A SPECTROSCOPIC STUDY OF THE POTASSIUM

NITRATE CRYSTAL SYSTEM

By

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CHAPTER I

INTRODUCTION

Scope of the Problem

The potassium nitrate crystal system has been shown to exhibit a thermal hysteresis loop between three crystalline phases (1) (2). The room temperature, orthorhombic phase and intermediate, ordered trigonal phases are well defined and understood (3) (4) (5). The high temperature, trigonal disordered phase has been the subject of numerous theoretical and experimental investigations which have mostly been directed toward relating this phase to a quasicrystalline structure or a disordered lattice concept which has been proposed for concentrated aqueous solutions and molten state forms of the salt (6) (7) (8) (9) (10).

To date, relatively few attempts have been made to explore the trigonal ordered phase of the salt in terms of its relation to the trigonal disordered phase. The occurrence of well-separated and sharp transverse and longitudianal optic mode Raman features for the ν_3 asymmetric stretching mode of this phase presents a unique opportunity to observe the degree of disordering in the ordered phase upon dilution with rubidium nitrate and $K^{15}NO_3$. The disordering of the trigonal ordered phase will hopefully lend insight into the analysis of the vibrational spectra of the trigonal disordered phase and therefore, into the concentrated solution and molten state forms of the salt.

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Attenuated Total Reflection

Infrared Spectroscopy

The technique of attenuated total reflection infrared spectroscopy (ATR) has become an established method for determining the absorption spectra of both organic molecules and inorganic salts (11) (12) (13) (14).

The technique of ATR, as applied to high temperature salts, is utilized by placing a silicon or Irtran$^®$ prism in the beam of an infrared spectrophotometer in the single beam mode. As shown in Figure 1, the geometry of the prism is such that the convergent infrared beam is focused on the prism surface, which is in contact with the sample, and then reflected into the optics of the spectrophotometer.
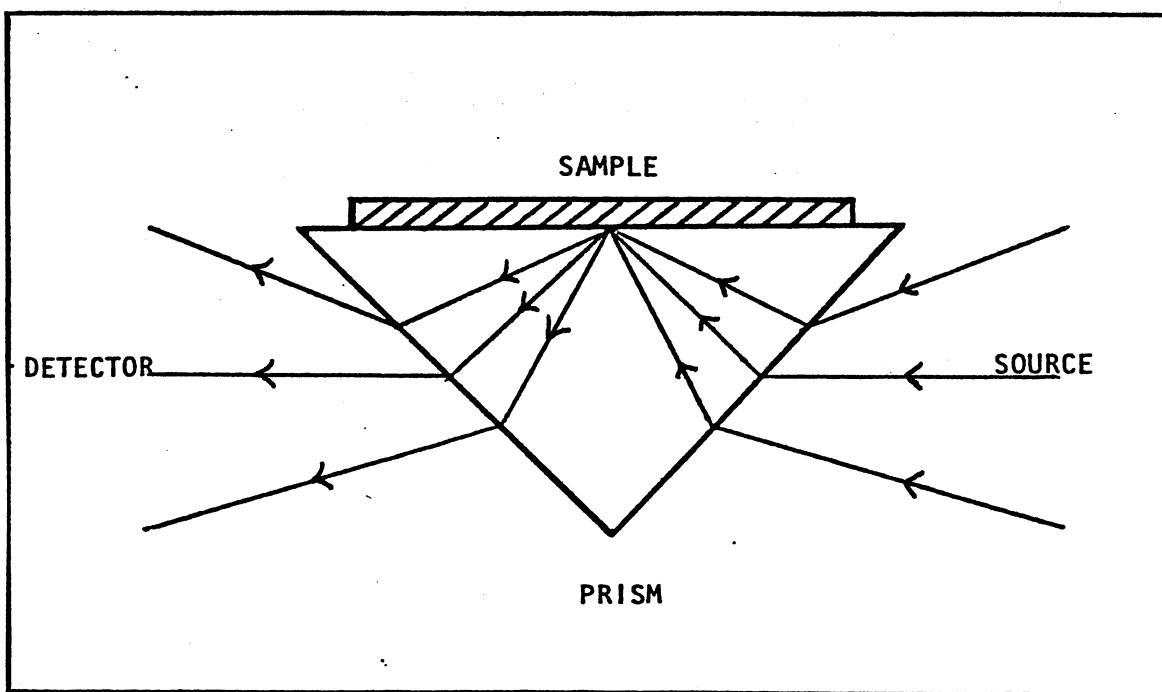

Figure 1. Convergent Infrared Beam at the ATR Element-Sample Interface

For the purpose of this study, ATR is a method by which the orientation of the nitrate C_3 axis in a crystal grown as a thin film on a silicon prism may be determined. The particular advantage of this method of orientation determination, as opposed to the commonly used polarizing microscope is twofold. Principally, sample preparation of nitrate crystals used for the studies later described require that the crystals be grown from the melt. One hundred to three hundred micron thick samples are easily prepared on the prism, with excellent optical and thermal contact at the element-sample interface by melting the sample on the heated prism surface and slowly cooling back to the high temperature phase of the potassium nitrate crystal. Secondly, growing a single bulk crystal from the melt is a slow and involved process requiring intricate thermal equipment. Also, the time and work involved in preparing the crystal may be lost if the optical properties of the crystal are destroyed by the temperature changes necessary for the Raman studies of the crystal's various phases. By the ATR method the crystals may be grown and orientationally checked within minutes, and immediately mounted for Raman studies.

Raman Spectroscopy

With the advent and development of the laser and its implementation into the field of Raman spectroscopy the field has expanded its applications almost without bound. This section is not meant to be a treatise on the theory of, or advances in Raman spectroscopy but merely a brief introduction into the field to familiarize the reader with the Raman effect as applied to this research. Excellent reviews of theoretical and experimental Raman spectroscopy are given by R. Loudon (15)

and S. Bhagavantam (16) (17).

We can define two areas of Raman activity in crystals. External modes, which are those modes charatcteristic of the crystal lattice itself, and internal modes characteristic of the molecules within the crystal lattice. For external modes, a source of incident light of frequency ω_i is focused on a crystal and creates or destroys a quantized lattice vibration called a phonon. The energy gained or lost by this process, ω, is reflected in the energy of the scattered light ω_s such that $\omega_s = \omega_i \pm \omega$. The scattered light of lower frequency compared to the incident light is refered to as the Stokes component, and conversely, the scattered light of higher frequency is known as the anti-Stokes component. The frequency of the scattered light is the entity measured in the Raman effect.

Internal modes are the molecular modes of the molecules residing in the crystal. Their activity in the Raman effect is symmetry governed in much the same way as infrared activity. Whereas infrared activity is determined by a change in the dipole moment of the molecule Raman activity is determined by a change in the polarizability of the molecule. Frequencies of molecular vibrations in the solid state usually closely parallel those in the gas phase in Raman activity with exceptions most generally noted in the lifting of degeneracies present in modes of the gas phase and a change in the activity of some modes between the two phases. These above exceptions are usually explainable in terms of the perturbations on molecular symmetry imposed by the surrounding crystal lattice and the molecular neighbors residing in the overall crystal. These effects are explained in much greater depth by Donald F. Hornig (18).

