THE VIBRATIONAL SPECTRA OF $LiNO_3$ AND KNO_3 IN VARIOUS INERT MATRICES

By

GARY DALE POLLARD

Bachelor of Arts

Oklahoma State University

Stillwater, Oklahoma

1969

Submitted to the Faculty of the Graduate College
of the Oklahoma State University
in partial fulfillment of the requirements
for the Degree of
MASTER OF SCIENCE
May, 1972

THE VIBRATIONAL SPECTRA OF $LiNO_3$ AND KNO_3 IN VARIOUS INERT MATRICES

Thesis Approved:

J. Paul Devlin
Thesis Adviser

Tom E. Moore

D. D. Durham
Dean of the Graduate College

ACKNOWLEDGEMENT

I would like to express my sincere appreciation to Dr. J. Paul Devlin for his advice, assistance, patience and encouragement during the course of this study.

Thanks is due to Paul C. Li for his technical assistance and many helpful discussions.

Finally, I wish to extend my gratitude to the National Science Foundation and the Oklahoma State University Research Foundation for their support of this project.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

CHAPTER I

INTRODUCTION

Purpose

This study was directed to the question of the nature of the environment experienced by the nitrate anion in various systems, but also included attempts to develop a good method of obtaining Raman spectra of matrix isolated species. Smith[6] attempted to develop techniques for the measuring of Raman spectra of the matrix isolated species without much success. However, the infrared spectra of the matrix isolated species gave a large amount of information. This study thus emphasized the infrared spectra in order to exploit their contribution to the understanding of the nitrate anion in various environments.

Although the determination of matrix isolation Raman spectra was a second goal, little progress was made in this area. This will be discussed in detail in Chapter II. The cell was designed so that both the infrared and Raman spectra could be run on the same sample. After the information from a particular sample was obtained from the infrared, the Raman spectrum was commonly attempted but without much success.

At present, good Raman spectra still has not been obtained. However, the new infrared spectra contains much information which is helpful in characterizing nitrate ion environments. Consequently, this thesis is an infrared study of the nitrate ion in the various environments.

Matrix Isolation

The matrix isolation technique was first applied by G. C. Pimentel[3] in 1954. The method consists of the co-condensation of a mixture of the absorbing substance (A) and a matrix gas (M). This is achieved by directing the mixture onto a NaCl or CsBr plate that is mounted on a cryogenic finger.

The M/A ratio is always very large. A person might think that perhaps 100 matrix molecules for every absorbing molecule would be sufficient to isolate the absorbing molecule from the other absorbing molecules. This has been found to be untrue; typical M/A ratios are 500:1 to 1000:1. Snelson[4] reports that to isolate monomeric LiF in neon a dilution of at least 80,000:1 is required, probably because of the high LiF kinetic energy at vaporization temperatures.

Matrix isolation was originally developed to study free radicals and other reactive species. Most matrix isolation work has been with unstable species, although more recently matrix isolation has been used to study molecular interactions and structure of stable species.

The absorbing material can be mixed with the matrix gas in a number of ways. When the absorbing material is a gas itself, it is mixed with the matrix gas and the two gases are deposited through one nozzle onto the cryotip. An advantage to this method is the M/A is easily determined because the gases are mixed before they are deposited. Liquids, however, must be mixed with the matrix gas at the time of deposition. The matrix gas must enter the cell through one nozzle and the liquid vapor through another nozzle. If the vapor pressure of the liquid is low enough or a solid is used then some type of heater must be used to vaporize the absorber. Obviously one cannot easily measure the

M/A ratio when using this method. One can, however, get an idea of the relative amounts of matrix gas and absorber by using a flowmeter with the matrix gas and measuring the temperature at which the absorber is being deposited from a Knudsen cell. Knudsen's equation is $K = PA/(2 RT/M)^{\frac{1}{2}}$ where K is the rate of effusion through the orifice in grams/second, A is the area of the orfice in square centimeters, M is the atomic weight of the gas and P is the vapor pressure of the gas in dynes/cm.^{2}. If vapor pressure data is available, the amount of absorber can be calculated. One can also tell from the infrared spectrum the relative amounts of matrix gas and absorber present by looking at the band intensities.

Matrix materials are chosen to keep interactions between the matrix and the absorber to a minimum. Other physical properties are important though. The matrix must be rigid so that the trapped species cannot diffuse through the matrix. A rough guide is that the temperature of the matrix must be less than half the matrix melting point (T_m) in ^oK. Tammann's rule, which relates the temperature at which diffusion first becomes appreciable (T_d) to the melting point, is for ionic compounds T_d is ca. 0.57 T_m and for covalent compounds T_d is ca. 0.90 T_m[1]. This is only a rough guide though and one should operate at the lowest temperature attainable. Another important physical property of the matrix is that it must be transparent in the infrared and not have bands which interfere with the absorber bands. Another desirable property of the matrix material is low heat of sublimation so that the matrix will not increase the temperature of the cryotip an appreciable extent. High thermal conductivity is also a desirable property so that heat can be dissipated quickly when the matrix material hits the cryotip. A thicker sample film can be made if the thermal conductivity is high and heat can dissipate through the matrix quickly.

The most commonly used matrix materials are the noble gases and nitrogen. Other materials that can be used are O_2, CO, N_2O, CH_4, CO_2, SF_6 and CCl_4. Liquid helium ($4^{o}K$) or liquid hydrogen ($20^{o}K$) temperatures are required for most matrix materials, but liquid nitrogen is sufficient for SF_6, CO_2, and CCl_4. Refrigerant liquids are now being replaced with miniature Joule-Tompson cryostats and closed cycle refrigerators which can be operated at any temperature desired. This is an advantage in that the matrix can be warmed until diffusion occurs to study spectral changes. They also are inexpensive to operate although a higher initial investment is required.

One cannot easily predict what effect the matrix will have on the results. In general, the frequencies obtained are close to the gas phase values, but exceptions do occur. One matrix may have sites that can accommodate monomers better than dimers or vice versa. Also a matrix may have multiple sites in which a species can be trapped which can complicate spectra to some extent. Although this phenomenon is quite common, bands from absorbers in different trapping sites can sometimes be identified by varying the matrix material.

An advantage of matrix isolation in the infrared is that bands are very sharp which affords good resolution of bands with similar frequencies.

The Alkali Metal Nitrates

In the past several years numberous papers based on the use of the nitrate anion as a molecular probe have appeared. The nitrate ion is valuable because of the relatively high symmetry (D_3h) of the undistorted anion. Provided the C_3 rotational axis is maintained, both $\nu_3(e)$ and $\nu_4(e)$ are doubly degenerate. Therefore, any splitting of these modes can be related to distortion of the anion. Also any shift in frequencies of the bands can be interpreted in terms of the symmetry and strength of forces perturbing the ion. A summary of the selection rules, frequencies and activity of the nitrate modes are given in Table I.

