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COMBUSTION CHARACTERISTICS OF CRYSTALLINE SOLID OXIDIZERS AND LATTICE DYNAMICS IN AMMONIUM PERCHLORATE

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Final Report by

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Introduction

This report presents the final results of two projects, a laser Raman and a mass spectral study, of the solid propellant oxidizer, ammonium perchlorate. The work was supported under the grant AF-AFOSR-71-2131. The grant was begun with Dr. E. E. Hackman, III, of Thiokol Corporation, Elkton, MD, and Dr. H. C. Beachell of the University of Delaware as principal investigators. Neither Dr. Hackman nor Dr. Beachell is any longer under the employ of these respective organizations, and neither has been engaged in propulsion research after January, 1973. In October, 1972, Dr. T. B. Brill became the principal investigator, and he felt that some other useful contributions could be made by carrying the research in a different direction than was proposed by Beachell and Hackman.

Under the original title, "Combustion Characteristics of Crystalline Rocket Oxidizers," a high resolution mass spectrometry study of UHP-AP was carried out and is described in Section I. This is primarily the work of Drs. Beachell and Hackman and Mr. Henry Hesser. With the change in principal investigators, the title of the project was modified to reflect the new direction of the research. The title "Lattice Dynamics in Ammonium Perchlorate" and the goals of the program were changed with the approval and encouragement of AFOSR personnel. The new intent of the project was to provide a concrete spectroscopic foundation upon which to base a fundamental model for the initial steps occurring in the degradation of solid AP. The results are described in Section II and are the work of Dr. T. B. Brill and Mr. F. Goetz. Each of these two sections is a complete body with its own abstract, introduction, results and discussion, experimental section, and bibliography. Most of the work reported here has appeared in literature papers, meeting presentations and annual reports to the AFOSR.

During the final few months of this grant period (February - June 1976), we began spectroscopic studies of nitramine propellants. These will be reported in the future under the grant AFOSR-76-3055.

Section I. Combustion Characteristics of Crystalline Oxidizers

Abstract

Time-of-flight and high resolution mass spectrometry of UHP-AP and its deuterated derivative were examined in an effort to identify some of the key decomposition species as proposed in thermal decomposition mechanisms. Of particular interest is the sure detection of HNO, the hydrides of nitrogen and the oxides of chlorine. HNO (mass 31) was found as a minor component at temperatures above 80°C and the species was confirmed by the presence of DNO (mass 32) when the deuterated compound was examined. It is considered highly improbable that HNO could have occurred by reactions other than surface thermal reactions. High resolution spectra were used to separate O_2^{2+} and O^+ from NH_2 at mass 16. The presence of NH_2^+ was confirmed along with NH_4^+, NH_3^+ and NH^+. $HClO_4^+$, Cl^+ and all the simple oxides of chlorine were found but Cl_2^+, $HClO^+$, $HClO_2^+$, $HClO_3^+$ and ClO_4^+ were not detected. Also not detected were N_2^+, N_2O^+ and NO_2^+ in the condensed phase. No parent $NH_4ClO_4^+$ was present. Evidence of strong exothermic reactions in the condensed phase was found, and this supports theories stating that this is the major source of energy to help balance the endothermic requirements for vaporization to sustain combustion.

Section I. Combustion Characteristics of Crystalline Oxidizers.

A. Introduction

For several decades there has been interest in clearly defining the important energy absorption, generation and transfer steps during solid propellant combustion.[1,2] Better understanding should lead to better control. Early simplified theories stated that ignition took place on a surface when a critical temperature was reached. The flame zone that was then established above the surface provided the sustaining energy by conduction and radiation for steady-state surface regression. For solid propellants there are many strongly exothermic reactions that can be proposed to take place in the flame zone to support such theories. Oxidation of hydrocarbons to CO_2 and H_2O and of aluminum to Al_2O_3 are good examples.

The experimental difficulties associated with detecting and measuring initial and midcourse reaction products, gas, and solid zone dimensions and temperature gradients for a burning solid propellant are numerous. In the late 1950's the final reaction products for simple systems were readily calculated by computer. By the mid-1960's reliable final product distributions were being calculated for complex propellant mixtures and were being confirmed as well as possible by chemical and spectral analyses.

The great experimental difficulty lies in capturing and identifying the proper quantity of a species before a loss of temperature or pressure, or before reactions with other species or with surfaces cause a change in mole fraction. Gas temperatures range from 2000 to 3500°K; the zones being observed range from 10^0 to 10^3 μm. The surface being observed regresses linearly at rates in centimeters per second and the ambient pressure is usually between 20 and 200 atm.

The high temperatures severely restrict the range of materials and processes usable for sampling and analysis. The minute dimensions being observed and the rapid movement of the reference vastly complicate the study of a given plane in the reacting system, while the customary high pressures reduce the dimensions and materials usable for viewing and spectrometry.

To circumvent some of these difficulties, spectral analyses of individual decomposition zones have been made at much lower temperatures and pressures; most of the effort has been concentrated on one material: ammonium perchlorate. This research deals with primary reactions occurring largely at the decomposing surface. Microcinematography of burning ammonium perchlorate surfaces and scanning electron microscopy of quenched surfaces have shown that important reactions other than sublimation are taking place at, and somewhat below, the surface.[3] Of most interest is the porous or noncrystalline surface zone, that even shows evidence of a liquidlike phase. This evidence of some condensed phase reactions supports some radiation heat transfer calculations. They showed[3] that the flame zone could not have the requisite temperature and emissivity to transfer enough heat to the surface and thus satisfy the endothermic requirements of solids gasification or sublimation. This meant that conduction and heat generation in other zones must be important processes. Since there is strong convection or mass transport away from the surface, there would appear to be only limited molecular back-diffusion from hot gas to surface. This means that important exothermic reactions must be occurring in the condensed phase to at least partially satisfy the endothermic requirements for steady-state gasification.

Further interest in the condensed phase springs from the conviction that if overall combustion rates are to be tailored or altered, the condensed phase reactions are the slowest and are also probably rate limiting, and therefore the best point for study and attack. Chemical analyses have been made of quenched propellant surfaces. They have not been too rewarding since they indicate largely undecomposed products, as well as other products that could have been condensed from the gas phase during quenching. But, of course, during quenching, severe changes of state are taking place.

Another reason for great interest in surface reactions is the desire to get at the very earliest stages of decomposition. Key transient or intermediate species might be present and detectable in the condensed phase, but may rapidly disappear and be lost to detection in the gas phase.

A detailed theoretical analysis of AP decomposition by Jacobs and Pearson[4] calls for the formation of nitroxyl, HNO, as

$$NH_2 + O_2 \rightarrow HNO + OH; \quad \Delta H = -6.2 \text{ kcal/mol}$$

but NH_2 has not been detected as a decomposition product. They point out that the method of production of the oxides of nitrogen in AP decomposition was first theorized[5] on the basis of HNO reactions as

$$HNO + HNO \rightarrow H_2O + \underline{N_2O}; \quad \Delta H = -85.8 \text{ kcal/mole} \qquad (1)$$

unimolecular decomposition to give nitric oxide

$$HNO \rightarrow H + \underline{NO}; \quad \Delta H = 49.6 \text{ kcal/mol} \qquad (2)$$

and oxidation to give nitrogen dioxide

$$HNO + O_2 \rightarrow \underline{NO_2} + OH; \quad \Delta H = -6.6 \text{ kcal/mol} \qquad (3)$$

Guirao and Williams[6] proposed an additional reaction for HNO leading to nitric oxide

$$HClO_4 + HN \rightleftharpoons ClO_3 + \underline{NO} + H_2O; \qquad \Delta H = -11.79 \text{ kcal/mol}$$

They state that the above reaction is essential to their gas phase kinetic scheme, in the sense that the overall reaction rate would be much lower without the postulated step. They point out, however, that HNO has never been observed in AP decomposition or combustion experiments.

Wilde[7] has also pointed out the importance of HNO in the gaseous H_2-NO reaction.

B. Principles of Experiment

The method holding good promise for further definition of overall reaction mechanisms and of surface decomposition products is mass spectrometry. Small samples can be heated to temperatures near the surface temperatures obtained during combustion. Such temperatures can be supplied to a small sample near the inlet to a mass spectrometer by resistance heating of the sample container or by radiant heating of the surface. Under the ambient high vacuum conditions, any surface decomposition should be rapidly followed by vaporization. Unfortunately, in the case of ammonium perchlorate, rapid sublimation will also be taking place. Once in the gas phase, under high vacuum, the species have little chance of collision reactions. They are ionized in the electron stream and carried to the detector. Hopefully, this occurs with a minimum of fragmentation or cracking. Pai Verneker and Maycock[8,9] and others have warned that electron bombardment of the sublimate can also produce many species. However, the ionizing voltage can be varied over a wide range to see if drastic changes in species take place for different electron energies. Species requiring bimolecular reactions should not occur due to bombardment. Also, as a check on the mass spectrometer operation, analyses can be run under test conditions in which other quantitative methods can be used. Check methods have revealed good correlation. However, the mass spectrometer also identifies a number of highly reactive species that could not exist long enough to be detected by the slower methods.

At any rate, time-of-flight and high resolution mass spectrometry hold the promise of providing data on primary species that have long been postulated to occur, but have not been proven. Time-of-flight analyses have been used in the past and have detected some of the primary species.[8-11]

Pellett[11] has shown that much the same kinds of products occur whether decomposition is caused by laser flash heating or by conduction heating of the sample in the spectrometer heater.

To simplify the species identification problem, neat, high purity ammonium perchlorate (AP) and its deuterated derivative as the candidate propellants were used. AP has been found to burn as a monopropellant under a variety of physical conditions and thus makes an ideal test case.[12] It is also a major component of most solid propellants.

It has been postulated that the following primary products are capable of being formed in the condensed phase: NH_4, NH_3, ClO_4, $HClO_4$, and the other hydrides and oxides of nitrogen and oxides of chlorine. None of these occur as final products of combustion, either by chemical analyses or by thermochemical calculation. As stated above, Jacobs and Pearson and Guirao and Williams have postulated detailed mechanisms for the combustion process depending on the existence of HNO in addition.

Time-of-flight spectrometry was chosen to scan all mass/charge values, while higher resolution methods were used to study regions of interest. Prior work reported has not used high resolution spectra. In the future, further isotopic tagging is to be used to assure separation of species with similar mass/charge values. Future work will also be devoted to anionic and cationic changes to the candidate propellant material. Mack and Guillory[13-15] have initiated some of this work, which will allow study of the reactivity of a variety of species to help strengthen the validity of the models proposed.

The usual combustion testing environment for ammonium perchlorate as a single crystal monopropellant has been about 65 atm in a bomb pressurized with nitrogen at about 25°. Under these conditions, the linear burning rate is about 1 cm/sec. The calculated equilibrium gas temperature is 1130°, the most prominent gas species being H_2O, O_2, HCl and N_2, Dode[16] and Levy[17] have partially confirmed the products by chemical analyses. Attempts at measurement have indicated that this temperature might be as low as 1000°, probably due to nonequilibrium conditions and mixing with surrounding cooler gases.

