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VIBRATIONAL SPECTRA OF MOLTEN SALTS

D. W. James

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CONTENTS

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D. W. James**

ABSTRACT

Vibrational spectra provide one of the most direct methods for the study of composition and structure of simple covalently bound species. In molten salts, where the presence of complex ionic species has been debated, the application of the powerful techniques of infrared and Raman spectroscopy has been hampered by severe experimental difficulty. The years since 1955 have seen a quickening interest in this field. This report reviews the literature from 1925 to the present time and covers unusual aspects of experimental techniques as well as the results obtained. The discussion is limited to ionic salts except where the spectra of molecular liquids make a direct contribution to the understanding of related ionic liquids. Literature references number 62.

I. INTRODUCTION

The study of vibrational spectra has long been an effective means of measuring the molecular characteristics of polyatomic molecules and ions. The vibrational frequencies may be measured by the Raman effect and by infrared absorption and emission. The application of Raman spectroscopy to molten salts has been an established field of research for many years, and several experimental arrangements have been described (*11*, *35*, *61*).*** The experimental problems involved in obtaining infrared spectra at high temperatures, however, have only recently been successfully overcome (*28*, *59*).

The vibrational spectra of molten salts have been studied principally to determine the vibrational frequencies of the fundamental modes of polyatomic ions. In many instances the very existence of strong vibrational frequencies has served as the first unambiguous evidence that the system contained strongly bound polyatomic ions (*61*, *62*). From the qualitative features of a spectrum, it is frequently possible to draw conclusions about the symmetry of a molecule ion. This is a first step toward determining the molecular structure. From the quantitative features of a spectrum, a reduced number of force constants can be determined, but a complete potential energy function cannot be derived, because there are usually more potential constants than vibrational frequencies. The theory of molecular vibrational spectra is treated extensively in a number of works (*34*, *60*).

In the harmonic approximation for gaseous molecules, the line intensity, given by the integrated area under the curve, may be related to the molecular bond dipole. In all real cases the line shape, and hence the line intensity, is modified by the interactions of the vibrator with the environment. The variation of line shape in gaseous spectra has been semiquantitatively analyzed in

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**D. W. James is a visitor from New Zealand.

***See Bibliography.

terms of such interactions (*10*). A similar analysis of liquid systems has not been attempted because of the complex nature of the interactions and the lack of a satisfactory distribution function. Qualitative information has, however, been obtained by comparison of the intensity of a given frequency in different salts (*58*).

Structural studies of high-temperature molecular, inorganic liquids (*21*, *27*, *44*), of glass-forming systems (*18*, *30*), and of network liquids (*13*) are outside the scope of this discussion. Only vibrational studies of ionic, inorganic liquids and only those experimental aspects peculiar to the production of the spectra at high temperatures are reviewed here.

II. EXPERIMENTAL TECHNIQUES

1. Introduction

Two problems of peculiar significance to molten-salt spectroscopy are containment of the sample and maintenance of a zone of high temperature. For a more general discussion than is given here, the reader is referred to texts on experimental vibrational spectroscopy (*33*, *49*).

2. Raman Spectroscopy

The intensity of a Raman spectrum depends on the intensity of the incident exciting radiation. It is essential therefore that the heating assembly surrounding the sample diminish the intensity as little as possible. Any high-temperature cell assembly will, of necessity, be a compromise between the production of a zone of uniform temperature and the maximum transmission of light to the sample. Spiral discharge lamps have been used predominantly in high-temperature Raman spectroscopy; their use limited the design of the cell assembly since it must be transparent and small enough to fit into the cylindrical space delineated by the lamp coils.

The experimental assembly, shown in Fig. II.1, was designed to meet the above specifications (*37*) and utilizes a hot zone surrounded by a static air space. The winding of fine resistance wire provides the primary source of heat, and convective temperature variations in the vertical tube are controlled by a countercurrent of preheated air. Efficient heating is possible only if the hot zone is kept small; therefore the radius of the silica furnace is kept as small as possible. Molten salts have been studied in this apparatus to the practical limit of Pyrex glass (500°C) with maximum thermal gradients of ±5°C. A similar apparatus whose heat source was preheated air was used for studies in which the temperature did not exceed 250°C (*61*).

In an assembly designed to study salts at temperatures approaching 1000°C* the sample cell was contained within a number of closely fitting stainless steel rings. When this stainless steel susceptor is subjected to a high-power radio-frequency field, it becomes hot by induction and the heat is transferred to the sample. Thermal gradients may be eliminated by varying the spacing of

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*G. E. Walrafen, Bell Telephone Laboratories, Murray Hill, N.J., private communication.

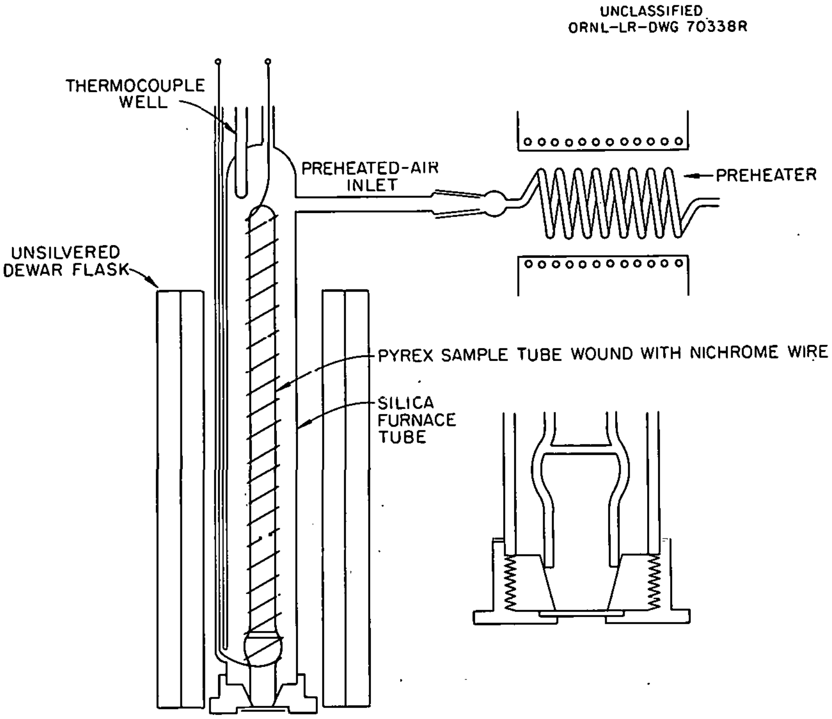

Fig. II.1. High-Temperature Cell Assembly for Use with a Toronto Arc. [Taken from G. J. Janz, Y. Mikawa, and D. W. James, *Appl. Spectry.* 15, 47 (1961).]

the stainless steel rings, with the temperature controlled by varying the field. Although this heating method sacrifices considerable light intensity because of the bulky nature of the susceptor, it has the great advantage of convenience and flexibility. However, with a spectrometer of high light-gathering power, such as the Cary model 81, the loss in intensity of the exciting radiation should not be a problem.

In the methods thus far described, the sample container must be transparent and resistant to attack by the salt under investigation, a restriction which makes studies of such corrosive salts as the carbonates not feasible. A unique method described by Bues (*11*) overcame this difficulty. In the experimental assembly shown in Fig. II.2, the surface of the liquid provides a transparent interface for both entry and exit of the light beam. The crucible containing the sample may be of any suitable container material. A well-formed silicon carbide crystal scatters the radiation from a horseshoe-shaped mercury arc. The scattered radiation, which includes the Raman radiation, passes through a slit into the spectrograph. This system has the advantage of great versatility but the disadvantage of a weak Raman spectrum because of the relatively low intensity of the exciting radiation.

