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"Lattice Dynamics in Ammonium Perchlorate"

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# Lattice Dynamics in Ammonium Perchlorate

**Title:** 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 $\text{ClO}_4^-$ ion seems to be intimately tied to the decomposition of AP. The effect of $\text{K}^+$ as an isomorphous dopant in the crystal lattice is to permit the $\text{ClO}_4^-$ ion to tumble at a lower temperature (0.8% $\text{K}^+$ 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...
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I. Abstract

The breakdown of the crystal lattice of ammonium perchlorate in the 300-625\textdegree{}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 \( \text{ClO}_4^- \) 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 \( \text{ClO}_4^- \) ion to tumble at a lower temperature (0.8\textdegree{}K produces a 60-70\textdegree{}K lowering in the tumbling temperature) and thus decompose at a lower temperature. Pressure effects on AP at 300\textdegree{}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.
II. 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.

Our approach to this problem 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.
Similar studies on the mechanism of breakdown of nitramine compounds such as HMX and RDX is to be the thrust of this research very soon. We have not included work on HMX in this report since our projects this past year most extensively dealt with ammonium perchlorate.

III. Background

A. 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 \( \text{NH}_4^+ \) and \( \text{ClO}_4^- \) to give \( \text{NH}_3 (g) \) and \( \text{HClO}_4 (g) \). 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. 

A great deal of information is available in the area of combustion rates and energies and the effects of catalytic dopants on AP. 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, permitting exothermic reactions to occur between the gases and the catalyst surface, catalyzing heterogeneous reactions between the gases and the propellant, modifying the pyrolysis mechanism, and formation of inert products on the surface. In still more detail, catalytic dopants can modify the electron transport properties of the crystal lattice, impede ion motions which are...
thought to be necessary for rapid combustion\textsuperscript{10}, and alter the proton transfer mechanism in AP decomposition\textsuperscript{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\textsuperscript{11}. They do not react directly with AP but appear to heterogeneously react with the NH\textsubscript{3} and HClO\textsubscript{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\textsuperscript{12}. Ag\textsuperscript{+}, Cd\textsuperscript{2+}, Br\textsuperscript{-}, I\textsuperscript{-}, and MnO\textsubscript{4}\textsuperscript{-} seem to catalyze the low temperature deflagration\textsuperscript{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 ammines has been advanced\textsuperscript{14}. This cannot account for the anion catalytic effect, however.

Pressure effects on AP 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)\textsuperscript{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 liquefication step to occur at a much lower pressure. The components of the melt phase are not known with any degree of certainty\textsuperscript{16}, although Selzer\textsuperscript{17} has speculated that NH\textsubscript{3}, ClO\textsubscript{3}, OH, and HClO\textsubscript{4} are likely to be present.
Only a few detailed vibrational spectroscopy studies have been made on AP. Most of these are infra-red studies which show the lines to be broad and poorly resolved. Raman spectral studies of AP at low temperature and room temperature have been reported but not with very high resolution. Two studies of the lattice region have been made, the second study showing the first study to be basically incorrect.

B. Laser Raman Spectroscopy

The technique which is being used in this work is the light scattering technique of laser Raman spectroscopy. Briefly, when a beam of light encounters an assembly of molecules or ions, the photons of energy, hv, are either scattered elastically with energy, hv, 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, has made it possible to achieve a reasonable degree of light scattering and hence to obtain quality spectra. Photon counting and a Spex 1401 double monochromometer were used for spectral analyses.
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 N₂ 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 the N₂ gas.

The variable pressure infrared 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.

