

# Nuclear Quantum Effects on Surface-Assisted Water Dissociation

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The study of molecules adsorbed on inorganic surfaces is an active research field, mainly motivated by its promising applications. Molecular devices employing molecular switches based on proton transfer [1] and energy conversion based on water splitting reactions [2, 3] are two such examples. Recent work on the last class of system has shown that zero point energy may be key to explain proton dissociation mechanisms [3, 4, 5, 6].

In this work, we employ ab initio path integral molecular dynamics to understand quantitatively the role of nuclear quantum effects of water wires adsorbed on stepped surfaces of Pt(221). Our results are based on density-functional theory (DFT) with the all-electron code FHI-aims and path integral molecular dynamics (PIMD) coupled to acceleration schemes [7, 8, 9]. We tailor PIMD acceleration schemes for systems containing adsorbates on surfaces and discuss its successes and limitations.

Here, we focus on hydrogen dissociation from the water wires. By considering the effects of different coverages and performing calculations at finite temperatures, we explore the local free energy surface and find structures of the wire that were not previously considered, as well as stabilisation of the dissociated hydrogen on empty steps. We find that nuclear quantum effects indeed favour the dissociated structures even at finite temperature and including anharmonicities. We also find that while in the intact structures nuclear quantum effects are only weakly modulated by the interaction with the surface, this is not true in the case of the dissociated structures, due to a strong orbital hybridisation involving the dissociated hydrogen and the oxygen atoms. Finally we find that zero point energy changes in a substantial way the dissociation rate, and show possible paths to be explored by instanton theory.

- [1] T. Kumagai, F. Hanke, S. Gawinkowski, J. Sharp, K. Kotsis, J. Waluk, M. Persson, L. Grill., *Nat. chem.* **6**, 41 (2014).
- [2] J. Jia, L. C. Seitz, J. D. Benck, Y. Huo, Y. Chen, J. W. Desmond, T. Bilir, J. S. Harris, T. F. Jaramillo, *Nat. Comm.* **7**, 13237 (2016).
- [3] D. Donadio, L. M. Ghiringhelli, *J. Am. Chem. Soc.* **134**, 19217 (2012).
- [4] X. Li, M. Probert, A. Alavi, A. Michaelides, *Phys. Rev. Lett.* **104**, 066102 (2010).
- [5] R. Peköz, S. Wörner, L. M. Ghiringhelli, D. Donadio, *J. Phys. Chem. C.* **118**, 29990 (2014).
- [6] W. Lew, M. C. Crowe, C. T. Campbell, J. Carrasco, A. Michaelides, *J. Phys. Chem. C.* **115**, 23008 (2011).
- [7] M. Ceriotti, G. Bussi, M. Parrinello, *J. Chem. Theory Comput.* **6**, 1170 (2010).
- [8] O. Marsalek, T.E. Markland, *J. Chem. Phys.* **144**, 054112 (2016).
- [9] V. Kapil, J. VandeVondele, M. Ceriotti, *J. Chem. Phys.* **144**, 054111 (2016)