
QUARTERLY REVIEWS

VIBRATIONAL SPECTRA OF IONIC MELTS

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Introduction. RESEARCH into molten salts has been, and is still, stimulated largely through problems of "extractive electrolysis". Chemical syntheses and co-ordination chemistry in the molten state are the least explored areas. A reflection of the trend towards problems in chemistry rather than electrochemistry is seen in the increasing physicochemical study of this field. Knowledge of the structure, thermodynamic and transport properties, and behaviour of molten salts is basic to the advancement of the chemistry as well as the electrochemistry of molten inorganic salts.

A salient difference of a one-component electrolyte, *e.g.*, sodium chloride, from an aqueous electrolyte is that, in the molten system, there is no covalently bonded or "molecular" electrolyte present to make the coulombic charge of the ionic electrolyte more diffuse. Such physicochemical studies as those of electrical transport, viscosity, phase-change calorimetry, and cryoscopy have been largely directed to the structural problems raised in such highly ionic melts; sufficiently enhanced, the ionic interactions should be experimentally realisable as deviations from thermodynamic ideality and possibly detectable spectroscopically.

Until recently, studies of the vibrational spectroscopy of molten systems were sporadic¹ and not directed towards problems currently attracting attention. It is apparent that purely ionic melts with spherical monatomic ions (*e.g.* sodium chloride) should not exhibit infrared or Raman activity;* there are no bonded atomic species of sufficient covalency to give rise to vibrational motion. One aspect of the present trend has been the use of known polyatomic *molecular* or *ionic* solute species (*e.g.*, HgCl_2 , NO_3^-) as spectroscopic "detectors" for ionic interactions and chemical bonding in such melts. The correlation of the vibrational force constants with the

* Infrared spectra for alkali halide monomers in the vapour state have been reported—see Klemperer *et al.*, *J. Chem. Phys.*, 1960, **33**, 1534; 1957, **26**, 618. Rittner's ionic model gives a good representation of the potential energy.

¹ (a) Gerding and Nijveld, *Rec. Trav. chim.*, 1937, **56**, 968; (b) *idem, ibid.*, 1940, **59**, 1198; (c) Pattabhiramayya, *Proc. Indian Acad. Sci.*, 1938, **7a**, 229; (d) Nedungadi, *ibid.*, 1938, **8a**, 397; (e) Moses, *ibid.*, 1939, **10a**, 71; (f) B. S. R. Rao, *ibid.*, p. 167; (g) K. V. K. Rao, *ibid.*, 1941, **14a**, 521; (h) Salstrom and Harris, *J. Chem. Phys.*, 1935, **3**, 241; (i) Vassas-Dubuisson, *J. Phys. Radium*, 1948, **9**, 91; (j) Petrikaln and Hochberg, *Z. phys. Chem.*, 1929, **B3**, 217; (k) *idem, ibid.*, 1929, **59**, 114; (l) A. Braune and G. Engelbrecht, *Z. phys. Chem.*, 1932, **B19**, 303.

degree of ionicity of the bonding interactions in inorganic melts illustrates another feature receiving attention. Formation of new chemical species in two-component inorganic melts as well as the identification of the nature of the species in pure one-component systems are also of current interest in high-temperature spectroscopy.

In this Review, some aspects and principles of vibrational spectroscopy applied to the qualitative and quantitative interpretation of results are described. Features of experimental work indicating differences from conventional practice are summarised. The status and scope of the vibrational spectroscopy of inorganic melts forms the main part of this review. For this purpose the melts have been grouped in increasing order of phase-rule complexity (as determined by the number of independently variable components).

Principles.—Vibrational spectroscopy is used both as an analytical aid and for more precise quantitative studies of the structure and bonding of polyatomic species. The analytical method is based on the uniqueness of the spectrum of a molecule and on the relative insensitivity of force constants and vibrational frequencies as the environment about a particular group is changed.² Quantitative analyses rest on the concentration-dependence of band intensities as given by the Beer–Lambert law in ideal cases.² This analytical approach is particularly useful in high-temperature spectroscopic problems where, not infrequently, the possibility arises of new species formed through inorganic reactions in the molten state.

Knowledge of chemical bonding and stereochemistry in inorganic melts can be advanced through the theory of molecular vibrations.^{2,3} Group-theoretical considerations show that it is often feasible to distinguish the arrangements of atoms in a polyatomic species from the number of vibrational bands observed in its infrared and Raman spectra by reference to the point group, *i.e.*, the totality of symmetry elements present in the species. In highly symmetrical systems, some vibrations may be active in either infrared or Raman spectra, but not both. Degeneracy of vibrations may also limit the number of frequencies observed. In the least symmetrical systems, degeneracy will not exist and all vibrations will be active in both infrared and Raman spectra. Tri-, tetra-, and penta-atomic species are most frequently encountered in ionic melts, and the vibrational spectroscopy of these is of particular interest in this review. The point groups, number of fundamentals of each type, and selection rules for various configurations of these species are given in Table 1. The loss of degeneracy in the transition from a D_{3h} system to a C_{2v} system is also shown.

² (a) Bellamy, "The Infra-red Spectra of Polyatomic Molecules," John Wiley and Sons, Inc., New York, 1954; (b) Barrow, "Introduction to Molecular Spectroscopy," McGraw Hill Book Company, New York, 1962; (c) Bauman, "Absorption Spectroscopy," John Wiley and Sons, Inc., New York, 1962; (d) Herzberg, "Molecular Spectra and Molecular Structure, Vol. II, Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Company, Inc., New York, 1945.

³ Wilson, jun., Decius, and Cross, "Molecular Vibrations," McGraw Hill Book Company, New York, 1952.

The selection rules based on "isolated" species hold best for molecules in the vapour phase. In condensed states, interactions between particles are often sufficient to cause splitting of degenerate frequencies and

TABLE 1. Selection rules for XY_2 , XY_3 , and XY_4 configurations.

