Structure of Molten Nitrates: Temperature Variation of Raman Spectrum of Sodium Nitrate

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ALTHOUGH the vibrational spectra of alkali-metal nitrates in the crystalline and molten phases have been much investigated, the published data are not consistent enough to be accepted without reservation. A re-investigation of single crystalline samples at room temperature has been completed[1] and we report the effect of change in temperature on some of the bands of sodium nitrate in both single crystal and molten state. It had been reported that the internal external modes did not change in energy with increasing temperature but had an abrupt change at the melting point.[2] The intensity of the internal and external modes in the crystal state were reported to decrease with increasing temperature[3] in contrast to the predictions of the theory of Placzek.[4]

The methods of crystal growing and examination of spectra have been reported.[1,5] The cell used collected light from a fixed volume of sample and the illumination was from an uncondensed laser beam 2 mm. in diameter. This arrangement allowed the relative intensities to be estimated from the band profiles photometrically recorded. The effect of density change with temperature has been corrected by multiplying the measured intensity by the factor $\rho 25/\rho t$ where ρ represents the density.[6] Spectra were obtained with a slit width of 5 cm.$^{-1}$ and as the smallest band halfwidth recorded was 17 cm.$^{-1}$ no appreciable error from beam divergence should be present. The intensities, which are referred to the intensity of the ν_1 band (A_{1g}) of the crystal at 25° taken as 100, were reproducible to $\pm 2\%$.

The experimental results are collected in the Table from which several trends are evident. There are two features of the spectrum in the melt at 310° which warrant special mention. The low-energy band at 170 cm.$^{-1}$ which has an obvious correspondence to one of the external frequencies in the crystal has not previously been observed in the melt. Also the appearance of a well-resolved low-frequency shoulder on the symmetrical stretching frequency is not expected from the symmetry of the crystal or the expected symmetry of the melt. The weaker of the two bands (1054 cm.$^{-1}$) remained evident as a shoulder on the low-energy side of the band when the melt was supercooled below the freezing point.

*Variation of Raman spectra with temperature**

T	25°	100	150	200	250	300	310	320	360	400
Mode										
L_1 (E_g)	100	94	91	82						
B I	25	40	45	50						
L_2 (E_g)	191	186	183	182	181	178	170			
B I	45 100	45	65 102	75	88	100 105	~100 ~90			
ν_1 (A_{1g})	1069	1068	1068	1067	1066	1064·5	1058 1054‡	1054	1053	1052
B I	17 100	19 101	21 102	21 103	23 104	25 105	25 105	26 124	28 139	30 153

*Frequencies are in cm.$^{-1}$, halfwidths, B in cm.$^{-1}$ and intensities, I, relative to ν_1 at 25°.
‡ Halfwidth and intensity are for the composite band.

For the three frequencies studied parallel trends in behaviour were noted and the variations are considered to have a common origin. The A_{1g} mode has been found to be sensitive to the state of aggregation and the nature of the counter ion,[2,7] and the variation has been correlated with an environmental polarization of the anion. In the crystal the packing does not change below 275°, only the ionic separation alters due to change in density. The change in polarization is reflected in the molar volume and when this is plotted against the frequency a straight-line relationship is obtained. This straight line also passes through the higher-energy melt frequency at 310°. A similar straight line, parallel to the first, may be drawn through the frequencies obtained in the melt, and this line passed through the lower of the two frequencies at 310°.

When the band profiles are examined in the crystalline sample a marked broadening with increasing temperature is noted particularly for the lattice modes. However, when the band areas are examined there is little apparent change. Due to the great increase in breadth of the lattice lines the band areas have considerable uncertainty. The increase in intensity which may be calculated from Placzek's polarizability theory would amount to 8% when the crystal is heated from 25° to 300° and this increase is similar to that observed. In the study by Venkateswarlu,[3] only peak heights were examined and in view of the change in profile it is evident that the assumption that intensity was proportional to peak height was unwarranted. The change in intensity noted in the melt is more dramatic than noted for the crystal. It has been assumed that there is no change in intensity on melting but, due to a change in effective sample volume when the crystal melts, it has not been possible to test this assumption. As the temperature of the melt is raised the intensity increase is much more rapid than expected from polarizability theory. It would appear that this increase reflects an increase in $\partial\alpha/\partial q$ rather than an increase in the number of vibrators in an excited state.

The spectral changes noted may be interpreted in terms of the structure of the crystalline and molten states. The changes in frequency and intensity in the melt are consistent with a constant packing arrangement which expands on heating and thus simultaneously reduces the anion–cation interaction and increases the population in the vibrationally-excited level. This behaviour is carried through the melting point and shows that just above the melting point there are crystallites which have a packing resembling that of the crystal. The observation of the lattice mode similar to the crystalline state reinforces this proposition. The simultaneous observation at 310° of the frequency characteristic of the crystal 1058 cm.$^{-1}$ and also a frequency which seems characteristic of the melt suggests strongly that the quasicrystalline order in the melt is different from that of the crystal. This has been proposed on the basis of i.r. measurements.[8] and the rapid increase in intensity of νA_{1g} in the melt with increasing temperature may reflect this change.

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[1] D. W. James and W. H. Leong, *J. Chem. Phys.*, to be published.

[2] *E.g.* G. J. Janz and D. W. James, *J. Chem. Phys.*, 1961, **35**, 739, and references therein.

[3] K. Venkateswarlu, *Proc. Indian Acad. Sci.*, 1941, **15***A*, 529; 1942, **16***A*, 45.

[4] C. Placzek, Handbuch der Radiologie 1934, **VI**, p. 205.

[5] D. W. James, W. H. Leong, and J. Buur, *Perkin-Elmer News*, to be published.

[6] "International Critical Tables" (crystal), McGraw Hill, New York, 1933; H. Bloom, I. W. Knaggs, I. J. Molloy, and D. Welch, *Trans. Faraday Soc.*, 1953, **49**, 1458 (melt).

[7] J. P. Mathieu and M. Lounsberry, *Discuss. Farad. Soc.*, 1950, **9**, 196; J. K. Ferraro, *J. Mol. Spectroscopy*, 1960, **4**, 99.

[8] K. Williamson, K. Li, and J. P. Devlin, personal communication.