

Temperature dependence of ^{79}Br NQR frequency in cadmium strontium, barium, zinc, magnesium and nickel bromates

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Abstract. The ^{79}Br quadrupole resonance in cadmium, strontium, barium, zinc, magnesium and nickel bromates is studied in the range 77 to 305 K. The temperature dependence of the resonance frequencies in these systems has been analysed on the basis of the torsional motion of the BrO_3^- groups. The torsional frequency and its temperature behaviour have been analysed.

Keywords. Nuclear quadrupole resonance; electric field gradient; resonance frequency; torsional mode of vibration; lattice frequency; bromates.

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1. Introduction

The theory of the temperature dependence of the nuclear quadrupole resonance (NQR) frequency has been developed for the axially symmetric case by Bayer (1951) and later extended to non-axially symmetric field gradient by Kushida (1955). Experimentally the problem of temperature variation of the NQR frequency was first undertaken by Dehmelt and Kruger (1951) and later by several workers (Wang 1955; Gutowsky and McCall 1960; Ramakrishna 1963; Chakrabani *et al* 1973; Tipsworth and Moulton 1963; Tipsworth *et al* 1964; Armstrong and Baker 1970). In these theories, only the variation in the amplitude of the librational motion with temperature has been considered. Kushida *et al* (1956) considered the volume changes that may accompany with temperature and which may change the electric field gradient at the site of interest. However, the temperature and pressure dependence of the NQR frequency investigations in bromates (Utton 1967; Tipsworth *et al* 1968) show that the volume variation in bromates is quite small. In 1960, Brown considered the volume variation effects by introducing a linear temperature dependence for the lattice frequencies. Ramamohan and Sobhanadri (1971) have modified Brown's theory taking into account the nonlinear variation of the lattice frequency with temperature by adopting a parabolic temperature dependence of the lattice frequencies.

NQR frequency of ^{79}Br in zinc, magnesium, nickel, strontium and barium bromates has been measured by Shimomura *et al* (1954) at 285 and 195 K. Burgiel *et al* (1961) have also reported the ^{79}Br NQR frequency in zinc and nickel bromates at 77 K and a few temperatures below 77 K. $\text{Sr}(\text{BrO}_3)_2 \cdot \text{H}_2\text{O}$ and $\text{Ba}(\text{BrO}_3)_2 \cdot \text{H}_2\text{O}$ are monoclinic (Sastry *et al* 1980; Kartha 1953) whereas $\text{Zn}(\text{BrO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Mg}(\text{BrO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Ni}(\text{BrO}_3)_2 \cdot 6\text{H}_2\text{O}$ are cubic (Beever 1936; Weigel 1963). In these systems only one crystallographic site of bromine in the unit cell is present and therefore only one line has been observed for each isotope of bromine. $\text{Cd}(\text{BrO}_3)_2 \cdot 2\text{H}_2\text{O}$ is orthorhombic

(Satyanarayana Murty and Murty 1978) and the room temperature x-ray data reveal the presence of two crystallographically inequivalent sites. Two resonances have been observed due to the two chemically inequivalent Br sites. From the Zeeman experiments carried out on these resonances at room temperature (Valli and Rama Rao 1983) it has been found that the high frequency line at room temperature corresponds to the bromine atom referred to as Br(1) in the structure (Satyanarayana Murty 1980) whereas the other line corresponds to the Br(2) atom.

In the present work, the temperature variation of the ^{79}Br NQR frequencies in $\text{Cd}(\text{BrO}_3)_2 \cdot 2\text{H}_2\text{O}$, $\text{Sr}(\text{BrO}_3)_2 \cdot \text{H}_2\text{O}$, $\text{Ba}(\text{BrO}_3)_2 \cdot \text{H}_2\text{O}$, $\text{Zn}(\text{BrO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Mg}(\text{BrO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Ni}(\text{BrO}_3)_2 \cdot 6\text{H}_2\text{O}$ has been carried out from 77 to 305 K. The volume effects have been considered following the procedures of linear and parabolic temperature-dependent lattice frequencies. These studies were carried out to compare the motional averaging of the electric field gradient and to obtain information about the librational frequencies of the bromate group in these system.

2. Experimental

A frequency-modulated, externally quenched super-regenerative oscillator (Schawlow 1954) has been employed to investigate the resonances. The resonance frequencies have been measured with an accuracy of ± 10 kHz using a Grunding frequency counter. The sample was cooled by nitrogen gas obtained by boiling liquid nitrogen. Copper-constantan thermocouple was used to measure the temperature with an accuracy of ± 1 K.

