

Atom-by-atom Synthesis of Cold Iron Oxide/Sulfide Clusters in the Gas Phase. Reactions of $\text{Fe}_2\text{O}_x\text{S}_y^+$, $x, y = 0-2$, $x+y = 2$, and Relevance to the Nitrogenase Enzymes

*Phillip Jackson*¹, *Detlef Schröder*² and *Helmut Schwarz*²

¹Mass Spectrometry, Australian National University, Canberra, ACT 0200, Australia

²Institut für Organische Chemie, Technische Universität-Berlin, Straße des 17. Juni 135, D-10623 Berlin, Germany

An area of great interest in mass spectroscopy is the replication of condensed-phase catalysis by mimetic ions. The goal of these studies is to develop 'tuned' and highly-specific catalysts for industrial applications. Enzymes exhibit both of these characteristics, in particular the nitrogenases, which possess iron-containing active sites.

We would like to reproduce the conversion achieved by the nitrogenase enzymes, in the gas-phase, using the smallest possible sub-unit of the active site. A convenient route to the synthesis of Fe-S and Fe-O clusters, recently exploited by Harvey *et al* [*Inorg. Chim. Acta* **1998**, 273, 111] involves (i) condensation reactions between $\text{Fe}(\text{CO})_5$ and an ablated metal ion, in this case Fe^+ (ii) oxidation of the $\text{Fe}_x(\text{CO})_y^+$ product with dioxygen or dinitrogen monoxide to yield Fe_xO_y^+ , and finally (iii) reaction with either H_2S or COS to generate an iron sulfide cluster or a mixed oxide-sulfide cluster. The MS^n capabilities of the FTICR-mass spectrometer are utilised to monitor the chemical evolution of the products, and further probe their chemistry. Pulsed valves (piezocrystal) were employed to introduce the reagents necessary to effect the cluster syntheses. A great advantage of this approach is that the intermediates, and the final product, undergo many non-reactive collisions with the pulsed reagents, which ensures the cluster ground states are populated. An example of a pulse-sequence is given below.

The results for the reactions of Fe_2O_2^+ , Fe_2OS^+ and Fe_2S_2^+ with dinitrogen, ammonia and selected hydrocarbons will be reported. Bracketed cluster-hydrogen bond strengths have been derived, and the structure of Fe_2O_2^+ determined from kinetic information.

