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UNIVERSITY OF DELAWARE

ENERGETICS SOLIDS DEGRADATION IN HIGH TEMPERATURE WATER

FINAL REPORT

THOMAS B. BRILL

JULY 1, 1992

U.S. ARMY RESEARCH OFFICE

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Strategies have been developed to determine the kinetics and mechanisms of degradation of energetic molecules in water up to 500°C. FTIR and FT-Raman spectroscopy enable *in situ* studies to be made and provide a wide spectral window in which many species can be followed simultaneously. Numerous spectroscopic and cell design hurdles have been encountered and surmounted so far. Cell designs and a process flow system that should provide clean kinetic studies are nearly completed at this time.

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FOREWORD

This report covers research performed under U.S. Army Research Office Contract DAAL03-89-K-0096 during the period July 1, 1989 to June 30, 1992. This contract was monitored by Dr. Robert W. Shaw, Chief, Chemical Diagnostics and Surface Science Branch who provided invaluable support, suggestions and patience relating to this challenging new endeavor.

Energetic Solids Degradation in High Temperature Water

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I. Summary

Strategies have been developed to determine the kinetics and mechanisms of degradation of energetic molecules in water up to 500°C. FTIR and FT-Raman spectroscopy enable *in situ* studies to be made and provide a wide spectral window in which many species can be followed simultaneously. Numerous spectroscopic and cell design hurdles have been encountered and surmounted so far. Cell designs and a process flow system that should provide clean kinetic studies are nearly completed at this time.

II. Introduction

The focus of this project has been to determine the decomposition chemistry of energetic materials in water at high temperature. The details sought are the reaction intermediates, mechanistic pathways, and kinetics. Although hot water reactors have been used for destruction of waste for some time, very little is understood about how they operate on a molecular level. At the outset of this project *in situ* diagnostic techniques were largely undeveloped for studying the details of such reactions in the laboratory. We began the task of designing and developing new techniques. From experience we know that the development of original techniques is fraught with pitfalls and hurdles. These frustrations are certainly present in this project. On the other hand, significant progress is being made toward making major advances toward understanding of kinetics and mechanisms of reactions in high temperature water.

III. Spectroscopic Developments

In situ, rapid-scan vibrational spectroscopy provides many advantages for characterizing reaction rates and sub-global mechanisms. This is because the broad spectral range allows the rate of change of many species to be monitored simultaneously. Alternative narrow band or single wavelength monitoring trades a high rate of data acquisition for the comprehensive view of the reactants, intermediates and products. In particular, FTIR and FT-Raman spectra of the reacting solutions allow us to observe both the disappearance of reactants as well as the appearance of products and transient reaction intermediates. In the future, our studies will also make use of GC/MS to analyze reaction products. The analysis of reaction products provides a means of determining mass balance and other information to complement the vibrational spectra.

A. FT-Raman Methods

At the start of ARO funding for this project, University funds were used to purchase a Nicolet FT-Raman Accessory for the currently existing 60SX FTIR. The Spex dispersive Raman instrument previously used for high temperature water studies by Spohn and Brill[1] had become obsolete and could not be used for transient studies. The new accessory scans much faster, collecting a full band width (6000-9394 cm^{-1}) at 1 cm^{-1} resolution and a rate of 1 scan per second. This capability allows us to observe multiple species simultaneously on a time scale suitable for kinetic studies.

The FT-Raman accessory was a prototype and proved to have many problems. The accessory included a NIC-Notch multi-reflection mirror for the attenuation of the Rayleigh scattering signal. The filter was designed to allow for the collection of Stokes shifts to within 75 cm^{-1} of the Rayleigh line. A regular band filter allows for the collection of Stokes shifts to within 300 cm^{-1} of the Rayleigh line. Because the Stokes shifts of concern in this experiment do not fall within 300 cm^{-1} of the Rayleigh line, the NIC-Notch filter was removed in order to achieve better signal-to-noise ratios. The FT-Raman spectrometer also had to be fitted with custom optics in the sample compartment because the optics normally supplied by Nicolet did not have adequate space for our cells, nor were they sufficiently far enough from heated cell parts to prevent the lens from heating and defocusing the scattered light. The optics configuration that we now have collects scattered radiation in the 180° back-scattering mode.

After a year and a half, Nicolet upgraded our original Raman accessory with a redesigned system. They did not charge us for this upgrade. The new unit provided more laser power, giving us about 0.95 watts at the sample. The new accessory also has a much better Rayleigh line filter. A new Germanium detector was installed to replace the indium/gallium/arsenide (IGA) detector in the original instrument. The germanium detector is about 10 times as sensitive as the IGA detector and was not commercially available when the original accessory was purchased. The germanium detector also has a plasma line filter to remove unwanted spectral lines produced by the flash lamps of the NdYAG laser.

A drawback discovered of the FT-Raman accessory is that it is sensitive to blackbody radiation produced by our heated cells. The radiative power output of a blackbody is proportional to its temperature raised to the fourth power. The exponential relationship causes little interference in the near IR between 25 and 200°C, but when the cell reached 250°C, bands of interest (e.g. the symmetric NO_3^- stretch) are no longer visible above the background (Figure 1). Heating much above 250°C causes saturation of the detector.

After discussing this problem with a number of experts in the fields of optics and spectroscopy, we surmise that it may not be possible to remove all of the blackbody interference. Thus our approach has been to manipulate the variables that we do have control over in order to raise the maximum working temperature.