In this study, we are chiefly concerned with the three crystalline phases of potassium nitrate. Raman spectroscopy of the internal modes is the tool by which we probe the phase transitions, the phases themselves, and the nitrate ions in the crystal. Each crystalline phase exerts a different perturbation on the internal modes and thus creates a spectral pattern specific to each phase.

Nitrates

The Symmetry and Selection Rules
for the Nitrate Anion

The nitrate system has been a subject of much study and research in the past decade. The nitrate systems have principally been studied as their alkali metal salts (19) (20). However, the nitrate anion has seen use as a molecular probe in matrix isolation studies (21) (22). One of the main reasons for the nitrate system's popularity is the relatively high symmetry, D_{3h}, of the undistorted nitrate anion, which lends itself to be particularly sensitive to pertrubation from its surroundings. As can be seen in Table I, the selection rules allow several vibrational modes to be monitored via infrared and Raman spectroscopy in order to observe the effects of environmental changes upon the nitrate anion.

A good example of the nitrate anion's sensitivity to its surroundings is the potassium nitrate crystal system. This crystal system exhibits a thermal hysterisis loop between its three crystalline phases as shown in Figure 2.

Phase II is the room temperature crystalline phase. It has an

TABLE I

FREE NITRATE ION SELECTION RULES

Mode	Symmetry	Activity	Degeneracy	Frequency (cm^{-1})	Description
ν_1	A_1	R	1	1050	Symm. Stretch
ν_2	A_2	I.R.	1	820	Out of Plane Bend
ν_3	E	I.R., R	2	1390	Assym. Stretch
ν_4	E	I.R., R	2	720	In Plane Bend
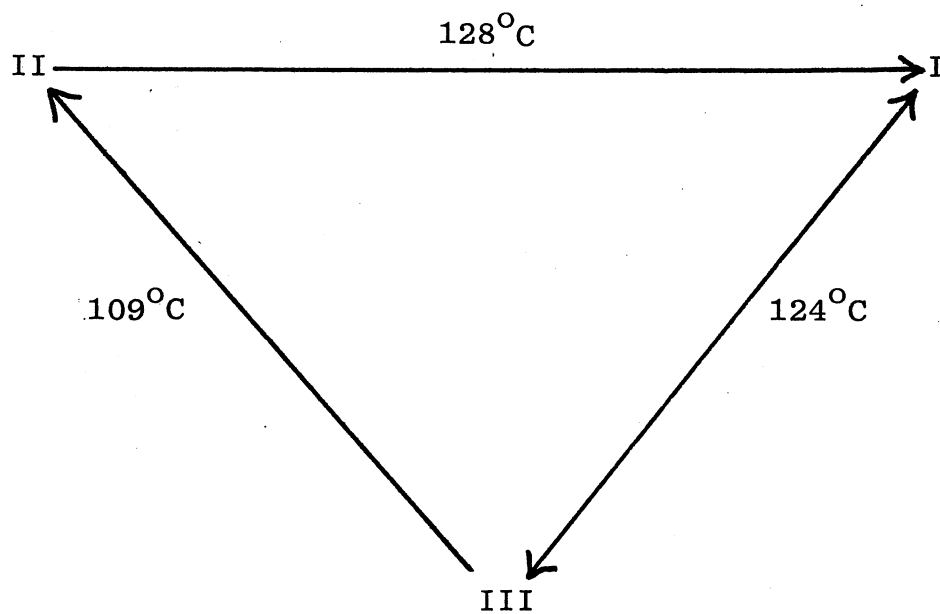
Figure 2. Hysterisis Loop Between the Three Crystalline
Phases of Potassium Nitrate

orthorhombic unit cell with space group D_{2h}^{16} containing four molecules

per unit cell (1). The nitrate ion site symmetry is C_s (1). Figure 3

is the correlation chart for Phase II showing the correlation between

the symmetry of the free nitrate ion to the symmetry of the nitrate ion

in the bulk crystal for this phase.

Free Nitrate Ion   Site   Space Group

D_{3h} C_s D_{2h}^{16}

Figure 3. Correlation Chart for Phase II for Potassium Nitrate

At 128 degrees centigrade, the crystal undergoes a second order

phase transition to Phase I. There has been much discussion about the

unit cell and symmetry of this phase. Karpov and Shultin (23) specify

a trigonal lattice with space group D_{3d}^5 containing two molecules per

unit cell. K. O. Stromme (24) agrees with the space group proposed but postulates three molecules per unit cell, while M. H. Brooker (2) agrees with the proposed space group also but, li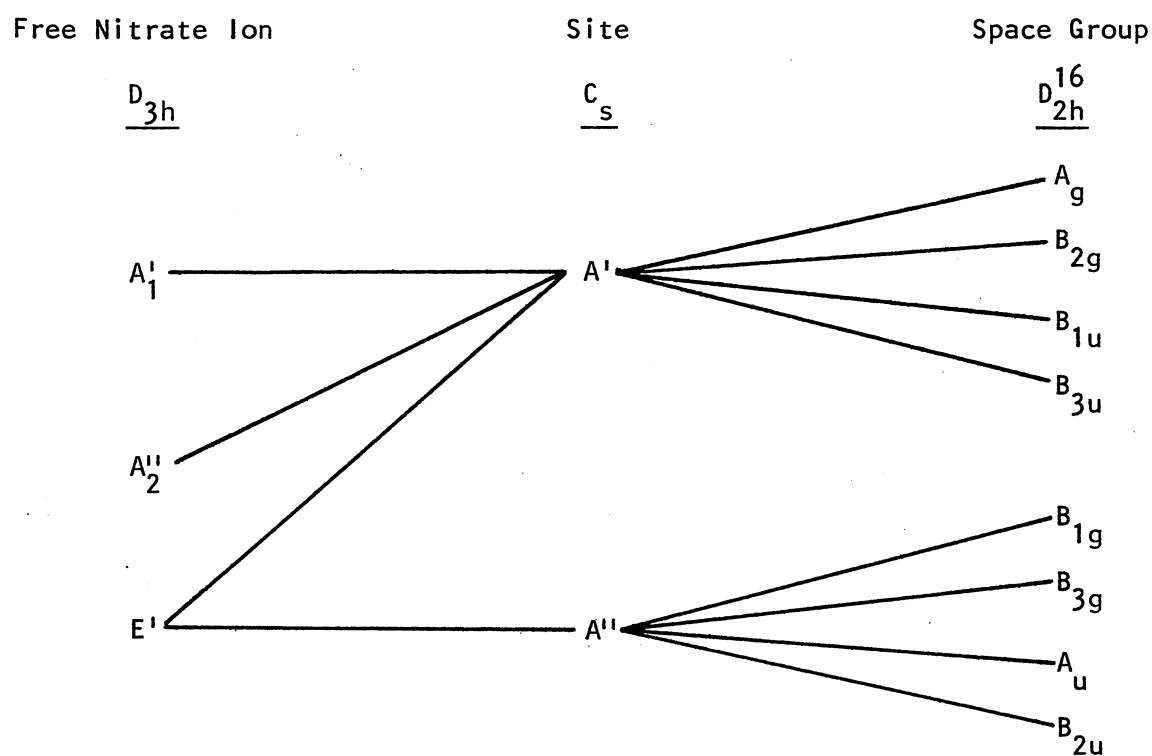ke Karpov and Shultin, postulates two molecules per unit cell. For the purpose of this study the controversy was resolved by Khanna, Lingscheid, and Decius (1). It is their contention that the spectrum of Phase I can be discussed in terms of the magnitude of the potential barrier to rotation about the trigonal axis of the crystal. If this barrier is negligable, the nitrate ion can be regarded as freely rotating, i.e. no interaction between nitrate ions and the D_{3h} selection rules should hold. However, in Phase I, ν_1 is still infrared active and ν_4 is split. Therefore, they deem it reasonable to postulate a finite barrier to rotation and assign a symmetry of D_{3d}^5 with one molecule per unit cell which satisfies the X-ray structure by a disordering of the nitrate orientation. This postulate is firmed up with ^{15}N - ^{14}N isotopic dilution studies.

