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QUANTIFICATION OF HYDROXIDE IN AQUEOUS SOLUTIONS
BY RAMAN SPECTROSCOPY

Carl D. Shaffer

U. S. Department of Energy Contract DE-AC11-93PN38195

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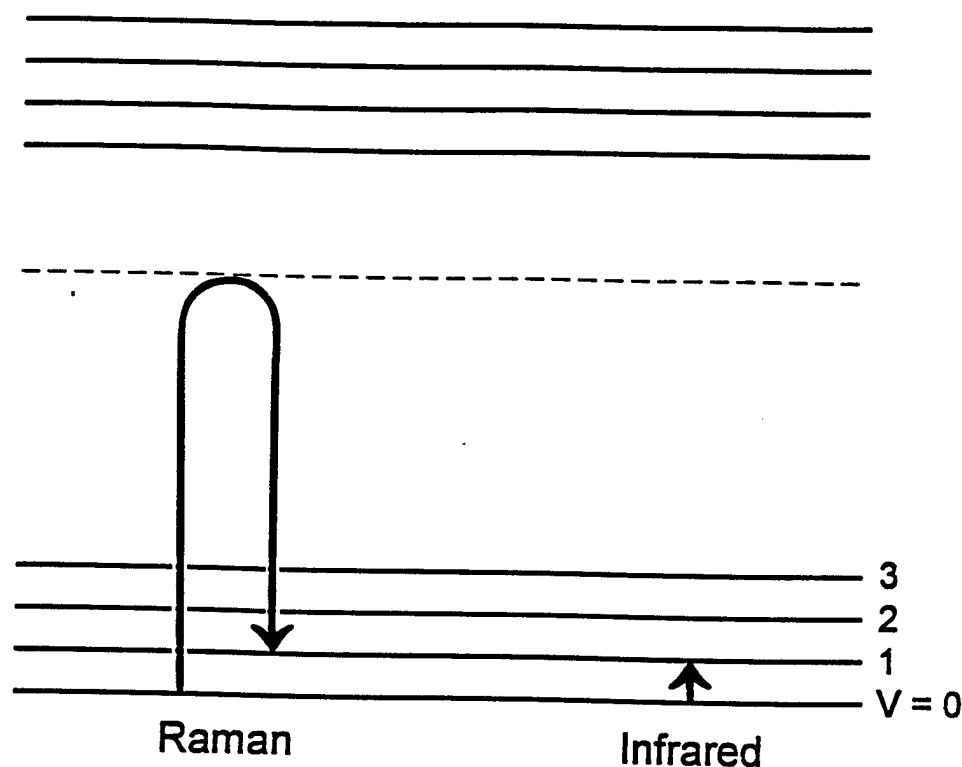
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DETAILED OUTLINE

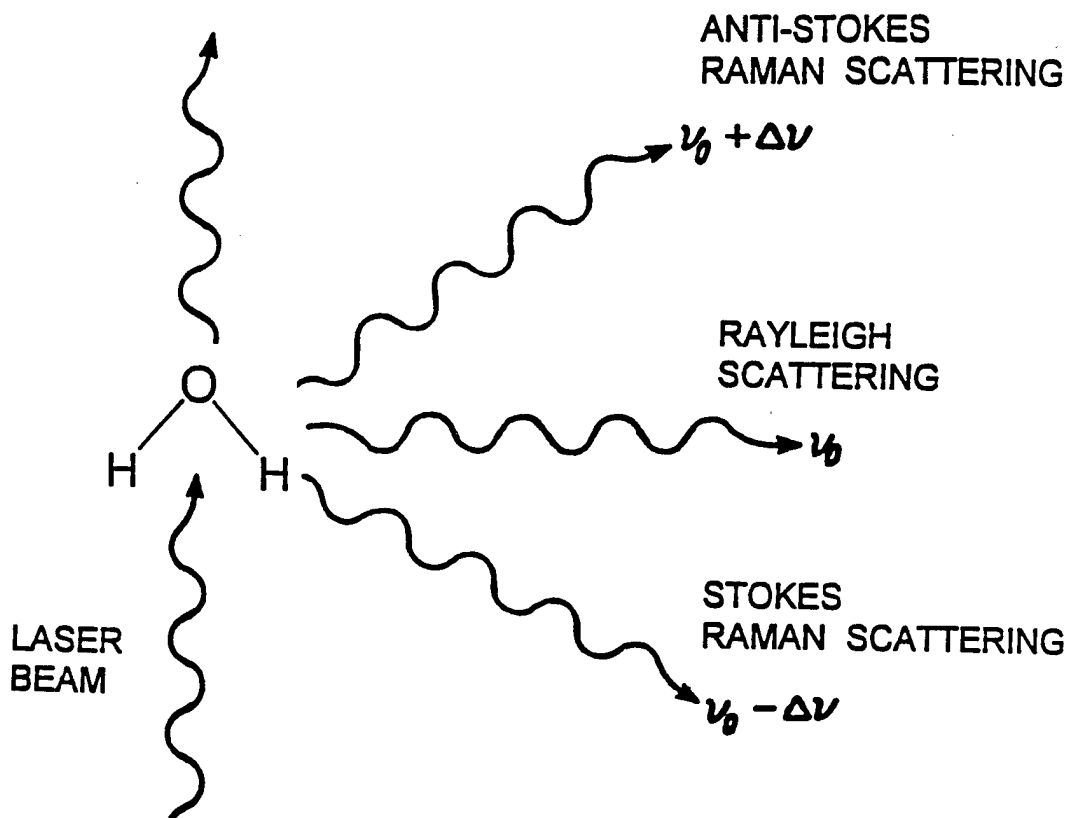
Introductory Comments

The following outline provides the details of the presentation on The Quantification of Hydroxide in Aqueous Solutions by Raman Spectroscopy at the Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy. This conference is being held in New Orleans, LA during March 1 - 6, 1998. The abstract for this presentation was approved on 7/11/97 and is included as an attachment. The presentation is strictly an oral presentation, while the abstract will be published in a book of abstracts by the conference. The abstract that was previously approved by Naval Reactors on 7/11/97 is provided as an attachment. Each of the following pages consists of the slides to be shown at the conference. Comments about what will be verbally presented about each slide are included on the same page. The typed comments will not be included on the slides to be given at the conference.



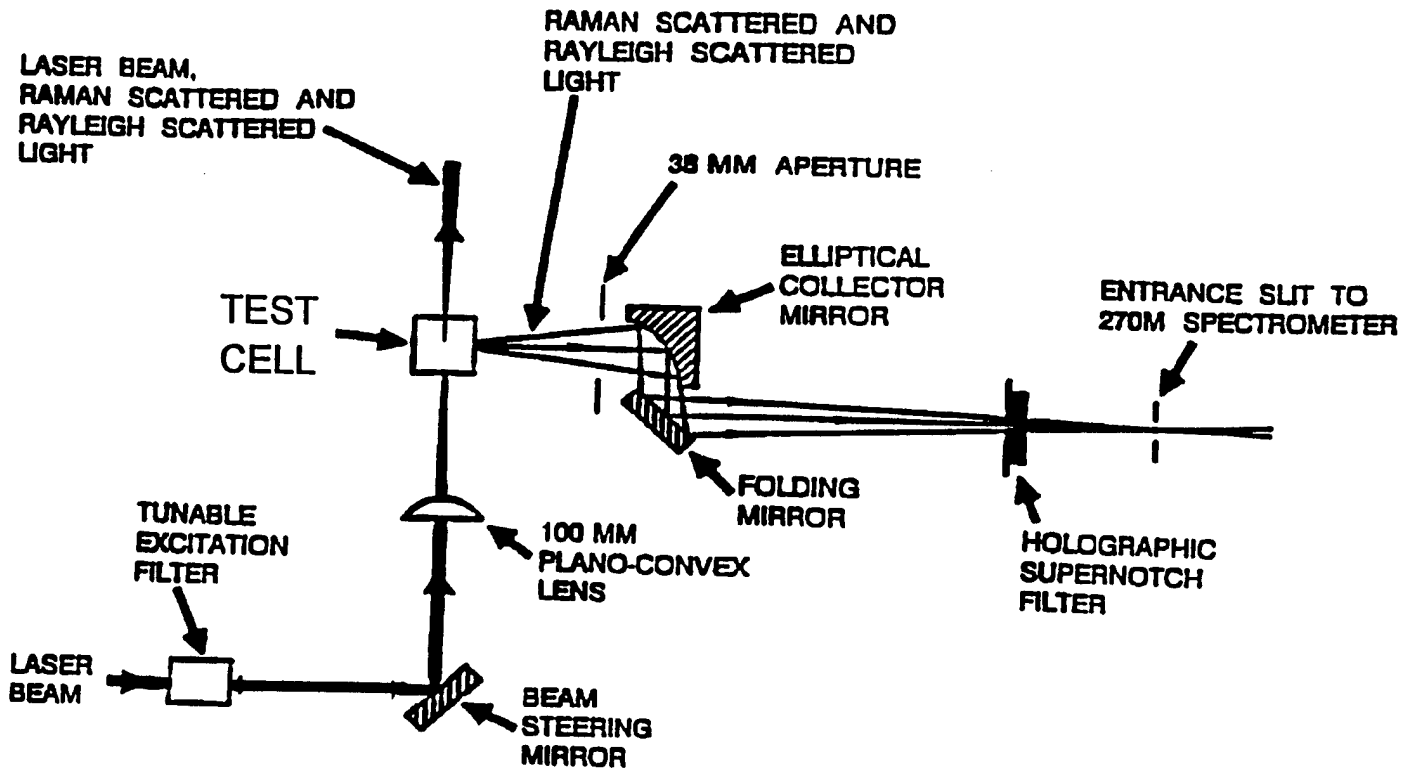
Slide 1

Since Raman spectroscopy is not as widely used as infrared spectroscopy (IR), this slide provides a comparison of Raman and infrared spectroscopy. Although both are based on exciting vibrational modes of molecules, Raman spectroscopy is a scattering effect while IR is based on the absorption of infrared radiation. Since visible light is scattered in the Raman effect, Raman spectroscopy is more suited for the analysis of aqueous solutions than IR due to the very strong absorption of infrared radiation by water.