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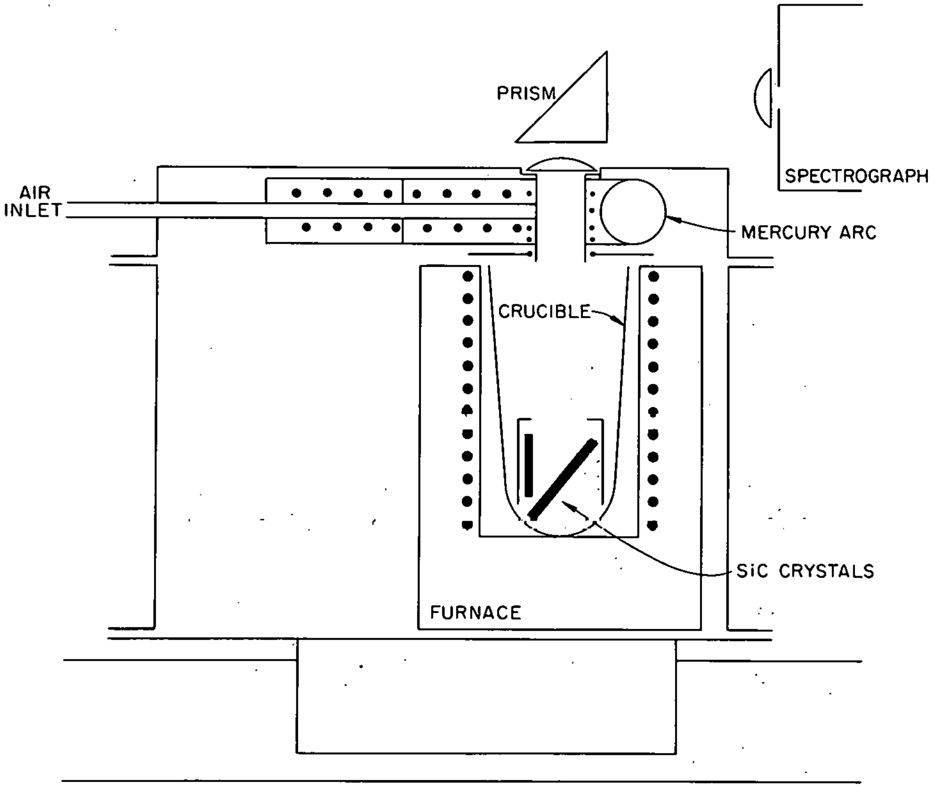

Fig. II.2. High-Temperature Raman Spectroscopic Assembly for Use with Corrosive Melts. [Taken from W. Bues, *Z. Anorg. Allgem. Chem.* **279**, 104 (1955).]

3. Infrared Spectroscopy

The study of infrared spectra of molten salts is made difficult by the lack of a satisfactory window material transparent to frequencies below 1000 cm^{-1}. Two systems have been designed which dispense with the use of windows: (1) a system involving a platinum-mesh screen on which the molten salt was suspended (*28*) and (2) a reflection system (*59*). In the first system a suitable heating device is used to keep the sample molten, and the radiation is chopped before it passes through the sample in order to prevent detection of thermal radiation; this permits the infrared spectra to be readily examined in transmission. Since molten salts in general are highly absorbing, a very short path length must be used so that good resolution can be obtained. The results (*29*) obtained by this method indicate the difficulty in achieving films that are thin enough.

In the second technique, which has proved the more successful, the infrared spectra of the liquids were observed in reflection (*59*). The experimental assembly is shown schematically in Fig. II.3, together with the optical path of the radiation. By rotation of the plane mirror, the reflectivity of the sample is directly compared with that of the standard mirror, the effects of all other

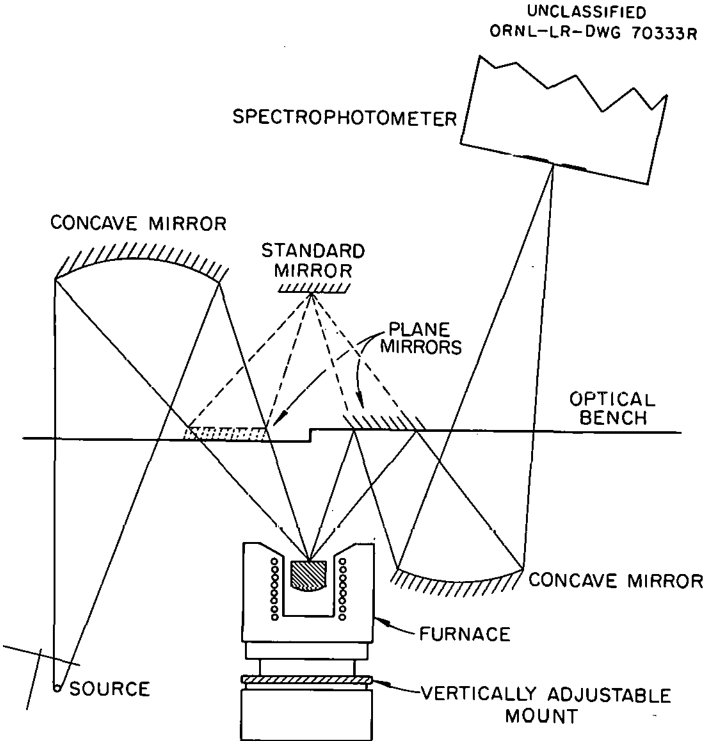

Fig. II.3. High-Temperature Infrared Cell Assembly. [Taken from J. K. Wilmshurst and S. Senderoff, *J. Chem. Phys.* 35, 1078 (1961).]

mirrors in the optical train being identical; the sample height is adjusted to give maximum reflection intensity. The reflection spectra were analyzed by the method of Robinson and Price (47) to provide the variation with frequency of both absorption coefficient and refractive index. The nature of the assembly allows the sample container to be of any suitable material; therefore highly corrosive liquids can be studied.

III. SPECTROSCOPIC DATA

Considerable data have been published on the vibrational spectra of molten salts, but they are scattered throughout the literature. They are assembled here in the form of easy-reference tables. Table III.1 shows vibrational frequencies of pure halides and complex halide anions, and Table III.2 shows the vibrations of oxyanions. The assignments given are those of the original publications and refer to the normal modes of particles with point-group symmetry stated in the tables. The point-group symmetries marked with an asterisk may be in doubt because of the incomplete nature of the spectra. The cationic species in Table III.2 are given because the spectra of oxyanions show a marked dependence on the nature of the cation. When the degenerate frequencies have been split into two components, they are both assigned to the original symmetry species and

Table III.1. Vibrational Frequencies of Halides

Molecule Ion	Symmetry	Vibrational Frequency (cm^{-1}) ν_1	ν_2	ν_3	ν_4	Bibliographical Reference
$ZnCl_2$	$D_{\infty h}$	233				(*11*, *48*)
$ZnBr_2$	$D_{\infty h}$	155				(*48*)
$CdCl_2$	$D_{\infty h}$	212				(*11*)
$HgCl_2$	$D_{\infty h}$	313	100	376		(*38*)
$HgBr_2$	$D_{\infty h}$	195	90	271		(*38*)
$ZnCl_3^-$	D_{3h}*	292			85	(*11*)
$CdCl_3^-$	D_{3h}*	259			83	(*11*)
$HgCl_3^-$	D_{3h}	282		287	210	(*38*)
$ZnCl_4^{2-}$	Td	280			92	(*11*)
$HgCl_4^{2-}$	Td	267	180	276	192	(*38*)
$AlCl_4^-$	Td	349	146	575	182	(*24*)
$GaCl_4^-$	Td	346	115	380	153	(*61*, *25*)
$GaBr_4^-$	Td	210	71	278	102	(*62*)

Table III.2. Vibrational Frequencies of Oxyanions

Molecule Ion	Cation	Vibrational Frequency (cm^{-1}) ν_1	ν_2	ν_3	ν_4	Bibliographical Reference
NO_3^- (D_{3h} symmetry)	Li^+	1067	821	1375, 1460	726	(*35*, *59*)
	Na^+	1053	827	1412	722	(*35*, *59*)
	K^+	1048	829	1391	718	(*35*, *59*)
	Rb^+	1046		1372	713	(*35*)
	Cs^+	1043		1356	708	(*35*)
	Ag^+	1035	800	1310, 1395	733	(*35*, *59*)
ClO_3^- (C_{3v} symmetry)	Li^+	938	620	977, 1018	478	(*58*)
	Na^+	932	611	988	482	(*58*)
	K^+	931	603	981	489	(*58*)
	Ag^+	895	595	931, 969	440, 477	(*58*)
ClO_4^- (Td symmetry)	Li^+	948	470	1139	627	(*58*)

are separated, in the appropriate column, by a comma. The reasons for this splitting will be discussed in a later section.