Upon cooling the crystal to 124 degrees centigrade, Phase I converts to Phase III. It is Phase III that is the principal phase of interest in this study. Phase III has a trigonal structure with space group C_{3v}^5 and contains one molecule per unit cell (1). The nitrate ion site symmetry is C_{3v}. Figure 4 shows the correlation between the symmetry of the free nitrate ion to the symmetry of the nitrate ion in the bulk crystal for this phase.

Further cooling of Phase III causes reversion to Phase II at 109 degrees centigrade. Phase III has been known to be preserved, in a metastable state, at temperatures well below 109 degrees centigrade for as long as two weeks if the crystal is kept away from moisture.
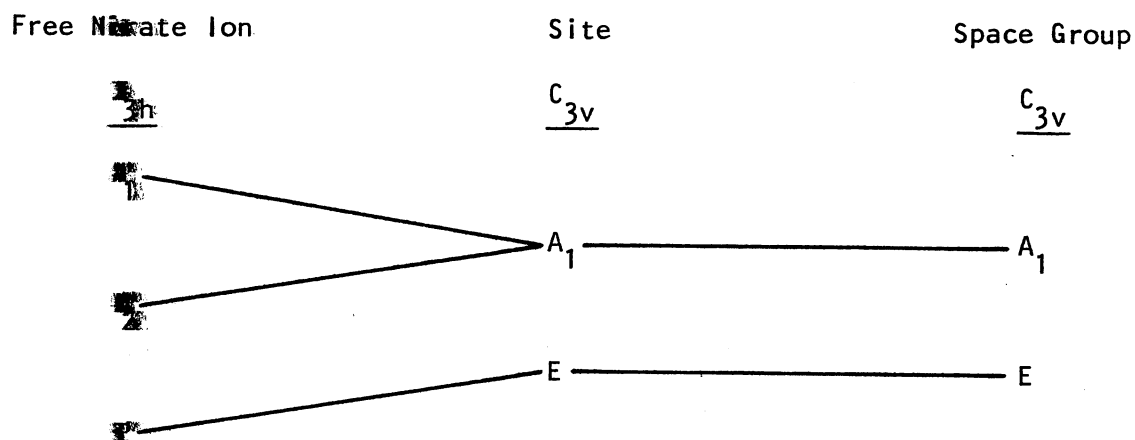
Free Nitrate Ion   Site   Space Group

D_{3h} C_{3v} C_{3v}

A'_1

A''_2 ——————————————— A_1 ———————————————————— A_1

E'

E'' ——————————————— E ————————————————————— E

Figure 4. Correlation Chart for Phase III for Potassium Nitrate

Figure 5 shows the Raman spectra for the ν_3 mode region of the three crystalline phases of potassium nitrate and one can see how drastically the nitrate anion is affected by the crystal geometry.

Mixed Crystals

For the purpose of this research, data for the metastable Phase III of the potassium nitrate crystal system will be presented in order to display the influence of rubidium substitution and isotopic nitrogen dilution on the dipole coupling of the nitrate ions in the bulk crystal. This coupling is responsible for the much greater restoring forces in the longitudinal modes (higher wavenumbers) relative to the transverse modes (lower wavenumbers) which appear as two distinct components in the ν_3 asymetric stretch mode of the metastable Phase III. The change in the shape and splitting, i.e. broadining reflects a disordering and a decrease in splitting reflects a decoupling of dipole moments, upon dilution will directly denote a change in the environment of the
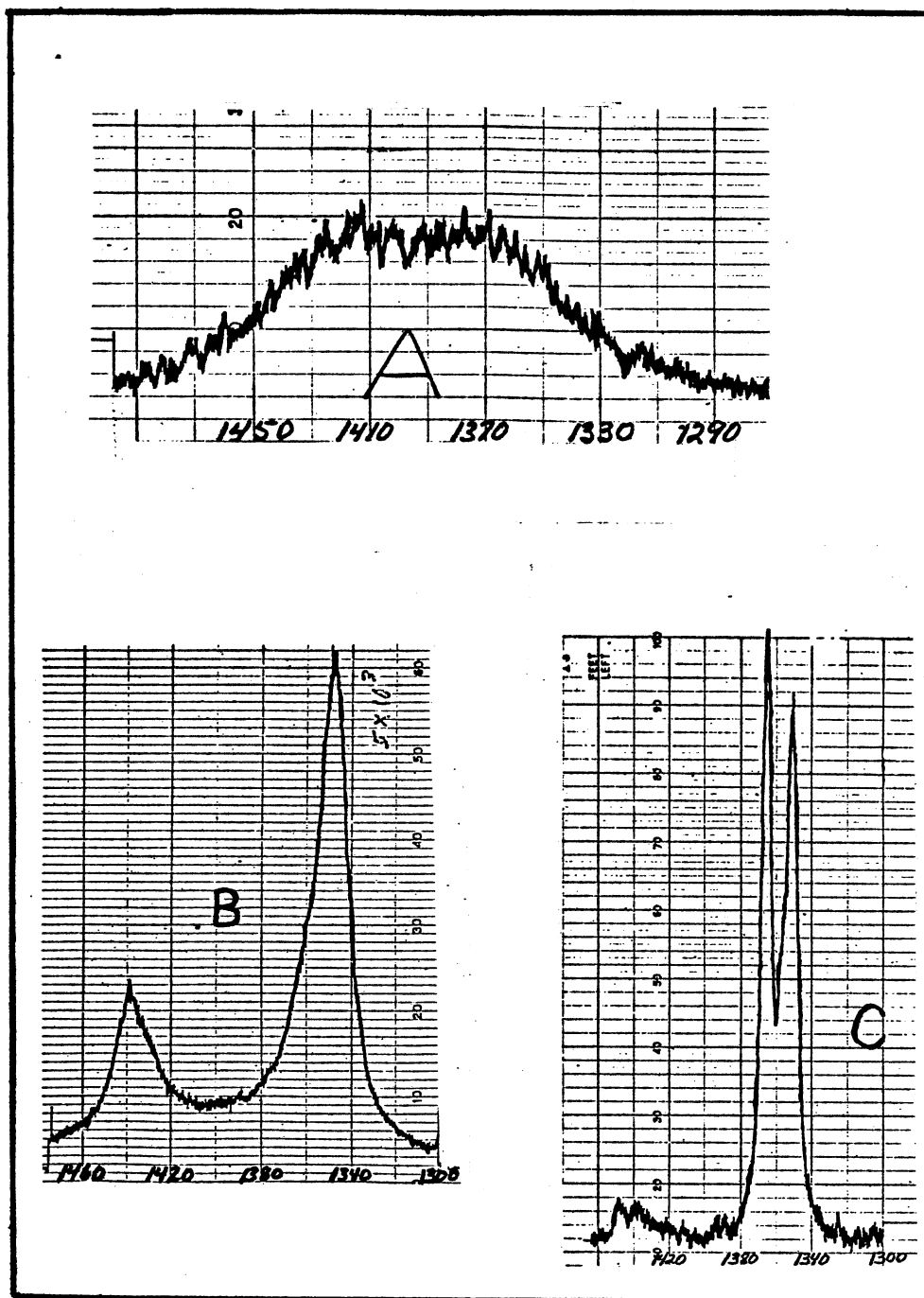
Figure 5. Raman Spectra of the Three Crystalline Phases of
Potassium Nitrate: (A) Phase I, Disordered Trigonal;
(B) Phase III, Ordered Trigonal; (C) Phase II,
Orthorhombic

nitrate ion.

