Furman - Los Alamos Collaboration

- Furman is a private liberal arts college of 2,500 students in Greenville, SC. The chemistry department has 9 faculty and produces about 30 graduates a year.
- Following a sabbatical leave at LANL in 1989-90, Tony Arrington has taken Furman undergraduates to Los Alamos for summer research. The students have worked with about a dozen LANL staff members in the CST and EES divisions.
- Most of our research has been in collaboration with Steve Buelow and other CST-6 staff members, who have worked in the area of hydrothermal processing of hazardous wastes.
- An EMSP proposal was submitted to continue the collaboration with the Los Alamos program. Our efforts are directed at developing an understanding of the fundamental chemistry involved in oxidation-reduction reactions in high temperature solutions.
- Two students worked on the project in 1997, and two more are working this summer. The work presented in this poster summarizes their results on the dissolution of chromium by oxidation of Cr(III) to Cr(VI) and related topics.

Characterization of samples of chromium oxide/hydroxides prepared in the laboratory

- Reducing chromium levels in Hanford tank wastes is essential for successful vitrification of high level wastes. See Steve Buelow's poster, number 46.
- Samples were prepared by Dr. Zhong Ding.
- They were characterized by Raman, infrared, and XPS spectroscopy. Infrared spectra were the most informative.

Sample Preparation

The Cr samples were prepared by dissolving 100 grams of $Cr(NO_3)_3$ $9H_2O$ in 500 ml of DI H_2O. 100 ml of a 7.5 M NaOH solution was added to the Cr solution and stirred. A precipitate formed, which was allowed to sit in the solution overnight (pH = 8.5). The precipitate was washed with DI H_2O, placed in a crucible, and dried in a 120°C oven for 24 hours.

Part of the dried precipitate was calcined separately at temperatures of 200 °C, 300 °C, 450 °C, and 700 °C.

Cal. Temp.	Orig. wt.	Final wt.	% wt. loss
200 °C	4.442	3.716	16.3
300 °C	7.902	5.638	28.6
450 °C	5.085	3.356	34.0
700 °C	4.672	3.026	35.2

The sample called $Cr(OH)_3$ was made by drying the precipitate at room temperature as $Cr(OH)_3$ $3H_2O$. This dried sample was then heated in an inert hydrothermal environment at 170 °C for five days to get CrOOH.

Treatment of laboratory samples of chromium oxide/hydroxide with H_2O_2 in basic solution

Reaction of Cr Samples with H_2O_2 in Basic Solution

$$CrO_xH_y + H_2O_2 + OH^- \rightarrow ?$$

10% 1.0 M

- Commercial Cr_2O_3 - green precipitate, clear pale green soln

- Calcined samples:
  120 °C - no precipitate; dark, clear, red-brown soln
  200 °C - no precipitate; dark, clear, red-brown soln
  300 °C - brown-black precipitate; brownish yellow soln
  450 °C - brown-black precipitate; dark brownish-yellow soln
  700 °C - light green precipitate; brownish-yellow soln

- "$Cr(OH)_3$" - no precipitate; dark, clear, red-brown-yellow soln
- "CrOOH" - black precipitate; clear orange-yellow soln

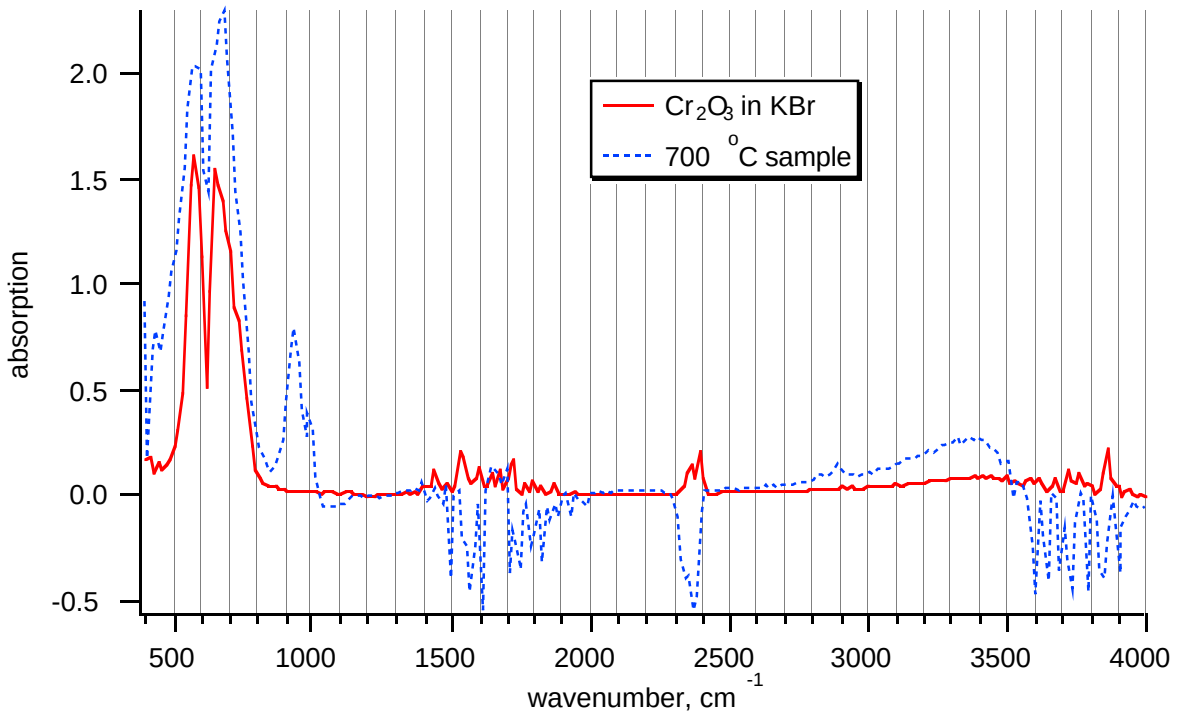
FTIR spectra of the remaining solid
450 °C and 700 °C - peaks at 900 cm^{-1} have decreased in intensity.
Spectra are more like the Cr_2O_3 spectrum.