Species	Point group	Number of fundamentals of symmetry type and selection rules*
$\begin{array}{c} Y-X-Y \\ X-Y-Y \\ X \\ / \quad \backslash \\ Y \quad Y \end{array}$	$D_{\infty h}$ $C_{\infty v}$ C_{2v}	$\sum_g^+ (R_p) + \sum_u^+ (I_r) + \Pi_u (I_r)$ $2\sum^+ (R_p, I_r) + \Pi (R_d, I_r)$ $2A_1 (R_p, I_r) + B_2 (R_d, I_r)$
$\begin{array}{c} Y \\ \\ X \text{ (planar)} \\ / \quad \backslash \\ Y \quad Y \end{array}$	D_{3h} Removal of degeneracy in transition from D_{3h} to C_{2v}	$\begin{array}{c} A_1' (R_p) + 2E' (R_d, I_r) + A_2'' (I_r) \\ \downarrow \quad \swarrow \quad \downarrow \quad \downarrow \\ 3A_1 (R_p, I_r) + 2B_2 (R_d, I_r) + B_1 (R_d, I_r) \end{array}$
$\begin{array}{c} Y \\ \\ X \text{ (planar)} \\ / \quad \backslash \\ Y \quad Y \end{array}$	C_{2v}	
$\begin{array}{c} Y \\ \\ X \text{ (pyramidal)} \\ / \quad \backslash \\ Y \quad Y \end{array}$	C_{3v}	
$\begin{array}{c} Y \\ \\ X \text{ (tetrahedral)} \\ / \quad \backslash \\ Y-X-Y \\ \\ Y \end{array}$	T_d	$2A_1 (R_p, I_r) + 2E (R_d, I_r)$ $A_1 (R_p) + E (R_d) + 2F_2 (R_d, I_r)$

* R = Raman-active; I_r = Infrared-active; _p = polarised; _d = depolarised.

appearance of forbidden vibrational bands. Generally, the intensities of the bands made allowed by such perturbations are less than those of active fundamentals. Due cognizance of this factor is important when assigning symmetry to condensed-state systems, based on the number of active frequencies.

In recent studies on silicate glasses,⁴ it has been shown that appearance of a new frequency in infrared absorption spectra can be predicted theoretic-

⁴ (a) Stepanov and Prima, *Optika i Spekt.*, 1958, 4, 734; 1958, 5, 15; (b) Zarzycki and Naudin, *J. Chim. phys.*, 1961, 58, 830.

ally from consideration of the gross structure of the melts and solids. The frequency and intensity of this band depend on the structure of the system as a whole. The Raman activity of the nitrate ion in molten thallos nitrate is such that two point-group symmetry classes, D_{3h} and C_{2v} , appear possible on first inspection; the latter is ruled out when nearest neighbour interactions are recognised in this ionic melt.⁵

The use of polarised radiation provides information about the symmetry type of a vibrational band. If polarised light is used in Raman spectroscopy, it can be shown² that the ratio of the intensity of light polarised perpendicular, I_{\perp} , to the XY plane to that polarised parallel, I_{\parallel} , to this plane can have a maximum value of $6/7$. In this it is assumed that the direction of the incident radiation is along the Z axis. In addition, anti-symmetric vibrations will be depolarised, *i.e.*, $\rho=6/7$, if they are permitted to occur at all. Only totally symmetric vibrations can be polarised, *i.e.*, $\rho \leq 6/7$. The state of polarisation of Raman lines is indicated for the systems of interest in Table 1.

Chantry and Plane⁶ have used absolute Raman intensities to gain information about the nature of the bonding in ionic species in aqueous solution. The derivatives of molecular polarisability with respect to changes in bond length determine the intensities of Raman bands. It is recognised that meaningful results can be obtained only when the environment of a changing bond does not change; an excellent example is an isoelectronic series. Thus, in this manner, the π -bonding contribution in NO_3^- , CO_3^{2-} and ClO_4^- , PO_4^{3-} was investigated.⁶ The results suggest that the π -bonding contributions in the ClO_4^- and NO_3^- ions are considerably greater than in CO_3^{2-} and PO_4^{3-} .

Normal co-ordinate vibrational analyses³ may provide information about chemical bonds. In this method, force constants are calculated by an iterative procedure, an assumed form of the potential function being used. The set of force constants obtained is usually not unique, but comparison of force constants for systems of the same symmetry gives an indication of the nature of the bonding in polyatomic systems. An illustration is the vibrational analysis of the planar XY_3 group, by using the Urey-Bradley potential field, for six inorganic species (BF_3 , BCl_3 , BBr_3 , NO_3^- , CO_3^{2-} , BO_3^{3-}).⁷ The repulsion force constants in these species are found to be correlated directly with the separation of the non-bonded atoms of the species XY_3 . The deviation of the NO_3^- ion from this correlation, due to the greatly shortened length of the N-O bonds, is understood in terms of the enhanced localisation of positive and negative charge densities in the resonance hybrids, relative to the species considered. This type of analysis is also required as a preliminary to the interpretation of intensity measurements, such as those made by Chantry and Plane.⁶

⁵ Wait, Kozlowski, and Janz, *J. Chem. Phys.*, in press.

⁶ Chantry and Plane, *J. Chem. Phys.*, 1960, **32**, 319; 1960, **33**, 736; 1961, **35**, 1027.

⁷ Janz and Mikawa, *J. Mol. Spectroscopy*, 1960, **5**, 92.

The preceding principles illustrate some aspects of the direct insight into the nature of chemical-bonding interactions and the symmetry of the species to be gained by vibrational spectroscopy. Significant contributions in the structural problems in inorganic molten-salt systems may be foreseen with the advance of spectroscopic methods into the area of high-temperature chemistry.

Experimental.—The techniques used in the experimental study of molecular vibrations fall into two categories: infrared absorption and Raman scattering studies. An excellent review of infrared spectral methods has been given by Conn and Avery.⁸ Some of the experimental approaches to the application of these methods to high-temperature systems have been considered specifically in two recent monographs.⁹

Infrared spectral methods. In inorganic melts, the high temperatures and enhanced reactivities make special techniques necessary, since conventional cell windows, *e.g.*, NaCl, KBr, CsI, etc., are either chemically attacked or are themselves molten. The simplest method appears to be the use of the melts themselves both as cell windows and as samples. Use of a platinum-mesh screen as a heater to melt the inorganic salt and to retain the liquid film has been reported.¹⁰ A simple platinum loop ($\frac{3}{4}$ in. diam.), mounted either vertically or horizontally in a sealed furnace, has been successfully used¹¹ for more viscous melts (*e.g.*, B₂O₃) up to 1000°. Use of an anhydrous atmosphere in the furnace chamber and formation of the liquid films *in situ* makes this approach attractive for work with highly hygroscopic materials. An infrared reflection method has been described for studies in molten salts.¹² The technique corresponds to the use of very thin films since it is estimated that the infrared radiation penetrates the melt to a depth of about 10 microns. Related physicochemical properties for inorganic melts, such as refractive indices and dielectric constants, can be determined by this technique.

Raman spectral methods. The Toronto-type mercury arc is the excitation source most generally used in Raman spectroscopy. The basic experimental problem in the extension of the Raman spectral method to high-temperature systems is the design of a molten-salt cell assembly to be placed within the cylindrical volume defined by the lamp coils. In principle this is achieved^{1,13} by heating the Raman tube electrically with a fine coil of

⁸ Conn and Avery, "Infrared Methods," Academic Press, Inc., New York, 1960.