$\text{Ba}(\text{BrO}_3)_2 \cdot \text{H}_2\text{O}$ was prepared by the double decomposition of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ and KBrO_3 (Sneed and Brasted 1958). The other bromates, except $\text{Sr}(\text{BrO}_3)_2 \cdot \text{H}_2\text{O}$, were prepared by double decomposition of $\text{Ba}(\text{BrO}_3)_2 \cdot \text{H}_2\text{O}$ and the corresponding metal sulphate and later purified by recrystallization from water. $\text{Sr}(\text{BrO}_3)_2 \cdot \text{H}_2\text{O}$ was procured from Cerac, USA. Table 1 gives the ^{79}Br and ^{81}Br NQR frequencies in these systems measured at 77 and 305 K.

3. Theory of temperature variation of NQR frequencies

Bayer (1951) considered an axially symmetric field gradient tensor, where a simple torsional mode of vibration about the principal field gradient axis is assumed to be responsible for the averaging of the field gradient. Kushida modified this to include a number of lattice modes in the general case of non-axially symmetric field gradient. The temperature dependence of the NQR frequency as given by Kushida (1955) is

$$\nu_T = \nu_0 (1 + bT + c/T), \quad (1)$$

where

$$b = \frac{-3k}{2} \sum_{i=1}^M \frac{A_i}{\omega_i^2}, \quad (2)$$

and

$$c = -\frac{\hbar^2}{8K} \sum_{i=1}^M A_i.$$

Here $(A_i)^{-1}$ is the i th moment of inertia of the BrO_3^- group, ν_T is the NQR frequency at T K, ν_0 is the NQR frequency at 0 K and ω_i is the i th frequency of vibration of the BrO_3^-

Table 1. NQR frequencies of bromine in $\text{Cd}(\text{BrO}_3)_2 \cdot 2\text{H}_2\text{O}$, $\text{Sr}(\text{BrO}_3)_2 \cdot \text{H}_2\text{O}$, $\text{Ba}(\text{BrO}_3)_2 \cdot \text{H}_2\text{O}$, $\text{Zn}(\text{BrO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Mg}(\text{BrO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Ni}(\text{BrO}_3)_2 \cdot 6\text{H}_2\text{O}$.

System	Site	Temperature (K)	NQR frequency* (MHz)	
			^{79}Br	^{81}Br
$\text{Cd}(\text{BrO}_3)_2 \cdot 2\text{H}_2\text{O}$	Br(1)	305	174.48	145.76
		77	177.63	148.39
	Br(2)	305	174.37	145.67
		77	178.54	149.16
$\text{Sr}(\text{BrO}_3)_2 \cdot \text{H}_2\text{O}$		305	175.04	146.23
		77	177.24	148.07
$\text{Ba}(\text{BrO}_3)_2 \cdot \text{H}_2\text{O}$		305	173.55	144.99
		77	176.21	147.22
$\text{Zn}(\text{BrO}_3)_2 \cdot 6\text{H}_2\text{O}$		305	176.88	147.77
		77	181.24	151.41
$\text{Mg}(\text{BrO}_3)_2 \cdot 6\text{H}_2\text{O}$		305	176.15	147.16
		77	180.59	150.87
$\text{Ni}(\text{BrO}_3)_2 \cdot 6\text{H}_2\text{O}$		305	177.25	148.09
		77	181.25	151.49

* Accuracy of measurement ± 10 kHz.

group. The summation is carried out over the M modes which contribute significantly to the temperature dependence of NQR frequencies.

Following Brown (1960), the volume effects can be indirectly included by taking the temperature dependence of ω_i explicitly as

$$\omega_i = \omega_i^0 (1 - \alpha_i t), \quad (3)$$

where t is the temperature measured from any origin and ω_i^0 is the lattice frequency at $t = 0$. Ramamohan and Sobhanadri (1971) assumed a parabolic equation of the form

$$\omega_i = \omega_i^0 (1 - \alpha_i t - \beta_i t^2) \quad (4)$$

for the variation of the NQR frequency with temperature. A series of differentiations of (1) coupled with (3) or (4) yields the b_0 value, where b_0 is the b value at $t = 0$, from which the lattice frequency at $t = 0$ can be obtained if the moment of inertia is known. To find the derivatives, the experimental data are fitted to an equation of the form

$$v_t = a_0 + a_1 t + a_2 t^2. \quad (5)$$

By finding the value of the moment of inertia from the known geometry of the BrO_3^- group and determining the derivatives from the experimental data, the differentiations of (1) coupled with (3) or (4) can be solved to obtain b_0 , α and β . Using (3) or (4), the lattice frequencies at different temperatures can be calculated.