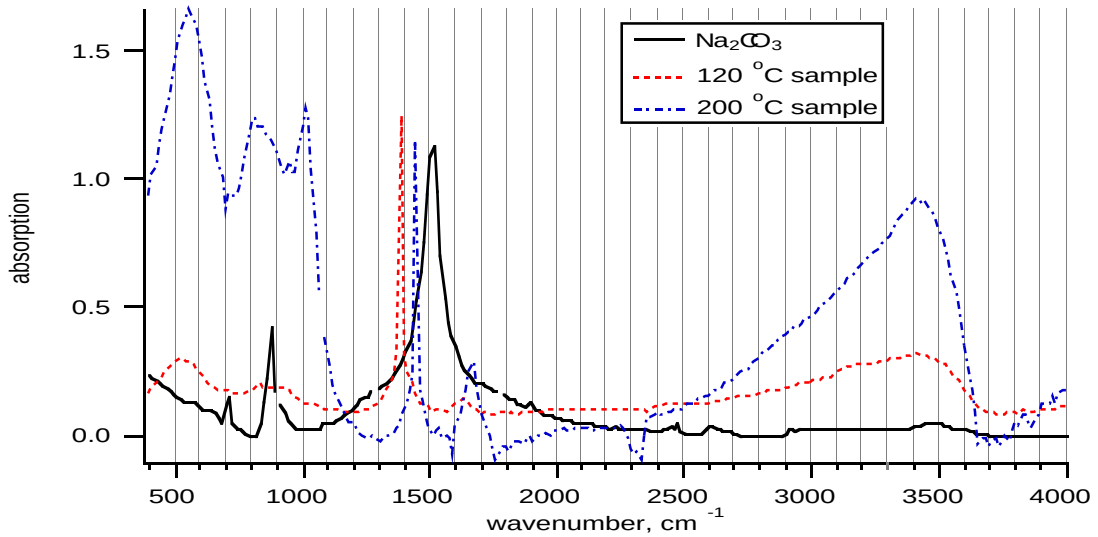
UV-visible spectra of the solution
Stronger absorbance at 372 nm for 120 °C and 200 °C samples

Weight loss from reaction with H_2O_2 in 1.0 M NaOH.

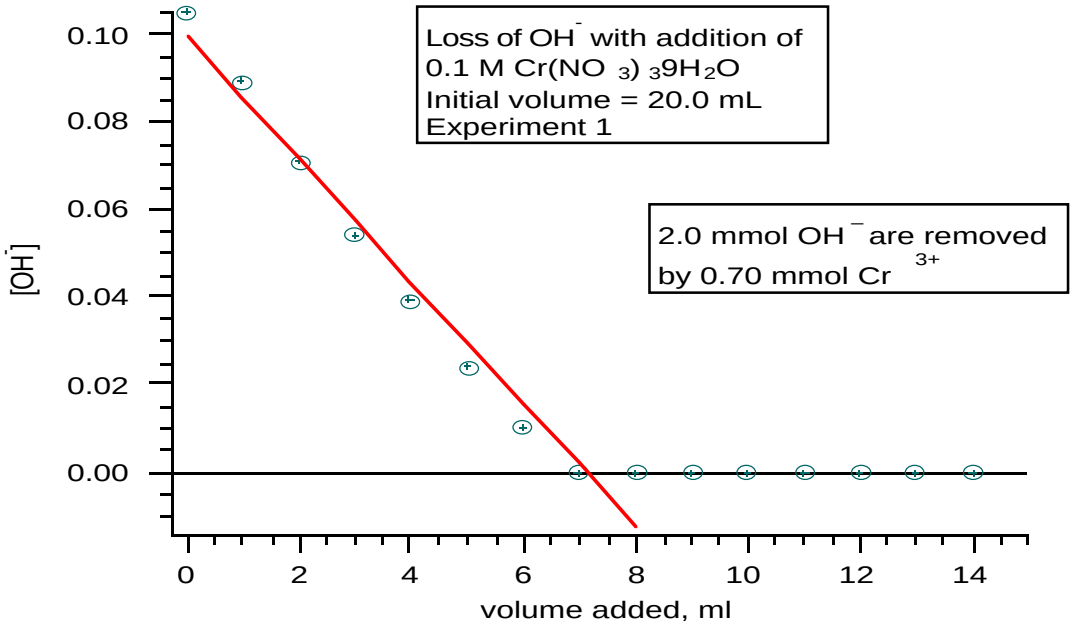
Sample	Original Weight (g)	Final Weight (g)	% Weight Loss
Cr_2O_3	0.1010	0.0988	2.18
120 °C	0.1068	0	99.9
200 °C	0.1061	0.0066	93.2
300 °C	0.1025	0.0826	19.4
450 °C	0.1058	0.1022	3.4
700 °C	0.1073	0.0971	9.51
CrOOH	0.1005	0.067	33.3

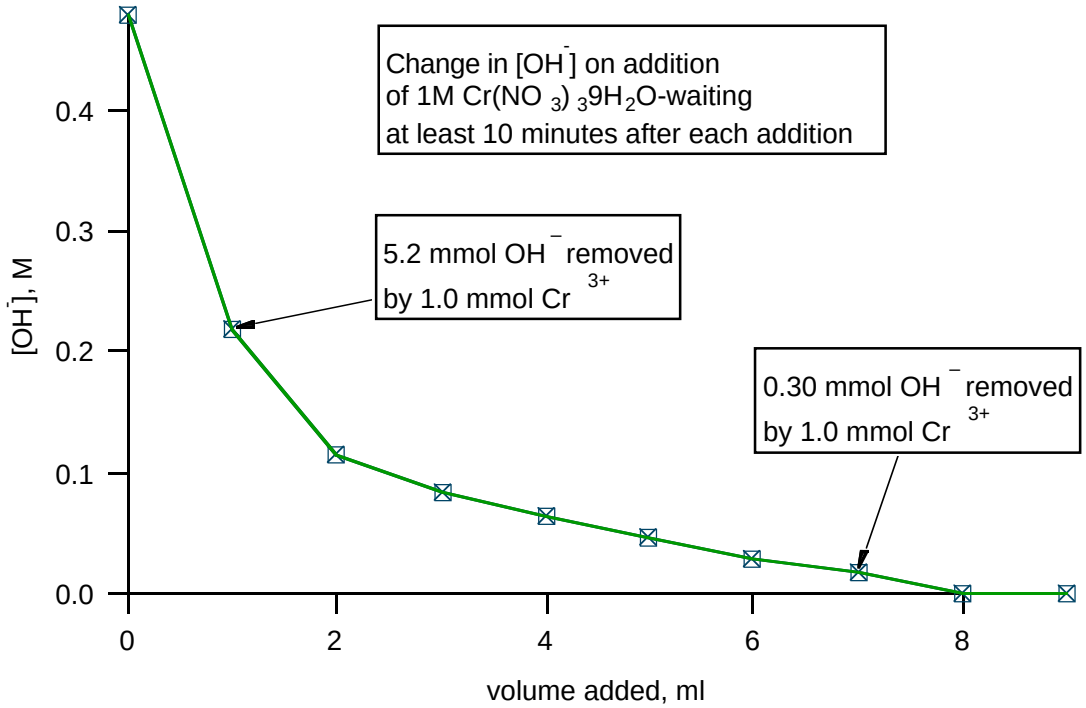
Infrared spectra of prepared chromium oxide/hydroxide samples