The surface temperature is known from photographs to be well beyond the orthorhombic-to-cubic phase transition temperature of 240° and is probably close to the fast decomposition temperature recorded by differential thermal analysis of 300 to about 450°, depending strongly on the purity of the AP. Apparently, at temperatures greater than about 300°, the steady-state, self-sustaining decomposition reaction we call combustion can take over. Below that temperature, only about 30% of the AP decomposes, and then reaction stops. Maycock[8] has proposed a theory for this behavior. It was assumed that in working at temperatures of 100 to 300°, which is about the only practical range for examination by mass spectrometers, unless a flash heating method is used, is that the majority of the nonelectronic reactions will be the same, at least initially, while the 30% decomposition is taking place. The higher combustion temperatures simply remove surface decomposition products fast enough by vaporization to allow steady-state and complete decomposition to take place.

The pressure effect on combustion rates is very strong. In fact, single AP crystals of millimeter dimensions will not burn at all below about 10 atm. Reasons for this were analyzed by Olfe and Penner.[18] Even though some of the bases they used for calculations have been later found to be somewhat in error, their fundamental conclusions seem valid. In addition to the first effect one would predict--that of increasing reaction rates with increasing pressure due to greater reacting mass concentrations--the greatest effect is on the emissivity of the hot gases. Pressure would be expected to have little effect on the hot surface emissivity, but its value would be much larger than that of the gas cloud for small dimensions and low pressures. Olfe and Penner showed that radiation from the gas cloud to the surface for millimeter size dimensions increases tenfold when pressure is increased from 25 to 300 atm. Even more striking is the effect of increasing the simple geometric (not necessarily the physical size with all its irregularities) size of the burning surface from a square of 20 mm on a side to one of 20 cm on a side. This increases the radiant energy flux from gas to surface by about 30,000 times because the larger gas cloud above the larger surface has a larger beam length, which increases the gas cloud's emissivity greatly.

Thus, it can be seen that where a surface temperature of greater than 300° is required, the hottest source available is the hot gas, and its effectiveness can be increased several hundred thousandfold by nonchemical changes; factors like pressure and geometry are merely acting as a hotter source to stimulate and sustain surface reaction.

Therefore, it was assumed that in mass spectrometry, although the pressures used are very many times lower than those used in combustion, we are compensating for the lost thermal input from the gas phase by providing a direct input to the sample by the mass spectrometer heater.

It is realized that dissociative sublimation will be very strong under the mass spectrometer conditions. Here it was hoped that the high sensitivity of the devices being used will enable detection of the surface decomposition products amid an anticipated flood of ammonia and perchloric acid, the first products of decomposition.

It is interesting that most ammonium perchlorate containing propellants burn quite well, although very slowly, at 1 atm. This may indicate that, in comparison with pure AP, condensed phase exothermic reactions are stronger and more controlling for the propellant (as opposed to gas phase radiant heating). The likely candidates are the oxidations $C \rightarrow CO_2$ and $Al \rightarrow Al_2O_3$.

C. Equipment and Experimental Procedures

The three experimental features of the study were the mass spectrometers used, the special sample probe designed to get surface decomposition products to the detector with minimum delay, and the high purity of the sample materials.

Mass Spectrometers. Time-of-Flignt (TOF). For screening studies of wide temperature ranges, probe experimental work, and the like, two time-of-flight mass spectrometers were used. This gave an opportunity to compare background traces and to determine the presence of any equipment artifacts in the scans. The instruments were Bendix Model 12-101 spectrometers operating with ionizing currents of 70 eV. This level of electron energy gave good reproducible spectra. We realize that this energy level may be causing some cracking of the gas species in addition to causing ionization sufficient for detection. Room temperature is associated with only about 0.025 eV.

Expected surface temperatures of burning AP (400-900°) might be considered to have an energy level of approximately 0.10 eV. The energy associated with the highest gas combustion temperatures would be less than 0.33 eV, so the electron beam energies used in any spectrometer have a far higher potential for causing decomposition than the thermal stress applied. The critical difference between the electron beam and thermal energy is that there is usually only one electron impact with a species, but thermal radiation impinges on the species for a finite time.

Other investigators have already recorded the chlorine oxides spectra produced by hot $HClO_4$. Guillory and King refer to the spectra as a cracking pattern quite similar to the species we find from AP. Other investigators have used very low electron beam energies in the region of 20 eV. This is further discussed in section D.

The time-of-flight instruments had a capture sensitivity of 10^{-8} A. A Bendix Model 843 hot filament sample controller was used to control sample temperatures. A sample of approximately 10 mg was used. When the desired test temperature was reached and stabilized, a number of spectra were run until they were reproducible.

Time-of-Flight (TOF) Sample Probe. Sample orientation and thermal conditioning within the spectrometer are critical to reproducibility. The probe we used is discussed elsewhere.[19] In our studies we endeavored to assure that the sample was heated uniformly and placed as near as possible to the electron beam. The limitation on nearness was to restrict the beam from being able to impinge directly on the solid sample. Our goal was to know the temperature of the solid phase, to operate at temperatures that would cause measurable decomposition of the condensed phase and production of gaseous species, and then to identify those species before any further decomposition or collisions could take place. The short period of time (10^{-6} sec) and high vacuum (10^{-5} Torr) during the period from vaporization to detection would tend to preserve the species from collision reactions. On the other hand, the high vacuum and the electron impact will tend to cause decomposition that is an artifact of the analytical method. Our hope is that the artifact will be quantitative, rather than qualitative. That is, we are tacitly assuming at this stage that the degree of decomposition we are measuring for a given temperature is really that for a somewhat higher temperature--if higher pressures and no electron beam were the ambient conditions. Thus, we are putting emphasis on detecting condensed phase decomposition rather than gas phase reactions.

High Resolution Spectrometry. A CEC DuPont 211-110B instrument was used for these studies. A molecular leak of perfluorokerosene was used in the background as a reference. With high resolution spectroscopy a number of runs are required to give assurance that peak heights at a given mass/charge are meaningful, particularly with solid samples. A burst of decomposition occurring when the detector was measuring a given mass/charge would make that peak unrealistically large. The vacuum in the sample region was 10^{-5} Torr and at the detector it was 10^{-8} Torr.

High Resolution Sample Probe. The solid sample of AP to be tested is placed as near as possible to the electron stream. As the sample is depleted during the test, it recedes somewhat from the ionization area, but in no case is it farther than about 20 mm. As shown, a Knudsen effusion cell is available, although it was not used during these tests.

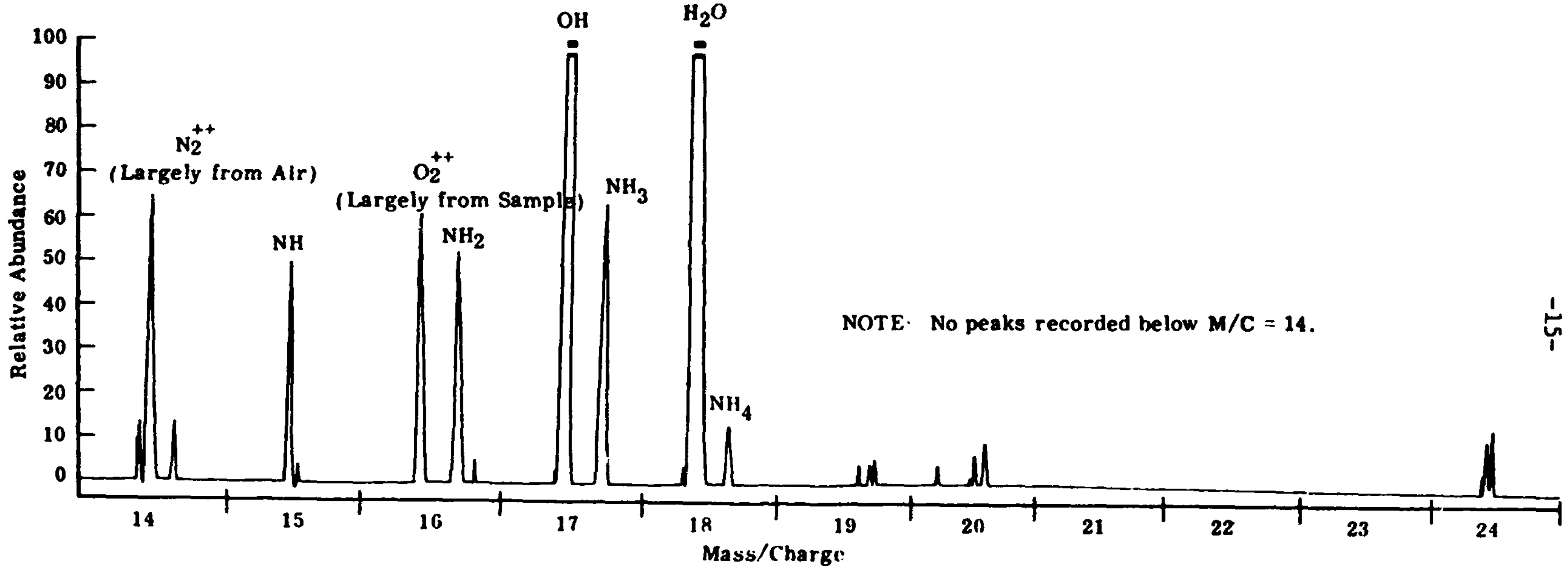
Materials. The ammonium perchlorate used was ultra high-purity grade prepared by American Potash Corp. This material had previously been used to prepare very pure single crystals. The deuterated version was prepared by triple recrystallization from D_2O. After vacuum drying, it gave no detectable proton signal on nmr analysis.

D. Discussion

A typical higher resolution (complete peak separation between OH and NH_3) scan of the lower mass numbers is shown in Figure 1. Additional spectra and their interpretation appear separately.[19] In these studies, as compared with those conducted at atmospheric or higher pressures, we should be producing larger quantities of NH_3 and $HClO_4$ due to dissociative sublimation. If we did not detect these two as initial and major species as temperature was raised, we would suspect that the low pressure in the mass spectrometer and the electron beam energy were cracking the ammonia and perchloric acid known to be formed and were producing the decomposition species. A review of the data shows that NH_3 and $HClO_4$ are among the first species formed, and they remain as major species at all temperatures tested.

Maycock and Pai Verneker[9] have proposed a point defect mechanism to explain the fact that at atmospheric pressure only 30% of ammonium perchlorate decomposes below 300°. At temperatures above 350°, decomposition is complete. The species we have found and the mechanisms to account for them are in accord with their mechanism, which calls for production of species such as NH_4, NH_3, H_2O, $HClO_4$, and ClO_3 in the condensed phase.

In this set of experiments we did not find a temperature at which NH_3 and $HClO_4$ were the only products. In the first appearance of $HClO_4$ at 95°, ClO_3, the first decomposition product of $HClO_4$, is already equally abundant and ClO_2 is possibly one-third as abundant. Our spectra seemed to correlate quite closely with the figures and descriptions given by Guillory and King.[14] This includes the chlorine oxide species "reversal effect" they referred to. Guillory and King also gave the spectrum for



NOTE: No peaks recorded below M/C = 14.

High resolution mass spectra; ammonium perchlorate at 165°, *m/c* 14–24.

perchloric acid itself. However, they state that $HClO_4$ produced as an evaporated product remains relatively stable up to 320°. Therefore, they attribute chlorine oxide species in the 200° region and below to $HClO_4$ cracking by the electron beam. This may well be, but Levy[17] reports heterogeneous $HClO_4$ reactions below 300°, the rate depending on the nature of the surface with which it is in contact. It might be expected that the surface of decomposing AP, containing NH_4 and NH_3 species, and probably NH_2 and NH species, could provide an environment favoring $HClO_4$ decomposition. The abstraction of OH at the weaker Cl-OH bond would start the formation of the three chlorine oxides.