4. Experimental results and analysis of data

The variation in the NQR frequency of the ^{79}Br resonance is shown in figure 1 for $\text{Cd}(\text{BrO}_3)_2 \cdot 2\text{H}_2\text{O}$, $\text{Sr}(\text{BrO}_3)_2 \cdot \text{H}_2\text{O}$ and $\text{Ba}(\text{BrO}_3)_2 \cdot \text{H}_2\text{O}$ and in figure 2 for other

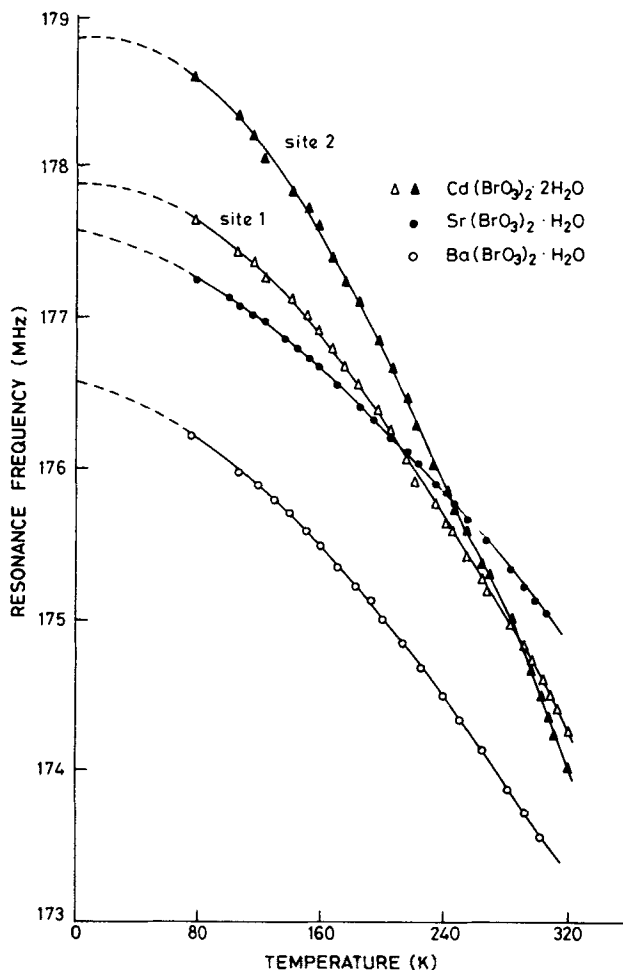


Figure 1. Temperature variation of ^{79}Br NQR frequency in $\text{Cd}(\text{BrO}_3)_2 \cdot 2\text{H}_2\text{O}$, $\text{Sr}(\text{BrO}_3)_2 \cdot \text{H}_2\text{O}$ and $\text{Ba}(\text{BrO}_3)_2 \cdot \text{H}_2\text{O}$.

bromates. The constants a_0 , a_1 and a_2 obtained for these bromates are tabulated in table 2. Following Kushida (1955), two torsional modes of vibration of the bromate group have been assumed to be responsible for the motional averaging of the EFG at the Br site. The Z axis is assumed to be normal to the oxygen plane, Y axis parallel to the line joining two oxygens and X axis mutually perpendicular to Y and Z axes. The moment of inertia of the BrO_3^- group has been calculated in these crystals from the geometry of the BrO_3^- group and the structural parameters of these crystals.

The unit cell of $\text{Cd}(\text{BrO}_3)_2 \cdot 2\text{H}_2\text{O}$ has the dimensions $a = 12.495 \text{ \AA}$, $b = 6.172 \text{ \AA}$ and $c = 9.24 \text{ \AA}$ (Satyanarayana Murty and Murty 1978), whereas in $\text{Sr}(\text{BrO}_3)_2 \cdot \text{H}_2\text{O}$ and $\text{Ba}(\text{BrO}_3)_2 \cdot \text{H}_2\text{O}$ the unit cell dimensions are $a = 9.06 \text{ \AA}$, $b = 7.97 \text{ \AA}$, $c = 9.66 \text{ \AA}$, $\beta = 93.5^\circ$ and $a = 12.703 \text{ \AA}$, $b = 7.609 \text{ \AA}$, $c = 9.375 \text{ \AA}$, $\beta = 135.71^\circ$ respectively (Sastry *et al* 1980; Kartha 1953). $\text{Zn}(\text{BrO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Mg}(\text{BrO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Ni}(\text{BrO}_3)_2 \cdot 6\text{H}_2\text{O}$ belong to cubic system with unit cell dimensions $a = 10.316 \text{ \AA}$, $a = 10.415 \text{ \AA}$ and $a = 10.3 \text{ \AA}$ respectively (Beevers 1936; Weigel 1963). The BrO_3^- groups

