

AD-A131 574

CHARACTERIZATION OF HYDROXYLAMMONIUM NITRATE (HAN) AT
VARIOUS PRESSURES AND TEMPERATURES(U) GEO-CENTERS INC
NEWTON UPPER FALLS MA C A VAN DIJK MAY 83 GC-TR-83-266
N00014-82-C-2150

1/1

UNCLASSIFIED

F/G 21/9. 1

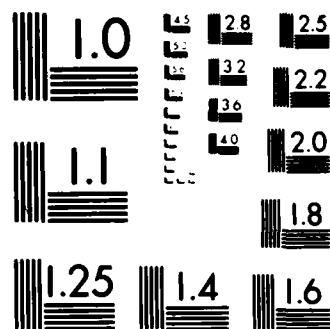
NL

END

FORMED

14

DATE



MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

6

AD A131574

CHARACTERIZATION OF HYDROXYLAMMONIUM NITRATE (HAN) AT VARIOUS PRESSURES AND TEMPERATURES

BY
C.A. VAN DIJK

PREPARED FOR
U.S. NAVAL RESEARCH LABORATORY
4555 OVERLOOK DRIVE
WASHINGTON, DC 20375

CONTRACT NUMBER N00014-82-C-2150

PREPARED BY
GEO-CENTERS, INC.
320 NEEDHAM STREET
NEWTON UPPER FALLS, MA 02164

DTIC FILE COPY

MAY 1983

DTIC

AUG 22 1983

C-10

A

GEO-CENTERS, INC.

83 06 22 218

GC-TR-83-266

CHARACTERIZATION OF HYDROXYLAMMONIUM NITRATE (HAN) AT VARIOUS PRESSURES AND TEMPERATURES

BY
C.A. VAN DIJK

PREPARED FOR
U.S. NAVAL RESEARCH LABORATORY
4555 OVERLOOK DRIVE
WASHINGTON, DC 20375

CONTRACT NUMBER N00014-82-C-2150

PREPARED BY
GEO-CENTERS, INC.
320 NEEDHAM STREET
NEWTON UPPER FALLS, MA 02164

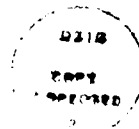
MAY 1983

GEO-CENTERS, INC.

TABLE OF CONTENTS

	<u>Page</u>
List of Figures	ii
List of Tables	ii
Acknowledgments	iii
Abstract	iv
1. Introduction	1
2. Experimental Procedure	3
3. Results and Discussion	7
a. Assignments	7
b. Pressure and Temperature Dependence	12
c. Electron Beam Heating	20
4. Conclusions and Recommendations	23
5. References	24

Attch on file



A

LIST OF FIGURES

	<u>Page</u>
1. Raman spectra from the diamond anvil cell filled with a sugar solution having a refractive index of 1.4728, matching that of an 11 molar HAN-H ₂ O mixture.	5
2. Raman spectra of HAN and H ₂ O. Samples were contained in a glass capillary at ambient conditions.	8
3. Raman spectra of deuterated HAN and D ₂ O. Samples were contained in a glass capillary at ambient conditions.	9
4. Raman spectra of AN, HAC and IPAN. Samples were contained in a glass capillary at ambient conditions.	10
5. Raman spectra from a sample of 11 molar HAN-H ₂ O mixture at various pressures and temperatures. Spectra were taken in the order a, b, c, d, spread out over three days, in which the cell was repeatedly cooled down to ambient temperature. No external pressure adjustments were made other than the initial pressure setting of a.	14
a. Sample at 5.9 kbar and ambient (22°C) temperature.	14
b. Sample at 5.9 kbar and 65°C.	14
c. Sample at 7.2 kbar and 79°C.	14
d. Sample at 4 kbar and ambient temperature.	14
6. Detailed transition in the 900-1400 cm ⁻¹ region of 11 molar HAN-H ₂ O mixture to the reacted state. Spectra were taken in the order a, b, c, d. Pressure was 7.2 kbar, temperature was 79°C. Total time span is approximately 1 hour.	16
7. Temperature versus time profile for a confined 11 molar HAN-H ₂ O mixture, when this mixture is exposed to a 40 MeV ² electron beam.	21

TABLE

1. Assignments for the Raman Spectrum of HAN.	13
---	----

ACKNOWLEDGMENTS

The author is indebted to Dr. A. Stolovy and Dr. E. C. Jones for assistance with the electron beam experiments. He also wishes to express his appreciation for helpful discussions with Dr. R. Priest and Dr. N. Klein.

ABSTRACT

Assignments of spectral features pertaining to ambient and unconfined conditions have been determined for an 11 molar hydroxylammonium nitrate mixture in H_2O in the $400\text{--}4000\text{ cm}^{-1}$ region, using Raman spectroscopy. For experiments at elevated pressures, the sample was contained in a diamond anvil cell. Pressure and temperature of the cell were varied over the range of 2-7 kbar, $22\text{--}120^\circ\text{C}$, respectively. At pressures around 6 kbar and temperatures around 90°C a significant and irreversible change in the spectra was observed. This change is interpreted as the result of a chemical reaction occurring within the sample. The disappearance of features related to oxygen-bonds was observed. Evidence of nitrous oxide formation was found.

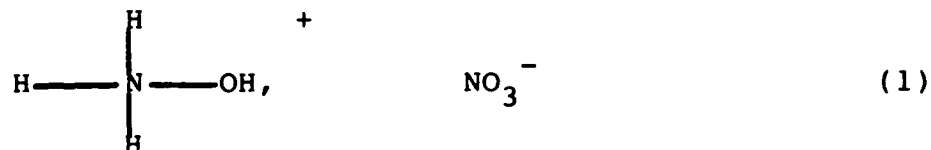
In a separate experiment, a cell containing about 0.7 cm^3 of HAN mixture was exposed to an electron beam having an energy of 40 MeV. Initiation thresholds of approximately 130°C were observed, in agreement with known values obtained by other researchers.

1. INTRODUCTION

For many years, the military has recognized the potential advantages of using self-contained liquid propellants in gun systems. For instance, liquid charges can be continuously varied to achieve the desired range. Also, the logistics of liquid propellants is presumably more manageable than that of solid propellants. In addition, the volumetric impetus of liquid propellants is expected to be greater than that of solid propellants. However, these advantages have been offset by the major problem of accidental detonation under both storage and handling conditions. The causes of these accidents are not understood and, to date, little information has been obtained from standard characterization methods. As a result, the advantages of these promising materials have not been fully explored.

→ A summary of some characteristics of various liquid propellants has been given by Klein (1). In the present report, attention is focused on hydroxylammonium nitrate, which is the more important component in HAN-based propellants (1,2).

The structural formula of HAN is



Under ambient conditions, this salt can be dissolved in H_2O up to 95% by weight. The concentration most often used in the present report is 11 molar (73.6%).

Both ions of HAN are oxygen-rich and therefore the predominant mode of reaction with most other compounds is oxidation (1). Although HAN is a propellant by itself, the fuel component isopropylammonium nitrate (IPAN) is often used in a mixture with HAN, to form a stoichiometric mixture.

Raman spectroscopy was used to study the HAN- H_2O mixture under various conditions. Slow reaction sequences were also monitored using Raman spectroscopy.