⁹ (a) James, "Selected Topics in Molten Salt Chemistry," Ed. M. Blander, Interscience Publishers, New York, in press, Ch., "Vibrational Spectra of Molten Salts"; (b) Bockris, White, and MacKenzie, "Physico-Chemical Measurements at High Temperatures," Academic Press, Inc., New York, 1959, Ch., W. Bues, "Raman Spectroscopy."

¹⁰ Greenberg and Halgren, *J. Chem. Phys.*, 1960, **33**, 900; *Rev. Sci. Instr.*, 1960, **31**, 444.

¹¹ MacKenzie, McDonald, and Murphy, *Rev. Sci. Instr.*, 1961, **32**, 118.

¹² Wilmshurst and Senderoff, *J. Chem. Phys.*, 1961, **35**, 1078.

¹³ (a) Rolfe and Woodward, *Trans. Faraday Soc.*, 1954, **50**, 1030; (b) Janz, Mikawa, and James, *Appl. Spectroscopy*, 1961, **15**, 47.

resistance wire wound directly on the cell walls and an unsilvered vacuum jacket to serve as a thermal barrier to the Toronto arc. A hot-air stream, countercurrent to natural convection in such an assembly, has been found valuable in smoothing out temperature gradients,^{13b} an important consideration for measurements near the fusion temperature or when samples have rather short liquid-state ranges (e.g., HgCl_2 ; m.p. 280° , b.p. 302°).

A radiofrequency heating assembly for Raman studies up to 1000° has been described.¹⁴ When the molten salts are too reactive to be contained in Pyrex or silica, a radically different Raman cell assembly is necessary. A technique in which the molten salt itself is the optical window has been used successfully¹⁵ in the temperature range $400\text{--}1000^\circ$. The melt is contained in a refractory crucible and the scattered radiation from the melt is observed by focusing the spectrograph on a virtual slit in the body of the melt.

Best results with a mercury arc can be obtained only with colourless water-clear melts. The need for different sources to extend the Raman technique to the visible and near-infrared regions is a problem attracting interest. The yellow and red lines of helium and the yellow doublet of sodium have been found useful in obtaining the Raman spectra of moderately coloured compounds.^{16,17} The experimental advances may be broadly grouped into three classes: the use of (a) high-voltage cold-cathode discharge tubes,¹⁶ (b) microwave radiation for excitation of the Raman lamps,^{17a,18} and (c) resonance lamps excited by radiofrequency radiation.^{17b} A unique feature common to the last two techniques is that annular electrodeless Raman lamps are used. The Raman spectra of such coloured compounds as liquid bromine¹⁹ and iron pentacarbonyl²⁰ have been gained by this technique. Extension of the microwave and radiofrequency excitation techniques to the high-temperature area is in progress.²¹

The advent of lasers has introduced a fourth experimental approach. Their use as possible excitation sources in Raman spectroscopy has recently been discussed.²²

One-component Ionic Melts.—Melts from pure salts may be classified broadly in two groups: those from salts recognised as essentially ionic in the crystalline state (e.g., NaCl) and those from salts having a pronounced covalent component of bonding in the solid (e.g., ZnCl_2 , HgCl_2). The

¹⁴ Young and Westerdahl, "The Structures of Liquid and Vitreous Boric Oxide (B_2O_3)," Aeronautical Research Laboratory Report ARL 135, 1961.

¹⁵ Bues, *Z. Anorg. Chem.*, 1955, **279**, 104.

¹⁶ Stammreich, *Pure Appl. Chem.*, 1962, **4**, 97.

¹⁷ (a) Ham and Walsh, *Spectrochim. Acta*, 1958, **12**, 88; (b) King and Lippincott, *J. Opt. Soc. Amer.*, 1956, **46**, 661.

¹⁸ Miller and Carlson, *Spectrochim. Acta*, 1960, **16**, 6.

¹⁹ Stammreich and Forneris, *J. Chem. Phys.*, 1954, **22**, 1624.

²⁰ Powell, Lippincott, and Steele, *Spectrochim. Acta*, 1961, **17**, 880.

²¹ Janz and his co-workers, unpublished work, 1962.

²² Porto and Wood, Symposium on Molecular Structure and Spectroscopy, the Ohio State University, June, 1961.

former liquids consist predominantly of ions corresponding to the simple constituents of the solid-state lattice; in the latter, the melt may retain "fragments" of the original solid-state species as molecular entities and complex ions, as well as the simpler anionic and cationic components. Studies with salts in the first group have been directed largely to investigations of nearest-neighbour interactions, to contribute to the concepts of liquid-state theory, *e.g.*, the quasicrystalline model. Salts from the second group are more suited to investigations of problems of chemical bonding and co-ordination interactions and of the inorganic chemistry of the molten state. The nitrate ion has been used as a spectroscopic "detector" in ionic melts in the former studies; the halides of the metals of Groups II and III appear best suited for the latter type of investigations.

Nitrates. In studies of both the electronic^{23a} and vibrational^{9a,23b} spectra of alkali nitrates, the nitrate ion may act as a sensitive detector of coulombic interactions and packing effects. In the bonding of the nitrate ion there is a framework formed by overlap of sp^2 hybrid orbitals on the nitrogen atom with p orbitals on the oxygen atoms, and π bonds in which there is a large measure of delocalisation. The model of the nitrate ion suggested for the molten nitrates^{23b} is a planar disc-like species (diam. 4.62Å, thickness 2.2 Å) evolved by rotation of the ion about its C_3 axis. The volume, 24.8 Å³, corresponds exactly to that of a spherical Cl⁻ ion. Spectroscopically, the nitrate ion in its "free" state belongs to the point group D_{3h} and, accordingly, should have one fundamental active in the Raman effect (A_1'), one in the infrared spectrum (A_2''), and two active in both the infrared and Raman spectra (E'), as listed in Table 1. If covalently bonded, as in methyl nitrate or certain nitrate-co-ordination compounds, the nitrate group obtains the C_{2v} group symmetry. The transitions and correlation between these two point groups are summarised in Table 1. A partial transition from point group D_{3h} to point group C_{2v} symmetry may be related in part to the bonding interactions in the molten salts, *i.e.*, a transition from cationic-anionic (coulombic) bonding to a covalently linked nitrate group.

The vibrational spectra of nitrate ions have been extensively investigated in aqueous solution²⁴ and in crystals.²⁵ The past decade has seen the

²³ (a) G. P. Smith, "Selected Topics in Molten Salt Chemistry," Ed. M. Blander, Interscience Publishers, New York, in press, Ch., Electronic Absorption Properties of Molten Salts; (b) Janz and James, *Electrochim. Acta*, 1962, 7, 427.

