Kinetics of the Reaction of Chromium(III) Hydroxide with H_2O_2 in Basic Solutions

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The Hanford Tank Wastes

Hazardous waste generated during the production of plutonium is stored in steel tanks near the Columbia River at Hanford, Washington.

Waste is stored in 177 tanks that hold 55 million gallons of liquid, sludge, and solids.

The waste solution is kept at a high pH to prevent corrosion of the steel tanks.

Radioactive components of this waste will be concentrated and formed into glass logs for storage at Yucca Mountain in Nevada.

Some Hanford tanks contain chromium in substantial concentration.

Chromium causes cracks in glass ingots.

Cr(VI) compounds are more soluble than those of Cr(III).

Oxidation of chromium hydroxides and oxides is necessary for removal of chromium before vitrification.

Hydrogen peroxide readily oxidizes chromium(III) hydroxide in basic solution.

The product is chromate, CrO_4^{2-}.

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

The reaction is strongly favored thermodynamically.

$\Delta G^o = -624.18$ kJ/mol;

$\Delta S^o = 417.1$ J/K mol;

$\Delta H^o = -499.88$ kJ/mol

In this reaction Cr must lose 3 electrons, and hydrogen peroxide must gain 2 electrons. The overall reaction must be a sequence of elementary reactions involving intermediates such as Cr(IV) and Cr(V).

Hydrogen peroxide is a somewhat stronger acid than water and loses a proton to the hydroxide ion to form HOO^-. The overall reaction can be written as:

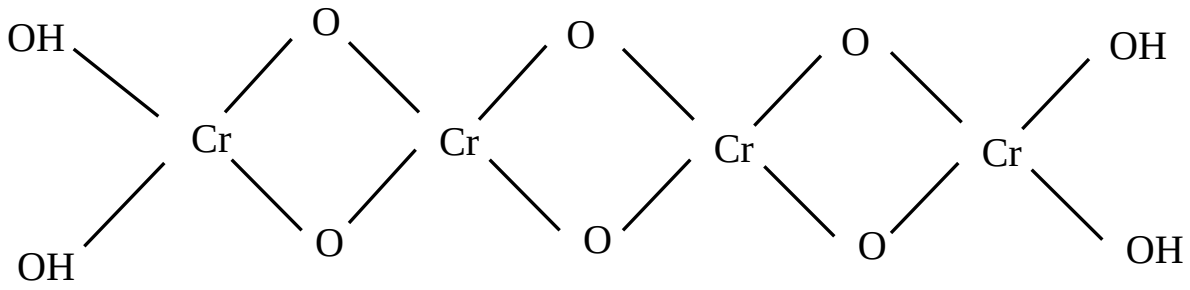
$2\ Cr(OH)_4^- + 3\ HO_2^- \rightarrow 2\ CrO_4^{2-} + 5\ H_2O + OH^-$

Chromium(III) hydroxide aqueous chemistry

$Cr(OH)_3$ is an insoluble solid.

In the presence of hydroxide ion the complex ion, $Cr(OH)_4^-$, forms and is soluble in water.

Basic solutions of chromium(III) hydroxide on aging form amorphous precipitates or gels that are oligomers formed by hydroxide ion linkages between chromium ions.



Simple, schematic representation of an oligomer

General Kinetic Considerations

For decay of $Cr(OH)_4^-$ the general rate equation is of the general form

$$d[\mathrm{Cr(III)}]/dt = -k\,[\mathrm{Cr(III)}]^m\,[H_2O_2]^n\,[OH^-]^p$$

We want to determine the reaction order with respect to each reactant. If hydrogen peroxide and hydroxide ion are present in substantial excess, their concentrations are effectively constant as chromium hydroxide is removed. The decay of Cr(III) can be treated as pseudo first order with an effective rate constant that includes the initial concentrations of other reactants as constants.

$$k_{eff} = k\,[H_2O_2]^n\,[OH^-]^p$$

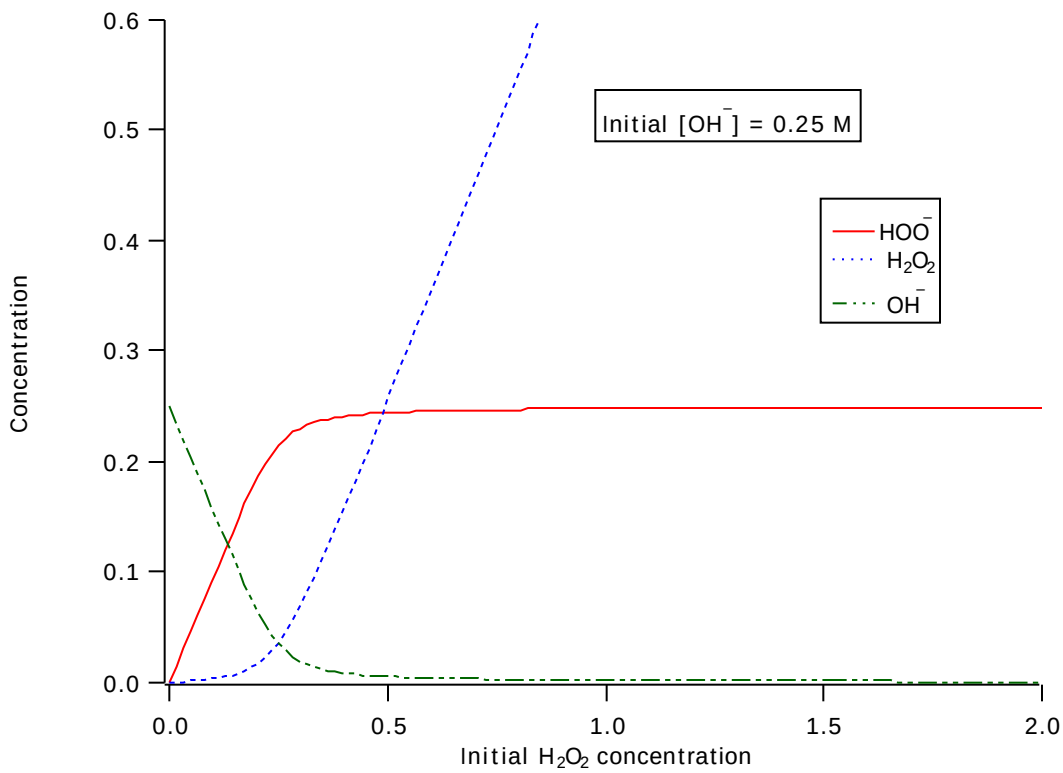
The rate equation is developed by measuring k_{eff} as a function of reactant concentration.

Acid-base Equilibrium

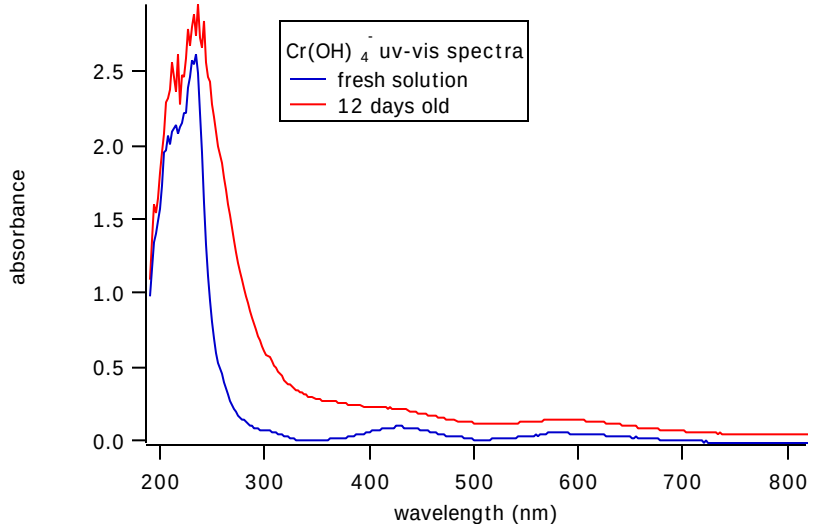
The concentration of HO_2^- must be determined by solution of a quadratic equation. If K is the equilibrium constant, a the initial hydrogen peroxide concentration, and b the initial hydroxide ion concentration, the concentration of HO_2^- is given by the expression

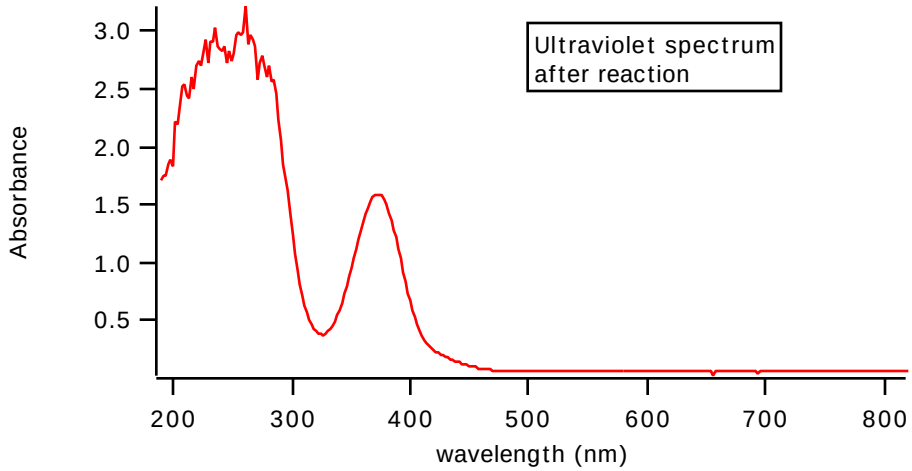
$$\left[HO_2^-\right] = c = K \times (a - c) \times (b - c)$$

$$c = \frac{\left(a + b + 1/K\right) \pm \sqrt{\left(a + b + 1/K\right)^2 - 4ab}}{2}$$



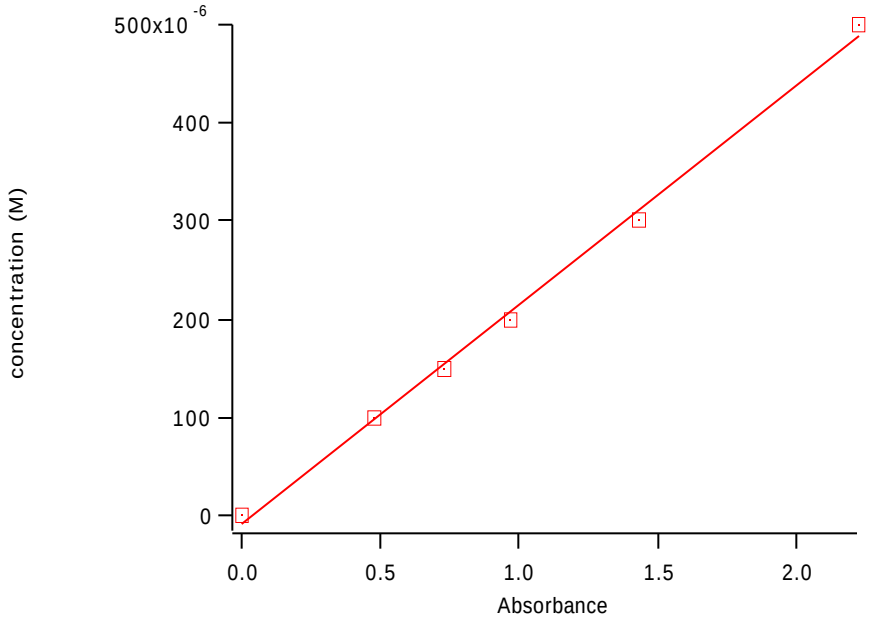
UV-Visible Spectra of $Cr(OH)_4^-$ and CrO_4^{2-}





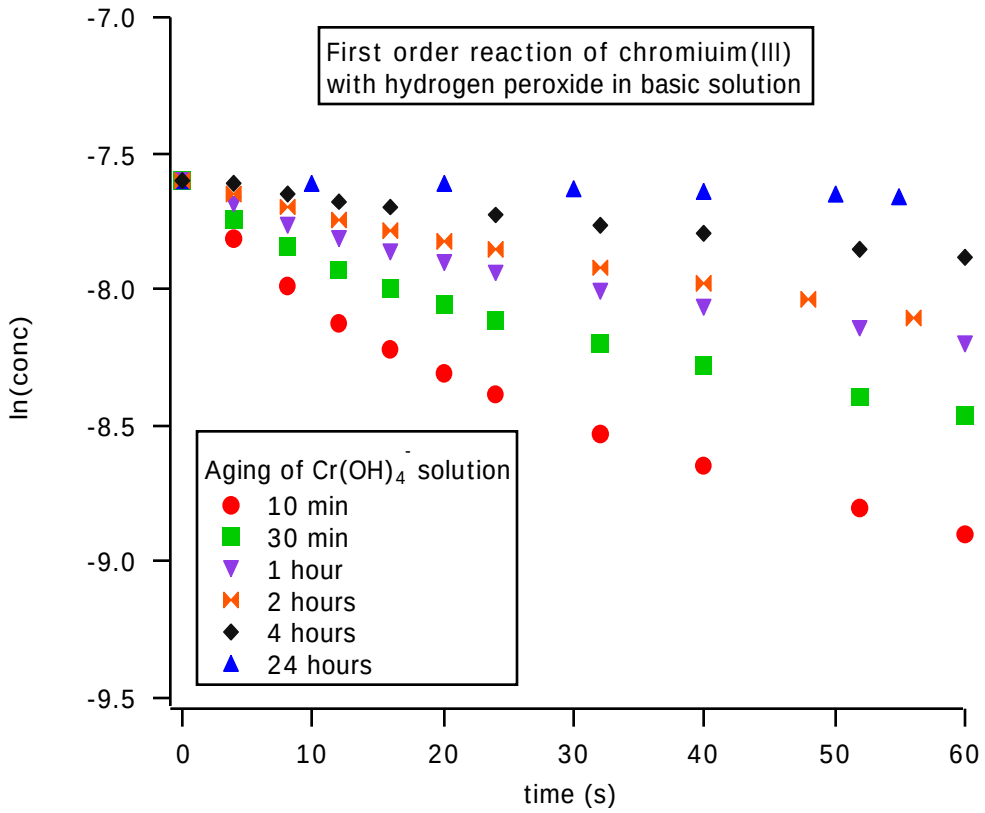
The chromate ion absorbs at 372 nm.

Rate Measurement and Chromate Calibration Curve



The rate of reaction is followed by measuring the ultraviolet band of the chromate ion at 372 nm. The concentration of $Cr(OH)_4^-$ remaining in solution is calculated and plotted as a function of time. The rate of decay of OH^- is determined by measuring pH and calculating OH^- concentration as a function of time.