Apparently, we cannot yet say for certain what portion of the $HClO_4$ decomposition species (and by analogy the hydrides of nitrogen species) is due to thermal decomposition and what portion is due to electron beam cracking. We do know that the intensities of the species grow in a striking fashion as the temperature is increased from 95 to 165°. Also Pellett and Saunders[11] have reported not much difference in the relative abundance of the species when reducing electron beam energy from 70 down to 20 eV. They also state that cracking products and solid decomposition products can be differentiated. It must be realized, however, that 20-eV electrons are approximately several hundred times more powerful than the thermal environment for initiating uncatalyzed decomposition.

The factor that adds credence to thermal decomposition as the source of many species--as opposed to cracking--is the presence of species such as HCl, HNO, and NO. Perchloric acid has not been shown to produce HCl as a decomposition product. HNO and NO almost certainly require a number of decomposition steps by NH_3 and $HClO_4$, followed by oxidation of nitrogen hydrides. Such reasoning leads us to believe that many of the species detected actually were formed on the surface of the thermally decomposing NH_4ClO_4. Once such species are formed on the surface, it requires only that they be vaporized, usually as a radical, struck with an electron which strips off one electron and forms the positive ion. Then, with almost no chance of any further reaction, the ion is accelerated to the identification sector of the mass spectrometer. Thus, surface reactions should be the last reactions occurring.

Table I gives a series of reactions we believe could occur on the surface of thermally decomposing ammonium perchlorate at temperatures as low as about 100° when under high vacuum. Although direct spectral evidence for mobile ClO_4^- has not been found, the detection of small quantities of NH_4^+ both with and without the electron beam turned on indicate that the perchlorate ion might have been present. Reaction 1c indicates pathways by which both NH_4 and NH_4^+ might have been formed. To make the perchlorate ion a positive ion so that it can be detected requires stripping off an electron pair

$$ClO_4^- \xrightarrow{-2e} ClO_4^+$$

This is much less likely to occur than

$$ClO_4^- \xrightarrow{-e} ClO_4\cdot\text{(radical)}$$

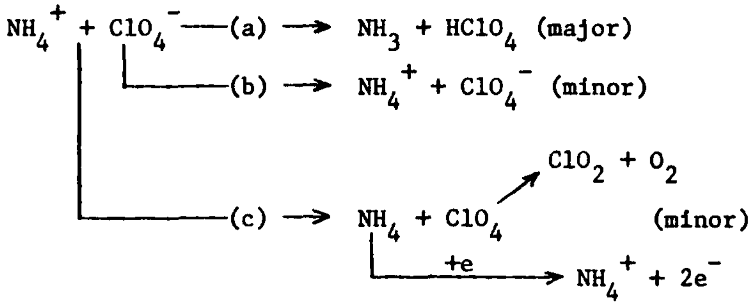
and the radical would not be detected. On the other hand, any NH_4^+ leaving the surface in the high resolution apparatus would be immediately accelerated to the detector. Such was found with the electron beam turned off. Further work will be required to determine the proportions of NH_4 and NH_4^+ being formed.

The presence of NH_4 and absence of ClO_4 might seem to militate

Table I.

AP Condensed Phase Decomposition Reaction Steps Justified by Mass Spectral Studies

1.



2. $HClO_4 \longrightarrow OH + ClO_3$

3. $ClO_3 + NH_3 \longrightarrow ClO_2 + OH + NH_2$

4. $ClO_3 + ClO_3 \longrightarrow 2ClO_2 + O_2$

5. $ClO_2 \longrightarrow Cl + O_2$

6. $NH_3 + Cl \longrightarrow NH_2 + HCl$

7. $NH_2 + Cl \longrightarrow NH + HCl$

8. $NH_2 + O_2 \longrightarrow HNO + OH$

9. $NH_2 + O_2 \longrightarrow NO + H_2O$

10. $ClO_3 \longrightarrow ClO + O_2$

against the interpretation that radicals left the surface because, in that case, one might assume a nearly equal probability of detecting either ammonium or perchlorate. However, ClO_4 is highly unstable, decomposing unimolecularly to ClO_2 and O_2. The second reaction producing OH and ClO_3 has been widely proposed and is well supported by our findings. Our reaction steps suggest that all decomposition starts with this step.

In $HClO_4$, the symmetry of the perchlorate ion is upset. The Cl-O bond, which was 1.408 Å for each of the oxygens, is lengthened to a Cl-OH bond length of 1.630 Å. This sets the stage for $HClO_4$ decomposition to ClO_3 and OH radicals. The third and fourth reactions providing two pathways to ClO_2 formation tend to explain the presence of more ClO_2 and ClO. Reaction 10 suggests one method of ClO formation. Reaction 5 shows how ClO_2 could decompose without going to ClO. Reactions 6 through 9 show reasonable ways for forming the various hydrides that are found, plus HCl, HNO, and NO. Oxygen was found to substantiate its usage in several reactions.

The reaction steps shown as occurring allow for the formation of most of the stable end products of equilibrium combustion except nitrogen. Tables II and III show the calculated combustion temperatures, gas molecular weights, and species distribution for three pressures. It can be seen that low pressures favor formation of HCl and Cl at the expense of Cl_2. Thus, where reactions are carried out at very low pressure, we would not expect to see Cl_2.

Table IV shows a series of nine reaction steps that are not justified based on the mass spectral analyses. The formation of Cl_2 (reaction 5) probably would take place at higher pressure. The underlined species represent those species not detected. NO_2, N_2O, HOCl, N_2, and Cl_2 have been reported as decomposition products by other investigators. We believe this

Table II.

Ammonium Perchlorate Monopropellant Combustion Equilibrium Calculations[a]

Combustion species, mol/100 g	Pressure		
	1 atm	34 atm	68 atm
Cl	0.0054	0.0022	0.0019
HCl	0.8168	0.7301	0.7005
ClO	0.0001	0.0002	0.0002
Cl_2	0.0144	0.0593	0.0742
OH	0.0002	0.0001	0.0001
H_2O	1.2937	1.3371	1.3519
NO	0.0011	0.0013	0.0013
N_2	0.4250	0.4249	0.4249
O_2	1.0546	1.0329	1.0254

[a] Other products less than 0.00005: H, NH, H_2, NH_3, N, and O.

Table III.

Ammonium Perchlorate Monopropellant Combustion Equilibrium Calculations

	H_f = -70.69 kcal/mol		
	Pressure		
Parameters	1 atm	34 atm	68 atm
Temp, °K	1375	1397	1403
Temp, °F	2015	2054	2066
Av. mol. wt.	27.691	27.871	27.930

Table IV.

Typical Nonjustified AP Condensed Phase Decomposition Reaction Steps

1. (Condensed) $NH_4 + ClO_4^- \longrightarrow \underline{NH_4ClO_4}$ (gas phase)[a]
2. $NH_3 + ClO \longrightarrow NH_2 + \underline{HOCl}$
3. $OH + Cl \longrightarrow \underline{HOCl}$
4. $HNO + O_2 \longrightarrow \underline{NO_2} + OH$
5. $Cl + Cl \longrightarrow \underline{Cl_2}$
6. $NH_2 + \underline{NO_2} \longrightarrow \underline{N_2O} + H_2O$
7. $NH_2 + O_2 \longrightarrow NH + \underline{HO_2}$
8. $N + NO \longrightarrow \underline{N_2O}$
9. $NH_2 + HNO \longrightarrow \underline{N_2O} + H_2O$
10. $NH + Cl \longrightarrow \underline{N} + HCl$

[a] Underlined species not detected.

may be the differentiation between condensed phase or surface reactions and gas phase reactions. We know that nitrogen is a major end product. However, we find no evidence of either N or N_2 coming from the surface. We theorize that the oxidation of the nitrogen hydrides just does not proceed beyond NH at the surface.

E. Conclusions

1. Most of the species postulated as occurring in AP decomposition were found. The spectrometers recorded only positive ion species. Therefore, the species detected were position ions or were formed by electron-impact stripping of one or more electrons from the actual thermal decomposition species.

2. The species HNO and NH_2 were found as condensed phase products providing support for two theories of decomposition mechanisms.

3. Small quantities of NH_4 were found, but no ClO_4. NH_4^+ leaving the condensed phase was detected with the electron beam turned off. ClO_4^-, on theother hand, could only have been detected by the loss of two electrons. ClO_4 could have been formed, but unimolecularly decomposed so rapidly as not to be detected.

4. No evidence for Cl_2 was found. Atomic chlorine was formed among all decomposition species. This is probably due to the low pressure studied. This checks with the results of Guillory and King, but is at variance with the results of a number of other investigators.

5. Nitrogen, N_2O, NO_2, and HOCl were not detectable as condensed phase decomposition products.

6. There is evidence that the majority of all proposed reactions of AP decomposition take place in the condensed phase at least to some extent. Thus, sufficient exothermic reactions can be made available under

proper pressure conditions to feed energy to the prime condensed phase endothermic reactions and to sustain combustion once the reaction chain is established.

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Section II. Lattice Dynamics in ~~Ammonium Perchlorate~~ AP

Abstract

The breakdown of the crystal lattice of ~~ammonium perchlorate~~ AP in the 300-625°K range has been studied by laser Raman spectroscopy. Detailed examination of the external and internal modes of the ion reveals that the onset of essentially unhindered tumbling of the $ClO_4^{(-)}$ ion seems to be intimately tied to the decomposition of AP. The effect of K^+ as an isomorphous dopant in the crystal lattice is to permit the $ClO_4^{(-)}$ ion to tumble at a lower temperature (0.8% $K^{(+)}$ produces a 60-70°K lowering in the tumbling temperature) and thus decompose at a lower temperature. Pressure effects on AP at 300°K show normal behavior and we do not believe that pressure plays a very large role in the decomposition of the crystal. All vibrational modes found in ~~ammonium perchlorate~~ AP including several not here-to-fore reported are discussed and insofar as possible assigned.

Section II. Lattice Dynamics in Ammonium Perchlorate.

A. Brief Description and Objectives

The thrust of this research program has been to gain a detailed and fundamental understanding of the crystal lattice dynamics of the principal solid propellant oxidizer, ammonium perchlorate (AP), under normal and pure conditions and under a variety of stress and impure conditions. Properties of the oxidizer are known to trigger the decomposition and thus the combustion of the propellant materials. It is the key component in the description of the pre-burn behavior propellant. Detailed information on the mechanism of breakdown of AP is important in formulating models to describe propellant performance and thermal stability, structural changes during temperature and pressure stress prior to deflagration, and the mechanism of the catalytic impurity effect on low temperature decomposition.

In the period from late 1972 to late 1974 the level of new data production was low largely because of instrumentation problems. In July 1974 we received enough funding through a cost sharing arrangement involving AFOSR and the University of Delaware to purchase a new Spectra Physics 4-watt Ar^+ laser source. Up until this time we were forced to operate with an intermittant and low power laser. In December of 1974 the new laser was installed so that the level of activity could be greatly increased.

Our approach to identifying the initial steps in AP crystal lattice decomposition has been through the technique of laser Raman spectroscopy. The study of decomposition of materials using this technique is virtually uncharted in spite of its very great potential. The spectra must be taken with very great care to obtain maximum information and can at times be very tedious. We have made a complete study of ultra-high purity AP to identify the origin and detailed characteristics of the internal and external modes of vibration of the ions. Spectroscopy was done on AP as a function of temperature in the 300-625°K range, as a function of pressure in the 0-40 Kbar range, and as a function of isomorphous dopants in the catalytic level concentration. With these results we are able to present a simple model to describe how the oxidizer begins to decompose and thus indicate the reactions leading to rocket propulsion.