²⁴ (a) Couture, *Compt. rend.*, 1945, 220, 646; (b) Young, Maranville, and Smith, "Structure of Electrolytic Solutions," Ed. Hamer, John Wiley and Sons, New York, 1959, p. 35.

²⁵ (a) Schroeder, Weir, and Lippincott, *J. Chem. Phys.*, 1962, 36, 2803; (b) Hexter, *Spectrochim. Acta*, 1958, 10, 291; (c) Buijs and Schutte, *ibid.*, 1962, 18, 307; (d) Vratny, *Appl. Spectroscopy*, 1959, 13, 59; (e) Gatehouse, Livingstone, and Nyholm, *J. Chem. Soc.*, 1957, 4222; (f) Ferraro, *J. Mol. Spectroscopy*, 1960, 4, 99; (g) Keller and Halford, *J. Chem. Phys.*, 1949, 17, 26; (h) Couture, *Ann. Phys.*, 1947, 2, 94; (i) Theimer, *Monatsh.*, 1950, 81, 424; (j) Mathieu and Lounsbury, *Discuss. Faraday Soc.*, 1950, 9, 196; (k) Doucet and Vallier, *Compt. rend.*, 1962, 255, 2935.

extension of such studies to molten nitrates.²⁶ Table 2 lists the data for the melts of the pure alkali-metal nitrates and the silver and thallos salts. The bar graph representation in Fig. 1 shows the spectral changes as

TABLE 2. *Vibrational spectra of molten nitrates.**

	ν_1^\dagger	ν_2	ν_3	ν_4	"Lattice" mode	Ref.
LiNO ₃	1067	821	1375, 1460	726	343	26
NaNO ₃	1053	827	1412	722	238	26
KNO ₃	1048	829	1391	718	<220	26
RbNO ₃	1046	—	1372	713	<220	26
CsNO ₃	1043	—	1356	708	—	26
AgNO ₃	1043	800	1310, 1395	727	—	26
TlNO ₃	1036	813	1328, 1383	708	—	26

* D_{3h} point group symmetry. † All values in cm^{-1} .

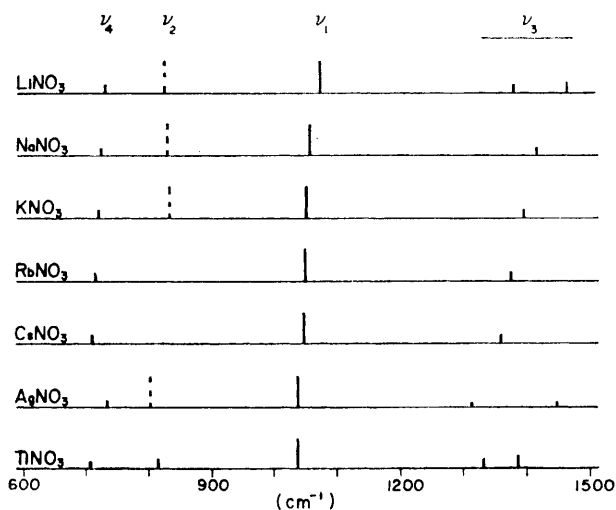


FIG. 1. *Vibrational frequencies of the nitrate ion in molten nitrates. The relative intensities are those noted in the Raman spectra; with the exception of TlNO₃, the frequency ν_2 is observed only in the infrared spectra.*

the cationic species is varied in these molten nitrates. There are three salient features: (i) loss of degeneracy of the E' modes in certain nitrates; (ii) the observation of a low frequency, *i.e.*, a band in the range 300—

²⁶ (a) Bues, *Z. phys. Chem. (Frankfurt)*, 1957, **10**, 1; Grossman, *Z. Physik*, 1932, **77**, 616; (b) Wilmshurst and Senderoff, *J. Chem. Phys.*, 1961, **35**, 1078; (c) Greenberg and Hallgren, *ibid.*, 1960, **33**, 900; (d) Janz and James, *ibid.*, 1961, **35**, 739; (e) Wait, Kozłowski, and Janz, in press.

200 cm^{-1} ; and (iii) correlation of the shift of the symmetrical stretching frequency with change in the cationic species in the molten nitrates.

For the alkali-metal nitrates, the degeneracy of the ν_3 fundamental mode is not lost except for lithium nitrate (Table 2). In this case, both infrared and Raman spectral studies confirm the presence of two bands, one centred at about 1375cm^{-1} and the other at about 1455cm^{-1} . Molten thallos nitrate^{26e} has bands at 1328 and 1383cm^{-1} , whereas molten silver nitrate has bands at 1310 and 1395cm^{-1} . Many solid nitrates exhibit splitting of this fundamental.²⁵

Absorption bands have been observed in the infrared spectrum of molten lithium, sodium, potassium, and silver nitrates at 343 , 238 , <220 , and $<220\text{cm}^{-1}$, respectively.^{26b} These bands have been assigned to "lattice-like" vibrations in the melt, presumably not unlike the lattice vibrations of a crystalline solid. The existence of such modes does not necessarily imply long-range order in the molten salt, but is attributed to the pronounced short-range, strong cation-anion interactions between the nitrate ion and its nearest neighbours. Schroeder, Weir, and Lippincott^{25a} have shown that a librational mode in solid nitrates might be expected in the vicinity of $20\text{--}40\text{cm}^{-1}$. Librational modes are normally weak and occur in a portion of the spectrum difficult to observe by Raman and conventional infrared techniques; application of the methods of far-infrared spectroscopy are needed to advance studies in this region.

The symmetrical stretching frequency, ν_1 , shows a definite correlation with the properties of the cation.²⁶ A systematic variation in ν_1 is observed for the series of molten nitrates: LiNO_3 (1067cm^{-1}); NaNO_3 (1053cm^{-1}); KNO_3 (1048cm^{-1}); RbNO_3 (1046cm^{-1}); and CsNO_3 (1043cm^{-1}). Various correlations have been advanced. Fig. 2 shows the regular variation of ν_1 with the cationic polarising power, P . The latter has been defined^{26d} as the product of the ionic potential²⁷ and the shielding efficiency²⁸ for the cationic species, *i.e.*, $P = (z/r)(5z^{1.27}/r^{1/2}I)$, where I is the ionisation potential, and r and z are the ionic radius and charge, respectively. For those cations containing d or f electrons, the polarising power may be expected to show a more general correlation than the simple ionic potential (z/r), since the second term corrects for the poor shielding of nuclear charge by these electrons.

