Heavy-atom tunnelling in spin crossovers from cryogenic to ambient temperatures

Heller, E.R.,[1]* Richardson, J.O.[2]
*presenter
[1] eric.heller@phys.chem.ethz.ch, ETH Zürich, Switzerland
[2] ETH Zürich, Switzerland

Intersystem-crossing reactions involving the transition between electronic states of different spin are essential processes in nature. In two recent matrix-isolation experiments at cryogenic temperatures convincing evidence has been presented for reactions of nitrenes in which the spin crossover is mediated by heavy-atom quantum tunnelling.[1] The correct theoretical description of such reactions, however, still poses a major challenge…until now!

We applied our recently developed golden-rule instanton theory in conjunction with high-level on-the-fly electronic-structure calculations to describe the $T_1 \rightarrow S_0$ spin crossovers in the matrix-isolation experiments on two nitrenes[2] and a pump–probe experiment on thiophosgene.[3] Where standard methods such as the weak-coupling (WC) method failed, we achieved excellent agreement of calculated and experimental rates for the first time (see Figure 1). Interestingly, we did not only find substantial tunnelling of carbon, nitrogen and oxygen atoms at cryogenic temperatures, but unveiled speed-ups due to tunnelling of up to 1000 even at room temperature.

The spin crossover of thiophosgene exhibits particularly strong tunnelling effects since it is in the *inverted regime*.[4] By locating the "ideal tunnelling pathways" or *instantons* at a range of temperatures, we discovered the critical role of corner cutting. The reaction thus proceeds via a tunnelling trajectory that substantially deviates from the minimum-energy pathway. This change of mechanism is not captured by commonly applied 1D tunnelling corrections, which are hence in error by orders of magnitude. In the inverted regime, the part of the instanton trajectory that is located on the product surface exhibits negative temperature**,** or alternatively travels in negative imaginary time giving rise to an interpretation involving particle–antiparticle creation and annihilation events.

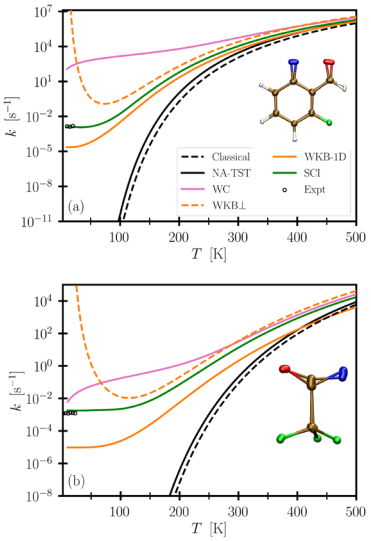

Figure 1: Reaction rates computed with semiclassical instanton theory (SCI) and other methods compared to experiment. The insets illustrate the instanton pathways, where the delocalization of individual atoms is due to tunnelling.

[1] (a) Nunes, C. M. et al. Heavy-Atom Tunnelling Through Crossing Potential Energy Surfaces: Cyclization of a Triplet 2-Formylarylnitrene to a Singlet 2,1-Benzisooxazole. *Angew. Chem. Int. Ed.* **2020**, *59*, 17622–17627; (b) Wu, Z. et al. Fast Heavy-Atom Tunnelling in Trifluoroacetyl Nitrene. *Angew. Chem. Int. Ed*. **2017**, *56*, 15672–15676.

[2] Heller, E. R.; Richardson, J. O. Heavy-Atom Quantum Tunnelling in Spin Crossovers of Nitrenes. *ChemRxiv*. **2022**, doi: 10.26434/chemrxiv-2022-2gcgx.

[3] Heller, E. R.; Richardson, J. O. Spin Crossover of Thiophosgene via Multidimensional Heavy-Atom Quantum Tunneling. *J. Am. Chem. Soc.* **2021**, *143*, 20952–20961.

[4] Heller, E. R.; Richardson, J. O. Instanton formulation of Fermi's golden rule in the Marcus inverted regime. *J. Chem. Phys.* **2020**, *152*, 034106.