I. REVIEW OF PROGRESS

Except for considerable data, both infrared and Raman, which has accumulated for the glassy mixture of $Ca(NO_3)_2$ (45%) and KNO_3(55%), most of the notable results of the past two years under contract AT (11-1)-1615 have been reported in the four papers listed under "Publications" at the end of this proposal. Briefly, the rather diverse results can be characterized as being consistently indicative of a perturbed lattice structure for the molten alkali metal nitrates. This interpretation was originally emphasized in a 1968 paper[1] which appeared nearly simultaneously with a report that lattice phonon features are carried over into the far infrared spectra of molten sodium and cesium nitrate.[2] The interpretation has been further substantiated by Raman studies in our laboratory, as well as those of James[3] and Clark,[4] and, also, by isotopic dilution data from our laboratory.[5] Angell et. al. have interpreted extensive far-infrared data for several inorganic glasses from a similar viewpoint.[6]

Thus, the concept emerging of the molten salt state is that order is sufficient to support phonon waves and permit the identification of vibrational modes which differ in their phase relationships within "unit cells." This view requires that such liquids retain vestiges of a lattice structure, but in no sense is the possibility of specific interactions ruled out. Just as for solids, the basic molecular unit may be either a simple, possibly polyatomic, ion (eg. NO_3^-) or a more complex entity resulting from specific interactions.

Apparently some progress is being made in characterizing melt structures but there has been no equivalent application of vibrational spectroscopy to the chemistry of molten salts, at least not in our

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laboratory, although it was expected that our interest would shift in this direction. The delay is not a result of a shortage of interesting chemical questions to be considered, but rather from a fascination with structural aspects that has yet to be dulled. Of course, it is naturally anticipated that, when feasible structural studies have been exhausted, chemical insights will evolve in a more logical and systematic fashion.

The growing body of evidence that spectroscopic properties of certain ionic melts bear a close analogy to those of the corresponding solids prompted the principal investigator to spend a six month sabbatical during the past year studying solid state spectroscopic theories in the laboratory of Professor J. C. Decius. Insights gained during that period have served to draw attention to other previously unsuspected analogies which may prove informative regarding melt structures. Thus, the emphasis in this proposal is on determining the significance of these apparent analogies, so that the emphasis continues to be on structural rather than chemical aspects of molten salts.

II. PROPOSED RESEARCH

It has been mentioned that, like solids, ionic melts are apparently capable of supporting optical phonons[2] and, further, features in the infrared and Raman internal mode frequency range seem to indicate a dynamical coupling of internal modes of neighboring nitrate ions as in the solid state.[1] Basically, the research proposed herein is directed to confirming or disproving the existence of yet another analogy that is suspected between the molten salt and solid state spectra. What is suggested here and will be argued in the succeeding

paragraphs is that one can identify features produced by both longitudinal and transverse modes in the spectra of molten salts (both in the infrared and Raman). Further, the appearance of spectral features produced by such modes and their subsequent misinterpretation has led to serious misconceptions regarding the degree of anion distortion in melts such as that of lithium nitrate.

To understand the arguments that follow, as well as the proposed experiments designed to test these ideas, one must be aware of several aspects of solid state spectroscopy:

1. Vibrational modes in crystals break down into pure transverse, pure longitudinal and mixtures thereof. Modes with wave vector perpendicular to the dipole moment change are pure transverse and are normally responsible for absorption loss from an electromagnetic wave. On the other hand, corresponding to each internal anion mode for crystals such as the trigonal forms of lithium, sodium and potassium nitrate, there is also a longitudinal optical mode with wave vector parallel to the mode dipole moment change. Although longitudinal modes do not normally cause absorption loss,[7] they are detectable by reflection measurements[8] or by noting reflection loss in transmission measurements.[9]

   As an example of absorption from a pure transverse wave, consider a light wave incident on a trigonal nitrate crystal with the wave vector parallel to the crystal three-fold axis. Momentum conservation permits interaction with a crystal mode with wave vector parallel to the C_3 axis. The nitrate planar modes, such as υ_3, have transverse components with the proper wave vector and with

dipole moment change perpendicular to the direction of wave propagation. The latter condition permits effective coupling of the ν_3 transverse wave to the infrared electromagnetic wave. On the other hand, the ν_2 (out-of-plane) mode that satisfies the momentum conditions is the longitudinal mode with wave vector and dipole moment change both oriented along C_3. No absorption is possible for this pure longitudinal mode, assuming an infinite plane wave and infinite crystal.[7] However, a ν_2 mode, largely longitudinal with a slight transverse admixture, becomes active when the wave propagation is slightly off the three-fold crystal axis. The transverse character is necessary for coupling of the mode dipole moment change with the electromagnetic field, but the absorption peak frequency approximates the longitudinal modal frequency.