Normal co-ordinate vibrational analyses for the nitrate ion have been carried out by several investigators.^{26a, d, 25k, 29} All have assumed "free" nitrate ions of symmetry D_{3h} , thereby predicting a single frequency for each of the fundamentals. A need exists for a vibrational analysis which includes the effect of nearest neighbours on the force constants and frequencies.

The results of the studies have been related to possible environmental

²⁷ Cartledge, *J. Amer. Chem. Soc.*, 1928, **50**, 2855.

²⁸ Ahrens, *Nature*, 1954, **174**, 644.

²⁹ Janz and Mikawa, *J. Mol. Spectroscopy*, 1960, **5**, 92.

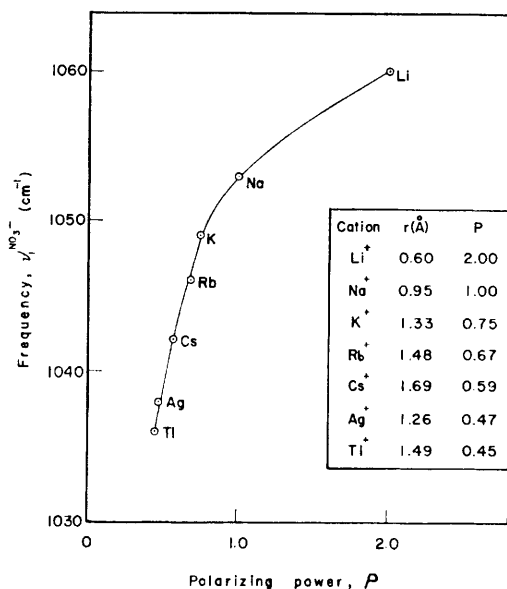


FIG. 2. Variation of ν_1 , with polarising power (P) of cations in fused salts. The relation between the symmetrical stretching frequency, ν_1 , and the polarising power of the cation is shown for LiNO_3 , NaNO_3 , KNO_3 , RbNO_3 , CsNO_3 , AgNO_3 , and TlNO_3 . The salts are represented by the chemical symbol for the cationic species.

factors, such as short-range order in the molten state and the existence of strong interionic forces. Support for this viewpoint is gained from solid-state spectral studies. For example, with solid sodium nitrate, no splitting of ν_3 is observed,²⁶ whereas in solid potassium nitrate, the degeneracy is removed.^{24,26a} This is understood in the light of the difference in crystal symmetries. Sodium nitrate belongs to the rhombohedral space group D_{3d}^6 (calcite type) while potassium nitrate is in the orthorhombic space group V_h^{16} (aragonite). The nitrate ion in the former lies on a three-fold symmetry axis. Accordingly, the spectrum should not lose its degeneracy. In the aragonite structure of potassium nitrate the nitrate ion is no longer on a three-fold crystal axis; it is subjected to an unsymmetrical environment and loss of the degeneracy for ν_3 of the isolated ion is a consequence. Extension of this concept to molten nitrates follows. Three "contact" sites seem most probable: (i) along the N-O bond; (ii) bisecting the O-N-O angle; or (iii) above the plane of the ion on the three-fold axis. These are shown in Fig. 3, as sites B, C, and A, respectively. Both of the first two positions give rise to an unsymmetrical field which might remove the degeneracy in the nitrate ion. Support for this viewpoint has recently been advanced from analyses of X-ray and neutron diffraction data and from physicochemical properties of molten nitrates³⁰ and molten carbonates.³¹

³⁰ Furukawa, *Discuss. Faraday Soc.*, 1961, **32**, 53.

³¹ Zarzycki, *Discuss. Faraday Soc.*, 1961, **32**, 212.

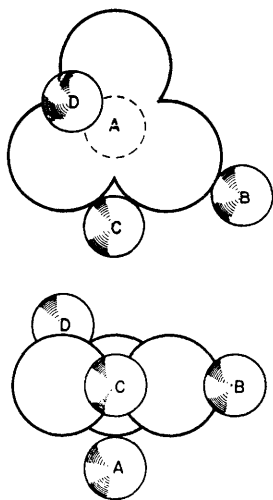


FIG. 3. Cation sites about the NO_3^- ion.

For molten nitrates near the melting temperatures, the radial distribution analyses of the diffraction data confirm that, for example, in sodium nitrate the most probable positions of Na^+ ions around NO_3^- ions are at position C (Fig. 3) and one intermediate to positions A and C, *e.g.*, site D. In molten carbonates it has been shown similarly that in passing from lithium to potassium salts the cations assume average positions about these planar disc-like anions which are increasingly close to the corner sites, *i.e.*, position B (Fig. 3). An alternative suggestion would be to assume a symmetry change in the nitrate ion from point group D_{3h} to C_{3v} or C_{2v} . The explanation why this occurs with some systems and not others is not obvious. Retention of D_{3h} symmetry by a nitrate ion in an unsymmetrical environment is more widely accepted.

Hydroxides, chlorates, perchlorates, and bisulphates. Molten alkali hydroxides,³² chlorates,³³ perchlorates,³³ and bisulphates³⁴ have been studied. The data are given in Table 3. In the infrared studies, the hydroxides, chlorates, and perchlorates all show a low-lying vibrational frequency similar to that observed with nitrate ion melts. It is significant that the bands at 440, 265, and 230 cm^{-1} , in lithium, sodium, and potassium hydroxide, respectively, are the most intense absorptions in the hydroxide spectra. The O-H stretching frequency occurs at about 3500 cm^{-1} in these melts, but is weak and also is split by 350–400 cm^{-1} . This splitting has been variously interpreted as *P* and *R* branches of a freely rotating O-H⁻ ion or the appearance of a second vibration due to hydrogen bonding.

³² Wilmshurst, *J. Chem. Phys.*, 1961, **35**, 1800.

³³ Wilmshurst, *J. Chem. Phys.*, 1962, **36**, 9.

³⁴ Walrafen, Irish, and Young, *J. Chem. Phys.*, 1962, **37**, 662.

TABLE 3. *Vibrational spectra of molten hydroxides, chlorates, and perchlorate.*

<i>Hydroxides</i>						
	ν_1^*	"Lattice" modes			Ref.	
LiOH	(3652)†	440			32	
NaOH	(3295)†	265			32	
KOH	(3300)†	233			32	

<i>Chlorates</i>						
	ν_1	ν_2	ν_3	ν_4	"Lattice" mode	Ref.
LiClO ₃	938	620	1018, 977	478	338	33
NaClO ₃	932	611	988	482	200	33
KClO ₃	931	603	981	489	200	33
AgClO ₃	895	595	969, 969	477	200	33

<i>Perchlorate</i>						
	ν_1	ν_2	ν_3	ν_4	"Lattice" mode	Ref.
LiClO ₄	948	470	1139	627	315 260	33

* All frequencies in cm^{-1} .

