

A computational approach to the kinetics and dynamics of energy flow in large gas volumes.

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A prototype computational model of state-to-state energy flow in non-equilibrium gas mixtures containing up to 10^4 molecules will be described. The program follows changes in quantum state populations through successive cycles of collisions to equilibrium. At each stage of ensemble evolution, vibration and/or rotational state populations for each component species are available, giving kinetic data, insight into the dynamics of ensemble evolution and constituent species population distributions at any stage of the equilibration. The modal temperatures of vibration, rotation and translation also are available for each species, and their evolution through to equilibration gives a valuable overview of the complete energy transfer process. Up to three different atomic and/or diatomic molecules may comprise the gas mixture, with each diatomic initially in a specific (v;j) state and an ensemble collision energy that may be varied over a very wide range.

The model has been tested on a number of gas mixtures of current interest and found to give unprecedented insight into the dynamics of the equilibration process. Examples will be shown of relevance to atmospheric and astrophysical chemistry and will include e.g. the equilibration of highly excited N_2^* in a range of bath gases,¹ the disposal of OH^* energy from the $H + O_3$ reaction in atmospheric gases² and a novel translational energy cooling mechanism for H_2 in post-recombination early Universe.³ Data obtained thus far indicate that the equilibration process is often complex and multi-staged with a strong dependence on the chemical nature of the species involved.

(1). J. Chem. Phys. **134**, 044317 (2011); (2) J. Phys. Chem. (A) **116**, 2006 (2011); (3). J. Chem. Phys. **143**, 104306, (2015).