Cells for *in situ* FT-Raman work are constructed out of low emissivity materials. We also utilize bandpass filters and instrument modifications to increase the ratio of the

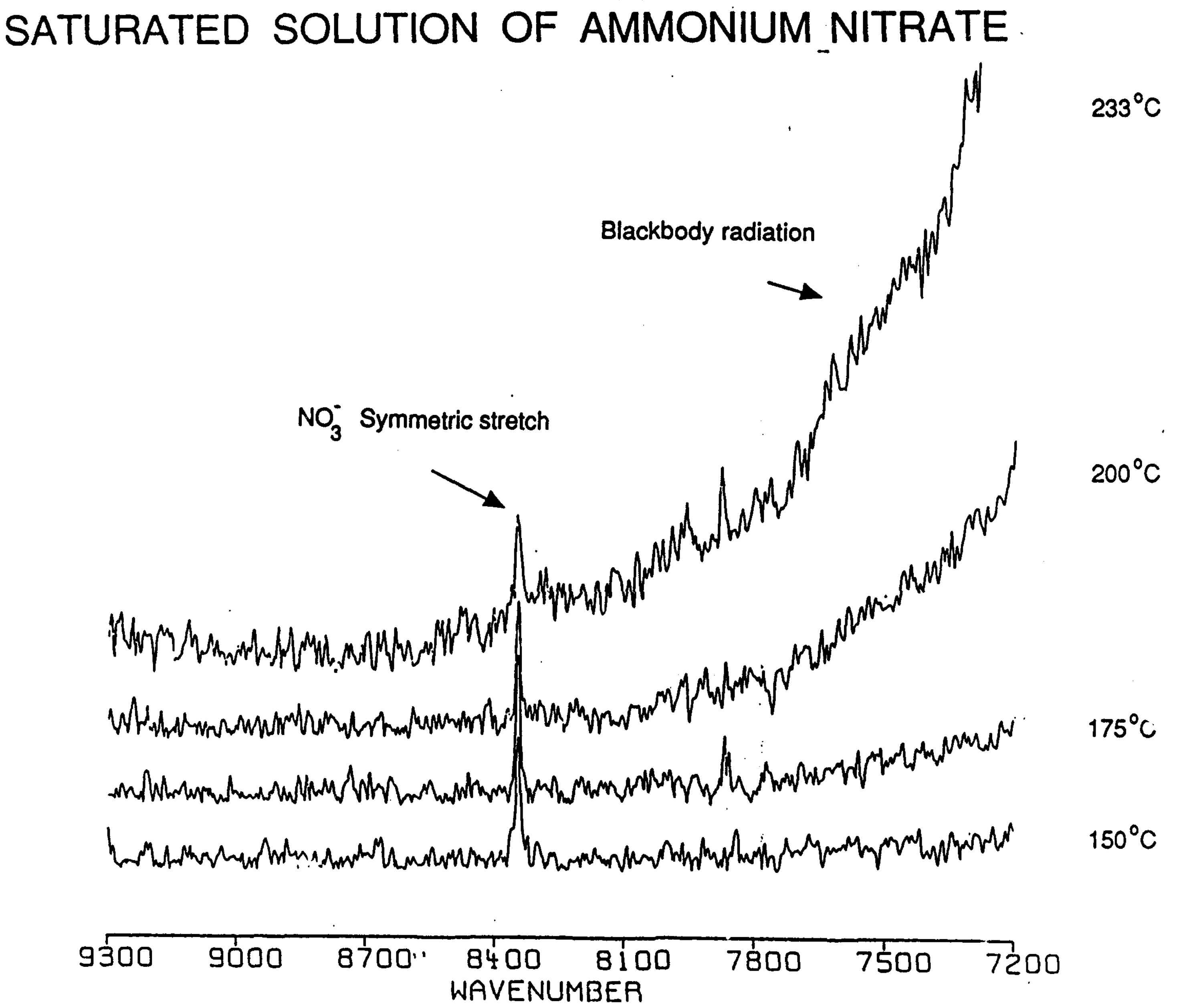

Figure 1 : FT-Raman spectra of saturated aqueous ammonium nitrate showing the blackbody radiation problem

Raman signal-to-blackbody interference. For compounds that need to be heated above 270°C in order to achieve appreciable decomposition rates, we have developed another means for collecting *in situ* data. This method utilizes FTIR spectroscopy and will be discussed later in this report. The first experiments employing the FT-Raman accessory were carried out on saturated aqueous solutions of NH_4NO_3 by using a cell designed by Brill and Spohn. It was in these experiments that we first observed the blackbody interference problem. Subtraction of the background from the sample spectrum proved to be of no use for removing the blackbody radiation. The detector cannot distinguish the thermal radiation from the Raman excitation radiation because both occur in the same region and have similar intensity. By the temperature that the nitrate stretch is largely masked by the thermal radiation background, the detector is nearing saturation. Spectral subtraction at this point gives the difference between two large numbers which is subject to a large error, and gives little or no reliable information about the changes in the characteristics of the nitrate stretch.

After the subtraction routine was discarded, we began working toward increasing the ratio of Raman scattering to blackbody radiation. The Spohn-Brill cell has a polished sapphire sample chamber which has relatively low emissivity in the spectral range of interest. Therefore, we tried constructing a simple aperture in an attempt to block the thermal radiation emitted by the other parts of the cell. These other, more strongly emitting materials were darkened-steel, tantalum, and inconel used in the cell holder, and a ceramic fiber that was used for thermal insulation. The apertures were simple paper cards punched with different sized holes. The apertures were affixed to the cell about 1.5

inches from the sapphire window. In this configuration, the aperture was between the cell window and the collection lens. This aperturing method, however, proved to be much too crude. If the aperture was large, no beneficial effect was observed; if the aperture was too small, intensity of Raman scattering was greatly compromised. However, an optical consultant with whom we have discussed this project is confident that a properly sized aperture positioned correctly in the instrument should have the effect we desire. Therefore, we have been working with Nicolet to construct a more efficient aperture for FT-Raman spectroscopy.

