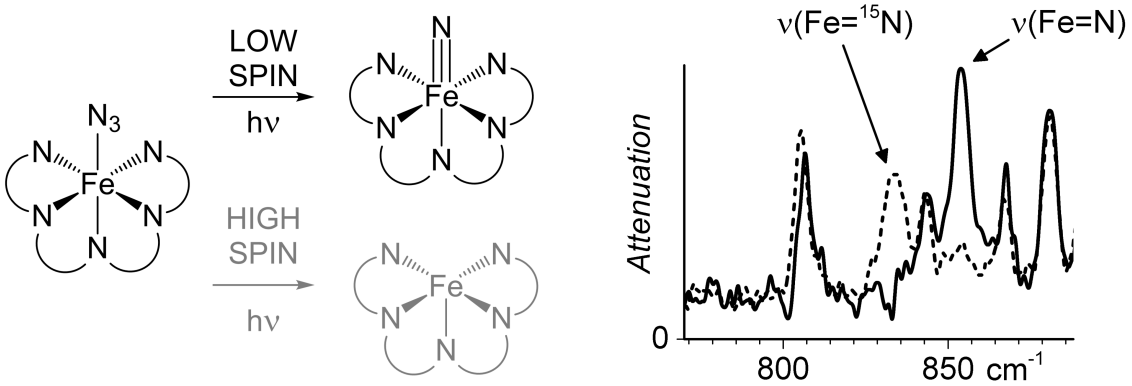
SPIN-STATE-DEPENDENT GENERATION AND SPECTROSCOPY OF TERMINAL IRON(V) NITRIDES

Erik Andris,[1] Rafael Navrátil,[1] Juraj Jašík,[1] Gerard Sabenya,[2] Martin Srnec,[3] Miquel Costas,[2] Jana Roithová[1]

[1]Department of Organic Chemistry, Charles University, Hlavova 2030/8, 128 43 Prague; [2]Departament de Quimica and Institute of Computational Chemistry and Catalysis (IQCC) University of Girona Campus Montilivi, Girona 17071 (Spain); [3]J. Heyrovsky Institute of Physical Chemistry of the CAS, v. v. i. Dolejškova 2155/3, 182 23 Prague 8 (Czech Republic).
e-mail: erik.andris@natur.cuni.cz

Study of terminal iron(V) nitrides with tetragonal ligand symmetry is a daunting task due to their extreme reactivity and instability above cryogenic temperatures.[1] We have overcome those obstacles by studying them in the gas phase. We examined, how the nitrides can be formed by iron(III) azide photodissociation.[2] By studying the wavelength and temperature dependence of the photodissociation reaction of various azides, we demonstrated that the the photodissociation outcome depends on the spin state of the iron azide, as previously suggested.[3] After establishing the crucial role of the spin state in the photodissociation process, we characterized the resulting iron(V) nitrides by gas-phase IR spectroscopy.[4] We assigned the weak Fe=N stretching vibrations of the iron nitrides using combination of isotopic labelling experiments and DFT/CASPT2 calculations. We identified, how the Fe=N band intensity can be diminished by coupling with by ligand vibrations, which precludes its measurement by conventional spectroscopic techniques.



1) J. M. Smith, D. Subedi, *Dalton Trans.* **2012**, *41*, 1423.
2) E. Andris, R. Navrátil, J. Jašík, G. Sabenya, M. Costas, J. Roithová, *Angew. Chem. Int. Ed.* **2017**, 56, 14057.
3) Y.-F. Song, J. F. Berry, E. Bill, E. Bothe, T. Weyhermüller, K. Wieghardt, *Inorg. Chem.* **2007**, *46*, 2208.
4) E. Andris, R. Navrátil, J. Jašík, G. Sabenya, M. Costas, J. Roithová, *manuscript in preparation*.