To obtain the spectral assignments, the sample was contained in a glass capillary tube. The Raman spectrum of various related compounds, such as ammonium nitrate, was also obtained for reference purposes.

In order to approach some of the conditions encountered in the field use of liquid propellants, some of the spectra were taken with the sample exposed to pressures of several kilobars and temperatures up to $100^{\circ}C$. This was done in a diamond anvil cell, equipped with heater and thermocouple.

The feasibility of heating a confined mixture of HAN and H_2O with an electron beam was investigated in order to find a possible method to observe reactions like those observed in the diamond anvil cell. A threshold for thermal initiation was obtained, in rough agreement with known values obtained with different methods. Also, the overall technical feasibility of the approach was confirmed.

2. EXPERIMENTAL PROCEDURE

For the spectroscopic part of the work, an Ar^+ laser was used as a radiation source. The 5145 Å line was selected and the power contained in this line was kept at 400 mW, after a warm-up period. As evidence became available that high intensity laser light interacted with the sample, the beam was attenuated with neutral density filters to about 10 mW at the location where it entered the sample. No deleterious effects were observed from the latter laser power. An optical filter in the beam removed spurious lines due to the Ar plasma.

A stainless steel (304) gasket, with a circular hole of 0.46 mm diameter and a thickness of 0.76 mm, served as the sample container. Total amount of sample was 0.13 μl , which would correspond to an energy content of about 2.6 joule for the stoichiometric mixture; based on numbers quoted by Fishman and Broadwell (3). Pressure was applied to the sample by means of two diamonds. These 1/5 carat diamonds were of the type IIB, as these are relatively free of spectral contaminations in the region of interest. Width of the diamond faces was 0.8 mm. The diamonds were epoxied onto steel rockers which could rotate in steel cradles; these rockers allow the diamond faces to be aligned with each other and also with the gasket surface. The diamonds were spectrally characterized by a strong, relatively narrow peak at 1330 cm^{-1} and a minor, broad structure centered around 2500 cm^{-1} , as shown in

Figure 1. Pressure is applied by tightening a nut which presses the cradle mounts together. Pressures up to about 30 kbar have been attained with this particular diamond anvil cell. However, in the present experiment, pressures were kept in the 2-10 kbar range.

A steel collar around the cell was attached to a heater element. For the temperature determination a copper-constantan thermocouple was inserted between the gasket and a free surface of a diamond, with its junction within 2 mm of the sample. Temperatures up to 120°C were achieved with this arrangement; the time to reach a stable temperature was about 45 minutes and the absolute precision of the temperature measurement was $\pm 2^\circ\text{C}$. An ice-bath with an identical thermocouple in series with the first one, served as a temperature reference. The temperature was varied by changing the voltage across the heater element.

The pressure in the cell was determined by the pressure shift of the ruby 14405 cm^{-1} line (4-6). A ruby chip, whose dimensions were kept below 50 μm , was immersed in the sample. Pressure measurements were made at ambient temperature, the coefficient used in the calculations was $-0.755 \text{ cm}^{-1}/\text{kbar}$. It was verified that, in the pressure and temperature range utilized, temperature and pressure shifts of the 14405 line were linearly superimposable, the temperature coefficient being $-0.149 \text{ cm}^{-1}/\text{K}$ (7).

The monochromator used was a Spex 1401 double monochromator with the slits set at 200 μm , giving a resolution of approximately 5 cm^{-1} . An RCA-C31034 photomultiplier, kept cool with a thermoelectric cooler, was used to detect the light; the signal from the photomultiplier was processed by a Pacific photon counter, Model 126, and displayed on a chart recorder.

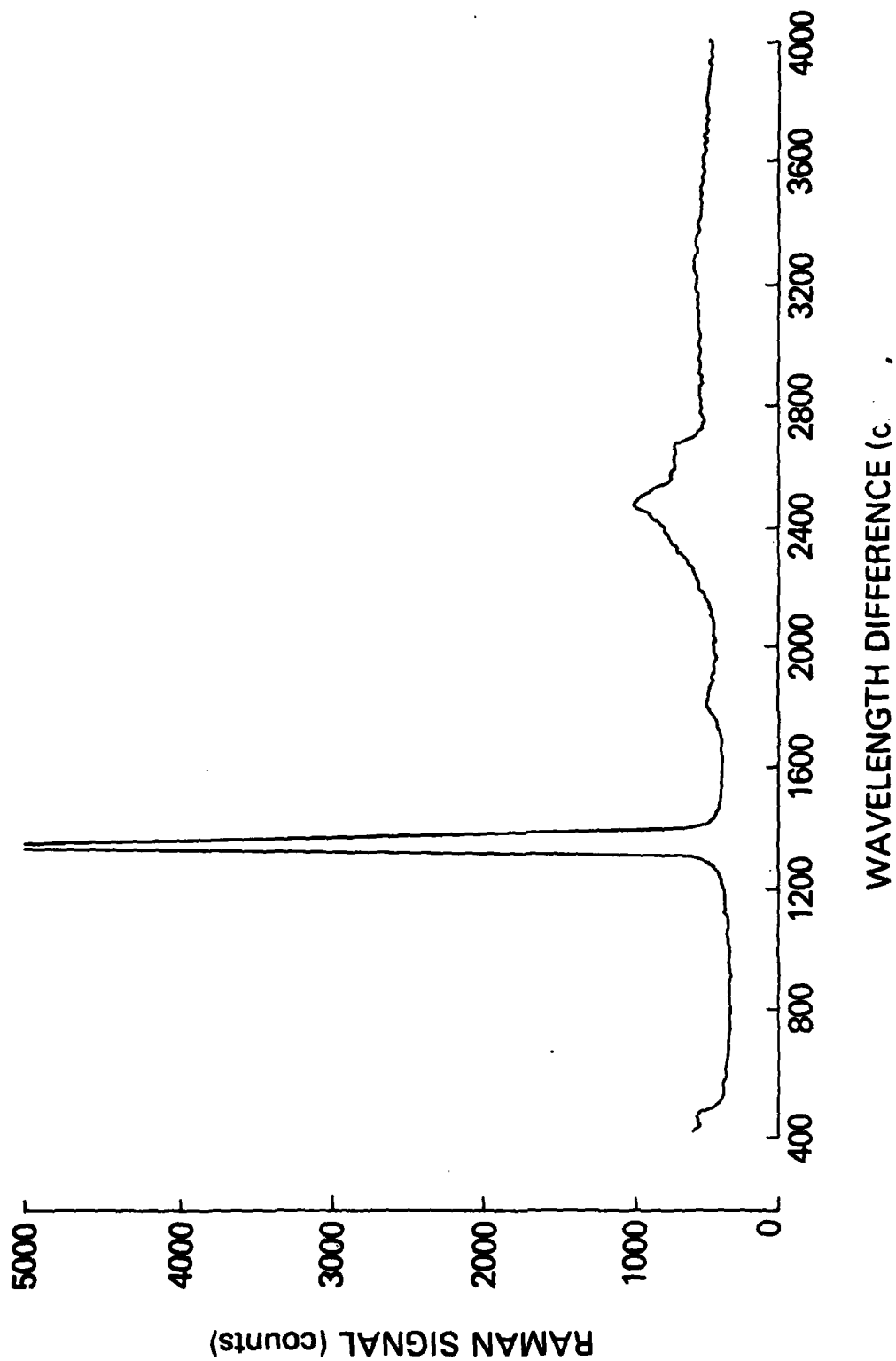


Figure 1. Raman spectra from the diamond anvil cell filled with a sugar solution having a refractive index of 1.4728, matching that of an 11 molar HAN-H₂O mixture.