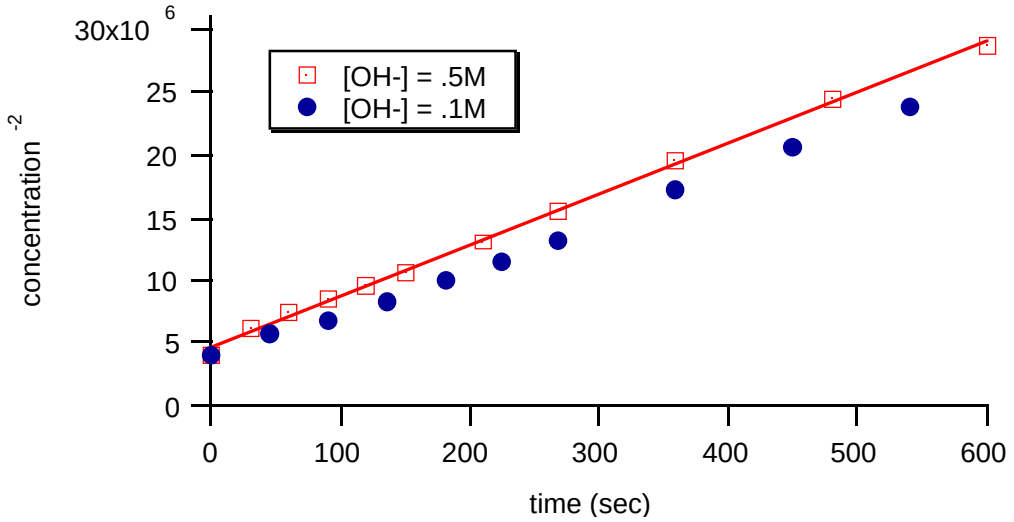


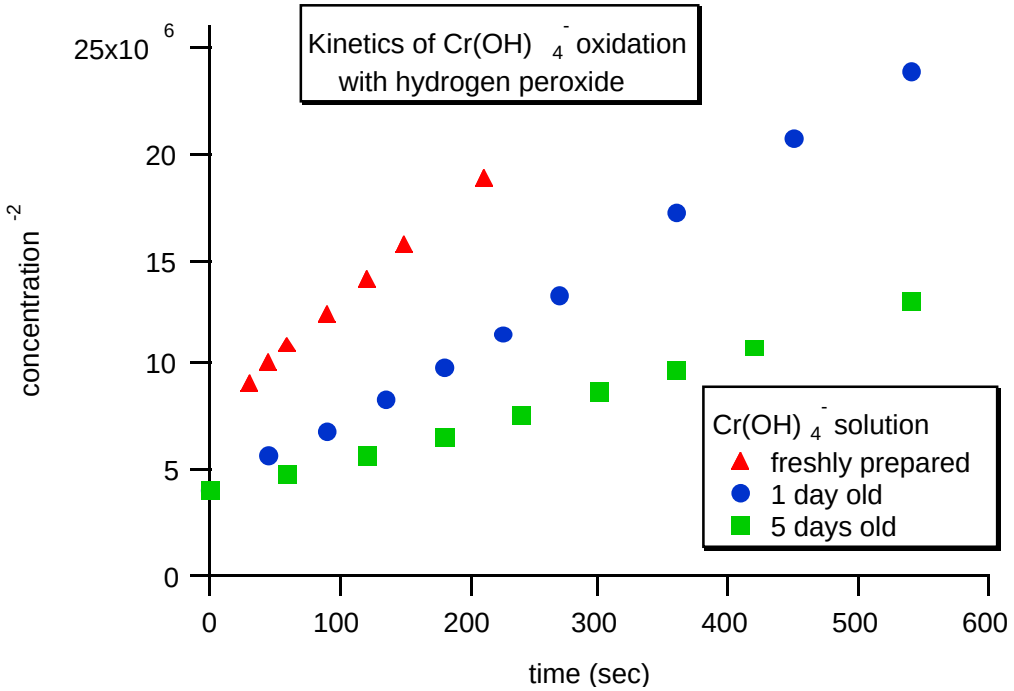
Stoichiometry of chromium hydroxide formation





Effect of hydroxide concentration and aging on oxidation of $Cr(OH)_4^-$ by hydrogen peroxide





Thermodynamic data for aqueous chromium chemistry

Chromium hydroxide and the complex anion, $Cr(OH)_4^-$, are stable in basic solutions of Cr(III).

$$Cr(H_2O)_6^{3+} + 3\ OH^- \rightarrow Cr(OH)_3\ (aq) \text{ or } Cr(OH)_3\ (s)$$

(aq) ΔG^0 = -147.41 kJ/mol; ΔS^0 = 287.25 J/K mol; ΔH^0 = -61.81 kJ/mol
(s) ΔG^0 = -185.45 kJ/mol; ΔS^0 = 430.25 J/K mol; ΔH^0 = -57.24 kJ/mol

$$Cr(H_2O)_6^{3+} + 4\ OH^- \rightarrow Cr(OH)_4^-\ (aq)$$

ΔG^0 = -161.93 kJ/mol; ΔS^0 = 252.2 J/K mol; ΔH^0 = -86.77 kJ/mol

Nitrate will not oxidize Cr(III) in acidic solutions.

$$2\ Cr^{3+}\ (aq) + 3\ NO_3^- + 5\ H_2O \rightarrow 2\ CrO_4^{2-} + 3\ NO_2^- + 10\ H^+\ (aq)$$

ΔG^0 = 545.77 kJ/mol; ΔS^0 = 267.87 J/K mol; ΔH^0 = 625.59 kJ/mol

But in basic solutions the formation of water makes the oxidation possible.

$$10\ H^+\ (aq) + 10\ OH^-\ (aq) \rightarrow 10\ H_2O$$

ΔG^0 = -798.89 kJ/mol; ΔS^0 = 806.6 J/K mol; ΔH^0 = -558.4 kJ/mol

Thermodynamic data for oxidation of chromium hydroxide

Chromium hydroxide in various forms can, in principle, be oxidized by nitrate.