A second strategy for collecting FT-Raman spectra at high temperature was to design a new cell that would hold more sample. We hoped that the larger sample volume would increase the nitrate stretching intensity relative to the thermal radiation. The cell we designed had flat sapphire windows and the high-pressure seal was made with gold gaskets. The cell was held together with allen bolts which made it easy to disassemble, clean, and reassemble without leaks. However, too much steel was exposed to the collection optics and blackbody radiation was still a problem. This cell did not raise the maximum temperature at which we could obtain useful spectra.

In order to determine the qualitative benefits of using a lower emissivity material for cell construction, we designed and built a cell that had a sapphire reaction chamber surrounded only by polished aluminum and gold. This cell did emit less blackbody radiation than the previous two designs. It was not good, however, at holding high pressures. Furthermore, due to the simplicity of its design, it could not be used in a flow mode and the pressure inside the cell could not be measured.

To take full advantage of lower emissivity materials, we designed a cell that has a solid gold reaction chamber, gold covered end caps, gold feed tubes and diamond windows only one third as thick as the sapphire windows used in the designs described above. The gold cell had a variable pathlength which could be altered by the thickness of the spacer placed between the diamond windows. The availability of different pathlengths would have allowed us to use this cell with both the FTIR and the FT-Raman instruments. Unfortunately, the pure gold used as the cell body proved to be too soft to hold the tight tolerances necessary for high pressure sealing. The gold block and the scraps from machining were sent back the caster and reformed into a cylinder. The gold cylinder was machined into a cell similar in design to the reliable stainless steel cell discussed above (Figure 2). This cell has been completed and we have begun pressure testing.

Another method of increasing the ratio of Raman scattering-to-blackbody radiation is to isolate the band of interest by using a narrow bandpass filter. This approach was tested employing a 1200±30 nm bandpass filter to isolate the totally symmetric nitrate stretch of an aqueous solution of ammonium nitrate. The filter had the effect of reducing the nitrate stretch intensity by about 30%, however, the ratio of Raman-to-blackbody radiation increased and we were able to raise the maximum usable temperature of FT-Raman spectroscopy from 245 to 265°C.

B. FTIR Methods

As mentioned earlier, even by manipulating the materials of cell construction and using a filter and an aperture, we still might not be able to attain the temperatures