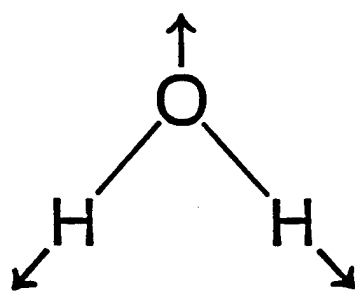
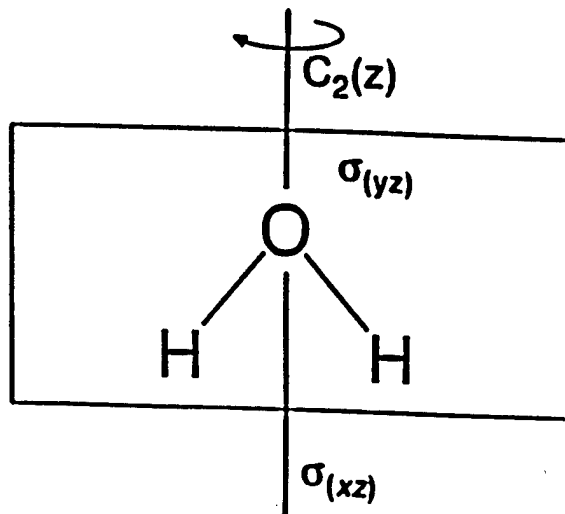
Slide 2

This slide presents a diagrammatic representation of the three types of light scattering that is of concern to this presentation. The Stokes Raman scattered light, which contains the vibration information, is the energy that will be measured. The anti-Stokes Raman scattering is of no consequence due to its energy being out of the detector range. The Rayleigh scattered light has to be filtered since it is so intense that it will mask the Stokes Raman light.

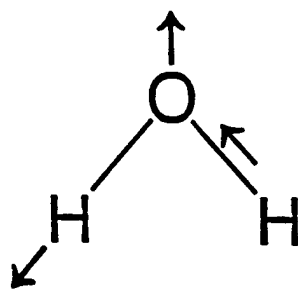


Slide 3

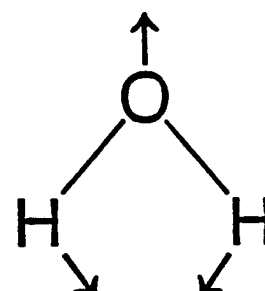
This slide illustrates the optical train that was used to collect the Raman scattered light for the measurement. This includes a tunable excitation filter to scrub the laser beam of spikes, beam steering mirrors to direct the laser beam, a plano-convex lens to focus the laser beam in the sample, a quartz test cell to hold the sample, an elliptical mirror and folding mirror to collect and direct Raman scattered light to the spectrometer, and a holographic supernotch filter to remove the Rayleigh scattered light. This type of optical train is commonly used in Raman spectroscopy.



SYMMETRIC



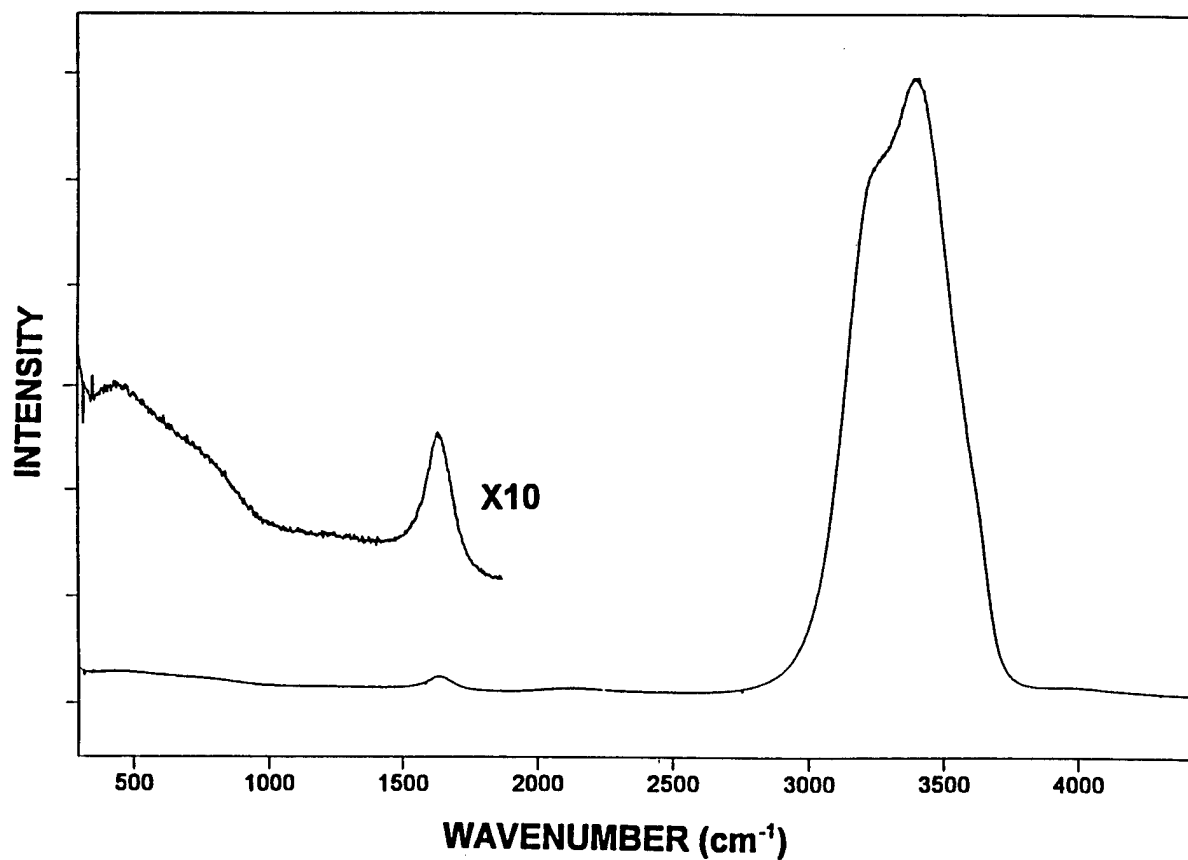
ANTISYMMETRIC



DEFORMATION

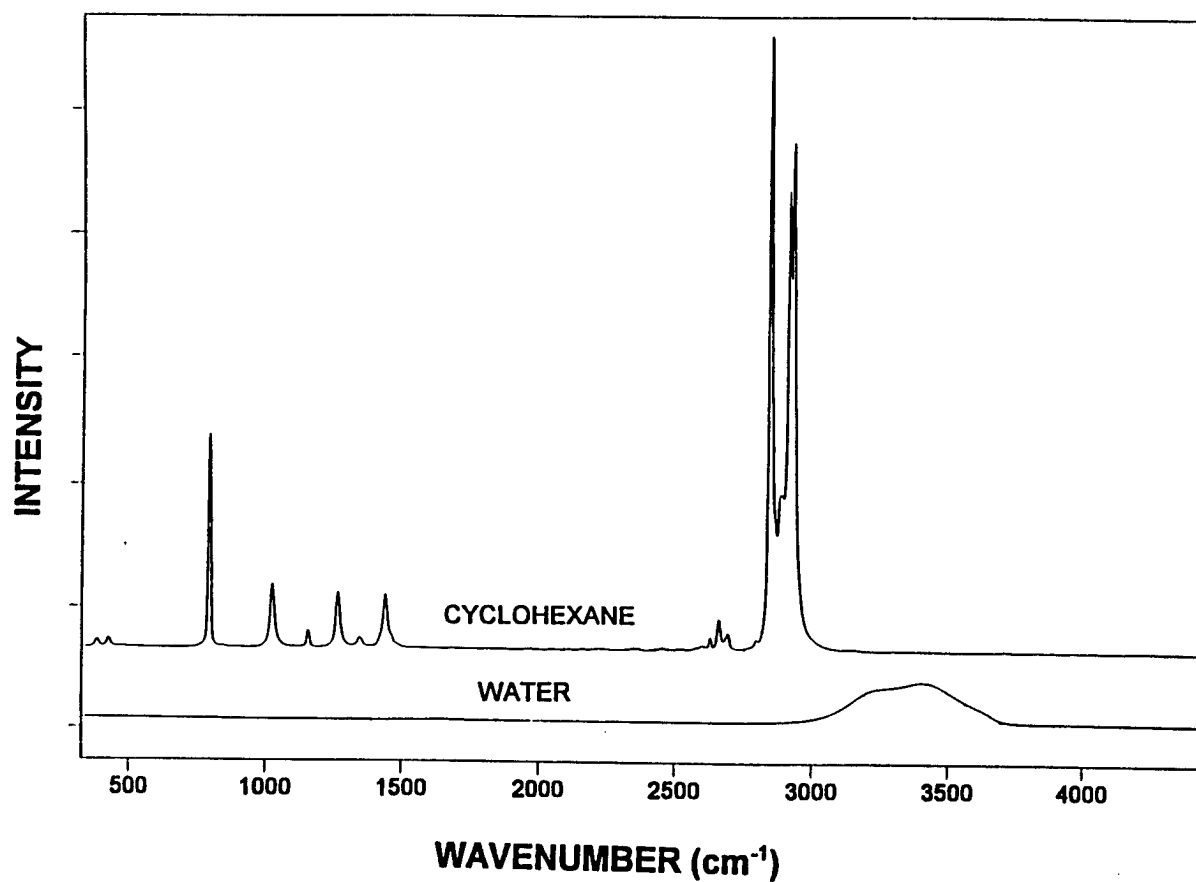
Slide 4

This slides illustrates the symmetry elements for water taken from group theory . This is used to predict the vibrations that are expected to be observed during the Raman analysis. The fact that there are only three vibrations predicted implies that the Raman spectrum of water should be rather simple.



