Nuclear quantum effects in intramolecular hydrogen dynamics

Mariana Rossi

MPI for the Structure and Dynamics of Matter, Luruper Chaussee 149, 22761 Hamburg, Germany

mariana.rossi@mpsd.mpg.de

The inclusion of nuclear zero-point-energy and tunneling effects in high-dimensional anharmonic systems represents a considerable challenge in atomistic simulations. I will discuss methodology based on the path integral formalism, that can give access to reaction rates and vibrational spectra, including nuclear quantum effects and that is fully applicable to systems where a high number of anharmonic degrees of freedom are relevant. As a paradigmatic example, I will show results for the intramolecular hydrogen transfer dynamics of the porphycene molecule. I will discuss how we unraveled the contribution of different tunneling paths to the reaction rates at lower temperatures [1], explained an unusual temperature dependence of its vibrational spectrum [2] and discovered that surface fluctuations can enhance the intramolecular hydrogen tunneling rate by orders of magnitude when these molecules are adsorbed on metallic surfaces [3].

[1] Y. Litman, J. O. Richardson, T. Kumagai, M. Rossi, *J. Am. Chem. Soc.* **141**, 6, 2526–2534 (2019).
[2] Y. Litman, J. Behler, M. Rossi, *Faraday Discuss.* **221**, 526-546 (2020).
[3] Y. Litman, M. Rossi, *Phys. Rev. Lett.* **125**, 216001 (2020).