The force constants of halide molecule ions in molten salts, presented in Table III.3, were calculated on the basis of the valence-force-field approximation (*34*) with cross term for symmetry $D_{\infty h}$ and the Urey-Bradley force-field (*5*, *34*, *40*) approximation for symmetry D_{3h} and Td. The correspondence of the terms F_1, F_2, and F_3 is as follows: for symmetry $D_{\infty h}$, $F_1 = k_1$, $F_2 = k\delta/l$, and $F_3 = k_{12}$; for symmetry D_{3h}, $F_1 = k$, $F_2 = H$, and $F_3 = F$; for symmetry Td, $F_1 = k_1$, $F_2 = k_2$, and $F_3 = \gamma$. This means, in effect, that F_1 is a stretching force constant, F_2 is a bending force constant, and F_3 is an interaction force constant between nonbonded atoms.

Table III.3. Force Constants for Halide Molecule Ions in Molten Salts

Molecule Ion	Symmetry	Force Constants (dynes/cm)			Bibliographical Reference
		F_1	F_2	F_3	
		$\times 10^5$	$\times 10^5$	$\times 10^5$	
$HgCl_2$	$D_{\infty h}$	2.11		−0.07	(*38*)
$HgBr_2$	$D_{\infty h}$	1.86		−0.07	(*38*)
~~$HgCl_3^-$~~	~~D_{3h}~~	~~1.27~~	~~0.21~~	~~0.13~~	~~(*48*)~~
$AlCl_4^-$	Td	2.06	0.31	0.06	(*24*)
$GaCl_4^-$	Td	2.15	0.18	0.05	(*61*)
$GaBr_4^-$	Td	1.73	0.19	0.05	(*62*)
$HgCl_4^{2-}$	Td	0.82	0.48	0.08	(*48*)

IV. DISCUSSION OF SPECTRA

1. Halides

The production of molecule ions in halide melts may occur in two ways: the salt may undergo a complex autoionization of the type

$$2M(X)_n \rightarrow [M(X)_{n-1}]^+ + [M(X)_{n+1}]^- , \qquad (IV.1)$$

or ionization may occur only in the presence of excess halide ion,

$$M(X)_n + X^- \rightarrow [M(X)_{n+1}]^- . \qquad (IV.2)$$

The formation of anionic complex ions by metals of Groups II-B and III-A has been investigated by Raman spectroscopy to establish the nature of the molecule ions present. Since the technique is not sensitive to vibrators present in low concentrations, only the dominant polyatomic species was detected.

The Group II-B metal ions may be expected to have a strong covalent component of bonding and consequently a tendency to form associated groups. The Raman spectra of molten $ZnCl_2$, $ZnBr_2$, $CdCl_2$, $HgCl_2$, and $HgBr_2$ (*8*, *11*, *38*, *46*, *48*) indicate that the dominant polyatomic species in the liquid form are the same as those in the crystalline form. The results from studies of vibrational spectra and of x-ray and electron diffraction (*7*, *11*, *50*) indicate the presence of a linear, symmetrical, triatomic species of symmetry $D_{\infty h}$ in the solid state of these salts.

The Raman spectrum of a triatomic species of symmetry $D_{\infty h}$ should consist of a single strongly polarized frequency (*34*). This is observed for the halides of zinc and cadmium (*11*). Crystalline mercuric chloride and bromide, however, display two weak frequencies in addition to the expected strong frequency (*11*, *17*). Neither crystal has all the elements of $D_{\infty h}$ symmetry. Thus the breakdown in selection rules may be attributed to the interaction of the crystal field with the vibrating particle. In the molten state, close to the melting point, the forbidden frequencies persist, but with reduced intensity. In the change of state, enough of the crystal symmetry is retained to cause relaxation of the selection rules for the $D_{\infty h}$ space group.

It is not possible to say, on the basis of the vibrational spectra, what the ionization process is in the weakly ionized zinc and mercury halides. Cadmium chloride, however, is sufficiently ionized that a mechanism similar to Eq. IV.1 would produce spectroscopically observable species. The absence of frequencies corresponding to such species indicates that the dominant ionic species present must be monatomic ions.

From measurements of vapor pressure (*5*), electrical conductance, and phase diagrams (*2*), it appears likely that when an alkali halide is added to a corresponding Group II-B halide, a complex ionization (Eq. IV.2) takes place. Vibrational spectral measurements may give two types of information in such cases: From the appearance of new frequencies, the presence of new polyatomic species may be postulated. If all frequencies of the new species are observed, both its constitution and conformation may be deduced.

The complex anionic chlorides of zinc and cadmium were investigated by Bues (*11*). The spectrum of zinc chloride showed progressive change with added potassium chloride. At a concentration of 50 mole % KCl, the spectrum of zinc chloride was no longer discernible, and two new frequencies had appeared. As the concentration of potassium chloride was increased to 67 mole %, these frequencies were replaced by two new lines of slightly different frequency. Further increase in potassium chloride concentration did not change the spectrum. Although not all the expected fundamentals were observed, these spectral changes were taken to indicate the presence of two new species, $ZnCl_3^-$ and $ZnCl_4^{2-}$, the formation of which was dependent on the chloride ion concentration. This interpretation has been questioned by Bredig and Van Artsdalen (*9*), who point out that the change in spectrum observed in going from $ZnCl_3^-$ to $ZnCl_4^{2-}$ is small enough to be attributed to an environmental change. In this case only a single, new species is necessary to explain the spectral changes. Irrespective of whether one or two new species are formed, it is not possible on the basis of these data to deduce the composition and nature of the particle. If relative intensity data were available, the composition could be deduced from the variation of intensity with melt composition, but this would still leave the conformation in doubt.

When potassium chloride was added to cadmium chloride, two new frequencies which were observed became the dominant frequencies at a 50 mole % composition, a further increase in the concentration of potassium chloride causing no further spectral change. The stable molecule ion in these melts was assumed to be $CdCl_3^-$, which should have three or four Raman-active fundamentals, depending on whether it is planar or pyramidal in conformation. Since the observed spectrum is not complete, the deductions made are open to doubt. As in the case of the zinc:potassium/chloride system a new spectroscopic species has been indicated, but neither its composition nor its conformation may be deduced.

Janz and James (*39*) investigated the spectra of the complex anionic chlorides of mercury by adding potassium or ammonium chloride to mercuric chloride to a maximum composition corresponding to $HgCl_2$:2MCl. They observed the change in spectrum with composition change and isolated the frequencies corresponding to two different species – three frequencies having maximum intensity at about 45 mole % MCl and four frequencies having maximum intensity at the highest concentration studied. These were taken to correspond to the species $HgCl_3^-$ and $HgCl_4^{2-}$. The intense Rayleigh wing prevented observation of frequencies lower than 170 cm^{-1}, and the elevated melting point associated with higher concentrations of MCl prevented the examination of such mixtures. The vibrations of an XY_3 species of D_{3h} symmetry divide into species $a_1(R,p) + a_2(I) + 2e(R,dp,I)$, where *R*, *I*, *p*, and *dp* denote Raman-active, infrared-active, polarized, and depolarized, respectively (*34*). The spectra observed (*39*) for the $HgCl_3^-$ species corresponded with that anticipated from the symmetry selection rules, and so the species was assigned a trigonal plane configuration. Similarly, the four observed vibrations of the $HgCl_4^{2-}$ may be assigned to the four Raman-active fundamentals [symmetry species $a_1(R,p,I)$, $e(R,dp,I)$, $2f_2(R,dp,I)$] of the tetrahedral point group (*34*). The tetrachloromercurate ion is thus assigned as a tetrahedral ion.

In the pure molten chlorides of aluminum and gallium, the molecular species occur as double molecules, thus enabling the metal atoms to have completed outer orbits of electrons. The structure of these molecular species has been investigated by Raman spectroscopy (*23*, *26*). When these halides are used as solvents for ionic salts, a complex ionization (Eq. IV.2) occurs, yielding an essentially completely ionic melt. The nature of this ionization is of interest to molten-salt chemists, since such mixtures provide a class of low-melting ionic media.