For some experiments at ambient pressure and unconfined conditions, a glass syringe was used instead of the diamond anvil cell. A small oven surrounded the syringe and a copper-constantan thermocouple in conjunction with a second, identical thermocouple and ice bath was used to determine the temperature.

Electron-beam heating was attempted using a linear accelerator, delivering a 40 MeV electron beam. This beam impinged on the aluminum windows of a closed cell which contained 0.7 cm³ of 11 molar HAN in H₂O. A calorimeter in front of the entry window was used to determine the total energy delivered to the sample. A chromel-alumel thermocouple with a wire diameter of 25 μm was used to monitor the temperature. As this thermocouple was immersed in the fused HAN salt, the compatibility of the thermocouple material and the HAN had been established prior to the experiment.

3. RESULTS AND DISCUSSION

(a) Assignments

In order to obtain the assignments of the 11 molar HAN-H₂O mixture, various Raman spectra of this mixture and of related compounds were recorded. The samples were contained in a glass capillary at ambient pressure and temperature.

From comparing the spectrum of 11 molar HAN with that of deionized H₂O, as shown in Figure 2, it is immediately obvious that the structure between 3100 cm⁻¹ and 3700 cm⁻¹ is mainly due to H₂O. Similarly, a structure between 2200 cm⁻¹ and 2800 cm⁻¹ in the spectrum of deuterated HAN is due to D₂O, as follows from comparing the spectra shown in Figure 3. Those structures are related to the O-H stretch mode in the water molecule, respectively related to the O-D stretch mode in the deuterated case (8-13).

A broad peak around 3000 cm⁻¹ is also found in the spectra of hydroxylammonium hydrochloride (HAC) and isopropylammonium nitrate (IPAN), as shown in Figure 4, and therefore seems to reflect the presence of the NH₃ complex; in addition, the spectrum of ammonium nitrate (NH₄NO₃), also shown in Figure 4, does not have similar features in the 2700 cm⁻¹ to 3000 cm⁻¹ region. According to the literature, the region 2700-3000 cm⁻¹ is the location of the NH₃ stretch frequency (14).

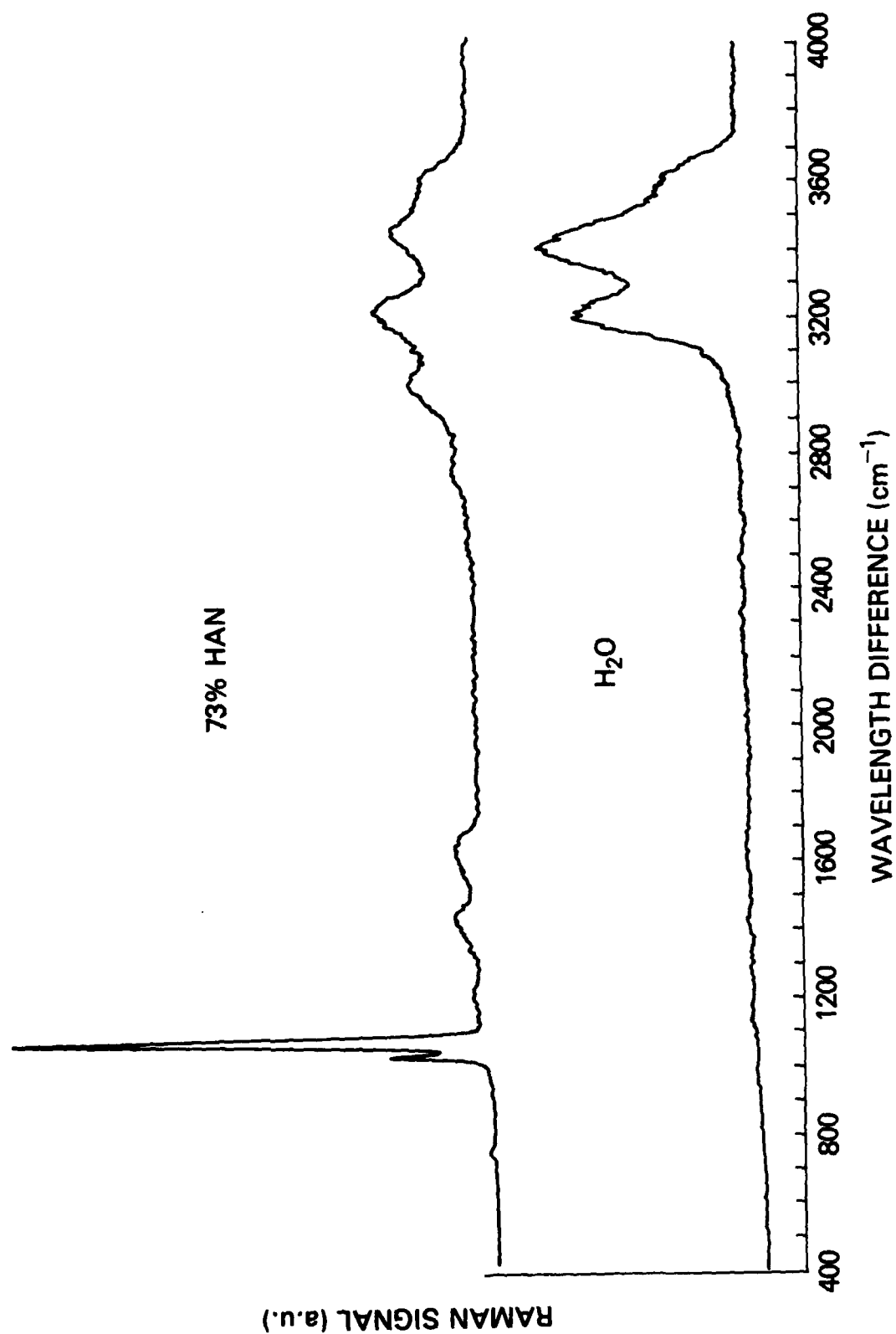


Figure 2. Raman spectra of HAN and H₂O. Samples were contained in a glass capillary at ambient conditions.