TABLE I

FREE NITRATE ION SELECTION RULES

Mode	Symmetry	Activity	Degeneracy	Approximate Frequency cm^{-1}	Description
$\nu 1$	A_1'	R, p	1	1050	symmetric stretch
$\nu 2$	A_2''	IR	1	820	out of plane bend
$\nu 3$	E'	IR, R, dp	2	1390	asymmetric stretch
$\nu 4$	E'	IR, R, dp	2	720	planar bend

The nitrate ion has been studied in a number of environments. The solid state of the nitrates is interesting in that they typically go through a number of phase transitions. KNO_3 is an interesting example with three solid state phase transitions (Figure 1). KNO_3(II) has an ordered orthorhombic structure with 4 nitrate ions per unit cell, KNO_3-(L) has a "discordered" trigonal structure and KNO_3(III) is an ordered trigonal structure. An important point here is the fact that when the nitrate is in the ordered trigonal crystal the nitrate ion is in an essentially unperturbed state because of the symmetric distribution of the cations around it. Therefore, the D_{3h} selection rules hold.

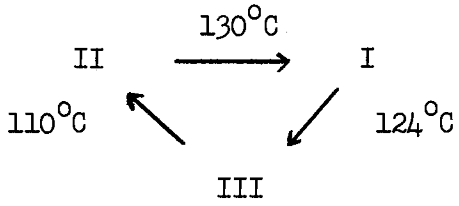


Figure 1. Solid State Phase Transitions in KNO_3

Recently a considerable amount of work has been done with the molten salts. The alkali metal nitrates are particularly good for this type of study because of their relatively low melting points and a large temperature range before decomposition occurs. Several interesting features of the liquid spectra are, the appearance of frequencies in both the infrared and the Raman which are forbidden by D_{3h} symmetry, the infrared and Raman ν_1 band frequencies are slightly different and there is a loss of degeneracy in the ν_3 and ν_4 bands. As a result of this several models for the liquid have been proposed. Devlin[8] says that there is evidence of some ordering in the melt. Wait, Ward, and Janz[9] assumed the melt was anion-cation pairs with the anion attached to one oxygen so that the molecule symmetry is C_{2v} or C_s.

Much work has been done on nitrates by attenuated total internal reflection (ATR) infrared spectroscopy[12]. It has recently been shown that longitudinal (LO) and tranverse (TO) phonon frequencies correspond to the peak and the inflection point on the wing of the ATR curve of crystalline trigonal nitrates[10]. The Raman spectra has a peak at each of these values in the ordered KNO_3 crystal and analogous features in the melt. This suggests that the splitting in the Raman is a TO-LO splitting rather than the result of an anion distortion which supports in the theory that the melt has some ordering because TO-LO wave propagation requires a latticelike structure.

In the matrix isolated case the TO-LO splittings cannot exist. Anion distortion and site splitting are important in the matrix isolated case. These will be discussed in detail in the interpretation of the results.

CHAPTER II

EXPERIMENTAL

The Cell

The cell that was used during this study was that designed by Smith[6]. Since he described it in detail, a brief description is justified here. It is basically a double dewar vacuum cell with an inner and outer jacket so that liquid helium temperatures can be obtained. A cryotip made from a hollow block of copper (for good heat conduction) in which a NaCl or CsBr plate can be mounted inserts into the double dewar. Indium gaskets were used to improve thermal contact. A 10° aluminum wedge was stuck to the copper with silicone grease. The aluminum was polished to a mirror shine. The sample was deposited on the salt plate and on the aluminum wedge at the same time. The infrared spectrum could then be taken through the salt plate and the laser beam reflected from the aluminum wedge for the Raman spectra. It should be noted that aluminum was chosen as a substrate only because it could be highly polished. Some other metal might serve the purpose better. Copper, nickel, stainless steel, chromium and even gold were placed in the spectrometer and the background was checked. Gold was found to have the lowest background, but this is not conclusive that one substrate is better than another since the background may depend on a number of factors such as how highly polished the surface is or the presence of an impurity such as grease on the surface.

The cryotip was surrounded by a copper shield which was connected to the outer dewar. During a run this shield was kept at liquid nitrogen temperatures.

The outer cell wall was made of stainless steel and had two NaCl windows and one quartz window for the Raman. One port was provided to evacuate the cell and two others for the deposition of matrix gas and nitrate. Apiezon T grease was used to attach the windows and Apiezon N was used on all other joints.

Procedure

A typical run was initiated by completely assembling the cell including the heater in which the nitrate was placed. The whole system was pumped to ca. 10^{-5} torr. This required three or four hours. If the salt was one that deliquesced the heater would be turned on and the salt heated to about 150°C with the pumping continued for about 24 hours to insure that the salt was dry. The portion of the vacuum that was to hold the matrix gas was then closed off and the matrix gas was introduced into the system. The pressure of the matrix gas was measured by a manometer. The gas used was directly from a Matheson bottle although initially attempts were made to purify the gas by passing it through a trap at dry-ice/acetone temperature. This made no difference in the infrared spectrum and did not lower the Raman background and was, therefore, abandoned. The liquid nitrogen was added to the cell at this point. Although the cell was designed for use at liquid helium temperatures, no runs were made with liquid helium in this study. At this time the salt plate was turned away from the heater. A shield which was attached to the cryotip blocked any nitrate or matrix gas from hitting the window while the cryotip was in this position. The heater voltage was increased to the temperature at which the deposition was to be made and the matrix gas was started and adjusted to the proper flow. One should note that when temperatures around 400°C were required an external cooler was used to keep the outer portion of the cell from becoming too hot. A small fan was sufficient. After ca. 15 minutes (enough time for the salt to reach the temperature desired) the cryotip was rotated so that the matrix gas and nitrate could hit the window and aluminum wedge. The deposition time was from 2 to 4 hours depending on the type of sample desired. At the completion of the deposition the cryotip was again rotated so that the nitrate and matrix gas was blocked. Both the nitrate oven heater and matrix gas needle valve were turned off. After the nitrate had cooled to below the melting point the cryotip was rotated into position for the spectrum to be taken. When the spectrum had been run and all information that could be gained from the sample was complete, the liquid nitrogen was poured out. Air was blown into the jackets to increase the rate of warming and the matrix gas was pumped off. The cell was then disassembled and cleaned. The windows were run to see if any nitrate had been deposited on them. If not they were not removed. Commonly the oven did not require refilling with nitrate so that it was not disassembled each time.

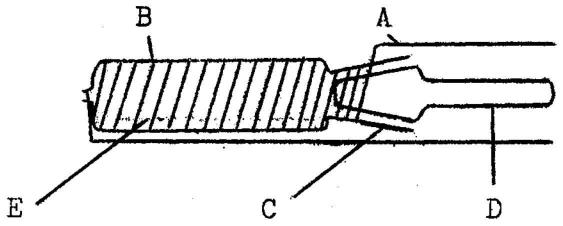
Some experimental conditions are as follows. The pressure of the vacuum system was measured by a Consolidated Vacuum Corporation ionization vacuum gauge using a GIC-015 ion tube. Before deposition the pressure was ca. 1 X 10^{-5} torr but during deposition the maximum pressure was ca. 3 X 10^{-4} torr. The temperature of the nitrate oven was measured with an iron-constantan thermocouple and a potentiometer.

