Kinetics of hot electron induced reactions on gold nanoparticles

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"Hot electrons", which are generated in the decay of localized surface plasmon resonances (LSPRs) of gold nanoparticles (AuNPs), can be transferred to adsorbed molecules and trigger chemical reactions therein [1]. Surface enhanced Raman scattering (SERS) is an established method to track hot electron induced reactions in real-time and identify the reaction products by their vibrational fingerprint [2]. However, as the sites on the AuNPs with the highest signal enhancement correlates with the sites, where the hot electrons are mainly generated, the determination of the reaction kinetics with SERS is challenging [3].
We will present a combined approach of SERS, atomic force microscopy and finite difference time domain simulations, to examine the kinetics of hot electron induced reactions in well-defined AuNP-arrays. Moreover, due to the strong dependency of the observed reaction constants on the wavelength of the incident laser light, the role of the accessible electronic states of the NP-ligand system in the plasmon mediated reactions has been evaluated. For this purpose, synchrotron XPS measurements of isolated AuNP clusters in the gas-phase have been performed [4]. A strong dependence of the reaction rates on the density of states in the valence band of the NP-ligand has been observed.
These findings will help to derive a mechanistic understanding of hot electron induced reaction and pave the way for applications in plasmon mediated catalysis and SERS based sensing.

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[1] G. V. Hartland, L. V. Besteiro, P. Johns, A. O. Govorov, ACS Energy Lett. 2, 1641 (2017).
[2] C. Zhan, X.-J. Chen, J. Yi, J.-F. Li, D.-Y. Wu, Z.-Q. Tian, Nat. Rev. Chem. 2, 216 (2018).
[3] R. Schürmann, I. Bald, Nanoscale 9, 1951 (2017).
[4] T. T. Meiling, R. Schürmann, S. Vogel, K. Ebel, C. Nicolas, A. R. Milosavljević, I. Bald, J. Phys. Chem. C, 122, 10217 (2018)