Quantum Dynamics of Gas Phase S_N2 Reactions

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Abstract

Nucleophilic bimolecular substitution (S_N2) reactions (e.g. the exchange reactions between halide ions and halomethanes $X^- + CH_3Y \rightarrow XCH_3 + Y^-$) belong to the most important reaction mechanisms in organic chemistry. There is evidence for strong solvent effects of S_N2 reactions in solution which prompted the investigation of those reactions in the gas phase. Here, the strong electrostatic interaction between the charge of the ion and the dipole moment of the halomethane leads to the formation of intermediate complexes, a pre-reaction and a post-reaction complex with deep wells which support scattering resonances. Classical trajectory calculations have shown that a detailed dynamical treatment is necessary for complex-forming bimolecular reactions.

We present quantum studies on the symmetric X = Cl = Y and asymmetric X = Cl, Y = Br reactions. The first reaction has a sharp central barrier and two equivalent wells, whereas the second one has the peculiarity that the barrier is below the asymptotic energy of the reactants.

Time independent quantum scattering calculations have been carried out on the reactions $X^- + CH_3Y\ (v,k) \rightarrow XCH_3\ (v',k') + Y^-$ with special emphasis on the rotational motion of the symmetric tops CH_3Hal. The two C-Hal stretching degrees of freedom (quantum numbers v and v') and the azimuthal angle describing the rotation of the CH_3 group (quantum numbers k and k') are treated explicitly. Since the k-levels are more widely spaced than the j-levels for a prolate symmetric top, an Infinite Order Sudden Approximation was introduced for j-rotation and orbital motion. This is accomplished by transforming the C-Hal distances into Radau coordinates which are democratic and orthogonal and suitable for strongly collinearly dominated systems. The potential energy surfaces of Hase and coworkers are used. The scattering problem is formulated in hyperspherical coordinates.