Briefly, substitution of rubidium ions for potassium ions in the crystal lattice will destroy the translational symmetry of the crystal and create non-equivalent anion environments, that is to say that different nitrate anions will have a different potassium -rubidium cation environment within the crystal. If the behavior of the nitrate anion is strongly governed by the potassium crystal lattice then this treatment should cause drastic changes in the appearance of the internal mode spectra. It was also wondered if the partial substitution with rubidium would produce a change in the stability of the metastable Phase III of the crystal.

After observing the effects of changing the external cation environment of the nitrate anion, the potassium nitrate crystal system was isotopically diluted with $K^{15}NO_3$ under a total potassium lattice. The effect of this dilution would be a decrease in the coupling of the internal mode vibrations between neighboring unit cells due to the vibrational frequency differences between the two isotopic nitrate ions. The random substitution of $^{15}NO_3^-$ ion would destroy the translational symmetry of the $^{14}NO_3^-$ dipoles necessary to produce the observed transverse and longitudinal spectral components. This effect should always manifest itself by a decrease in the transverse-longitudinal component splitting of the ν_3 internal mode and lend some insight into the magnitude of the interaction forces between unit cells.

The results of these studies will be presented and discussed in a later section.

CHAPTER II

EXPERIMENTAL

ATR and Raman Apparatus and Proceedure

The experimental portion of this work consisted of two parts. The first part involved the preparation of oriented potassium nitrate crystals on a silicon prism and subsequent characterization of the orientation and phase for these crystals by infrared spectroscopy. The second part involved obtaining the spectra of the crystal in its metastable phase using Raman spectroscopy.

The experimental setup for preparing the oriented films is shown in Figure 6. The resistor-heater was controlled using two Variacs® in series. This supplied the ability to vary the temperature of the heater with the second Variac® while the first Variac® guarded against supplying too much voltage to the heater and burning it out. Baker Analyzed® reagent grade potassium nitrate was placed on the prism at ambient temperature and then slowly heated, via the Variacs®, until fused. The fused salt was spread across the element using a nickel spatula and then slowly cooled to the high temperature crystalline Phase I.

The entire assembly and crystal was next mounted in the beam condenser of an unmodified infrared spectrophotometer in the single beam mode (second chopper stopped). Except for the silver chloride polarizer no special foreoptics were required. Orientation of the C_3 rotation
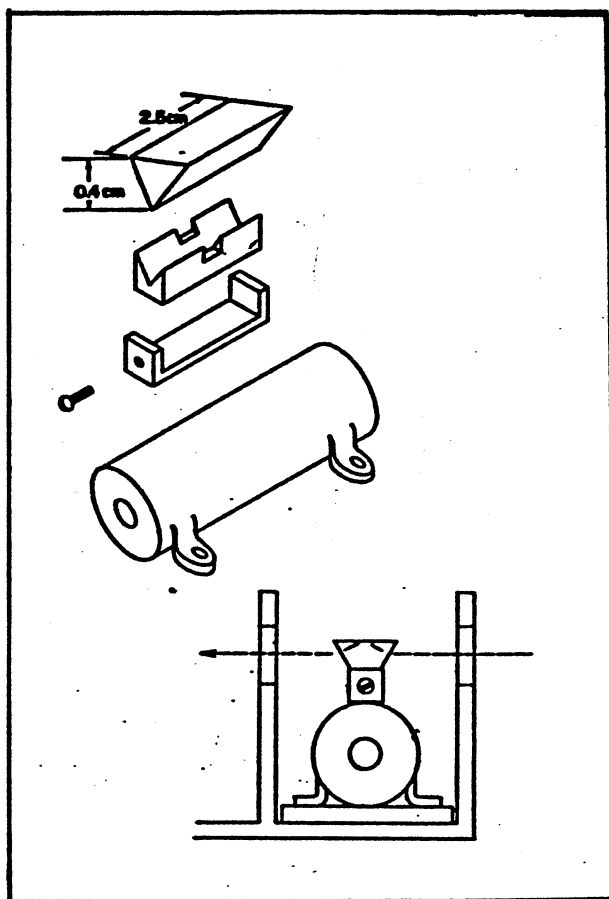
12

Figure 6.   Resistor-Heater, Prism Mount,
            and Prism Used in ATR
            Studies

axis purpendicular to the prism surface, was determined by observing the vibrational dipole moment change parallel to the C_3 axis of the crystal with polarized infrared radiation in the frequency range of 820 cm^{-1}. If the crystal was oriented, the ν_2 out-of-plane mode would be observed at one polarization and be completely absent at a polarization ninety degrees away from the first.

Once a properly oriented crystal was obtained, the prism and crystal were transfered to the assembly shown in figure 7 in order to obtain the Raman spectra of the crystal. Here again, two Variacs® in series were used for temperature control.

Raman spectra were obtained using a one hundred eighty degree scattered light to incident light angle (backscatter). All samples reported in this work were prepared and studied in this manner.

Instrumentation

The infrared spectra were recorded with a Beckman IR-7 Spectrophotometer® which is a prism-grating instrument that covers the range from 600 to 4000 cm^{-1}. The instrument was equipped with a silver chloride polarizer for polarization studies.

