The influence of nuclear quantum effects on proton hopping kinetics in the H-SSZ-13 zeolite through ab initio derived machine learning potentials

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Computing accurate kinetics for zeolite-catalysed reactions is of primary importance to provide mechanistic insights and strengthen the bridge connecting theory and experiment.[1] While, on the one hand, there is a desire of moving towards complex models capable of reproducing the actual working catalyst,[2] even the simplest reaction in pristine Brønsted-acidic zeolites can hide some unexpected challenges. Arguably, such a reaction is represented by the BAS (Brønsted Acid Site) hopping around the oxygens in the first coordination sphere of the Al substitution. Because of its simplicity, extensive theoretical and experimental investigation has been performed during the past few decades but, by comparing the activation energies reported in the literature, one quickly realizes that a large spread in the datapoints is present – especially when comparing theoretical and experimental data.[3]

The reasons underlying this discrepancy can be manifold but, from a purely theoretical point of view, calculations performed so far never explicitly accounted for the quantum nature of the hydrogen nucleus that, thanks to tunneling effects, is known to significantly reduce proton transfer barriers. Unfortunately, the Path Integral Molecular Dynamics (PIMD) approach – commonly used to introduce Nuclear Quantum Effects (NQEs) in the calculation[4] – is generally too computationally expensive to be routinely applicable when the potential energy surface is evaluated at an *ab initio* level of theory. Luckily, Machine Learning Potentials (MLPs) have recently permeated the field of computational chemistry, as they can reproduce the *ab initio* accuracy for a fraction of the computational cost.[5]

In this contribution, we used high-temperature advanced-sampling *ab initio* simulation to train a reactive MLP, capable of accurately describing the BAS hopping reaction in the H-SSZ-13 zeolite. Thanks to its extreme speed-up, we were able to retrieve activation energies for the reaction over a large interval of temperatures (273-873K) both with classical MD and with PIMD, to explicitly take into account the quantum behavior of the nuclei. Accurate rate constants were then computed in the reactive flux formalism, providing a final hopping rate that should be comparable with experiment.

We showed that explicitly including NQEs has a severe impact on the computed kinetics, even at temperatures well above room temperature. The final hopping rate follows an Arrhenius behavior, with low deviations from linearity over the large span of temperatures considered.

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5. Schütt, K. T. et al. *J. Chem. Phys.* **2018**