

Abstract

In this thesis results for the reaction of a ground state carbon atom, $C(^3P_J)$, with ground state nitric oxide, $NO(X^2\Pi)$, and the reaction of a ground state oxygen atom $O(^3P_J)$, with a ground state cyanogen radical, $CN(X^2\Sigma^+)$ are presented. These results have been obtained by using ab initio (CASPT2) and long-range intermolecular potential methods. Initially, about 2400 data points, different molecular configurations with corresponding potential energies, have been calculated for two potential energy surfaces (of $^2A'$ and $^2A''$ symmetries). These points have then been used to construct analytical representations of the global potential energy surfaces by fitting them to a functional form of the Many Body Expansion (MBE) type. Dynamics calculations have in most cases been performed using the quasiclassical trajectory (QCT) approach, but we also report on quantum mechanical wavepacket calculations on the O+CN reaction. From these kinetic (thermal rate coefficients) and dynamic data (reaction cross sections and product energy distributions) have been obtained and are compared to experiment. For most cases good agreement with experiment is found, and where this is not the case possible reasons for this are thoroughly discussed considering the approximations that have been made prior to performing the calculations. One of the most central concepts in this context is the Born-Oppenheimer approximation, which is discussed in depth.

A central part of thesis is the construction and evaluation of potential energy surfaces. An interpolation scheme, the Generalized Discrete Variable Representation (GDVR) method, has been developed to efficiently construct accurate potential energy surfaces. Some applications of this method are presented.