AQUEOUS FT - RAMAN CELL

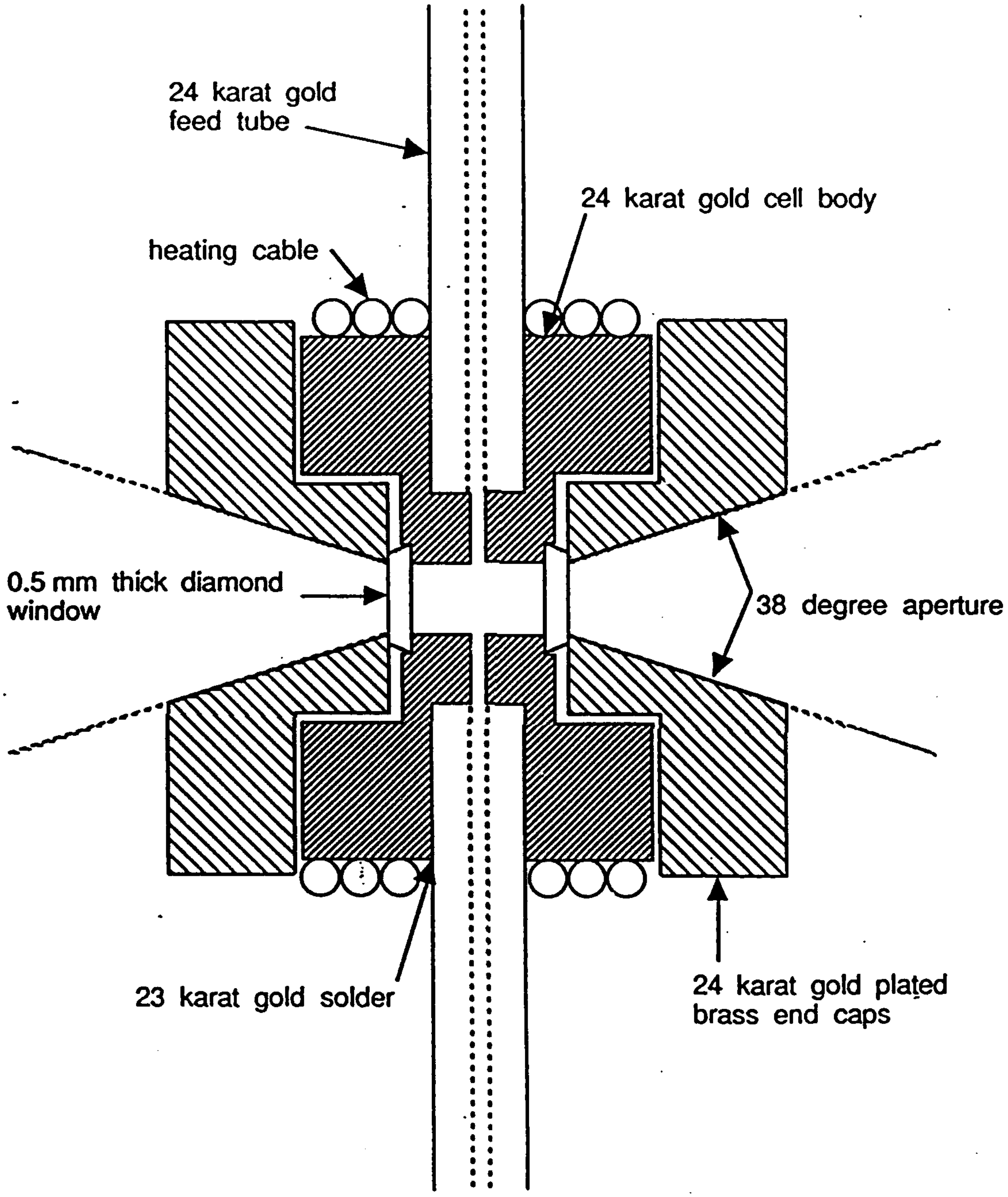

Figure 2 : High temperature aqueous FT-Raman cell constructed from low emissivity materials

needed for decomposition of some compounds. FTIR spectroscopy operates in the mid-IR and has no blackbody interference problem at the temperatures of interest. Water, however, very strongly absorbs IR radiation at various regions of interest. Initial FTIR studies of aqueous solution were conducted with a variable pathlength cell that we built from spare ZnSe windows. We found that a pathlength of 25μ worked well for subtraction of water bands and was long enough to allow observation of the asymmetric stretching fundamental of solutions containing the nitrate ion. 2-Azidoethanol was synthesized and solutions of 0.01 - 1M concentration were studied. The azide stretch was observable at a lower limit of concentration of about 0.01 molar (Figure 3). Nitro groups could be seen in 2-nitroethanol at 0.1 molar concentration (Figure 4).

Once we were certain that we could detect the functional groups characteristically present in energetic molecules with a short pathlength, we designed an FTIR cell for aqueous solutions that has diamond windows (Figure 5). For corrosion resistance, the cell walls are made of 90/10 platinum-iridium alloy. The platinum-iridium alloy has an extremely low coefficient of thermal expansion that should maintain a nearly constant pathlength over the temperature range of interest (25 - 400 °C). Platinum-iridium is also resistant to acid attack. This cell is currently under construction and should be completed during the Summer of 1992.

In order to study the mechanisms decomposition of materials in hot, pressurized water, the platinum-iridium cell was designed not only with spectroscopic considerations in mind, but also to function as a chemical flow reactor (Figure 6). The intention was to obtain spectra of the solutions at a known temperature while the reaction takes place. A

