

# Vibrational Blue Shift of coordinated N<sub>2</sub> in [Fe<sub>3</sub>O(OAc)<sub>6</sub>(N<sub>2</sub>)<sub>n</sub>]<sup>+</sup>: “Non Classical” Dinitrogen Complexes

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The N<sub>2</sub> stretching vibration responds to coordination to (transition) metal centers. Vibrational red shifts indicate conceivable precursors to activate N-N bonds[1] on the road to catalytic ammonia synthesis under mild conditions[2]. In contrast, blue shifts indicate Lewis acid coordination sites as utilized in N<sub>2</sub> probing of heterogeneous catalysts (e.g. alumina[3]). In organometallic chemistry blue shifts of two atomic ligands are pretty rare and appear so far mainly in the case of CO coordination (so called “non classical” carbonyl complexes[4]).

Here, we present “non classical” dinitrogen complexes [Fe<sub>3</sub>O(OAc)<sub>6</sub>(N<sub>2</sub>)<sub>n</sub>]<sup>+</sup> (n=1,2,3) in the gas phase. Infrared photo dissociation (IR-PD) as well as density functional theory (DFT) calculations reveals blue shifted N<sub>2</sub> stretching bands in comparison to the (IR inactive) free N<sub>2</sub> stretching frequency (cf. Fig.1). A detailed analysis of the electronic and steric interplay between N<sub>2</sub> and the [Fe<sub>3</sub>O(OAc)<sub>6</sub>]<sup>+</sup> unit indicates a polarization of the N<sub>2</sub> orbitals towards the iron center. This increases the electron density in the vicinity of the N-N bond. The N-N bond order increases as antibonding N<sub>2</sub> electrons delocalize into the complex. Both findings rationalize the strengthened N-N bond.

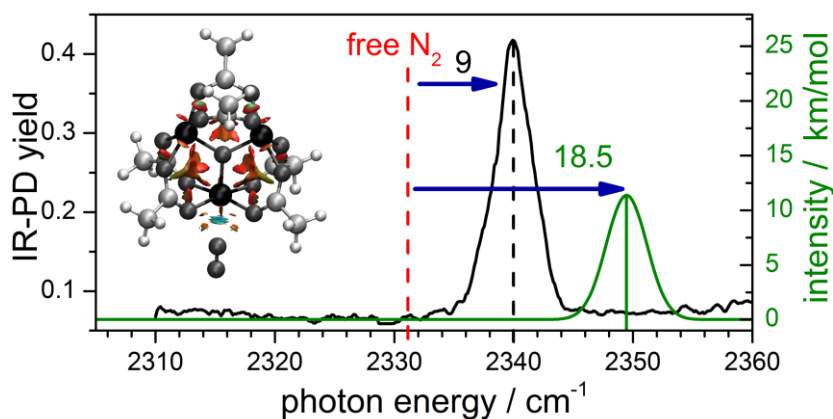


Figure 1: IR-PD spectra of [Fe<sub>3</sub>O(OAc)<sub>6</sub>(N<sub>2</sub>)<sub>1</sub>]<sup>+</sup> at 26 K (black curves) and calculated IR absorption spectra of geometry optimized [Fe<sub>3</sub>O(OAc)<sub>6</sub>(N<sub>2</sub>)<sub>1</sub>]<sup>+</sup> (green curves) in the N<sub>2</sub> stretching vibration region. The calculations were performed at the B3LYP/cc-pVTZ (H, C, N, O) and Stuttgart 1997 ECP (Fe) level of theory.

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