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## Raman study of NaClO<sub>3</sub> as a function of temperature into the melt and the novel high temperature phase

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Received 28 March 1989, in final form 19 October 1989

**Abstract.** Raman spectra have been measured for oriented single crystals of NaClO<sub>3</sub> II from 77 K to the melting temperature, for the molten salt and the high temperature phase, NaClO<sub>3</sub> I. The results for NaClO<sub>3</sub> II were in excellent agreement with unit-cell group analysis. Apparent anomalies associated with the presence of weak bands due to naturally abundant <sup>37</sup>Cl and <sup>18</sup>O substituted ions have been accounted for on the basis of intermolecular coupling models. The unusual high temperature, ambient pressure phase transition for NaClO<sub>3</sub> has been characterised by spectroscopic and thermal methods. The novel feature about the high temperature phase is the fact that it may only be reached by cooling the melt and it transforms back to the room temperature phase at about 510 K as the sample is cooled. The longitudinal optical mode at about 1030 cm<sup>-1</sup> which was characteristic of the acentric room temperature phase (P2<sub>1</sub>3, T<sup>4</sup>) was conspicuously absent in the Raman spectrum of the high temperature phase. The Raman spectrum of the high temperature phase indicated that the crystal has a centric structure but the similarity of many bands with the spectrum of the room temperature phase suggested that the phase transition involved only small changes in atomic positions. The structure remained ordered but there was evidence of considerable band broadening due to increased thermal motion. The Raman results are consistent with the diffraction studies of Meyer and Gasperin who reported a monoclinic structure similar to room temperature KClO<sub>3</sub>, space group P2<sub>1</sub>/a. Measurements of the heats of fusion and transition by differential scanning calorimetry gave values of  $\Delta H_f = 21.7 \text{ kJ mol}^{-1}$ ,  $\Delta S_f = 40.6 \text{ J mol}^{-1} \text{ K}^{-1}$ ,  $\Delta H_t = 4.1 \text{ kJ mol}^{-1}$ ,  $\Delta S_t = 8.2 \text{ J mol}^{-1} \text{ K}^{-1}$ . The relatively small values of the heat and entropy of transition compared to those of fusion also indicated that the high temperature phase was not disordered.

### 1. Introduction

Sodium chlorate represents a class of crystals with interesting properties because it has a non-centric crystal structure [1, 2]. These non-centric crystals may exhibit piezoelectric, pyroelectric, ferroelectric, linear and non-linear electrooptic properties. In addition, separate longitudinal optical (LO) modes of vibration may be Raman active for polar modes (i.e. modes which also have infrared activity) because the long-range electric field associated with the vibrational motion splits the phonon into transverse and longitudinal components at different frequencies [3–5]. Mason [6] measured the elastic, piezoelectric and dielectric properties of NaClO<sub>3</sub> over the temperature range 173 to 473 K. The

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temperature dependence of the static dielectric constant was found to be typical of that of a ferroelectric with an extrapolated Curie temperature  $T_c = 593$  K which was unfortunately above the melting temperature of 536 K. Detailed studies of the optical phonons in  $\text{NaClO}_3$  have to be made by infrared reflection and Raman scattering methods to determine the optical constants and to test the generalised Lyddane–Sachs–Teller relationship [5] between the dielectric constant and the frequencies of the transverse optical (TO) and longitudinal optical (LO) modes [7–14]. Several vibrational studies [9, 11, 15] have been performed in an attempt to establish whether the predicted transition was displacive or order-disorder. Rao *et al* [9] have studied the low frequency Raman spectrum of  $\text{NaClO}_3$  up to the melting point but did not find any evidence for a propagating soft mode which would have indicated the onset of a displacive transition. From a study of all the vibrational modes as a function of temperature Dawson [11] has reported that the observed dielectric behaviour of  $\text{NaClO}_3$  could be accounted for fully on the basis of contributions from polar phonons without the need to postulate other dielectric mechanisms in the region between the microwave and infrared regions. Dawson claimed that there really was no evidence to confirm that  $\text{NaClO}_3$  was in fact ferroelectric (i.e. exhibits an electric dipole even in the absence of an external electric field) since a crystal may be non-centric and exhibit piezoelectric properties and not be ferroelectric [16]. The evidence for a noncentric crystal class may be achieved by vibrational spectroscopy through the observation of LO modes but it is doubtful that unequivocal statements on ferroelectric properties are possible by these indirect methods. It is clear that  $\text{NaClO}_3$  is noncentric and piezoelectric but whether or not it is ferroelectric awaits confirmation by direct methods.

Although the predicted high temperature phase cannot be realised by heating  $\text{NaClO}_3$  II there is an unusual high temperature phase (phase I) that can be reached by cooling the melt [17, 18]. Meyer and Gasperin [17] reported that the phase I structure was monoclinic and similar to  $\text{KClO}_3$  with space group  $P2_1/a$  and four formula units per unit cell. Meyer and Rimsky [18] have proposed that the mechanism for the transition back to the acentric room-temperature phase (phase II) occurs without disruption of the structure by a sliding of layers which results in the change of coordination number of sodium from nine to six but leaves the sodium and chlorate ions in octahedral environments. Schamm and Todheide [19] have reported a high pressure form of  $\text{NaClO}_3$  with a triple point at 541 K and 750 bar but the structure has not been determined.

The present study was initiated in part to investigate the temperature dependence of LO modes in crystals and to follow their demise at phase transitions in an effort to establish whether or not the claim for LO modes in amorphous solids and liquids has any basis [20]. Several problems associated with this concept have been addressed [21]. Raman spectra of phase I should not exhibit LO modes if the crystal is paraelectric because for centric crystals the rule of mutual exclusion applies and infrared active modes cannot be Raman active. It has also been demonstrated that Raman spectroscopy may be used to characterise disordered structures [21–23]. Since both  $\text{RbClO}_3$  and  $\text{CsClO}_3$  have disordered high temperature phases [24, 25] this possibility for  $\text{NaClO}_3$  must be considered. Thermal measurements may also give evidence for ordered-solid to disordered-solid phase transitions because these transitions have relatively large transition enthalpies and entropies compared to those of melting [26].