Chromium Reaction Rates as a Function of Aging



The rate of reaction decreases with aging time for the chromium hydroxide solutions.

This change of rate is attributed to the formation of oligomers of chromium hydroxide.

Kinetic Analysis

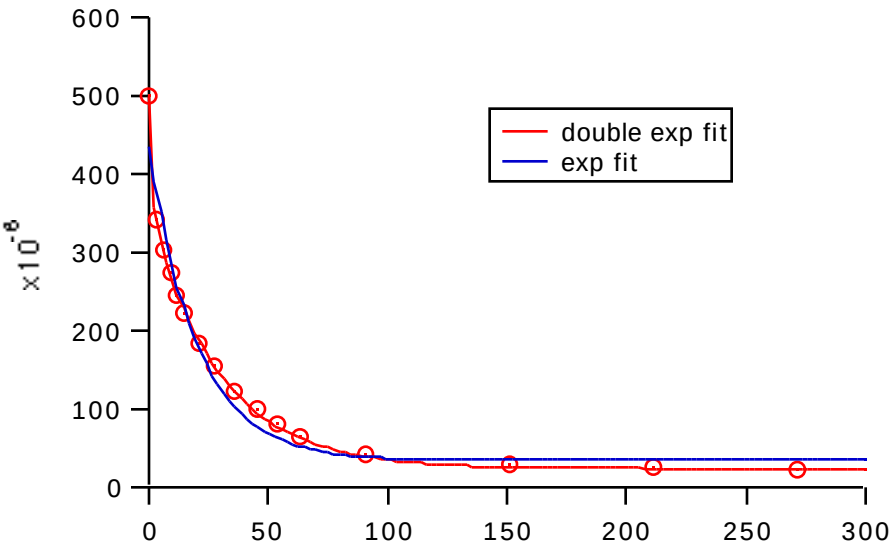
The rate of reaction decreases with aging of the solution.

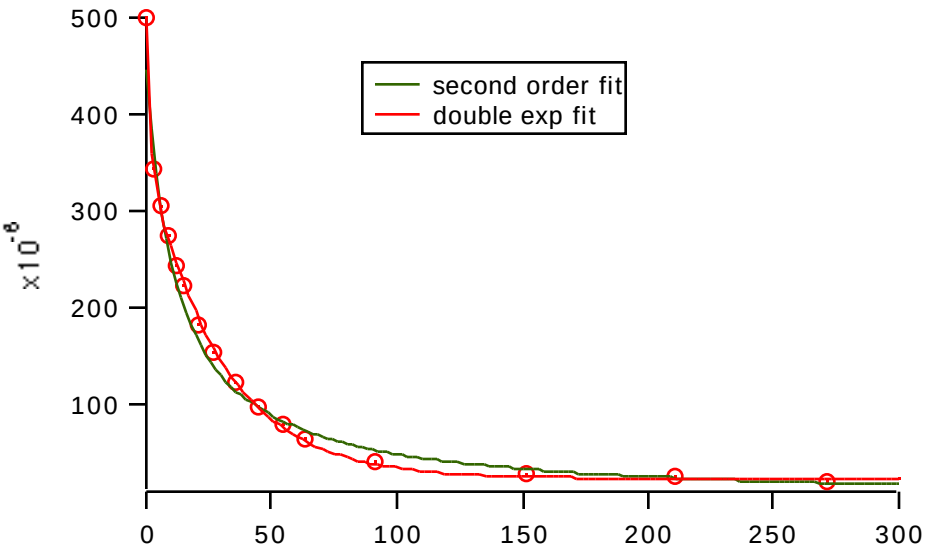
Different oligomers of chromium(III) hydroxide react at different rates.

Decay kinetics fit a multi-exponential function.

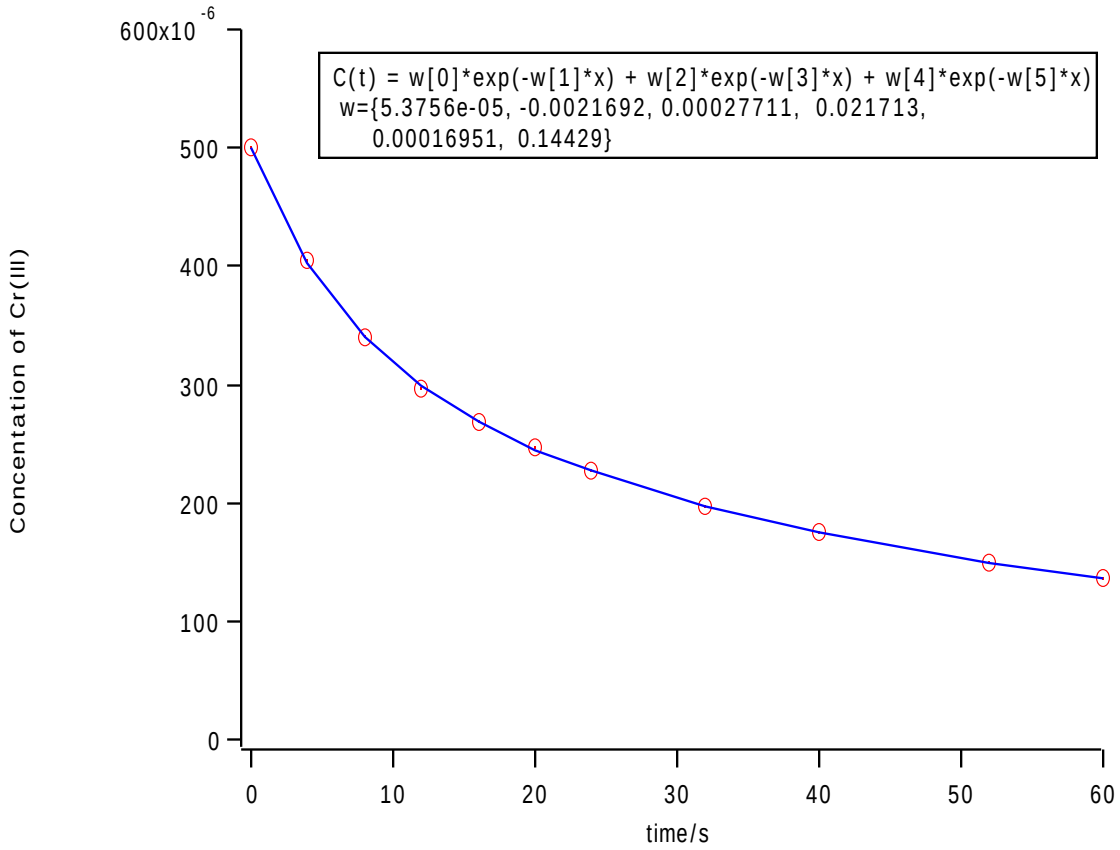
$$[Cr(OH)_4^-](t) = C_0 + C_1 e^{-k1 \cdot t} + C_2 e^{-k2 \cdot t}$$

Simple first or second order functions do not fit the data.



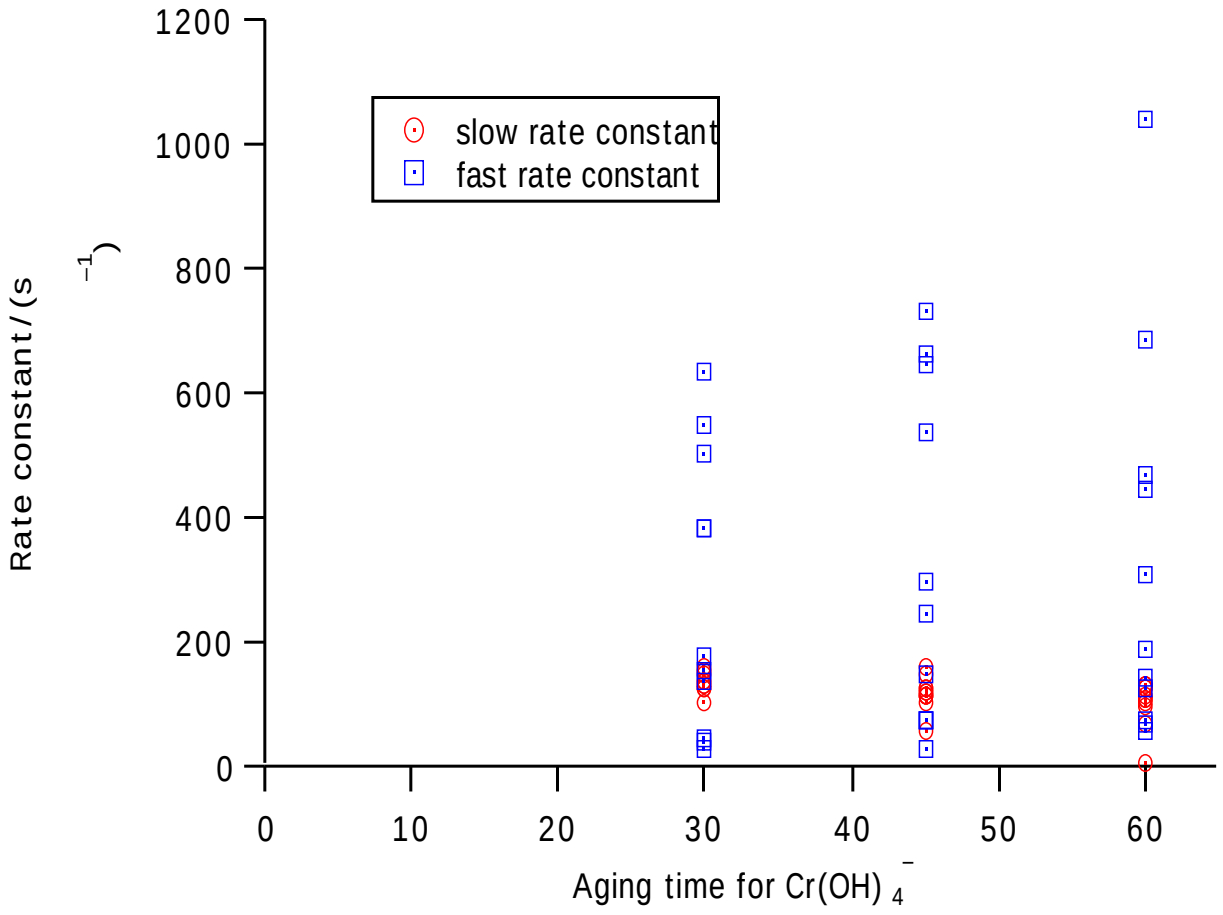


Multi-exponential Decay

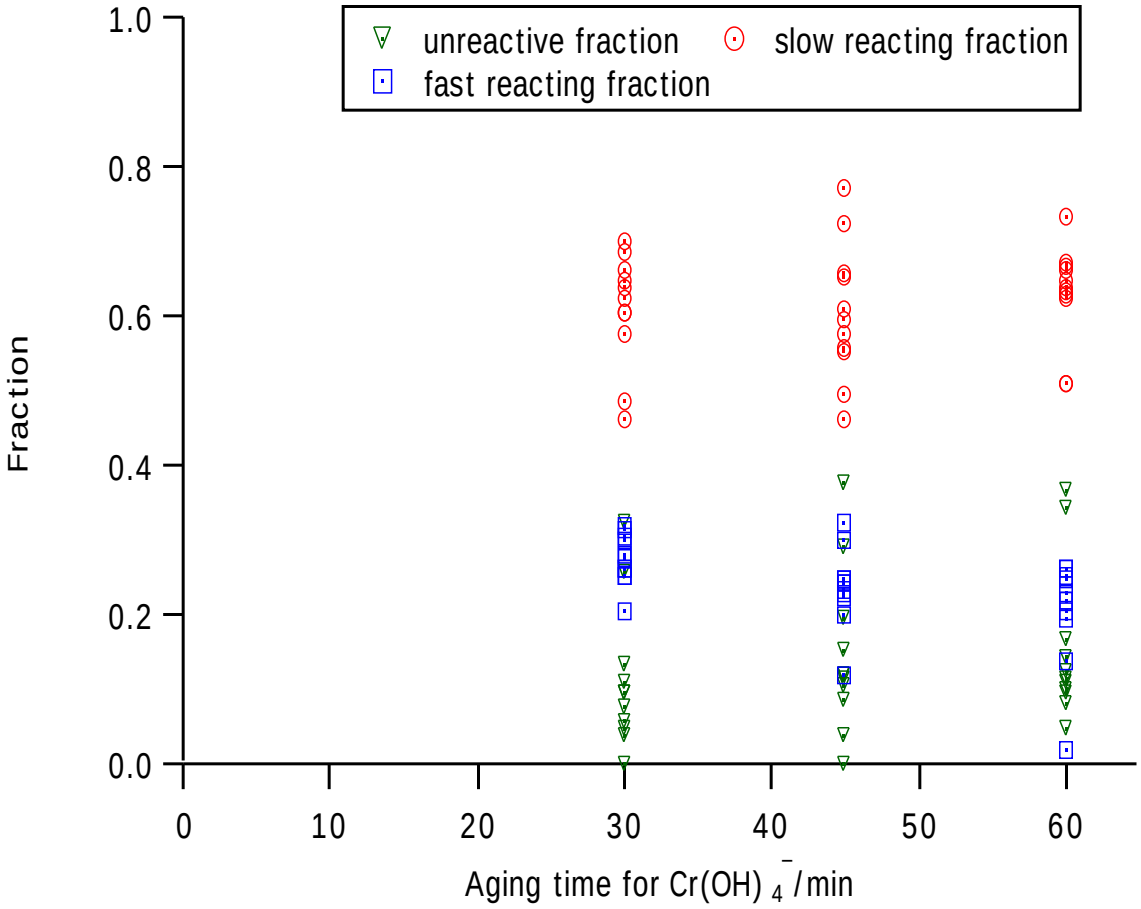


Data analysis provides the fraction of chromium species and the effective rate constant for slower and faster reactions.

