

## Abstract

Collisional ro-vibrational activation/deactivation plays a major role in the kinetics of many chemical reactions. For unimolecular or recombination reactions in low pressure gas phase the amount of energy transfer in the intermolecular collisions is of primary importance for the reaction rate. The development of unimolecular reaction rate theory and of conceptual models for estimating collisional energy transfer is summarised and the corresponding statistical theories are compared to molecular dynamics simulations with respect to energy transfer efficiency and to detailed dynamical features of the collisions. Typically collisions between a highly energetic target molecule and a thermal bath molecule are considered. Initially, three systems are studied: *i*)  $\text{H}_2\text{O}-\text{H}_2\text{O}$ , a system with high capture strength, dipole-dipole coupling and non-spherical symmetry, using a high quality potential function; *ii*)  $\text{CF}_3\text{I}$ -propane, a system with intermediate capture strength, using a *3-body* representation as well as an *all-atom* model for the propane and a simple generic intermolecular potential function; *iii*)  $\text{CF}_3\text{I}-\text{Ar}$ , with a low capture strength and adjustable hardness of the repulsive part of the intermolecular interaction. Our results quantify the relevance to the energy transfer of the number of atom-atom encounters during a molecular collision. The correlations of the energy transfer with the geometry of the collision and the dynamical hardness of the interaction are treated as possible extensions of the models of energy transfer. Further investigation into the finer details of collisional dynamics is made by addressing the importance of the intermolecular repulsive hardness and collision energy to the energy transfer efficiency. Colinear collisions between diatomic molecules and rare gas atoms are treated using classical trajectory calculations compared to quantum dynamical close coupling calculations and an excellent classical/quantum agreement is found for the average energy transfer. A simple pair-potential model allowing for the repulsive hardness to be correctly represented, the mBq-potential, is suggested. It is based on counterpoise corrected MP2 energies in symmetry directions and extensively compared to state of the art potentials and interaction energies based on electron gas density functional theory. Finally trajectory calculations using the mBq potential are carried out to obtain energy transfer probabilities,  $P(E', E)$ , for the thermal activation of  $\text{CH}_3$  radicals. The kinetics of the decay process of  $\text{CH}_3$  to  $\text{CH} + \text{H}_2$  and  $\text{CH}_2 + \text{H}$  has been treated with a discrete energy master-equation to filter out the quantum mechanically forbidden energies in the low energy range giving  $P(E', E)$  information comparable to the classical trajectory results. The agreement is shown to be remarkably good. The future development of statistical theory is discussed.