In the present study the Raman spectra of  $\text{NaClO}_3$  II has been measured at a series of temperatures from 77 K to 535 K to check the previous assignments and frequencies. Peaks due to the naturally abundant isotopically different forms of chlorate with  $^{37}\text{Cl}$  and  $^{18}\text{O}$  were studied in an attempt to resolve the uncertainty associated with the reported

presence and absence of these peaks [8, 12, 27, 28]. In addition the peaks due to the isotopically different ions provide an insight into the extent of intermolecular coupling. Raman spectra have been obtained for the melt and the high temperature  $\text{NaClO}_3$  I. These measurements indicated that  $\text{NaClO}_3$  I has a centrosymmetric, ordered structure similar to  $\text{KClO}_3$  and in good agreement with the X-ray studies of Meyer and co-workers [17, 18]. Although the phase transition appears to be displacive and an E-type band at  $60\text{ cm}^{-1}$  appeared abruptly at the phase I to phase II transition, the associated soft mode behaviour could not be established. There was no evidence for LO modes in phase I or in the molten phase but the LO mode at  $1023\text{ cm}^{-1}$  characteristic of phase II reappeared abruptly at the phase transition.

## 2. Experimental details

Single crystals of  $\text{NaClO}_3$  were grown from a saturated solution of the reagent grade salt in double distilled water. The solution was treated with activated carbon to remove fluorescent impurities and filtered through a fine glass grit. Clear crystals with well developed natural faces were obtained. A crystal about  $4 \times 4 \times 4\text{ mm}^3$  parallel to the major crystallographic axes was used for the single crystal study. Several smaller crystals were placed in a 4 mm id pyrex tube, carefully melted just above the melting temperature, cooled, evacuated and sealed. In this work and in related studies of the molten salt there was no evidence of decomposition when the crystals were heated as much as 30 degrees above the melting temperature of 536 K. It was also noted that the phase transition was not sensitive to whether or not the sample was open to the atmosphere. Occasionally the molten phase supercooled sufficiently to transform directly to phase II. It was also observed that if a small amount of phase II material was left in equilibrium with the melt that the crystals that formed on cooling were also phase II not phase I. Attempts to grow single crystals from the melt were unsuccessful.

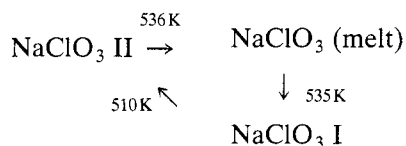
Raman spectra were measured with a Coderg PHO Raman spectrophotometer for both the polycrystalline samples of phase I and II in the pyrex tube and the single crystal of  $\text{NaClO}_3$  II. The 488.0 and 514.5 nm lines of a Control laser model 52 argon ion laser was used to excite the sample. Plasma lines were removed with a narrow band-pass interference filter. Peak positions were calibrated against laser plasma lines. The slit widths were set at  $1.0\text{ cm}^{-1}$  for survey scans but detailed studies for each region were performed with  $0.25\text{ cm}^{-1}$  slits. The power level at the sample was about 500 mw. There was no evidence of local heating or sample degradation at the beam focus. Raman spectra of the oriented single crystal were obtained at 77 K and 298 K on the copper cold tip of an evaporating liquid nitrogen cryostat. The crystal was oriented for the incident and scattered light to be perpendicular to principle planes to give the  $x(zz)y$ ,  $x(zx)y$ ,  $x(yx)y$  and  $y(zy)y$  scattering geometries. Polarisation of the incident beam was controlled by a halfwave plate and the  $90^\circ$  scattered light was analysed with Polaroid films which accepted parallel or perpendicular polarised light. A quarter waveplate before the entrance slit served to compensate for grating polarisation preference. The high temperature studies were performed on the polycrystalline sample sealed under vacuum in the pyrex tube and heated in an insulated furnace regulated with a proportional temperature controller. Temperatures were monitored with a chromel-alumel thermocouple and the quoted temperature at the sample was constant at one degree and accurate to about three degrees for the Raman measurements.

The Raman scattered light was detected with a PMT cooled to 250 K connected to a photon counter. The analogue spectra were recorded on a strip-chart recorder. Digital data files were also created after the counts were integrated and processed with a home-built box-car averager interfaced to the Memorial University VAX 8800 computer. Either two or four data points were collected per wavenumber. At least two sets of data were collected for each spectrum to assure reproducible results. Spectra were signal averaged and smoothed once with a three point Savitsky–Golay smoothing function. A baseline program was applied which corrected the measured intensity for the fourth power frequency factor and then set the lowest data point to zero and the highest data point to 999 on a relative intensity scale. This form of the data is defined as our  $I(\omega)$  spectrum which should be independent of excitation frequency. The same baseline program was applied with the option to correct for the fourth-power scattering factor, the Bose–Einstein temperature factor,  $B = [1 - \exp(-hc\omega/kT)]$  and the frequency factor,  $\omega$ , to give the reduced or  $R_Q(\omega)$  spectrum which is directly proportional to a point by point relative scattering activity  $S_Q(\omega)$  in terms of mass weighted normal coordinates,  $Q$ , in the double-harmonic approximation.  $R_Q(\omega)$  is the form of the Raman spectrum that most closely approaches the vibrational density of states [29]. The relationship between the  $I(\omega)$  and  $R_Q(\omega)$  forms of the spectra is given by