B. Background

Ammonium Perchlorate. Low temperature decomposition of pure AP is known to begin to a significant extent just below the 500°K and to involve a proton transfer between NH_4^+ and ClO_4^- to give $NH_{3\,(g)}$ and $HClO_{4\,(g)}$.[1] An orthorhombic-to-cubic phase transition occurs at 513°K. At higher temperature (>530°K) and depending on the catalyst present, ignition occurs and yields a wide variety of combustion products containing reduced chlorine and oxidized nitrogen.[1,2]

A great deal of information is available in the area of combustion rates and energies and the effects of catalytic dopants on AP.[3] The process is extraordinarily complex in the combustion zone. Superficially it appears that the enhancement of the rate of heat release and the increase in temperature are the most important contributions the positive catalysts make to combustion. Presumably negative catalysts reverse these processes. More detailed reasons for these general responses include accelerating gas phase reactions,[4] permitting exothermic reactions to occur between the gases and the catalyst surface,[5] catalyzing heterogeneous reactions between the gases and the propellant,[6] modifying the pyrolysis mechanism,[7] and formation of inert products on the surface.[8]

In still more detail, catalytic dopants can modify the electron transport properties of the crystal lattice,[9] impede ion motions which are thought to be necessary for rapid combustion,[10] and alter the proton transfer mechanism in AP decomposition.[11] In point of fact probably no single explanation can be advanced to account for all catalytic effects, however. For instance, the high temperature decomposition is catalyzed by copper chromite, copper oxide and various other metal oxides.[11] They do not react directly with AP but appear to heterogeneously react with the NH_3 and $HClO_4$ in the high temperature combustion. Still other metal oxides react directly with AP to form metal perchlorates which subsequently react in the high temperature decomposition scheme.[12] Ag^+, Cd^{2+}, Br^-, I^-, and MnO_4^- seem to catalyze the low temperature deflagration.[13] No concrete proposals regarding this low temperature action have been made although a suggestion that the cation may facilitate the proton transfer mechanism through the formation of amines has been advanced.[14] This cannot account for the anion catalytic effect, however.

Pressure effects on solid AP material properties have not been very extensively investigated. An important observation has been made concerning the fact that AP can be made to melt at pressures similar to those of a rocket combustion chamber (~1000 psi).[15] This property may also be important in the catalytic effects of dopants and on the decomposition scheme. Dopants which destroy crystallinity could cause the liquification step to occur at a much lower pressure. The components of the melt phase are not known with any degree of certainty,[16] although Selzer[17] has speculated that NH_3, ClO_3, OH, and $HClO_4$ are likely to be present.

Only a few detailed vibrational spectroscopy studies have been made on AP.[17-19] Most of these are infra-red studies which show the lines to be broad and poorly resolved.[17-19] Raman spectral studies of AP at low temperature and room temperature[19] have been reported but not with very high resolution. Two studies of the lattice region have been made,[20,21] the second[21] study showing the first study[20] to be basically incorrect.

Laser Raman Spectroscopy. The technique which is being used in this work is the light scattering technique of laser Raman spectroscopy.[22] Briefly, when a beam of light encounters an assembly of molecules or ions, the photons of energy, hν, are either scattered elastically with energy, hν, or inelastically with higher or lower energies in amounts equal to vibrational motions in the compound. Elastic light scattering is known as Rayleigh scattering while inelastic scattering is called Raman scattering. The fact that the intensity of light inelastically scattered from a material is less than 10^{-6} of the intensity of elastically scattered light necessitates a high intensity light source. Ammonium perchlorate was found to be a rather feeble scatterer of light, particularly in the lattice region, probably because the NH_4^+ and ClO_4^- ions approximate rotating spheres and are not greatly distorted by the crystal lattice. Thus the magnitude of the polarizability change for them is small. The acquisition of a Spectra-Physics 4-watt Ar^+ laser in November, 1974, made it possible to achieve a reasonable degree of light scattering and hence to obtain quality spectra. Photon counting and a Spex 1401 double monochrometer were used for spectral analysis, and the spectral slit widths were maintained at 150 μ for this work.

The thermal decomposition of AP produces certain complications to optical spectroscopy, particularly because of the formation of a sublimate which fogs the windows of the optical cell. A system was designed that would simultaneously allow controlled heating of the crystal and maintenance of a low optical density of the cell. Figure 1 is a block diagram of the system used. A small crystal (10-20 mg) of AP was mounted in a thin wall capillary funnel which was itself held in glass variable temperature cell. The arrangement was made so that the crystal position can be varied by moving the mount at the back end of the cell. A flow of N_2 gas was passed through a furnace and allowed to flow over the crystal. This method serves to both heat the crystal and blow off the decomposition products which otherwise fog the cell. The temperature of the crystal can be controlled within several degrees by merely varying the flow rate of N_2 gas.

The variable pressure infra red work was carried out using a Perkin-Elmer 301 spectrometer and a Beckman IR-12 spectrometer at Argonne National Laboratory. Diamond anvil presses were used to obtain pressures in the 0-40 Kbar range.

C. Results and Discussion

AP Spectra and Assignments. The band assignments and the orientational dependence of the internal and lattice motions in a single crystal of AP were carried out. It was necessary to repeat all previous Raman work done on AP to determine its reproducibility and relationship to the present study. Table 1 contains the Raman spectral frequencies and their assignments for a single crystal of AP at 25°C.

The spectra obtained are a vast improvement over the internal mode spectrum that is in the literature at present.[19,20] The external or lattice region appears to be a very complicated problem to assign.[21] The following factor group analysis[23] for the orthorhombic phase of AP was carried out in the hope of providing a complete picture of the lattice motions as well as the splittings in the internal modes.

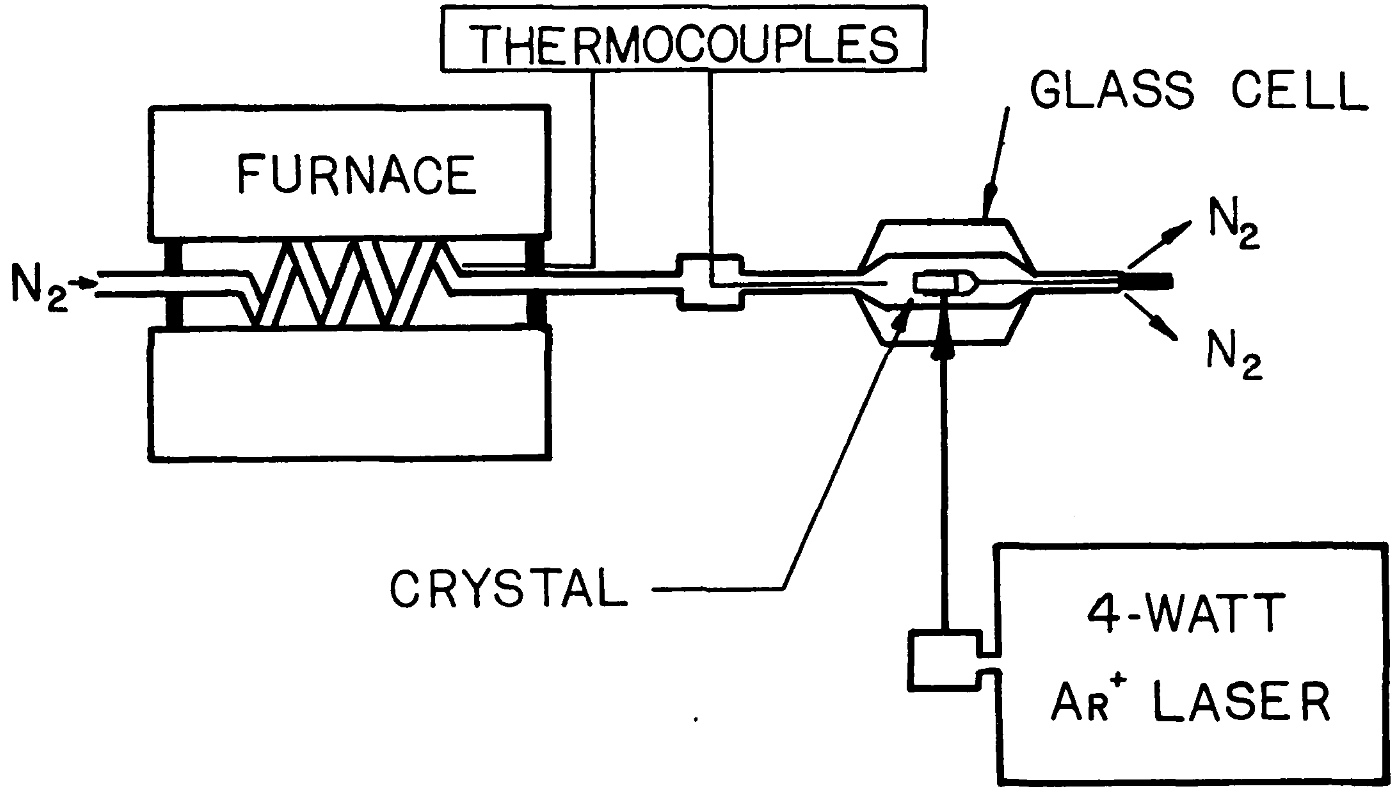
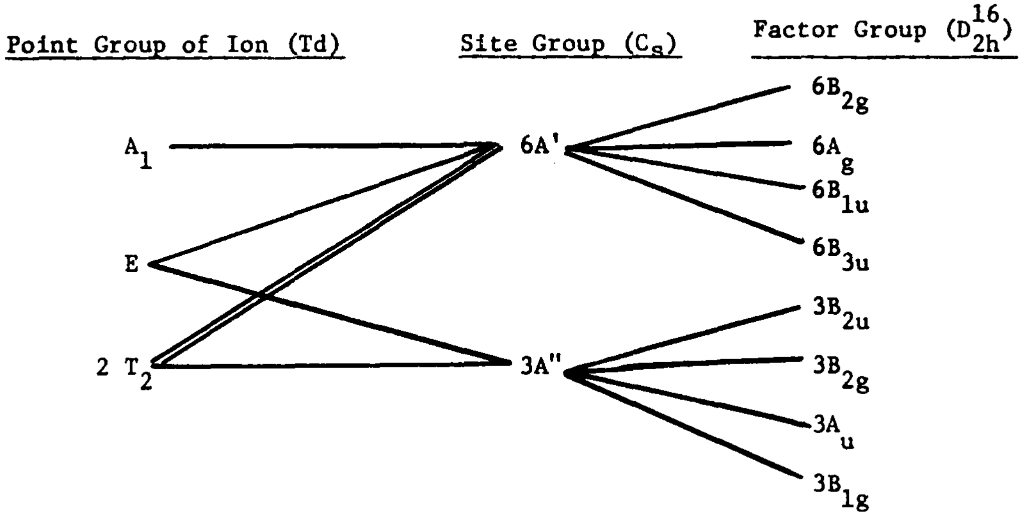


Figure 1. A Block Diagram of the Variable Temperature Raman Sample Cell.

