Photocatalytic water splitting with heptazine by Landau-Zener surface hopping simulations

Xiang Huang

Department of Chemistry, Technical University of Munich,

Lictenbergstr. 4, 85747 Garching, Germany

Graphitic carbon nitrides have become popular as organic photocatalysis in recent decades[1]. The heptazine ($C_6N_7H_3$) building block exhibits photoreactive charge transfer with H-atom donor molecules such as water[2] and phenol[3] as well as an inverted S_1/T_1 gap[4], which facilitates deexcitation *via* intermolecular channels.

In aqueous environment this opens the possibility to split water by absorbing a photon of near UV light. We found that two reduced HzH radical with sufficient excess energy can undergo a dark disproportionation process which restores one Hz molecule and produces a doubly-reduced heptazine (HzH_2). The HzH_2 is found to be photopredissociative in the $\pi\sigma^*$ state, generating a free H atom and a HzH radical that reenters the dark reaction. The overall process illustrates a photocatalytic cycle of water splitting by Hz molecules into free H atoms and OH radicals.

1. Wang, X.; Maeda, K.; Thomas, A.; Takanabe, K.; Xin, G.; Carlsson, J. M.; Domen, K.; Antonietti, M., A metal-free polymeric photocatalyst for hydrogen production from water under visible light. *Nat. Mater.* **2009,** *8* (1), 76-80.
2. Ehrmaier, J.; Karsili, T. N.; Sobolewski, A. L.; Domcke, W., Mechanism of photocatalytic water splitting with graphitic carbon nitride: photochemistry of the heptazine–water complex. *The Journal of Physical Chemistry A* **2017,** *121* (25), 4754-4764.
3. Rabe, E. J.; Corp, K. L.; Huang, X.; Ehrmaier, J.; Flores, R. G.; Estes, S. L.; Sobolewski, A. L.; Domcke, W.; Schlenker, C. W., Barrierless Heptazine-Driven Excited State Proton-Coupled Electron Transfer: Implications for Controlling Photochemistry of Carbon Nitrides and Aza-Arenes. *The Journal of Physical Chemistry C* **2019,** *123* (49), 29580-29588.
4. Ehrmaier, J.; Rabe, E. J.; Pristash, S. R.; Corp, K. L.; Schlenker, C. W.; Sobolewski, A. L.; Domcke, W., Singlet–Triplet Inversion in Heptazine and in Polymeric Carbon Nitrides. *J. Phys. Chem. A* **2019,** *123* (38), 8099-8108.