$$S_Q(\omega) \propto R_Q(\omega) = I(\omega)\omega B. \quad (1)$$

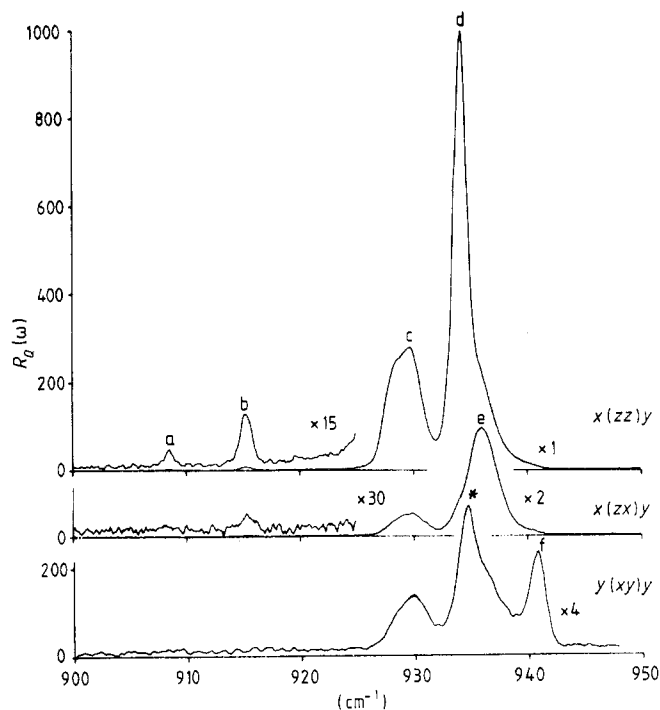
It is our preference to plot the spectrum in the  $R_Q(\omega)$  form because the Bose–Einstein factor removes the vibrational-state dependent temperature factor of the excited state transitions and leaves the effect that is due to concentration changes. Only in the low frequency region are the  $I(\omega)$  and  $R_Q(\omega)$  significantly different and both forms are presented and discussed.

Thermal measurement were made on a Perkin–Elmer DSC2. Scan rates of 5 and 10 K min<sup>-1</sup> for the heating and cooling cycles. Identical results were obtained for several different NaClO<sub>3</sub> samples including reagent grade solids used as received. The peak due to the phase transition was only observed on the cooling cycle and always occurred within a few degrees of 510 K. The DSC was calibrated with the heat of melting for indium. The phase transition characteristics can be summarised as follows:



### 3. Results and discussion

The Raman spectra from an oriented single crystal of NaClO<sub>3</sub> II at room temperature and at 77 K (figures 1–4, table 1) were in good agreement with previous measurements [8, 10, 11] although some minor differences have been noted. Peaks due to different isotopic forms of ClO<sub>3</sub><sup>-</sup> have been assigned and are discussed below with reference to intermolecular coupling effects. Since it was only possible to obtain Raman spectra of the high temperature phase for polycrystalline samples it was also necessary to study the low temperature phase for polycrystalline samples for comparative purposes. Raman spectra of the polycrystalline phase II sample were measured at selected temperatures from 77 K to 535 K, for the molten phase at 545 K and for the phase I salt at 520 K.



**Figure 1.** Raman spectra obtained from an oriented single crystal of  $\text{NaClO}_3$  II at 77 K (\*, spill-over due to misalignment). Key: a,  $^{37}\text{Cl}^{18}\text{O}^{16}\text{O}_2^-$ ; b,  $^{35}\text{Cl}^{18}\text{O}^{16}\text{O}_2^-$ ; c,  $^{37}\text{Cl}^{16}\text{O}_3^-$ ; d,  $^{35}\text{Cl}^{16}\text{O}_3^-$ ; A; e,  $^{35}\text{Cl}^{16}\text{O}_3^-$ , E(TO); f,  $^{35}\text{Cl}^{16}\text{O}_3^-$ , E(LO).

Spectra for the  $\nu_1$  and  $\nu_3$  regions in the  $R_Q(\omega)$  format (figure 2) and in the external lattice mode region in both the  $I(\omega)$  and  $R_Q(\omega)$  formats (figures 3 and 4) serve to illustrate the basic differences in the spectra among the  $\text{NaClO}_3$  II,  $\text{NaClO}_3$  I and  $\text{NaClO}_3$  molten phases. In particular the appearance of the external lattice E mode at  $60\text{ cm}^{-1}$  and the F(LO) component of  $\nu_3$  at  $1023.5\text{ cm}^{-1}$  marked the I to II phase transition. The spectra in the  $R_Q(\omega)$  format have been normalised for temperature and permit a comparison based on structural differences. Peak frequencies and assignments based on the single crystal measurements are collected in table 1. Although there was considerable band overlap in the spectra for the polycrystalline sample it was possible to make reasonable assignments. In general the bands due to the LO modes were weak and not easily identified in the polycrystalline material. Only the LO mode at about  $1030\text{ cm}^{-1}$  in the  $\nu_3$  region of  $\text{ClO}_3^-$  was sufficiently intense and isolated to study as a function temperature.

The Raman spectrum of  $\text{NaClO}_3$  has possible complications from extra peaks due to the presence of naturally abundant isotopically different ions  $^{35}\text{ClO}_3^-$  and  $^{37}\text{ClO}_3^-$  and  $^{35}\text{Cl}^{18}\text{O}^{16}\text{O}_2^-$  and  $^{37}\text{Cl}^{18}\text{O}^{16}\text{O}_2^-$ . Fortunately the bands due to these isotopically different ions provide information about the correlation field coupling of vibrational modes in an ordered single crystal. Belousov, Pogarev and Shultin [28] have shown theoretically, and demonstrated experimentally that isotopically dilute molecules in an ordered lattice can couple with the host molecule for small frequency shifts. For example, if the frequency shift which accompanies isotopic substitution does not take the band