IV. Results to Date

A. AP Spectra and Assignments

We have essentially completed the assignment and the orientational dependence of the internal and lattice motions in a single crystal of AP. It has been necessary to repeat all previous work that we and others have carried out on AP to determine its reproducibility. Table 1 contains the Raman spectral frequencies and their assignments for a single crystal of AP at 25°C.
Figure 1

Diagram of a system with labeled parts:
- Glass Cell
- Thermocouples
- Furnace
- Crystal
- 4-Watt Ar^+ Laser
- N_2 flows indicated
<table>
<thead>
<tr>
<th>Vibrational Frequency (cm(^{-1}))</th>
<th>Assignment</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>42</td>
<td>C(_{10})(^{-}) lattice mode</td>
<td>No shift from ND(<em>{4})C(</em>{10})(^{-}) (Ag)</td>
</tr>
<tr>
<td>64</td>
<td>C(_{10})(^{-}) lattice modes</td>
<td>No shift from ND(<em>{4})C(</em>{10})(^{-}) (Ag)</td>
</tr>
<tr>
<td>74</td>
<td>C(_{10})(^{-}) lattice modes</td>
<td>Weak &amp; very broad. Shift 0.85-0.9 lower in ND(<em>{4})C(</em>{10})(^{-})</td>
</tr>
<tr>
<td>147</td>
<td>NH(_{4})(^{+}) lattice modes</td>
<td>Appear mostly non-totally symmetric</td>
</tr>
<tr>
<td>175</td>
<td>v(<em>2) (C(</em>{10})(^{-}))</td>
<td>Very strong. Doubly degenerate bending motion.</td>
</tr>
<tr>
<td>462</td>
<td>v(_2) + lattice</td>
<td>Very weak combination band.</td>
</tr>
<tr>
<td>550</td>
<td>v(<em>4) (C(</em>{10})(^{-}))</td>
<td>Triply degenerate bending (resolution of the three bands not always noted.)</td>
</tr>
<tr>
<td>622</td>
<td>v(_2) + lattice</td>
<td>Very weak combination band</td>
</tr>
<tr>
<td>631</td>
<td>v(<em>1) (C(</em>{10})(^{-}))</td>
<td>Cl-0 symmetric stretching motion, and Fermi resonance enhanced first overtone of v(_2).</td>
</tr>
<tr>
<td>710</td>
<td>v(_2) + lattice</td>
<td>Cl-0 antisymmetric stretching motion</td>
</tr>
<tr>
<td>921</td>
<td>v(<em>1) (C(</em>{10})(^{-}))</td>
<td>Cl-0 antisymmetric stretching motion</td>
</tr>
<tr>
<td>936</td>
<td>v(<em>3) (C(</em>{10})(^{-}))</td>
<td>Cl-0 antisymmetric stretching motion</td>
</tr>
<tr>
<td>1065</td>
<td>v(<em>4) (NH(</em>{4})(^{+}))</td>
<td>Weak and broad</td>
</tr>
<tr>
<td>1106</td>
<td>v(<em>2) (NH(</em>{4})(^{+}))</td>
<td>Weak and broad</td>
</tr>
<tr>
<td>1131</td>
<td>v(<em>1) (NH(</em>{4})(^{+}))</td>
<td>Strong</td>
</tr>
<tr>
<td>1421</td>
<td>v(<em>4) (NH(</em>{4})(^{+}))</td>
<td>Very weak shoulder</td>
</tr>
</tbody>
</table>
The spectra obtained are a vast improvement over the internal mode spectrum that is in the literature at present.\textsuperscript{19,20} The external or lattice region appears to be a very complicated problem to assign.\textsuperscript{21} The following factor group analysis\textsuperscript{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.

The crystal structure has a space group $P_{nma}$ ($D_{2h}^{16}$) with four formula units per cell.\textsuperscript{24,25} The $\text{NH}_4^+$ and $\text{ClO}_4^-$ ions occupy sites of $C_s$ symmetry in the lattice.\textsuperscript{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 $A_1 + E + 2T_2$.\textsuperscript{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.