The crystal structure has a space group P_{nma} (D_{2h}^{16}) with four formula units per cell.[24,25] The NH_4^+ and ClO_4^- ions occupy sites of C_s symmetry in the lattice.[24] For each isolated ion there are 9 internal modes (3n-6) or 36 internal modes 4(3n-6) for all four ions of that type in the factor group. The nine internal modes for a tetrahedral ion are well established as $A_1 + E + 2\ T_2$.[26] How these modes will be affected by the site symmetry of each ion, which is not tetrahedral in the lattice but rather C_s symmetry, and, further, how these ion motion symmetries will translate into the factor group, D_{2h}^{16}, for the entire lattice was derived in the following correlation table.



The 36 internal modes for NH_4^+ or ClO_4^- have the irreducible representations

$$6B_{2g} + 6A_g + 6B_{1u} + 6B_{3u} + 3B_{2u} + 3B_{3g} + 3A_u + 3B_{1g}$$

It is clear from this that no internal mode is wholly degenerate in orthorhombic ammonium perchlorate, which is in accordance with our spectral observation.

Turning to the external modes for NH_4^+ or ClO_4^-, there are 24 translational and rotational optical modes for each ion that are allowed. There are also a total of three acoustic modes (B_{1u}, B_{2u}, B_{3u}) for each ion that cannot be observed in an optical experiment. The optical modes for A' and A" for any set of four common ions in the cell evolve from correlation of the C_s site group to the D_{2h}^{16} factor group as follows:

External Modes for Site Group, C_s (NH_4^+ or ClO_4^-)	Factor Group D_{2h}^{16}	Number of Modes Translational	Number of Modes Rotational
A'	B_{2g}	2	1
	A_g	2	1
	B_{1u}	2	1
	B_{3u}	2	1
A"	B_{3g}	1	2
	A_u	1	2
	B_{1g}	1	2
	B_{2u}	1	2

The last two columns indicate how many translational and how many rotational modes appear of each symmetry for each ion. Since we are doing a Raman experiment, only the g modes will be detected so this reduces the number of modes likely to be observed by a factor of two.

The two correlation tables above summarize the group theoretical restrictions on the symmetry and number of unique modes in NH_4ClO_4 (orthorhombic). It is not critically important to this work to determine the exact assignment of each. Rather, it gives a formalism from which irregularities can be traced. There are no irregularities in the assignment of the internal modes and splitting of them given in Table 1. However, in the lattice region the situation has proven to be very complex (see Figure 2). Comparison of the AP spectrum to the deuterium analog, AP-d_4, identifies the broad bands in the 145-175 cm^{-1} region as NH_4^+ in origin because of the frequency decrease by a factor of about 0.9 upon deuteration. The magnitude of this shift suggests that it is a translatory motion and its degree of polarization ($\parallel$ vs. $\perp$ in Figure 2) is suggestive of non-totally symmetric modes of the B_{1g}, B_{2g}, B_{3g} class. However, very low temperature Raman spectral work[21] has shown that the situation is very much more complex. In fact, the mode shifts much more in frequency upon deuteration if studied at low temperature (<100°K). Thus some rotatory character is suggested for the NH_4^+ ion in this energy region. Moreover, there is also some A_g symmetry motion present at low temperature.[21]

The split mode in the 65-75 cm^{-1} region has been previously assigned to a NH_4^+ mode[20] but this is clearly not the case because it is rigorously unaffected by deuteration. Its strong dependence on polarized light shows it to arise from a totally symmetric mode of the Ag symmetry species. The mode at 42 cm^{-1} is primarily ClO_4^- in origin and is polarized. We note, however, that the temperature dependence at low temperature of these modes is very complex and that not all of the modes correspond to one phonon processes. Since it is not important to the general conclusion of this work, we have not pursued further the analysis of this complex lattice motion region.

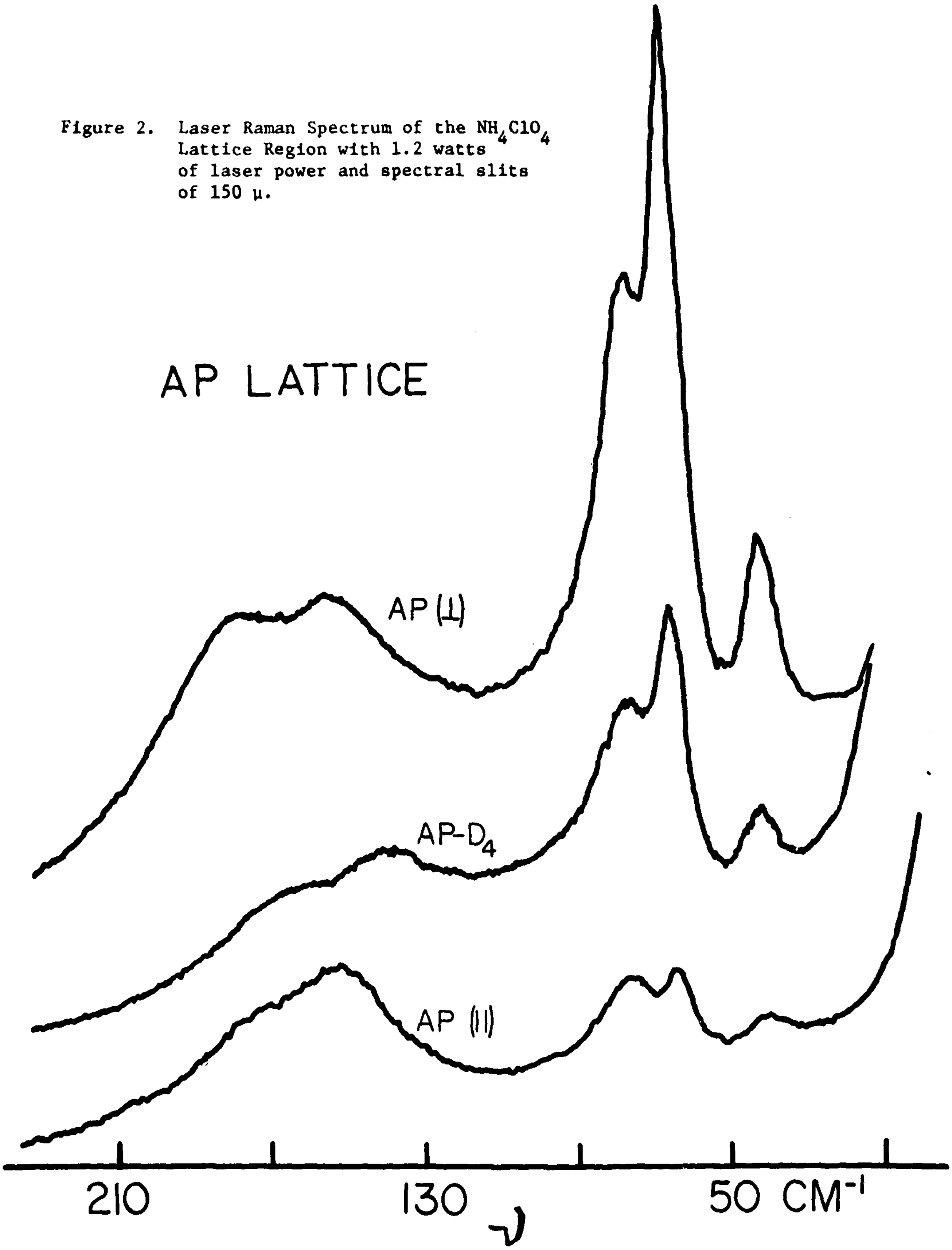
Two weak bands not here-to-fore reported appear at 550 and 710 cm^{-1}. They are not fundamental modes because all of those have been

Table 1.

Raman Spectral Assignments in a Single Crystal of Ammonium Perchlorate at 300°C

Vibrational Frequency (cm^{-1})	Assignment	Remarks
42	ClO_4^- lattice mode	No shift from ND_4ClO_4 (Ag)
64 74	ClO_4^- lattice modes	No shift from ND_4ClO_4 (Ag)
147 175	NH_4^+ lattice modes	Weak & very broad. Shift 0.85-0.9 lower in ND_4ClO_4 Appear mostly non-totally symmetric
462	$\nu_2(ClO_4^-)$	Very strong. Doubly degenerate bending motion.
550	ν_2 + lattice	Very weak combination band.
622 631	$\nu_4(ClO_4^-)$	Triply degenerate bending (resolution of the three bands not always noted.)
710	ν_2 + lattice	Very weak combination band
921 936	$\nu_1(ClO_4^-)$	Cl-O symmetric stretching motion, and Fermi resonance enhanced first overtone of ν_2.
1065 1106 1131	$\nu_3(ClO_4^-)$	Cl-O antisymmetric stretching motion
1421	$\nu_4(NH_4^+)$	Weak and broad
1700	$\nu_2(NH_4^+)$	Weak and broad
3210	$\nu_1(NH_4^+)$	Strong
3273	$\nu_3(NH_4^+)$	Very weak shoulder

Figure 2. Laser Raman Spectrum of the NH_4ClO_4 Lattice Region with 1.2 watts of laser power and spectral slits of 150 μ.



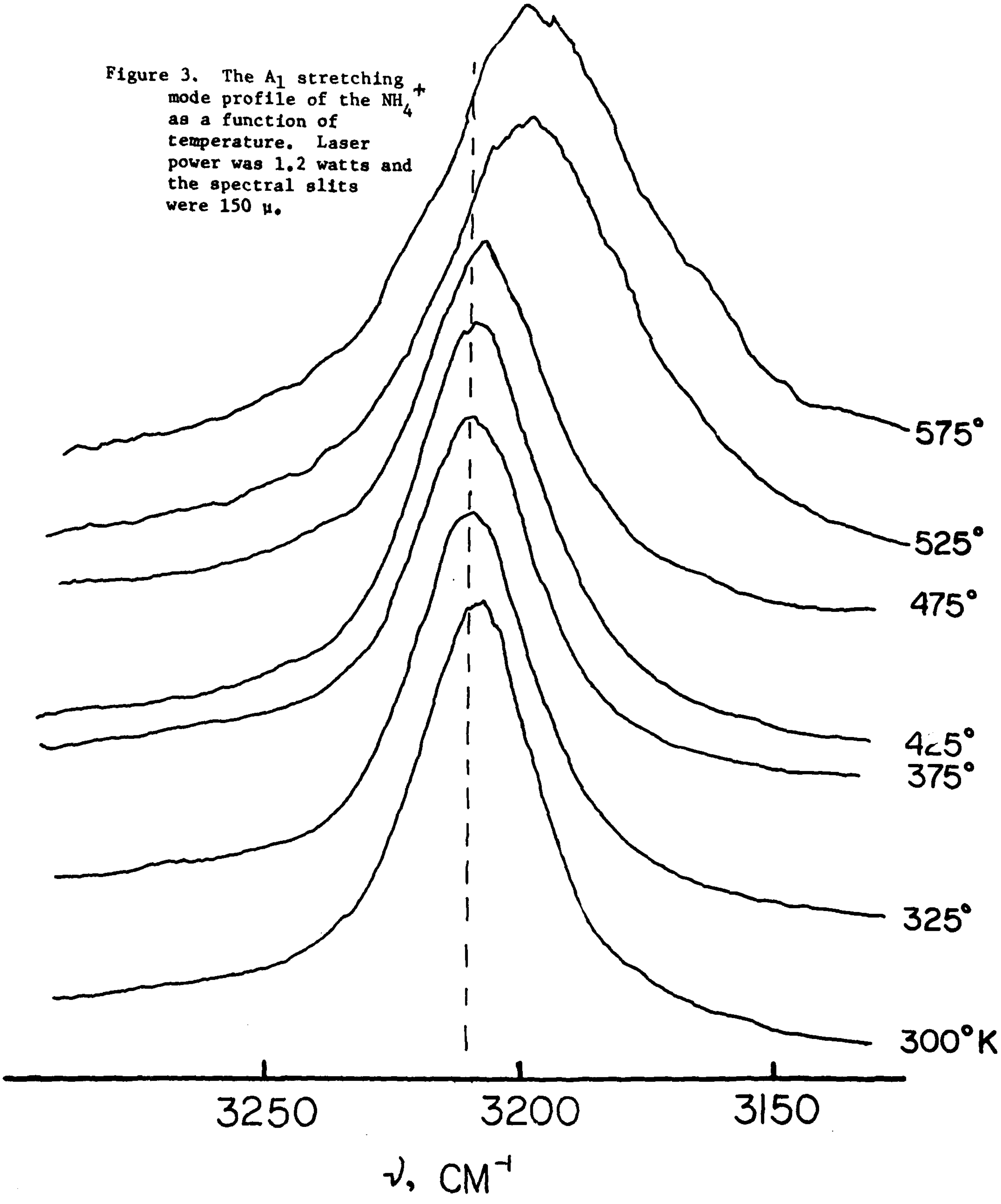
accounted for. The fact that both appear at about the same frequency above a bending mode of the ClO_4^- ion is perhaps a clue. Also, both are rigorously unshifted in the ND_4ClO_4 spectrum which identifies them as being perchlorate in origin. The identity of these modes is not certain but the best assignment would seem to be to call them summation modes of the bending modes and the highest energy ClO_4^- mode in the lattice region.