Equimolar mixtures of aluminum chloride and sodium chloride or nitrosyl chloride have been shown, by phase studies (*15*, *24*), to form compounds of the type $MAlCl_4$ where M is Na^+ or NO^+. The Raman spectra of both these mixtures in the molten state were qualitatively similar (*24*) but were quite distinct from the spectrum of pure aluminum chloride (*26*). When the vibrational frequencies were assigned on the basis of a tetrahedrally symmetric species, frequency checks with both the central force field and the Urey-Bradley force field (*34*) gave reasonably good agreement between observed and calculated values. The spectrum of the mixture $NOCl\cdot AlCl_3$ also included the fundamental frequency characteristics of the NO^+ ion. It seems relatively certain, therefore, that both melts were predominantly ionic in nature, with the anionic species being the tetrahedral tetrachlor-aluminate ion. This species was also formed in a variety of other media (*22*).

In addition to having a normal valence of III, gallium shows an apparently anomalous valence of II in gallium dichloride and gallium dibromide. Woodward *et al.* (*61*, *62*), using Raman spectroscopy, made structural studies of these salts in the molten state and report that the spectra did not show the presence of either triatomic GaX_2 species or polyatomic $(GaX_2)_n$ species involving Ga–Ga bonds but, rather, were in accord with a tetrahedral tetrahalo-gallate ion GaX_4^-. They examined the spectrum of the corresponding ions in aqueous solution and obtained analogous spectra. These liquids, undoubtedly, therefore are composed of Ga^+ and GaX_4^- ions in which the gallium metal shows valences of I and III respectively.

When normal gallium chloride (empirical formula, $GaCl_3$) is mixed with sodium chloride in the molten state, the electrical conductance is found to increase markedly. The Raman spectra of these mixtures (*25*) show, in addition to the characteristic frequencies of Ga_2Cl_6, the frequencies of $GaCl_4^-$. In this case, then, the gallium is not completely converted to an anionic complex, in contrast to the findings with aluminum chloride.

2. Nitrates

The molten nitrates of Group I metals have been among the most extensively studied molten salts (*3*, *36*, *41*, *52*), doubtlessly because they are noncorrosive and low melting with reasonable thermal stability. Spectroscopically, these salts have several features which make them particularly interesting. They are examples of highly ionic salts in which the ionic species are simple cations and polyvalent anions. The highly polarizable stable anion acts as an ideal detector of changes in electrostatic forces within the melt as either the cationic or anionic composition is altered.

The vibrational spectra obtained from nitrate melts may be associated with the nitrate ion, which has symmetry D_{3h} in dilute aqueous solution. The vibrations of this symmetry class divide into nondegenerate species, a_1' and a_2'', together with two doubly degenerate species of class *e*, as enumerated earlier. Two types of environmental perturbations may be differentiated by the effect produced in the spectrum: those produced by a symmetric field and those produced by a nonsymmetric field. If the environmental symmetry is at least D_{3h} (symmetric field), the selection rules for the D_{3h} nitrate ion will be obeyed. In this case, changes in interionic forces will be manifest as small changes in frequency and alteration of line profile. When the environmental symmetry is less than D_{3h} and the nitrate ion is not able to rotate, so that it is subject to the unsymmetric field, the selection rules for D_{3h} symmetry will no longer be strictly obeyed. A perturbation of this type may result in removal of the degeneracy of the vibrations of class *e* or in the appearance of forbidden frequencies, or in both (*32*).

Molten nitrates have been studied by both Raman and infrared spectroscopy. Only the nitrates of Group I are treated in detail in this section. [Two studies dealing with glassy mixtures of nitrates of potassium and calcium (*18*, *30*) are not discussed, but are referred to with regard to their results.] Early studies of the Raman spectra of molten nitrates did little more than establish that the liquids are composed predominantly of ions (*45*). The nitrates of lithium, sodium, potassium, and silver were studied by Bues (*12*) (Raman spectra) and Wilmshurst and Senderoff (*59*) (infrared spectra). Janz and James (*35*) studied all the Group I-A nitrates and silver nitrate (Raman spectra). The spectra obtained for potassium nitrate by both Raman and infrared spectroscopy are shown in Fig. IV.1.

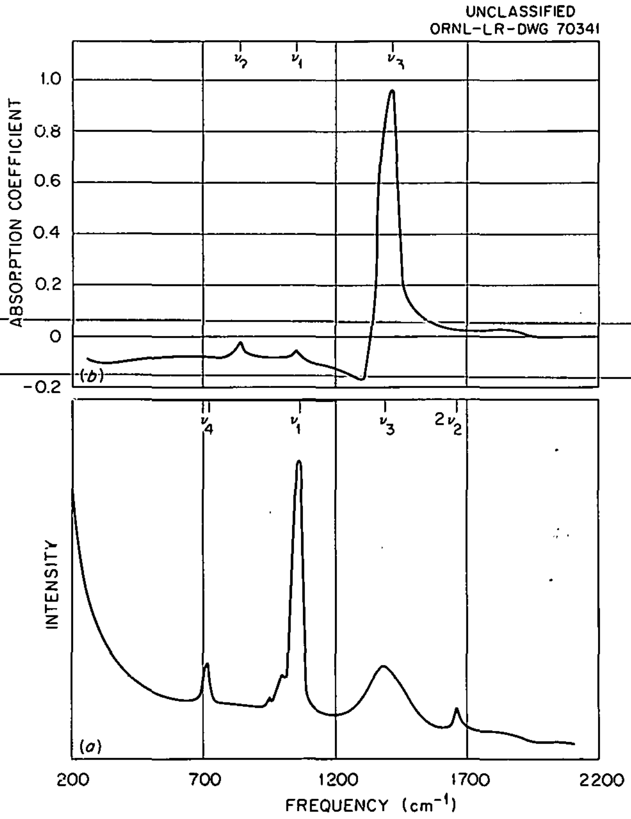

Fig. IV.1. Vibrational Spectra of Molten Potassium Nitrate. (*a*) Raman spectrum [taken from W. Bues, *Z. Physik. Chem. (Frankfurt)* 10, 1 (1957)], and (*b*) infrared spectrum [taken from J. K. Wilmshurst and S. Senderoff, *J. Chem. Phys.* **35**, 1078 (1961)].

The fundamental vibration frequencies all showed regular variations with change of cation. The a_2'' bending frequency increased as the size of the cation increased; all other frequencies decreased. It was found in all investigations that for lithium nitrate and silver nitrate there is a loss of degeneracy in the frequency ν_3. This was observed as a splitting of the band into two components, as shown in Fig. IV.2, and has been discussed in different terms by each investigator (*12*, *35*, *59*); however, the general points of all discussions are similar. The selection rules governing the nature of the spectrum are determined not only by the point group of the particle but also by the

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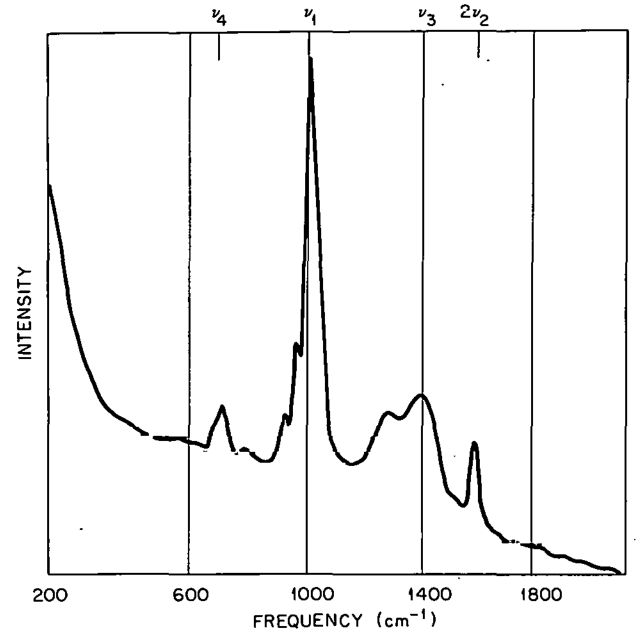

Fig. IV.2. Raman Spectrum of Silver Nitrate. [Taken from W. Bues, *Z. Physik. Chem. (Frankfurt)* 10, 1 (1957).].

symmetry of the environment about the particle. If the symmetry of the environment is lower than the D_{3h} symmetry of the nitrate ion and if the nitrate ion does not have free rotation about the C_3 axis, a loss of degeneracy may be anticipated for ν_3.

