RESONANCES IN S_N2 REACTIONS: TWO-DIMENSIONAL QUANTUM CALCULATIONS ON A NEW POTENTIAL ENERGY SURFACE FOR $CL^- + CH_3CL$

J. HAUSCHILDT, R. SCHINKE, *Max-Planck-Institut für Strömungsforschung, Bunsenstr. 10, D-37073 Göttingen, Germany*; P. BOTSCHWINA and S. SCHMATZ, *Institut für Physikalische Chemie, Universität Göttingen, Tammannstr. 6, D-37077 Göttingen, Germany*.

A new potential energy surface (PES) has been constructed for the collinear symmetric S_N2 reaction $Cl^- + CH_3Cl \rightarrow ClCH_3 + Cl'^-$. It is based on coupled cluster calculations with a large basis set. In the quantum dynamics calculations Radau coordinates were employed for the description of the two C$-$Cl stretching degrees of freedom. Making use of the filter diagonalisation method and an optical potential the wavefunctions of bound states as well as resonances states far above the barrier have been calculated. For many continuum states lifetimes are reported. Gerade states have strongly delocalized wavefunctions and decay faster than their ungerade counterparts with wavefunctions characterized by a node on top of the barrier. Removing the degeneracy by using different Cl isotopes reveals that the lifetimes of the resonance states are similar to those of the gerades states in the symmetric reaction.

Furthermore, first results on a new PES for the S_N2 reaction $Cl^- + CH_3Br \rightarrow ClCH_3 + Br'^-$ are presented. Using the coupled cluster method in conjunction with a large basis set of 257 contracted Gaussian$-$type orbitals the stationary points of the reaction have been characterized.