Spectrum of the Oxidizer in the 300-625°K Region. The main thrust of this work has been to provide a fundamental model for the breakdown of the AP crystal as it heats toward combustion. Having provided the above analysis of the assignment of bands in pure AP at room temperature we turned our efforts to their temperature dependence upon heating to the decomposition region in order to determine how the decomposition is triggered.

All temperature dependence work in the Raman of AP here-to-fore has been done at room temperature and below.[19-21] It is known that most of the unusual activity of the NH_4^+ ion as regards tumbling variations occurs below 150°K. Its barrier to rotation is believed to be less than 1 kcal/mole. In accordance with this we find little useful information in the NH_4^+ region at elevated temperatures. With the exception of the totally symmetry N-H stretching motion of the NH_4^+ ion, all bands are weak in the Raman. Hence, only the A_1 stretch was examined as a function of temperature. Figure 3 shows this dependence. Some broadening probably due to increased disorder does occur as the temperature is increased but it does not appear to do so abruptly at any temperature. The frequency shift of 10 cm^{-1} downward is rather abrupt at the phase transition probably because of the expansion of the crystal lattice. These changes are basically normal ones corresponding to a more energized NH_4^+ ion as the temperature increases.

It is the temperature dependence of the ClO_4^- region which seems

Figure 3. The A_1 stretching mode profile of the NH_4^+ as a function of temperature. Laser power was 1.2 watts and the spectral slits were 150 μ.



to offer the clue to the onset of NH_4ClO_4 decomposition. Figure 4 shows the orthorhombic phase of AP (300°K) and for the first time the cubic phase of AP (585°K). The cubic phase appears to be an inherently poorer scatterer of light compared to the orthorhombic phase. This results in a lower intensity spectrum for the temperatures above 513°K. The lower intensity is not a result of the increased optical density of the crystal due to decomposition because it is reversible; i.e., upon cooling a badly decomposed crystal from the cubic phase to the orthorhombic phase the intensity of the modes markedly increases again.

As is required by group theory, the T_2 antisymmetric Cl-O stretching motion becomes fully degenerate in the cubic phase whereas the factor group analysis for the internal modes presented above requires the degeneracy to be removed in the orthorhombic phase. No temperature dependence work was carried out on this mode because its breadth and relatively low intensity complicate extraction of accurate results. The other stretching motion of the ClO_4^- ion is the strongest band in the Raman and corresponds to totally symmetric motion, A_1. The temperature dependence of the mode is shown in Figure 5. It is deceptive that the band profile changes with temperature. The A_1 mode does, in fact, decrease in frequency with temperature by about 5 cm^{-1} but the Fermi resonance enhanced first overtone of the E bending mode at 921 cm^{-1} also moves but at a different rate. Thus, the shape of the band varies with temperature. On the whole, these modes do behave normally as a function of crystal symmetry and temperature.

The T_2 and E bending modes are extremely interesting and unusual, however. At the phase transition at 513°K we note a dramatic base broadening occurring in these motions. The only plausible explanation for this is

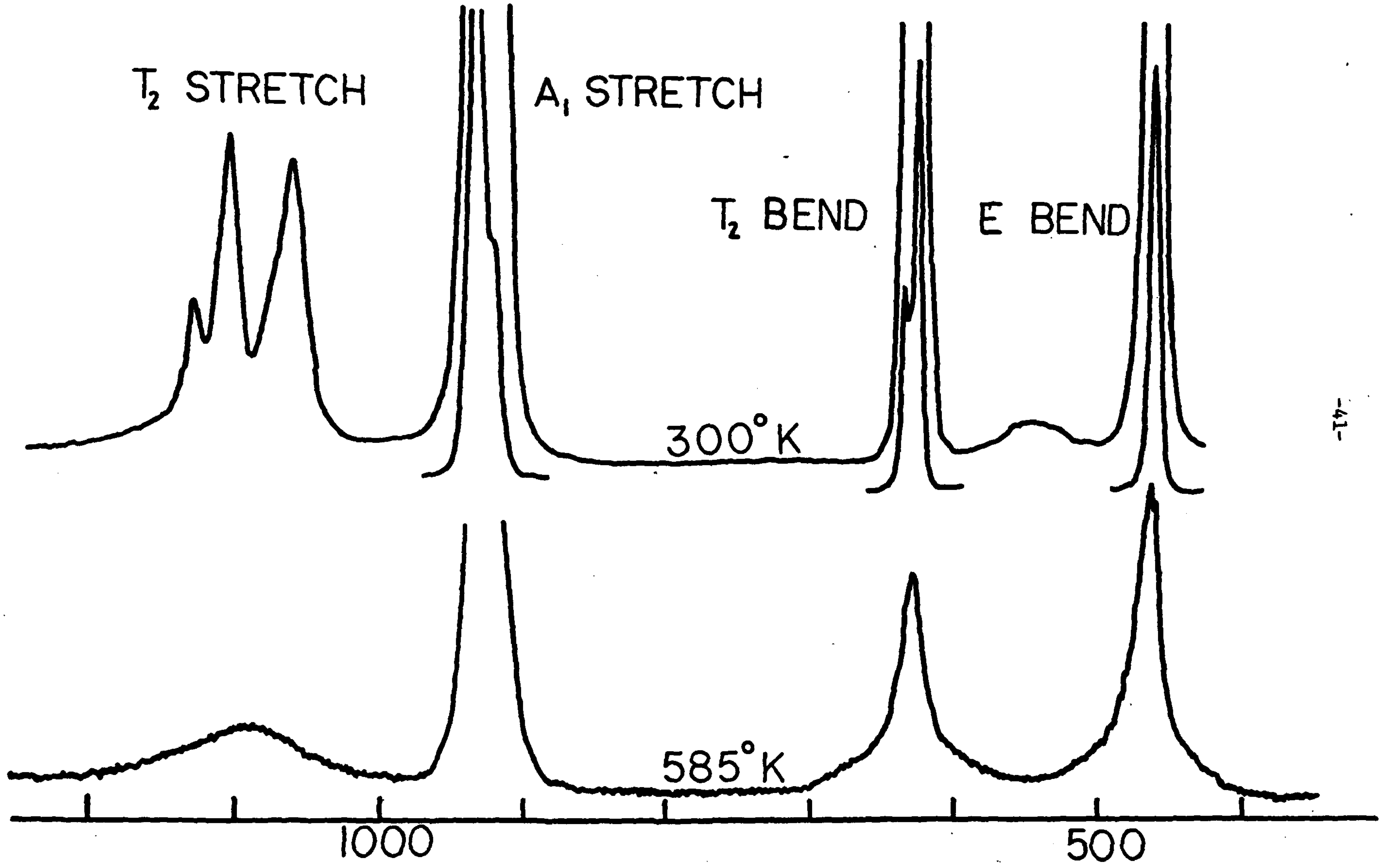


Figure 4. The ClO_4^- fundamental mode region in the Orthorhombic (300°K) and Cubic (585°K) phases.