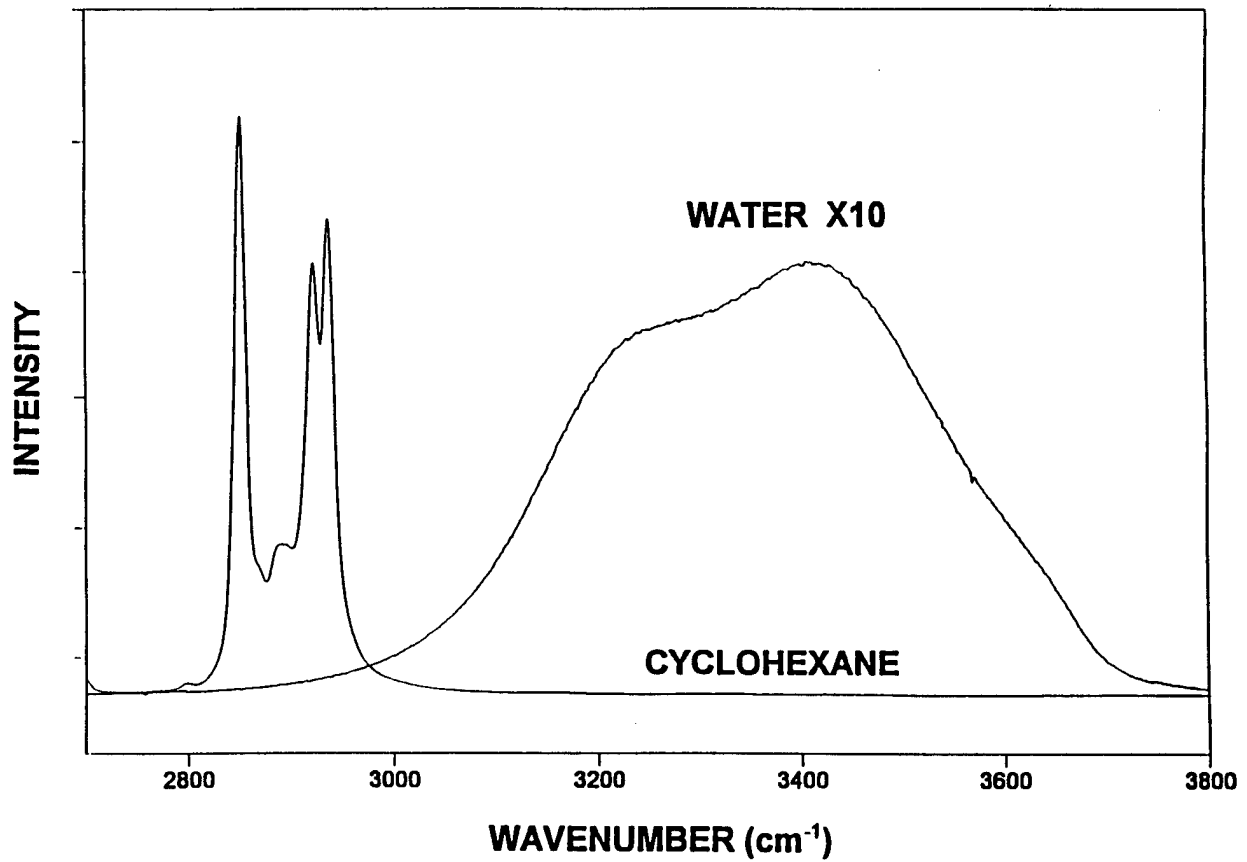
Slide 5

Slide 5 presents the Raman spectrum of water. Although the spectrum will be related to the vibrations that were presented in the previous slide, the important feature of this spectrum is the very wide peak that occurs at approximately 3400 cm⁻¹.



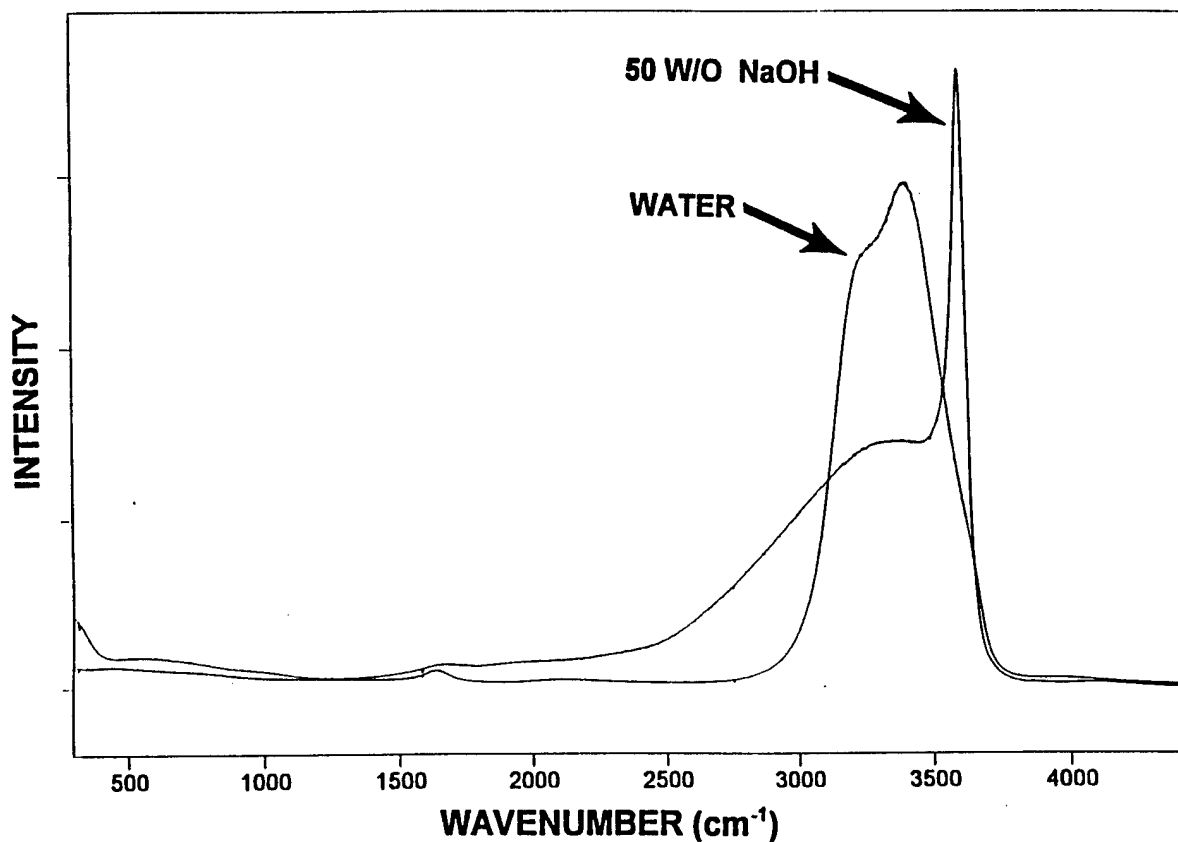
Slide 6

This slide compares the Raman spectrum of cyclohexane, a typical organic solvent, with that of water to help illustrate the unique spectrum of water.



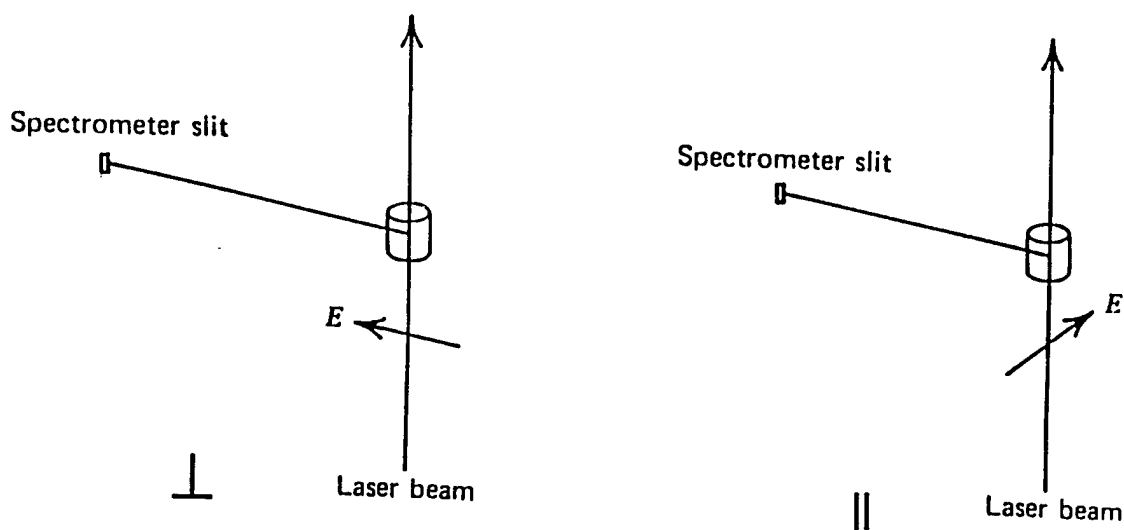
Slide 7

This slide is an enhancement of the 2700 - 3800 cm⁻¹ region. This dramatizes how the water peak is unusually wide and that the asymmetric nature of the peak indicates that it consists of more than one component.