The extent of free rotation of nitrate ions in molten Group I nitrates is not certain. It appears probable, from calculations of energy barriers to rotation (*59*) and x-ray diffraction studies (*20*), that the nitrate ions in lithium and silver nitrates cannot rotate freely when the salts are close to the melting point. Thus the loss of degeneracy of the ν_3 band may be attributed to the symmetry perturbation of the cation field, with the contribution of the Ag–O covalent forces probably being significant in silver nitrate. In spectra of mixtures of potassium nitrate and calcium nitrate, both frequencies of type *e* lose degeneracy (*30, 35*). In this case the introduction of a divalent cation must produce a stronger symmetry perturbation of the cationic environment than is possible with mixtures of 1:1 salts.

In discussing variations in frequency with change in cationic species, Bues (*12*) used the frequencies of the nitrate ion in dilute aqueous solution as reference. He discounted the possibility that the observed frequency variation was due to a change in the force constants of the nitrate ion, because, whereas the stretching frequency ν_1 in crystalline lithium nitrate is 4% greater than that observed in aqueous solution, the bending frequency ν_3 is greater by only 0.8%. A force-constant variation may be expected to have a comparable effect on both frequencies.

In dilute aqueous solution the nitrate ion, although not subject to a strong cation field, is far from being in a field-free state. The solvent field has associated with it strong ion-dipole and ion-quadrupole forces. In addition, there is evidence for hydrogen bonding between water molecules and nitrate ions in aqueous nitrate solutions (*53*). The effect of these various forces on the vibrational frequencies is not known; consequently, the spectrum observed in dilute aqueous solution must be considered as an unsuitable reference for molten-salt spectra.

The volume requirements for the nitrate ion change during the vibration ν_1 but not during the vibration ν_3. Bues (*12*) used this characteristic in correlating the free volume of the melt (total volume minus hard-core ion volume) with the variation of ν_1 in both the solid nitrates at room temperature and the molten nitrates at their melting points, as shown in Fig. IV.3. If the variation of ν_1 is purely a function of the free volume of the melt, the stretching frequencies observed for the molten nitrates should show a temperature dependence because of the change in liquid density with temperature change. Later studies (*35*) showed that the vibrational frequencies are independent of temperature over a considerable temperature range.

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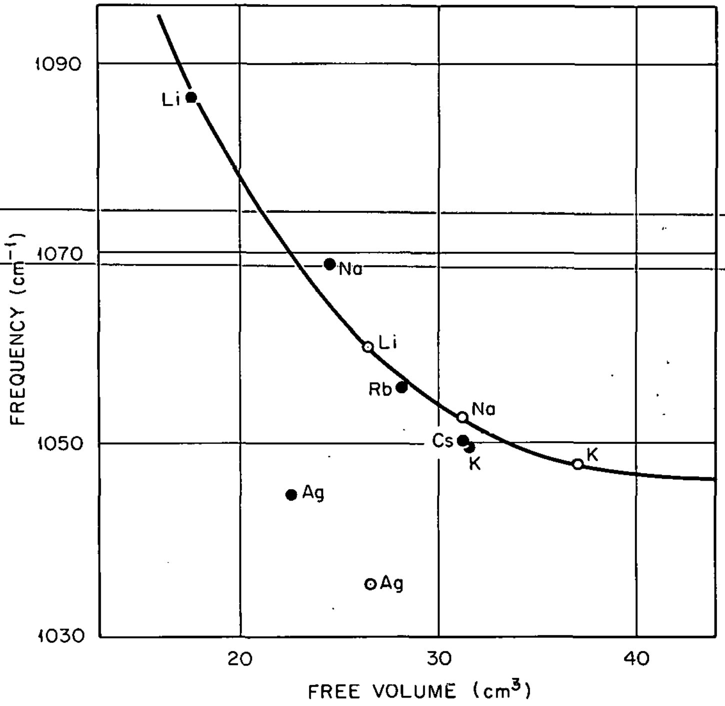

Fig. IV.3. Correlation of Free Volume of Melt with Symmetrical Stretching Frequency ν_1 for Group I Nitrates. Closed circle, crystalline salt; open circle, molten salt. [Taken from W. Bues, *Z. Physik. Chem. (Frankfurt)* 10, 1 (1957).]

Janz and James (*35*) discussed the variations in spectrum from salt to salt in terms of the variations in the cation-anion interactions. They assumed the perturbing field to be due only to the cationic environment, and the distribution of cations to be uniform about any anion. Under these circumstances the field at the anion is proportional to the ionic potential* (Φ) of the cations (*14*). This quantity was modified by a screening factor S_{eff}, the shielding efficiency** (*1*), designed to

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*Ionic potential Φ is defined as cation charge/cation radius.

**Shielding efficiency is defined as $S_{eff} = 5Z^{1.27}/\sqrt{rI}$, where Z is ionic charge, r is ionic radius in A, and I is ionization potential in volts.

make allowance for the poor shielding of the nucleus by *d* electrons in silver nitrate. The modified ionic potential, designated by *P*, showed a monotonic increase with increase in frequency ν_1 for all systems studied (Fig. IV.4).

All the Raman-active fundamentals show about the same relative change with change of cation. Janz and James (*35*) made a force-constant analysis of the data for both the solid and the liquid state by means of the Urey-Bradley force-field approximation (*40*). The stretching force constant displays the same behavior whether in the solid phase or in the liquid phase, an increase of about 7% being observed as the cation is changed from cesium to lithium as shown in Fig. IV.5. The change of force constant with change of state is also relatively constant, irrespective of the cation

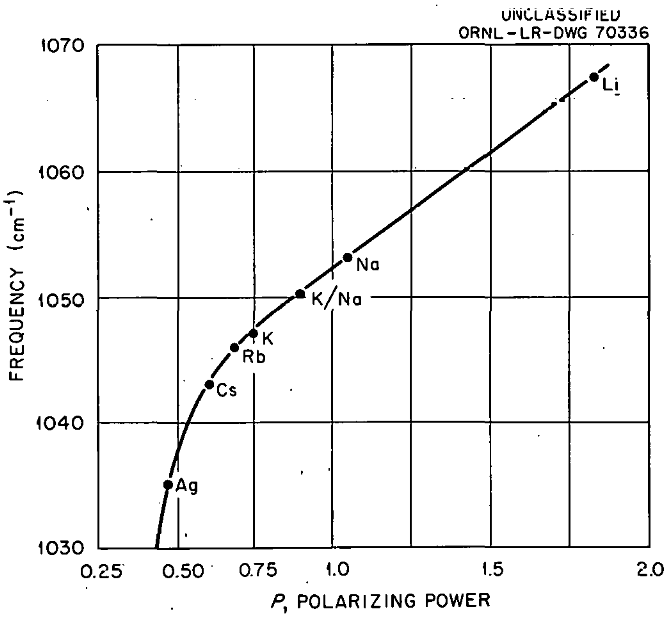

Fig. IV.4. Correlation of Cationic Polarizing Power *P* with Symmetrical Stretching Frequency ν_1 for Molten Group I Nitrates. [Taken from G. J. Janz and D. W. James, *J. Chem. Phys.* 35, 739 (1961).]

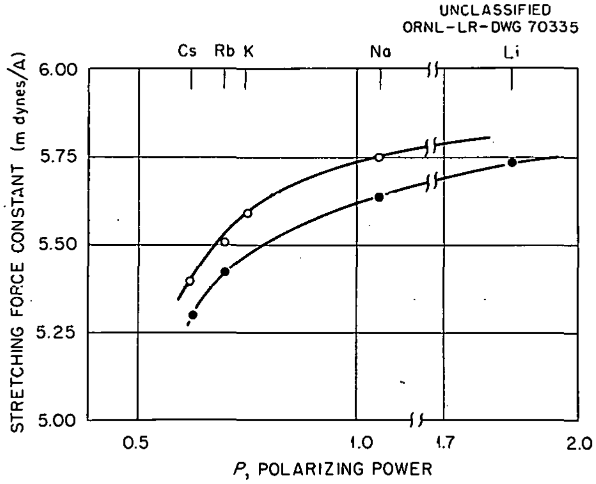

Fig. IV.5. Correlation of Cationic Polarizing Power *P* with Stretching Force Constant for Group I Nitrates. Closed circle, crystalline salt; open circle, molten salt. [Taken from G. J. Janz and D. W. James, *J. Chem. Phys.* 35, 739 (1961).]

involved. These changes in force constant were interpreted as being due to two mechanisms. In the molten state, a change to a more polarizing cation was assumed to cause an increase in electron density in the region of the N–O bonds, with consequent increase in the stretching force constant. The increase in force constant when the salt melted was attributed to a similar increase in the polarization of the anion due to a decrease in the anion-cation separation. A decrease in anion-cation distance has been observed in the alkali halides by x-ray and neutron diffraction (*42*). Data purporting to show the same thing for the alkali nitrates are of dubious accuracy (*16*).

