Energy Transfer and Reaction Dynamics in Solution: Molecular Dynamics Simulations

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In this talk, I will present recent work in my group focused on using molecular dynamics simulations to address the topics of energy transfer between solutes and solvent, and of reaction dynamics. We use molecular mechanics, empirical valence bond, and hybrid quantum mechanical/molecular mechanical (QM/MM) potential energy surfaces for studying reaction dynamics. I will discuss two main topics:

A) Reaction of the fluorine atom with solvents acetonitrile or dichloromethane, yielding hydrogen fluoride and the radical derived from the solvent [1,2,3]. I will show that EVB methods yield reliable and efficient potential energy surfaces for these reactions. Also, the simulations shows that the hydrogen atom transfer occurs in a manner similar to that found in similar gas phase reactions, with the nascent hydrogen fluoride molecule being formed with a large amount of vibrational energy. The rate of vibrational cooling is extremely sensitive on the details of the potential energy surface, with timescales ranging from the experimental ~5ps to hundreds of ps.

B) Cycloaddition of ethene with butadiene to yield cyclohexene [4]. Here I will focus on the role of solvent friction in influencing barrier crossing rates. This will be discussed in the context of results relating to the speed of energy transfer between organic solutes and common solvent [5].

Relevant recent publications:

[1] *Vibrational relaxation and micro-solvation of DF after F-atom reactions in polar solvents*, G. T. Dunning, D. R. Glowacki, T. J. Preston, S. J. Greaves, G. M. Greetham, I. P. Clark, M. Towrie, J. N. Harvey and A. J. Orr-Ewing, *Science*, 2015, **347**, 530 – 533

[2] *EVB and polarizable MM study of energy relaxation in fluorine–acetonitrile reactions,* X. Zhang and J. N. Harvey, *Phys. Chem., Chem. Phys.*, 2019, **21**, 14331 -14340

[3] *Vibrational Energy Relaxation of Deuterium Fluoride in d-Dichloromethane*, X. Zhang, S. A. Vázquez, J. N. Harvey, to be submitted

[4] *Solvent Friction Effects in Diels-Alder Cycloaddition*, X. Zhang and J. N. Harvey, work in progress.

[5] *Rates of Molecular Vibrational Energy Transfer in Organic Solutions*, S. Essafi and J. N. Harvey, *J. Phys. Chem. A*, 2018, **122**, 3535 - 3540