<table>
<thead>
<tr>
<th>Point Group of Ion (Td)</th>
<th>Site Group ($C_s$)</th>
<th>Factor Group ($D_{2h}^{16}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1$</td>
<td></td>
<td>$6A'$</td>
</tr>
<tr>
<td>$E$</td>
<td></td>
<td>$6A_1g$</td>
</tr>
<tr>
<td>$2T_2$</td>
<td></td>
<td>$6B_{2g}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$6A_g$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$6B_{1u}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$6B_{3u}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$3B_{2u}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$3B_{2g}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$3A_u$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$3B_{1g}$</td>
</tr>
</tbody>
</table>
The 36 internal modes for NH$_4^+$ or ClO$_4^-$ have the irreducible representations

$$6B_{2g} + 6Ag + 6B_{1u} + 6B_{3u} + 3B_{2u} + 3B_{3g} + 3Au + 3B_{1g}$$

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 Cs site group to the $D_{2h}^{16}$ factor group as follows:

<table>
<thead>
<tr>
<th>External Modes for Site Group, Cs (NH$_4^+$ or ClO$_4^-$)</th>
<th>Factor Group</th>
<th>Number of Modes</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$D_{2h}^{16}$</td>
<td>Translational</td>
</tr>
<tr>
<td>$A'$</td>
<td>B$_{2g}$</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>Ag</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>B$_{1u}$</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>B$_{3u}$</td>
<td>2</td>
</tr>
<tr>
<td>$A''$</td>
<td>B$_{3g}$</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>Au</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>B$_{1g}$</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>B$_{2u}$</td>
<td>1</td>
</tr>
</tbody>
</table>
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 NH₄ClO₄ (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-d₄, identifies the broad bands in the 145-175 cm⁻¹ region as NH₄⁺ 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 (|| vs. \perp\) in Figure 2) is suggestive of non-totally symmetric modes of the B₁g, B₂g, B₃g 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 NH₄⁺ ion in this energy region. Moreover, there is also some Ag symmetry motion present at low temperature.\(^{21}\)

The split mode in the 65-75 cm⁻¹ region has been previously assigned to a NH₄⁺ 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 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\(_4\)ClO\(_4\) 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.

B. Spectrum of the Oxidizer in the 300-625\(^\circ\)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. 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 does occur as the temperature is increased but it does not appear to do so abruptly at any temperature. The frequency shift of 5 cm$^{-1}$ downward is also a gradual one. 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 is really the clue to the NH$_4$ClO$_4$ 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
T₂ STRETCH

A₁ STRETCH

T₂ BEND

E BEND

300°K

585°K

1000

500

Fig 4
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 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. This base broadening is thus 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 and $T_2$ bending motions in much greater detail. The frequency dependence is not accurately represented in
E BEND
ClO$_4^-$

600°
553°
523°
510°
273-500°K

485  435  CM$^{-1}$

T$_2$ BEND
ClO$_4^-$

575°
525°
300-500°K

.650  600  CM$^{-1}$
this plot in order that we can clearly demonstrate the broadening. 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 and we wish to determine this with some more accuracy.

There is a frequency shift which also occurs and this will be better represented below. It does appear, however, that the $\text{ClO}_4^-$ tumbling motion determines the stability of the $\text{NH}_4\text{ClO}_4$ 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 to map the temperature profile and extent of heat transmission into the propellant using the line width change and frequency shift. We intend to pursue this application before terminating the project.

Having examined the spectrum of the lattice modes in AP, we have investigated their temperature dependence also. 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.
AP LATTICE

550°
475°
425°
375°
300°

200 CM⁻¹  120  40
C. Dopant Effects on the AP Lattice

Considering our proposal that the $\text{CIO}_4^-$ 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., dealing with decomposition of single crystals AP doped with $\text{K}^+$, $\text{Cr}_2\text{O}_7^{2-}$, and $\text{MnO}_4^-$. 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 has concentrated on the $\text{K}^+$ doped crystals to date.