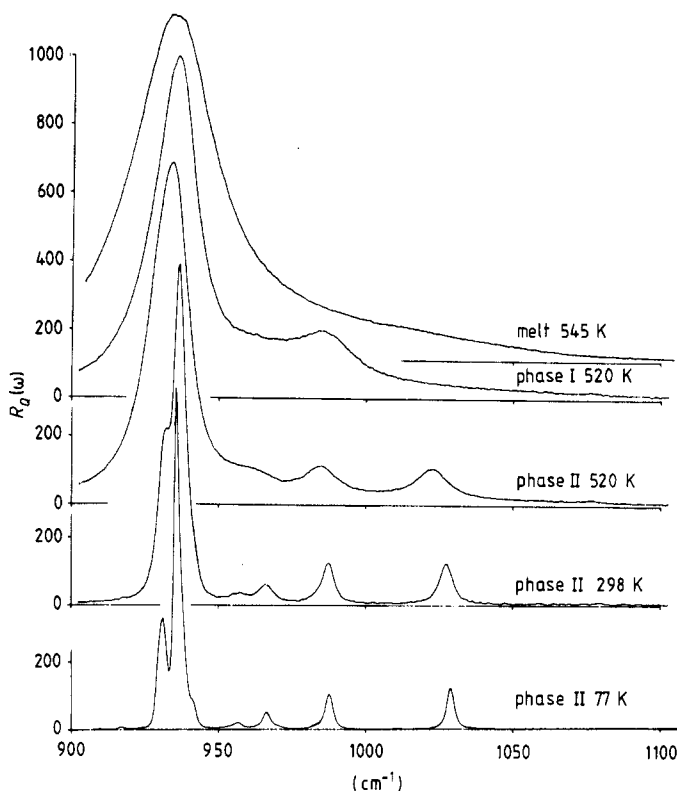
**Table 1.** Raman frequencies ( $\text{cm}^{-1}$ ) and assignments for  $\text{NaClO}_3$  in phase II for single-crystal and polycrystalline samples, for phase I as polycrystalline sample, and for the melt.

	Single crystal 77 K	Phase II 298 K	Phase II 520 K	Phase I 520 K	Melt 545 K	
E	69	66	60	—		$T_{\text{ClO}_3^-}$
F (TO, LO)	77, 83	74, 78				
A	87	86				
F (TO, LO)	124, 125	122				
F (TO, LO)	137, 138					
A	139	133	117	105	90 dp	$R_{\text{ClO}_3^-}$
E	142					
F	166					
F	a					
E	192	180	160	145		
F (TO, LO)	204, 206					
A	208	190 sh				
F	216					
	~472					
E	479.7	481.5	481	484	484 dp	$\nu_4 {}^{35}\text{Cl}^{18}\text{O}^{16}\text{O}_2^-$
F (TO, LO)	482.0, 487.6 <sup>b</sup>					
F (TO, LO)	487.3, 481	488.0	486	489		
					500 (sh) dp	
A	616.4	620	621	618	618 p	$\nu_2 \text{ClO}_3^-$
F (TO, LO)	623.6, 630.8	624, 628				
A	908.9					$\nu_1 {}^{37}\text{Cl}^{18}\text{O}^{16}\text{O}_2^-$
A	915.3					$\nu_1 {}^{35}\text{Cl}^{18}\text{O}^{16}\text{O}_2^-$
A	929 (sh)					$\nu_1 {}^{37}\text{ClO}_3^-$
A	930.1	931.5 (sh)				
A	934.6	936.0	933.5	934.5	937 p	$\nu_1 {}^{35}\text{ClO}_3^-$
F (TO, LO)	936.5, 941.2	940 (sh)				
E	955.6	958.0				
F (TO, LO)	965.4, 1029.6 <sup>b</sup>	966.5, 1027.5	962, 1023.5	960	~985 dp	$\nu_3 \text{ClO}_3^-$
F (TO, LO)	986.6, 983.0	987.5	985.5	985	~1000 dp	

<sup>a</sup> It was not possible to confirm or disprove the presence of an F mode at  $192 \text{ cm}^{-1}$  as reported by Miller and Khanna [10].

<sup>b</sup> Assigned on the basis of the most intense infrared band associated with the largest TO–LO splitting.

due to the isotopically dilute molecule out of the region of that particular branch of the vibrational density of states of the more abundant molecule the isotopically different molecule will still couple to the host molecule and give rise to a single set of correlation field components with mass weighted average frequencies. In this case the isotopically different molecule is *invisible* and does not give rise to a separate band or set of bands and the species can be classified as a shallow well impurity. However if the isotopic shift puts the frequency outside the branch of the vibrational density of states of the mode of the more abundant molecule the isotopically different molecule will give rise to a separate uncoupled band(s) and the molecule can be treated as a deep well impurity centre for that mode. A single isotopic species such as  ${}^{35}\text{ClO}_3^-$  may give rise to a separate peak in some regions of the spectrum and not in others. Whether or not there is a separate peak for the isotopically different ion depends on the magnitude of the correlation field effects and therefore on the crystal structure. For instance, in  $\text{KClO}_3$  it was possible to detect a band due to the  ${}^{37}\text{ClO}_3^-$  in the  $\nu_2$  region because in  $\text{KClO}_3$  the correlation field splitting in this region is only  $1 \text{ cm}^{-1}$  [30, 31]. A study of O-18 substituted  $\text{NO}_3^-$  in



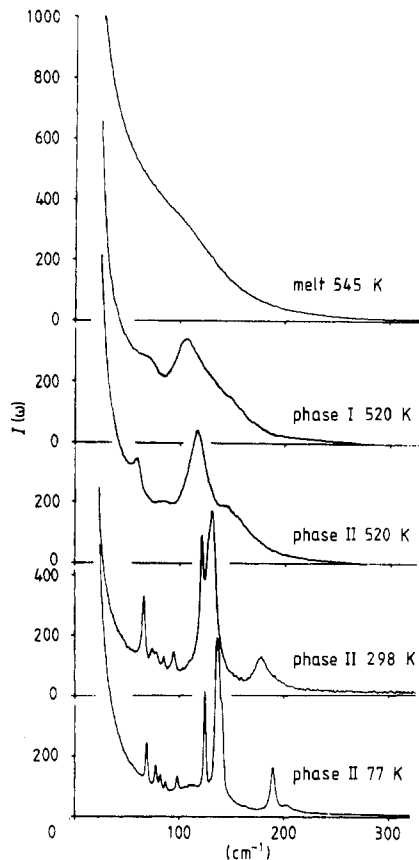
**Figure 2.** Raman spectra in the 900 to 1100  $\text{cm}^{-1}$  region obtained for polycrystalline  $\text{NaClO}_3$  at different temperatures.

$\text{Sr}(\text{NO}_3)_2$  has demonstrated the usefulness of isotope dilution for differentiating between static and correlation field effects [23]. The present results for isotopic molecules in  $\text{NaClO}_3$  at 77 K are consistent with the predictions of Belousov, Pogarev and Shultin [28]. The results for the sample at 77 K are discussed because band overlap presented a serious problem at room temperature.