The amount of matrix gas was measured on a Fischer and Porter 1/8 inch tri-flat variable-area flowmeter. The normal reading was 3-6 for CO_2 and 1-3 for CCl_4. Knowing the viscosity and density of the gas the flow rate can be calculated. For CO_2 the flow rate was calculated to be ca. 5×10^{-4} moles/minute. Voltage was supplied to the oven heater by two variacs used in series. The primary variac was set at 15 and the second variac was plugged into the first so that full scale on the second represented ca. 15 volts. The heater was made from 24 gauge nichrome wire and its resistance was around 30 ohms. It was found that a setting of ca. 100 on the second variac gave ca. 400°C. $LiNO_3$ was deposited at temperatures from 380° to 420° and KNO_3 was deposited from 400° to 450°C.

Difficulties Encountered

A chief difficulty involved the NaCl outer cell windows. When the nitrate is vaporized in the cell some of it will collect on any surface at room temperature. Therefore, the outer windows usually had a small amount of nitrate on them. After each run the cryotip was removed and the infrared spectrum of the cell windows was run. Many times there was little enough nitrate on the windows that another run was possible without removing and polishing the windows. Since the nitrates could be deposited onto a surface at room temperature, the idea was proposed that possibly a compound could be found that would isolate the nitrates at relatively high temperatures. Several straight chain hydrocarbons (with melting points above room temperature) were tried. The conclusion from this experiment was that anything that has a high melting point is much more difficult to work with because two heaters are required and one cannot pump the matrix away as the cell warms. The matrix material as well as the nitrate contaminates the whole cell so that it must be completely disassembled after each run.

Another difficulty with the windows was that they leaked very easily. It was found that the best way to attach the windows was, along with grinding them very flat and repolishing each time, to mark them so that they were invariably put on in the same manner and with a thick even coat of grease on the surface to which they are to be applied. One might note here that the windows are also a potential problem when designing a greaseless system.



A - nichrome wire

B - glass Knudsen cell

C - 7/25 standard taper joint

D - glass rod

E - molten nitrate level

Figure 2. Oven Heater Assembly

Also, a major difficulty was the heater. Designing a heater which was vacuum tight with electrical leads that could be easily removed and that could withstand temperatures of 450°C was a problem. The same basic design described by Smith[6] was used, but some modifications were made. Smith used a stainless steel Knudsen cell to contain the nitrate. The stainless steel Knudsen cell seemed to be a poor design. When the nitrate becomes molten it is very fluid and will leak through any small opening. When the nitrate leaks out of the Knudsen cell, it can be deposited at a very fast rate or run behind the Knudsen cell and not deposit at all. This problem was solved by using a glass Knudsen cell in which there was no way for the nitrate to leak out. A disadvantage to this type of assembly is that there is no good place to attach the thermocouple (Figure 2).

Another problem with the Knudsen cell is that solid nitrate may stop up the orifice and deposition will stop, nullifying the whole run. To avoid this problem the tip of the cell must be at least as hot as any other part of the cell and one must be careful not to cover the orifice with the salt crystals when loading the cell.

Another point to keep in mind is the angles at which the matrix gas and the nitrate are directed at the NaCl window. The cell was designed such that the nitrate port and the matrix gas port were side by side. If the window is turned such that the angle is different for different runs, for the same experimental conditions the M/A ratio will be different and the film may not be even. A great improvement would be obtained by having the matrix gas port directly under the nitrate port. In this study a mark was made on the cell so that the cryotip was rotated to the same position each time.

While discussing difficulties, it might be well to recall that the Raman spectra has not been obtained. The problem is that the background radiation is very large with respect to the Raman scattering from the matrix isolated species. Several things contribute to the background.

One source of background is primary reflective scattering. This, however, has been shown to be a minor source of background. An etalon was installed in the argon laser which was used as a light source in the Raman spectrometer. The etalon permits single mode operation. When an iodine vapor filter at ca. 120°C is placed between the sample and the monochromator, one of the modes can be filtered out because iodine vapor has a narrow band which is accidently at the proper frequency to couple with one of the modes of the laser. By tuning the laser to the proper mode, the primary reflective scattering can be filtered out.

Since the primary reflective scattering has been shown to be the minor source of background, fluorscence is the major problem. Apiezon grease used in vacuum system connections has an intense fluorescence spectrum and this seems to be the source of the fluorscence. At present it seems that a greaseless system might be the answer.

CHAPTER III

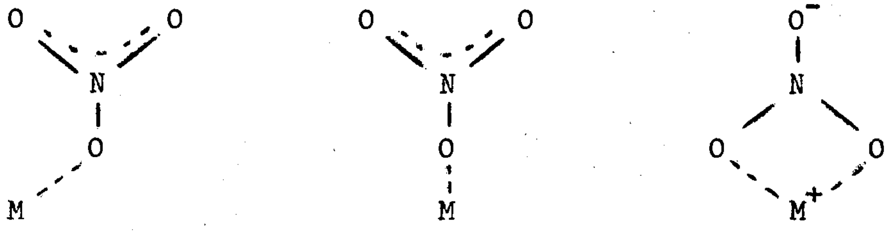
RESULTS

Review and Previous Results

Since this study is a continuation of work done by Smith[6], a review of his results is in order. No work was done at liquid helium temperatures in this study, and much of the work done by Smith at liquid helium temperatures is needed to help in the interpretation of the spectra gained from this study. More specifically, the nitrates isolated in argon give another system to which one can compare data. Carbon dioxide and carbon tetrachloride were the two matrix gases used in this study.

One should recall that when the nitrate ion is undistorted i.e. the C_3 rotational axis is maintained, that ν_3 is doubly degenerate. Any perturbation on the nitrate ion causes a splitting of ν_3. Smith deduced that the frequency of the monomer and dimer bands of KNO_3 are not strongly dependent on any of the matrices used. In all three cases the splitting of ν_3 is about the same. However, the high frequency ν_3 component intensity and position differs a small amount in each case. For the other nitrates Smith noted that going from Li, Na, to K there is an increase in the frequency of ν_1, and a decrease in the splitting of ν_3. Also, the dimer band splitting was about half that of the monomer and by changing the M/A ratio, the relative intensities of the KNO_3 1291-1462 cm^{-1} (monomer) pair and the 1334-1417 cm^{-1} (dimer) pair can be altered. Smith concluded that the monomer form is probably the planar monodentate C_{2v} (Figure 3) but the dimer structure is still not clearly understood although a center of symmetry seems to be present because of the non-coincidence of ν_1 in the infrared and Raman.

