EXCITED STATE PHOTODYNAMICS OF SUB-NANOMETER METAL OXIDE CLUSTERS

SCOTT G SAYRES, *School of Molecular Sciences and Biodesign Center for Applied Structural Discovery, Arizona State University, Tempe, AZ, USA*.

I will present our recent work[1−3] on the ultrafast dynamics of sub-nanometer neutral metal oxide clusters investigated with femtosecond pump-probe spectroscopy and supported by theoretical calculations. Absorption of a UV (400 nm) photon initiates several relaxation processes, with excited state lifetimes that are strongly dependent on the nature of the electronic transition. The atomic precision and tunability of gas phase clusters highlights how the simple picture of sequential oxidation of the metal atoms reveals a linear tunability to the contributions of each relaxation component to the total transient signal. In chromium oxides, a 30 fs transient signal fraction grows linearly with oxidation, matching the amount of O to Cr charge transfer character of the photoexcitation and highlighting a gradual transition between semiconducting and metallic behavior at the molecular level. The lifetimes of nickel oxide clusters exhibit a unique reliance on the nature of the atomic orbital contributions, providing new insights to the analogous band edge excitation dynamics of strongly correlated bulk material. Short lived dynamics in stoichiometric (NiO)n clusters are attributed to excitation between Ni-3d and Ni-4s orbitals, where their strong exchange coupling produces metallic-like electron-electron scattering. Oxygen vacancies introduce 3d to 4p transitions, which increases the lifetimes of the sub-picosecond component by 20-60 percent and enables the formation of long-lived (lifetimes greater than 2.5 ps) states.

(1) Garcia, J. M.; Heald, L. F.; Shaffer, R. E.; Sayres, S. G. Oscillation in Excited State Lifetimes with Size of Sub-Nanometer Neutral $(TiO_2)_n$ Clusters Observed with Ultrafast Pump–Probe Spectroscopy. J. Phys. Chem. Lett. 2021, 12, 4098–4103.

(2) Garcia, J. M.; Sayres, S. G. Increased Excited State Metallicity in Neutral Cr_2O_n Clusters (n $<$ 5) upon Sequential Oxidation. J. Am. Chem. Soc. 2021, 143 (38), 15572–15575.

(3) Garcia, J. M.; Sayres, S. G. Orbital-Dependent Photodynamics of Strongly Correlated Clusters. Phys.Chem.Chem.Phys. 2022, 24, 5590-5597.