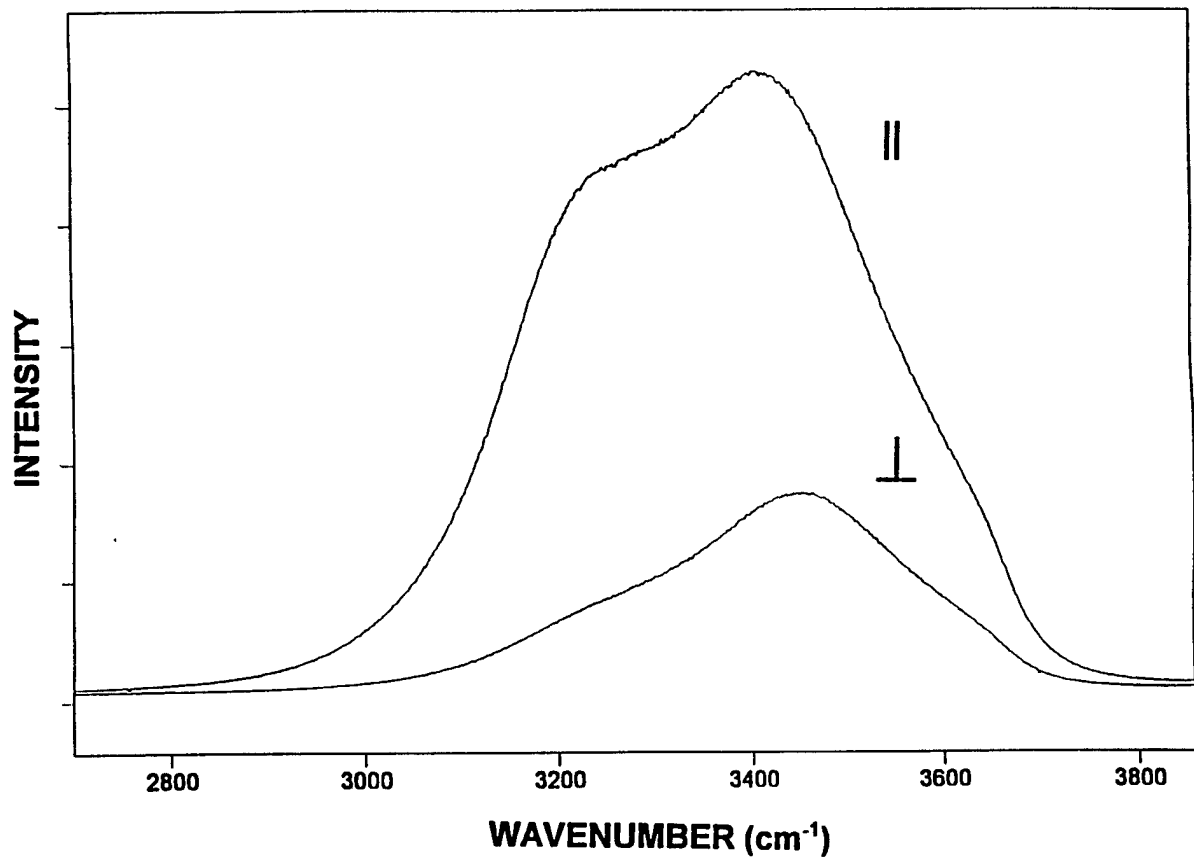
Slide 8

This slide introduces the influence on the Raman spectrum of adding hydroxide to water. A sharp peak occurs at approximately 3600 cm⁻¹ due to the hydroxide. The hydroxide peak overlaps with the water peak. In addition, the water peak becomes significantly broader in the lower wavenumber region.



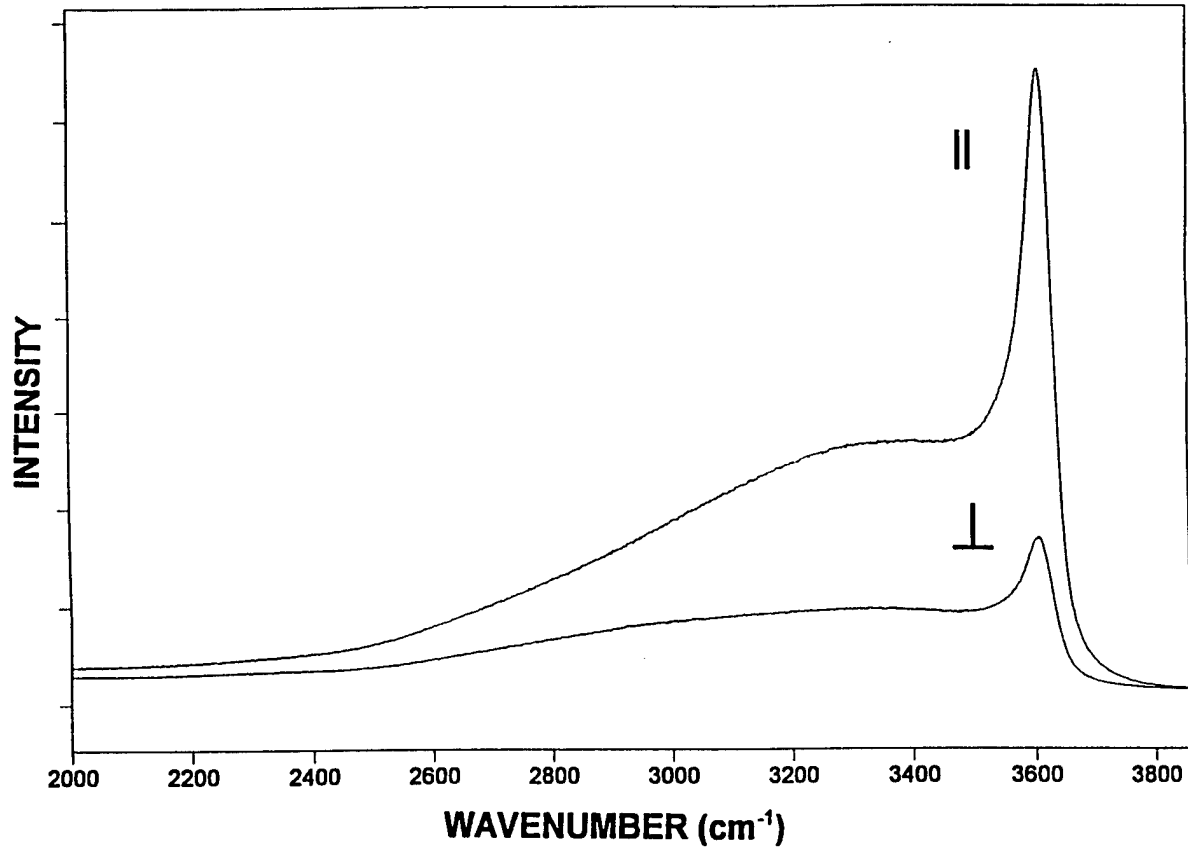
Slide 9

This slide illustrates how the direction of the polarization of the laser beam was changed to allow the investigation of the nature of the laser beam polarization on the water and hydroxide peak profiles. This change in configuration was tried to determine if the resolution between the hydroxide and water peak could be improved.



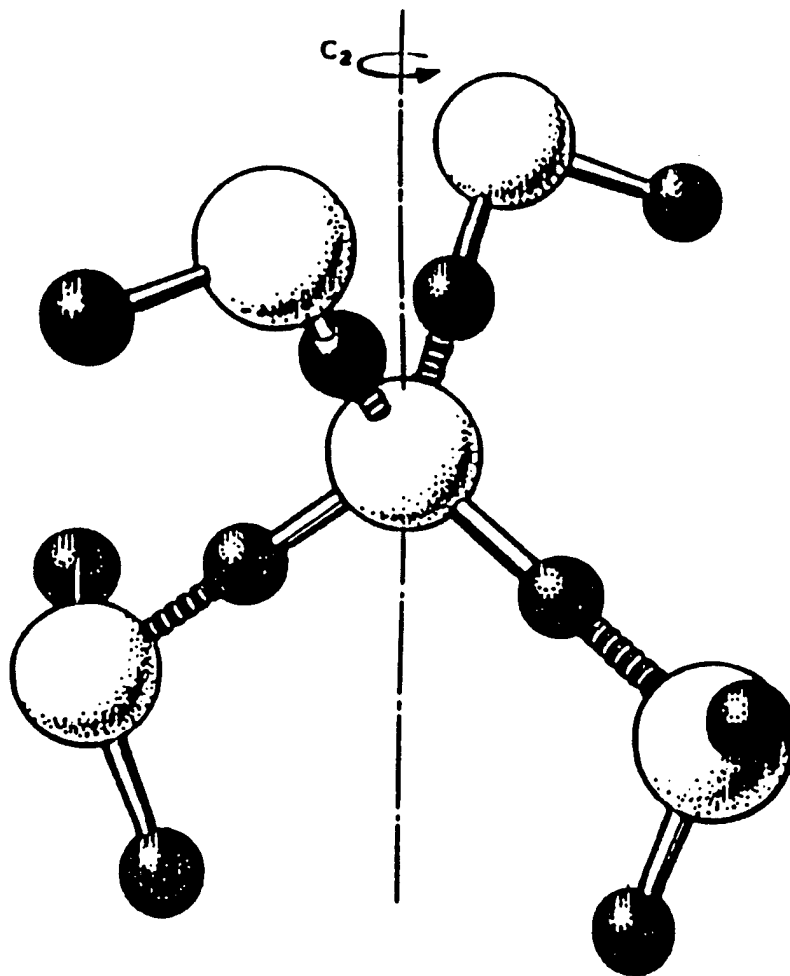
Slide 10

This slide illustrates the effect of changing the direction of polarization of the laser beam on the Raman spectrum of water.