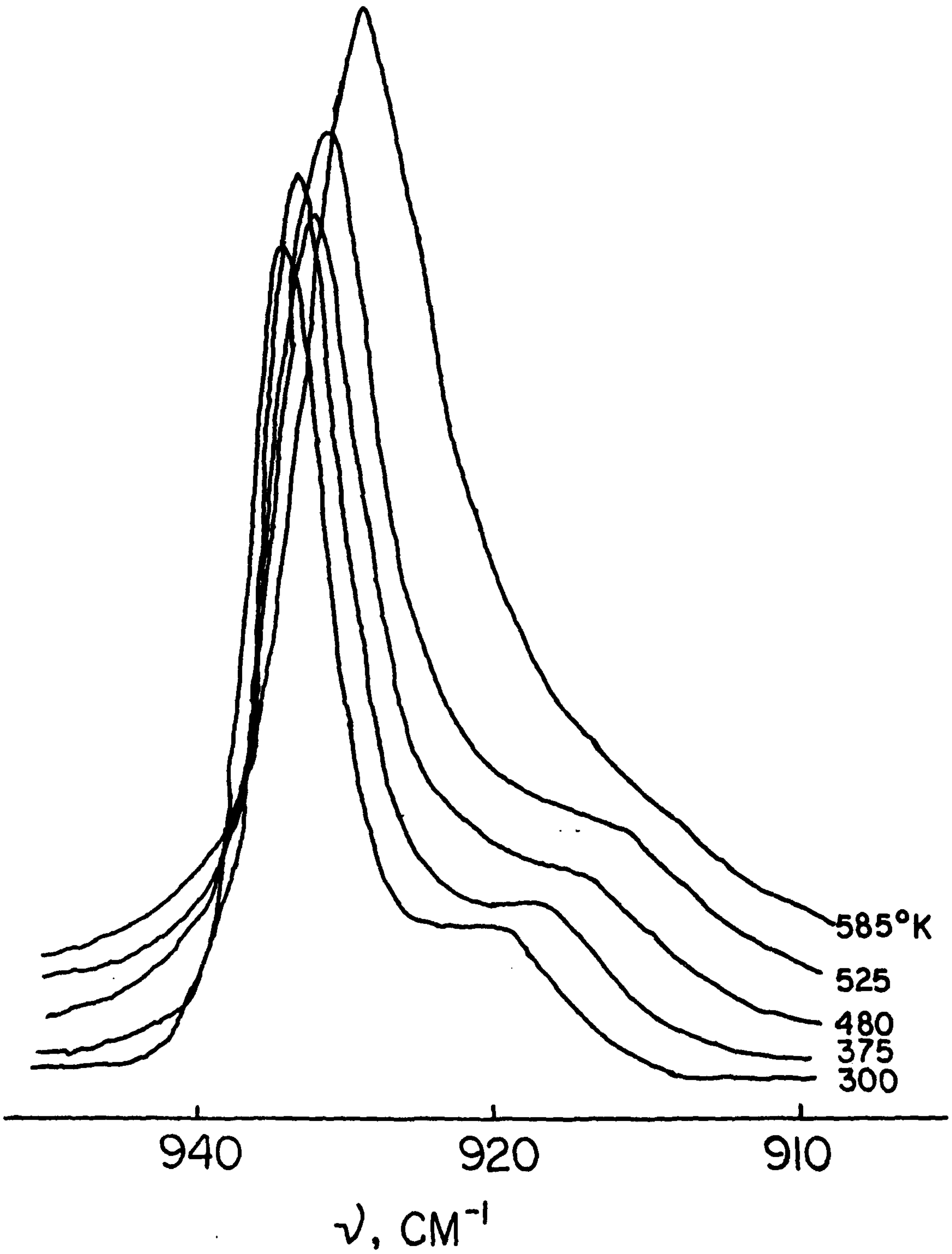
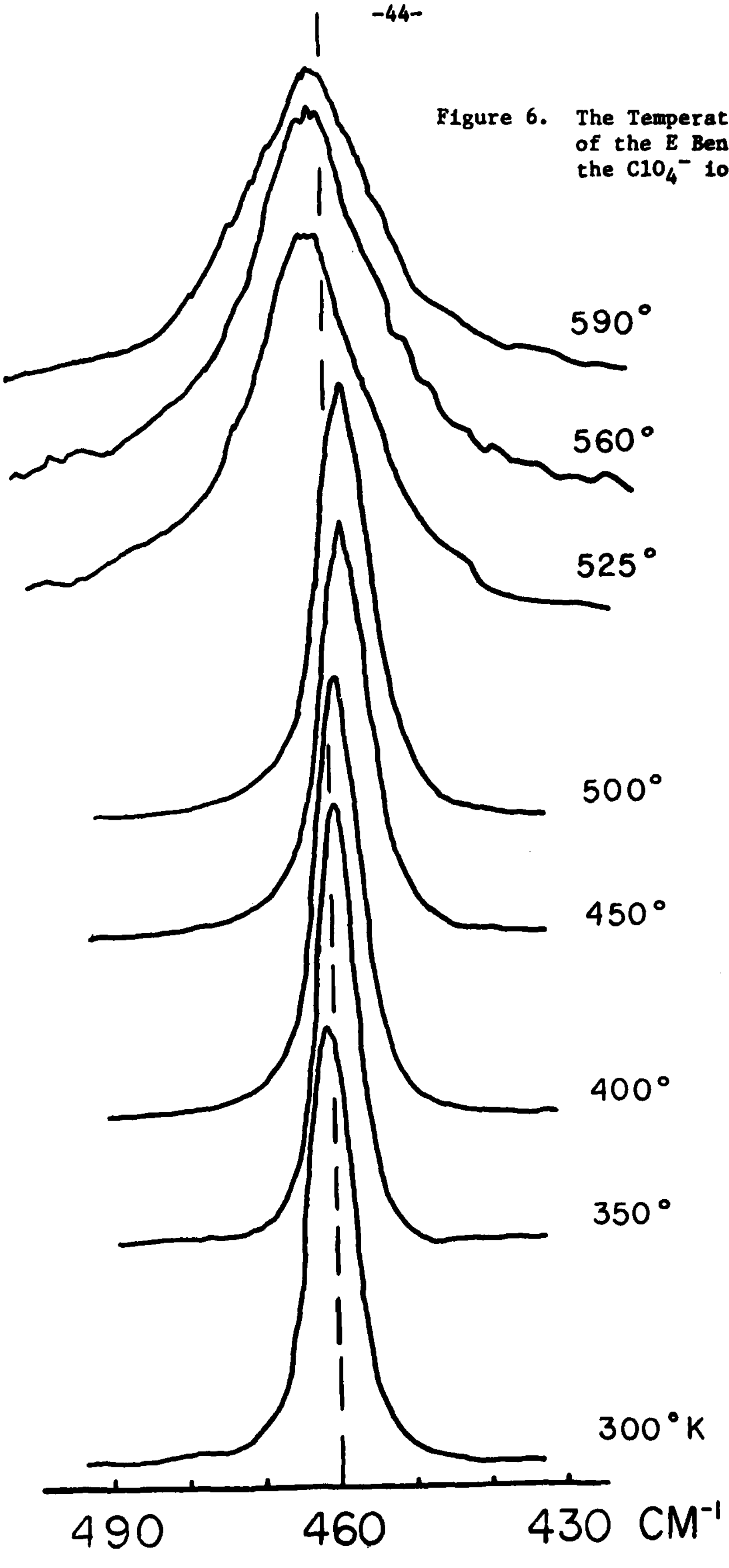


Figure 5. The Temperature Dependence of the A_1 Stretching Mode Profile of the ClO_4^- Ion. Slits were 150 μ.

that we are seeing rotational wings appearing on the vibrational modes which distort the ClO_4^- ion from tetrahedral symmetry. The distorted ion can then pick up rotational angular momentum and become Raman active. An attempt was made to fit these bands to the OPQRS rotational-vibrational progression but because of the lack of resolution of the shoulders, a large error in rotational constant values is incurred. Base broadening of this type occurs in the bending modes of solid methane just below its melting point.[27]

This base broadening in AP is a key to the fact that the phase transition represents the onset of essentially unhindered rotation of the ClO_4^- ions. This also happens to occur at about the same temperature that rapid crystal decomposition is observed. We thus propose that tumbling characteristics of the ClO_4^- ion are a major factor in determining the stability of AP and thus in triggering the decomposition of the oxidizer in the propellant. Figure 6 shows this broadening characteristic of the E bending motion in much greater detail. Up to the phase transition the lines show only slight broadening. However, at 513°K the base broadens rapidly and continues to do so up to the highest temperatures studied. We do have some evidence that the broadening levels off, however, at higher temperatures. It appears, however, that the ClO_4^- tumbling motion determines the stability of the NH_4ClO_4 lattice and thus is responsible for triggering the propellant combustion. An application of this fact in propellant combustion diagnostics is the potential for using the nature of this mode (the frequency shift in the orthorhombic phase and the line width in the cubic phase) to map the temperature profile and extent of heat transmission into the propellant. We had hoped to pursue this application of these modes as a crystal thermometer before terminating

Figure 6. The Temperature Dependence of the E Bending Mode of the ClO_4^- ion in NH_4ClO_4.



the project but did not.

Having examined the spectrum of the lattice modes in AP, we have also investigated their temperature dependence. Figure 7 shows the lattice modes as a function of T in the orthorhombic and cubic phases. The modes are unusually sensitive to temperature in an absolute sense and decrease very rapidly in frequency as the temperature increases. At the phase transition temperature, the modes rapidly disappear. In the cubic phase we have been unable to detect any lattice vibrations above 40 cm^{-1} where the stray light from the Rayleigh line of the light scattering swamps all Raman lines. This is a qualitative indication that the energy required to set the ions into translatory and rotatory motion is very small in the cubic phase, and hence, reactions between them should be made facile.

Dopant Effects on the AP Lattice. Considering our proposal that the ClO_4^- tumbling motion triggers the decomposition of AP it should be possible to understand some of the details of isomorphously incorporated catalytic dopants on the decomposition of AP. We were particularly drawn to the work of Boggs, et al.,[8] dealing with decomposition of single crystals AP doped with K^+, $Cr_2O_7^{2-}$, and MnO_4^-. We obtained from the NWC samples of these crystals which were from the very same batch as was used for the combustion work. Our work concentrated on the K^+ doped crystals.

It would follow from our ClO_4^- tumbling model that any dopant which tended to destroy the dynamic hydrogen bonding network between NH_4^+ and ClO_4^- would cause ClO_4^- to tumble at a lower temperature and thus decompose at a lower temperature. K^+ would be a candidate since it replaces NH_4^+ in the lattice and cannot hydrogen bond to the ClO_4^- ion. The temperature dependence spectrum of the E bending mode in 0.8% K^+ doped in AP is shown in Figure 8. The ClO_4^- bending is essentially