Raman scattering was recorded on a system constructed around a Jarrel-Ash 25-100 dual monochromater® fitted with an ITT FW-130PM photomultiplier tube and a Hamner photon counting instruments. Excitation was achieved with a Coherent Radiation Model 52® argon ion laser using both the 5145 Å (green) and the 4880 Å (blue) lines.
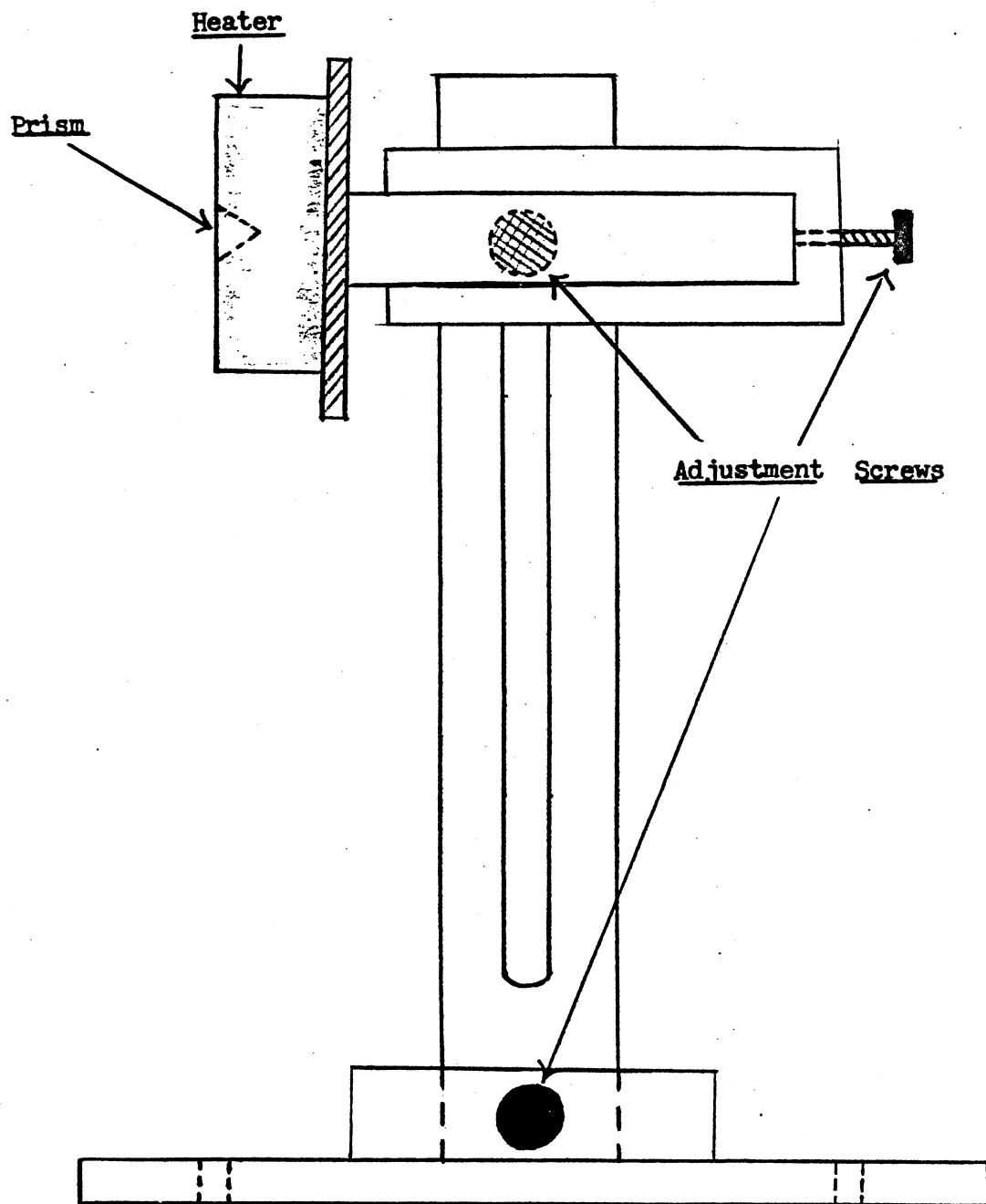
Figure 7. Prism Mounting Stage Used in Raman Studies

CHAPTER III

RESULTS

As mentioned in Chapter I, it was the intent of this research to explore the potassium nitrate crystal system by observing, spectroscopically, the effects of altering the system both anionically and cationically. Let us review the results obtained by treating the pure potassium nitrate system and the diluted systems independently and then compare the diluted systems to the pure systems in order to correlate the results.

One should recall that when the nitrate ion is unperturbed, i.e. the C_3 rotational axis is maintained, the ν_3 vibrational mode is doubly degenerate. In Phase III, the degeneracy of the ν_3 vibrational mode is maintained but dipole-dipole coupling gives rise to a transverse and longitudinal component splitting of approximately 90 cm^{-1}. It is the shape of these components and the magnitude of their separation (splitting) in Phase III of the crystal that we will focus on.

When potassium nitrate is prepared in the manner previously described the Raman spectra for the metastable Phase III of the salt exhibits two sharp, intense transverse and longitudinal components at 1348 and 1438 cm^{-1}, respectively, as seen in Figure 8. These component positions give rise to a splitting of 90 cm^{-1}. The position and intensity of these two components can be shown to be a function of the bulk crystal's orientation with respect to the Raman optics. However, the
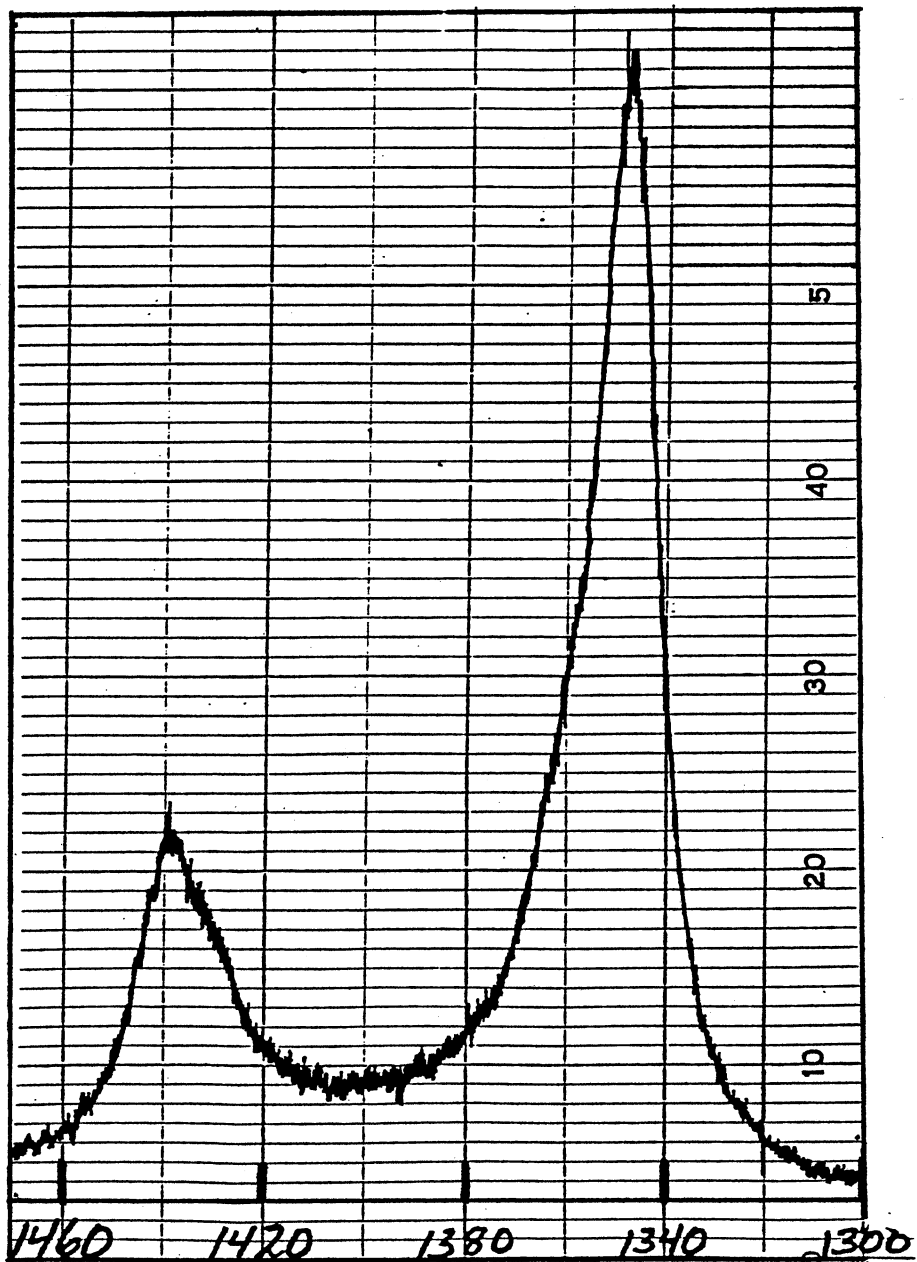
16

Figure 8.   Raman Spectra of $K^{14}NO_3$, Phase III

magnitude of the transverse-longitudinal splitting remains nearly constant with various orientations.