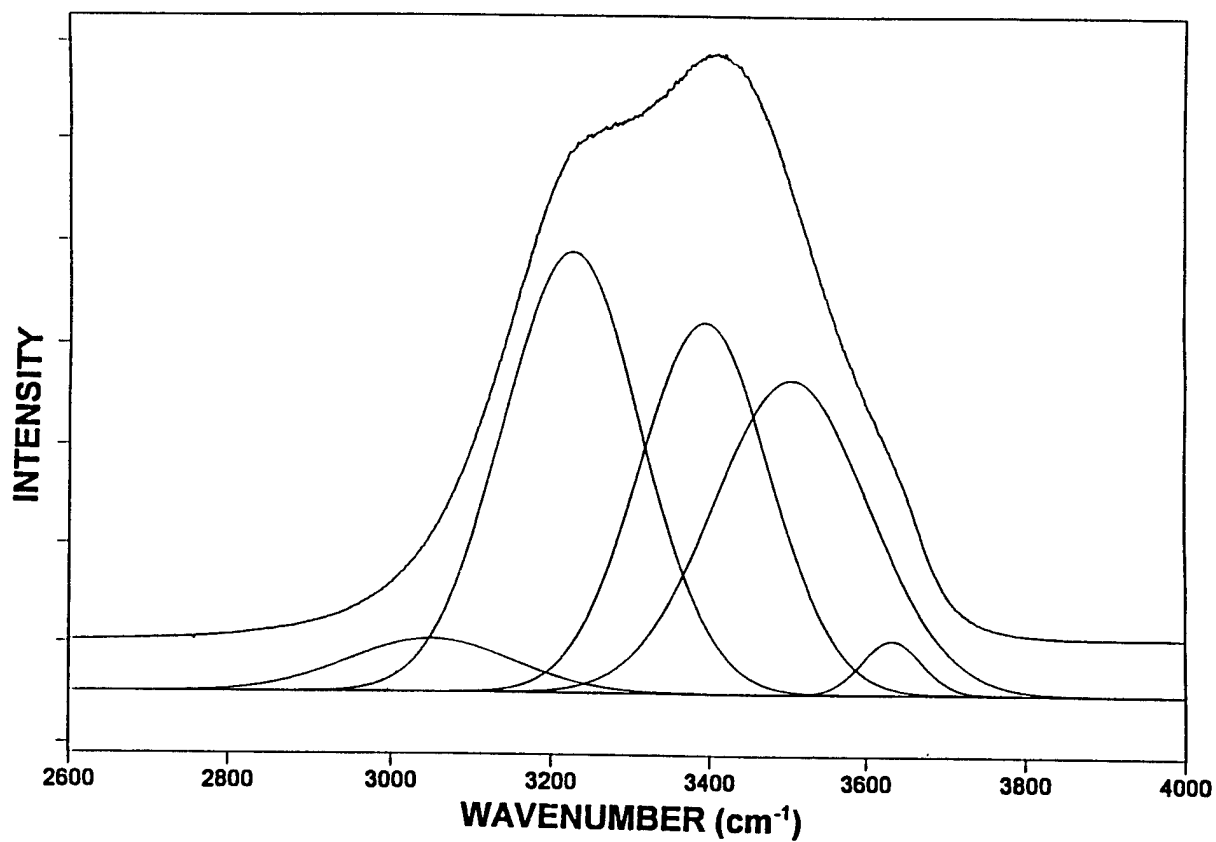
Slide 11

This slide illustrates the effect of changing the direction of polarization of the laser beam on the spectrum of 50 w/o sodium hydroxide. The conclusion of the study was that changing the polarization of the laser beam from the normal parallel orientation did not provide any benefit.



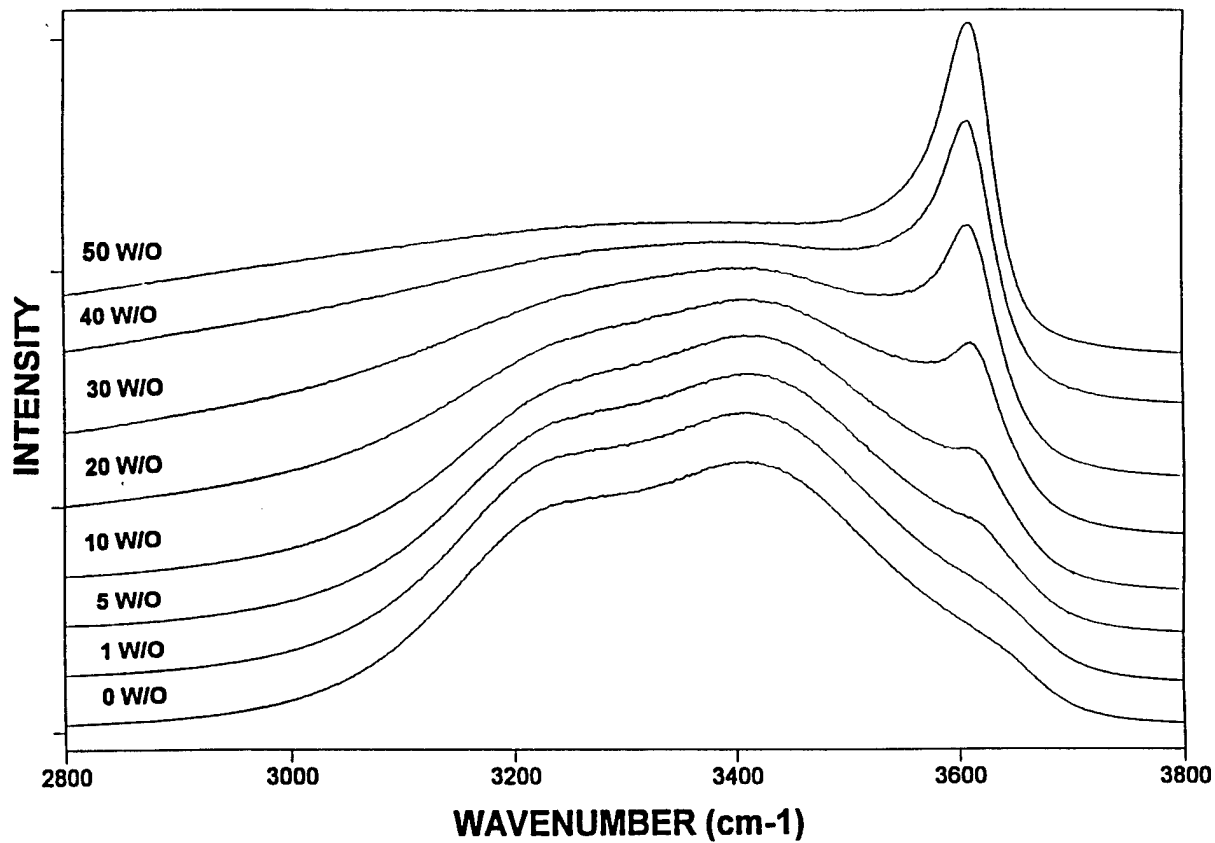
Slide 12

This slide illustrates a model of the water structure that is believed to be the cause of the unusual Raman spectrum obtained for water. This model consists of a central water molecule that is hydrogen bonded to four surrounding water molecules. Based on this structure, it is postulated that water peak at 3400 cm^{-1} is due to five vibrational components.



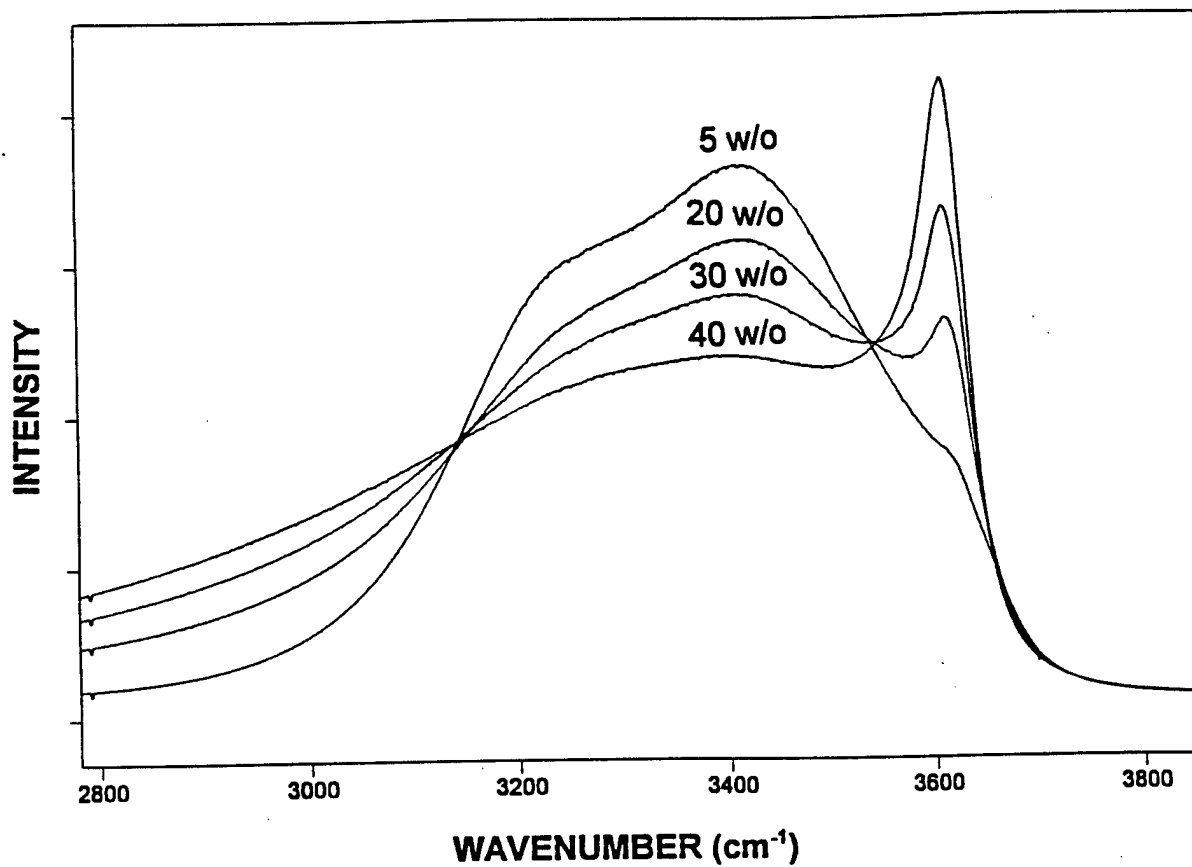
Slide 13

This slide illustrates the five gaussian peaks that were used to curve fit the water peak based on the model provided in the previous slide.