A possible reason that the nitrates have not been previously studied in the vapor is that they were presumed to decompose rather than volatilize upon heating. Recent work shows this to be untrue. Nolta, Schubring and Dork[13] report depositing KNO_3 from a V-shaped tantalum boat at slightly above the melting point (340°C). Hardy and Field[14] also demonstrated the volatility of the alkali metal nitrates in distillation experiment at 450°C. Büchler et al.[15] recently reported the mass spectra of vapors of $LiNO_3$ at 400°C and $NaNO_3$ at 480°C. The spectra indicated the prescence of ions of the type M^+, MX^+, M_2X^+, O_2^+, NO^+, N_2^+ and NO_2^+. This pattern is typical of those of the alkali halide vapors containing monomers and dimers[16]. From the mass spectra, Büchler concluded that monomers and dimers do exist in the vapor phase, that the monomer/dimer ratio is a function of temperature and the monomers and dimers exist in approximately equal amounts at 450°-500°C.



(a) monodentate C_s model

(b) monodentate C_{2v} model

(c) bidentate C_{2v} model

$\Gamma_{vib} = 7A' + 2A''$

$\Gamma_{vib} = 4A_1 + 3B_1 + 2B_2$

$\Gamma_{vib} = 4A_1 + 3B_1 + 2B_2$

Figure 3. Theoretical Models for MNO_3

Several models for the monomers have been proposed [17] (Figure 3).

The irreducible representations of the fundamental vibration modes show that all modes of each species are both infrared and Raman active. All three models of the monomer predict 9 infrared bands so that one cannot know which model is correct by counting the number of bands in the spectrum. Wong[19] suggests that the bidentate model can be distinguished from the monodentate models by the highest fundamental frequency of the NO symmetric stretch because the double bond character should cause the frequency of that band to be higher. One can tell the C_s model from the C_{2v} models because the C_s model predicts 7 polarized Raman lines while the C_{2v} model has only 4 polarized lines. However, one should remember that this experiment has not been done to date.

Little is known about the structure of the dimer, but for reason of symmetry the D_{2h} model (Figure 4) is generally used. Smith[6] favored this model because his data suggested that the Raman and infrared bands were non-coincident. The D_{2h} models irreducible representation is $\Gamma_{vib} = 5A_g + 4B_{1g} + 2B_{2g} + B_{3g} + 3B_{1u} + 4B_{2u} + 4B_{3u}$. Thus the model predicts 12 Raman active modes and 11 infrared active modes, the Raman and infrared frequencies being mutually exclusive. One can see that the monomer would have a larger ν_3 splitting than the dimer because the perturbation on the nitrate ion would be less for a dimer structure than a monomer.

Experimental Results and Interpretations

When one studies the infrared spectrum of the matrix isolated alkali metal nitrates he finds the bands of several chemical species. The species are: (1) the nitrate in its crystal structure; (2) the monomers, dimers and possibly trimers, tetramers etc.; (3) a glass or

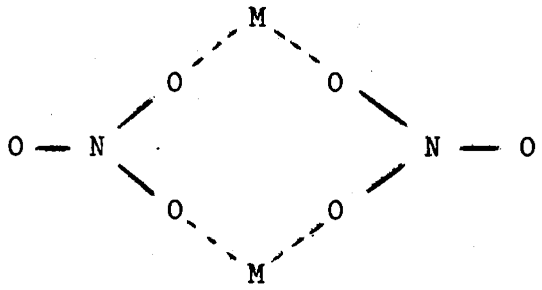


Figure 4. D_{2h} Model of the MNO_3 Dimer

polymer structure; (4) the matrix gas; and (5) sometimes some decomposition products. Some factors which affect the relative amounts of the species present are the temperature of the molten salt, the matrix gas flow rate, the length of the deposition and perhaps even the choice of matrix gas. Figure 5 shows $LiNO_3$ in carbon dioxide as the M/A ratio is changed. One can see that the pure $LiNO_3$ thin film has a band at 840 cm^{-1} and one at 1360 cm^{-1}. The 720 cm^{-1} ν_4 band could not be seen because the film was thin and the band is very weak. The 1050 cm^{-1} band is not present in the thin film because the NO_3^- ion is in a symmetric environment so that the mode is infrared inactive. When a relatively small amount of carbon dioxide is introduced (Figure 5b), the polymer (or glass) bands appear along with the monomer, dimer, trimer etc. bands. The glass bands are broad and intense whereas the monomer and dimer bands are characterized by very sharp peaks. The monomer bands are those of lowest frequency in the ν_1 and ν_2 region. They are also the ν_3 bands (1400 cm^{-1} region) with the largest splitting because the splitting can be looked upon as a measure of the distortion of the nitrate ion and the monomer nitrate would experience the largest conceivable distortion by the cation. The dimer (ν_3) bands are somewhere between the monomer bands depending on the matrix and the cation. In the case of $LiNO_3$ in CO_2 (Figure 5a), there are four different component pairs. The largest splitting is for the monomer pair (1275-1521 cm^{-1}). The other three pairs are probably produced by dimer in different sites in the matrix or possibly by the dimer, trimer and tetramer. As one increases the amount of CO_2 the glass bands disappear and in the high dilutions the glass bands are absent.

The polymer or glass bands are interesting in that they are almost identical to those of the liquid spectrum. Quite a large quantity of work has been done on liquid structures [10, 12, 20]. The structure of the glass is probably similar to the liquid, although looking at ν_1 in Figure 5b, one might suggest that the structure of the glass is a statistical distribution of monomers, dimers, trimers etc. However, an important point to remember here is that for ν_1 to be infrared active the nitrate ion must be distorted. Therefore, anything one sees in that region is in an environment (such as the dimer) which causes distortion. The peak value of the glass is 1037 cm^{-1} whereas the Raman liquid peak is 1062 cm^{-1}. One might suggest that the difference is caused by the Raman signal being produced dominantly by undistorted nitrate ions in a symmetrical environment while the infrared signal is caused by nitrate ions in an environment which causes distortion. As a result of this interpretation, one must predict that there exists a strong Raman line at ca. 1062 cm^{-1} in the glass spectrum. The glass band of $LiNO_3$ in CO_2 in the ν_3 region is split about 70 cm^{-1}. Two possibilities exist as the source of the splitting. There is a possibility of a lattice structure which could give rise to a TO-LO splitting, but anion distortion could also cause the splitting. Devlin et al.[10] concluded that liquid alkali metal nitrate systems may reflect TO-LO splitting of the ν_3 phonon degeneracies rather than anion distortion. Since the glass spectra has

