

Interplay of theory and spectroscopy:

Study of an Fe^V-nitride complex and its photolytic formation

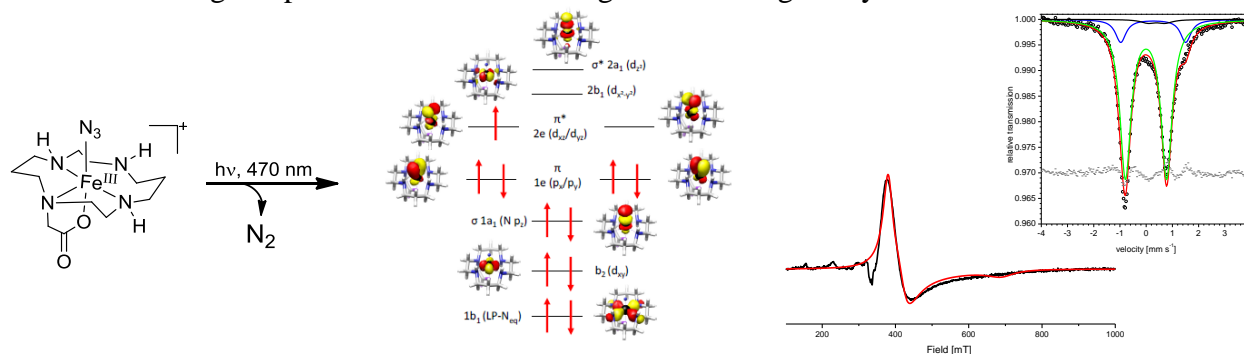
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In bioinorganic chemistry a wide range of highly developed spectroscopic methods have been used in the study of bio-relevant complexes and over the last two decades, computational chemistry has gained prominence as a powerful tool to provide insight into e.g. bio-relevant reactions from an additional perspective. DFT is of course the most frequently used method, but with contemporary computers and software it is possible to handle bio-relevant systems with higher level theory, such as correlated single- and multi reference methods.

Both fields, spectroscopy and theory, are individually very powerful, but a combination of both can facilitate the interpretation of data and permits an even more detailed understanding of the studied systems. The ORCA software package developed in our group features all common standard functionality, but is particularly well suited for the calculation of spectroscopic parameters.[1] Therefore we can experimentally verify our calculated electronic structures and confirm or rule out proposed intermediates by comparing calculated and experimental parameters.

We are interested in iron nitrides, which are believed to be key intermediates in the industrial and biological fixation of N₂. [2] Given the difficulties in isolating and characterizing transient intermediates, model complexes of low molecular weight are synthesized and studied and the results have a high impact on the understanding of real biological systems.



The nitridoiron model system we have chosen to focus upon is a six coordinated Fe^V-nitride supported by a cyclam derived ligand which is formed by photolysis of its Fe^{III}-azide counterpart in frozen solution with 470nm light[3]. Combining spectroscopy and theory we have been investigating the formation process of Fe^V by N₂ elimination and the electronic structure of the resulting high-valent iron complex. Using DFT we are able to accurately model the measured Mössbauer parameters, but a more sophisticated insight in the electronic structure was obtained by multi-reference calculations (CASSCF/NEVPT2), which also made it possible to reproduce the measured g-values accurately. To map the processes that accompany photo excitation, resonance Raman spectroscopy is a very applicable method, with DFT once again very useful in band assignment.

The presentation will demonstrate how theory and spectroscopy was combined in the study of an Fe^V-nitride complex.

[1] Neese, F. et al. ORCA – *an ab initio, DFT and Semiempirical Program Package*.

[2] Ertl, *Chem. Rec.* **2001**, *1*, 33.; Hoffman, Dean, Seefeldt, L. C. , *Acc. Chem. Res* **2009**, *42*, 609.

[3] Grapperhouse, Mienert, Bill, Weyhermüller, Wieghardt, *Inorg. Chem.* **2000**, *39*, 5306; Aliaga-Alcalde, DeBeer, Mienert, Bill, Wieghardt, Neese, *Angew. Chem., Int. Ed.* **2005**, *44*, 2908.