$$2\ Cr(OH)_4^- (aq) + 3\ NO_3^- + 2\ OH^- \rightarrow 2\ CrO_4^{2-} + 3\ NO_2^- + 5\ H_2O$$

ΔG^o = -85.27 kJ/mol; ΔS^o = 570.07 J/K mol; ΔH^o = 84.61 kJ/mol

$$2\ Cr(OH)_3 (aq) + 3\ NO_3^- + 4\ OH^- \rightarrow 2\ CrO_4^{2-} + 3\ NO_2^- + 5\ H_2O$$

ΔG^o = -114.31 kJ/mol; ΔS^o = 499.97 J/K mol; ΔH^o = 34.68 kJ/mol

$$2\ Cr(OH)_3 (s) + 3\ NO_3^- + 4\ OH^- \rightarrow 2\ CrO_4^{2-} + 3\ NO_2^- + 5\ H_2O$$

ΔG^o = -36.23 kJ/mol; ΔS^o = 213.97 J/K mol; ΔH^o = 27.53 kJ/mol

Even chromium(III) oxide can be oxidized by nitrate.

$$2\ Cr_2O_3 (s) + 3\ NO_3^- + 4\ OH^- \rightarrow 2\ CrO_4^{2-} + 3\ NO_2^- + 2\ H_2O$$

ΔG^o = -18.09 kJ/mol; ΔS^o = 111.54 J/K mol; ΔH^o = 15.15 kJ/mol

Chromium hydroxide can be oxidized by hydrogen peroxide.
ΔG^o is very negative for this reaction.

$$2\ Cr(OH)_4^- (aq) + 3\ H_2O_2 + 2\ OH^- \rightarrow 2\ CrO_4^{2-} + 8\ H_2O$$

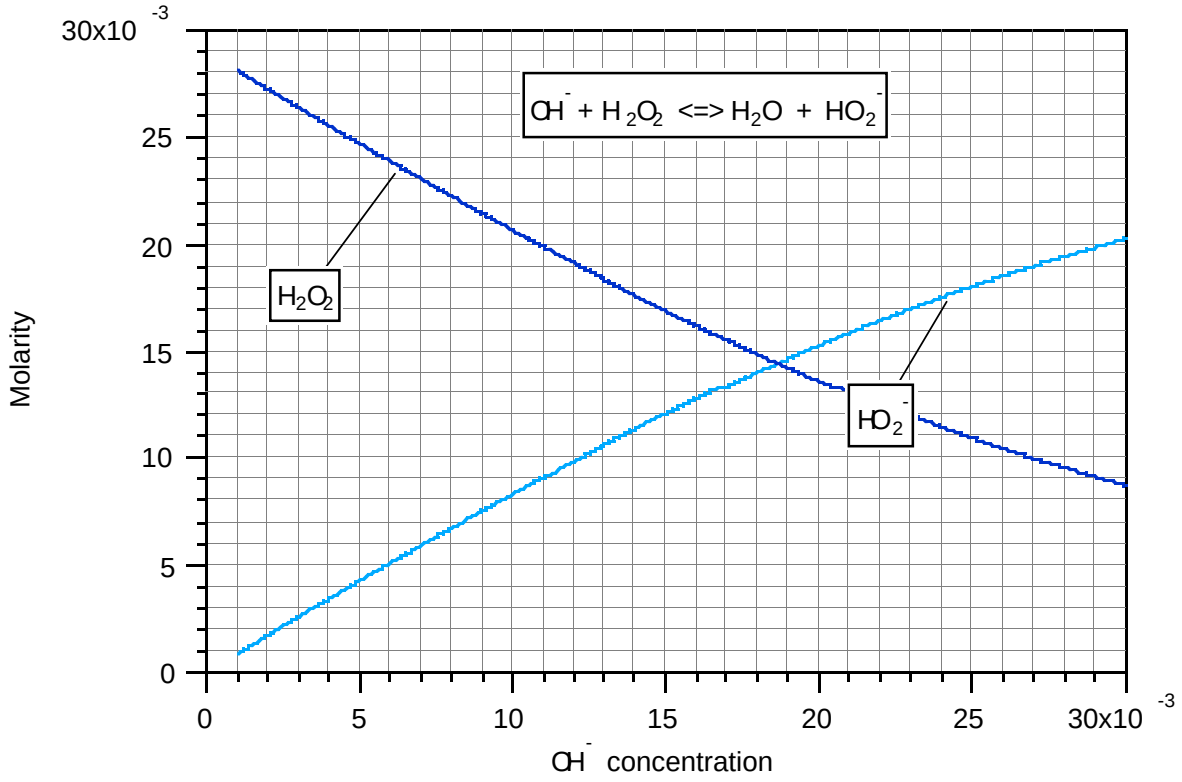
ΔG^o = -624.18 kJ/mol; ΔS^o = 417.1 J/K mol; ΔH^o = -499.88 kJ/mol

Observation of the hydroperoxide anion, HO_2^-, the conjugate base of hydrogen peroxide

- In studying the oxidation of chromium hydroxide by hydrogen peroxide we collected the Raman spectrum of the solution. This spectrum included to O-O stretch of hydrogen peroxide at 876 cm^{-1} and a nearby intense band at 850 cm^{-1}. We have assigned this band as the O-O stretch of HO_2^-.
- Recent literature does not report any vibrational data of this species. A number of theoretical studies cite only a value of 775 $\pm$ 250 cm^{-1} obtained from photoelectron detachment.
- A more thorough literature search turns up an assignment of a band at 836 cm^{-1} as the O-O stretch in solid ammonium hydroperoxide.
- We have carried out experiments to verify this assignment. It is important to determine the role of the hydroperoxide anion in oxidation reactions that take place in strongly basic solutions.

Acid-base chemistry of hydrogen peroxide in basic solutions.

- Hydrogen peroxide is somewhat more acidic than water. Its pK_a value is about 11.6.
- In basic solutions the hydrogen peroxide will lose a proton to the hydroxide ion.
- $H_2O_2 + OH^- \rightarrow HO_2^- + H_2O$
- In solutions at high pH the predominant species is the conjugate base, HO_2^-.