Another aspect of the pure potassium nitrate, Phase III, ν_3 spectra is shown in Figure 9. This spectra is the product of backscattering from films that crystallized with the nitrate planes non-parallel to the prism surface. The phonons produced are scattered at an angle to the trigonal axis such that a component arising from a mixture of transverse and longitudinal phonons is observed between the pure transverse and longitudinal components which are still present.

After careful measurements on the ν_3 vibrational mode of the potassium nitrate system the effects of a dilution of the potassium system with rubidium was determined. The ratio of potassium to rubidium was chosen to give a mixed salt of compostion $K_{0.7}Rb_{0.3}NO_3$. This mixture was dicided on since some work had already been done in this area, with this mixture, by Shultin and Karpov (25). Figure 10 shows a representative example of the spectra of the mixed salt. Components of ν_3 are seen at 1347 and 1436 cm^{-1} giving a component splitting of 89 cm^{-1}.

Shultin and Karpov reported an increased stability of Phase III upon rubidium dilution relative to reported stability of pure potassium nitrate, Phase III. Attempts were made to verify this statement but no difference in relative stability could be found. Since Shultin and Karpov observed the stability of Phase III using a Sawyer-Tower circuit as opposed to optical observance of the ferroelectric phase, we believe that herein lies the descrepancy of results. Kohnke, Baum, and Northrip (26) reported that an electric field imposed across a ferroelectric material prolongs the stability of the material by lowering the Gibbs' free energy and thereby increase the stability of the phase. This hy-
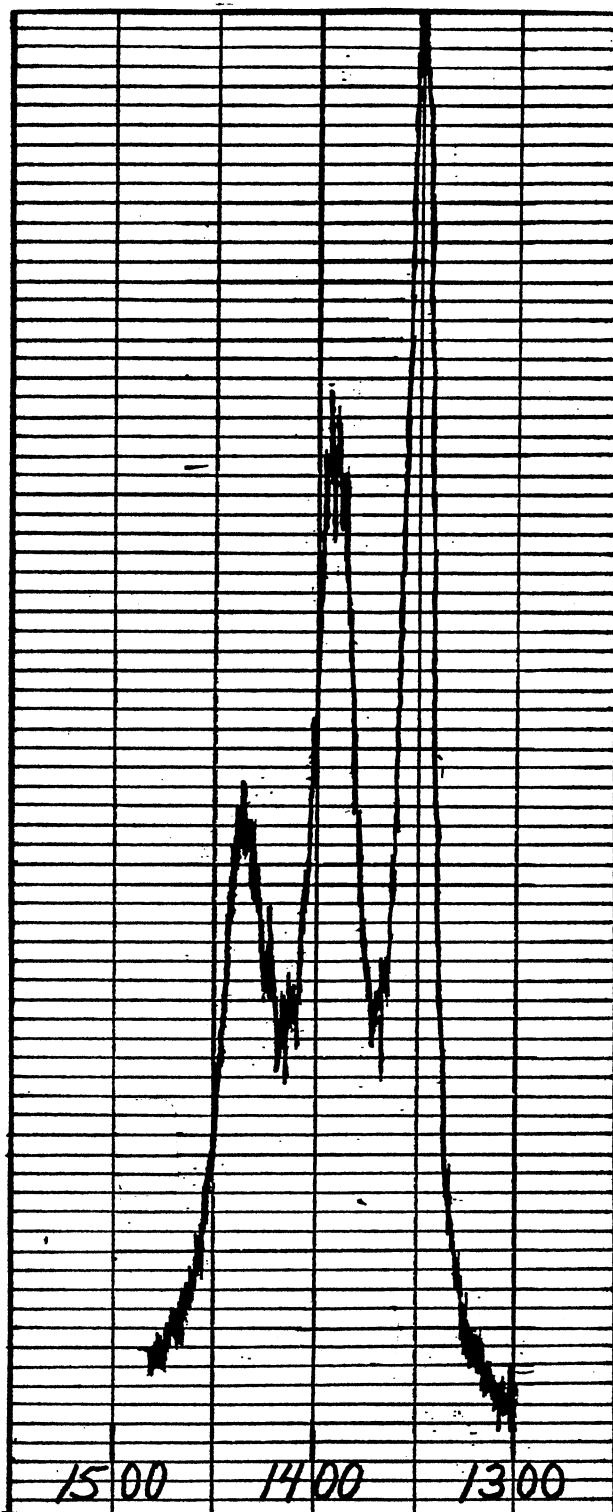
Figure 9.   Raman Spectra of $K^{14}NO_3$, Phase
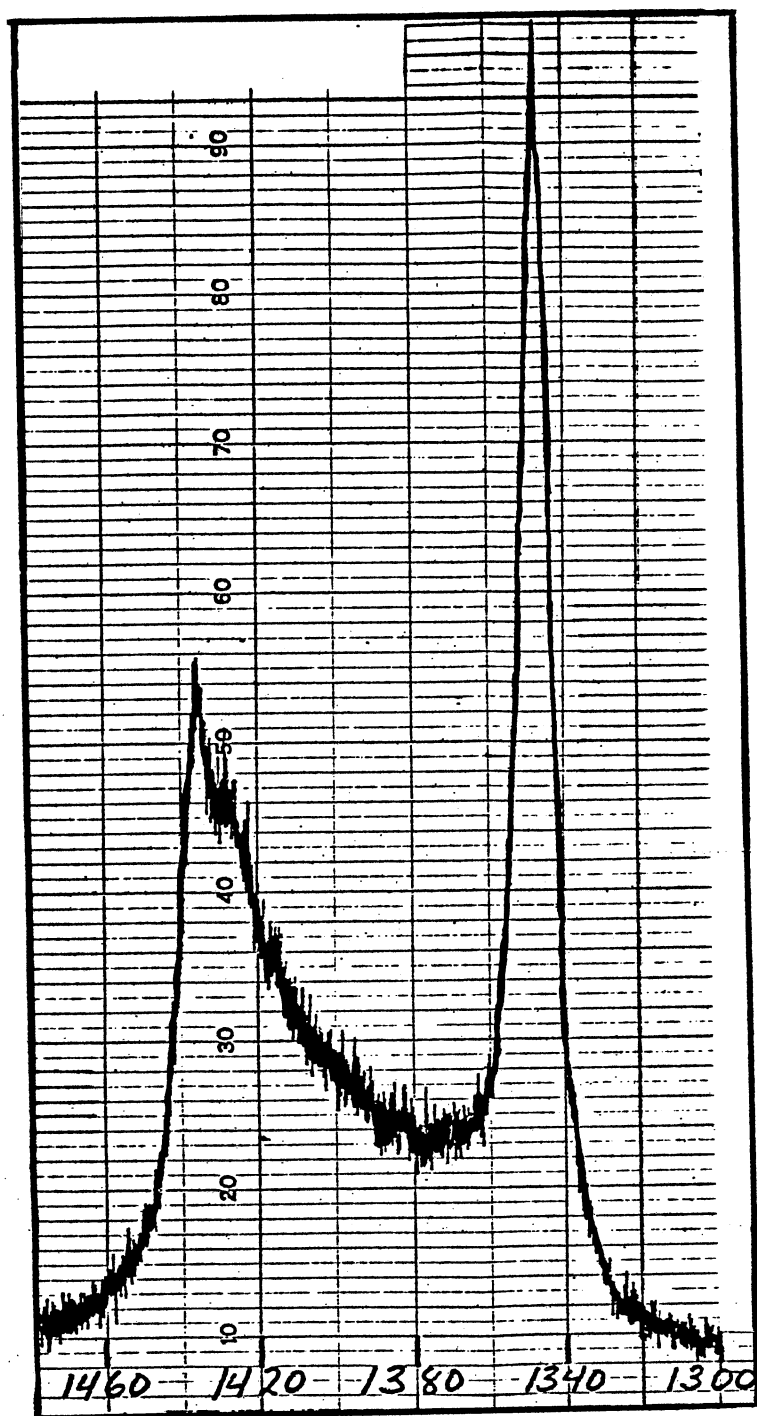III, Showing the Mixed
Component