2. The frequency difference between longitudinal (LO) and transverse (TO) optical modes is directly related to the magnitude of the dipole moment change of the mode in question. For intense absorption bands such as ν_3 of the NO_3^- ion this splitting is of the order of 100 cm^{-1}. The values for lithium and sodium nitrate at 25° C are as indicated in Table I. This table shows that the splitting is an order of magnitude smaller for the much less intense ν_2 mode.

TABLE I

	ν_3(TO)	ν_3(LO)	Δ
$LiNO_3$	1360 cm^{-1}	1475 cm^{-1}	115 cm^{-1}
$NaNO_3$	1353	1455	102
	ν_2(TO)	ν_2(LO)	Δ
$LiNO_3$	849	834	15
$NaNO_3$	840	836	4

3. Attenuated total reflection (ATR) bands for the nitrate υ_3 mode obtained with light polarized in the plane of incidence and with trigonal nitrate crystals having the nitrate ions oriented parallel to the ATR prism surface are sharply peaked at υ_3(TO) but also have a high frequency wing with an inflection point at υ_3(LO). (Fig. 1). This observed quality of the υ_3 ATR band is precisely what one predicts from Fresnel's equations using a damped harmonic oscillator model and the appropriate band intensity parameter.[10] Thus, both υ_3(TO) and υ_3(LO) contribute to the ATR band profile and can be immediately identified from it.

4. Orientational disorder in a solid leads to a breakdown of selection rules[11b] such that not only $k \neq 0$ modes become optically active but longitudinal as well as transverse modes may be activated. This feature of the infrared spectra of methylammonium halides has been examined in detail.[11b] It seems quite probable that activation as a result of orientational disordering is also important in determining the spectra of the high temperature disordered forms of solid trigonal $NaNO_3$ and KNO_3. Thus, despite the preservation of a three-fold symmetry axis and, presumably, the degeneracy of the υ_3 and υ_4 modes, υ_3 appears as a doublet in the Raman spectrum.[12]

Chisler, impressed by this υ_3 splitting, in spite of the presumed three-fold symmetry axis, has suggested that the anion distortion indicated by the Raman doublet is the result of a Jahn-Teller effect. A more likely source of the second Raman component is the activation of υ_3(LO) as a result of the relaxation of selection rules accompanying orientational disordering. The latter view is supported by the reasonably close comparison of the magnitude of

the splitting of the Raman components with the known T - L splitting of the low temperature form of $NaNO_3$. Also, like the Raman doublet,[12] the T - L splitting is known to decrease in frequency in the series $LiNO_3$ - $NaNO_3$ - KNO_3 since the magnitude of the T - L splitting is correlated with the NO_3^- particle density. Table II emphasizes the close comparison between the spacing of the Raman doublet and the known T - L splittings. Warming of these nitrates decreases the Raman doublet spacing,[13]

TABLE II

	Infrared[a] (ATR)		Raman[b]	
	υ_3(TO)	υ_3(LO)	υ_3'	υ_3''
KNO_3(130°)	1350	1430	1360	1420
$NaNO_3$(25°)	1353	1455	1370	1450

a - from reference 10

b - peak frequencies for υ_3 Raman doublet from references 12 and 13.

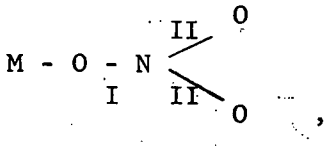
a phenomenon that is expected from a T - L assignment since crystal expansion decreases particle density and, thus, the T - L splitting.

5. The ATR spectrum of $NaNO_3$ (υ_3 region) changes very little upon the order-disorder phase transition, which suggests that NO_3^- ion distortion is unlikely. By attributing the Raman doublet to the T - L split, anion distortion need not be invoked.

Points (1) through (5) emphasize that both the TO and LO modes must be considered in the interpretation of solid state vibrational spectra, particularly when intense absorption bands are involved, and the

LO mode, or admixtures of it with the TO mode, may become of nearly equal concern with the TO mode for orientationally disordered crystals. The latter is a proposition rather than a confirmed fact at this stage. With one other fact in mind, we are prepared to defend the proposition that T - L effects rather than anion distortion are responsible for certain features in the vibrational spectra of molten salts (the alkali metal nitrate melts in particular).