The vibrational frequencies obtained from the infrared spectra by Wilmshurst and Senderoff (*59*) are in agreement with those found by Bues (*12*) and Janz and James (*35*). The change in spectrum with change in cation species was reflected in the variation in line intensity. From the integrated intensity of ν_2, Wilmshurst and Senderoff calculated the molecular-dipole derivative and the N–O bond dipole. The latter was higher than the value estimated for the solid and was found to decrease in the series $Li^+ > Na^+ = K^+ > Ag^+$. Thus the variation in the N–O bond dipole is the same as that in the stretching force constant (*35*) (Fig. IV.5).

The analysis of the infrared reflection spectra (*59*) provided, in addition to the vibrational-frequency data, the variation of refractive index as a function of both temperature and frequency. The refractive indices obtained at the frequency of the sodium *D* line agreed quite well with those obtained by the usual methods (*4*, *54*). The limiting value of the refractive index of lithium nitrate at zero frequency was estimated, and from this the dielectric constant was found to lie in the range $1.96 < \epsilon < 3.13$.

3. Hydroxides and Chlorates

The infrared reflection spectra of silver chlorate, lithium perchlorate, and the hydroxides and chlorates of lithium, sodium, and potassium have been investigated by Wilmshurst (*57*, *58*). In the spectra of the molten hydroxides, two regions of absorption were noted (see Fig. IV.6): a very

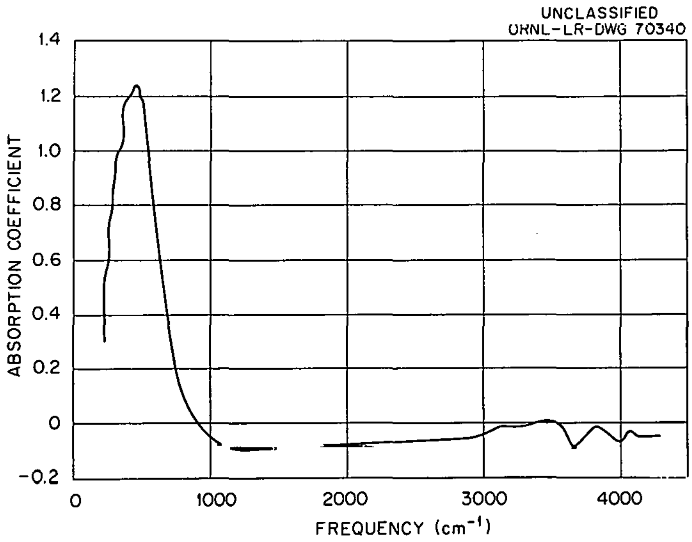

Fig. IV.6. Infrared Spectrum of Lithium Hydroxide. [Taken from J. K. Wilmshurst, *J. Chem. Phys.* **35**, 1800 (1961).]

weak region around 3500 cm^{-1} corresponding to the OH^- stretching vibrational band and a very intense region below 600 cm^{-1} due to latticelike vibrations. The OH^- stretching band did not consist of a single frequency, as anticipated from the $C_{\infty v}$ symmetry of the OH^- ion, but of two prominent, though weak, broad bands flanked by one or two weaker bands. The possible configurations of the hydroxide ion in the melt were considered in assigning these frequencies (Table IV.1). In the original assignment the band was described as the unresolved *P* and *R* rotational branches of the hydroxide stretching frequency, with the band centers at 3652, 3295, and 3300 cm^{-1} for lithium, sodium, and potassium hydroxide melts, respectively. It is not obvious why the band center in lithium hydroxide should be so much higher than in the other two melts; Wilmshurst suggested* that hydrogen bonding was present in the liquids. The low frequency in all melts (~3180 cm^{-1}) is assigned to the stretching mode of the hydrogen-bonded hydroxyl group, the frequency at approximately 3540 cm^{-1} in sodium and potassium hydroxides assigned to the vibration of the free hydroxyl at the end of the chain, and the remaining two frequencies in lithium hydroxide assigned as the *P* (3495 cm^{-1}) and *R* (3840 cm^{-1}) branches arising from the rotation of some free hydroxyl ions, with the *P* branch overlapping the vibrational band of the hydroxyls at the ends of the chains. This assignment is somewhat more satisfactory than the original one, although the O–H–O bending modes should be active in the infrared and observable.

Table IV.1. Components of the Hydroxyl Stretching Band in Molten Alkali Hydroxides

Vibrational Band Component (cm^{-1})		
LiOH	NaOH	KOH
3195	3155	3180
3495		
	3545	3536
3840	3845	
4060		

In this investigation, commercial anhydrous salts were used without being subjected to further dehydration. It has been shown (*51*) that, even above the melting point, sodium hydroxide has a surprising affinity for water and that dehydration below 400°C is difficult. In common with other lithium salts, lithium hydroxide may be expected to be even more difficult to dehydrate than sodium hydroxide. In view of the relative weakness of the hydroxyl stretching bands, the fact that the H–O–H bending vibration was not observed at about 1600 cm^{-1} does not constitute evidence for the absence of water in the melt. Little is known concerning the effects of low concentrations of

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*J. K. Wilmshurst, Parma Research Laboratories, Cleveland, Ohio, private communication.

water on vibrational spectra of molten salts, but profound spectral modifications have been observed in very concentrated aqueous solutions (*43*). For these reasons some uncertainty is introduced into the interpretation of the spectral data.

The structure of the chlorate ion has been well established in the solid state and in solution as being pyramidal with point-group symmetry C_{3v}. As such, the six possible vibrational modes must divide into symmetry species as $2a_1 + 2e$, all modes being active in both infrared and Raman spectra. The infrared spectra of the Group I chlorates observed by Wilmshurst (*57*) are in accord with this point-group assignment. He further observed that the strong degenerate frequency ν_3 of lithium chlorate was split into two components and that both degenerate frequencies ν_3 and ν_4 of silver chlorate were split. By an analysis analogous to that used for molten nitrates, this loss of degeneracy was interpreted as a result of an unsymmetrical charge field about the chlorate ion and a lack of free rotation of the same ion..

4. Potassium Bisulfate

~~The Raman spectrum of potassium bisulfate has been studied as a function of temperature (*56*)~~ and provides evidence for the reactions

$$2HSO_4^- \rightarrow S_2O_7^{2-} + H_2O\ , \qquad (IV.3)$$

$$S_2O_7^{2-} \rightarrow SO_4^{2-} + SO_3\ . \qquad (IV.4)$$

The strongest frequencies of the three molecule ions HSO_4^-, $S_2O_7^{2-}$, and SO_4^{2-} were integrated at various temperatures, and the intensities thus obtained were plotted as a function of temperature (Fig. IV.7). The variation in concentration of a species in solution can be measured by the intensity variation of its vibrational frequencies. Thus Fig. IV.7 shows that, as the temperature is raised from 300 to 620°C, HSO_4^- decomposes according to reaction IV.3 up to 500°C and, subsequently, according to reaction IV.4. Analysis of gaseous products showed the formation of SO_3 in the terminal step.

The spectrum of HSO_4^- showed the same general form in the molten salt as in aqueous solution, and the ion was assigned to the C_s point group. There were, however, slight differences in frequency, which were attributed to the different hydrogen bonding in the two media. The bonding occurred between HSO_4^- ions in the molten salt and H_2O molecules and HSO_4^- ions in aqueous solution. The most probable point group of the $S_2O_7^{2-}$ molecule ion was C_2, and the seventeen frequencies observed for the vibrator were assigned on this basis. Many close correspondences were noted between the frequencies of $S_2O_7^{2-}$ in molten $KHSO_4$ and those of the related species $HS_2O_7^-$ and $H_2S_2O_7$.