2-AZIDOETHANOL

Resolution = 0.5 cm^{-1}

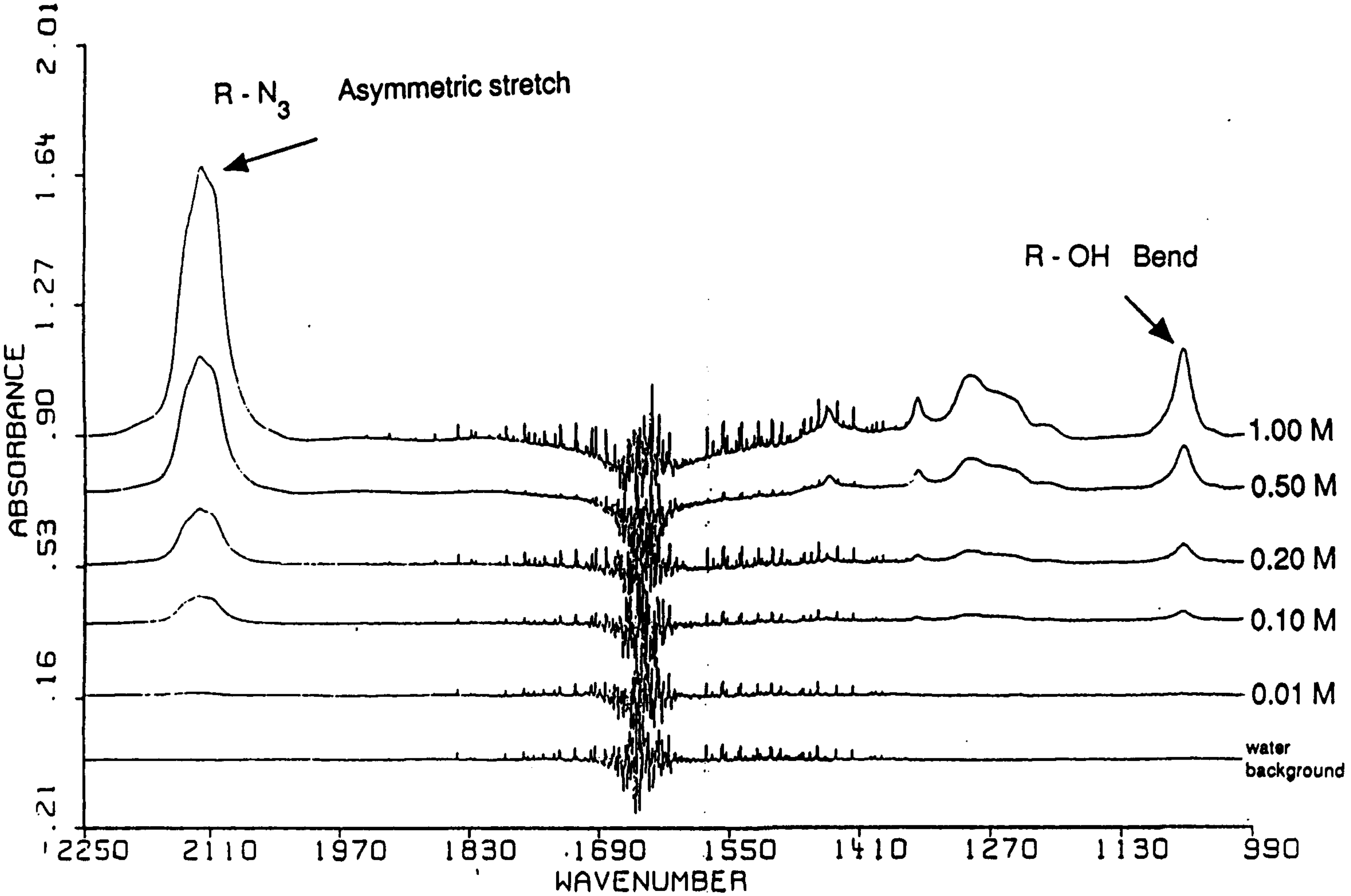

Figure 3 : FT-IR spectra of aqueous solutions of 2 azidoethanol at various concentrations

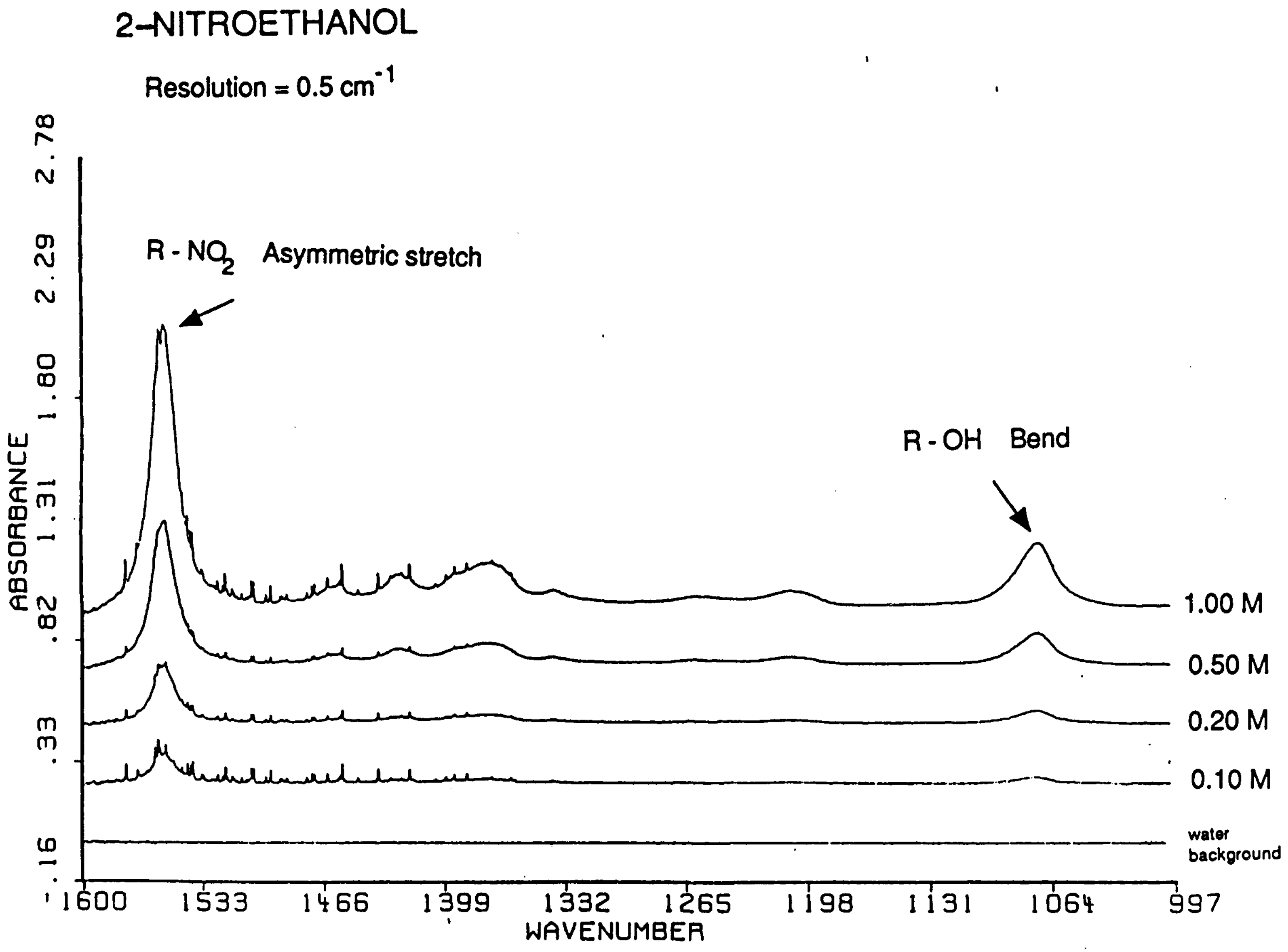

Figure 4 : FT-IR spectra of aqueous solutions of 2 nitroethanol at various concentrations