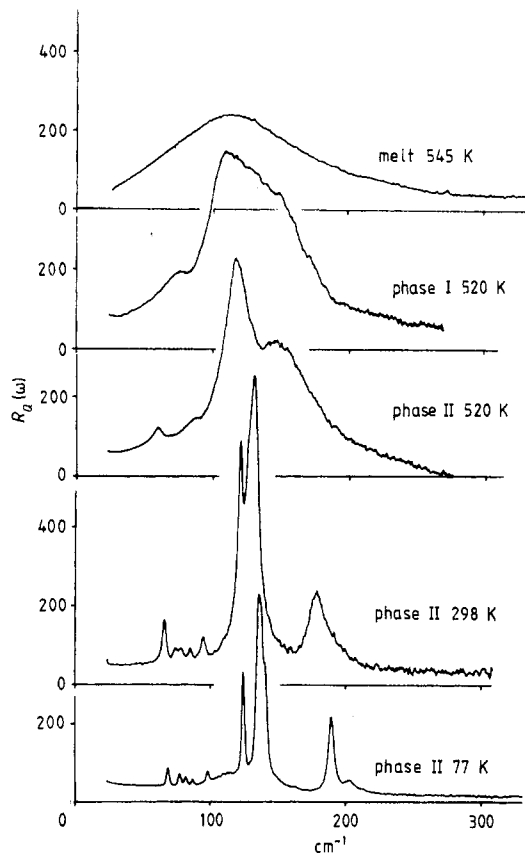
Studies of  $^{35}\text{ClO}_3^-$  and  $^{37}\text{ClO}_3^-$  in matrix isolation [32] have shown that the differences in the vibrational frequencies for the  $\nu_1$ ,  $\nu_2$ ,  $\nu_3$  and  $\nu_4$  modes are 7.0, 4.9, 10.1 and 1.5  $\text{cm}^{-1}$ , respectively. On the basis of these frequency shifts it can be predicted that the  $^{37}\text{ClO}_3^-$  ion should give rise to a separate peak in the  $\nu_1$  region where the isotope shift is greater than the correlation and TO/LO splitting (4  $\text{cm}^{-1}$ ) but separate peaks due to the  $^{37}\text{ClO}_3^-$  should not appear in the  $\nu_2$ ,  $\nu_3$  and  $\nu_4$  regions of the spectra where the isotopic shifts are not greater than the separation of correlation field components of about 11, 70 and 8  $\text{cm}^{-1}$ , respectively.

The  $\nu_1$  mode for  $^{37}\text{ClO}_3^-$  appears as separate band at 930.1  $\text{cm}^{-1}$ , uncoupled from the A (934.6  $\text{cm}^{-1}$ ) and F (936.5  $\text{cm}^{-1}$  TO, 941.2  $\text{cm}^{-1}$  LO) components due to the modes of the coupled  $^{35}\text{ClO}_3^-$  ions on the ordered lattice (figure 1). The 7  $\text{cm}^{-1}$  isotope shift was sufficient to decouple the  $\nu_1$  mode of  $^{37}\text{ClO}_3^-$  from the  $\nu_1$  mode of  $^{35}\text{ClO}_3^-$ . The  $\nu_1$  mode of the ordered lattice of  $^{35}\text{ClO}_3^-$  ions clearly exhibits the A and F correlation field





**Figure 3.** Raman spectra in the  $I(\omega)$  format in the external lattice mode region obtained from polycrystalline  $\text{NaClO}_3$  at different temperatures.



**Figure 4.** Raman spectra in the  $R_Q(\omega)$  format in the external mode region obtained from polycrystalline  $\text{NaClO}_3$  at different temperatures.

components and the F(TO)–F(LO) separation (figure 1). A 25%  $^{37}\text{ClO}_3^-$  concentration was not sufficient to place the  $^{35}\text{ClO}_3^-$  ions far enough apart on average to decouple the  $\nu_1$  vibrational modes of  $^{35}\text{ClO}_3^-$  region of the ordered lattice. Although the  $\nu_1$  mode of the  $^{37}\text{ClO}_3^-$  did not exhibit the correlation field and TO–LO modes of the  $^{35}\text{ClO}_3^-$  ion, the  $\nu_1$  mode of  $^{37}\text{ClO}_3^-$  ion did have an anomalous shoulder about  $1\text{ cm}^{-1}$  below the peak maximum but only in the  $x(zz)y$  orientation. This shoulder could be caused by resonance energy exchange between pairs or clusters of  $^{37}\text{ClO}_3^-$  ions that are in close proximity by chance. It may be noted that the peak maximum for the  $\nu_1$  mode of  $^{37}\text{ClO}_3^-$  was at the same frequency ( $930.1\text{ cm}^{-1}$ ) for each of the different polarisation geometries (figure 1). The weak intensity of the  $\nu_1$  mode of  $^{37}\text{ClO}_3^-$  in the  $x(yx)y$  and  $y(z)y$  geometries is more consistent with the depolarisation ratio of the  $\nu_1$  (A) mode of free chlorate in solution than possible F mode character. In matrix isolation and aqueous solution the  $^{35}\text{ClO}_3^-$  and  $^{37}\text{ClO}_3^-$  ions are decoupled and should appear as separate peaks. Two peaks at  $947.6$  and  $940.6\text{ cm}^{-1}$  have been reported [32] in KBr matrix but in aqueous solution band broadening prevents resolution of the two components [25, 33]. Separate peaks due to the decoupled  $\nu_1$  modes of the  $^{35}\text{Cl}^{18}\text{O}^{16}\text{O}_2^-$  and