† Approx. band centre.

The chlorate ion, in aqueous solution, has been studied by Shen and his co-workers³⁵ and, in the solid, by Rocchiccioli.³⁶ The assignments were made on the basis of C_{3v} symmetry, *i.e.*, all three oxygen atoms being equivalent. The investigation of molten chlorates³³ seems to confirm that C_{3v} symmetry is retained in the melt, if allowance is made for splitting of the degenerate vibrations due to environmental effects.

The totally symmetric vibrations (ν_1, ν_2) show a decrease in the series lithium, potassium, silver, the frequencies being (938, 620), (931, 603), and (895, 595) in these cases, respectively. The higher of the two doubly degenerate fundamentals, ν_3 , shows a similar decrease; the lower fundamental, ν_4 , shows a definite increase, *e.g.*, Li^+ (478), K^+ (489), and in the molten silver salt loses its degeneracy (477, 440).

In molten lithium perchlorate, the tetrahedral (T_d point group) symmetry of the ClO_4^- ion is apparently retained. The spectrum consists of two strong bands at 1139 and 627cm^{-1} and two weaker bands at 948 and 470cm^{-1} . The last two are probably the infrared-inactive fundamentals; the appearance of these forbidden frequencies as weak infrared lines is undoubtedly due to condensed-state environmental factors.

Raman spectral studies of potassium bisulphate have been reported by Walrafen, Irish, and Young³⁴ for the temperature range 300—700°. The

³⁵ Shen, Yao, and Wu, *Phys. Rev.*, 1937, **51**, 235.

³⁶ Rocchiccioli, *Compt. rend.*, 1956, **242**, 2922.

spectra indicate that reactions occur to form the $S_2O_7^{2-}$ and SO_4^{2-} ions. Assignments of the vibrations of HSO_4^- , $S_2O_7^{2-}$, and SO_4^{2-} are made and correlated with results in aqueous solution. It appears that the $S_2O_7^{2-}$ and HSO_4^- ions possess C_2 and C_s point group symmetries, respectively.

Molten Halides. The halides of metals of Group II B are predominantly covalent in the solid state,³⁷ the vapour state,³⁸ and, as has been recently shown, also in the liquid state.^{39,40} The halides of zinc, cadmium, and mercury are symmetrical linear molecules of point group $D_{\infty h}$. In the solid layer-type structure for cadmium chloride (illustrated in Fig.4), the triatomic linear species can be recognised, and the unsymmetrical

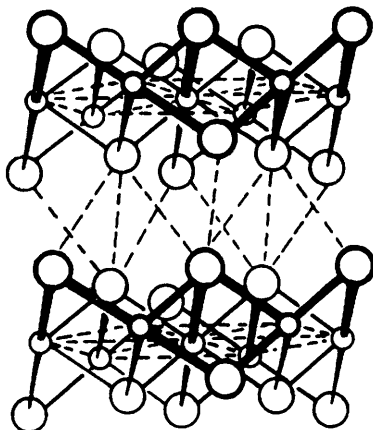


FIG. 4. The layer type structure in solid $CdCl_2$.

cationic environment is evident. Selection rules for "free" molecules of this type are given in Table 1. Spectral data for these compounds in the molten state are summarised in Table 4.

TABLE 4. *Vibrational spectra of molten halides.*

	ν_1	ν_2	ν_3	Ref.
$ZnCl_2$	233			48b
$ZnBr_2$	155			48b
$CdCl_2$	212			48b
$HgCl_2$	313	376	100	40
$HgBr_2$	195	271	90	40
$HgBrCl^*$	236 (ν_1)	335 (ν_3)	111 (ν_2)	40

* $C_{\infty v}$ Symmetry. ν_1, ν_3 , are stretches; ν_2 is a bending mode.

³⁷ Bues, *Z. anorg. Chem.*, 1955, **279**, 104.

³⁸ (a) Klemperer and Lindemann, *J. Chem. Phys.*, 1956, **25**, 397; (b) Buchler, Klemperer, and Emslie, *ibid.*, 1962, **36**, 2499.

³⁹ Janz and McIntyre, *Ann. N.Y. Acad. Sci.*, 1960, **79**, 790; *J. Electrochem. Soc.*, 1962, **109**, 842.

⁴⁰ Janz and James, *J. Chem. phys.*, 1963, **38**, 902.

The vibrational spectra of molten HgCl_2 and HgBr_2 ^{40,41} are understood if the melts are considered to consist of linear triatomic species. The finite electrical conductance of these melts has been attributed to the dissociation of the molecular solvent species with the formation of species MX^+ , MX_3^- , MX_4^{2-} in amounts less than 0.01%. In this concentration range, the ionic species are below the level necessary for spectroscopic detection. The symmetric stretching frequency, ν_1 , is broad in the Raman spectrum of the melts (e.g., HgCl_2 ; ν_1 , 313 cm^{-1} , line width $\sim 80\text{cm}^{-1}$). The band broadening has been attributed to the heteropolar nature of the M–X bond and the possibility of perturbation of the halide orbitals by molecular rotational interactions.⁴⁰ The appearance of the Raman forbidden frequency, ν_2 , is additional support for this viewpoint.

The nature of the bonding processes in Group II halides can be discussed in terms of the solvent shift of the totally symmetrical stretching vibration⁴² and the magnitude of the angle bending force constant in gaseous halides.³⁸ The degree of ionicity of the Hg–Cl bond has been estimated as 23% from studies of “solvent-shift” spectra.⁴³ It is clear from such observations that the bonding orbital of the mercury should not be regarded as a purely covalent *sp* hybrid, but rather as formed by the interaction of a repulsive lower state with an attractive *sp* upper state. It is apparent from the precise values gained for the gaseous state³⁸ and the solid state⁴⁰ of the interaction force constant (HgCl_2 , $k_{12} = 0.037$ dyne cm^{-1} , gas, and -0.06 dyne cm^{-1} , solid) and from the estimated value for the molten state (HgCl_2 , $k_{12} = -0.07$ dyne cm^{-1}),⁴⁰ that the spectra of these salts in the molten state are evidence for interparticulate force-fields due to the chemical bonding processes in the mercuric halides. High-temperature infrared spectral studies for molten mercuric halides remain an outstanding need.