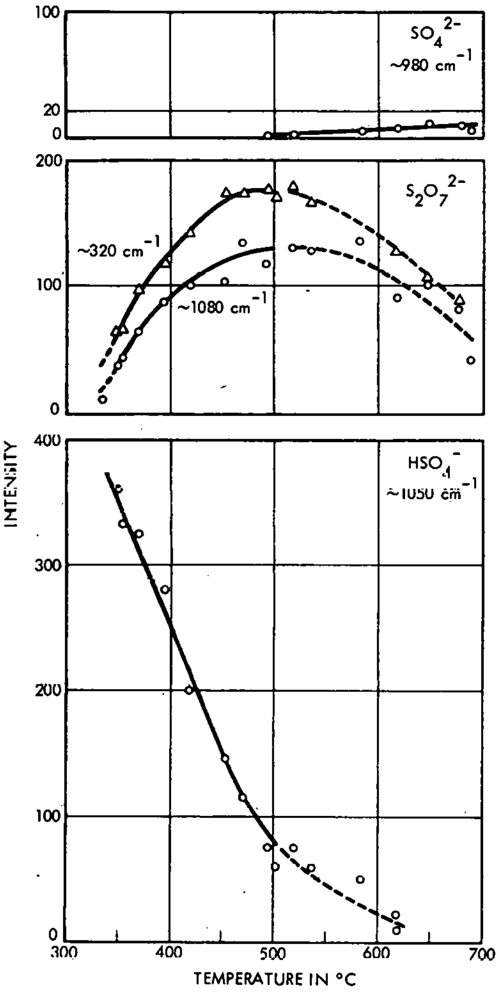

Fig. IV.7. Integrated Relative Intensities of Raman Frequencies Assigned to HSO_4^-, $S_2O_7^{2-}$, and SO_4^{2-} as Functions of Temperature. [Taken from G. E. Walrafen, D. E. Irish, and I. F. Young, *J. Chem. Phys.* 37, 662 (1962).]

5. Selenious Acid

Photoelectric Raman spectra of molten selenious acid (55) obtained in the range of 70 to 175°C provide evidence for the existence of a new species, $H_2Se_2O_5$. Comparisons of Raman bands of molten selenious acid with those of very concentrated aqueous solutions of sodium biselenite indicate common frequencies. In concentrated aqueous solutions the equilibrium

$$2HSeO_3^- \longrightarrow Se_2O_5^{2-} + H_2O$$

provides $Se_2O_5^{2-}$ ions in considerable concentrations. Similarly, in molten selenious acid the reaction

$$2H_2SeO_3 \longrightarrow H_2Se_2O_5 + H_2O$$

produces $H_2Se_2O_5$ molecules in quantity. Raman lines common to the two spectra arise from vibrations that are characteristic of the Se_2O_5 grouping, such as the bending and stretching motions of the Se–O–Se linkage.

V. STRUCTURE OF MOLTEN SALTS

All the investigations reviewed have led to information regarding the structure and conformation of constituent particles in a molten salt. Information concerning the nature and variation of interparticulate forces and the short-range structure present in molten salts is exceedingly difficult to obtain, and this field of research is in but an early state. Spectroscopically, such variations are manifest as modifications of the primarily observed quantity, the vibrational frequency. This can occur as small frequency shifts (*35*, *59*), as splitting of degenerate frequencies (*12*, *35*, *59*), or as changes in profile shape (*59*). Consequently, the derived information cannot lead to unequivocal interpretations but must be used in conjunction with other physicochemical information to provide a best-fit interpretation.

In Raman spectroscopic studies of molten nitrates (*12*, *35*), small changes in frequency with change in cationic environment were interpreted in terms of ionic packing and the anion-cation interactions. The observed variation of frequency is small with change of cation and the interpretations therefore lead to only very qualitative conclusions. The smooth correlations found by Bues (Fig. IV.3) and by Janz and James (Fig. IV.4) may be a reflection of the insensitivity of the analysis methods used.

The variation of line shape as reflected in the change in line intensity has been measured by Wilmshurst (*58*, *59*). From the integrated intensity of a given fundamental, he calculated the dipole derivative corresponding to that vibration and then, by treating the vibrating species as a gaseous particle, calculated the bond dipole, μ. This quantity may be expressed as

$$\mu = \mu_0 + \mu_{\text{induced}} ,$$

where μ_0 is the value in the field-free state, and μ_{induced} is the product of the bond polarizability and the strength of the cation field at the bond. The variation in μ may thus be related to variations in the strength of the cation field or, in other words, to the anion-cation interaction forces. At present, there is no reliable way to estimate μ_0, and so no attempt was made to calculate the variation of μ_{induced} with change of cation composition.

In addition to vibrational frequencies attributable to fundamental modes of the polyatomic vibrator, the infrared spectra of Wilmshurst (*57–59*) disclose the presence of low-frequency vibrations in all melts studied. The frequencies for lithium hydroxide are evident in Fig. IV.6. Similar frequencies observed in nonpolar crystals and liquids (*31*) were assigned as vibrations of the crystal lattice. It is well-recognized that in crystals, out-of-phase vibrations of oppositely charged ions in the lattice give rise to the so-called "optical modes" of lattice vibrations (*6*). Because of the associated large change in dipole, these vibrations are strongly absorbing in the infrared. Wilmshurst assigned the low-frequency vibrations as latticelike modes in the liquid and found support for such assignment by noting that these vibrations are cation sensitive.

While the presence of lattice frequencies in ionic liquids does not necessarily presuppose the existence of a long-range-ordered lattice structure, it does indicate that strong anion-cation forces are operative. The relative sharpness of these bands indicates that only a small range of first-and second-nearest-neighbor distances can occur from a given ion. Further study of the temperature variation of these frequencies and the determination of lines of lower frequency give promise of yielding valuable structural information concerning molten salts.

VI. SUMMARY

Vibrational spectroscopy is a useful technique for examining the particulate properties of a molten salt, in contrast to many physicochemical techniques which measure the bulk time-average properties. Its usefulness lies in the measured quantity being the fundamental vibrational frequency of a molecule ion, which has only a narrow range of values about the most probable value. The two types of measurements made are the most probable vibrational frequencies of the particle and the distribution of frequencies about this most probable value (line-profile studies).

The characterization of a vibrational line requires determination of its activity in infrared or Raman spectra and its depolarization ratio if it is Raman active. From the symmetry species of a vibration of a particle with a given point-group symmetry, the activity as infrared or Raman frequencies and the depolarization ratio may be predicted. On this basis the observed spectral lines may be assigned to the normal modes of vibration of the particle. By matching the characteristics of the observed spectrum with the spectrum anticipated for a number of point-group symmetries, the nature of the polyatomic species can be determined. Spectral studies in molten salts have been mainly directed toward determination of the nature of the polyatomic species by the above technique. Melts, where the existence of complex anionic species has been postulated by other physicochemical techniques, are of particular interest since their vibrational spectra should enable both the constitution and the conformation of the molecule ion to be established. This, however, is possible only when the complete vibrational spectrum is observed. In those experiments (*11*, *19*) in which not all the fundamentals were observed, the conclusions derived from analysis of the data are only speculative and are in no way superior to those obtained from other measurements.

The intense interactions between vibrators in molten salts affect both the frequency and the shape of a spectral line. The frequency for a field-free vibrator is, in general, not accessible, and so the nature of the forces can be estimated only by the way in which they change from one medium to another. Changes in frequency with change in cationic species have been associated qualitatively with the anion-cation forces (*12*, *23*). No attempt has been made to use the variation in line profile to gain insight into the nature of the interionic forces. In all molten salts the line shape is modified by the interactions of the molecule ion with its environment. Some of the ways in which this can occur are broadening by the electric fields (ion, dipole, and quadrupole) of the perturbing entities, resonance broadening by the coupling of corresponding vibrations of neighboring molecule ions, and combination broadening caused by combination of the fundamental molecule-ion vibration with the low-frequency rotational and interparticulate modes. At present, it is not possible to quantitatively analyze a vibrational spectral line in terms of a natural line shape modified by environmental forces. However, by observing a given fundamental of the same molecule ion in a variety of media, variations in interactions will be manifest in the profile of the line. By choosing the medium from a wide variety of nonpolar, polar, and ionic liquids, it may be possible to separate the contributions of the different types of electrostatic forces. With the availability of recording spectrophotometers and high-speed computing techniques, studies such as those outlined should become more feasible and provide a powerful technique to aid in unraveling the problems of internal forces in molten salts.

