determined by regions of the potential energy surface that are far from the saddle point. Such cases will be presented in the talk.

1. In reactions of vibrationally highly excited diatomic molecules, during the reactive encounters the atoms do not even approach the saddle point. Moreover, in many cases a phenomenon called roaming can be observed: after a successful reactive encounter the products first depart from each other, their flight slows down because of slight attractive forces that arise due to the high vibrational amplitude until they stop finally return from a distance as large as 5 Å, and another collision occurs that can yield new products [1].

2. On the PES of the reaction of H atoms with electronically excited O₂, there is a barrier on the reactant side of the deep potential well corresponding to electronically excited HO₂. The rate of the reaction is determined not by the chance of crossing of the SP region but by the intramolecular motion of HO₂.

3. In the photodecomposition of CH₄ the excited-state PESs are repulsive. In such cases TST is not applicable. Dynamical simulations are needed to understand the molecular mechanism of the reaction. The product distribution depends on nonadiabatic transitions between the excited PES. Near conical intersections the reacting system can be reflected back from the repulsive side of the lower cone, which leads to roaming [2].

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[2] Mayes M.L., Lendvay G., Schatz G.C., *J. Chem. Phys.* 131:224320, 2009; Ziolkowski M., Vikár A., Mayes M.L., Bencsura Á., Lendvay G., Schatz G.C., *J. Chem. Phys.* 137:22A510, 2012.