

Electronic Structure Analyses of Complexes for Nitrogen and Oxygen Activation

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Catalysts for the efficient activation and transformation of small molecules are essential stepping stones towards a future society that is independent of fossil resources. In this talk, case studies for quantum chemical studies on inorganic complexes capable of small molecule activation reactions are presented, focusing on the electrochemical reduction of dioxygen and the light-driven activation of dinitrogen.

Fuel cells, for instance for automotive applications, rely on the oxygen reduction reaction. While cost-intensive platinum-based catalysts are considered state-of-the-art, single-atom catalysts (SACs) have shown competitive activity albeit at lower stabilities. SACs are prepared by pyrolysis of earth-abundant precursors and rendered as amorphous powders, which significantly hampers the precise identification of active sites and hence a strategic optimisation of activity and stability.¹ For Fe-SACs, the active sites are considered as single iron ions ligated by four nitrogen donors embedded in a graphene-like environment; open questions concern the number and nature of axial ligands and the presence of dopants. This talk will illustrate how computational chemistry and theoretical spectroscopy can aid in unravelling the identity of active sites using the first iron complex with a pyridinic, conjugated, square-pyramidal coordination sphere as an example.²⁻⁵

The activation of the nitrogen molecule has been a long-standing challenge in inorganic chemistry. Besides Nature's FeMo/FeV cofactors and the well-established Haber-Bosch-process, many molecular complexes capable of N₂ activation are known which operate by thermal energy input. A much less explored route towards nitrogen fixation is the use of light.⁶ By promoting a transition metal catalyst into an electronically excited state, the N₂ bond can be weakened and made more basic to facilitate protonation, or even be photocleaved completely leading to metal nitride complexes as versatile platforms for further syntheses. Several synthetic examples for nitrogen photoactivation are known, however the underlying photophysical and photochemical processes are not fully resolved. This talk will report on progress in the quantum chemical analyses of complexes for nitrogen photoactivation.⁷⁻¹⁰

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