Determination of fundamental photophysical parameters of gold nanoclusters

L. Llanes Montesino¹, T. Bürgi¹*, A. Rosspeintner¹*

¹Department of Physical Chemistry, University of Geneva

Atomically precise metal nanoclusters (NC) in general and gold nanoclusters (AuNC) specifically have many advantages which allows their uses in areas such as photocatalysis, biosensing, or solar energy conversion [1]. A comprehensive description of their photophysics will strongly benefit all these three branches of applications. However, the basic photophysics of AuNC is currently not clearly understood, according to the previously published results in the area. This work intends to achieve such a level of understanding of their photophysical properties. To this end, the absorption and fluorescence spectra (steady-state and time-resolved) were obtained for the most commonly studied cluster, Au₂₅PET₁₈. A series of deviations from conventional molecular photophysics was observed, in particular the discrepancy between absorption and luminescence excitation spectra, the violation of Kasha's rule (i.e. a strong dependence of emission spectra and lifetimes on excitation energy) and clearly multi- or nonexponential behavior for the ns-µs emission decays. A tentative Jablonski diagram and kinetic scheme are proposed to explain these findings.

[1] Chakraborty, I.; Pradeep, T. Atomically Precise Clusters of Noble Metals: Emerging Link between Atoms and Nanoparticles. *Chem. Rev.* **2017**, 117 (12), 8208–8271.