

## Abstract

I used helium-tagging infrared photodissociation spectroscopy of ions in the IR (IRPD) and vis (visPD) range in conjunction with gas-phase reactivity studies to study biomimetic terminal iron-oxo complexes. In first part of the work, I measured IRPD spectra of iron(IV)-oxo complexes of TMC, N4Py and PyTACN amine ligands in different charge states. Results show that the gas-phase Fe=O stretching frequencies are, on average, blue-shifted by  $9\text{ cm}^{-1}$  with respect to the condensed phase. I prepared stereoisomers of  $[(\text{PyTACN})\text{Fe}^{\text{IV}}(\text{O})(\text{X})]^+$  complexes ( $\text{X} = \text{CF}_3\text{COO}, \text{NO}_3$ ) that were in quintet and triplet state using nitrate cleavage method and showed that the Fe=O frequency of these iron(IV)-oxo complexes is not affected by the spin state. Gas-phase reactivity shows that dicationic complexes react with 1,4-cyclohexadiene by hydride transfer and monocationic complexes engage in hydrogen atom transfer (HAT) from the methylene group and oxygen atom transfer to the C=C bond. Variation of the ligand *trans* to the Fe=O unit has the greatest influence on reactivity, whereas the spin state has a modest effect. In the second part of the work, I prepared and studied gas-phase iron(III)-oxo complexes with N4Py, TPA, TQA and TMC ligands. IRPD and visPD spectra in conjunction with DFT calculations allowed me to assign the spin state of the former two complexes as quartet and the latter two complexes as sextet. Whereas the Fe=O stretching frequencies in quartet complexes are essentially the same as in iron(IV)-oxo complexes, the frequencies in sextet complexes are red-shifted by  $\sim 70\text{ cm}^{-1}$ . Moreover, I showed that coordination of water molecule to the quartet complexes triggers a spin flip to sextet. Finally, I showed that iron(III)-oxo complexes do not engage in HAT with 1,4-cyclohexadiene, but they react in a net HAT with ethanethiol via proton transfer – electron transfer mechanism. In conclusion, this thesis demonstrates the applicability of gas-phase spectroscopy of ions to bioinorganic chemistry and sets the stage for the future work in this field.