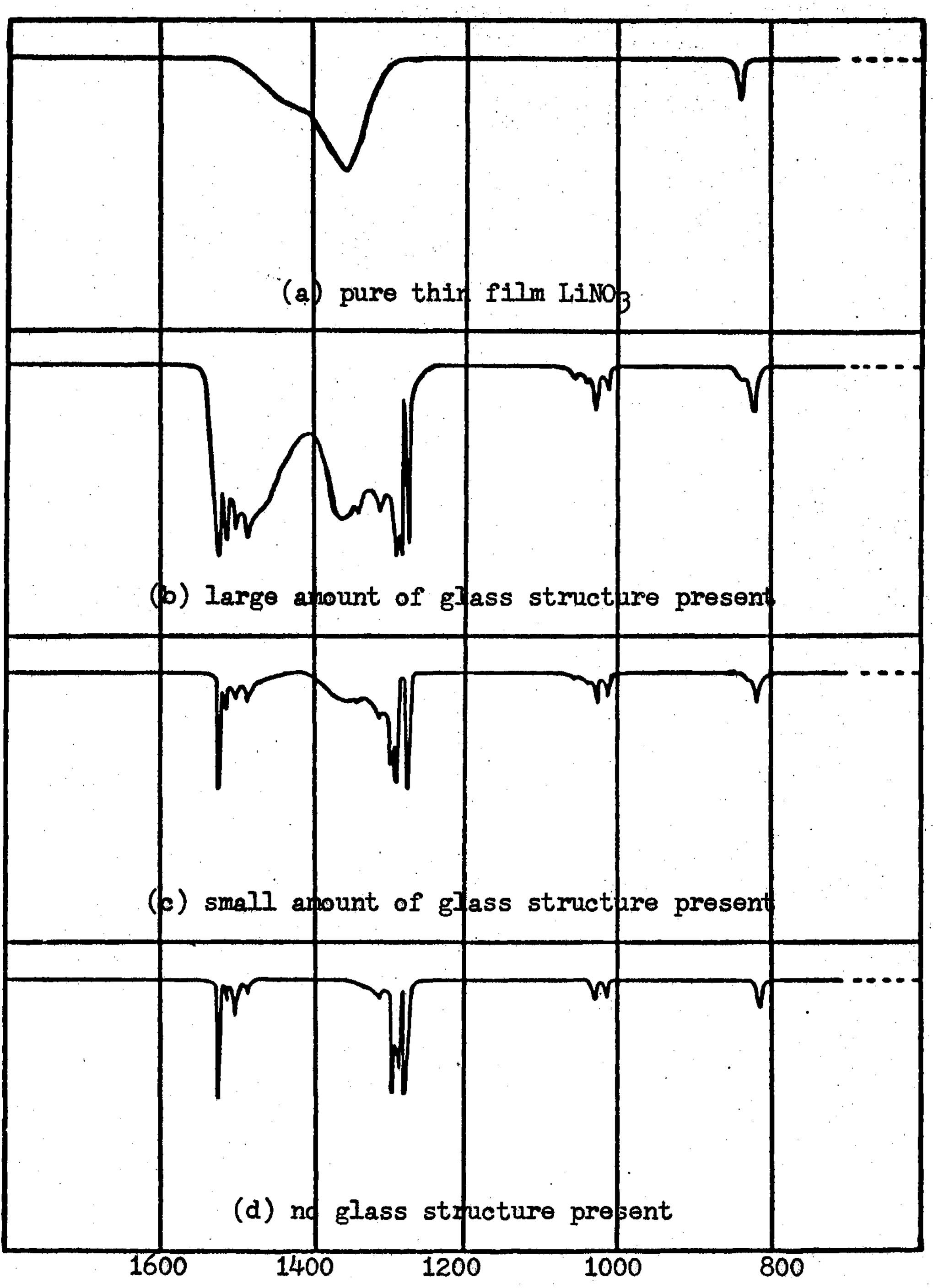


Figure 5. $LiNO_3$ in Carbon Dioxide with Varying M/A Ratios

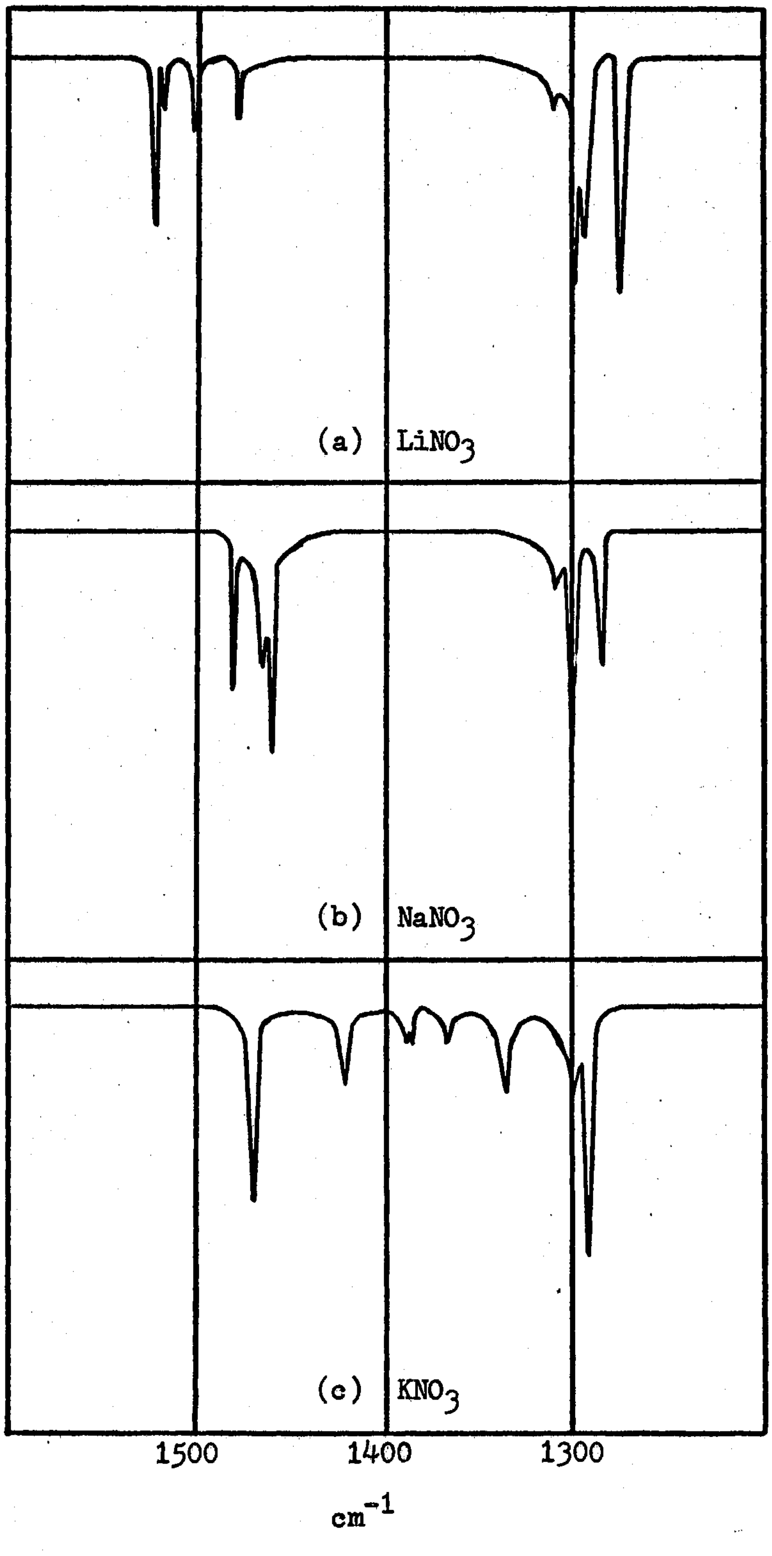


Figure 6. The ν_3 Region of the Alkali Metal Nitrates Isolated in Carbon Dioxide

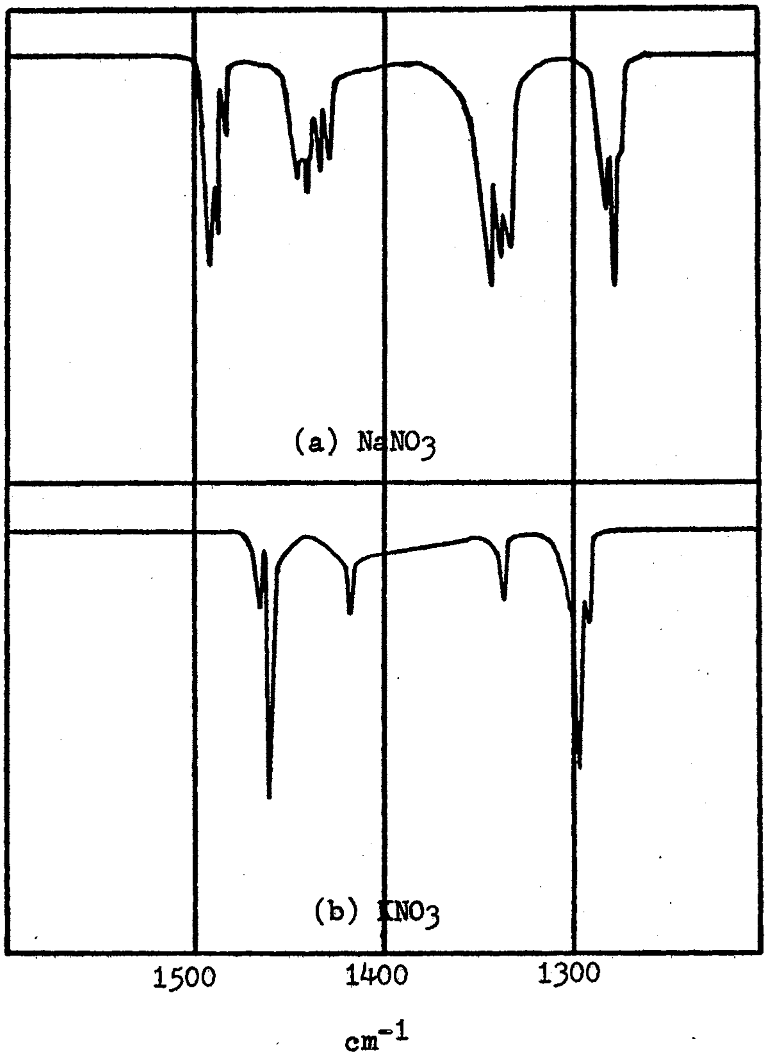


Figure 7. The ν_3 Region of KNO_3 and $NaNO_3$ Isolated in Argon

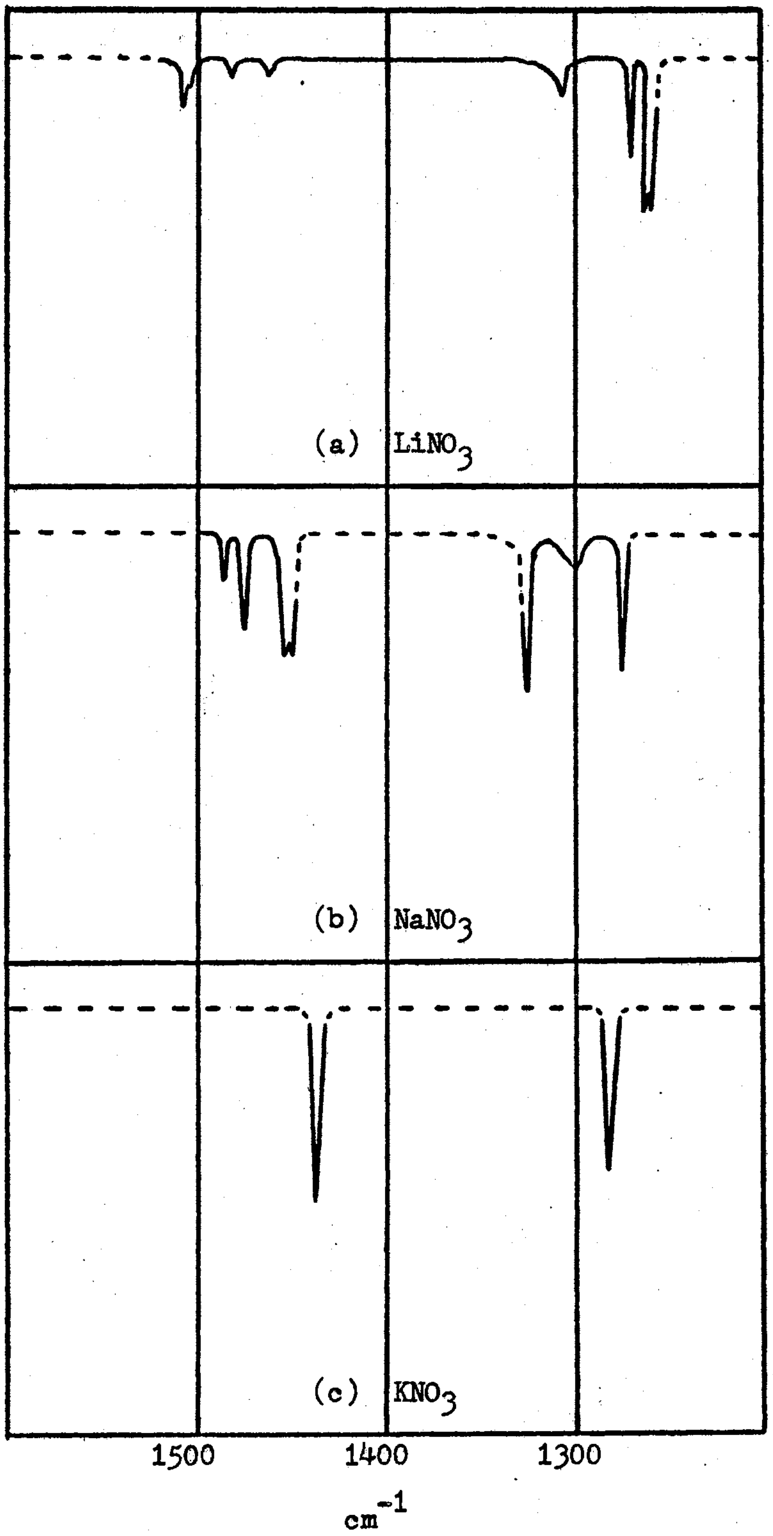


Figure 8. The ν_3 Region of the Alkali Metal Nitrates Isolated in CCl_4

similar features, one might make the same conclusion for the glass. A point to remember here is that KNO_3 has three phases in the solid state, and the structure of the glass may be related to the phase in which the pure nitrate thin film would normally be deposited. A study of pure nitrate thin films is currently in progress.