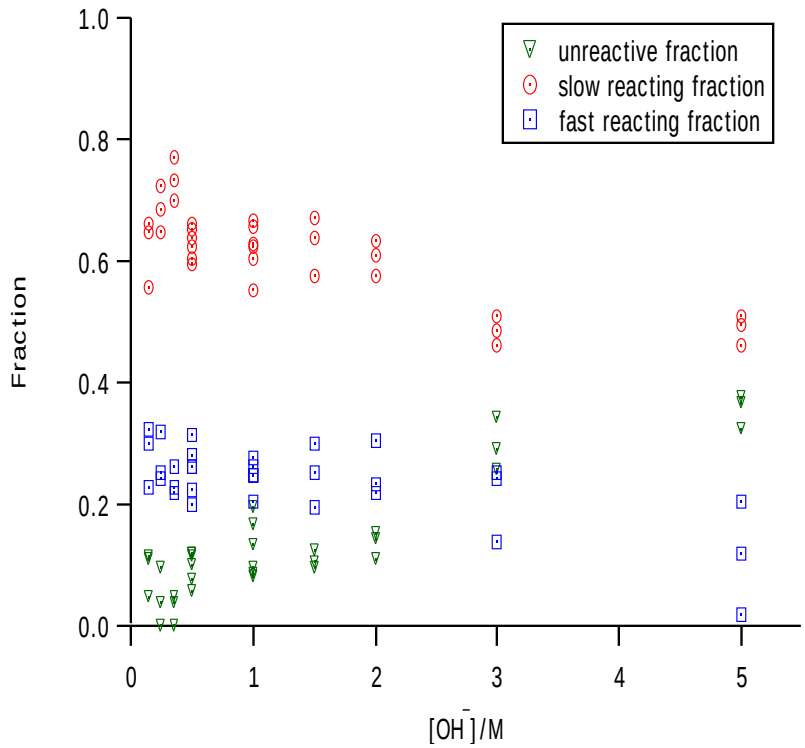
Effective first order rate constants show some dependence on aging time.

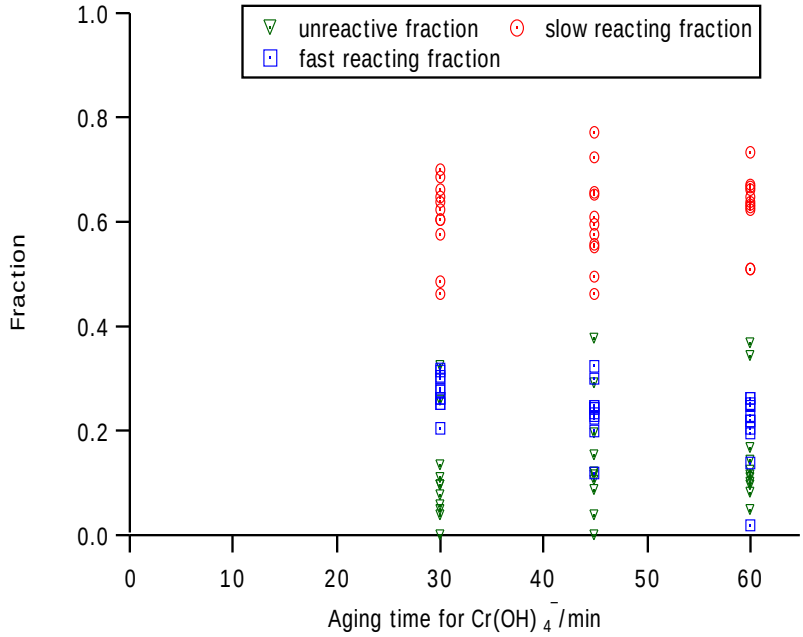


Reactive fractions change some with aging time.

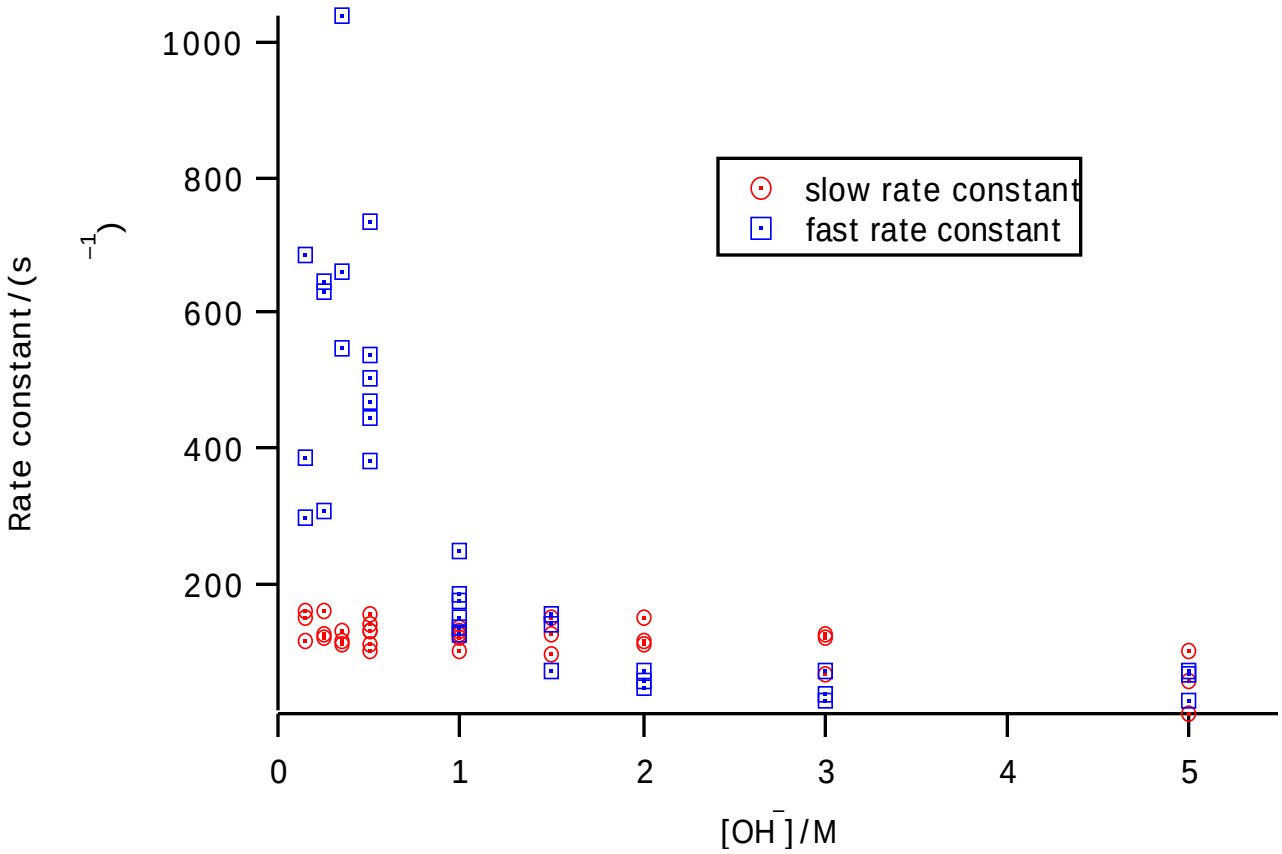


Reactive fraction as a function of [OH^-] and aging time



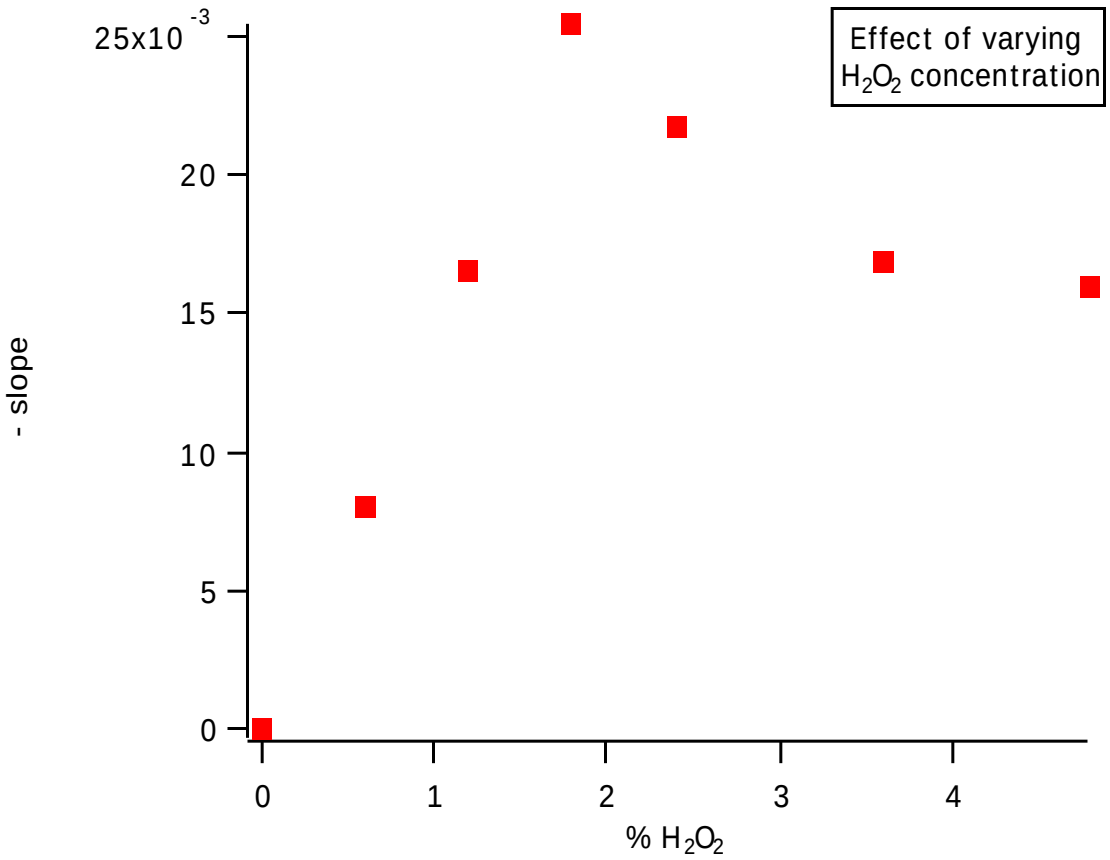


Effective first order rate constants decrease as a function of OH^- concentration.



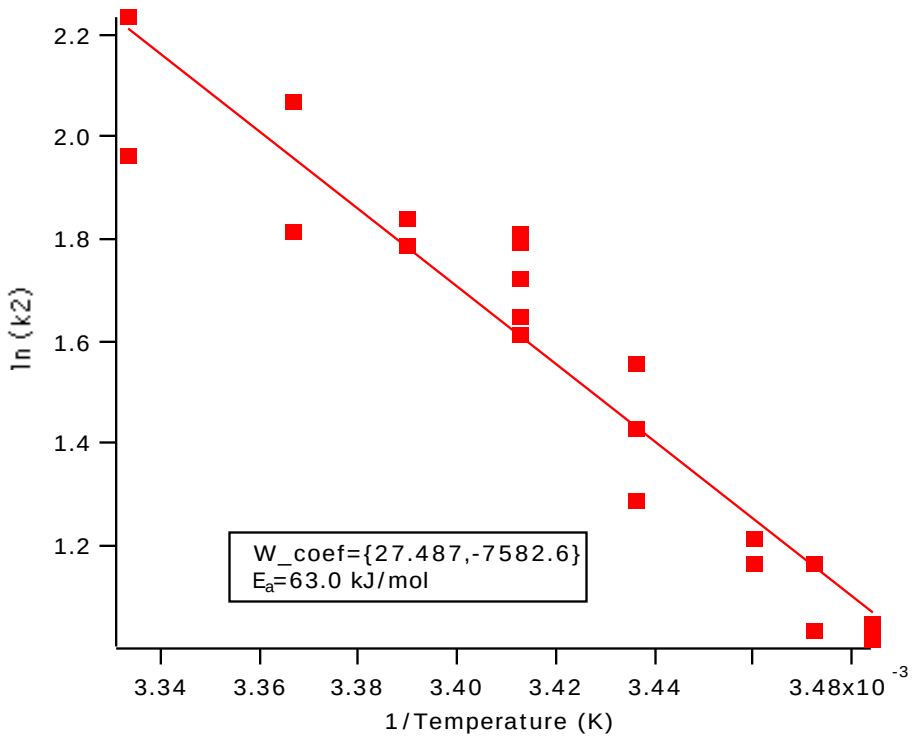
The fast effective rate constant initially increases with increasing hydroxide ion concentration then decreases with further increases in hydroxide ion concentration. The slow rate constant is not strongly dependent on hydroxide concentration.

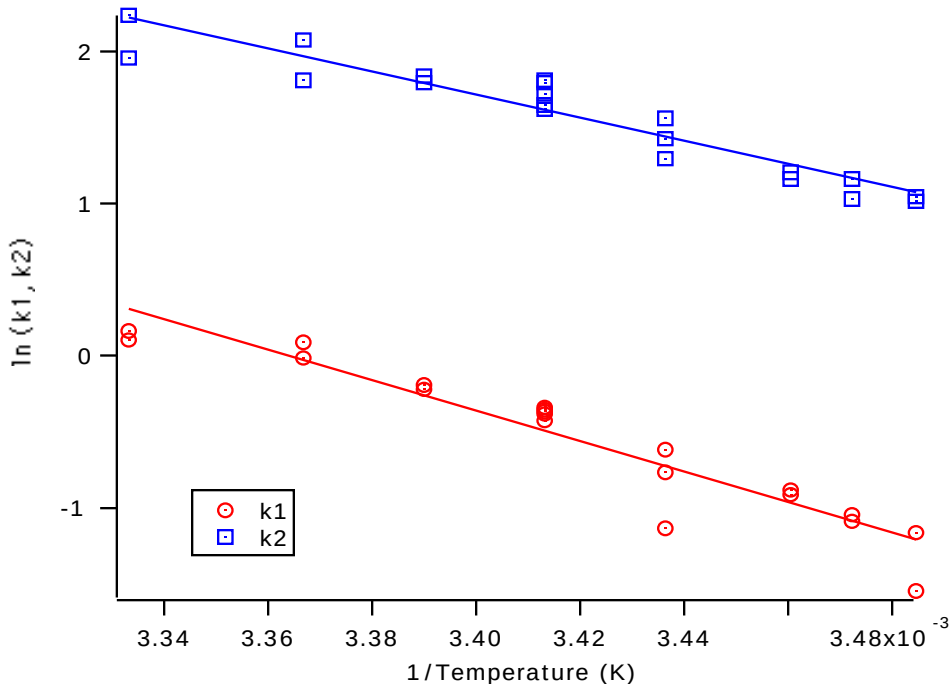
Dependence of Rate on $[H_2O_2]$



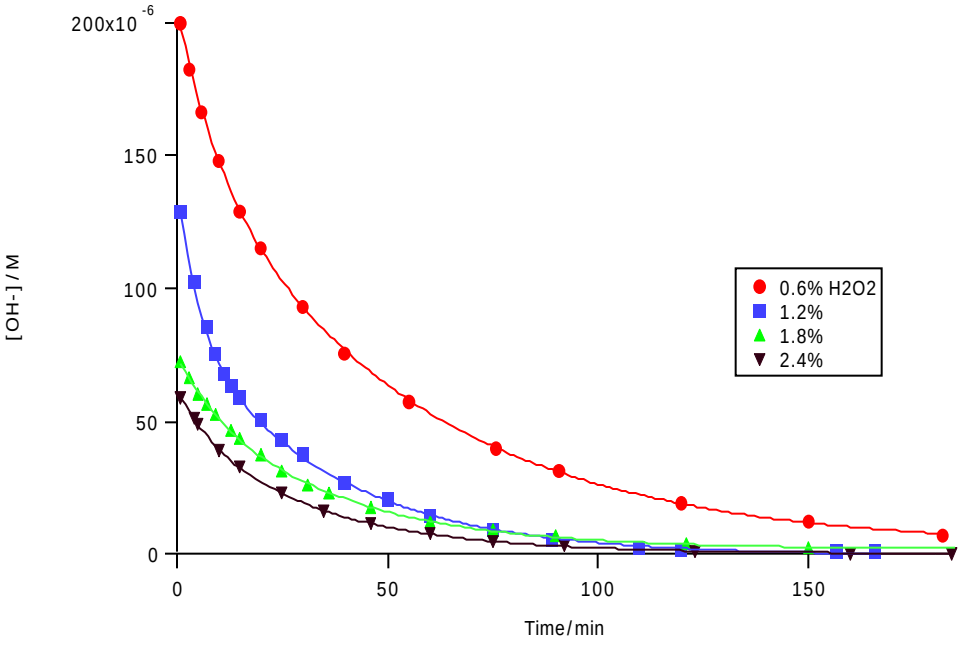
The effective rate constant has a complex dependence on the concentration of hydrogen peroxide.