VII. BIBLIOGRAPHY

(*1*) Ahrens, L. H., *Nature* **174**, 644 (1954).

(*2*) Belyaev, I. N., and K. E. Mirnov, *Zhur. Obshch. Khim.* **21**, 1484 (1951); **22**, 1529, 1734 (1952).

(*3*) Bloom, H., *et al.*, *Trans. Faraday Soc.* **49**, 1458 (1958).

(*4*) Bloom, H., and D. C. Rhodes, *J. Phys. Chem.* **60**, 791 (1956).

(*5*) Bloom, H., and B. J. Welch, *J. Phys. Chem.* **62**, 1594 (1958).

(*6*) Born, M., and K. Huang, *Dynamical Theory of Crystal Lattices*, p 57, Oxford University Press, Oxford, 1954.

(*7*) Braekken, H., and W. Scholten, *Z. Krist*, **89**, 448 (1934).

(*8*) Braune, H., and G. Engelbrecht, *Z. Physik. Chem. (Leipzig)* **B19**, 303 (1932).

~~(*9*) Bredig, M. A., and E. R. Van Artsdalen, *J. Chem. Phys.* **24**, 478 (1956).~~

~~(*10*) Breene, R. G., Jr., *Rev. Mod. Phys.* **29**, 94 (1957).~~

(*11*) Bues, W., *Z. Anorg. Allgem. Chem.* **279**, 104 (1955).

(*12*) Bues, W., *Z. Physik. Chem. (Frankfurt)* **10**, 1 (1957).

(*13*) Bues, W., *et al.*, *Z. Anorg. Allgem. Chem.* **288**, 292, 307 (1956); **308**, 62 (1961).

(*14*) Cartledge, G. H., *J. Am. Chem. Soc.* **50**, 2855 (1928).

(*15*) Chrétien, A., and E. Lous, *Compt. Rend.* **217**, 451 (1943).

(*16*) Danilov, V. I., and S. Y. Krasnitskii, *Dokl. Akad. Nauk SSSR* **101**, 661 (1955).

(*17*) Delwaulle, M. L., *Compt. Rend.* **206**, 1965 (1938).

(*18*) Dietzel, A., and H. J. Poegel, *Atti. Congr. Intern. Vetro, 3°, Venice* **1953**, 219.

(*19*) Ellis, R. B., *et al.*, *J. Phys. Chem.* **65**, 1186 (1961).

(*20*) Furukawa, K., *Discussions Faraday Soc.* **32**, 53 (1962).

(*21*) Gaunt, J., *et al.*, *Trans. Faraday Soc.* **50**, 209 (1954); *Spectrochim. Acta* **10**, 52, 57 (1957).

(*22*) Gerding, H., *Rec. Trav. Chim.* **75**, 589 (1956).

(*23*) Gerding, H., H. G. Haring, and P. A. Renes, *Rec. Trav. Chim.* **72**, 78 (1953).

(*24*) Gerding, H., and H. Houtgraaf, *Rec. Trav. Chim.* **72**, 71 (1953).

(*25*) Gerding, H., and J. A. Koningstein, *Rec. Trav. Chim.* **79**, 46 (1960).

(*26*) Gerding, H., and E. Smit, *Z. Physik. Chem. (Leipzig)* **B50**, 171 (1941).

(*27*) Gerding, H., *et al.*, *Rec. Trav. Chim.* **56**, 968 (1937); **60**, 701 (1941); **61**, 412 (1942); **64**, 191 (1945); **73**, 737 (1954).

(*28*) Greenberg, J., and L. J. Hallgren, *Rev. Sci. Instr.* **31**, 444 (1960).

(29) Greenberg, J., and L. J. Hallgren, *J. Chem. Phys.* **33**, 900 (1960).

(30) Gross, E., and V. A. Koleskova, *Pamyati Sergeya Ivanovicha Vavilova, Akad. Nauk SSSR* **1952**, 231.

(31) Gross, E., and M. Vuks, *Nature* **135**, 100, 431, 998 (1935).

(32) Halford, R. S., *J. Chem. Phys.* **14**, 8 (1946).

(33) Harrison, G. R., R. C. Lord, and J. R. Loofbourow, *Practical Spectroscopy*, Prentice-Hall, New York, 1948.

(34) Herzberg, G., *Infrared and Raman Spectra*, Van Nostrand, New York, 1945.

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

(36) Janz, G. J., and D. W. James, *Electrochim. Acta* **7**, 427 (1962).

(37) Janz, G. J., Y. Mikawa, and D. W. James, *Appl. Spectry.* **15**, 47 (1961).

(38) Janz, G. J., and D. W. James, "Vibrational Spectra of Molten Halides of Mercury, Pt I," to appear in the *Journal of Chemical Physics.*

(39) Janz, G. J., and D. W. James, "Vibrational Spectra of Molten Halides of Mercury, Pt II," to appear in the *Journal of Chemical Physics.*

(40) Janz, G. J., and Y. Mikawa, *J. Mol. Spectry.* **1**, 92 (1960).

(41) Kleppa, O. J., *et al.*, *J. Phys. Chem.* **64**, 1937 (1960); **34**, 357 (1961); **35**, 175 (1961).

(42) Levy, H. A., *et al.*, *Ann. N. Y. Acad. Sci.* **79**, 762 (1960).

(43) Mathieu, J. P., and M. Lounsbury, *Discussions Faraday Soc.* **9**, 196 (1950).

(44) Moureu, H., P. Sue, and M. Magat, *Contrib. Etude Struct. Mol., Vol. Commem. Victor Henri* **1947–48**, 125.

(45) Nedungadi, T. M. K., *Proc. Indian Acad. Sci., Sect. A* **8**, 397 (1938).

(46) Rao, K. V. K., *Proc. Indian Acad. Sci., Sect. A* **14**, 521 (1941).

(47) Robinson, T. S., and W. C. Price, *Molecular Spectroscopy*, ed. by G. Sell, Institute of Petroleum, London, 1955.

(48) Salstrom, E. J., and L. Harris, *J. Chem. Phys.* **3**, 241 (1935).

(49) Sawyer, R. A., *Experimental Spectroscopy*, Prentice-Hall, New York, 1944.

(50) Scholten, W., and J. M. Bijvouet, *Z. Krist.* **103**, 415 (1941).

(51) Smith, G. P., *Problems Pertaining to the Dehydration of Sodium Hydroxide by Volatilization of Water,* USAEC Report ORNL-2130 (Aug. 28, 1956).

(52) Smith, G. P., and C. R. Boston, *J. Chem. Phys.* **34**, 1396 (1961).

(53) Strickler, S. J., "Spectra and Structure of the Nitrate and Nitrite Ions," *Dissertation Abstr.* **21**, 3649 (1961).

(54) Wagner, O. H., *Z. Physik. Chem. (Leipzig)* **131**, 409 (1928).

(55) Walrafen, G. E., D. E. Irish, and T. F. Young, *J. Chem. Phys.* **37**, 1468 (1962).

(56) Walrafen, G. E., D. E. Irish, and T. F. Young, *J. Chem. Phys.* **37**, 662 (1962).

(57) Wilmshurst, J. K., *J. Chem. Phys.* **35**, 1800 (1961).

(58) Wilmshurst, J. K., *J. Chem. Phys.* **36**, 2415 (1962).

(59) Wilmshurst, J. K., and S. Senderoff, *J. Chem. Phys.* **35**, 1078 (1961).

(60) Wilson, E. B., J. C. Decius, and P. C. Cross, *Molecular Vibrations*, McGraw-Hill, New York, 1952.

(61) Woodward, L. A., G. Garton, and H. L. Roberts, *J. Chem. Soc.* **1956**, 3723.

(62) Woodward, L. A., *et al.*, *J. Chem. Soc.* **1958**, 1505.

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