Figure 6 gives a comparison of the alkali metal nitrate ν_3 infrared spectra in the carbon dioxide matrix. When going from Li^+ to Na^+ to K^+ the splitting for the monomer and dimer decreases. This indicates that lithium exerts the largest perturbation on the nitrate ion and potassium the smallest. One may note that in $LiNO_3$ four pairs of bands are seen while in $NaNO_3$ only three are apparent. This is probably caused by the cations of different sizes fitting into the matrix sites differently. Also in a particular matrix a monomer may fit better (for a particular cation) than the dimer or vice versa. In Figure 6b the $NaNO_3$ dimer bands are stronger than the monomer bands. One must keep in mind, however, that the temperature affects the monomer/dimer ratio.

Figure 7 shows the ν_3 bands for $NaNO_3$ and KNO_3 in argon. $NaNO_3$ in argon shows a large number of splittings for both the monomer and the dimer. The dimer splitting is about half of the monomer splitting for both KNO_3 and $NaNO_3$. The $NaNO_3$ monomer splitting is greater than the KNO_3 which is in accordance with the carbon dioxide matrix results. Note that the dimer splitting (Table II) for KNO_3 is about half of the monomer splitting in both carbon dioxide and argon, but the same is not true for $NaNO_3$. The implication here is that the CO_2 matrix has a larger stress on the dimer for a cation the size of sodium than for potassium i.e. the dimer of KNO_3 can fit into a CO_2 matrix better than $NaNO_3$. $LiNO_3$ in argon has not been studied but would likely make the reason for the variation in dimer splittings more apparent.

TABLE II

SPLITTINGS FOR MATRIX ISOLATED ALKALI METAL NITRATES

Species	$LiNO_3$		$NaNO_3$			KNO_3		
	CO_2	CCl_4	Ar	CO_2	CCl_4	Ar	CO_2	CCl_4
Monomer	246	245	201	196	207	171	167	154
Dimer	205	190	105	160	125	83	85	---

Although admittedly sketchy, some work has been done in a CCl_4 matrix. CCl_4 is not as good a matrix as CO_2 and Ar in that it has some interfering bands. The dotted lines in Figure 8 represent areas where CCl_4 bands have been omitted or where the data is not conclusive. An interesting trend is noticed; in going from argon to carbon dioxide to carbon tetrachloride, there is a shift to lower frequency for the monomer bands. Although clearly a matrix effect, the reason for the shift is not understood. Perhaps the more polarizable matrices change the force constants in the nitrate molecule by some type of interaction with the matrix.

CHAPTER IV

SUMMARY AND CONCLUSIONS

Method

The infrared spectra of the matrix isolated alkali metal nitrates has been shown to be a very powerful tool in the study of the nitrate ion under the distorting influence of various cations. Although there are many inherent problems, good infrared spectra have been obtained. A large amount of study is still needed, however, since there are features in the spectra which are unexplained. Different matrix materials should be tried so that matrix effects, particularly on the dimer, can be better understood. When the Raman spectra of the matrix isolated species has been obtained, one will be able to better understand the structure of the nitrate ion in the different environments. For example, the C_s structure can be distinguished from the C_{2v} model of the monomer by the number of polarized Raman lines. Matrix isolation spectroscopy has permitted an initial study of the glass spectra of the alkali metal nitrates and their correlation with the liquid spectra. It also gives some information as to the structure of the vapor above the molten salt i.e. the monomers and dimers exist in the vapor. The bands in the infrared spectra of matrix isolated species are very sharp and therefore, one can detect very small splittings. This is one of the many advantages to the matrix isolation technique over conventional spectral sampling techniques. In conclusion, with its many experimental difficulties, matrix isolation is a very good method for studying the nitrate ion.

Factors Affecting the Spectra

One should recall that the spectra are a composite of the spectra of the nitrate in its crystal structure, the isolated monomers, dimers, trimers etc., the glass structure, the matrix gas, and sometimes some decomposition products. Therefore, anything that affects the relative amounts of the species causes a change in the spectra i.e. the intensity of some bands increase or decrease relative to the others. Factors that fall in this category are temperature, size of the orifice in the Knudsen cell, matrix gas flow rate and the angle at which the cryotip is turned during deposition. One should keep in mind that the crystal nitrate on the outer windows of the cell is the source of the crystal bands in the spectra.

The spectra is also affected by the environment of the trapped species. For example, a monomer may give two different spectra because there are two possible types of sites in the matrix it can occupy. The experimental parameters that control this are difficult to determine. One might suggest temperature of the cryotip, rate of deposition of nitrate and matrix gas flow rate. Some more work needs to be done to determine exactly how the experimental parameters affect the site that the species occupy.

Nitrate Structure in Different Environments

The purpose of this study was to better understand the effect of different environments on the nitrate ion. The various environments correspond to the various stable phases, the involvement of the different cations, isolation in different matrix materials, the glass and the monomer, dimer, trimer etc.

The vapor phase could be studied because the species that exist in the vapor phase are trapped in the matrix. Evidence shows that monomers, dimers, trimers, etc. exist in the vapor phase and when the temperature is increased the vapor equilibrates in favor of the monomer.

In certain solids (eg. $NaNO_3$ D_{3d}^6) the nitrate ion is in an unperturbed state because of the symmetric distribution of the cations around it. Consequently, the D_{3h} selection rules hold and ν_3 is not split. In the liquid spectra, bands appear in both the infrared and Raman which are forbidden by D_{3h} symmetry. Also, there is a loss in the degeneracy of ν_3. This is an indication that the anions (or some of the anions) are distorted. One should remember, however, that the liquid may have some structure since the ν_3 Raman splitting corresponds to the TO-LO ATR frequencies.

The various cations cause a substantial change in both dimer and monomer splitting. As one goes down the periodic table, the splitting for both monomer and dimer decrease i.e. Li^+ causes the largest anion distortion and K^+ the smallest.

By changing matrix materials, one can distinguish what effects are caused by the matrix i.e. one matrix may have more sites that the nitrate can occupy than another. It was found that the matrix has little effect on the frequency of the monomer bands, but the dimer band frequencies seem to be more dependent on the matrix.