Figure 10. Raman Spectra of $K_{0.7}Rb_{0.3}NO_3$ Mixed
Salt, Phase III

pothesis was not tested in our laboratory.

The next step in the investigation was to isotopically dilute the ^{14}N nitrogen in the nitrate ion with ^{15}N nitrogen in order to study any effect on the internal modes brought about by this alteration. Spectra showing 20%, 50%, and 80% dilutions of ^{14}N with ^{15}N are shown in Figure 11 along with the spectra for 100% K^{15}NO$_3$. Table II shows the various dilutions, the frequency of their transverse and longitudinal component splitting, and the magnitude of the component splitting for pure ^{14}N potassium nitrate, the three dilutions with ^{15}N potassium nitrate in ^{14}N potassium nitrate, and pure ^{15}N potassium nitrate, Phase III.

TABLE II

TRANSVERSE AND LONGITUDINAL COMPONENTS FOR THE
POTASSIUM NITRATE SYSTEM, PHASE III

System	Transverse	Longitudinal	Splitting
K^{14}NO$_3$	1348 cm^{-1}	1438 cm^{-1}	90 cm^{-1}
20% K^{15}NO$_3$*	1347 cm^{-1}	1433 cm^{-1}	86 cm^{-1}
50% K^{15}NO$_3$*	1330 cm^{-1}	1425 cm^{-1}	95 cm^{-1}
80% K^{15}NO$_3$*	1323 cm^{-1}	1415 cm^{-1}	92 cm^{-1}
K^{15}NO$_3$	1319 cm^{-1}	1404 cm^{-1}	85 cm^{-1}

* All percentages are balanced with K^{14}NO$_3$

As can be seen, both components shift toward the values of pure $K^{15}NO_3$ as more $K^{15}NO_3$ is added to the $K^{14}NO_3$ as a diluent.

Here again, backscattering from $K^{15}NO_3$-$K^{14}NO_3$, $K^{15}NO_3$ and the $K_{0.7}Rb_{0.3}NO_3$ films which crystallized with the nitrate planes not parallel to the prism surface show phonon mixing. This effect is shown in Figure 12. This fact supports the contention that these spectral features result from a mixture of transverse and longitudinal phonons as observed in the pure $K^{14}NO_3$ system.

Table III shows a listing of all nitrate frequencies for all systems investigated.
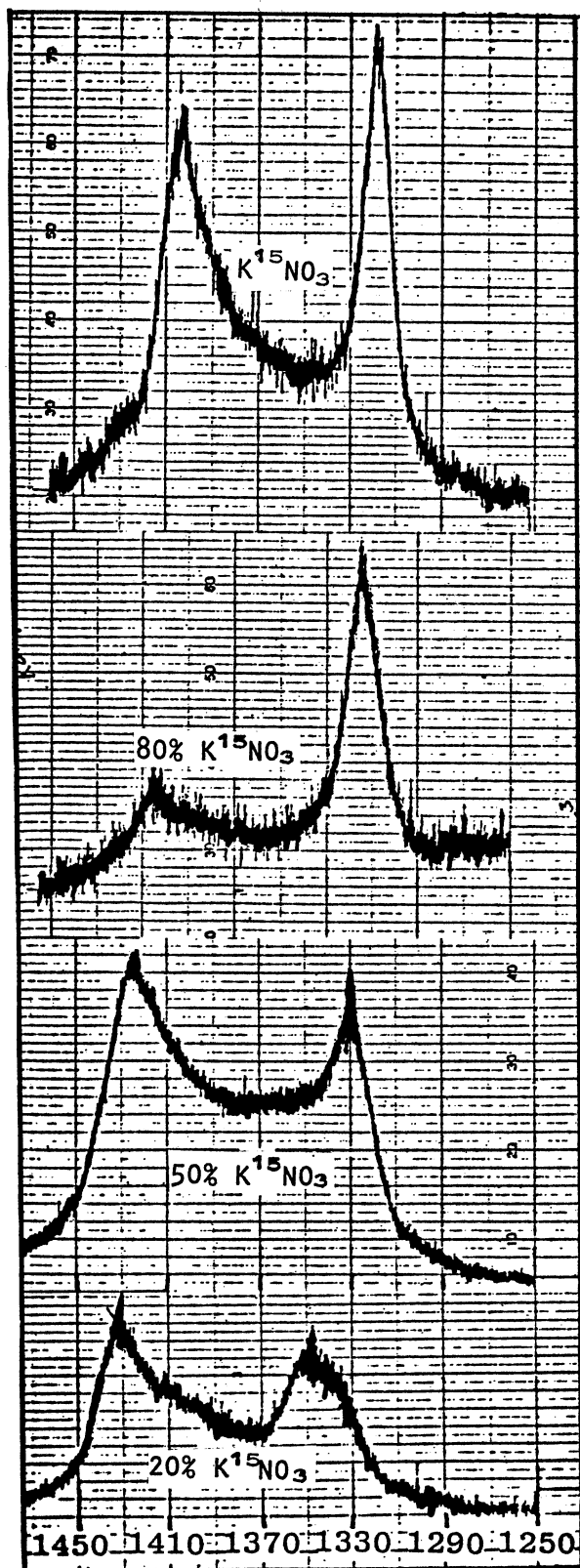
Figure 11.　Raman Spectra of Isotopically
Diluted Potassium Nitrate
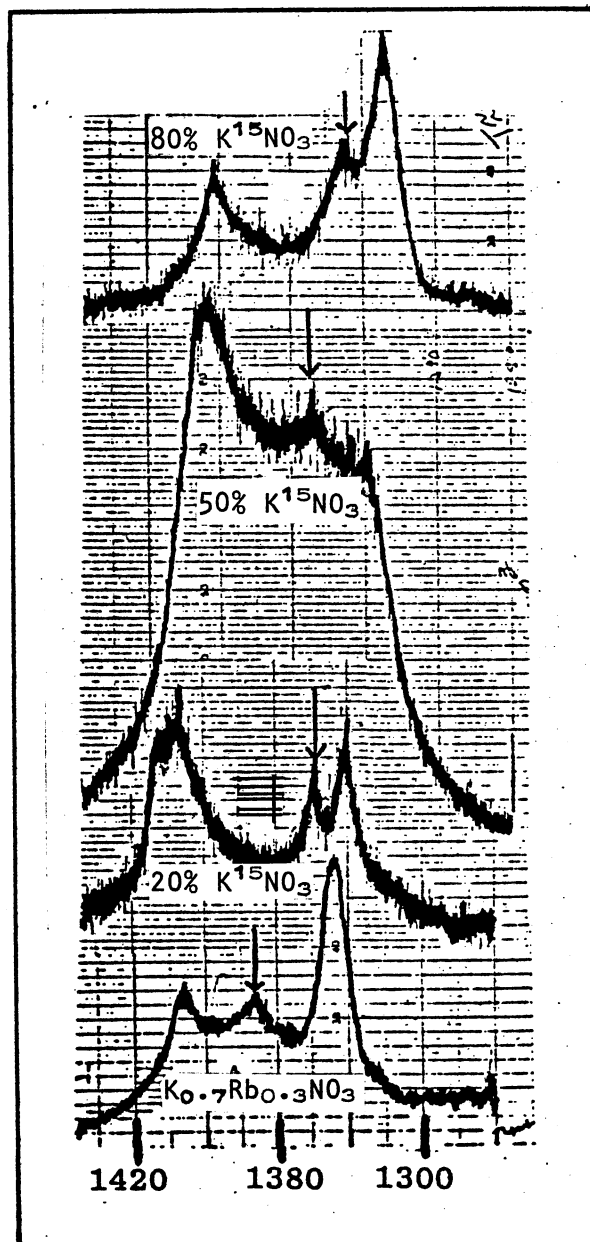
Figure 12. Raman Spectra of All Mixed
Systems Studied Showing
the Transverse and
Longitudinal Component
Mixing