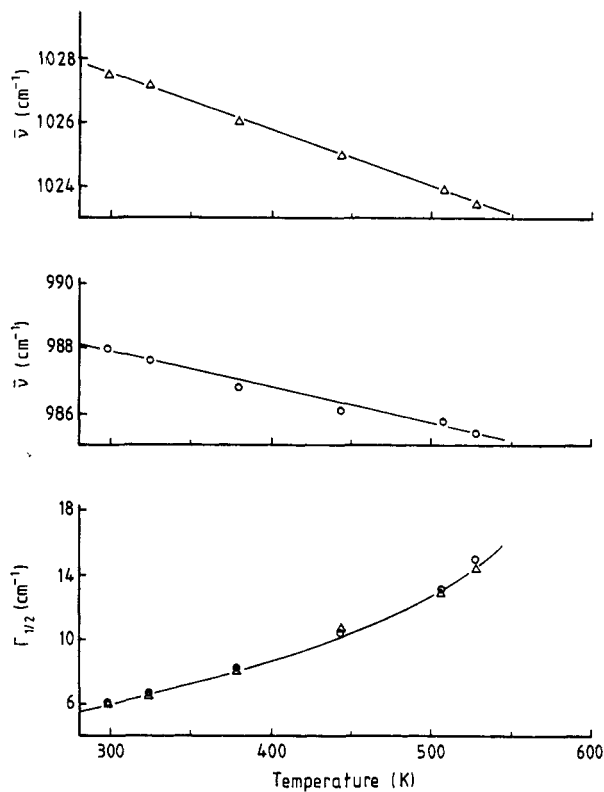
<sup>37</sup>Cl<sup>18</sup>O<sup>16</sup>O<sub>2</sub><sup>-</sup> ions in NaClO<sub>3</sub> have also been detected at 915.3 and 908.9 cm<sup>-1</sup> (figure 1, table 1). Bates and Stidham [27] have studied the O-18 substituted chlorate and bromate ions for several salts. Orientational splitting has been observed for the Cl<sup>18</sup>O<sup>16</sup>O<sub>2</sub><sup>-</sup> ions in KClO<sub>3</sub> because of the C<sub>s</sub> site symmetry. The single sharp lines for <sup>35</sup>Cl<sup>18</sup>O<sup>16</sup>O<sub>2</sub><sup>-</sup> and <sup>37</sup>Cl<sup>18</sup>O<sup>16</sup>O<sub>2</sub><sup>-</sup> in NaClO<sub>3</sub> is consistent with the fact that the chlorate ion occupies a C<sub>3</sub> lattice site and it does not matter in which direction the O-18 atom points. The frequency differences between the pairs of ions <sup>37</sup>Cl<sup>18</sup>O<sup>16</sup>O<sub>2</sub><sup>-</sup> and <sup>37</sup>Cl<sup>16</sup>O<sub>3</sub><sup>-</sup>, and <sup>35</sup>Cl<sup>18</sup>O<sup>16</sup>O<sub>2</sub><sup>-</sup> and <sup>35</sup>Cl<sup>16</sup>O<sub>3</sub><sup>-</sup> also indicate that the ν<sub>1</sub> mode of <sup>37</sup>ClO<sub>3</sub><sup>-</sup> is decoupled, i.e. the 21.2 cm<sup>-1</sup> difference between the bands at 908.9 and 930.1 cm<sup>-1</sup> is in agreement with predictions of a normal coordinate calculation for the free ions but the 915.8 cm<sup>-1</sup> peak from <sup>35</sup>Cl<sup>18</sup>O<sup>16</sup>O<sub>2</sub><sup>-</sup> must be compared to the mean of the three components A (934.6 cm<sup>-1</sup>), F TO (936.5 cm<sup>-1</sup>) and F LO (941.2 cm<sup>-1</sup>) of <sup>35</sup>Cl<sup>16</sup>O<sub>3</sub><sup>-</sup> for similar agreement.

It appears that the ν<sub>1</sub> modes of <sup>35</sup>ClO<sub>3</sub><sup>-</sup> and <sup>37</sup>ClO<sub>3</sub><sup>-</sup> begin to couple to each other as the bands broaden with increased temperature. The halfwidths of the ν<sub>1</sub> A mode for <sup>35</sup>ClO<sub>3</sub><sup>-</sup> increased from a value of 2.5 cm<sup>-1</sup> at 77 K to 6 cm<sup>-1</sup> at 300 K. At room temperature the isotope structure was just detectable and at high temperature only one symmetric band with a halfwidth of 15.3 cm<sup>-1</sup> was observed.

The ν<sub>3</sub> region of NaClO<sub>3</sub> was studied in detail because the bands due to the correlation field components and their TO LO components are well resolved although the LO component at 983 cm<sup>-1</sup> was too weak to be observed in the spectrum of the polycrystalline sample (figure 2). The assignments (table 1) of the TO/LO pairs was based on the principle of alternative pairs and the association of the greatest TO-LO separation with the most intense infrared band [34]. Peak frequencies and halfwidths for an oriented single crystal were unaffected by the angle of the incident and scattered light. In fact the peak frequencies and halfwidths for the polycrystalline sample and the oriented single crystal were identical. These results corroborate those of Hartwig *et al* [8] and confirm the fact that mixed TO + LO modes with intermediate frequencies do not exist in cubic crystals such as NaClO<sub>3</sub>. In crystals of lower symmetry mixed modes can give rise to peak frequencies that may range from that of the pure TO mode to that of the pure LO mode [35]. In the ν<sub>3</sub> region there was no evidence of bands due to separate <sup>35</sup>ClO<sub>3</sub><sup>-</sup> and <sup>37</sup>ClO<sub>3</sub><sup>-</sup>, therefore the motions of these ions must be tightly coupled for this mode. In matrix isolation studies the chlorate ions are decoupled and two peaks have been observed at 1004.5 and 994.4 cm<sup>-1</sup> with the appropriate three to one intensity ratio [32]. In aqueous solution the <sup>35</sup>ClO<sub>3</sub><sup>-</sup> and <sup>37</sup>ClO<sub>3</sub><sup>-</sup> ions should also be decoupled but band overlap with ν<sub>1</sub> obscures the region [25, 33].