Arrhenius Plots and Activation Energy





Cr (III) Reaction Rate as Measured by pH Decay



Measurement of the rate of reaction has also been followed by the rate of consumption of hydroxide ion my measuring the pH. These decay curves also fit a multi-exponential function.

Kinetic Analysis with Mathcad

Hydrogen peroxide concentration (y) increasing

$y := 0, .02 .. 2$ $\quad a := 2$ $\quad b := .25$ $\quad k := 225$

[OH^–] initial $\quad$ Equilibrium constant

$i := 0 .. 10$

$kr_i :=$	$c_i :=$
7.9	.044
17.2	.088
27.8	.132
30.2	.176
35.1	.176
26	.221
18.2	.265
15.3	.294
15.3	.353
12.8	.441
14.1	.529

Algebra for equilibrium

$$x = k\cdot(y - x)\,(b - x)$$

$$\left[\frac{-1}{(2\cdot k)}\cdot\left(-1 - k\cdot y - k\cdot b + \sqrt{1 + 2\cdot k\cdot y + 2\cdot k\cdot b + k^2\cdot y^2 - 2\cdot k^2\cdot y\cdot b + k^2\cdot b^2}\right)\right]$$

Solve for HO2^– concentration

$$hoo(y) := \frac{1}{(2\cdot k)}\cdot\left[(1 + k\cdot y + k\cdot b) - \sqrt{1 + 2\cdot k\cdot y + 2\cdot k\cdot b + k^2\cdot y^2 - 2\cdot k^2\cdot y\cdot b + k^2\cdot b^2}\right]$$

$$k1_i := \frac{kr_i}{14000}$$

$$hp(y) := y - hoo(y) \qquad oh(y) := b - hoo(y)$$

$$k2_i := \frac{kr2_i}{14000}$$

Rate equations

$$s(y) := oh(y)^{2.0}\cdot hoo(y)^2$$

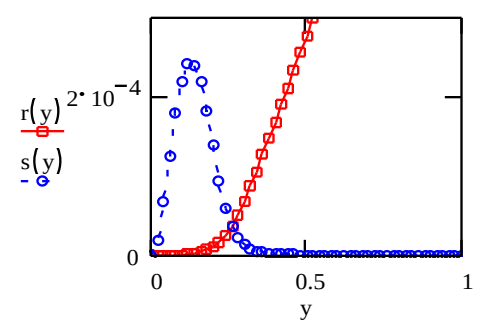
$$r(y) := oh(y)^{1}\cdot hp(y)^2\cdot hoo(y)^0$$

$$t2(y) := 220\cdot s(y) + 130\cdot r(y)$$

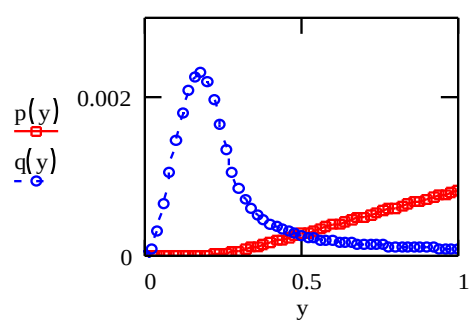
$$p(y) := oh(y)^{1}\cdot hp(y)^2$$

$$q(y) := oh(y)^{1}\cdot hoo(y)^2$$

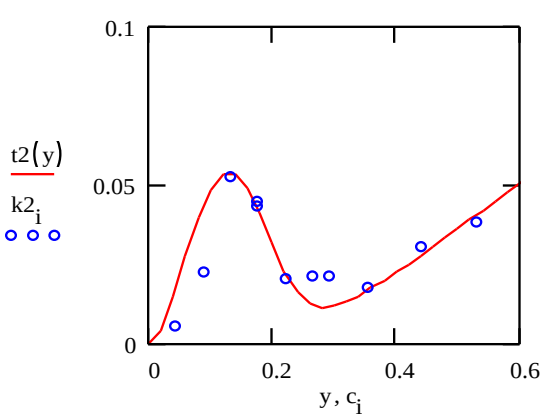
$$t(y) := 1.0\cdot q(y) + 2.5\ p(y)$$

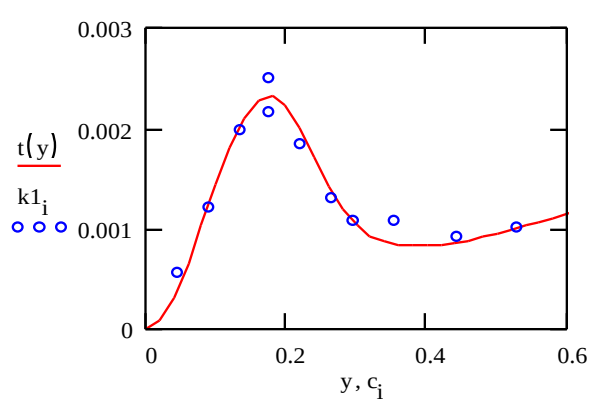


Fast effective rate constant
fit to experimental data



Slow effective rate constant
fit to experimental data





Kinetic Analysis with Mathcad

Simulation for hydrogen peroxide at 0.176 M and increasing hydroxide ion concentration.

Experimental data

$i := 0 .. 10$

$kr_i :=$

296
644
660
733
539
150
247
72
72
29.9
74.1

$c_i :=$

.15
.25
.35
.5
.5
1
1
1.5
2
3
5

$j := 0 .. 14$

$kr2_j :=$

384
347
465
632
632
600
547
502
383
175
135
154
46.3
39.4
28.8

$c2_j :=$

.15
.15
.2
.25
.25
.251
.35
.5
.5
1
1
1.5
2
3
5

$y := 0, .02 .. 5 \quad a := .4 \quad b := .25$

$k := 225$

Initial [H2O2] must be adjusted to achieve a fit.

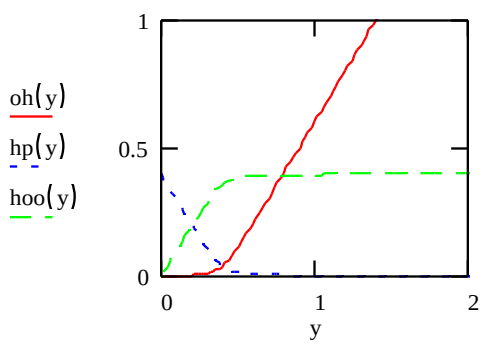
$k1_i := \frac{kr_i}{8000}$

$k2_j := \frac{kr2_j}{8000}$

Solve for [HO2^–]

$$hoo(y) := \frac{1}{(2\cdot k)}\cdot\left[(1 + k\cdot y + k\cdot a) - \sqrt{1 + 2\cdot k\cdot y + 2\cdot k\cdot a + k^2\cdot y^2 - 2\cdot k^2\cdot y\cdot a + k^2\cdot a^2}\right]$$

$hp(y) := a - hoo(y) \quad oh(y) := y - hoo(y)$



Rate equations

$p(y) := oh(y)^{1.5}\cdot hp(y)^{2.}$

$q(y) := oh(y)^{1.5}\cdot hoo(y)^2$

$r(y) := hoo(y)\cdot hp(y)$

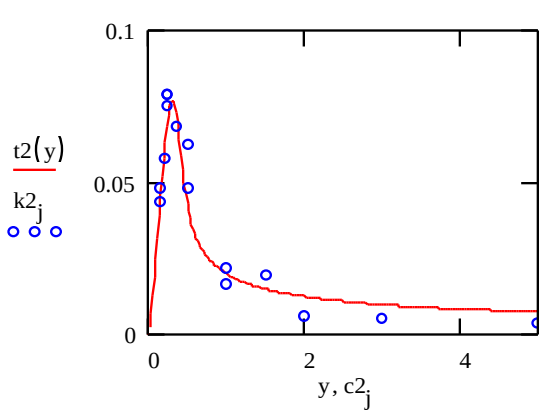
$s(y) := hoo(y)\cdot oh(y)\cdot hp(y)$

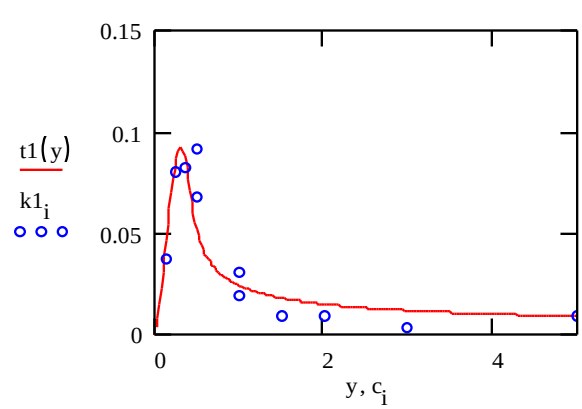
$t2(y) := 0\cdot q(y) + 5000\ p(y)$

$t1(y) := 0\cdot q(y) + 6000\ p(y)$

Fast effective rate constant fit to experimental data for 30 min aging.

Fast effective rate constant fit to experimental data for 45 min aging.





Conclusions

- **Chromium(III) hydroxide is readily oxidized to chromate by hydrogen peroxide at ambient temperatures.**
- **The rate of reaction decreases with aging of the chromium hydroxide solution.**
- **The rate equation is complex with respect to the concentrations of hydrogen peroxide and hydroxide ion.**
- **For a given hydroxide ion concentration the rate of reaction increases then decreases with increasing hydrogen peroxide concentration.**
- **The acid-base equilibrium between hydrogen peroxide and its conjugate base, HO_2^-, plays a major role in the rate equation.**
- **The model generally fits the trends in dependence of rate on concentration of reactant, but quantitative agreement has not been achieved for all conditions.**

Acknowledgments

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- **We greatly appreciate the wonderful, varied opportunities provided by northern New Mexico.**

Vibrational Spectroscopy of HOO^-, the Conjugate Base of Hydrogen Peroxide

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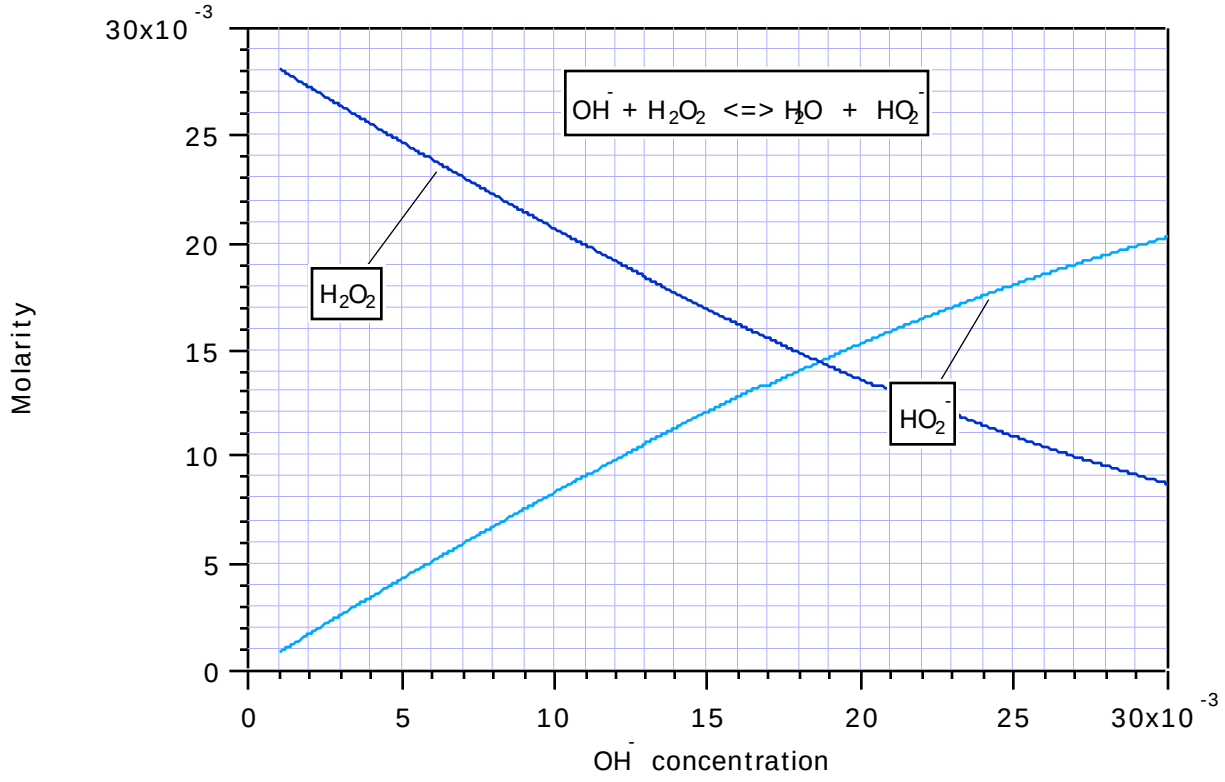
Observation of the hydroperoxide anion, HO_2^-, the conjugate base of hydrogen peroxide

- 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 Ellison's value of 775 ± 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.
- $H_2O_2 + OH^- \text{-->} HO_2^- + H_2O$
- In solutions at high pH the predominant species is the conjugate base, HO_2^-.



Formation of hydroperoxide ion

Reaction conditions

$$H_2O_2 + OH^- \longrightarrow HO_2^- + H_2O$$

Hydrogen Peroxide was added to a solution of sodium hydroxide at room temperature. The reaction formed bubbles and the spectrum of the solution was recorded. Upon desiccation, a solid could be obtained.