TABLE III

TRANSVERSE AND LONGITUDINAL COMPONENTS FOR ALL
SYSTEMS INVESTIGATED

System	Transverse	Longitudinal	Splitting
$K^{14}NO_3$	1348 cm^{-1}	1438 cm^{-1}	90 cm^{-1}
$K_{0.7}Rb_{0.3}NO_3$	1347 cm^{-1}	1436 cm^{-1}	89 cm^{-1}
20% $K^{15}NO_3$*	1347 cm^{-1}	1433 cm^{-1}	86 cm^{-1}
50% $K^{15}NO_3$*	1330 cm^{-1}	1425 cm^{-1}	95 cm^{-1}
80% $K^{15}NO_3$*	1323 cm^{-1}	1415 cm^{-1}	92 cm^{-1}
$K^{15}NO_3$	1319 cm^{-1}	1404 cm^{-1}	85 cm^{-1}

* All percentages are balanced with $K^{14}NO_3$

CHAPTER IV

SUMMARY

It has been shown that in two major respects that the experimental ν_3 vibrational spectra for a potassium nitrate crystal, Phase III, with 30% rubidium and with 20%, 50%, and 80% $K^{15}NO_3$ mixtures is analogous to that for $K^{14}NO_3$, Phase III, and can be interpreted as being produced by an average resonant ν_3 frequency (27) arising from dynamic coupling of the dipole moments between neighboring nitrate ions as described by Decius (28) and Frech and Decius (29) (30) (31). It was expected that these dilutions would alter or destroy the coupling of the nitrate ions by disordering the system with respect to the phonon propigation within the crystal. However, this was not what was observed.

In all four cases the Raman spectra taken along the trigonal axis shows two sharp components analogous to the transverse and longitudinal features of $K^{14}NO_3$ and $K^{15}NO_3$, Phase III. The spectra taken from phonon scattering well off the trigonal axis of the crystal produces a third distinct component, appearing between the transverse and longitudinal features of the pure $K^{14}NO_3$ and $K^{15}NO_3$, which arises from a combination of the transverse and longitudinal components which were observed in both perturbations and in the $K^{14}NO_3$ and $K^{15}NO_3$ spectra.

As seen in Table III, upon dilution the transverse and longitudinal components of the isotopically diluted salts approach the frequencies of the transverse and longitudinal components for pure $K^{15}NO_3$ without

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sharing features of both, simultaneously. For both pure $K^{14}NO_3$ and $K^{15}NO_3$ the transverse and longitudinal component splitting is about 86 cm^{-1}.

The only anomaly arises in the fact that for the 50% and 80% $K^{15}NO_3$ in $K^{14}NO_3$ dilutions, the spectra show the transverse and longitudinal component splitting to be about 95 cm^{-1}, which is greater than in any other systems studied. It is thought that the explanation for this un-expected behavior lies further in the realm of dipole-dipole coupling theory, on the inter-crystalline level. Similar interactions between neighboring dipoles of similar symmetry and frequency are described by Devlin, Ritahaupt, and Hudson (32).

From the results presented it can be concluded that the substituted metastable Phase III of potassium nitrate behaves as the pure potassium nitrate ordered crystal, Phase III. Since the dilution of the system with both rubidium and isotopic $^{15}NO_3^-$ caused no appreciable effect on the transverse and longitudinal component splitting, which is theoreti-cally inversly proportional to particle density and was expected to decrease upon dilution, we can only determine that the spectra of Phase III, ν_3 region, is a product of a delocalized average resonant frequency since the pattern of ν_3 is largely unaffected by the dilutions studied.

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Candidate for the Degree of

Master of Science

Thesis: A SPECTROSCOPIC STUDY OF THE POTASSIUM NITRATE CRYSTAL SYSTEM

Major Field: Chemistry

Biographical:

Personal Data: Born in Oklahoma City, Oklahoma, Feburary 25, 1947, the son of Mr. and Mrs. R. B. Hudson.

Education: Graduated from C. E. Donart High School, Stillwater, Oklahoma, in May, 1965; received Bachelor of Science degree from Oklahoma State University, Stillwater, Oklahoma with a major in Chemistry and minors in Mathematics and Physics, in May, 1972; completed requirements for the Master of Science degree at Oklahoma State University in May, 1976.

Professional Experience: Graduate Teaching Assistant, Oklahoma State University, Janurary, 1972 to December, 1973; National Science Foundation Research Assistant, Oklahoma State University, September, 1972 to December, 1973; Chemist, The Dow Chemical Company, U.S.A., Freeport, Texas, January, 1974 to May, 1976; Laboratory Supervisor, The Dow Chemical Company, U.S.A., Freeport, Texas, September, 1975 to May, 1976.

Membership in Professional Societies: Member and Local Section Officer in the American Chemical Society.

Military Service: United States Navy, September, 1967 to March, 1969; Viet Nam Veteran; Honorable Discharge, March, 1972.