The Raman spectral studies of molten gallium dichloride and dibromide by Woodward and his co-workers⁴⁴ provide a clear illustration of the information to be gained on the structural nature of the species present in inorganic melts. Possible species suggested were $\text{X}_2\text{Ga}-\text{GaX}_2$, GaX_4^- , and related ionic entities, such as $(\text{X}_2\text{Ga}-\text{GaX})^+$. The results, summarised in Table 5 together with the data for the species GaX_4^- in aqueous solution, leave no doubt as to the nature of the ionic species in these molten halides. The stability of GaCl_4^- was further confirmed in that, even after long exposure, no Raman activity characteristic of gallium trichloride was observed in molten gallium dichloride. Some evidence for

⁴¹ (a) Braune and Engelbrecht, *Z. Phys. Chem.*, 1931, **B10**, 1; 1932, **B19**, 303; (b) K. V. K. Rao, *Proc. Indian Acad. Sci.*, 1941, **A14**, 521; (c) Salstrom and Harris, *J. Chem. Phys.*, 1935, **3**, 241.

⁴² Allen and Warhurst, *Trans. Faraday Soc.*, 1958, **54**, 1786.

⁴³ Rolfe, Sheppard, and Woodward, *Trans. Faraday Soc.*, 1954, **50**, 1275.

⁴⁴ (a) Woodward, Garton, and Roberts, *J. Chem. Soc.*, 1956, 3273; (b) Woodward, Greenwood, Hall, and Worrall, *J. Chem. Soc.*, 1958, 1505; (c) Nixon and Plane, *J. Amer. Chem. Soc.*, 1962, **84**, 4445.

TABLE 5. *Raman spectrum of gallium dichloride and dibromide.**

Assignment (T_d)	Aqueous solution		Molten	
	GaCl_4^-	GaBr_4^-	"Dichloride"	"Dibromide"
ν_2 (E)	114	71	115 s, dp, sh.†	79 s, dp, sh
ν_4 (F_2)	148	102	153 w, dp, dif	107 s, dp, sh
ν_1 (A_1)	346	210	356 vs, p, sh	209 vs, p, sh
ν_3 (F_2)	386	278	380 vw, dp, dif	288 w, dp, dif

* Ref. 44. All values in cm^{-1} .

† s = strong, dp = depolarised, p = polarised, sh = sharp, dif = diffuse, w = weak, v = very.

nearest-neighbour ionic interactions in these melts was seen, in that the triply degenerate fundamentals for GaX_4^- , *i.e.*, ν_3 , were weaker and more diffuse in the melts relative to the corresponding species in aqueous solutions.

Two-component Molten Systems.—Spectroscopic investigations of molten two-component systems are fewer than for pure molten salts. These studies may be broadly divided into three types: (i) melts of two or more compounds, each of which is predominately ionic; (ii) melts formed from one ionic compound as a solute in a covalent inorganic solvent; and (iii) melts formed from two or more covalent compounds. There follows a survey of the systems most recently examined, with specific reference to chemical interactions and the formation of new species.

In the first class of melts, the predominant spectroscopic interest has been the investigation of changes in vibrational spectra with composition. Bues⁴⁵ examined the spectrum of an equimolar melt of silver nitrate and potassium nitrate. The vibrational frequencies were intermediate between those for pure silver nitrate and pure potassium nitrate, and the spectrum retained the same general features, *i.e.*, splitting of degeneracy and intensity ratios, as for pure silver nitrate. Mixtures of sodium nitrate and lithium nitrate in the concentration range 5% to 60% of lithium nitrate have been studied.⁴⁶ A linear variation in ν_1 , the symmetrical stretching frequency, was noted as the composition was changed. For potassium nitrate–calcium nitrate mixtures, glassy systems with complex spectra are reported.⁴⁷ The removal of degeneracy of both ν_3 and ν_4 in this mixture has also been observed.⁴⁶ A summary of the data is given in Table 6.

The melts formed from mixtures of ionic and covalent halides have received more attention.⁴⁸ A striking feature is the appearance of new bands as the ionic halide is added to the covalent melt. In the case of molten mercuric chloride–potassium (or ammonium) chloride systems, it

⁴⁵ Bues, *Z. phys. Chem. (Frankfurt)*, 1957, **10**, 1.

⁴⁶ Janz and James, *J. Chem. Phys.*, 1961, **35**, 739.

⁴⁷ Borgen, Grjotheim, and Urnes, *Glastechn. Ber.*, 1960, **33**, 52.

⁴⁸ (a) Janz and James, *J. Chem. Phys.*, 1961, **38**, 905; (b) Bues, *Z. anorg. Chem.*, 1955, **279**, 104; (c) Bredig and Van Artsdalen, *J. Chem. Phys.*, 1956, **24**, 478; (d) Gerding, Haring, and Renes, *Rec. Trav. chim.*, 1953, **72**, 78; (e) Gerding and Smit, *Z. phys. Chem.*, 1941, **B50**, 171; (f) Janz and Kozlowski, *J. Chem. Phys.*, in press.

has been shown^{48a} that the species HgCl_3^- and HgCl_4^{2-} are formed. Studies on mercuric halide-alkali halide in aqueous and organic solvent systems confirm the formation of these complex ions.⁴⁹ The variation of the symmetrical stretching frequency, ν_1 , for each of three species, HgCl_2 , HgCl_3^- , and HgCl_4^{2-} , in the molten salt mixtures is illustrated in Fig. 5

TABLE 6. *Vibrational spectra of molten nitrate mixtures.*

System	ν_1	ν_2	ν_3	ν_4	$2\nu_2$	Ref.
$\text{AgNO}_3 : \text{KNO}_3 (1 : 1)$	1043	817	1312, 1425	720	1633	45
$\text{NaNO}_3 : 5\% \text{LiNO}_3$	1054	—	1308–1472	723	1665	46
$\text{NaNO}_3 : 10\% \text{LiNO}_3$	1057	—	1319–1484	724	1656	46
$\text{NaNO}_3 : 30\% \text{LiNO}_3$	1061	—	1319–1493	723	1650	46
$\text{NaNO}_3 : 60\% \text{LiNO}_3$	1061	—	1305–1398 1398–1495	724	1646	46
$\text{NaNO}_3 : 50\% \text{KNO}_3$	1050	—	1396–1492	718	1655	46
$\text{Ca}(\text{NO}_3)_2 : 60\% \text{KNO}_3$	1049	—	1300–1361 1407–1500	713 733	1646	46

as a function of the excess of chloride ion being added as an additional ligand. The ν_1 intensity being taken as a measure of concentration, it is apparent that the molecular molten salt (*i.e.*, pure mercuric chloride) is transformed almost completely into an ionic melt in the presence of about 70% of added halide.