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

$$D_2O + O_2^{2-} \longrightarrow DO_2^- + OD^-$$

Sodium peroxide was added to both H_2O and D_2O at room temperature. The spectra of the solutions were recorded and then upon desiccation spectra of the solids were recorded.

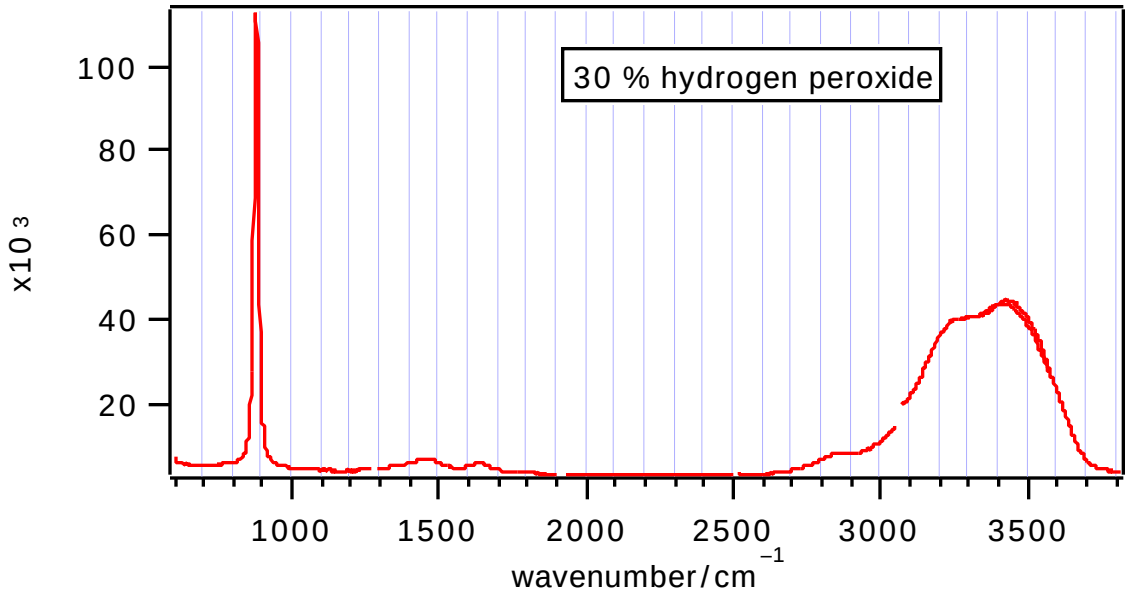
Vibrational spectrum of the hydroperoxide anion

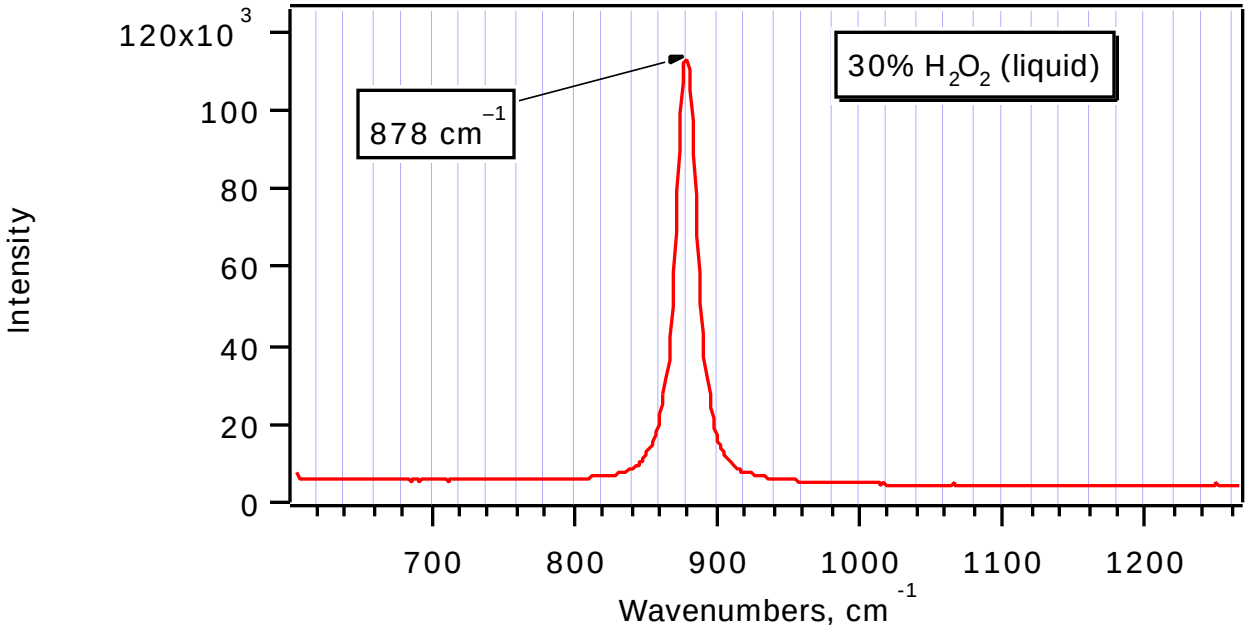
- The O-O stretch of the hydroperoxide anion is the most readily observed of the three vibrations.
- The H-O stretch is obscured by the strong H-O stretches of water, and the HOO bend is weak.
- Deuteration of HO_2^- should shift the bending mode to lower wavenumber. This vibration will mix more strongly 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.

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

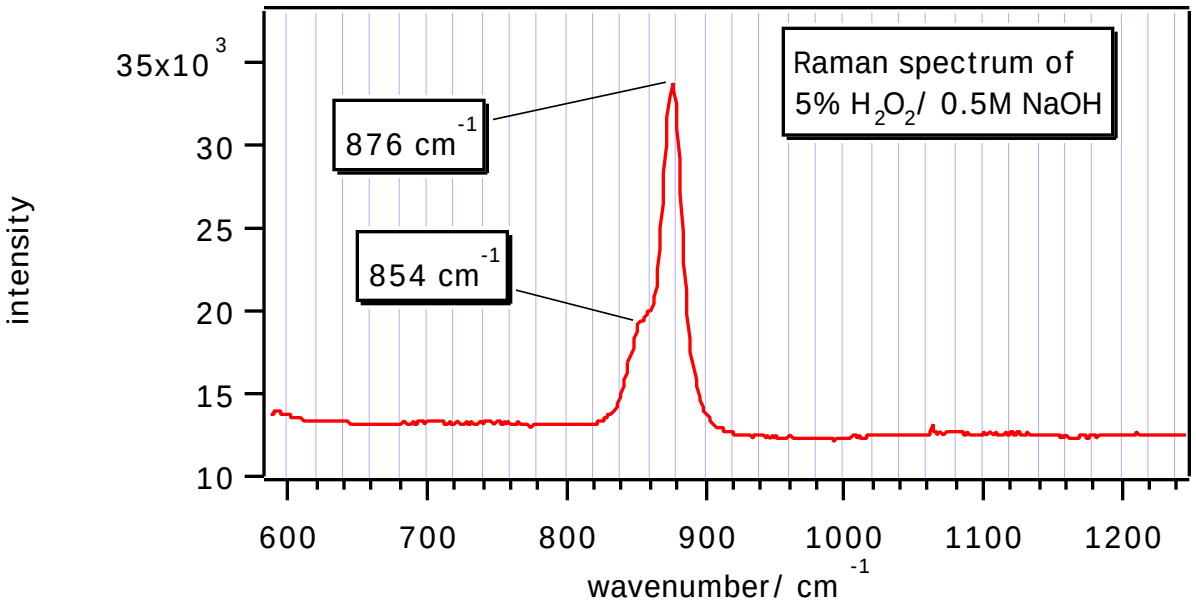
- The same reaction with D_2O forms DO_2^- .
- We observe the same 850 cm^{-1} band for DO_2^-. There is no shift on deuteration.
- Solids formed by evaporation of water should contain crystalline $Na^+ HO_2^-$. Spectra of these solids include vibrations of solvent in the crystals.

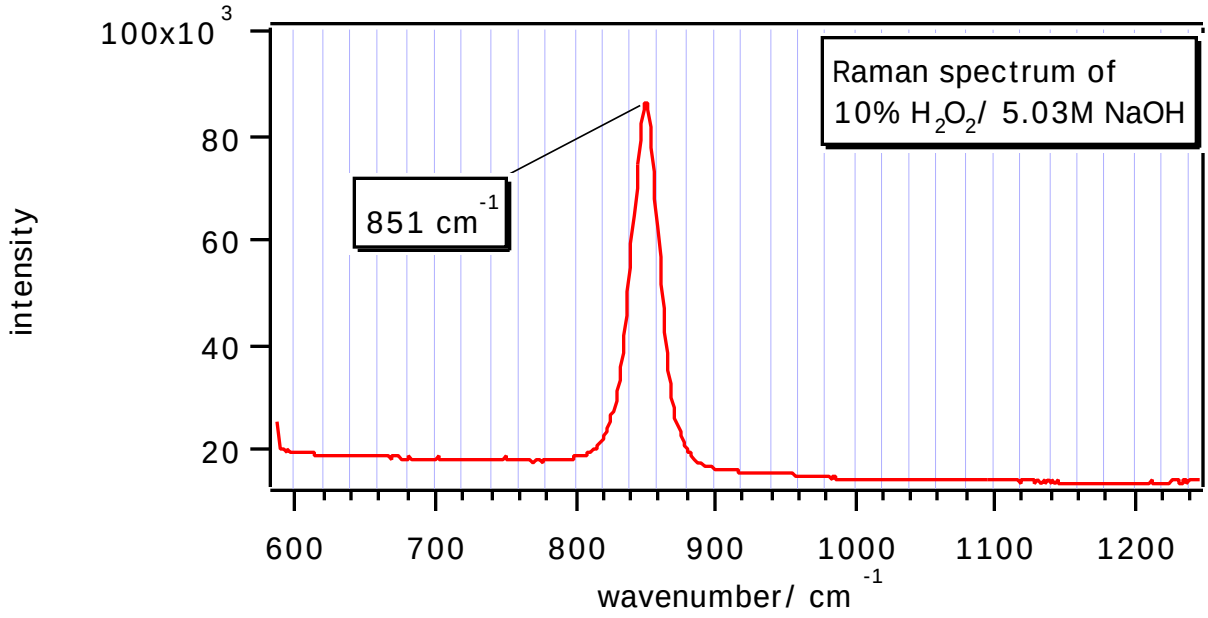
Raman spectrum of hydrogen peroxide in water