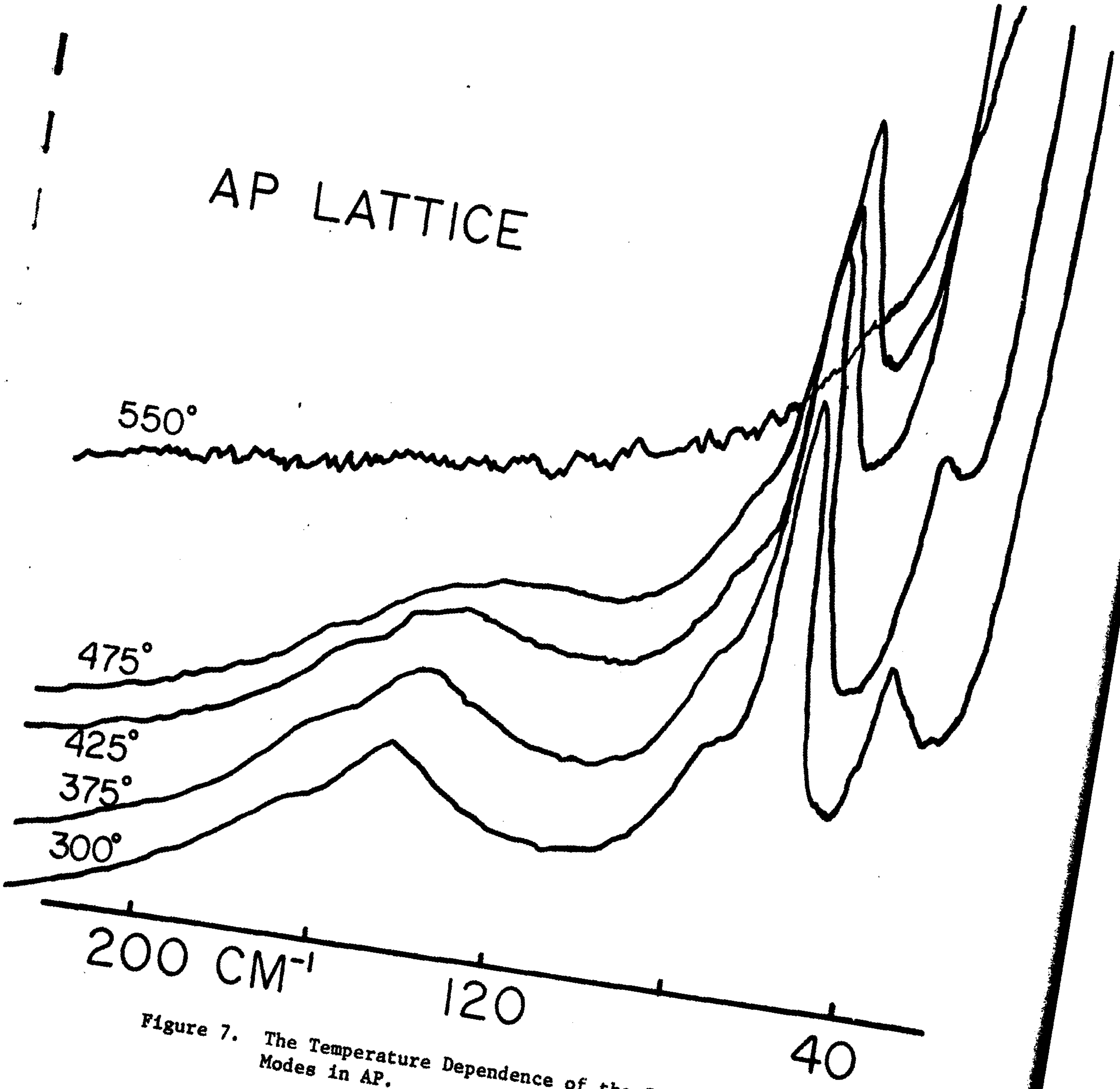
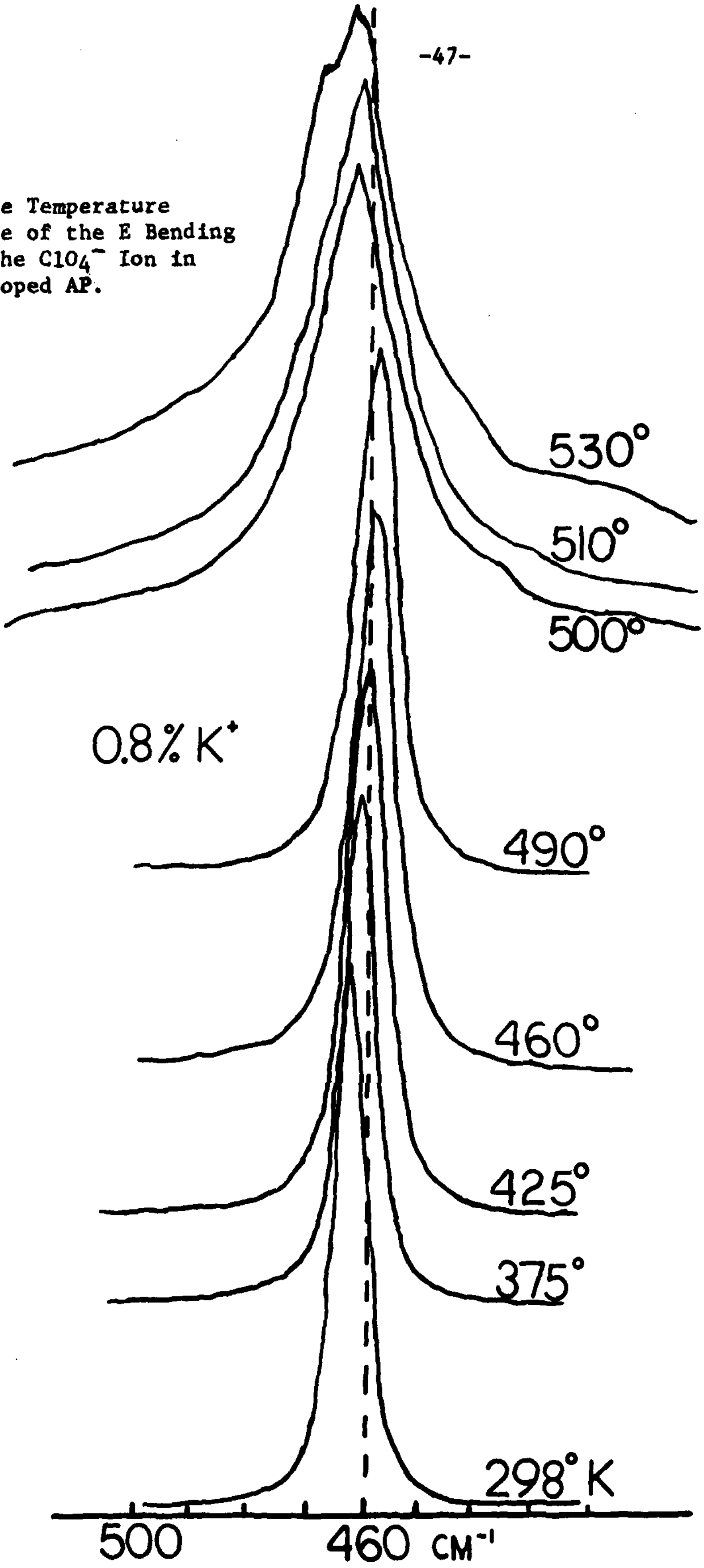


Figure 7. The Temperature Dependence of the Crystal Lattice Modes in AP.

Figure 8. The Temperature Dependence of the E Bending Mode of the ClO_4^- Ion in 0.8% K^+ Doped AP.



uneffected by T up to 500°K where broadening begins to occur. The phase transition is thus 10-15°K lower in this crystal than in pure AP and therefore the onset of ClO_4^- tumbling is 10-15°K lower. The model of lattice breakdown is able to predict and explain the affect of K^+ on crystal stability in AP.

Another feature demonstrated in Figure 8 is the appearance of a second mode in the 530°K spectrum. Boggs, et al.,[8] noted that extinguishment took place in burning crystals with a high K^+ content, such as 0.8%. The shoulder appearing on the 530°K spectrum is due to $KClO_4$ building on the surface which is most likely the source of extinguishment. Boggs proposed this and we find such a feature occurring.

We were concerned with whether we could also detect static changes in crystals with these various dopants. Some intensity differences in the ClO_4^- bands are seen and it is tempting to ascribe these to real distortions in the ClO_4^- site. We do not believe, however, that these differences arise from such effects, but rather that they come from slight variations in the crystal orientations in the laser beam. The morphologies of the crystals are all different and it is very difficult to reprodubibly align each crystal in the same way.

Pressure Effects on AP. AP is known to melt under the pressure and temperature conditions of a rocket motor.[15] We sought to learn the potential effect of pressure on crystal decomposition as well as the composition of this melt layer. It does not appear to be possible to do spectroscopy on the melt layer at the present time and we have abandoned this aspect. The pressure dependence of the modes was the subject of some effort on our part, however. Raman pressure work is not reported here because of the lack of a suitable cell design, although we have attempted some. Instead, the infra red technique was used. There have been reports of infra red studies on AP but none have involved pressure work.[17,18] We quickly found that ir spectroscopy is a vastly inferior technique for doing decomposition studies when compared on a one-to-one basis with Raman spectroscopy. Thus what might appear here to be an incomplete analysis of all bands is actually the best that one can do given the broad poorly resolved bands found in the infra red. Table 2 is a summary of the pressure dependence of several NH_4^+ and ClO_4^- internal modes in the 0-40,000 bar region. Normal pressure behavior would result in the modes which change the volume of the ion (stretching modes) being more sensitive to pressure than modes which do not (bending modes). ν_3 for ClO_4^- and NH_4^+ do indeed show very significant increases in frequency as the ions become compressed in the 0-40 Kbar range. ν_2 (ClO_4^-) and $\nu_4(NH_4^+)$ are the only bending modes which can be studied with any degree of certainty and they show no significant pressure dependence. $\nu_1(ClO_4^-)$ is detectable in the 0-10 Kbar range as a weak spike. The mode should be inactive in the ir except for crystal symmetry distortions which exist in the orthorhombic phase but not in the cubic phase. Indeed, the mode disappears above 10 Kbars. This locates the orthorhombic-to-cubic phase transition in the 10-24 Kbar region at 300°K. We stress, however, that most of these bands are broad and the errors in their frequencies are about ± 5 cm^{-1} in some cases. Infra red analysis of crystal details is very much poorer than the Raman analysis.

The principal conclusion to be drawn from the effect of pressure on the AP lattice is that, insofar as the details of the changes are observable, pressure is not a major contributor to the decomposition of solid AP. It certainly is very important in gaseous decomposition products and in the burning rate of AP. The pressure effects on the solid are normal

Table 2.

Pressure Dependence of Internal Mode Frequencies in NH_4ClO_4

Mode	Pressure (Kbars)					
	0	2	6	10	24	40
$\nu_3(NH_4^+)$[a]	3310	---	3310	3300	3327	3330
$\nu_4(NH_4^+)$	1425	---	1430	1435	1435	1435
$\nu_1(ClO_4^-)$[b]	939	---	940	940	Not seen	Not seen
$\nu_3(ClO_4^-)$[a]	1085	---	1095	1105	1125	1130
$\nu_4(ClO_4^-)$	634	630	635	638	635	635

[a] Very broad, errors can be ±5 cm^{-1}.

[b] Band becomes in-active due to crystal symmetry above 10 Kbars.

and predictable for this system which is in contrast to the temperature effects. Literature reports discussing parts of our work have appeared.[28,29]

D. Conclusions

1. Highest quality Raman spectra of AP were obtained, and the methods for studying decomposition of solid materials by the technique have been worked out.

2. The onset of essentially unhindered tumbling of the ClO_4^- ion destabilizes the NH_4ClO_4 crystal lattice and appears to be the first step in oxidizer decomposition.

3. The band profile of the doubly degenerate E bending mode of the ClO_4^- ion can be used as a "crystal thermometer" to map the extent of heat transmission into the crystal lattice of NH_4ClO_4. Below the orthorhombic-to-cubic phase transition the frequency position is diagnostic, while above it, the line width is sensitive to temperature.

4. Doping of the crystal lattice with 0.8% K^+ causes the ClO_4^- ion to tumble freely at 15-20°K lower than the temperature in pure AP. The buildup of $KClO_4$ on the crystal surface at higher temperatures is clearly evident.

5. Static pressure up to 40 Kbars on the crystal lattice does not result in decomposition and appears to produce only normal effects on the vibrational motions of the ion.

6. Raman spectroscopy appears to be a vastly superior technique compared to infra red spectroscopy for doing crystal lattice degradation studies.

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Time-of-flight and high resolution mass spectrometry of UHP-AP and its deuterated derivative were examined in an effort to identify some of the key decomposition species as proposed in thermal decomposition mechanisms. Of particular interest is the sure detection of HNO, the hydrides of nitrogen and the oxides of chlorine. HNO (mass 31) was found as a minor component at temperatures above 80°C and the species was confirmed by the presence of DNO (mass 32) when the deuterated compound was examined. It is considered

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highly improbable that HNO could have occurred by reactions other than surface thermal reactions. High resolution spectra were used to separate O_2^{2+} and O^+ from NH_2 at mass 16. The presence of NH_2^+ was confirmed along with NH_4^+, NH_3^+ and NH^{+2}. $HClO_4^+$, Cl^+ and all the simple oxides of chlorine were found but Cl_2^+, $HClO^+$, $HClO_2^+$, $HClO_3^+$ and ClO_4^+ were not detected. Also not detected were N_2^+, N_2O^+ and NO_2^+ in the condensed phase. No parent $NH_4ClO_4^+$ was present. Evidence of strong exothermic reactions in the condensed phase was found and this supports theories stating that this is the major source of energy to help balance the endothermic requirements for vaporization to sustain combustion.

The breakdown of the crystal lattice of ammonium perchlorate in the 300-625°K range has been studied by laser Raman spectroscopy. Detailed examination of the external and internal modes of the ion reveals that the onset of essentially unhindered tumbling of the ClO_4^- ion seems to be intimately tied to the decomposition of AP. The effect of K^+ as an isomorphous dopant in the crystal lattice is to permit the ClO_4^- ion to tumble at a lower temperature (0.8% K^+ produces a 60-70°K lowering in the tumbling temperature) and thus decompose at a lower temperature. Pressure effects on AP at 300°K show normal behavior and we do not believe that pressure plays a very large role in the decomposition of the crystal. All vibrational modes found in ammonium perchlorate including several not here-to-fore reported are discussed and insofar as possible assigned.