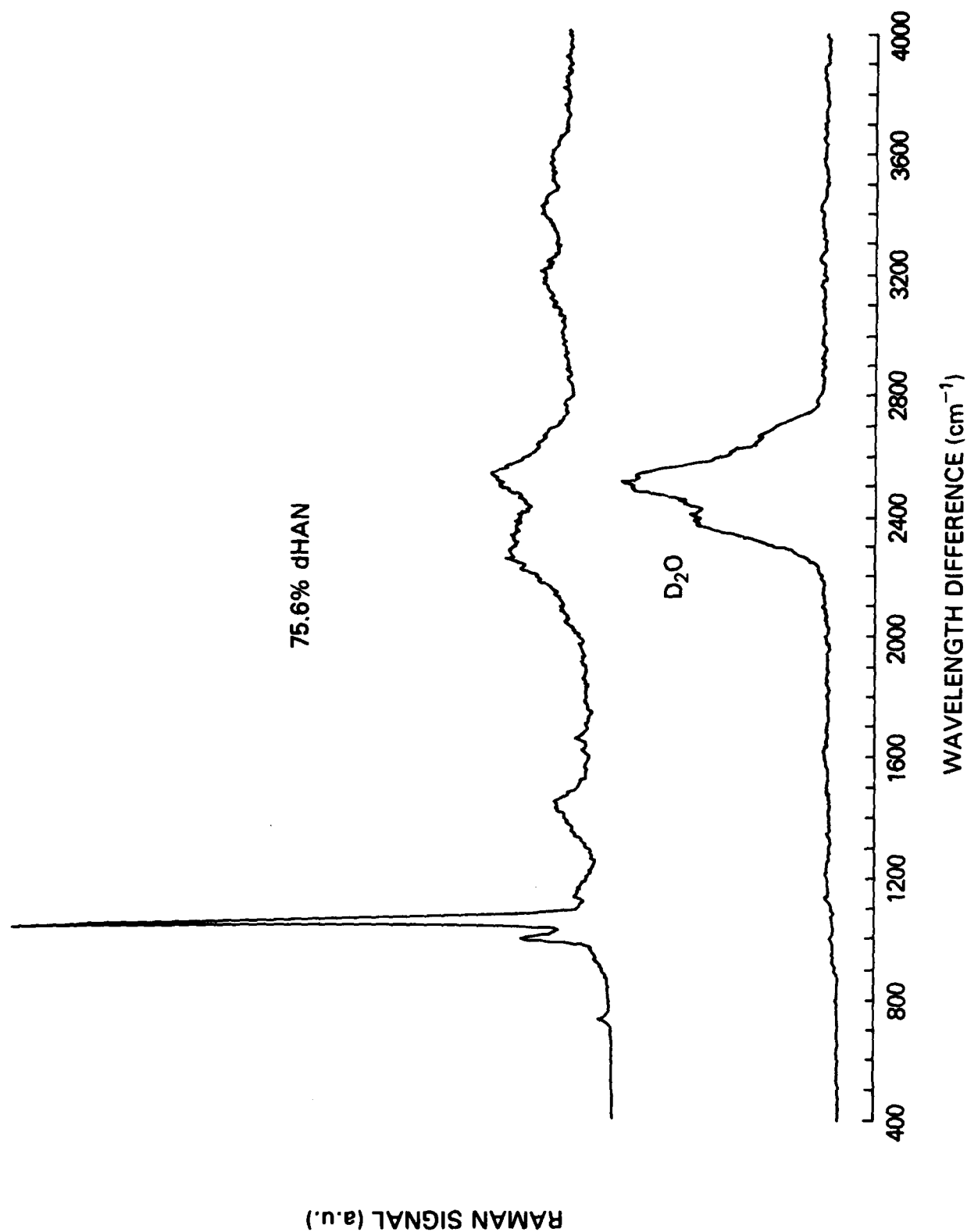


Figure 3. Raman spectra of deuterated HAN and D₂O. Samples were contained in a glass capillary at ambient conditions.

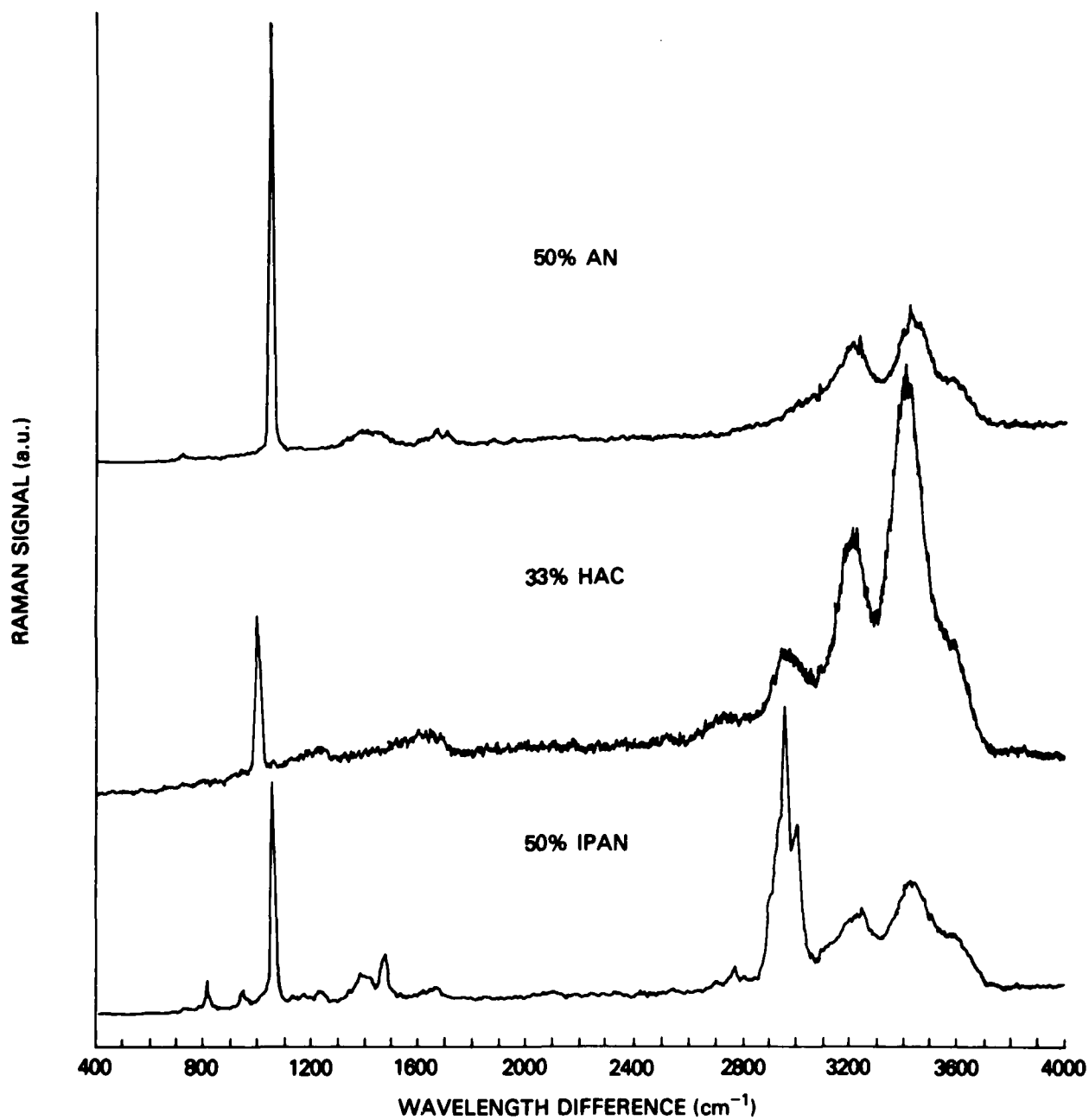


Figure 4. Raman spectra of AN, HAC and IPAN. Samples were contained in a glass capillary at ambient conditions.