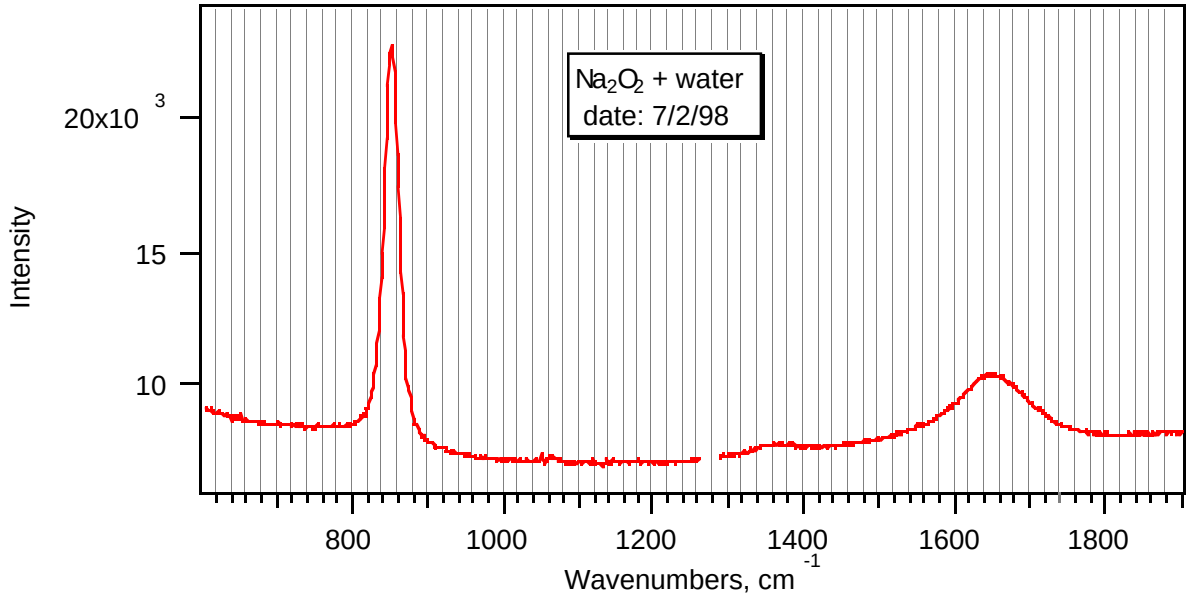
Vibrational spectrum of the hydroperoxide anion

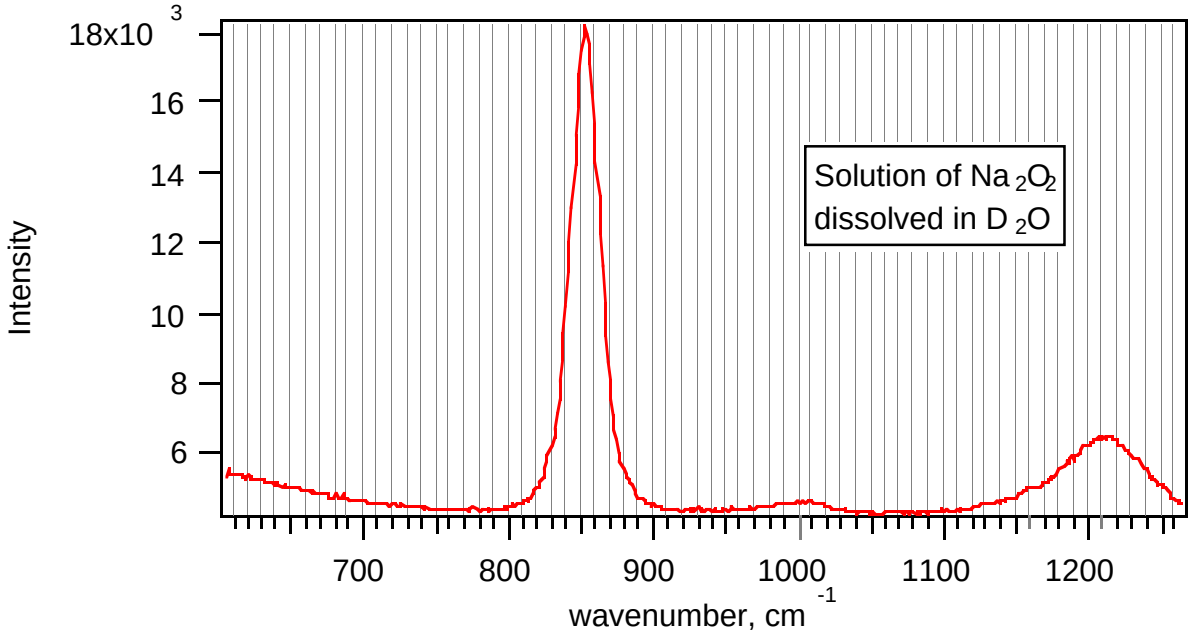
- The O-O stretch of the hydroperoxide anion is the most readily observed of the three vibrations.
- The H-O stretch will be obscured by the strong H-O stretches of water, and the HOO bend will be weak.
- Deuteration of HO_2^- will shift the bending mode to lower wavenumber. This vibration will mix more strongly with the O-O stretch so that the O-O stretch should show a shift upon deuterium labeling.
- The addition of sodium peroxide to water produces the same 850 cm^{-1} band formed by addition of hydroxide ion to hydrogen peroxide.

$$O_2^{2-} + H_2O \text{ --> } HO_2^- + OH^-$$

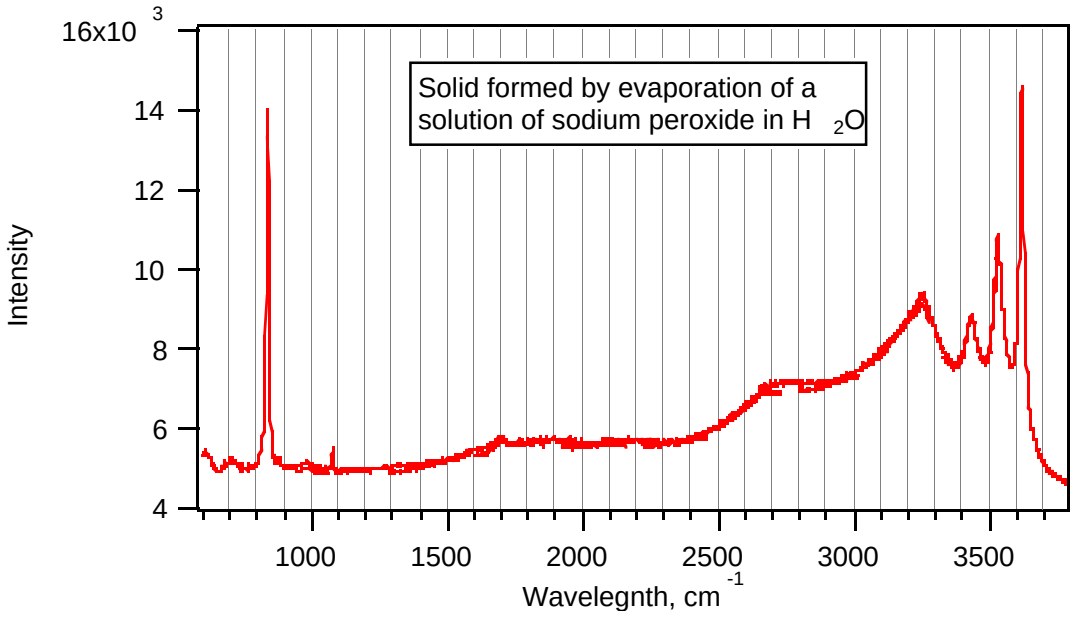
- The same reaction with D_2O forms DO_2^- .
- We observe the same 850 cm^{-1} band for DO_2^-. There is no shift on deuteration.
- Solids formed by evaporation of water should contain crystalline $Na^+ HO_2^-$. We have obtained Raman and infrared spectra of these solids.