The presence of a glass structure has been shown. Although the structure of the glass is unknown, evidence shows that it is similar to the liquid structure. The splitting of ν_3 in the glass for KNO_3 and $LiNO_3$ is about the same as the Raman liquid ν_3 splitting. The splitting of the ν_3 glass band may be TO-LO rather than anion distortion, but $LiClO_4$ in $LiNO_3$ dilution experiments seem to indicate the splitting is anion distortion since the splitting is invariant. Another indication that there is some anion distortion present in the glass is the fact that there is a broad ν_1 infrared band that should not appear if the anion is not distorted. A more extensive study of the glass may prove valuable in understanding the structure of molten salts.

The nitrate ion environment in the monomer causes thelargest distortion, such that ν_3 has the largest splitting of all cases considered. For KNO_3 the monomer splitting is ca. 170 cm^{-1}. The dimer splitting is about one half of the monomer in most cases. One can say from this that the distortion of the nitrate ion in the dimer environment is about half of that in the monomer. If one accepts the suggestion that the glass ν_3 splitting is anion distortion, he can say that the nitrate ion is distorted about the same amount in the glass as in the dimer since their splittings are about the same magnitude.

At the present a firm decision as to which model best describes the monomer still cannot be made, and perhaps even all three exist. Although little is understood about the dimer, the present information leads to the conclusion that a center of symmetry is present and the D_{2h} model best describes the dimer. The possibility of the existence of trimers, tetramers etc. is reasonable. Figure 6c shows two weak bands in the ν_3 region which have a splitting about half of the dimer splitting. One might suggest that these are evidence of a trimer. Also, since some weak bands that are unexplained exist, they might be trimer or tetramer bands. No model has been proposed for a trimer or tetramer.

Suggestions for Further Study

Only a small amount of data has been obtained in the CCl_4 matrix. To date the spectra that have been obtained show fairly weak monomer bands and the dimer bands are even weaker. Even though several attempts may be required before one can get good spectra, it is likely that matrix isolated species can be obtained in CCl_4. Perhaps more data will help explain the shift of the monomer ν_3 bands to lower frequency in CCl_4.

A new matrix always introduces new questions and gives a different system from which inferences can be made. Consequently, one seeks to find a matrix that has not been used before. Note that matrix effects in themselves are not the subject of interest, but rather the fact that a new environment in which the nitrate can be studied can be created. To be a good matrix there should be minimum matrix interactions, it must not have interfering bands in the infrared and have a fairly low heat of sublimation. One might suggest the halogens as a matrix. Even though they are very reactive at room temperature, they might not react with the nitrate at temperatures required for matrix isolation. Since chlorine is very reactive and iodine is a solid, bromine seems to be the most likely candidate. One attempt was made to isolate $LiNO_3$ in Br_2. The sample was too thick to obtain a good spectrum, but the Br_2 did make an even film and there were no signs of a reaction with the nitrate. When the sample was warmed, however, some reaction did occur because a black film was left after the Br_2 had been pumped off.

Another proposal one might make would be to pass the matrix gas through the Knudsen cell to make a deposit in which thermal equilibrium conditions did not exist in the Knudsen cell. This experiment might give some more insight into the composition of the vapor. One would suspect that this experiment would alter the monomer/dimer ratio. A note of caution here is to remember that since the matrix gas is passed over the hot molten salt, it has a greater chance to react than in the conventional experiment.

A related experiment would use the "double oven" technique [21,22]. The Knudsen cell has two parts that can be heated simultaneously by the same source or independently. The molten salt is contained in the back part of the Knudsen cell. The front compartment is heated to a higher temperature than the back compartment. The vapor from the molten salt pases from the back to the front compartment. Since the front compartment is hotter, the vapor will equilibrate in favor of the monomer. Therefore, the spectrum will be primarily that of the monomer.

Finally, a normal coordinate analysis needs to be done on the D_{2h} model of the dimer. Smith[6] did force constant calculations on the monomer and represented the distortion in terms of force constants. Perhaps a force constant analysis on the dimer would confirm the proposed structure.

A SELECTED BIBLIOGRAPHY

1. Barnes, A. J. and Hallam, H. E., Quart. Rev. (Chem. Society) 23, 392 (1969).
2. Ogden, J. S. and Turner, J. J., Current Awareness, 22, 186 (1970).
3. Pimentel, G. C., Dows, D. A. and Whittle, E. J., J. Chem. Phys., 22, 1943 (1954).
4. Snelson, A., J. Chem. Phys., 73, 1919 (1969).
5. Smith, D. E., James, D. W., and Devlin, J. P., J. Chem. Phys. 54, 4437 (1971).
6. Smith, D. E., PhD. thesis, Okla. State Univ. (1971).
7. Khanna, R. K., Lingscheid, J., Decius, J. C., Spectrachimica Acta, 20, 1109 (1963).
8. Devlin, J. P., Private Communication.
9. Wait, S. C., Wand, A. T., Janz, G. J., J. Chem. Phys., 45, 113 (1966).
10. Devlin, J. P., James, D. W., Frech, R., J. Chem. Phys., 53, 4394 (1970).
11. Hester, R. E., Krishnan, K., J. Chem. Phys., 46, 3405 (1967).
12. Devlin, J. P., Li, P. C., Pollard, G. D., 52, 2267 (1970).
13. Nolta, J. P., Schubring, N. W., Dork, R. A., from "Thin Film Dielectrics Symposium," Electrochem. Soc., 236 (1969).
14. Hardy, C. J., Field, B. O., J. Chem. Soc., 5130 (1963).
15. Büchler et. at., J. Phys. Chem, 70, 4092 (1966).
16. Berkowitz, J., Chupka, W. A., J. Chem. Phys., 29, 653 (1958).
17. Wait, S. C., Ward, A. T., Janz, G. J., J. Chem. Phys., 45, 133 (1966).
18. Brintzinger, H., Hester, K. E., Inorganic Chem., 5, 980 (1966).
19. Wong,. J., Private Communication.

20. Janz, G. J., James, D. W., J. Chem. Phys., 35, 739 (1961).

21. Freiberg, M., Ron, A., and Schnepp, O., J. Phys. Chem., 72, 3526 (1968).

22. Milne, T. A., J. Chem. Phys., 28, 717 (1958).

VITA

Gary Dale Pollard

Candidate for the Degree of

Master of Science

Thesis: THE VIBRATIONAL SPECTRA OF $LiNO_3$ AND KNO_3 IN VARIOUS INERT MATRICES

Major Field: Chemistry

Biographical:

Personal Data: Born in Batesville, Indiana, January 2, 1947, the son of Hollis E. and Glenna A. Pollard.

Education: Attended grade and junior high school in Elmore City, Oklahoma. Attended Madill and Plainview High School. Graduated from Plainview High School, Ardmore, Oklahoma in 1965. Received a Bachelor of Arts degree with a major in Chemistry at Oklahoma State University in 1969; completed the requirements for the Master of Science degree in May, 1972.

Professional Experience: Graduate Teaching Assistant, Oklahoma State University, from Fall 1969 to Spring 1972. National Science Foundation Research Assistant during Spring and Summer 1969, Summer 1970, and Spring and Summer 1971.