AQUEOUS FT-IR CELL

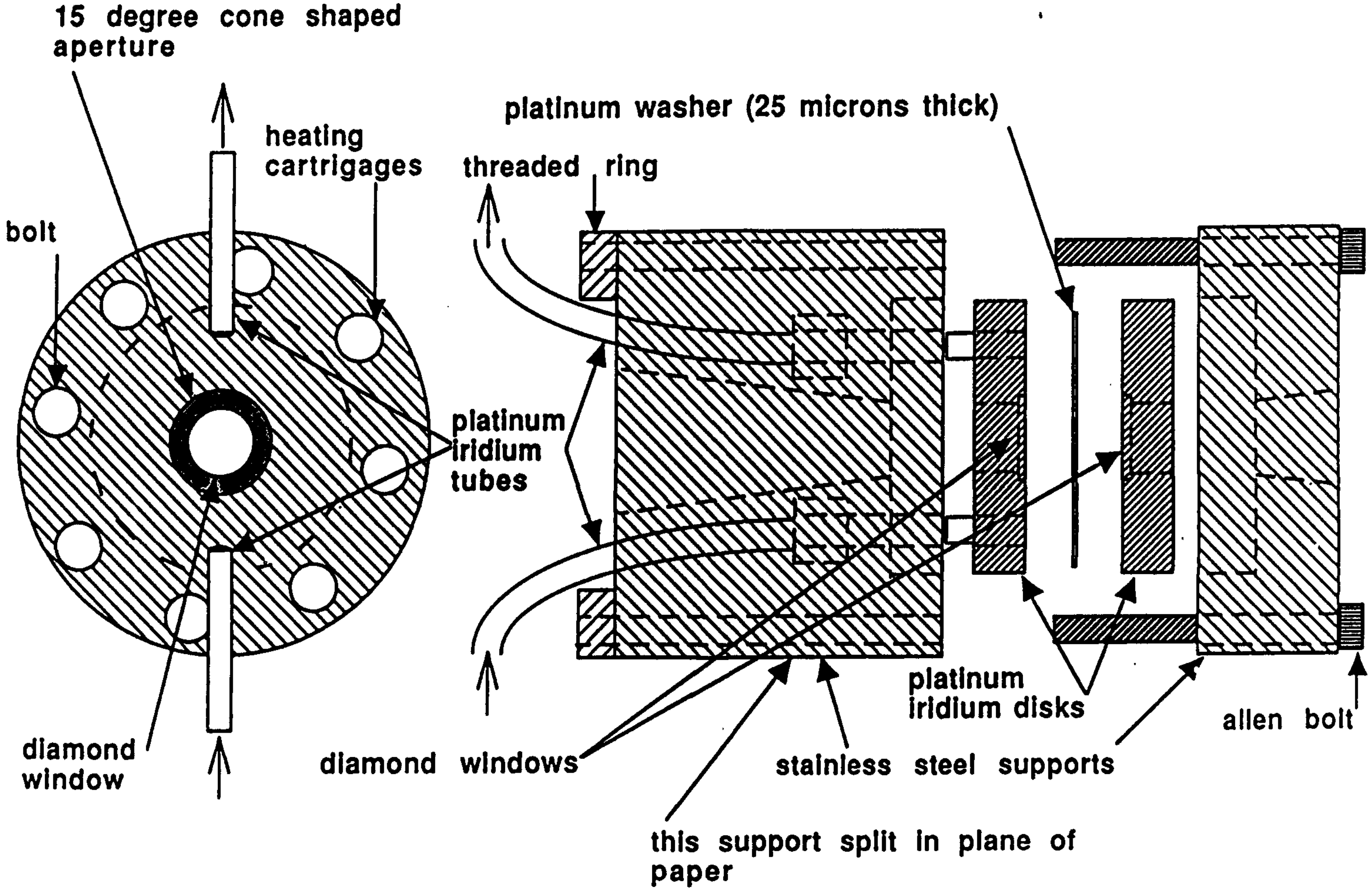

Figure 5 : Variable pathlength high temperature and pressure aqueous FT-IR cell

REACTOR SCHEMATIC

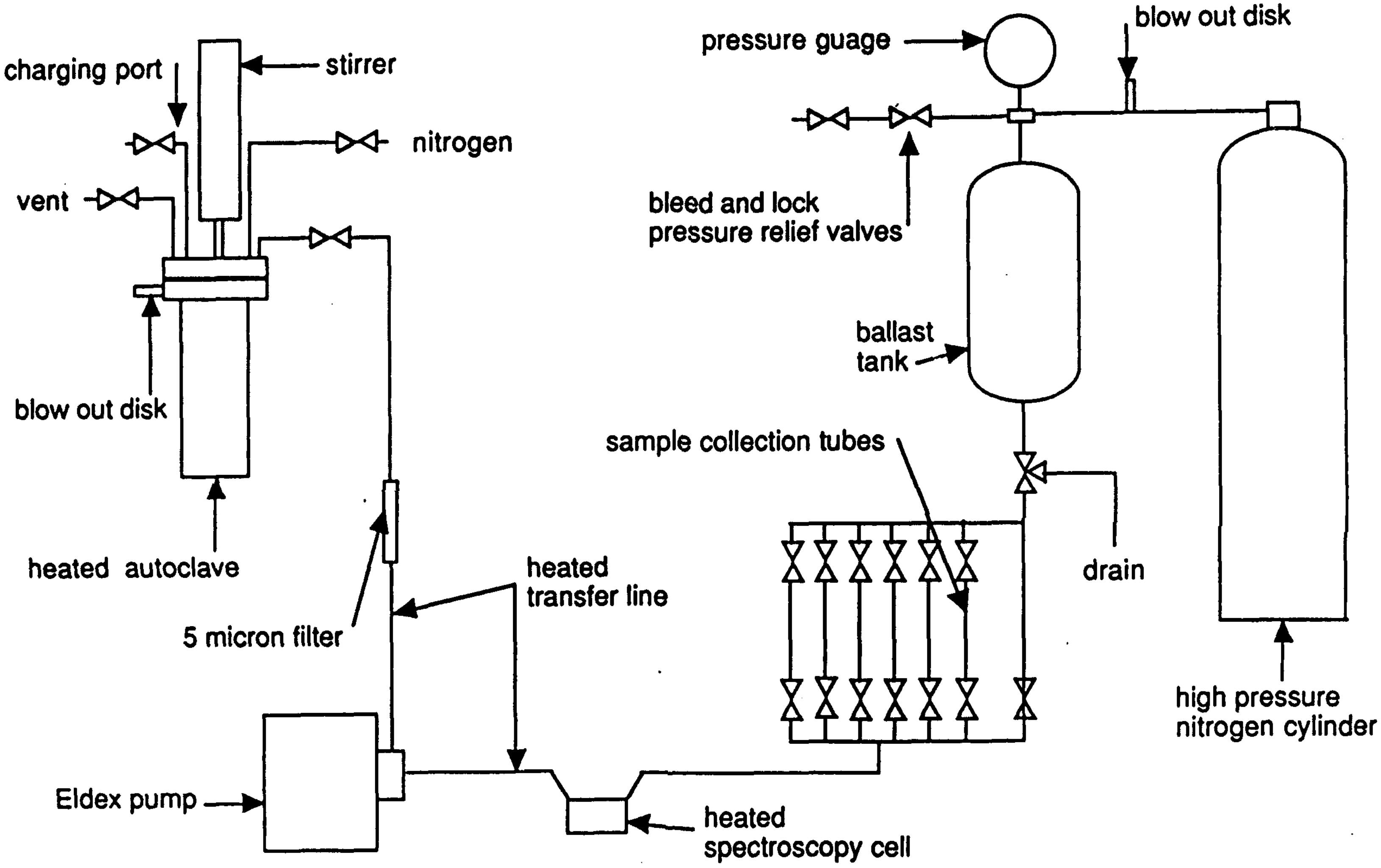

Figure 6 : Schematic diagram of high temperature and pressure flow reactor

secondary goal was to capture these samples as quickly as possible for component analysis such as by GC/MS. To accomplish these goals, it was necessary to understand the thermodynamics and fluid dynamics of the cell. To this end, we collaborated with a group from the Chemical Engineering Department headed by Michael Klein before constructing the cell. The main premise was to develop a flow cell in which the sample reached the set temperature at the cell windows. Conducted in this way, the experiment would best simulate the conditions of a larger scale reactor and would enable a wide variety of corollary experiments to be conducted. Our original design was modeled by one of Klein's graduate students so as to understand the heat transfer and flow properties of the cell. This model took into account factors such as flow profiles through both the entry/exit tubes and through the narrow channel between the diamond windows. It also accounted for such thermal factors as conductive heat transfer to the fluid at various flow rates and radiative losses of the cell body to the atmosphere.

By using the theoretical model, we were able to optimize several aspects of the final design. These included the length of the heated entry tube necessary to bring the fluid up to the chosen reaction temperature before it passes between the diamond windows, the amount of heat (via electric heating cartridges) required to maintain a constant temperature at a certain flow rate, and the shape of the fluid path between the two windows. We desired a laminar plug-flow profile. The model also provides us with a good understanding of the temperature, pressure, and flow at various points in the cell as we change the specific sets of conditions. By simply changing some of the variables in the model, we can predict how it will behave under a variety of conditions including different system temperatures, pressures, flow rates, and optical pathlengths allowing for a great deal of flexibility in the experiment. Of course, the model will be tested for validity once the cell is built. Some reparameterizing of the model will undoubtedly be necessary to obtain a predictive set of controlling equations.

C. Pumping System

