

Nucleophilic substitution dynamics by crossed-beam ion imaging

Roland Wester

Institute for Ion Physics and Applied Physics, University of Innsbruck, Austria

In this talk I will present recent studies of the dynamics of nucleophilic substitution reactions, which we have performed using crossed-beam velocity map ion imaging ^[1]. By analysing the differential scattering cross sections, we have identified several distinct reaction mechanisms for the reactions of Cl⁻, F⁻ and OH⁻ anions with CH₃I and a good agreement has been obtained with direct dynamics simulations ^{[2]-[6]}. The different mechanisms depend differently on the relative collision energy. This will be discussed with respect to the role of the energetics and the geometrical structure of the entrance channel complex. Recently, we studied the influence of the leaving group on an S_N2-reaction by comparing the reactants CH₃I and CH₃Cl and observed a profound difference for the two - in good agreement with dynamics simulations. This is explained by subtle differences in the interaction in the entrance channel ^[7].

In order to clarify the influence of spectator vibrational modes on the reaction dynamics we studied the reaction of F⁻ with CH₃I for CH-stretch excited reactant molecules. Both the S_N2-product and the proton transfer product were observed. For the latter a strong effect of the infrared excitation was manifest, whereas the former is only marginally affected by the vibrational excitation, which indicates spectator-like dynamics ^[8]. In crossed-beam experiments with larger alkyl halides we recently found evidence for the bimolecular elimination reaction (E2), which competes with the S_N2 reaction when more than one carbon atom is present ^[9].

References

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