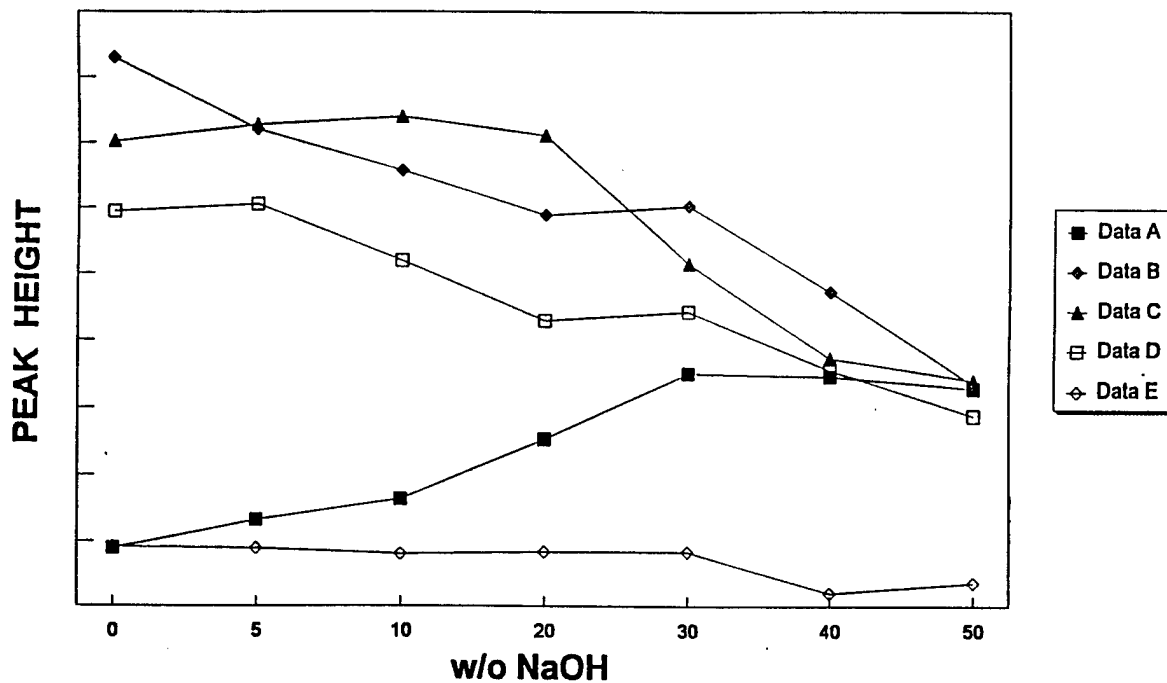
Slide 14

This slide illustrates the change in the profile of the water - hydroxide peak with changing hydroxide concentration.



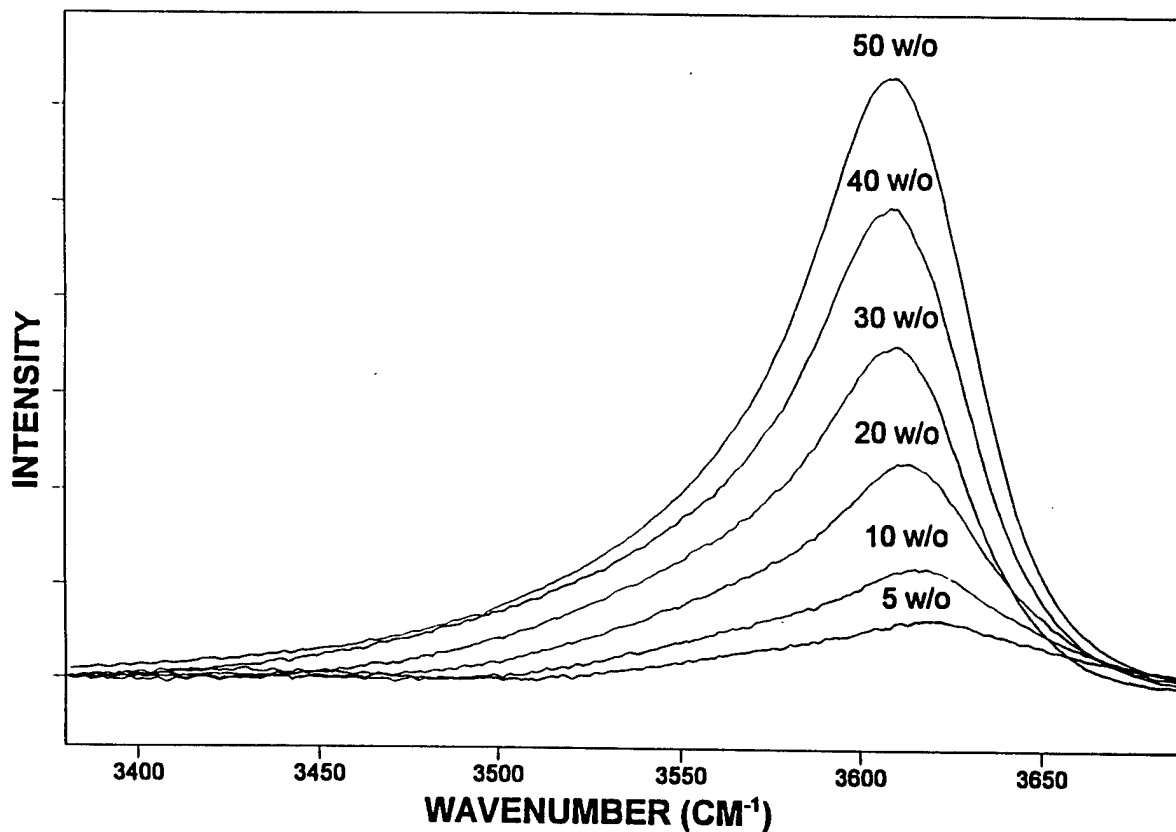
Slide 15

This slide illustrates the change in the profile of the water - hydroxide peak with changing hydroxide concentration in the 40 to 5 weight percent concentration range. The isobestic points imply that there is an equilibrium of species in this concentration region.



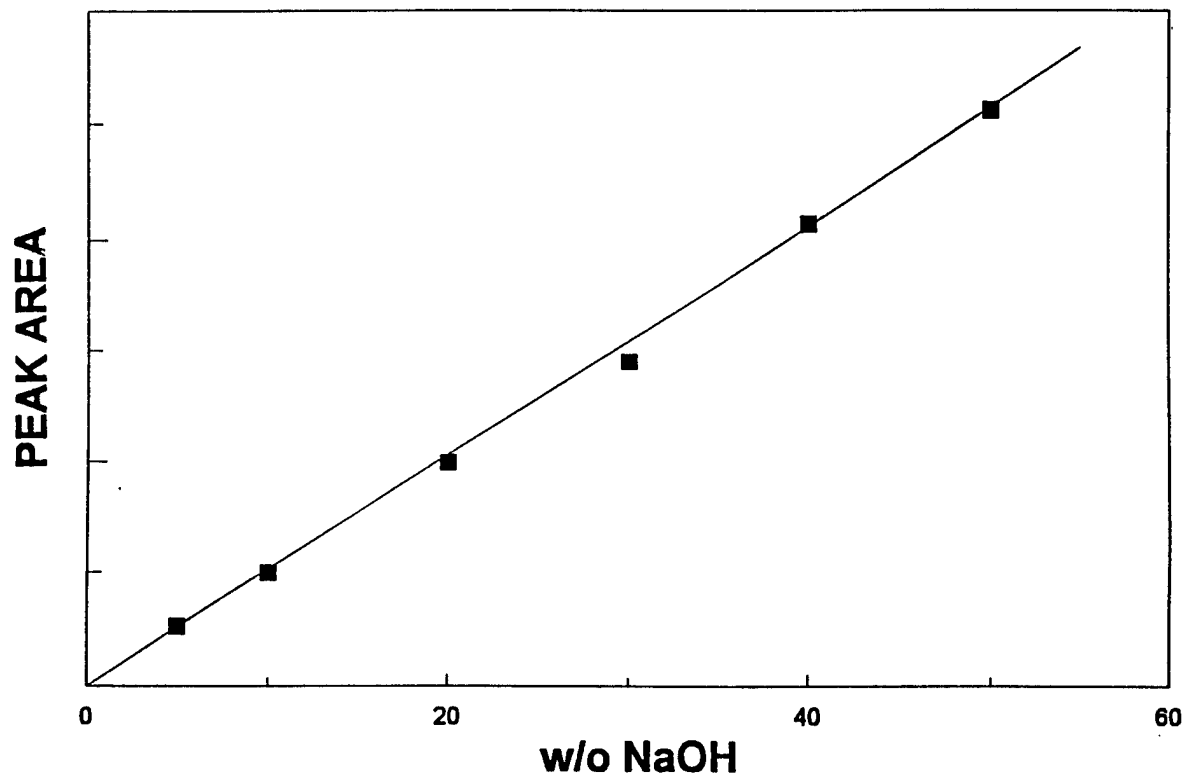
Slide 16

This slide provides the results of curve fitting the water - hydroxide peak with five gaussian peaks. This was accomplished by holding all the parameters at the values required to fit the water peak except the height of the peak. This figure shows the variation of the height of the five peaks with concentration of hydroxide.



