

# Spin, Charge and Structural Dynamics: Elements for the Control of Cluster-Mediated Chemical Reactions

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The optical control of a bimolecular reaction mediated in the environment of a metal site cluster is investigated [1,2]. Generally, the strategy of utilizing the distinct character of a series of different electronic states available to the metal center for guiding the reaction pathway is pursued. By sequential excitation through a set of electronic states in the reaction complex, the unique charge distribution and characteristic structural dynamics on the individual potentials can be utilized for dynamic control of the system. The experiment is carried out within the instrumentation of a tandem mass spectrometer and a radio frequency ion trap. The general strategy can hereby be expanded to include not only the neutral but also the electronic states of the anionic and cationic species. By optically driving a charge reversal process with a sequential electron photo-detachment from the anionic state and a multi-photon ionization process to the cationic state via the neutral system, changes in charge and spin are included to the degrees of freedom that control the reaction pathway. Specifically, an ultrafast photo-induced charge reversal in the  $[\text{Au}_2\text{O}_2\text{CH}_4]$  complex allows for the activation of oxygen in the negative doublet state, structural evolution in a variable ultrafast time window on the neutral state potentials and specific methane activation in the cationic doublet state of the gold cluster adsorbate system. A controlled, cold oxidation of methane is the objective of the optical manipulation of the system. This approach of an ultrafast sequential charge and spin modification allows for specifically addressing the significantly different nature of the reactants. Additionally, an optimization in the yield of a specific dissociation product from the cationic complex can be achieved with the structural rearrangements to a critical geometry in a neutral intermediate state. With the molecular scale analysis that can be gained from this approach, insight to the decisive electronic and geometric structures can be obtained for the rational design of heterogeneous catalytic systems. The application of a newly developed supercontinuum source will enhance these efforts [3].

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