The additional fact is that, when one assumes an anion distortion such as can be envisioned for the C_{2v} complex



then a normal coordinate analysis reveals two relevant features:

1) to produce a 120 cm^{-1} ν_3 split from such a distortion requires that $K_{II} - K_I = 2.5$ md/Å.[14,5] Since this is the splitting observed in the Raman spectrum of $LiNO_3$ melt, an interpretation of the Raman doublet as the result of anion distortion requires that the distortion be quite marked.

2) if, in this calculation, the total bonding in the anion is kept nearly constant by requiring that $\sum_i K_i$ = constant regardless of the amount of anion distortion, the calculated splitting in ν_3 is nearly symmetric about the ν_3 frequency of the limiting free nitrate.[14] Thus, if $\nu_3 = 1350$ cm^{-1} is assumed for the free NO_3^- anion, then $\nu_3' \approx 1410$ cm^{-1} and $\nu_3'' \approx 1290$ cm^{-1} when $K_{II} - K_I = 2.5$ mdyne/Å.

With this backgound it can be seriously suggested that certain of the dominant features in the infrared and Raman spectra of molten salts

result from the extension to the liquid salt state of yet another solid state property, the T - L splitting of vibrational modes, the reasons behind this suggestion can be listed as follows:

1. As can be seen in Figure 1, the ATR curve for molten $LiNO_3$ closely resembles that for solid $LiNO_3$ when the latter is obtained using in-plane polarized light (TM) with a sample having NO_3^- ions parallel to the prism-sample interface. As mentioned, theory relates the high frequency solid state ν_3 wing to $\nu_3(LO)$. The wing and its extension is very similar for the melt. Further, the extension of this wing falls off in the sequence $LiNO_3$, $NaNO_3$ KNO_3 for the melts, as for the solids, in a fashion consistent with the expected decrease in T - L splitting with the decrease in nitrate ion particle density.[1]
2. Dilution of molten $LiNO_3$ with LiCl is accompanied by a decrease in both the splitting of the Raman ν_3 doublet components and the extension of the ATR high frequency wing. Again, this is expected because of the decrease in NO_3^- particle density which would be accompanied by a decrease in T - L splitting, but cannot be understood from a cation-distortion-of-the-anion viewpoint since the cation identity is unchanged.
3. The 120 cm^{-1} ν_3 split for $LiNO_3$ (and the corresponding 80 cm^{-1} split for $NaNO_3$) requires, from an anion distortion view, a strong distortion of the anion and would logically signal a rather drastic overall structure change upon melting. Such a strong anion distortion, corresponding to $K_{II} - K_I \approx 2.5$

mdyne/Å, is thus inconsistent with the negligible change in far infrared (phonon) spectra upon melting.[2] On the other hand, the preservation of lattice (phonon) modes in the melt[2] might suggest that T and L modal characteristics also be identifiable in liquid salts.

4. As noted anion distortion alone should cause a reasonably symmetric splitting of the ν_3 degeneracy. However, the Raman melt doublets have one component fairly near the normal undistorted nitrate frequency while the second component, just like the ν_3(LO) mode in the solid state, invariably appears at a considerably higher frequency. From a distortion model this requires a significant increase in overall bond strength of the nitrate anion on melting. No reason for such an increase has been put forth and such a strengthening is inconsistent with the decrease in the symmetric stretching frequencies (ν_1) on melting.

5. The orientationally disordered solids may serve as a bridge to understanding between the ordered solids and the more randomized melts. If one accepts that the high frequency ν_3 Raman components for these disordered solids (eg. KNO_3 I and $NaNO_3$I) arise from ν_3(LO) then it is a more modest jump to the assignment of the corresponding features in the Raman melt spectra to modes having longitudinal characteristics. Such an assignment for the disordered solids seems more appealing than other extant interpretations, and Chisler has already remarked on the strong similarities between the disordered solid and liquid Raman spectra.[12]

To this point, we have only presented a new and somewhat radical view of molten salt vibrational spectra in the fundamental range. It is perhaps impossible to pinpoint a definitive experiment to irrevocably either affirm or rule out the suggested T - L assignments, but there are a number of rather obvious studies suggested by the T - L viewpoint. Only three of these are considered here.