A shoulder around 2730 cm^{-1} in the spectrum of HAN is also found in the spectrum of HAC, but is absent from the spectrum of AN; the dHAN case shows a similar shoulder around 2050 cm^{-1} . This shoulder therefore seems to be associated with the O-H group attached to the positive ion.

NH_3 frequencies are also known to occur at somewhat higher wavenumbers, therefore, NH_3 frequencies might also contribute a minor fraction of the structure between 3100 cm^{-1} and 3700 cm^{-1} .

In the dHAN case, a weak structure is observed between 3200 cm^{-1} and 3600 cm^{-1} . This structure is by some authors attributed to NH stretch frequencies (15); this would mean, however, that either this structure is hardly affected by deuteration, or our samples were not completely deuterated, or possibly both.

A broad structure around 1620 cm^{-1} is also found in the spectra of HAC, NH_4NO_3 , and IPAN, as shown in Figure 4. A small, rather narrow feature occurs in the dHAN spectrum at a slightly higher frequency (1650 cm^{-1}). Some authors list NH frequencies for this region (14,15).

The spectra of HAN and dHAN, as well as the spectra of AN and IPAN, all show a broad feature in the region of 1400 cm^{-1} . Each of these samples contains the NO_3^- ion in the solvated state, and it therefore seems justified to attribute this feature to the NO_3^- ion. An analogous observation can be made for two other features in the spectra of each of the above mentioned four compounds, namely: a sharp, predominant line at 1050 cm^{-1} and a minor, but obvious line at 730 cm^{-1} . The occurrence of this triplet has also been noted by Hester and Plane (16) and attributed by them to complexation of the NO_3^- ions in concentrated solutions. This

complexation is assumed to distort the symmetry of the ion and thus give rise to additional frequencies, which are approximately symmetrically located at distances of 350 cm^{-1} on each side of the main line at 1050 cm^{-1} . The latter line is assigned to the symmetric stretch mode of the NO_3^- ion (16-18).

A sharp peak occurs at 1010 cm^{-1} in the spectra of both the HAN and the HAC. This peak appears to be downshifted by about 20 cm^{-1} in the spectrum of the deuterated HAN. Various authors have attributed this feature to the N-OH stretch mode (14), which is consistent with our observation that the peak occurs in the HAN- and HAC spectra, but is absent from the AN and IPAN spectra.

A minor hump around 1200 cm^{-1} is found in the HAN spectrum; it appears to be downshifted by 50 cm^{-1} in the dHAN spectrum. The origin of this feature is not obvious and might also be connected with NH modes, like the feature around 1620 cm^{-1} .

In conclusion, all of the main features observed in the Raman spectrum of HAN have been assigned with fair certainty, and are summarized in Table 1.

(b) Pressure and Temperature Dependence

In this part of the experiment, the diamond anvil cell was filled with an 11 molar $\text{HAN-H}_2\text{O}$ mixture. Raman spectra in the range $400\text{-}4000\text{ cm}^{-1}$ were taken, the cell being at various pressures and temperatures. These spectra were complicated by features from the diamond, which tend to obscure sample features in some regions, as is evident from Figure 1.

In Figure 5 a sequence of spectra is shown taken at pressures in the 4-7 kbar range, and temperatures up to 79°C . This variation in the pressure range is partially due to changing stresses

Table 1. Assignments for the Raman Spectrum of HAN.

Assignment	Wavenumber (cm^{-1})
NO_3^- Deformation	730
N-OH Stretch	1010
NO_3^- Symmetric Stretch	1050
OH Bend (From HAN), NH_3 Rock	1190
Asymmetric NO_3^- Stretch	1420
NH_3 Deformation	1620
OH Stretch (From HAN)	2730
NH_3 Stretch	3000
OH Stretch (From H_2O)	3200
OH Stretch (From H_2O)	3430
OH Stretch (From H_2O)	3600

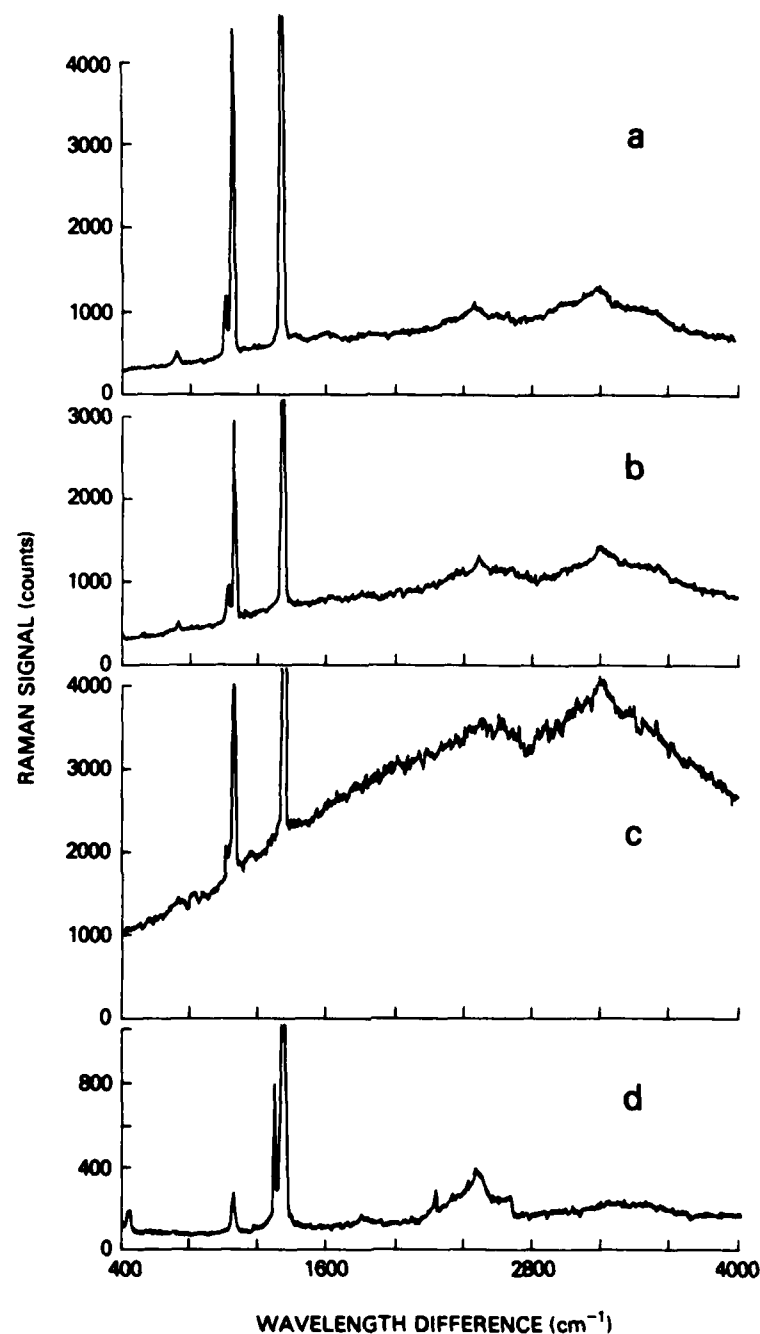


Figure 5. Raman spectra from a sample of 11 molar HAN-H₂O mixture at various pressures and temperatures. Spectra were taken in the order a, b, c, d, spread out over three days, in which the cell was repeatedly cooled down to ambient temperature. No external pressure adjustments were made other than the initial pressure setting of a.

