# Energy Transfer in Molecular Collisions - Statistical Theory of Activation and Deactivation in Gas Phase

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**Abstract**

Ever since the realization that molecular collisions in general are weak not strong an accurate description of this collisional energy transfer (CET) process has been one of the major obstacles in the development of a predictive unimolecular reaction rate theory.

In this thesis we have explored the possibility to describe, what may seem to be a highly dynamical quantity, energy transfer in molecular collisions by the use of approximate statistical mechanics. The *ergodic collision theroy* (ECT) and *partially ergodic collision theory* (PECT) have been developed on the basis of an assumption of complete or restricted microcanonical relaxation between the molecules in the collision event.

We have made extensive test of ECT/PECT against what we belive to be benchmark experimental data measured using the very reliable and accurate method of *kinetically controlled selective ionization* (KCSI). We have in general found a good and systematic agreement between theory and experiments. Some deviations have been noted but none that could not be explained from within theory presented.

Investigations along the predictive line of our statistical approach have also been carried out. Both ECT and PECT successfully predict the energy and temperature dependence of collisional energy transfer under thermal conditions. This is important in efforts where one would like to extrapolate and obtain collisional energy transfer quantities, such as the collisional energy transfer kernel $P(E', E)$, for systems where no or only limited experimental or theoretical data is available.

One apparent strength of our statistical model is that it can readily be implemented with our without quantum effects which may enable the use of classical MD simulations to predict quantized energy transfer in real molecular collisions. We have also explored this possibility of ECT/PECT forming a bridge between MD simulations and experiment.

**Keywords:** Collisional energy transfer, energy transfer kernel, unimolecular reactions, master equation, reaction rates.