The dilution studies of $LiNO_3$ with LiCl mentioned under point 2 above have been limited by solubility to less than 25% LiCl. This dilution of the NO_3^- particle density needs to be extended. This is possible by introducing a second more or less innocucous anion such as Br^-. The collapse of the Raman υ_3 doublet with dilution would offer strong support for the T - L approach.

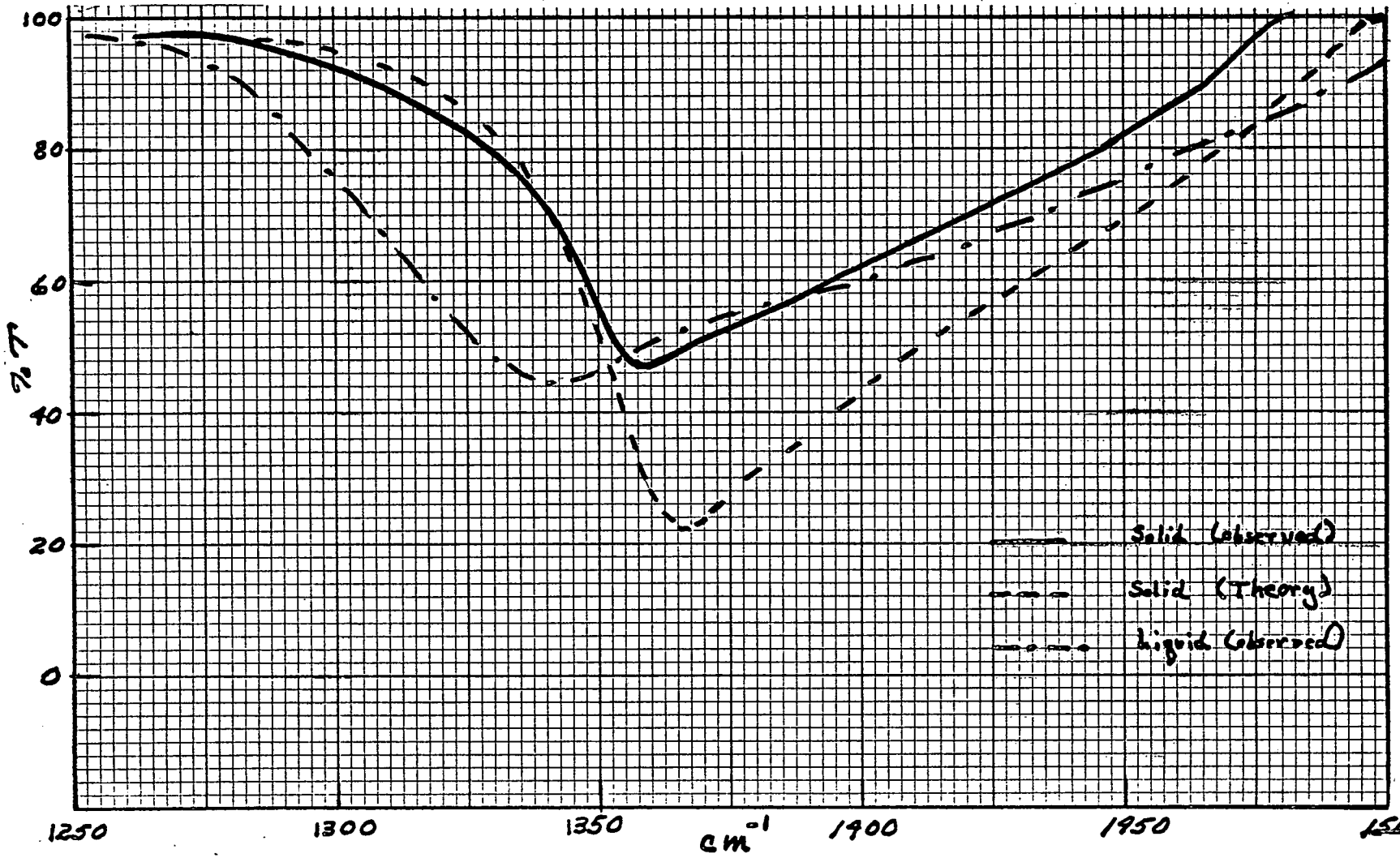
Should the second υ_3 Raman component in the disordered solid nitrates have a longitudinal origin then one would expect the relative intensities of the doublet components to be strongly orientation dependent. The necessary Raman orientation studies can be easily completed using a laser source but to date, the spectra are limited to an instrument equipped with a helical mercury lamp source.[12] We are prepared to make the necessary laser Raman study.