- a. Sample at 5.9 kbar and ambient (22°C) temperature.
- b. Sample at 5.9 kbar and 65°C.
- c. Sample at 7.2 kbar and 79°C.
- d. Sample at 4 kbar and ambient temperature.

in the sample gasket and other cell components when the temperature of the cell is varied. No external adjustment of the pressure was made. These spectra were taken sequentially in the order a-d, spread out over three days, in which the cell was repeatedly brought up to the quoted temperature and subsequently cooled down to ambient temperature. Many more spectra were taken of this sample during these three days; these spectra represent various intermediate stages. The spectra shown represent typical stages in the development.

Figure 5a depicts a Raman spectrum of the sample at ambient temperature ($\sim 22^{\circ}\text{C}$) and at a pressure of 5.9 kbar. This spectrum does not differ substantially from the HAN spectrum of Figure 2, the main differences being an enhanced background and the presence of features due to the diamond at 1330 cm^{-1} and around 2500 cm^{-1} . The OH stretch peaks in the $3100\text{--}3200\text{ cm}^{-1}$ region appear to be more smeared out in the pressurized case. In Figure 5b the temperature of the cell was set at 65°C . An increase in background signal and consequently a drowning of the smaller features in the noise signal generated by this background is observed. The increase in the background and associated noise signal is quite dramatic in Figure 5c, where the temperature was at 74°C . By the time the spectra of Figure 5c were taken, the sample had been in the cell for several days and had undergone several heating-cooling cycles. However, the transition shown in the sequence of spectra of Figure 6 took place within an hour or less. In these spectra a collapse of the background is observed, together with the appearance of a new feature at 1290 cm^{-1} , superimposed on the red shoulder of the diamond line. Simultaneously, a disappearance of the NO-stretch feature at 1010 cm^{-1} has occurred.

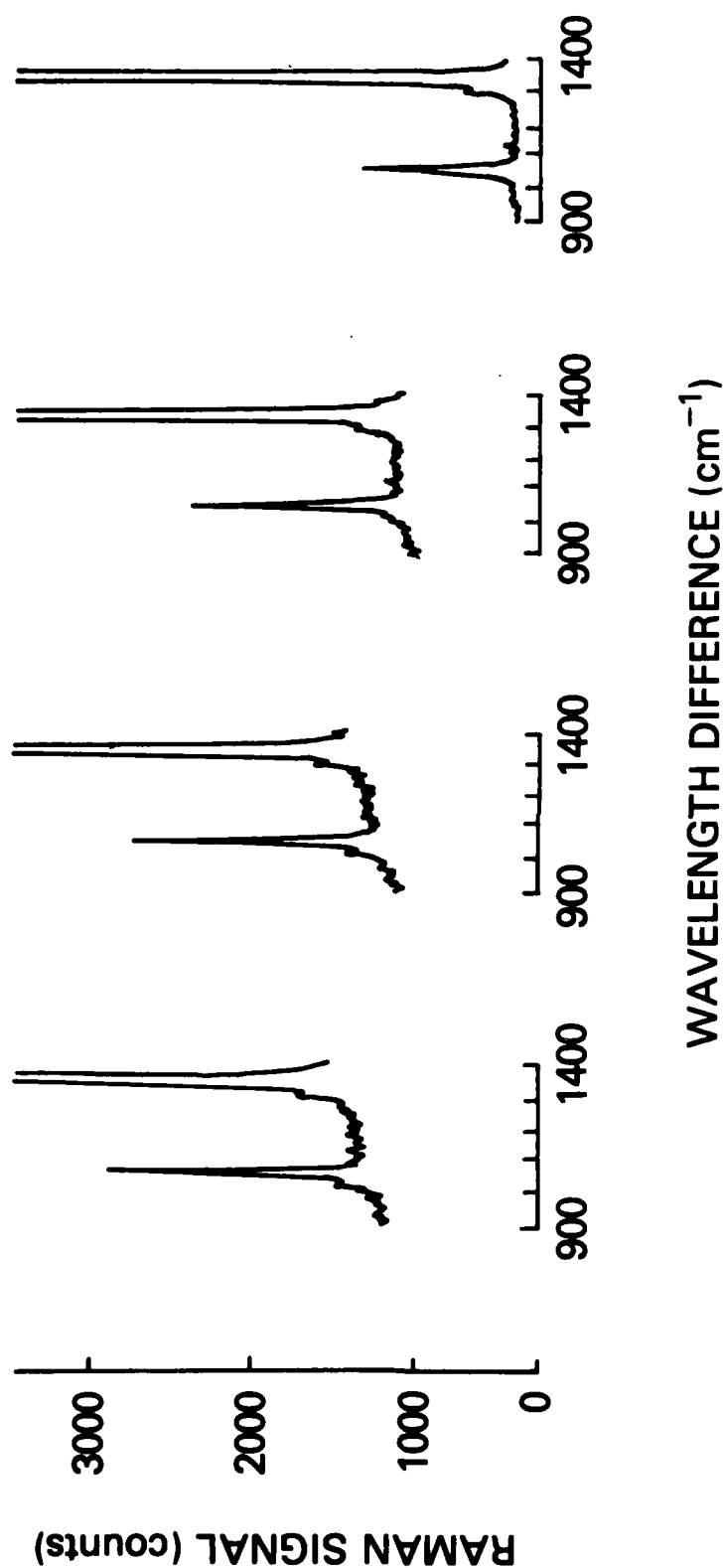


Figure 6. Detailed transition in the 900-1400 cm⁻¹ region of 11 molar HAN-H₂O mixture to the reacted state. Spectra were taken in the order a, b, c, d. Pressure was 7.2 kbar, temperature was 79°C. Total time span is approximately 1 hour.

The final spectrum is shown in Figure 5d. A substantial decrease in the features due to the nitrate ion is obvious. The appearance of new features with narrow line widths at 1290 cm^{-1} and 2224 cm^{-1} is remarkable. On an absolute scale, the features due to the OH stretch modes have diminished by a factor of about 6. Also, the pressure at the time the spectrum from Figure 5d was taken was down to about 4 kbar.

On other occasions, similar occurrences were observed, the main differences being that (1) the decrease in the signal of the nitrate ion was not as drastic and (2) the pressure drop was different. However, the appearance of the 1290 and 2224 cm^{-1} feature was observed, as was the disappearance of the 1010 cm^{-1} feature and also the growth and collapse of the background signal.

For the enumerated effects to occur, a pressure of about 6 kbar seems to be necessary in combination with a temperature above 70°C , as combinations at lower values of these parameters did not yield the reported results.

From the fact that the observed changes in the spectra persisted when pressure and temperature of the cell were brought back to their initial values, it can be concluded that a chemical reaction took place, rather than a phase change.

Inhomogeneities in the reacted sample were evident from spectra taken at different locations in the cell. These spectra showed variations up to a factor of 7 in the peak height ratio of the 1050 cm^{-1} line and 1290 cm^{-1} line.