Along with the cells, the design and construction of the pumping system is nearing completion. It was necessary to develop a method through which high, constant pressures could be maintained throughout the system. It was decided that fluids would be pushed through the cell using a piston type HPLC pump. It was necessary to find a pump that would operate at high pressures over a wide temperature range and that would be resistant to potentially corrosive aqueous solutions. The pump would also need to have fairly constant flow rate characteristics at a variety of flow settings. An Eldex single piston HPLC pump fitted with sapphire valve seats and a micrometer metering device was chosen for this purpose.

In order to maintain high pressures throughout the system, the HPLC pump would have to push against pressure resistance. This was provided by a one liter stainless steel ballast tank place at the distal end of the flow system. As well as providing a relatively large volume to act as pressure ballast, this tank was intended to serve as a receptacle for the reacted fluids exiting the cell reactor. The ballast tank was designed with a simple "bleed-and-lock"valve system to regulate the pressure rather than an automatic pressure relief valve. If this pressure regulation system is not satisfactory we will switch to a pressure relief valve. High pressure (6000 psi) nitrogen tanks and regulators have already been obtained to provide the system start-up pressure and to provide the back pressure in the ballast tank.

Initial studies of some model compounds have shown that in many cases, much better solubilities are obtained, not surprisingly, at higher temperature. It was decided that it would be best if the reactor design included a method by which hot, but non-reacting, solutions could be fed into the spectroscopic cell reactor where the actual degradation would take place. Therefore, a 300 cc Autoclave Engineers research autoclave is being used as a sample reservoir. This apparatus was overhauled and modified to fit our application. Since this device is able to stir and heat solutions at pressure, it will enable us begin the experiments with a wider variety of solution concentrations including those attainable only above 100°C.

In order to prevent the precipitation of the dissolved sample before it reaches the cell reactor, the lines and fitting must be wrapped with silicone coated fiberglass heating tapes. The tapes are covered with fiberglass insulation to provide more constant and even heating and to prevent the occurrence of hot spots. The temperature in the cell and the lines and the cell are monitored and controlled by separate Omega PID controllers.