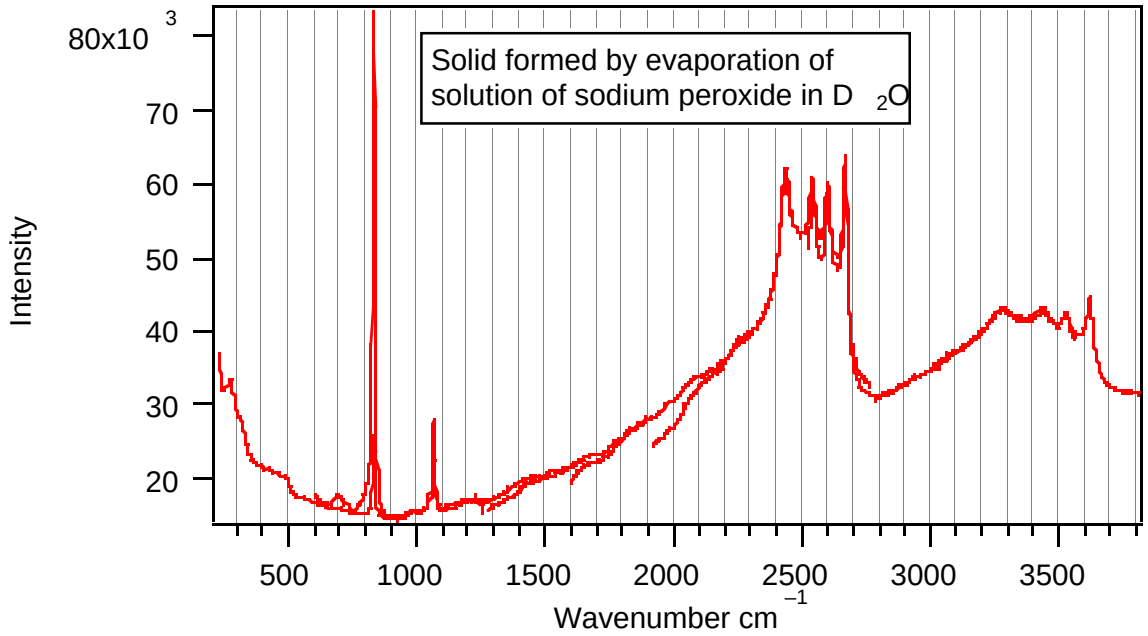
Raman spectra of sodium peroxide dissolved in H_2O and D_2O





Raman spectra of solids formed by evaporation of solutions of Na_2O_2 in H_2O and D_2O





Calculated vibrational wavenumbers for HO_2^- and related species

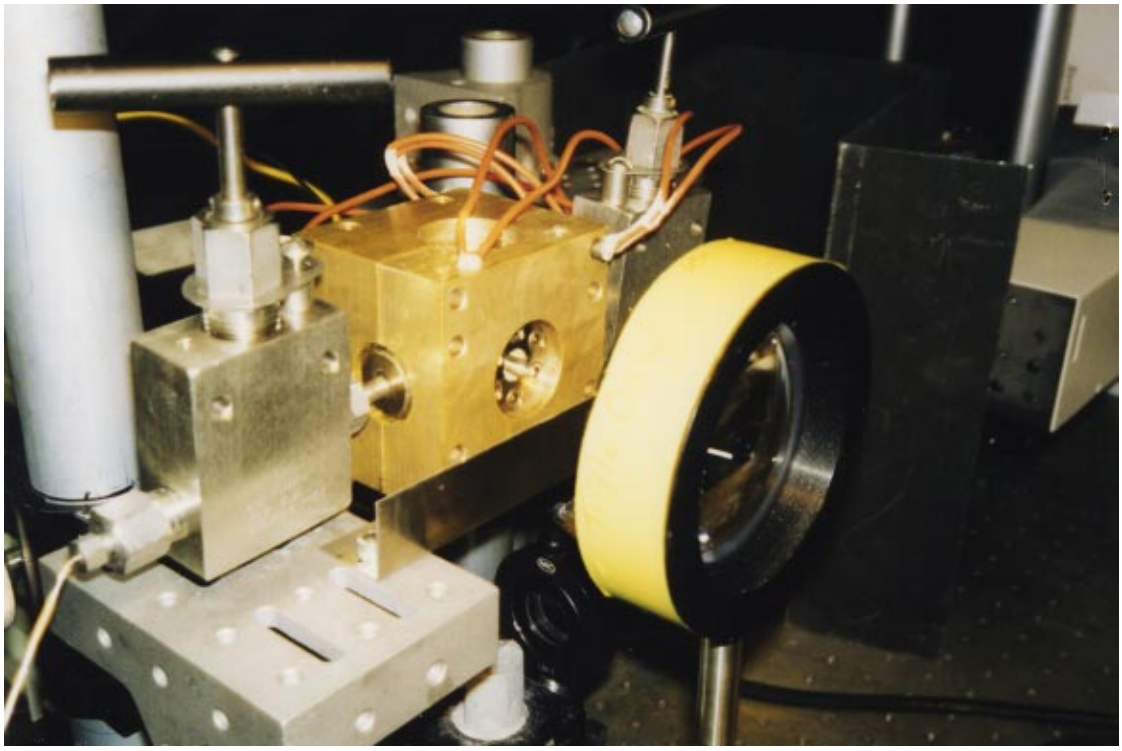
Calculated wavenumbers (cm^{-1}) for HO_2^- and related species