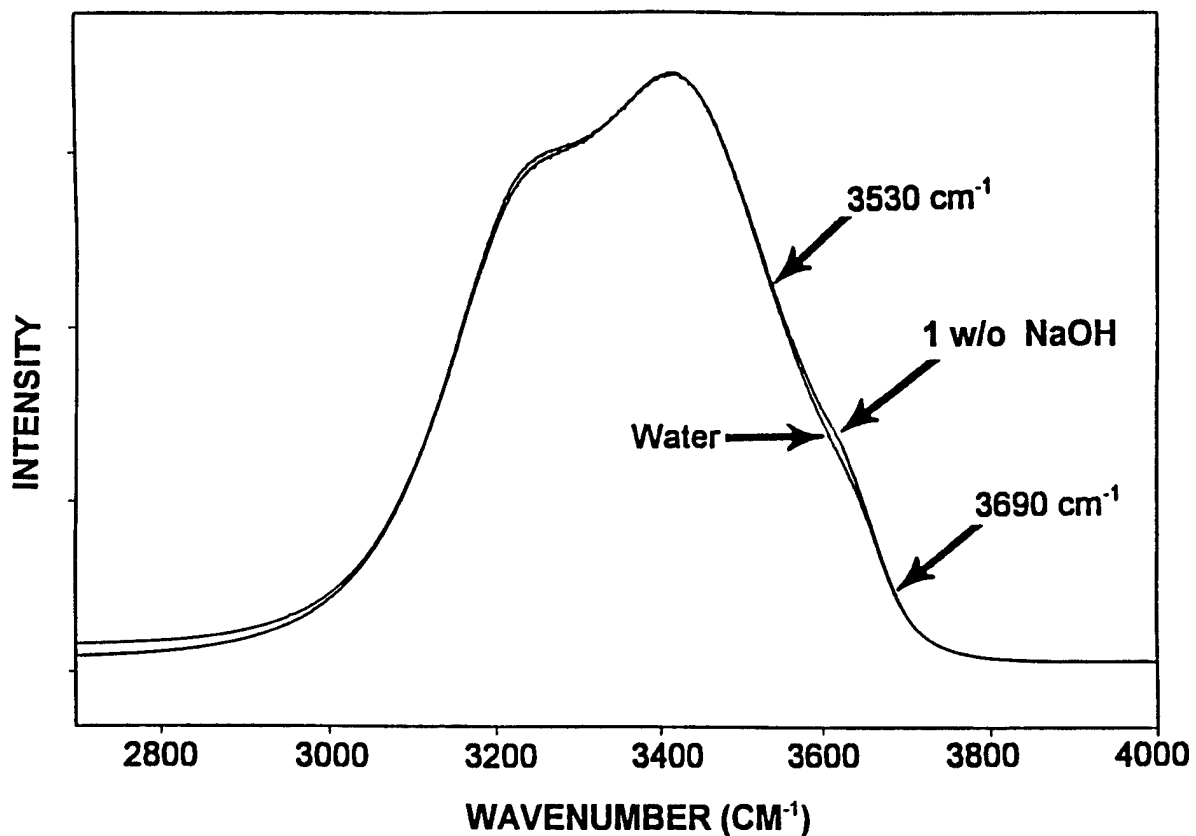
Slide 17

This slide illustrates the hydroxide peaks that were extracted from the water - hydroxide peak during the curve fitting procedure. The asymmetric nature of the peaks are similar to the peaks found for inorganic hydroxide compounds.



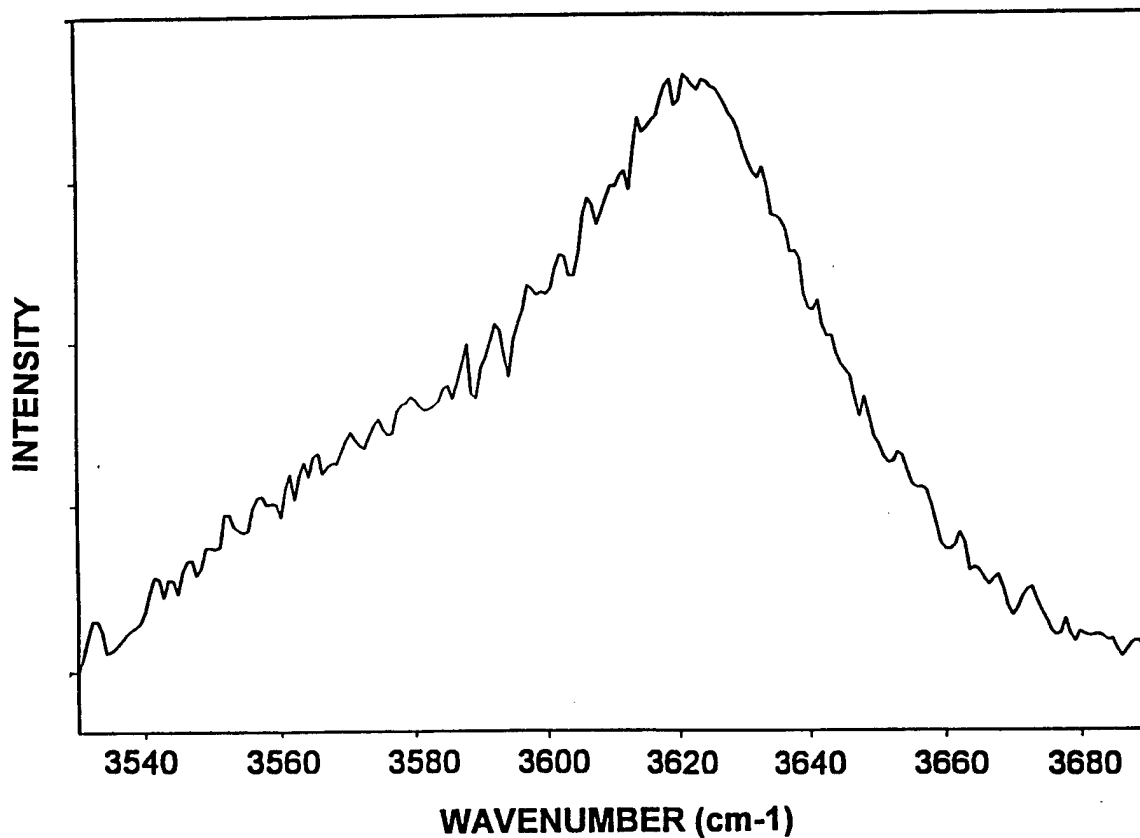
Slide 18

This slide illustrates the calibration curve obtained by plotting the areas of the hydroxide peaks from the previous slide versus the known sodium hydroxide concentration in the 50 to 5 weight percent concentration range. This provides a very linear relationship that can be used to obtain quantitative results. For concentrations below 5 weight percent, the uncertainty was too large to provide a linear relationship.



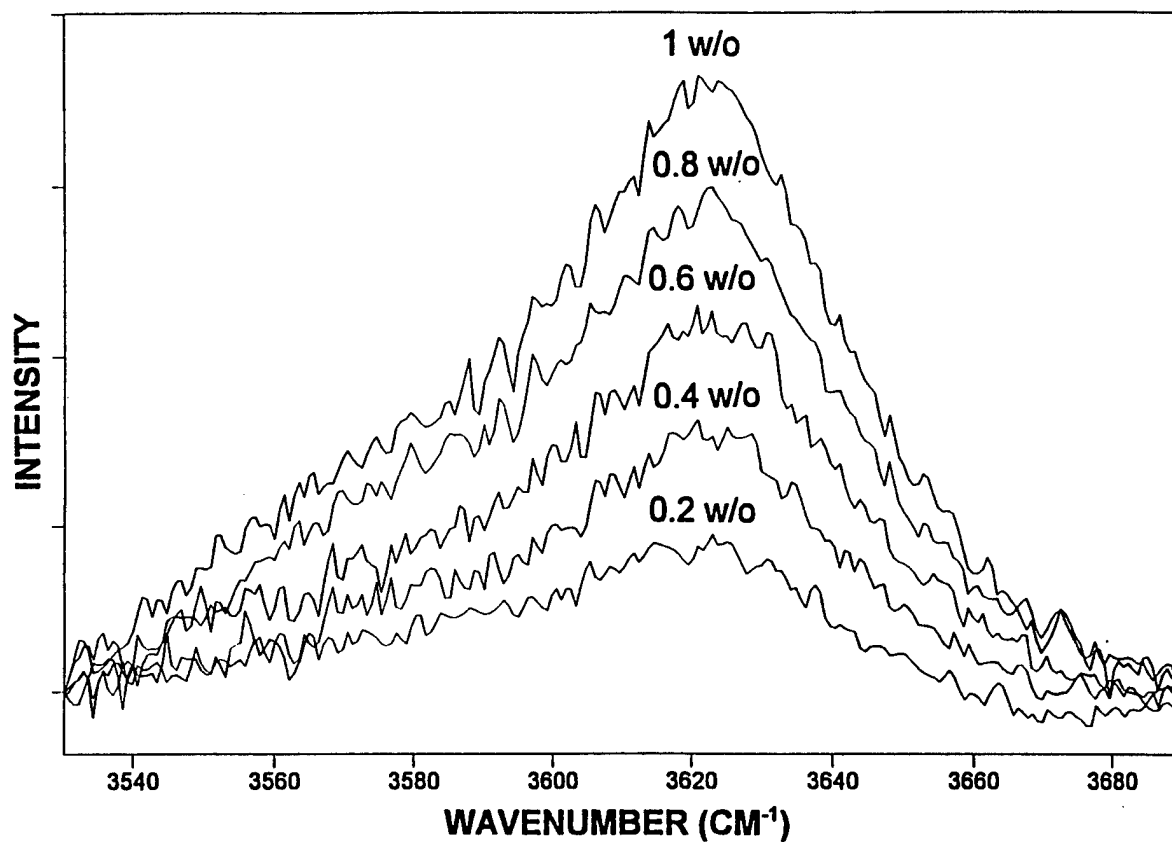
Slide 19

This slide illustrates the technique that was adopted to be able to obtain a calibration curve below 5 weight percent. In this method, the portion of the water spectrum between 3530 and 3690 cm⁻¹ was subtracted from the corresponding region of the sodium hydroxide solution spectrum.