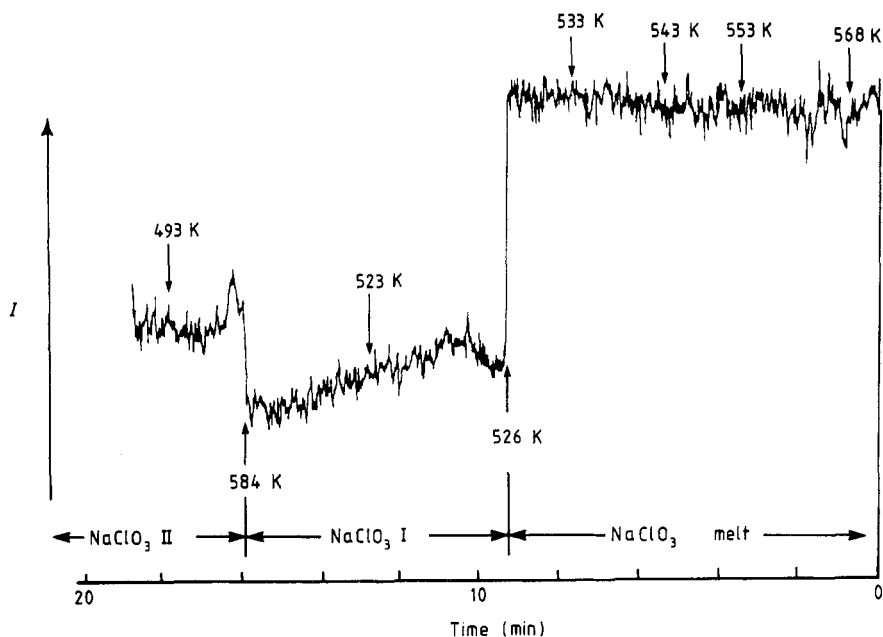
An increase in the temperature of the sample caused bands to broaden and overlap but there was no evidence for any structural change up to the melting point. At 530 K the two components of ν<sub>2</sub> were still resolved but ν<sub>4</sub> appeared as a broad band. In the ν<sub>3</sub> region the band of the E mode was overlapped by the ν<sub>1</sub> band and the band of the F(TO) mode at 962 was not well enough resolved to study quantitatively. A quantitative study of the bands at 1027.5 cm<sup>-1</sup> (LO) and 987.5 cm<sup>-1</sup> (TO) over the temperature range from room temperature to the melting point indicated that both bands had similar temperature dependence (figure 5); the LO mode shifted to lower frequency by 4 cm<sup>-1</sup> and the TO mode by 3 cm<sup>-1</sup> and both bands increased in halfwidth by about 9 cm<sup>-1</sup>. The temperature dependence of the peak positions and halfwidths were essentially linear and indicated the same phase was present until the sample melted.

Cooling of the melt almost always gave the high temperature phase which was relatively stable between 536 and 510 K but occasionally the phase change occurred spontaneously while studies of phase I were in progress. With normal cooling the I to II



**Figure 5.** Plots of peak maxima  $\bar{\nu}$  and halfwidths  $\Gamma_{1/2}$  versus temperature for the F(RO) mode at  $987\text{ cm}^{-1}$  and the F(LO) mode at  $1030\text{ cm}^{-1}$ .

phase transition always occurred near 508 K. The Raman spectrum of phase I differed from that of phase II at the same temperature by two significant differences—the absence of the LO peak in the  $1020\text{--}1030\text{ cm}^{-1}$  region (figure 2) and the absence of the band at about  $60\text{ cm}^{-1}$  (figures 3, 4). In the  $\nu_3$  region the maximum at  $985\text{ cm}^{-1}$  and the weak shoulder at about  $960\text{ cm}^{-1}$  are similar to features in  $\text{KClO}_3$  and the absence of isotope structure suggests that these are correlation field components of coupled chlorate ions of different isotopic forms. Two bands were observed in the  $\nu_2$  region which appear to be due to correlation field components because the separation is too large for isotope structure. Frequencies and assignments for phase I are listed in table 1. The absence of the LO mode indicates that phase I has a centric structure. The presence of band structure in the external mode region and the  $\nu_3$  and  $\nu_2$  regions indicates that the structure is not disordered beyond normal thermal motion. The three bands that can be resolved in the external mode region of phase I resemble the three bands at similar frequency in phase II at the same temperature (figures 3 and 4). The  $\nu_1$  band was too broad to resolve possible isotope structure and it should be noted that the peak maximum actually *increased* on transition from phase II to phase I. The similarity of most of the features in the Raman spectrum from  $\text{NaClO}_3$  I to those of  $\text{NaClO}_3$  II suggests that the transformation occurs with only small changes in atomic positions. The spectrum of  $\text{NaClO}_3$  I is similar to that of both  $\text{KClO}_3$  I and  $\text{KClO}_3$  II [30, 31]. The Raman results are



**Figure 6.** Recorder trace of the relative Raman intensity at  $1023.5\text{ cm}^{-1}$  for a sample of  $\text{NaClO}_3$  cooled from the melt monitored as a function of temperature and time.

consistent with the diffraction studies of Meyer and Gasperin [17] and the reported monoclinic structure, space group  $P2_1/a$  but the Raman measurements would also be consistent with the structure of the high temperature phase of potassium chlorate ( $\text{KClO}_3$  I) which has an orthorhombic structure, space group  $Pcmm$  [36]. The atomic positions in  $\text{KClO}_3$  I and  $\text{KClO}_3$  II are very similar [36] as are the Raman spectra [31].

The phase transition was studied as a function of temperature and time by fixing the monochromator to a  $1024\text{ cm}^{-1}$  setting and following the Raman intensity as the sample cooled from the melt (figure 6). It was observed that the intensity decreased instantly as the sample froze and increased instantly at the phase I to phase II transition. The decreased intensity on freezing was caused by the sudden sharpening of the broad distribution of states in the melt to the narrow distribution of states in the ordered high temperature phase. The increase of the intensity at  $1024\text{ cm}^{-1}$  at the phase transition was due to the sudden appearance of the LO mode as the acentric, room-temperature structure formed. The low frequency mode at  $60\text{ cm}^{-1}$  also appeared suddenly at the phase transition. The low frequency mode at  $60\text{ cm}^{-1}$  in phase II has been assigned to a Translatory mode of the  $\text{ClO}_3^-$  ion by analogy with assignment for  $\text{NaBrO}_3$  [37]. This mode appears to be associated with a displacive phase transition. Such a martensitic type mechanism has been proposed by Meyer and Rimsky [18]. Unfortunately it was not possible to determine whether or not this band exhibited soft mode characteristics.