Gaussian 94, 6-311G MP2**

Species	OO stretch	HOO bend	HOO bend	HO stretch	HO stretch
HO_2^-	826	1111		3891	
DO_2^-	747	901		2836	
H_2O_2	945	1311	1468	3872	3875
D_2O_2	940	966	1078	2819	2826
DOOH	942	1012	1399	2823	3873
O_2^{2-}	619				
Na^+ HO_2^-	847	1137		3960	
Na^+ DO_2^-	796	896		2886	
HO_2^--H_2O	883	1210		3895	
DO_2^--H_2O	833	1126		2838	
$HO_2\cdot$	1248	1460		3737	
$DO_2\cdot$	1261	1073		2723	
H_2O		1668		3902	4010
D_2O		1220		2815	2936
HOD		1462		2874	3958

Kinetics of high temperature reactions

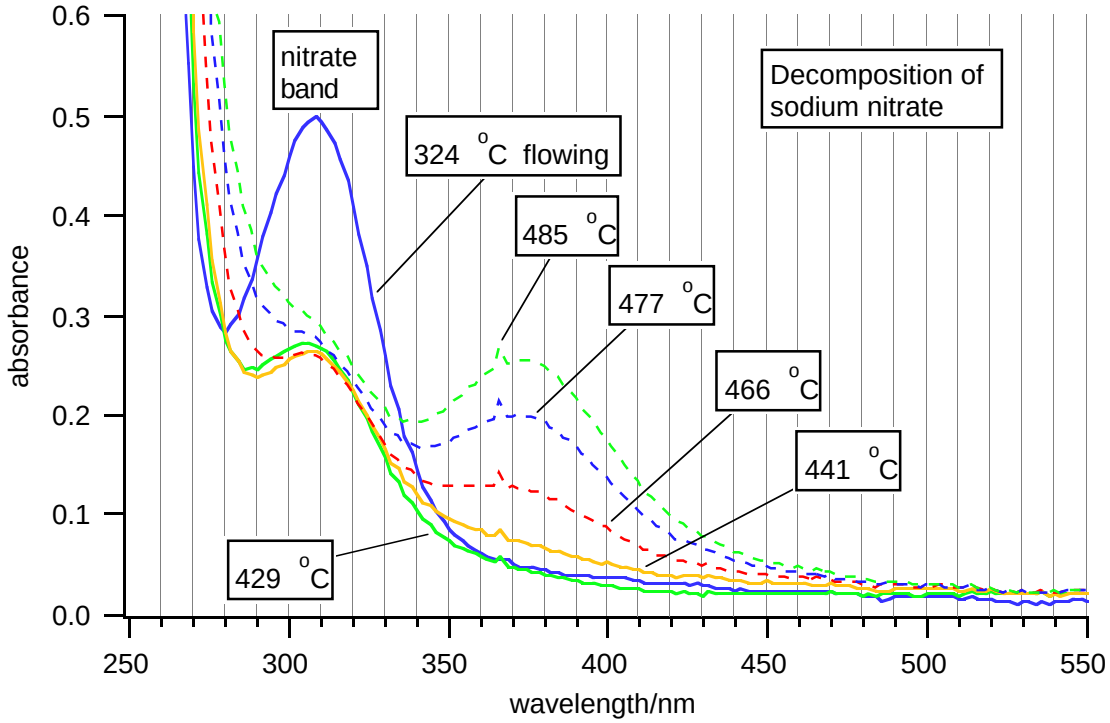
- Reactions are carried out in stainless steel or Inconel cells with diamond windows, flow connections, and a thermocouple. Flow rate and pressure are controlled with a syringe pump.
- We use optical spectroscopic methods, Raman and UV-visible spectroscopy, to probe the reactions.



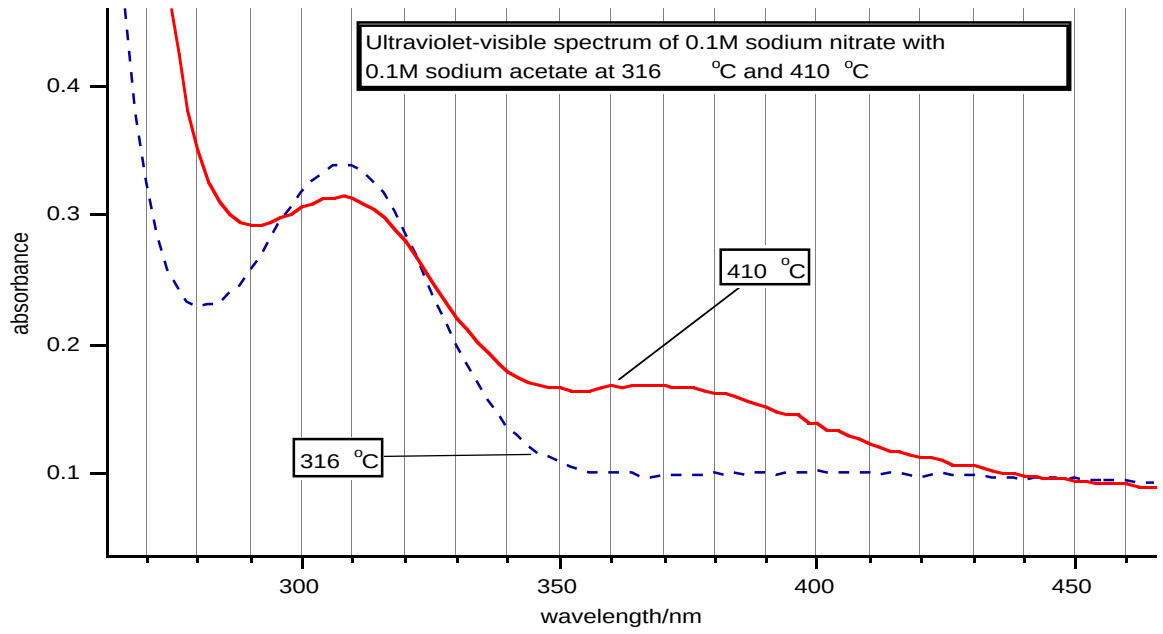
High temperature Raman cell with diamond windows.