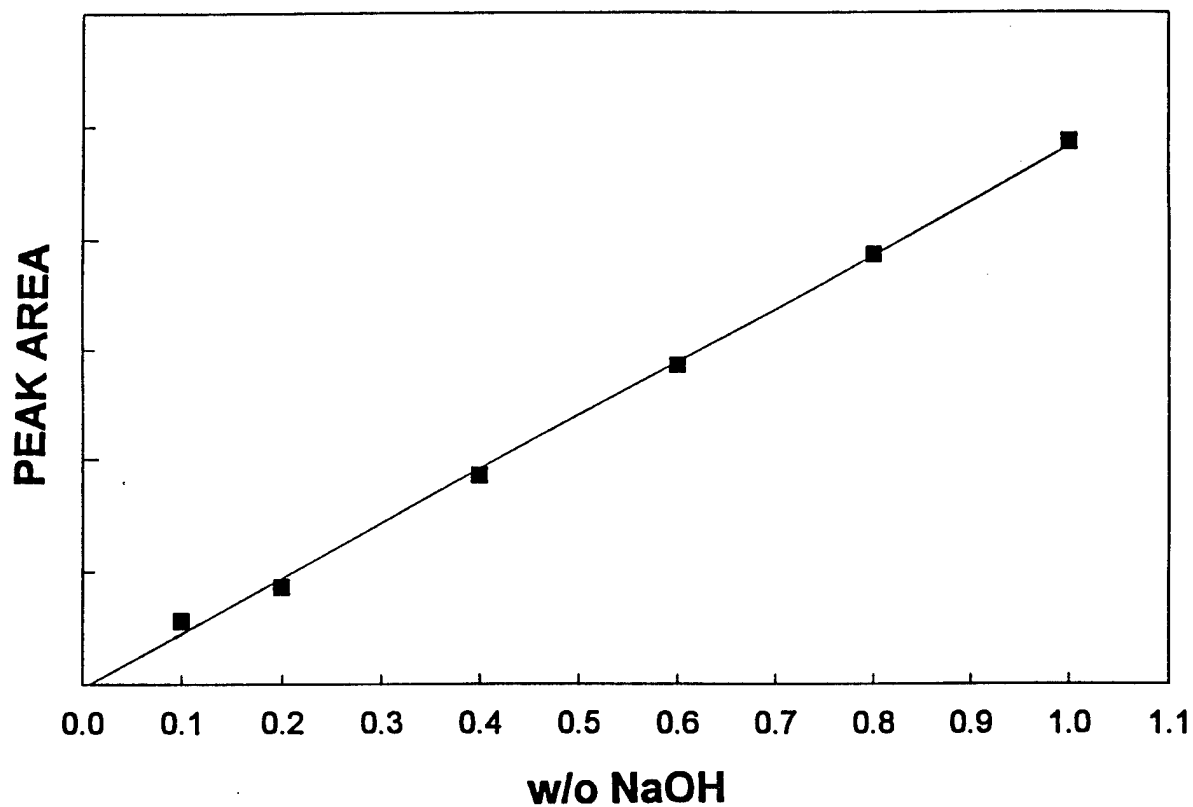
Slide 20

This slide illustrates the hydroxide peak obtained when the subtraction technique was applied to a one weight percent sodium hydroxide solution.



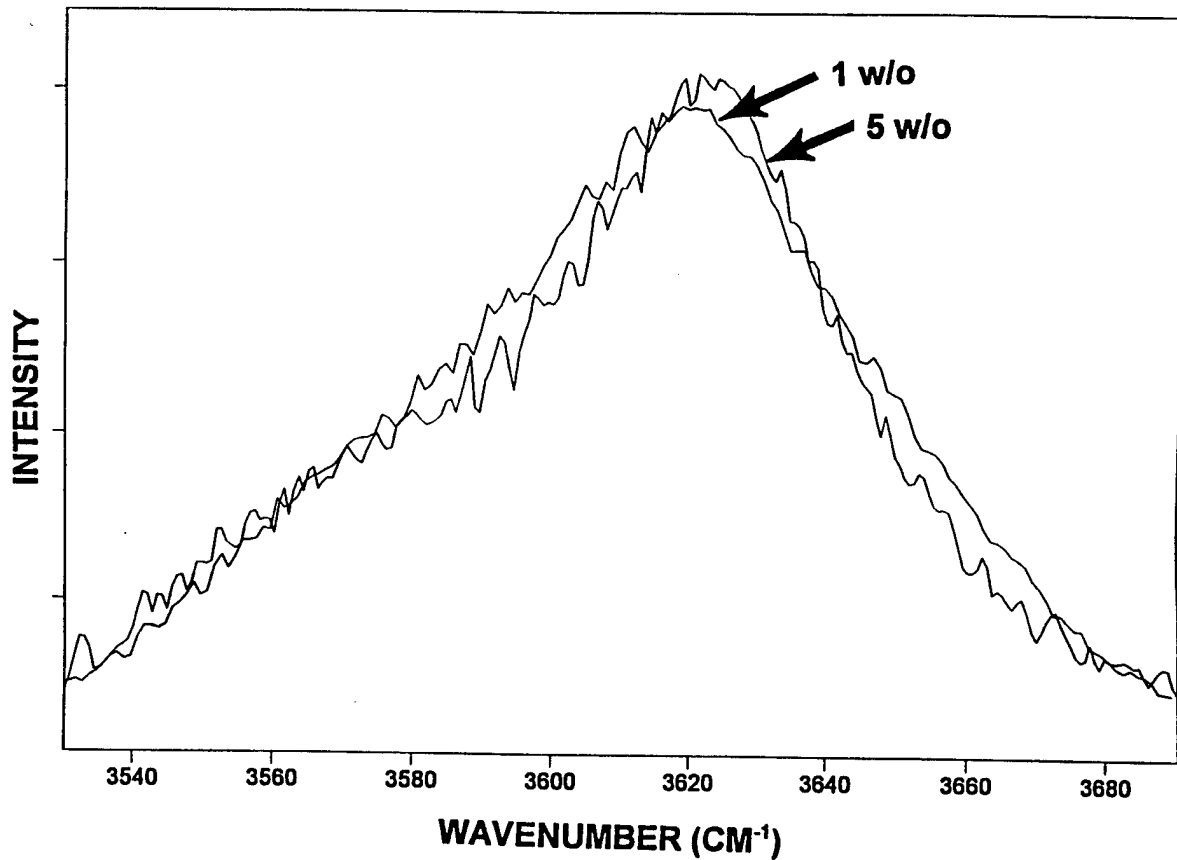
Slide 21

This slide illustrates the hydroxide peaks obtained when the subtraction technique was applied to solutions ranging from one to 0.2 weight percent sodium hydroxide solution. Below 0.1 weight percent the results were too uncertain to provide reliable quantitative results.



Slide 22

This slide illustrates the calibration curve obtained by plotting the areas of the hydroxide peaks from the previous slide versus the known sodium hydroxide concentration in the 1 to 0.1 weight percent concentration range. This provides a very linear relationship that can be used to obtain quantitative results. For concentrations below 0.1 weight percent, the uncertainty was too large to provide a linear relationship.



Slide 23

This slide compares the hydroxide peak shapes that were extracted from the water - hydroxide peak by the two different techniques. The 1 weight percent peak was enlarged to overlap with the 5 weight percent peak. The similarity of the peak shapes helps to validate the two techniques.

This attachment provides the abstract that was previously approved by Naval Reactors on 7/11/97.

Abstract

Quantification of Hydroxide in Aqueous Solutions by Raman Spectroscopy

Quantification of hydroxide in aqueous solutions by Raman spectroscopy is complicated by the fact that the O-H stretching band of hydroxide is overlapped by the broad, symmetric O-H stretching band of water. This overlap is further complicated by the fact that the shape of the O-H stretching band of water is strongly influenced by the concentration of hydroxide. The O-H stretching band of water is believed to consist of five components that result from differing configurations of intramolecular hydrogen bonding.

The Raman spectral region from 300 to 4450 cm^{-1} was investigated for NaOH solutions ranging in concentration from 0.2 to 50 weight percent. At approximately 5 weight percent NaOH, a distinct shoulder appears on the high energy side of the O-H stretching band of water. As the NaOH concentration increases, this shoulder becomes a sharp distinct band at 3600 cm^{-1} which is still not resolved from the O-H stretching band of water. As the O-H stretching band of hydroxide increases, the O-H stretching band of water broadens and its contour becomes smoother.

By curve fitting five gaussian functions to the O-H stretching band of water, the asymmetric band due to hydroxide was extracted from the composite band of the NaOH solution. The curve fitting routine resulted in a linear relationship for the area of the hydroxide band in the concentration range from 5 to 50 weight percent NaOH. The uncertainty in the curve fitting at concentrations below 5 weight percent was too large to establish a reliable calibration curve. Below 5 weight percent NaOH, direct spectral subtraction of the water band from the NaOH solution band resulted in a linear relationship in the range of 5 down to 0.2 weight percent NaOH. The peak shape obtained for the hydroxide band by the two different techniques was very similar. A comparison of the results obtained from peak fitting and spectral subtraction will be presented.

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