COMPUTATIONAL STUDIES OF THE $Cl(^2P) + HCl \rightarrow ClH + Cl(^2P)$ HYDROGEN EXCHANGE REACTION

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Over the years, the increase in computer power has led to increasingly extensive theoretical calculations on reactions of small molecular systems. Most of these calculations assume that the reaction takes place on a single electronic potential energy surface. However, in reactions where open-shell atoms or molecules take part, this approximation is generally not justified. Since for these systems multiple electronic surfaces become degenerate for certain geometries, a full description of such a reaction requires knowledge of all electronic states involved and of the couplings between them. A prototypical system for which such global potentials are available is the $Cl(^2P)$ + HCl system, in which there are three doublet surfaces that correlate to the ground state of reactants and products.[ab] An interesting feature of these surfaces is a shallow Van der Waals well in the reactant and product channels. The presence of such a well has been shown to be of great importance in the reaction rate of $Cl(^2P)$ with molecular hydrogen.[c]

We present results of time-dependent wave packet calculations on the hydrogen exchange reaction $Cl(^2P) + HCl \rightarrow ClH + Cl(^2P)$. In the calculations, the reaction is initiated by a vibrational excitation of the reactant HCl molecule. Total reaction rates and product distributions are calculated. All three potential energy surfaces and the non-adiabatic couplings between them are taken into account, as well as Coriolis and spin-orbit couplings.

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[b] T. W. J. Whiteley, A. J. Dobbyn, J. N. L. Connor, and George C. Schatz, *Phys. Chem. Chem. Phys.* 2, 549 (2000)
[c] D. Skouteris, D. E. Manolopoulos, W. Bian, H.-J. Werner, L.-H. Lal, and K. Liu, *Science* 286, 1713 (1999)