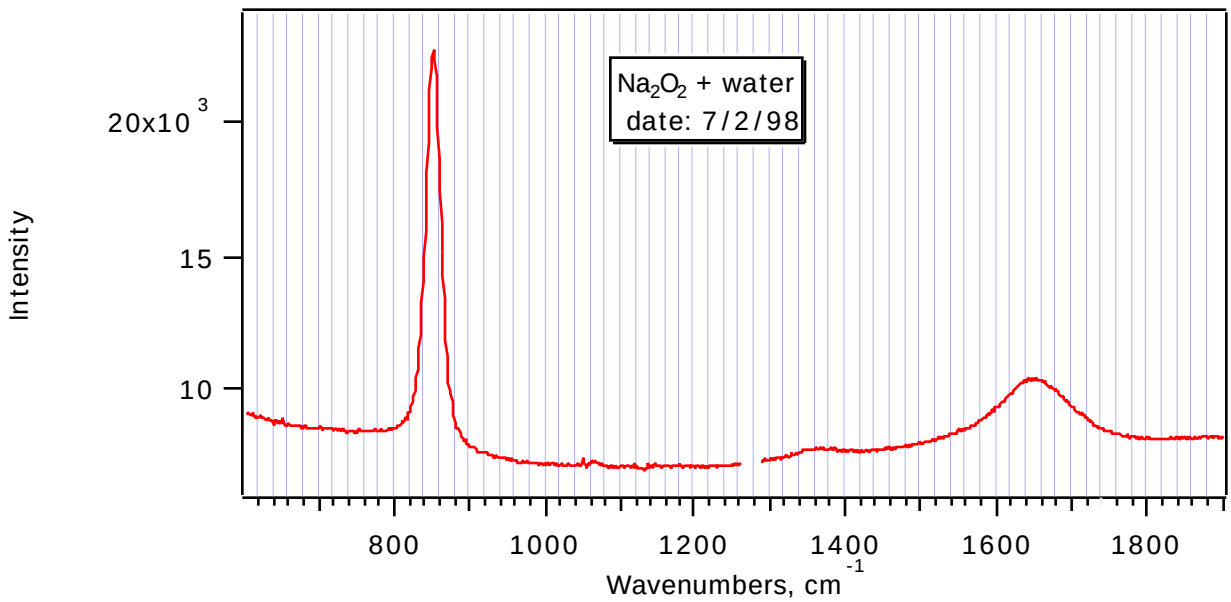


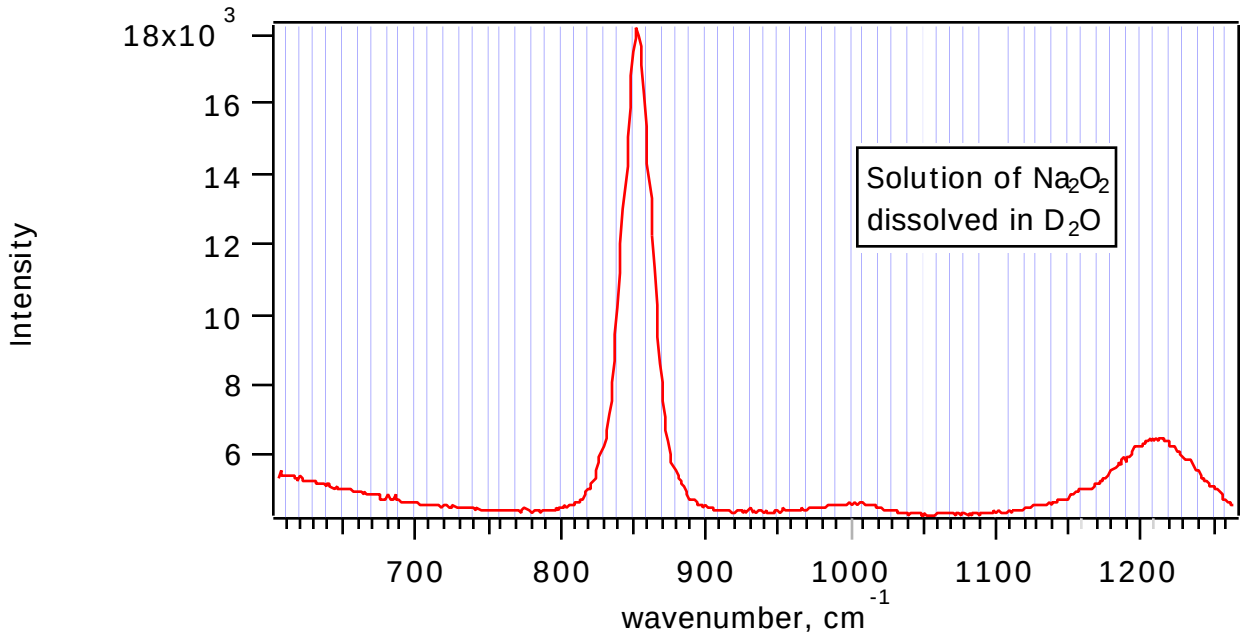
Adding NaOH to H_2O_2



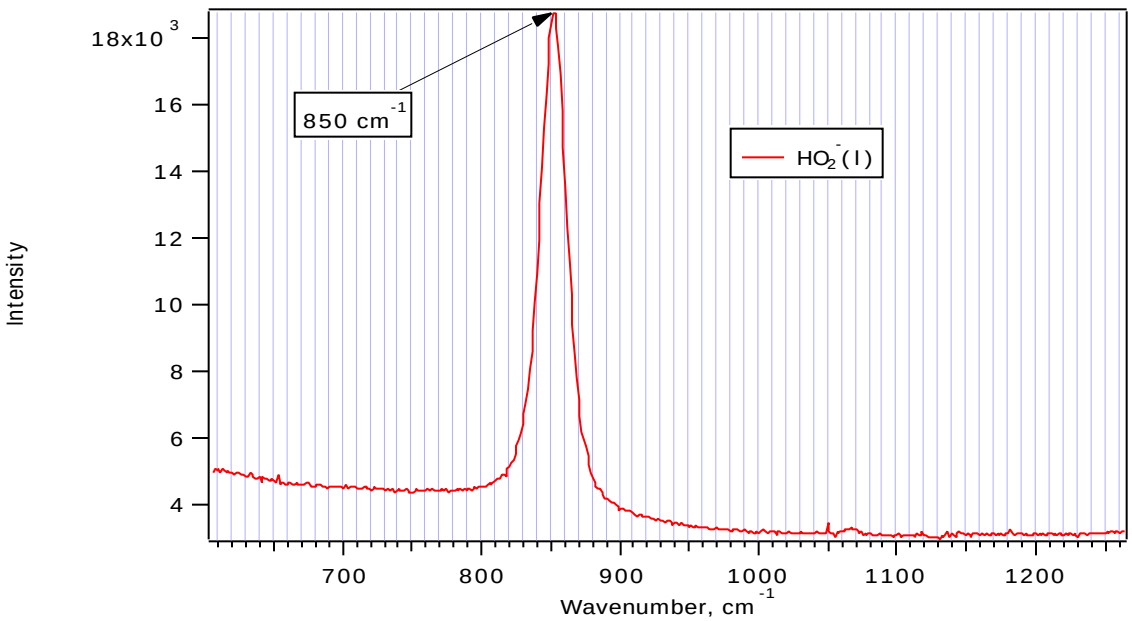


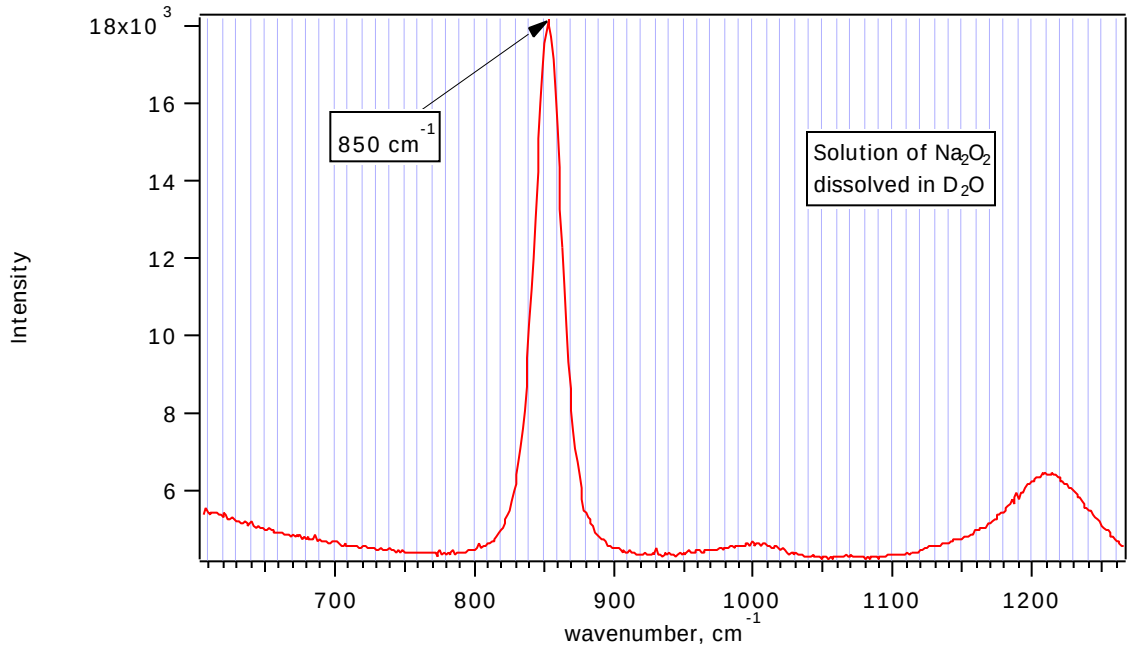
Raman spectra of sodium peroxide dissolved in H_2O and D_2O



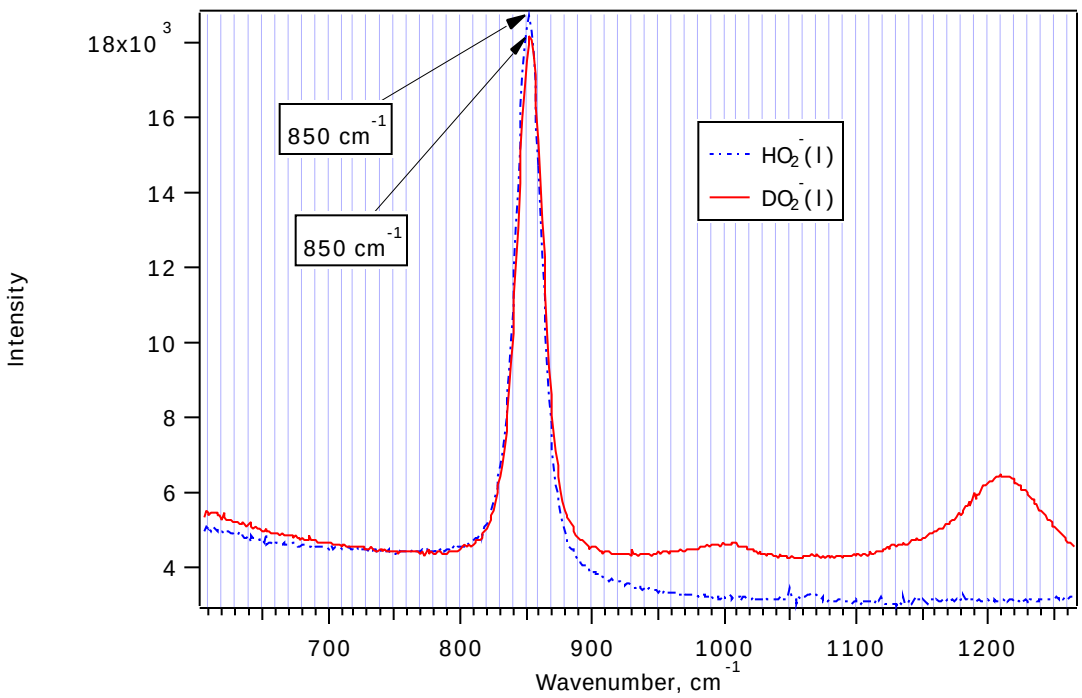


Raman Spectra of sodium peroxide dissolved in H_2O and D_2O

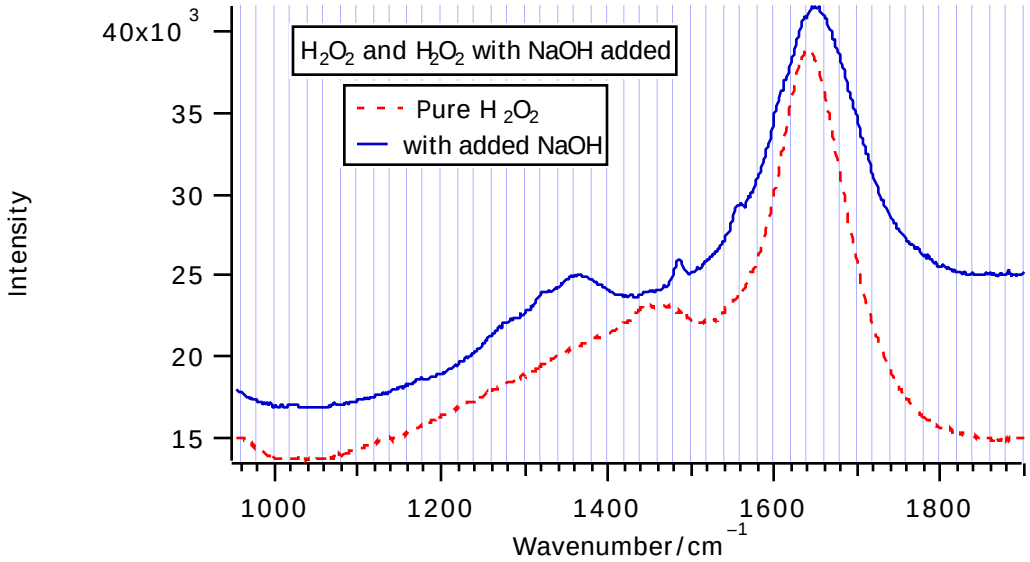




Raman Spectra of DO_2^-(aq) and HO_2^-(aq)

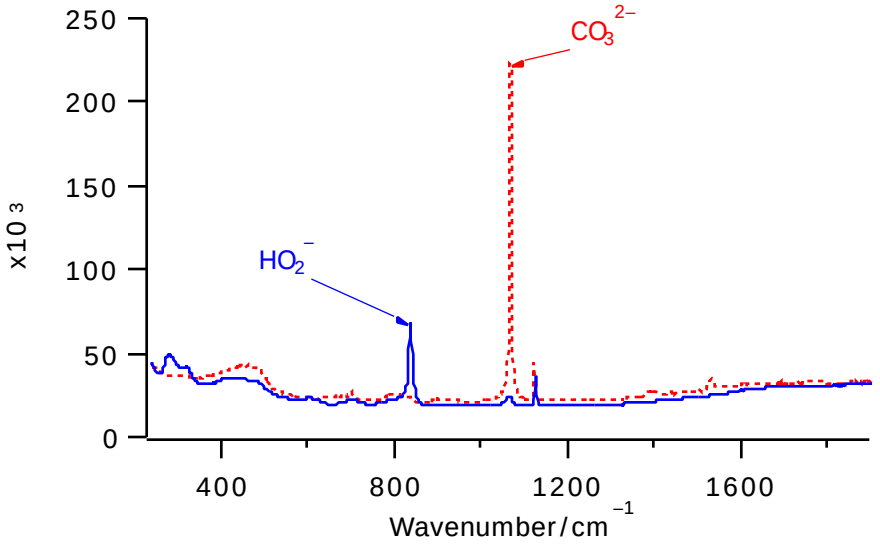


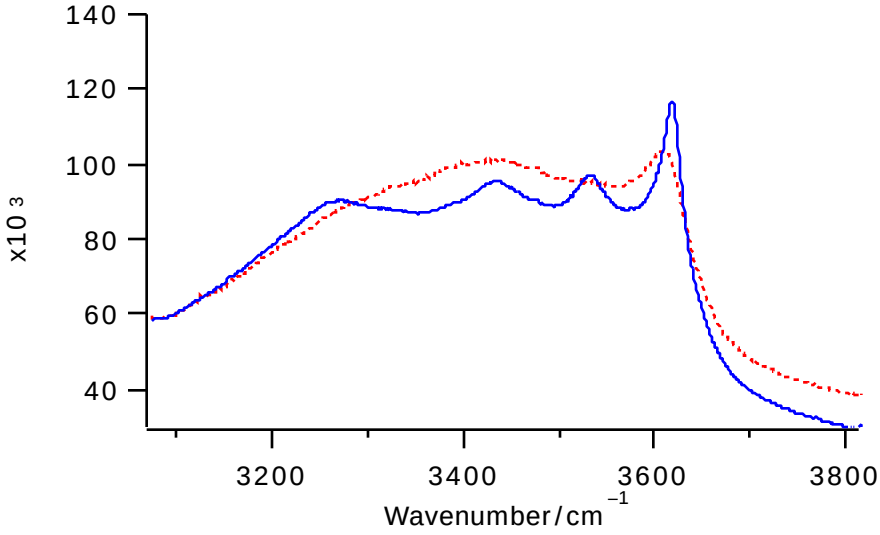
Both HO_2^- and DO_2^- have O-O stretch at 850 cm^{-1}



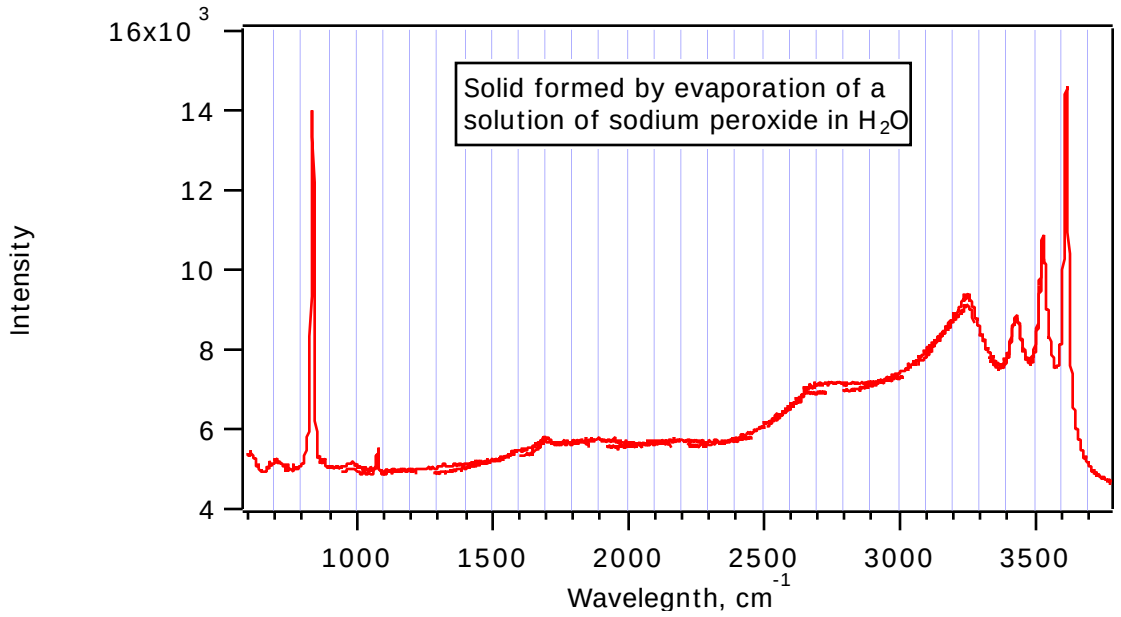
The HOO bend is at 1367 and DOO at 1000 cm^{-1}

