DETERMINING THE ROLE OF VIBRATIONAL EXCITATION ON THE DYNAMICS OF THE HYDROGEN-TRANSFER REACTION OF $F(^2P) + HCl \rightarrow FH + Cl(^2P)$

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In a series of studies, we have been investigating the possibility of promoting simple hydrogen-transfer reactions through vibrational excitation of the HCl bond in pre-reactive F···HCl or Cl···HCl complexes. Such open-shell species provide a challenge for quantum dynamical calculations due to the need to take into account multiple potential energy surfaces to accurately describe the system. Here, we focus on the $F(^2P)$ + HCl hydrogen-transfer reaction.

Previous studies on the hydrogen-transfer reaction of the $Cl(^2P)$ + HCl system focused on whether vibrational excitation of the HCl stretch would promote the reaction and if so, how the reaction dynamics reflects the coupling among the diabatic potential surfaces that describe this system.[a] The reaction mechanism involved coherent oscillations of the wave packet between the reactant and product channels. By going to $F(^2P)$ + HCl, we have broken the symmetry between the reactant and product channels which means we do not expect to see coherent oscillations. With this change, the question now becomes how does the reaction proceed.

A three-dimensional, fully-coupled potential energy surface has been constructed based on electronic energies calculated at the multireference configuration interaction+Davidson correction (MRCI+Q) level of theory with an aug-cc-pVnZ ($n = 2, 3, 4$) basis.[b] Spin orbit calculations have also been included[c]

We performed time-dependent quantum wave packet propagations involving all three potential surfaces, initiating the reaction with HCl in each of its three lowest vibrationally excited states ($v = 1 - 3$).

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[a] G. W. M. Vissers and A. B. McCoy *J. Phys Chem. A* **110** 5978 (2006).

[b] M. P. Deskevich, M. Y. Hayes, K. Takahashi, R. T. Skodje, and D. J. Nesbitt *J. Chem. Phys.* **124**(22) 224303 (2006).

[c] M. P. Deskevich and D. J. Nesbitt *private communication*(2007).