INITIATING THE HYDROGEN EXCHANGE REACTION $Cl(^2P) + HCl \rightarrow ClH + Cl(^2P)$ BY VIBRATIONAL EXCITATION OF THE MOLECULE

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In the quantum mechanical description of reactions, the most common approach is to assume that they take place on a single electronic potential energy surface (PES). However, in recent years interest in reactions in which open-shell species play a role is growing. In such reactions, there are often multiple surfaces that are degenerate for certain geometries and that are generally close in energy and strongly coupled. Thus the single surface approximation is no longer a good one, and a full description of an open-shell system requires multiple PESs and the non-adiabatic couplings between them.

A prototypical example of an open-shell system for which global potential surfaces have been constructed[a b] is $Cl(^2P) + HCl$. In this system, there are three doublet surfaces that correlate to the ground state of reactants and products. The potentials show a shallow Van der Waals well in both reaction channels, which has been shown to have a large effect on reaction rates in similar systems.[c]

We present results of a computational study to the feasibility of initiating the hydrogen exchange reaction $Cl(^2P) + HCl \rightarrow ClH + Cl(^2P)$ by vibrational excitation of the HCl molecule. The calculations involved a time-dependent wave packet propagation of the lowest $v_{HCl} = 2$ state, using all three potential energy surfaces and taking spin-orbit and Coriolis coupling into account. We find that the system does indeed react upon excitation of the HCl stretch, and that effects of the initial Cl isotopes and parity on the reaction rate are very small. Rotational and electronic product state distributions were computed and can be explained by features of the potential energy surfaces.

[a] A. J. Dobbyn, J. N. L. Connor, N. A. Besley, Peter J. Knowles, and George C. Schatz, *Phys. Chem. Chem. Phys.* 1, 957 (1999)
[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)