

P014 Enzymic H-tunnelling – a role for promoting vibrations?
**Linus O. Johannissen[†], Sam Hay[‡], Michael J. Sutcliffe[†]
and Nigel S. Scrutton[‡]**

[†]Chemical Engineering and Analytical Science, [‡]Faculty of Life Sciences, Manchester Interdisciplinary Biocentre, University of Manchester

Our understanding of enzyme catalysis has evolved tremendously since the early lock-and-key model. It is now well established that enzymes are inherently dynamic molecules, undergoing a wide range of internal motions – sub-picosecond atomic fluctuations to nanosecond domain motions and millisecond conformational rearrangements. Over the past decade, it has come to light that enzymically-catalysed H-transfers, which involve varying degrees of nuclear quantum tunnelling, are influenced by enzyme vibrations, but the nature and role of these vibrations is not clear. According to one school of thought, collective, thermally equilibrated motions are required to attain quantum degeneracy between the reactants and products, while faster “promoting” vibrations can enhance the probability of tunnelling once such a state has been achieved by compressing the donor-acceptor distance. The concept of promoting vibrations is contentious, however. For example, such compression might in fact arise from stochastic fluctuations rather than specific vibrational modes, and it has been suggested that the rate enhancement caused by such vibrations is not in fact due an increase in tunnelling. Here are presented results from numerical and molecular modelling studies of the role of promoting vibrations and their effect on H-tunnelling, both on model systems and specific enzymic H-transfers.