Modelling Atom Abstraction Dynamics in the Gas Phase and in Solution

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We will describe recent work aimed at modeling the dynamics of simple hydrogen atom abstraction reactions, in the gas phase and in solution. We use classical or quasiclassical trajectory methods on potential energy surfaces constructed using a simple version of the empirical valence bond (EVB) method.1 The potential energy is obtained as the lowest eigenvalue of a pseudo-Hamiltonian matrix. The diagonal elements of the matrix are diabatic potential energy surfaces calculated using force-fields, and the off-diagonal coupling elements are simple Gaussian functions of a few key coordinates.

This type of simple potential energy surface has not been much used for gas-phase reactions of small molecules, and hence the achievable accuracy of the method is not well known. Here we report reactions for the Cl + CH_4 reaction, for which extensive experimental data is available, and a high-quality potential energy surface has recently been described.[2] The EVB approach is shown to yield an accurate potential energy surface in terms of agreement with *ab initio* data. Quasi-classical trajectories on the EVB surface confirm the good quality of the surface, and differences from the global fit of reference 2 will be discussed.

Through the use of standard force-fields for the diabatic states, EVB is well suited to describing reactions in solution. Extending on our recent work on energy disposal in the CN + *c*-C_6H_{12} ➔ HCN + *c*-C_6H_{11} reaction,[3] we will discuss here the development of an accurate EVB potential energy surface for the F + CD_3CN ➔ DF + CH_2CN reaction, and the results of classical trajectory simulations of the reaction in liquid acetonitrile.

References

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