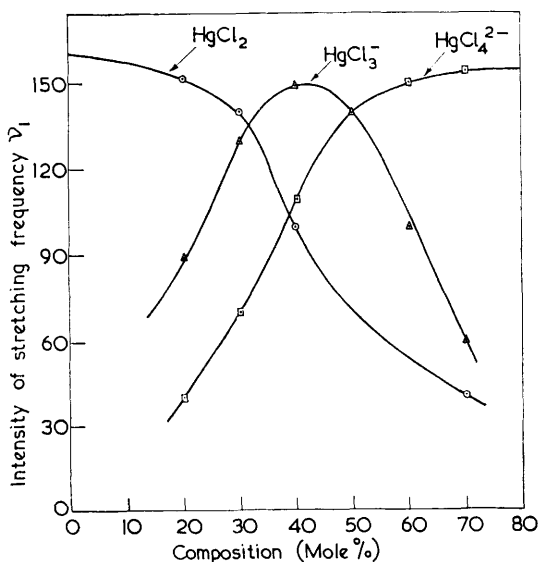


FIG. 5. *Variation of intensity of ν_1 with composition (excess of Cl^- as added ligand)*
 ○ HgCl_2 ◇ HgCl_3^- ■ HgCl_4^{2-} .

⁴⁹ (a) Sillen, *Acta. Chem. Scand.*, 1949, 3, 549; (b) Aggarwal, *Z. phys. Chem. (Leipzig)*, 1957, 207, 1; *Z. anorg. Chem.*, 1957, 291, 134; (c) Griffiths and Symons, *Trans. Faraday Soc.*, 1960, 56, 1752.

Normal co-ordinate vibrational analyses for HgCl_2 ,⁴⁰ HgCl_3^- ,^{48a} and HgCl_4^{2-} ^{48a} have been carried out by using the Urey-Bradley potential field. The symmetrical stretching force constant, k_1 , decreases in the series HgCl_2 (2.11), HgCl_3^- (1.27), and HgCl_4^{2-} (0.82). This decrease undoubtedly reflects the transition of the Hg-Cl bond to an increasingly mixed covalent-ionic type as the complex ions are formed. If the ionicity of the Hg-Cl bond is taken as about 23% in pure molten mercuric chloride, the ratio of the values of k_1 predicts the ionicity of this bonding in HgCl_3^- and HgCl_4^{2-} to be about 50% and 70%, respectively.

Relative to this work, the compositions of mercuric chloride-thallos nitrate mixtures have recently been investigated^{48f} by Raman spectroscopy in the complete range of concentrations from one component to the other. Cryoscopic measurements on thallos nitrate with mercuric chloride and bromide as solute species support the viewpoint that the mercuric halide solute remains molecular in molten thallos nitrate.⁵⁰ Raman spectral data^{48f} show clearly that the symmetrical stretching frequencies for the nitrate ion (1036 cm.^{-1}) of pure thallos nitrate and for molten mercuric chloride (313 cm.^{-1}) are present as the strongest Raman lines in mixtures of these two salts over the entire composition range; while species such as $\text{HgCl}_2(\text{NO}_3)^-$ and $\text{HgCl}_2(\text{NO}_3)_2^{2-}$ are not ruled out, it is suggested that the ion-molecule interactions are most likely limited to solvation-type forces in the thallos nitrate-mercuric halide molten-salt mixtures.

Studies of the last class, mixtures of two covalent compounds, seem virtually non-existent. A report of the spectrum of HgBrCl ⁴⁸ indicates that this compound tends to disproportionate in the molten state into mercuric chloride and mercuric bromide.

Molten complex salts of cadmium(I) with aluminium chloride have been investigated by Raman spectroscopy.⁵¹ The presence of Cd_2^{2+} was demonstrated by a strong band at 183 cm.^{-1} . The presence of complex ions in molten mixtures of cadmium(II) halide-alkali-metal halide has been confirmed by Raman studies⁵² and various physicochemical and electrochemical studies.⁵³ The stoichiometry and stereochemistry of these complex ions are current problems. The ions, CdCl_3^- , both as planar and pyramidal species, and CdCl_4^{2-} , of tetrahedral symmetry, have been suggested as the predominant species in 1:1 molar cadmium chloride-potassium chloride molten mixtures. The thermodynamics of these molten-salt mixtures have been qualitatively explained⁵⁴ on a model in which CdCl_4^{2-} is the important complex ion, and species such

⁵⁰ Rolla, Franzosini, and Riccardi, *Discuss. Faraday Soc.*, 1961, **32**, 84.

⁵¹ Corbett, *Inorg. Chem.*, 1962, **1**, 700.

⁵² (a) Bues, *Z. anorg. Chem.*, 1955, **279**, 104; (b) Bredig and Van Artsdalen, *J. Chem. Phys.*, 1956, **24**, 478; (c) Tanaka, Balasubramanyam, and Bockris, *Electrochim. Acta*, in press.

⁵³ (a) Bredig, *Electrochim. Acta*, 1961, **5**, 299; (b) Boardman, Doran, and Heymann, *J. Phys. Chem.*, 1949, **53**, 375; (c) Barton and Bloom, *Trans. Faraday Soc.*, 1959, **55**, 1792; (d) Bockris and Angell, *Electrochim. Acta*, 1959, **1**, 308.

⁵⁴ Bredig, *J. Chem. Phys.*, 1962, **37**, 451.

as CdCl_3^- and CdCl_6^{4-} are present in only minor concentration. Re-investigation of the Raman spectra of molten mixtures of cadmium chloride-potassium chloride (33-66 mole % of the latter) has shown^{52c} that the vibrational assignment, intensities, and polarisation data are in accord with a system where the dominant complex ion in this concentration range is CdCl_3^- , and that the symmetry of this species is pyramidal, rather than planar as previously suggested.^{52a}

Summary.—The vibrational spectra of molten salts are seen to yield two types of information. In the first instance, it has been shown that the ionic and molecular species, known to exist in aqueous solutions and solid phases, retain their identity in the molten state. More interesting and informative, on the other hand, are those effects which are definitely attributable to environmental perturbations and molecular or ionic interactions. These effects, in ionic melts, noted as shifts in vibrational frequencies, splitting of degenerate fundamentals, and the appearance of "forbidden" fundamentals, can be understood in terms of short-range ordering in the melt and strong cation-anion forces. Chemical co-ordination-type interactions in mixtures of ionic and covalent salts have been confirmed* in the molten state. High-temperature spectroscopy will assume increasing importance with the advance of the inorganic chemistry of the molten state.

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* See also ref. 23a, Gruen and his co-workers, *J. Phys. Chem.*, 1959, **63**, 393; *J. Inorg. Nuclear Chem.*, 1957, **4**, 74; *Nature*, 1956, **178**, 1181; and Ubbelohde, *Proc. Chem. Soc.*, 1960, 332, for electronic absorption spectra and complex ions in fused salts.