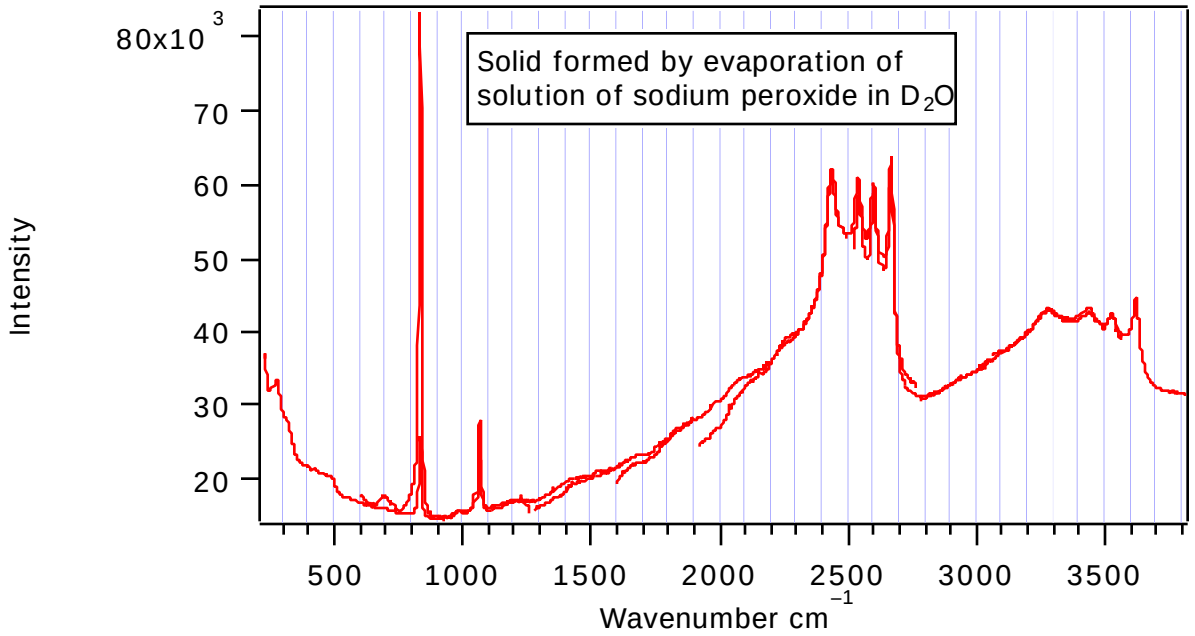
Spectra of Two Different Regions of Solid Precipitate from NaOH in H_2O_2



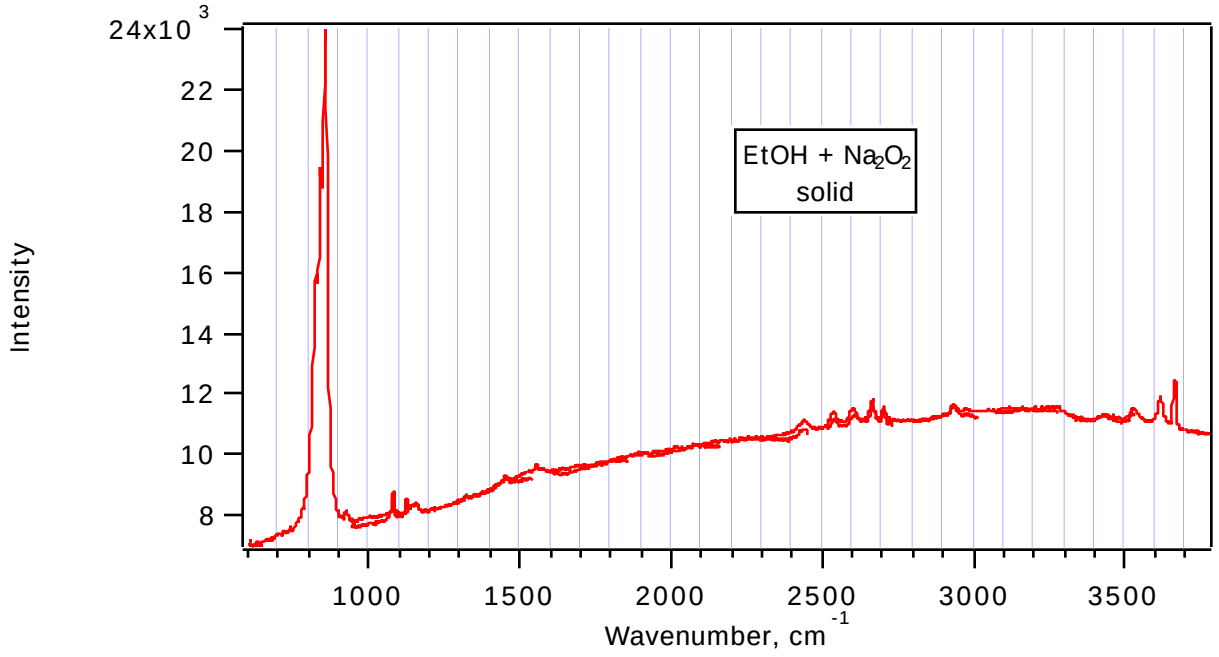


Raman spectra of solids formed by evaporation of solutions of Na_2O_2 in H_2O and D_2O



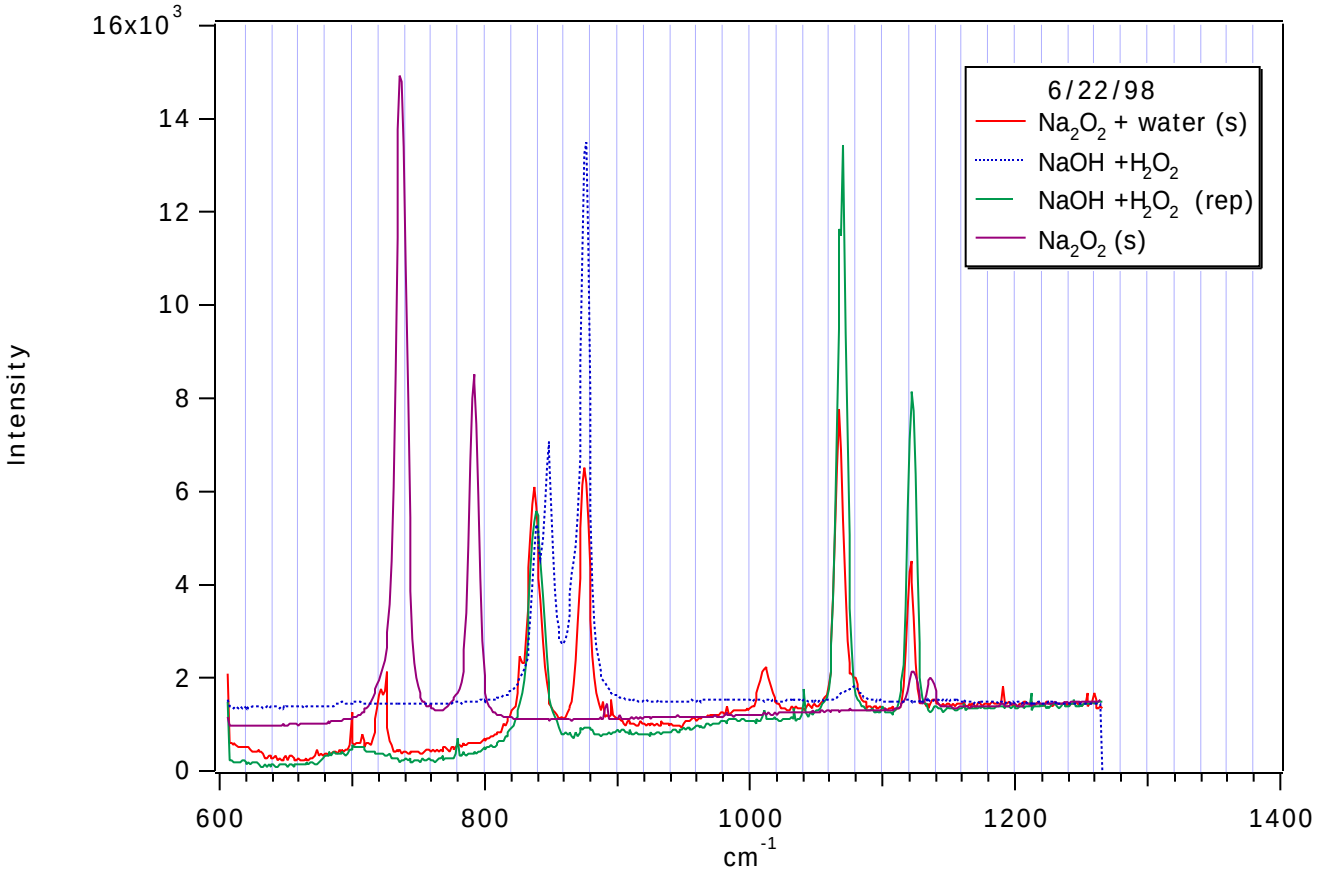


Solid formed from Ethanol

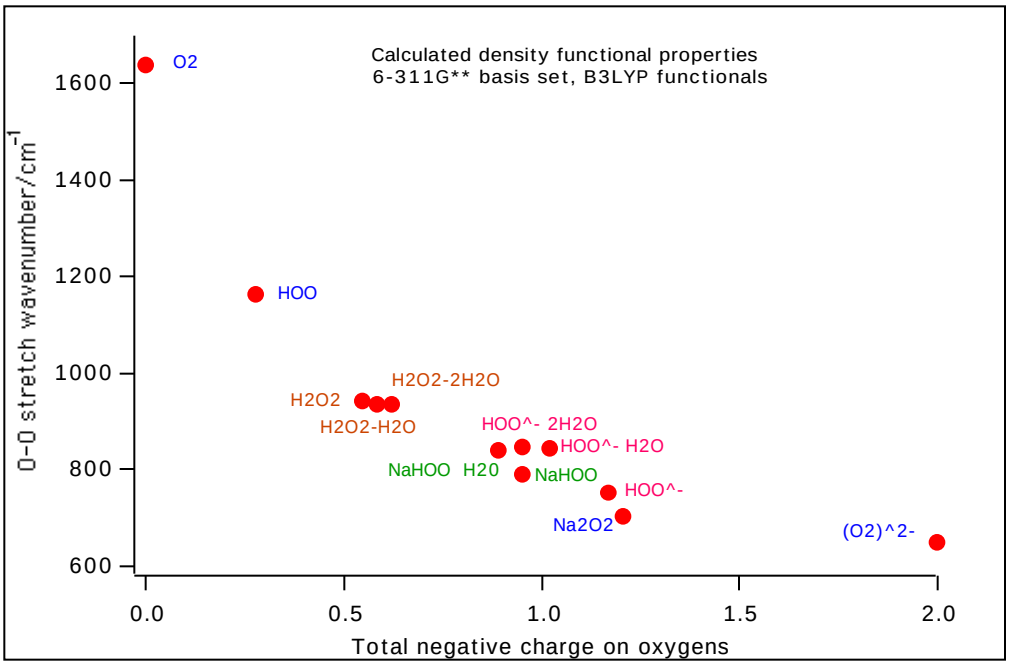


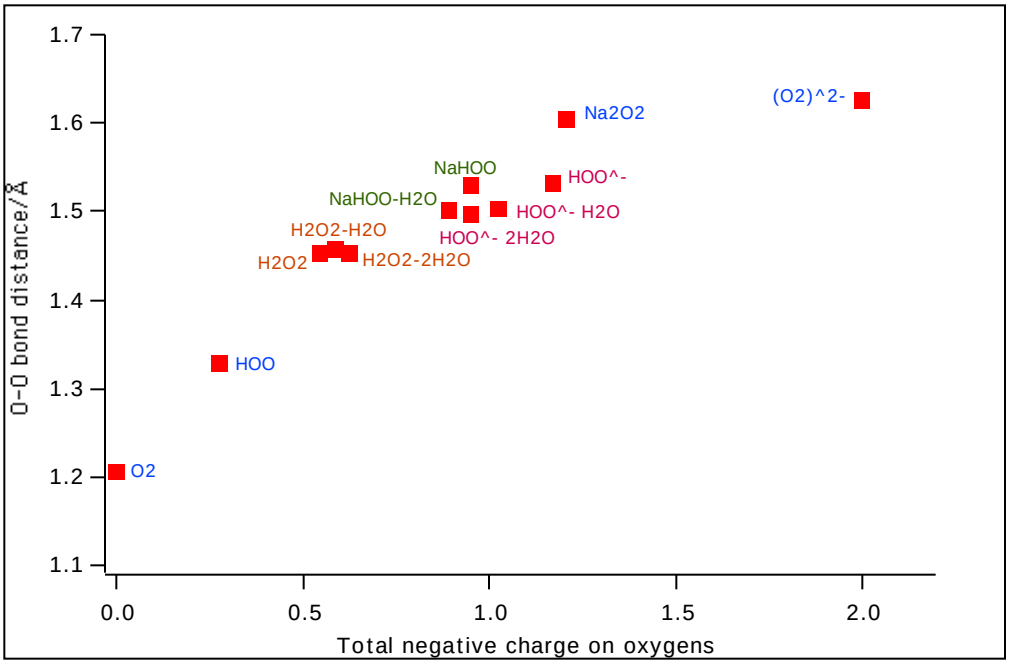
Sodium peroxide was added to ethanol and the solution was stirred at 4°C, causing a white solid to precipitate. The solution was then desiccated to remove any remaining ethanol.