On observing the cell with its reacted contents through a microscope, numerous bubbles in various sizes were visible, as opposed to prereaction conditons, when a clear and homogeneous

sample was observed. When the cell was opened, it appeared empty, with a miniscule deposit on the diamond faces. This finding seems to favor the hypothesis that most of the reaction products are gases under ambient conditions. A watery solution containing the deposit on the diamond faces was analyzed in an electron spin resonance apparatus in the range 3-4 kGauss, but without result. Probably not enough sample was present to produce a discernible ESR signal.

In an effort to observe the reaction under less stringent conditions, and with less experimental difficulty, an 11 molar HAN-H₂O mixture was heated in a glass syringe at ambient pressure. A thermocouple attached to the syringe monitored the temperature; a stationary temperature was reached in approximately 45 minutes. Similar to the experiments with the diamond anvil cell, a rise in the background signal with temperature was observed. However, when the temperature reached approximately 70°C, the mixture became unstable, and could not be contained in the syringe.

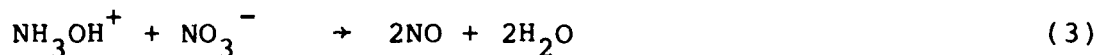
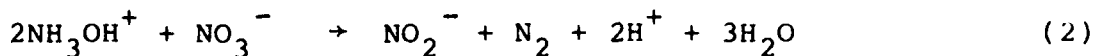
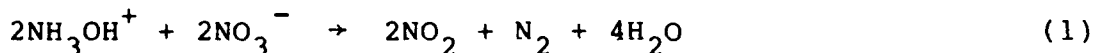
An observation which can be made from our results is that the 1290 cm⁻¹ and 2224 cm⁻¹ peaks closely match features due to stretch modes from nitrous oxide, N₂O.

The occurrence of nitrous oxides in certain reaction stages was also postulated by Fishman and Broadwell (3) in analyzing the results which Ed Fisher from Calspan Corporation obtained in a study of the combustion of HAN/IPAN mixtures. The "chemical shutter," due to NO₂ formation, as conjectured by the above authors, might be related to the observed increase and subsequent rapid decline in the background signal in our experiments.

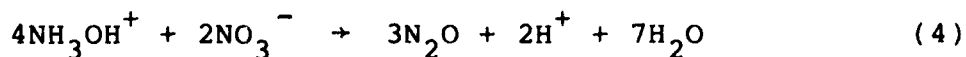
The formation of NO and NO₂ (among other things) was also observed by Kaufman and Koski (2) when decomposing HAN under confined conditions and 180°C.

The fact that in the high pressure case the reaction apparently slows down compared with ambient conditions might be related to an increase in the viscosity of the mixture. The pressure dependence of the viscosity of liquids is fairly substantial in many cases and is known to affect the rates of chemical reactions, especially those of rapid reactions with low activation energies (19). This means that high pressure measurements of the type reported here may offer an excellent opportunity to study the details of reactions on a convenient time scale.

Various models have been proposed for the decomposition of HAN. A number of reactions mentioned by Klein (1) is



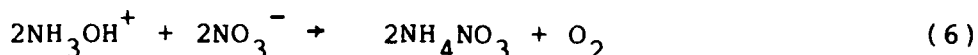
These reactions would explain the disappearance of features due to NH_3 , NO_3^- and the NO group attached to the HAN cation. An N_2O producing reaction is



Because of a difference in experimental conditions, here the analogy between Klein's and our experiments breaks down. However, a reaction mentioned by Kaufman and Koski (2) produces additional NO_2 :



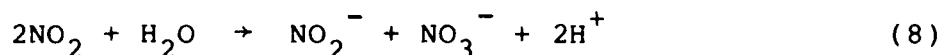
The minuscule, solid deposit observed on the diamond face might be due to the formation of ammonium nitrate (AN)



the oxygen would readily react to give NO_2 :



which would produce additional nitronium ions:



as NO_2 is unstable in the presence of H_2O .

From reactions 1-8 it appears that the main candidates for the observed reaction products are N_2 and NO , suspended in H_2O . A contribution from the symmetric stretch mode of NO_2 might be superimposed on the 1290 cm^{-1} line from the NO stretch mode, or swamped by the diamond line at 1330 cm^{-1} . The instability of NO_2 might also be related to the observed increase and collapse of the background in the spectra of Figure 5.

(c) Electron Beam Heating

Several attempts were made to obtain initiation curves with electron beam heating. Problems were encountered due to the viscosity of the sample, which tended to make filling of the cell difficult, especially in combination with the presence of a delicate ($25 \text{ }\mu\text{m}$) thermocouple in the cell. However, the curve of Figure 7 represents results from one of the successful attempts.