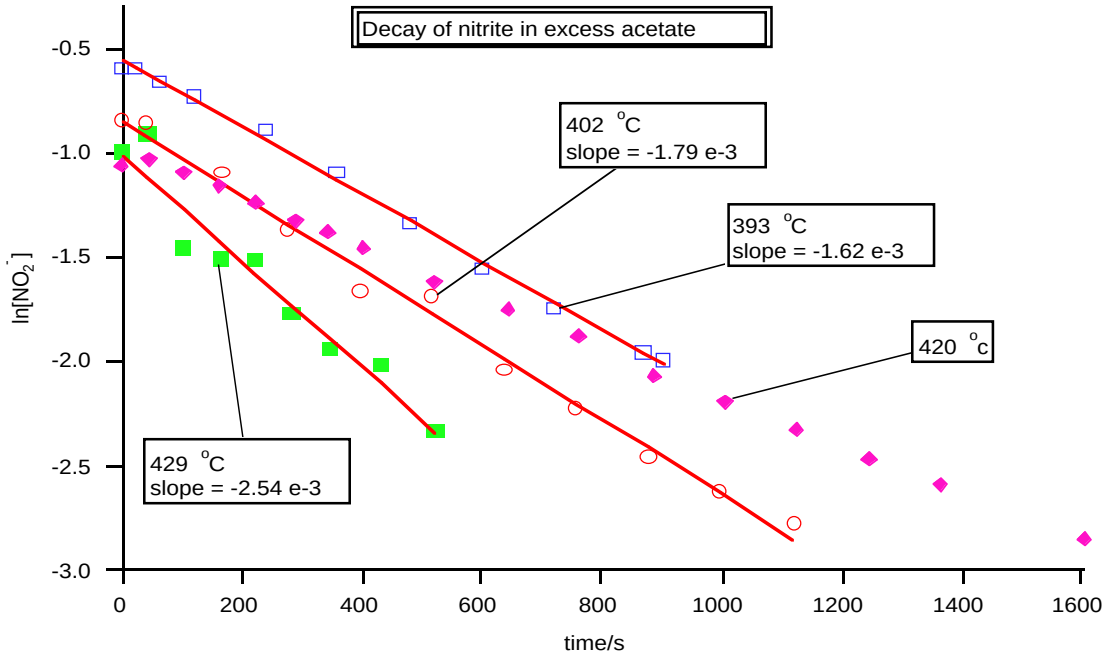
Following reactions in supercritical water by UV-visible spectroscopy

- Ultra violet-visible spectroscopy can be used to monitor the concentrations of nitrate, NO_3^-, and nitrite, NO_2^-, anions.
- Concentrations can be measured as a function of temperature in a continuous flow mode.
- Flow can be stopped by closing valves into and out of the cell, and the concentrations monitored in real time as a reaction proceeds.



Kinetic data for the reaction of nitrite anion with acetate





Significance of experimental results

- Mixtures of various chromium oxide/hydroxides can be readily characterized by infrared spectroscopy.
- Most components of such mixtures can be dissolved at room temperature by a rapid reaction of hydrogen peroxide in alkaline solutions. Cr_2O_3(s) does not react under these conditions.
- The kinetics of this reaction are complicated and depend on the extent of aging of the chromium solution.
- The hydroperoxide anion has been observed spectroscopically and may be significant in oxidation reactions of hydrogen peroxide in alkaline solutions.
- Thermodynamic considerations suggest that oxidation by the nitrate ion is possible at room temperature. This reaction has not been observed to occur at ambient temperatures but does take place at higher temperatures.

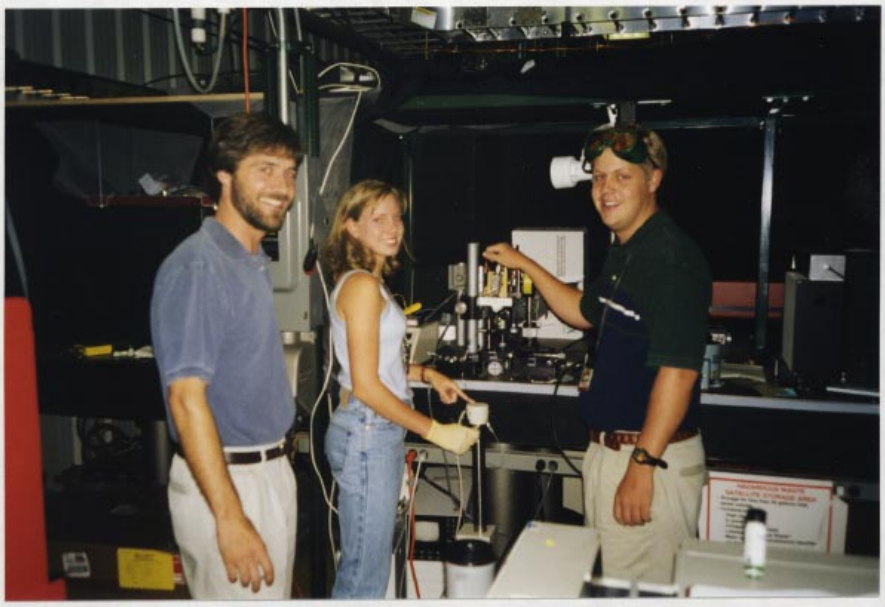
Plans for continuing work on this project

- A Raman spectrometer has been purchased and set up in an optical spectroscopy laboratory at Furman. Experiments will be carried out during the academic year using this equipment.
- Studies of the kinetics of the oxidation of Cr(III) in basic hydrogen peroxide will determine the Arrhenius parameters for the reaction and examine the role of the hydroperoxide anion in the reaction.
- UV-visible spectroscopy will be used to study the oxidation of Cr(III) by nitrate at elevated temperatures.
- Kinetics of the high temperature conversion of nitrate to nitrite will be studied using real-time "stopped flow" techniques.
- A manuscript will be submitted on the spectroscopy of the hydroperoxide anion.

Acknowledgment of people and agencies that are contributing to this project

- Los Alamos National Laboratory staff members who are wonderful scientific collaborators, generous with time and equipment and eager to share in the scientific enterprise:
  Steve Buelow, Bernie Foy, Jeanne Robinson David Harradine, Graydon Anderson, Mark Paffett
- Other LANL personnel who helped get experiments done:
  Zhong Ding, Mike Sedillo, Ron Martinez
- Furman undergraduates– hard working, curious, resourceful, and stimulating colleagues:
  Ginger Denison, Robb Lanning,
  Dana Olsen, David Pond
- Furman University for sustaining support
- Camille and Henry Dreyfus Foundation for financial support for purchase of a Raman spectrometer
- DOE EMSP program for generous project support

Robb Lanning at pyrolysis bench, Ginger Denison and Dave Pond with LANL scientist, Bernie Foy



Dana Olsen at the lab bench, extracurricular activities in northern New Mexico

Furman University