Raman spectra for the molten  $\text{NaClO}_3$  were similar to those reported by Bates and Quist [33] and were very similar to the Raman spectrum of the dilute aqueous solution [25, 33]. The similarity between the spectrum of  $\text{ClO}_3^-$  in aqueous and molten phases suggests that the Raman spectra of both phases may be interpreted in terms of independent uncoupled molecular ions (i.e., short-range order only) and similar to the

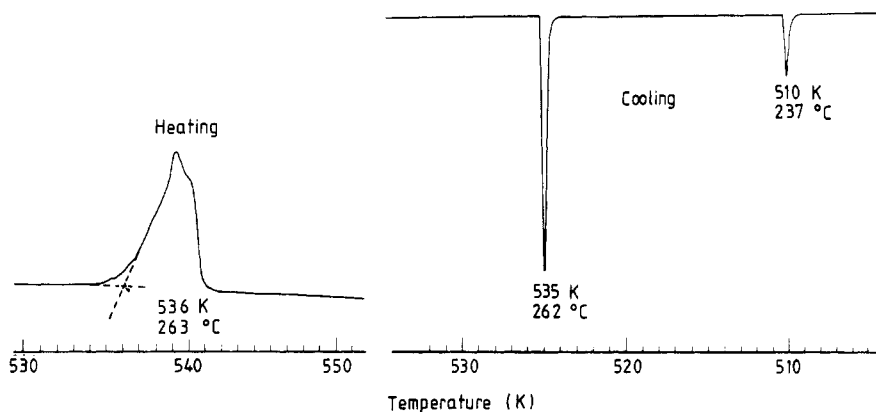


Figure 7. DSC trace for the heats of fusion and transition for  $\text{NaClO}_3$ .

interpretation of aqueous and molten nitrates [21]. Essentially the spectrum is that of a density of states unstructured by the effects of intermolecular coupling. The low frequency region exhibited a depolarised Rayleigh–Raman wing due to the reorientational motions of the anisotropic chlorate ion. The  $\nu_2$  region had a doublet structure due to a shoulder at about  $500\text{ cm}^{-1}$  which appears to be due to interaction with the sodium ion. The  $\nu_1$  region was broad and overlapped with the  $\nu_3$  region to such an extent that the  $\nu_3$  region was difficult to analyse. From consideration of the depolarised Raman spectrum there appeared to be two overlapped bands at about  $985$  and  $1000\text{ cm}^{-1}$  in the  $\nu_3$  region. Although the intensity of the  $\nu_3$  band extended to  $1100\text{ cm}^{-1}$  there was no indication to suggest a residual LO mode in the melt. The presence of an LO mode in a liquid is not expected since it would indicate the presence of considerable long range order. The  $\nu_3$  region should be complicated by the presence of bands due to both the  $^{35}\text{ClO}_3^-$  and  $^{37}\text{ClO}_3^-$  ions because of the absence of the coupling mechanism that is operative in the ordered solids and this is the suggested assignment for the components at about  $985$  and  $1000\text{ cm}^{-1}$ . In aqueous and molten nitrates the degeneracy of the  $\nu_3$  mode is lifted by interaction with water or cation and it is possible that the degeneracy of the  $\nu_3$  mode of  $\text{ClO}_3^-$  in molten  $\text{NaClO}_3$  is also lifted by interaction with sodium. A detailed study of the molten alkali metal chlorate melts is in progress.

Thermal measurements were performed by differential scanning calorimetry. The heating and cooling traces (figure 7) for the DSC measurements show peaks due to melting, freezing and the phase transition. The unusual structure associated with the heat of melting may reflect the presence of another solid phase just at the melting point. The values for the enthalpy and entropy of melting and of transition were found to be  $\Delta H_f = 21.7\text{ kJ mol}^{-1}$ ,  $\Delta S_f = 40.6\text{ J mol}^{-1}\text{ K}^{-1}$ ;  $\Delta H_t = 4.1\text{ kJ mol}^{-1}$ , and  $\Delta S_t = 8.2\text{ J mol}^{-1}\text{ K}^{-1}$ . The melting temperature was found to be  $536\text{ K}$ . The heat of fusion was in good agreement with the literature [38]. The heat of transition has not been reported previously. The fact that the enthalpy and entropy of transition were relatively small compared to those of melting may also be interpreted to mean that phase I is not disordered.

#### 4. Conclusions

Raman spectra of solid  $\text{NaClO}_3$  I and II over a wide range of temperatures has been interpreted on the basis of intermolecular coupling and correlation field models. The

results are in good agreement with reported crystal structures. With respect to the chlorine isotopes only the  $\nu_1$  mode of the  $^{37}\text{ClO}_3^-$  ion was found to be decoupled from the  $^{35}\text{ClO}_3^-$  host lattice and only at lower temperatures. In other regions the spectra indicated that the motions of these ions remained coupled to each other and did not give rise to separate peaks. Raman and thermal studies reaffirmed the novel property of the high temperature form of NaClO<sub>3</sub> to form only from the melt as a metastable ordered crystal. The disappearance of the longitudinal mode at the II to I phase transition indicated that NaClO<sub>3</sub> I has a centric structure. Evidence of correlation field components in NaClO<sub>3</sub> I indicated an ordered structure similar to KClO<sub>3</sub>. Heats and entropies of transition also indicated that NaClO<sub>3</sub> I was ordered. The similarity of the Raman spectrum of molten NaClO<sub>3</sub> to aqueous NaClO<sub>3</sub> suggested that intermolecular coupling between chlorate ions were not significant. The absence of longitudinal components in NaClO<sub>3</sub> I, the molten salt and aqueous solution suggested that longitudinal modes require both long-range translational symmetry and a non-centric crystal class for Raman activity.

### Acknowledgments

This work was supported in part by the Natural Sciences and Engineering Council of Canada. The authors wish to thank De Kevin Keough of the University Biochemistry Department for the use of the DSC.

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