Raman Spectra of Several Solids



Relation of Calculated Bond Distance and O-O Stretch to Charge on Oxygen Atoms





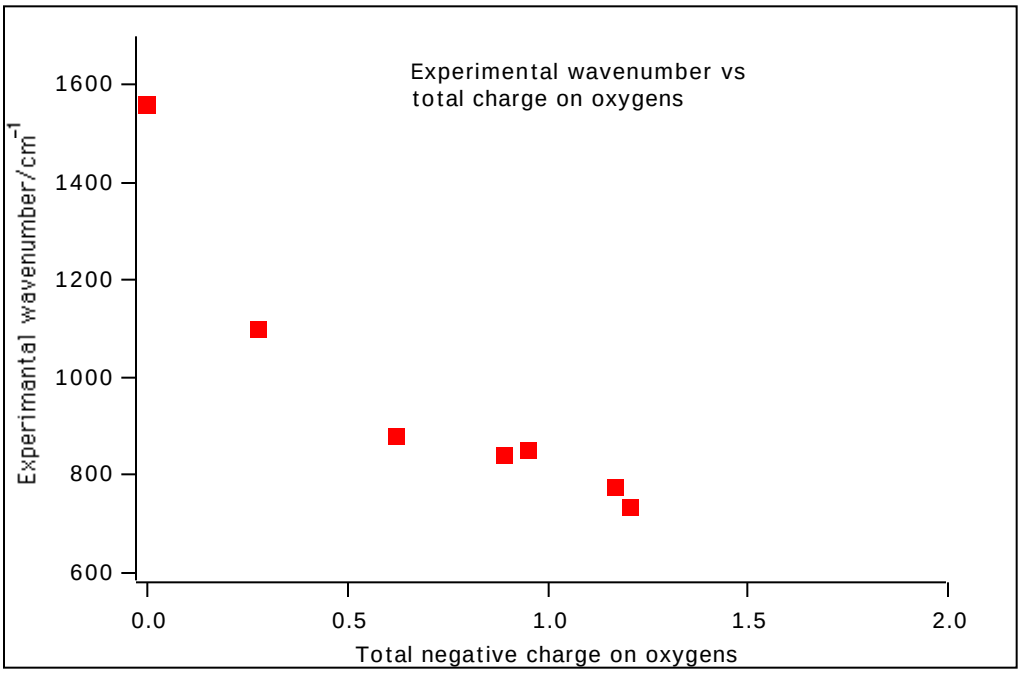
Observed Vibrations of HO_2^- and DO_2^- in Aqueous Solution

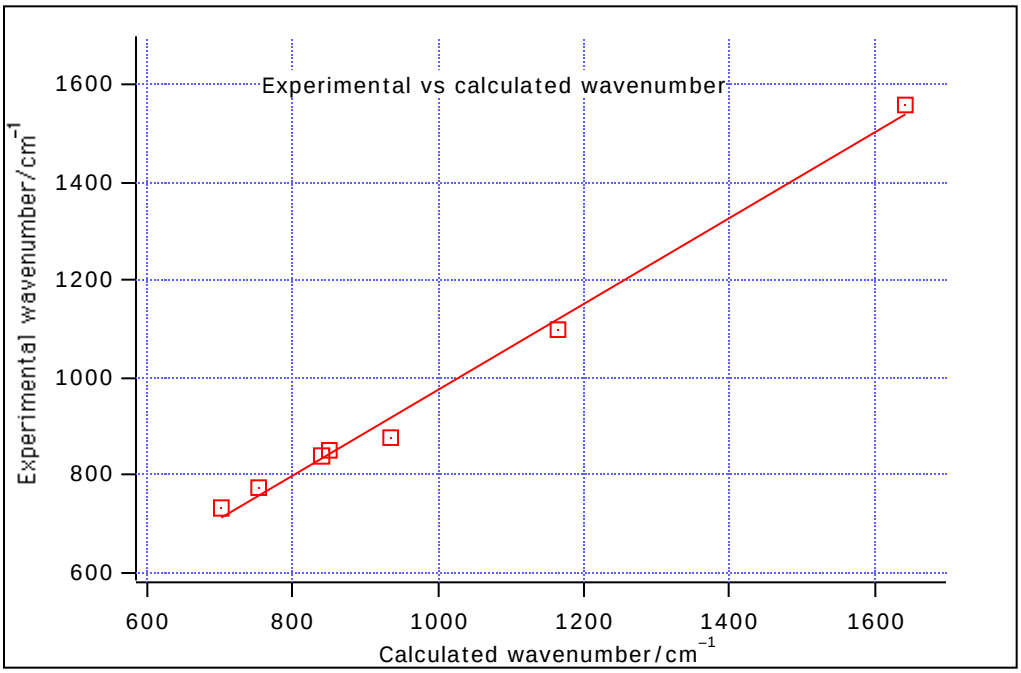
1. O-H stretching mode at 3620 cm^{-1}
   O-D stretching mode at 2670 cm^{-1}

2. H-O-O bending mode at 1367 cm^{-1}
   D-O-O bending mode at 1000 cm^{-1}

3. O-O stretching mode in HO_2^-
   at 850 cm^{-1}
   O-O stretching mode in DO_2^-
   at 850 cm^{-1}

Comparison of Experimental Wavenumber with Calculated Wavenumber for O-O Stretch





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

Calculated Properties for HO_2^-

HOO^-	Energy/ hartrees	Wave-number OO str(H)	Wave-number OO str(D)	Wave-number HOO bend	Wave-number DOO bend
DFT	-150.9514	754	710	1063	829
MP/2	-150.5816	826	747	1111	901
SCF	-150.1790	893	893	1269	934

H_2O Energy = -76.44745 (DFT)
HOO^- - H_2O ΔH = -30.7 kcal.mol for the first water

HOO^-. 1 H_2O	Energy/ hartrees	Wave-number OO str(H)	Wave-number OO str(D)	Wave-number HOO bend	Wave-number DOO bend
DFT	-227.4596	903	816	1182	900
MP/2	-226.8931	883	833	1210	948
SCF	-226.2633	983	981	1347	1000

HOO^- - 2 H_2O ΔH = –30.1 kcal/mol for the second water

HOO^-. 2 H_2O	Energy/ hartrees	Wave-number OO str(H)	Wave-number OO str(D)	Wave-number HOO bend	Wave-number DOO bend
DFT tight	-303.9432	851	849	1398	1007
MP/2	-303.2039	871	827	1213	939
SCF	-302.3489	973	972	1358	1001

Calculated Properties for H_2O_2

HOOH	Energy/ hartrees	Wave-number OO str(H)	Wave-number OO str(D)	Wave-number HOO bends	Wave-number DOO bends
DFT	-151.5918	943	895	1303 1456	814 1066
MP/2	-151.2313	945	941	1311 1468	966 1078
SCF	-150.8203	1166	1094	1480 1630	1157 1201

H_2O_2 - H_2O $\Delta H = -10.8$ kcal/mol for the first water

HOOH· 1 H_2O	Energy/ hartrees	Wave-number OO str(H)	Wave-number OO str(D)	Wave-number HOO bends	Wave-number DOO bends
DFT	-228.0565	935	932	1331 1552	982 1132
MP/2	-227.5114	939	933	1338 1550	989 1131
SCF	-226.8792	1159	1507 1687	1155	1113 1238

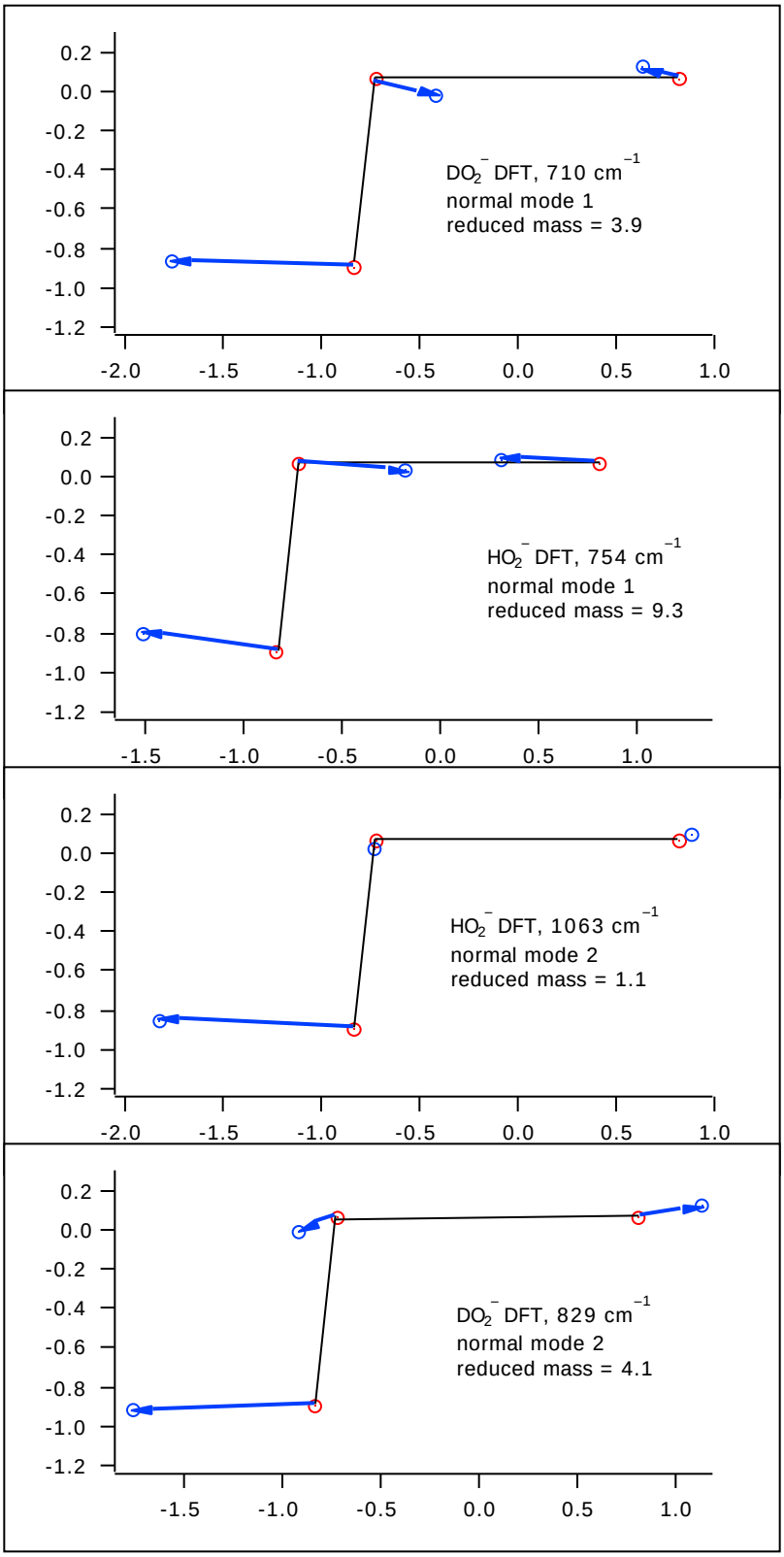
H_2O_2 - 2 H_2O $\Delta H = -14.7$ kcal/mol for the second water

HOOH· 2 H_2O	Energy/ hartrees	Wave-number OO str(H)	Wave-number OO str(D)	Wave-number HOO bends	Wave-number DOO bends
DFT	-304.5274	936	938	1334 1575	984 1146

Experimental Wavenumbers for HO_2^- and Related Species

	O-O stretch	O-O stretch	H-OO bend	H-O stretch	H-O stretch	H-O stretch	H-O stretch
HO_2^- (aq)	850		1367				3620
DO_2^- (aq)	850		1000				2670
HO_2^- (s) water	838			3250	3430	3528	3619
DO_2^- (s) water	840		990	2439	2537	2604	2667
HO_2^- (s) ethanol	855	841 825	1151 1450	3268	3435	3535	3620 3668
H_2O_2 (aq)	876		1457			3335	3525
Na_2O_2 (s)	735	792					
NaOH (s)							3631

Calculated displacements for normal modes of HOO^-



Calculated electrical charge, bond length, and Vibrational wavenumber for O-O species

	Calculated Charge on Oxygens	O-O Distance /Ångstrom	Calculated OO Stretch Wavenumber /cm^{-1}	Experimental O-O Stretch Wavenumber /cm^{-1}
O_2	0.0/0.0	1.2056	1641	1558(g)
$HO_2\cdot$	-0.135/-0.143	1.3280	1163	1098 (g)
$DO_2\cdot$			1179	1121(g)
H_2O_2	-0.274/-0.274	1.4536	943	864(g)
D_2O_2			895	867(g)
$H_2O_2\cdot H_2O$	-0.304/-0.280	1.4563	936	
$D_2O_2\cdot D_2O$			932	
$H_2O_2\cdot 2H_2O$	-0.292/-0.321	1.4528	935	876 (aq)
HO_2^-	-0.464/-0.706	1.5323	754	775 (g)
DO_2^-			710/829 mix with bend	
$HO_2^-\cdot H_2O$	-0.393/-0.630	1.5024	842	
$DO_2^-\cdot D_2O$			816	
$HO_2^-\cdot 2\ H_2O$	-0.381/-0.569	1.4964	851	850 (aq)
$DO_2^-\cdot 2\ D_2O$			849	850 (aq)
$Na^+\ HO_2^-$	-0.409/-0.527	1.5276	791	
$Na^+\ DO_2^-$			776	
Na^+ $HO_2^-\cdot H_2O$	-0.379/-0.515	1.4999	839	838 (s)
Na^+ $DO_2^-\cdot D_2O$			835	840(s)
Na_2O_2	-0.604/-0.604	1.6035	701	735/792 (s)
O_2^{2-}	-1.0/-1.0	1.6257	651	

Summary

- The conjugate base of hydrogen peroxide, HO_2^-, can be readily observed in aqueous solution by Raman spectroscopy.
- In aqueous solution the O-O stretch occurs at 850 cm^{-1} for both HO_2^- and DO_2^-.
- *Ab initio* calculations using density functional methods provide useful insight into the vibrational modes of HO_2^-.
- The O-O stretch and D-OO bend are strongly mixed for the free DO_2^- species.
- Water is strongly bound to HO_2^- through hydrogen bonding.
- When two waters are bound to HO_2^-, the mixing of stretching and bending modes is reduced so that the calculated O-O stretch shows no change on substitution of D for H.
- The O-O stretch wavenumber is related to the magnitude of negative charge on the oxygen atoms.

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 have worked on the project each summer since 1997.

Acknowledgment of people and agencies that have contributed to this project

- Camille and Henry Dreyfus Foundation for financial support for purchase of a Raman spectrometer
- DOE EMSP program for generous project support: Grant # 54828
- Los Alamos National Laboratory staff members: Steve Buelow, Bernie Foy
- Furman University for sustaining support