Vibronic and chemical properties of supported single metal atom catalysts

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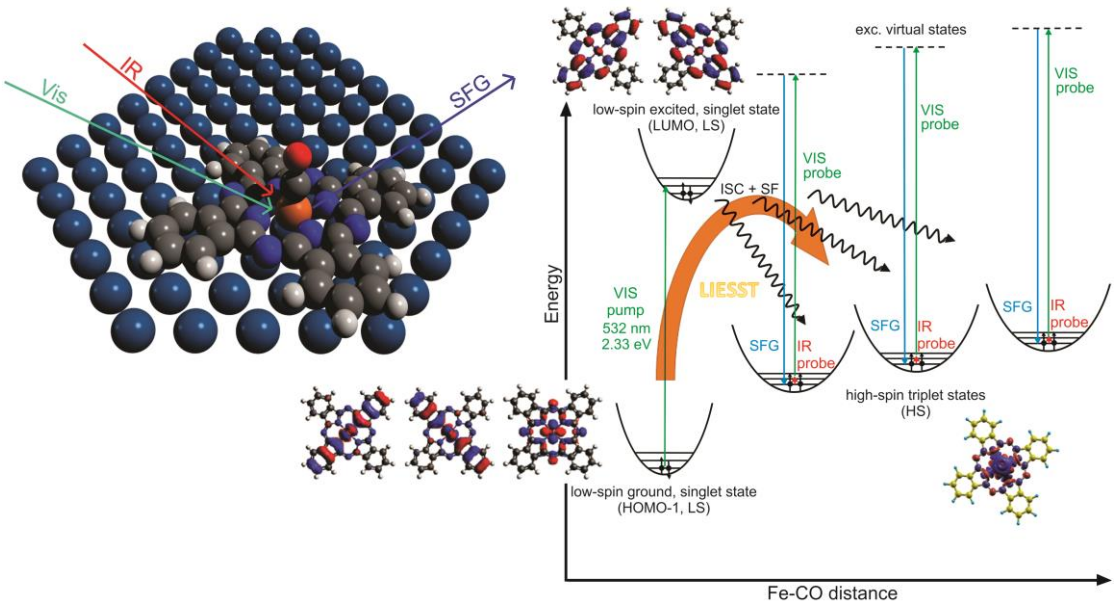
Innovative and stable catalysts can be prepared within the framework of a biomimetic approach, thus embedding an active single metal atom in a tetra-pyrrolic cage. From the surface science point of view, an *in situ* and *operando* characterization of heme-like, simplified model systems may represent a challenge. Besides investigations at cryogenic temperature, a thorough atomic-level experimental understanding is not straightforward so far due to the near-ambient pressure conditions that are necessary to yield a significant interaction of the active core with gas phase molecules at room temperature. By exploiting non-linear laser spectroscopy, access to the vibronic properties of interfaces is possible under realistic operative conditions, allowing the investigation of 2D metal-organic supported systems.

Self-assembled 2D layers of metal-N_4 complexes deposited at single crystal terminations [1] and over supporting templates like graphene [2] or oxide films [3] will be described, with a specific focus on the interaction with small gas-phase molecules. IR-Vis Sum Frequency Generation spectroscopy data combined with *ab initio* calculations provide a detailed insight into the structural and chemical behavior of the layers, including the role of Frenkel excitons [2]. The latter form upon illumination with visible light and, initially localized at the reactive centers, evolve through associated spin transition and singlet fission mechanisms, affecting the adsorbed ligand, i.e. the chemical reactant.



References:
[1] M. Corva and E. Vesselli, J. Phys. Chem. C **120** (2016) 22298.
[2] M. Corva, A. Ferrari, M. Rinaldi, Z. Feng, M. Roiaz, C. Rameshan, G. Rupprechter, G. Pastore, G. Comelli, N. Seriani, and E. Vesselli, *submitted*.
[3] M. Corva, F. Mohamed, Z. Feng, T. Skala, G. Comelli, N. Seriani, M. Peressi, and E. Vesselli, *in preparation*.