D. Product Analysis and Behaviors

As was mentioned earlier, another need for the kinetics models is capture the samples that have been analyzed spectroscopically so that a mass balance analysis can be made. A sample manifold was designed in which six aliquots can be trapped at pressure in a stainless steel tube between two high pressure, high temperature ball valves. This configuration will allow us to collect samples at several different temperatures during the same experiment. Careful flow studies of the completed apparatus will enable us to match the trapped aliquots with their corresponding IR spectra at reaction conditions. The lines running from the cell to the manifold and possibly the manifold itself could be heated, if necessary, in the same manner as the tubing from the reservoir to the cell. This should prevent the precipitation of the reaction products prior to trapping in the sample tubes.

We intended to analyze the reacted sample aliquots using the departmental GC/MS. We were advised that aqueous solutions will damage the column on the instrument so we have devised a special protocol for analyzing the solutions. The trapped aliquot will be released into a specially designed, evacuated, glass vessel fitted with a stopcock containing a septum and a glass-to-stainless fitting. A sample of the evolved gaseous products will then be drawn off and analyzed. The liquid portion will then be divided into thirds and extracted with an organic solvent, the first being acidified, the second made basic, and the third left neutral. Each of these solutions will be analyzed by GC/MS. This solution phase analysis, the analysis of the gaseous products, and the *in situ* IR spectra should give considerable insight into the kinetics and mechanisms.

Before samples are studied in the IR and Raman cells, preliminary studies of the reaction will be made in a batch reactor. Precipitation of products or a runaway exotherm could severely damage the cell. Three types of batch reactors have been developed so far. The first type is a 316 stainless steel tube with two fittings to allow flow into and out of the reactor. Once the tube is full of sample, flow is stopped and heating starts. Pressure is monitored with a gauge on the inlet side of the tube. After the initial experiments with NH_4NO_3 and EDDN, it was found that this batch reservoir was not practical. The dilution caused by flowing into the relatively large volume of the reactor required too much sample to achieve the desired sample concentration within the reactor.

Current batch studies use two batch reactors that do not fill by flowing solution through the reactor. The tube is simply loaded with reagents, closed and heated. Reactors of this type do not allow us to monitor the pressure during the reaction but they require less sample.

One of these reactors is a six inch long titanium pipe that has one threaded end. A cap is screwed tightly onto the threaded end and the whole reactor is lowered into a heated fluidized sand bath for 8-15 minutes. The cell is then removed from the sand bath and quenched in a bucket of ice water. The reactor is then opened and the products analyzed.

Our other batch reactor uses a heavy wall pyrex ampule that is sealed at one end, loaded and then sealed at the other end. The ampule is then placed in an aluminum heating block. After heating, the ampules are cracked open and products are analyzed. The pyrex ampules have the advantage that we can watch the reactants during heating and see at what temperature any tar-like deposits form.

We have conducted preliminary batch studies on 2-azidoethanol, DINA, NH_4NO_3, HAN, TEAN and EDDN. Of these six compounds, DINA, NH_4NO_3, and HAN were found to decompose cleanly. Azidoethanol, TEAN, and EDDN decomposed but left a sticky tar-like residue in the reactor. Detailed kinetic studies cannot be conducted on materials that decompose to a tar because they will plug the flow cell.

IV. Future Plans

This project is continuing under a University Research Initiative sponsored by the Army Research Office. Detailed plans are described in that proposal.

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1. Spohn, P.D.; T.B. Brill. Raman Spectra of the Species in Concentrated Aqueous Solutions of $Zn(NO_3)_2$, $Cd(NO_3)_2$, $LiNO_3$, and $NaNO_3$ up to 450°C and 30 MPa." J. Phys. Chem., 1989, 93, 6224.

V. Students Supported

Dr. Youlin Chen (Ph.D. Princeton University) was supported on this project from September 1989 to February 1990 as a post-doctoral student. From June, 1990 to the present Matthew Kieke, a Ph.D. candidate, has been supported as a research assistant. Joseph Schoppelrei, Ph.D. candidate, has been supported since June 1991 on this project. Matthew Kieke and Joseph Schoppelrei are continuing to work on this project as RA's until they complete their programs. Thomas Schwerdt is a freshman chemistry major and began working June 1, 1992, on this project.

VI. Conferences Attended and Contacts Established

Supercritical water reactions in relation to environmental problems have been a new thrust in our program. One avenue to gaining perspective has been attendence at meetings in which environmental problems and SCW reactors have been discussed. A second avenue has been to visit laboratories and attend seminars in this area where possible.

I attended an American Society of Mechanical Engineers meeting in Albuquerque, NM in April, 1989, in which various advanced methods of toxic waste destruction were discussed. A meeting specifically on SCW processes was held at Los Alamos National Laboratory in August, 1989, in which I presented a paper and was a panel member to discuss materials of fabrication. In September 1990, I participated in a NATO Advanced Research Workshop organized by ARO and the University of Leeds which was held at Bolton Abbey, U.K. Extensive discussion of key research issues took place. In April 1991, I took part in a technical exchange conference on supercritical water oxidation held at Tyndall AFB, FL organized by Dr. Joe Wander.

Because of the activity in critical phenomena at the University of Delaware, we have frequent visitors here to discuss activities. For example, Mike Antal from the University of Hawaii, Johannes Penninger from Groningen, The Netherlands, Ulrich Franck from Karlsruhe, Germany, and Greg Rosasco and Annecke Sengers from NIST - Gaithersburg have all visited for extended discussions. I have visited NIST-Boulder, the University of Karlsruhe and the ICT in Karlsruhe to see their facilities and gain insight. My most extensive contacts are with Sandia, Livermore where I visit Steve Rice and Dick Steeper about twice per year, and Los Alamos National Laboratory where I visit Steve Buelow's facility about twice per year.

VII. REPORT INVENTIONS

ARO Contract DAAL03-89-K-0096

none.