υ_2, like υ_3, shows a high frequency ATR wing in both the liquid and solid lithium nitrate spectra. This wing in the solid spectrum can be theoretically related to the T - L split, but not in any straightforward manner for the liquid. However, initial studies indicate that υ_2 is weakly Raman activated in the melt and may be peaked at a value close to the longitudinal frequency that one might deduce from the liquid ATR wing extension. This possibility needs further investigation perhaps using a more powerful argon laser source which we now have

available in our laboratory. Also, it would be exceedingly interesting to look for ν_2 in the Raman of the orientationally disordered solid nitrates to make comparisons with the known longitudinal frequencies.

The objectives stressed in this proposal may seem somewhat restricted since, again, most interest is expressed in the alkali metal nitrates. In fact, however, since these are the best characterized melts, they are the obvious objects of any study involving novel concepts of the source of vibrational spectroscopic features. It is not possible to foresee the particular gain in understanding of melt structures from this study, even assuming that the suggestion of T - L mode differentiation is affirmed. However, it is clear that such an affirmation (or negation) will serve as another piece in the complex picture puzzle of the liquid state. Only when more complete dynamical calculations for systems experiencing three dimensional disordering are available will the significance of the identification of T and L modes (if such is affirmed) be apparent. Dyson's one dimensional calculation may serve as a starting point for such a dynamical analysis.[15]

Figure 1. ATR curves for the ν_3 mode of $LiNO_3$. The solid curves are for a sample with trigonal axis $\perp$ to ATR element and using radiation polarized in the plane of incidence.



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Phi Lambda Upsilon
American Chemical Society
American Institute of Physics

RECENT PUBLICATIONS UNDER AT(11-1)-1615:

1. K. Williamson, P. Li and J. P. Devlin, "Vibrational Spectra and Structures of Ionic Liquids II. The Pure Alkali Metal Nitrates," J. Chem. Phys., 48, 3891 (1968).

2. P. Li and J. P. Devlin "--III. $AgNO_3$ and KNO_3 Mixtures," J. Chem. Phys., 49, 1441 (1968).

3. J. P. Devlin, R. P. J. Cooney and P. Li "Advances in the Infrared Spectroscopy of Molten Salts" Ch. 8 of "Molten Salts" (G. Mamantor, ed.) (Marcel-Dekker, 1969).

4. J. P. Devlin, P. C. Li and G. Pollard "---IV. Isotopic Dilution of the Alkali Metal and Ammonium Nitrates," J. Chem. Phys., to be published, February, (1970).

SYMPOSIA PRESENTATIONS AND RELATED ACTIVITIES:

1. "Advances in the Infrared Spectroscopy of Molten Salts" Invited Speaker A. C. S. Molten Salt Symposium, Fall National Meeting, Atlantic City, N. J. (1968).

2. "Isotopic Dilution, and the Choice of a Bravais Lattice for the Molten Alkali Metal Nitrates," Invited Speaker Gordon Conference on Molten Salts, August (1969).

3. Session Chairman, Gordon Conference on Molten Salts, August (1969).

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1. B. Ware, K. Williamson and J. P. Devlin. "An Infrared Study of Internal-Rotational Barriers in Solid π Complexes of Methylbenzenes." J. Phys. Chem., 72, 3970 (1968).

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3. R. P. J. Cooney, C. Thayer, P. Li and J. P. Devlin. "Spectroscopic Observation of Surface Distortion in Ionic Crystals," J. Chem. Phys., 51, 302 (1969).

FACILITIES:

Laboratory space with standard laboratory features plus built-in vacuum racks is available. Instrumentation includes a Beckman IR-7 infrared spectrometer with a CsI interchange, a Perkin-Elmer 12-C infrared spectrometer with NaCl and CsBr optics, a Cary 14 recording spectrometer, a Beckman D. U. quartz spectrometer, a Varian A-60 nmr spectrometer and several gas chromatographs. The Bartlesville branch of the Bureau of Mines has offered the use of their Perkin-Elmer far-infrared double-beam recording spectrometer. A new laser Raman instrument built around the Jarrell-Ash 25-100 double monochromator is also available, with both Argon and He-Ne laser sources.

A computer center equipped with an IBM 360-50 digital computer offers its services. A thoroughly tested program for the least-square fitting of force constants to frequencies in a normal coordinate analysis is ready for use. This program will handle several molecules or isotopic species simultaneously and enables the use of a variety of quadratic potential functions. A program for theoretical analysis of ATR infrared bands is also available.