universität innsbruck

Innsbruck Physics Colloquium

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Forcing the reversibility of a mechano-chemical reaction

Mechanical force modifies the free-energy surface of chemical reactions, often enabling thermodynamically unfavoured reaction pathways. Most of our molecular understanding of force-induced reactivity is restricted to the irreversible homolytic scission of covalent bonds and ring-opening in polymer mechanophores. Whether mechanical force can bypass thermodynamically locked reactivity in heterolytic bimolecular reactions and how this impacts the reaction reversibility remains poorly understood.

Using single-molecule force-clamp spectroscopy, here we show that mechanical force promotes the thermodynamically disfavored S_N2 cleavage of an individual protein disulfide bond by poor nucleophilic organic thiols. Upon force removal, the transition from the resulting high-energy unstable mixed disulfide product back to the initial, low-energy disulfide bond reactant becomes suddenly spontaneous, rendering the reaction fully reversible. By rationally varying the nucleophilicity of a series of small thiols, we demonstrate how force-regulated chemical kinetics can be finely coupled with thermodynamics to predict and modulate the reversibility of bimolecular mechano-chemical reactions.

Tuesday, 11.6.2019, at 17:15 h in lecture hall C

Innsbruck Physics Colloquium, Organisation: M. Beyer, H.-C. Nägerl, A. Reimer