It would follow from our $\text{CIO}_4^-$ tumbling model that any dopant which tended to destroy the hydrogen bonding network between $\text{NH}_4^+$ and $\text{CIO}_4^-$ would cause $\text{CIO}_4^-$ to tumble at a lower temperature and thus decompose at a lower temperature. $\text{K}^+$ would be a candidate since it replaces $\text{NH}_4^+$ in the lattice and cannot hydrogen bond to the $\text{CIO}_4^-$ ion. The temperature dependence spectrum of the E bending mode in 0.8% $\text{K}^+$ doped in AP is shown in Figure 8. The $\text{CIO}_4^-$ bending is essentially unaffected by $T$ up to 450$^\circ$K where broadening begins to occur. The phase transition is thus 60-70$^\circ$K lower in this crystal than in pure AP and therefore the onset of $\text{CIO}_4^-$ tumbling is 60-70$^\circ$K lower. Moreover, the frequency shifts are here accurately represented and they, too, can be used as a diagnostic for the presence of $\text{CIO}_4^-$ tumbling motion. In the orthorhombic phase a frequency decrease is noted up to the phase transition, then a jump to higher frequency occurs when the broadening occurs. Thus both the frequency and the line width can be used as a crystal "thermometer." The model of lattice breakdown is able to predict and explain the affect of $\text{K}^+$.
on crystal stability in AP.

Another feature demonstrated in Figure 8 is the appearance of a second mode in the 500\textdegree K spectrum. Boggs, et al., noted that extinguishment took place in burning crystals with a high $K^+$ content, such as 0.8%. The shoulder appearing on the 500\textdegree K spectrum is due to $\text{KClO}_4$ 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 $\text{ClO}_4^-$ bands are seen and it is tempting to ascribe these to real distortions in the $\text{ClO}_4^-$ 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 reproducibly align each crystal in the same way.

D. Pressure Effects on AP

AP is known to melt under the pressure and temperature conditions of a rocket motor. We have been concerned with 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 has been 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.\textsuperscript{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\textsubscript{4}\textsuperscript{+} and ClO\textsubscript{4}\textsuperscript{-} 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). $v_3$ for ClO\textsubscript{4}\textsuperscript{-} and NH\textsubscript{4}\textsuperscript{+} do indeed show very significant increases in frequency as the ions become compressed in the 0-40 Kbar range. $v_2$ (ClO\textsubscript{4}\textsuperscript{-}) and $v_4$ (NH\textsubscript{4}\textsuperscript{+}) are the only bending modes which can be studied with any degree of certainty and they show no significant pressure dependence. $v_1$ (ClO\textsubscript{4}\textsuperscript{-}) 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\textsuperscript{-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
Table 2.

Pressure Dependence of Internal Mode Frequencies in NH$_4$ClO$_4$  

<table>
<thead>
<tr>
<th>Mode</th>
<th>Pressure (Kbars)</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
<td>2</td>
<td>6</td>
<td>10</td>
<td>24</td>
<td>40</td>
<td></td>
</tr>
<tr>
<td>$\nu_3$(NH$_4^+$)\textsuperscript{a}</td>
<td>3310</td>
<td>---</td>
<td>3310</td>
<td>3300</td>
<td>3327</td>
<td>3330</td>
<td></td>
</tr>
<tr>
<td>$\nu_4$(NH$_4^+$)</td>
<td>1425</td>
<td>---</td>
<td>1430</td>
<td>1435</td>
<td>1435</td>
<td>1435</td>
<td></td>
</tr>
<tr>
<td>$\nu_1$(ClO$_4^-$)\textsuperscript{b}</td>
<td>939</td>
<td>---</td>
<td>940</td>
<td>940</td>
<td>Not seen</td>
<td>Not seen</td>
<td></td>
</tr>
<tr>
<td>$\nu_3$(ClO$_4^-$)\textsuperscript{a}</td>
<td>1085</td>
<td>---</td>
<td>1095</td>
<td>1105</td>
<td>1125</td>
<td>1130</td>
<td></td>
</tr>
<tr>
<td>$\nu_4$(ClO$_4^-$)</td>
<td>634</td>
<td>630</td>
<td>635</td>
<td>638</td>
<td>635</td>
<td>635</td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{a} Very broad, errors can be ±5 cm$^{-1}$.

\textsuperscript{b} Band becomes in-active due to crystal symmetry above 10 Kbars.
decomposition of AP. The pressure effects are normal and predictable for this system which is in contrast to the temperature effects.
VI. References


