Title: Quantitative Estimates of Chemical Kinetics With Metadynamics

In this talk, we present application of the infrequent metadynamics [1] method to studying chemical reaction kinetics. This method combines the theoretical framework of the well-known acceleration factors [2] approach with the versatility of convenient collective variable selection and transient bias potential construction of metadynamics. The approach allows for calculation of mean escape times from free-energy basins, leading to enormous effective speedups of ab initio (AIMD) calculations, sometimes up to eight orders of magnitude.

The first part of the presentation will discuss the fundamentals of the method and demonstrate determination of Arrhenius-like activation energies for a model gas-phase S_N2 reaction using semi-empirical PM6 [3]. A systematic study of the algorithm and optimization of parameters required over 5000 reaction events to be sampled. Exact agreement with unbiased high-temperature kinetics will be presented. Furthermore, we will demonstrate that previously suggested approaches for using Metadynamics to obtain estimates of reaction barriers may not provide reliable results. Following this, the feasibility of using the approach on actual AIMD calculations is then shown by using CPMD+MetaD to sample the same reaction using only 10-20 calculations of the rare event. Finally, extension to other more complicated systems will be presented.

[1] Tiwary, P. and M. Parrinello, Phys. Rev. Lett, 2013. **111**, 230602.

[2] A. Voter, Phys. Rev. Lett., 1997, **78**, 3908.

[3] K. Fleming, P. Tiwary, J. Pfaendtner, "A New Approach for Investigating Reaction Dynamics and Rates with Ab Initio Calculations", *under review,* 2015.