Low-Energy Electron Impact Dissociation of Molecules and Molecular Ions

J. Royal, V. Ngassam and A. E. Orel
Department of Applied Science
University of California, Davis, USA

Electron collisions with molecules and molecular ions that lead to dissociationand excitation play a key role in a number of environments, since they produce the radicals and molecular fragments that initiate and drive the relevant chemistries. Examples of such systems can be found in biology as well as in chemistry and physics; they range from the technologically important plasmas used in plasma enhanced chemical vapor deposition, to planetary atmospheres and interstellar clouds, to DNA damage driven by secondary electron cascades produced by radiation. Since the mass of the electron is some three orders of magnitude less than that of the nuclei, it is a general prediction that in electron-molecule or electron-molecular ion collisions, there is little vibrational energy transfer or dissociation. However, there is an important exception to this rule, namely, systems where there is an intimate coupling between the electron interaction with the target and the nuclear dynamics of the target. The results of such an interaction can be quite dramatic. In these cases, the electron can temporarily attach to the molecule and change the forces felt between its atoms for a period of time comparable to a vibrational period. This can lead to resonant vibrational excitation and dissociative attachment, for neutral targets, or dissociative recombination in the case of ions.

We will outline the basic theory that underlies these processes, and our approach to study them. In the systems presented here, there exists one or more resonant states that lead to dissociation. The resonance parameters, the position and autoionization widths are taken from accurate electron scattering calculations using the Complex Kohn variational method. These parameters are then used as input to the dynamics calculations. The dyamics were studied using time-dependent wave packet methods, Multi-Channel Quantum Defect Theory (MQDT) and the solution of the time-independent equation using a Discrete Variable Representation (DVR) and exterior complex scaling. We will illustrate these methods with application to dissociative attachment in ClCN and BrCN, and dissociative recombination in the rare gas diatomic ions, He_2^+ and Ne_2^+ and in the HCN^+ and HNC^+ systems.