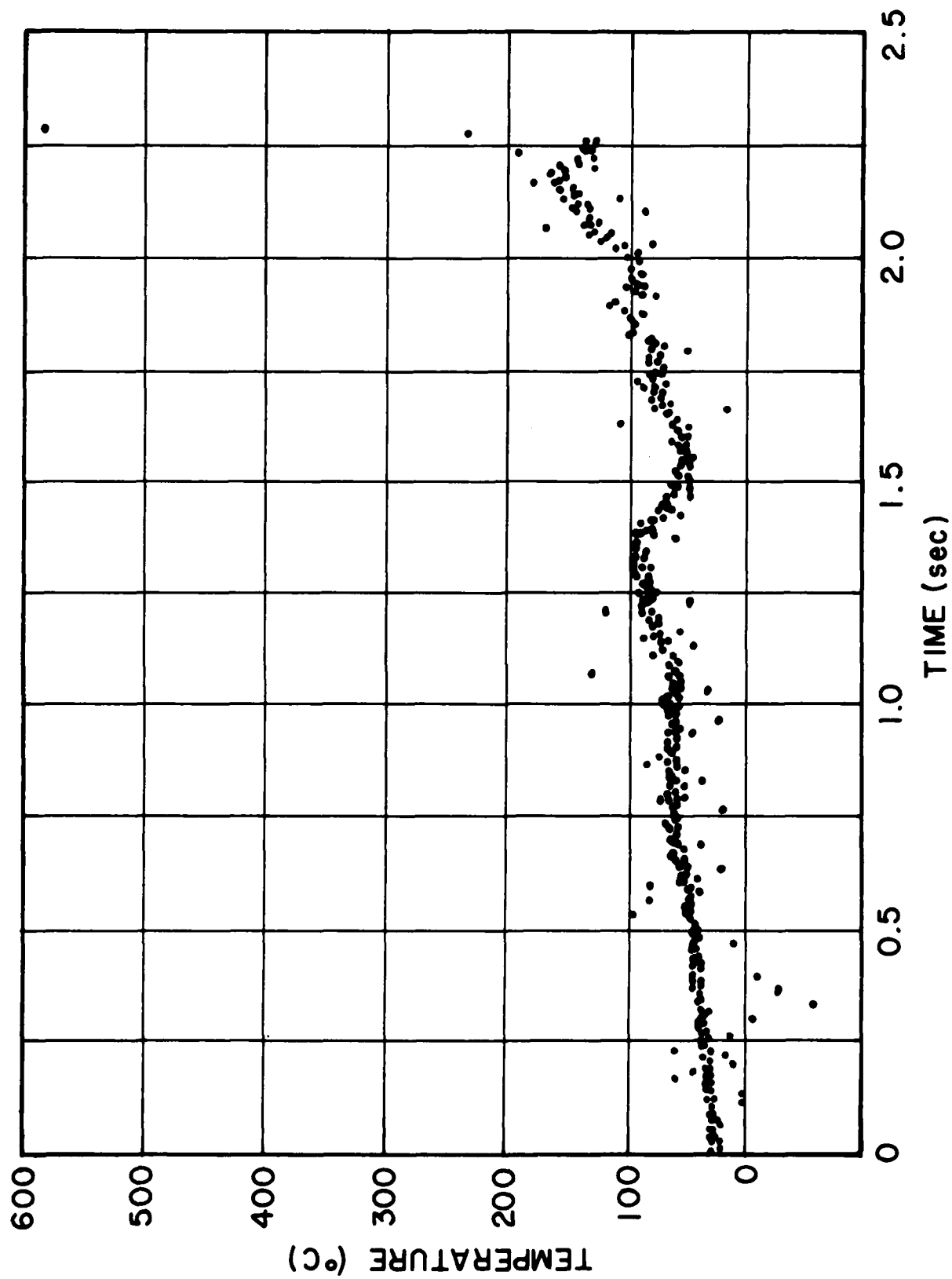


Figure 7. Temperature versus time profile for a confined 11 molar HAN-H₂O mixture, when this mixture is exposed to a 40 MeV electron beam.

The sample, consisting of an 11 molar HAN-H₂O mixture in about 0.7 cm³, is seen to heat up to about 130°C prior to initiation, which value is in approximate agreement with known values for mixtures of HAN and aliphatic amines (1). The temperature of the calorimeter rose practically linearly from 22°C to approximately 180°C in the time shown in Figure 7. The energy absorbed in this experiment was 42 cal/cm³.

The negative slope of the curve between 1.4 and 1.6 sec could be related to vaporization of H₂O from the mixture. The desiccated sample is expected to be unstable (1), which would be reflected in the irregular behavior between 1.6 and 2.3 sec.

The scattering in the temperatures, observed in Figure 6, is probably related to electrical grounding problems of the thermocouple, which tends to pick up noise from the electron beam.

4. CONCLUSIONS AND RECOMMENDATIONS

The evidence of reactions as observed in HAN samples under conditions at high pressures and above ambient temperatures could contain a clue to the cause of accidental detonations. These reactions occurred at pressures and temperatures which are in the range of those occurring in guns. The fact that these reactions seem to appear on extended time scales compared with reactions under unconfined conditions might be related to a pressure effect on the sample viscosity. Further work to confirm this hypothesis would be useful. A stretched time scale simplifies the study of intermediate stages in the reaction.

As discussed in Section 3b, the observed spectral changes exhibit minor but obvious differences between various occurrences. This could in part be related to spatial inhomogeneities of the reacted cell contents, but seems to be real for another part. Varying conditions, such as pressure and temperature, will presumably influence the degree to which the reactions proceed. This in turn might yield information on the nature of the reactions and therefore merits pursuing.

Results from electron beam heating experiments suggest the presence of processes taking place prior to initiation. Subsequent experiments are necessary to identify these processes and possibly link the results with those from Raman spectroscopy.

5. REFERENCES

1. Nathan Klein, "Preparations and Characterization of Several Liquid Propellants,": Technical Report ARBRL-TR-02471, Ballistic Research Laboratory, Aberdeen Proving Grounds, Maryland.
2. Joyce J. Kaufman and Walter S. Koski, "Study of the Hydroxylammonium Nitrate-Isopropylammonium Nitrate Reaction," The Johns Hopkins University, Baltimore, Maryland.
3. E. Fishman and J. E. Broadwell, "Liquid Propellant Gun Performance Analysis," Defense and Space Systems Group, TRW, Redondo Beach, California.
4. J. D. Barnett, S. Block, and G. J. Piermarini, "An Optical Fluorescence System for Quantitative Pressure Measurement in the Diamond Anvil Cell," Rev. Sc. Instr. 44, 1 (1973).
5. G. J. Piermarini, S. Block, J. D. Barnett, and R. A. Forman, "Calibration of the Pressure Dependence of the R_1 Ruby Fluorescence Line to 195 kbar," J. Appl. Phys. 46, 2774 (1975).
6. G. J. Piermarini and S. Block, "Ultrahigh Pressure Diamond Anvil Cell and Several Semiconductor Phase Transition Pressures in Relation to the Fixed Point Pressure Scale," Rev. Sc. Instr. 46, 973 (1975).
7. Stephanie L. Wunder and Paul E. Schoen, "Pressure Measurement at High Temperatures in the Diamond Anvil Cell," J. Appl. Phys. 52, 3772 (1981).
8. G. E. McGraw, D. L. Bernitt, and I. C. Hatsune, "Vibrational Spectra of Isotopic Nitric Acids," J. Chem. Phys. 42, 237 (1965).
9. G. E. Walrafen, "Raman Spectral Studies of the Effect of Solutes and Pressure on Water Structure," J. Chem. Phys. 55, 768 (1971).

10. Babu Ram S. Sengar and Gopal Narain, "Magneto-chemistry and Infrared Spectra of Ammonium and Primary Aliphatic Amine Complexes of Copper (II) Chromate," Bull. Chem. Soc. Japan 48, 1087 (1975).
11. Norman B. Colthup, Lawrence H. Daly, and Stephen E. Wiberley, "Introduction to Infrared and Raman Spectroscopy," Academic Press, 1975.
12. Y. Yeh, J. H. Bilgram, and W. Kanzig, "Raman Spectra of Super-cooled H_2O from 0 to $-21^\circ C$," J. Chem. Phys. 77, 2137 (1982).
13. Paul A. Giguere and J. G. Guillot, "Raman Spectrum of H_3O^+ Ions in Aqueous Acids," J. Chem. Phys. 86, 3231 (1982).
14. D. L. Frasco and E. L. Wagner, "Interpretation of the Infrared Spectra of the Solid Hydroxylammonium Halides," J. Chem. Phys. 30, 1124 (1959).
15. R. E. Nightingale and E. L. Wagner, "The Vibrational Spectra and Structure of Solid Hydroxylamine and Deutero-Hydroxylamine," J. Chem. Phys. 22, 203 (1954).
16. R. E. Hester and R. A. Plane, "A Raman Spectrophotometric Comparison of Interionic Association in Aqueous Solutions of Metal Nitrates, Sulfates and Perchlorates," Inorg. Chem. 3, 770 (1964).
17. D. E. Irish and G. E. Walrafen, "Raman and Infrared Spectral Studies of Aqueous Calcium Nitrate Solutions," J. Chem. Phys. 46, 378 (1967).
18. D. E. Irish, A. R. Davis, "Interactions in Aqueous Alkali Metal Nitrate Solutions," Can. J. Chem. 46, 943 (1968).
19. K. E. Weale, "Chemical Reactions at High Pressures," E. & F. N. Spon Ltd, London, 1967, p. 22.

END

FILMED

9-83

DTIC