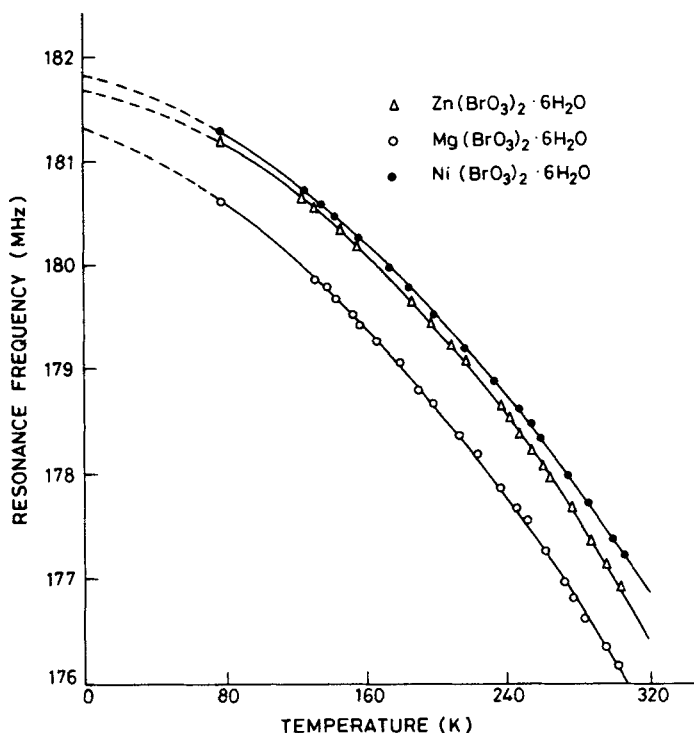


Figure 2. Temperature variation of ^{79}Br NQR frequency in $\text{Zn}(\text{BrO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Mg}(\text{BrO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Ni}(\text{BrO}_3)_2 \cdot 6\text{H}_2\text{O}$.

Table 2. Coefficients of the equation $\nu_i = a_0 + a_1t + a_2t^2$ that fits the temperature variation data.

System	Site	a_0 (MHz)	a_1 (MHz/deg)	$a_2 \times 10^4$ (MHz/(deg) ²)
$\text{Cd}(\text{BrO}_3)_2 \cdot 2\text{H}_2\text{O}$	Br(1)	175.5961 ± 0.0002	-0.0196 ± 0.0001	(-0.2620 ± 0.0005)
	Br(2)	174.5085 ± 0.0002	-0.0253 ± 0.0001	(-0.3181 ± 0.0005)
$\text{Sr}(\text{BrO}_3)_2 \cdot \text{H}_2\text{O}$		175.0944 ± 0.0002	-0.0131 ± 0.0001	(-0.1483 ± 0.0005)
$\text{Ba}(\text{BrO}_3)_2 \cdot \text{H}_2\text{O}$		173.5610 ± 0.0002	-0.0163 ± 0.0001	(-0.1971 ± 0.0005)
$\text{Zn}(\text{BrO}_3)_2 \cdot 6\text{H}_2\text{O}$		179.9510 ± 0.0002	-0.0309 ± 0.0001	(-0.5906 ± 0.0005)
$\text{Mg}(\text{BrO}_3)_2 \cdot 6\text{H}_2\text{O}$		176.2064 ± 0.0002	-0.0279 ± 0.0001	(-0.3716 ± 0.0005)
$\text{Ni}(\text{BrO}_3)_2 \cdot 6\text{H}_2\text{O}$		177.3508 ± 0.0002	-0.0252 ± 0.0001	(-0.4158 ± 0.0005)

in $\text{Cd}(\text{BrO}_3)_2 \cdot 2\text{H}_2\text{O}$, $\text{Sr}(\text{BrO}_3)_2 \cdot \text{H}_2\text{O}$ and $\text{Ba}(\text{BrO}_3)_2 \cdot \text{H}_2\text{O}$ form a tetrahedron with the three oxygens forming a triangle whereas in $\text{Zn}(\text{BrO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Mg}(\text{BrO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Ni}(\text{BrO}_3)_2 \cdot 6\text{H}_2\text{O}$ the three oxygens form an equilateral triangle. The moment of inertia about X and Y axes are nearly the same in these crystals and therefore the two torsional modes have been considered as two degenerate modes with the same frequency. The moment of inertia of the BrO_3^- group in these bromates has been calculated assuming different positions of the torsional axis below the centre of mass of the bromate group and the average of all the values has been taken. In $\text{Zn}(\text{BrO}_3)_2 \cdot 6\text{H}_2\text{O}$, for example, the moments of inertia about the centre of mass and

about the points which are at distances 0.3, 0.4, 0.5 and 0.667 Å (which is on the $O_1O_2O_3$ plane) from Br atom along the Z axis are 100.79, 101.27, 105.38, 113.70 and $136.90 \times 10^{-40} \text{ g cm}^2$ respectively and an average value of $111.63 \times 10^{-40} \text{ g cm}^2$ is taken in the present work. Similarly the average value has been used for other bromates. Knowing the values of the derivatives of the resonance frequency and the geometrical moment of inertia, solutions have been obtained for α , β and b_0 . The ω_i value has been obtained from b_0 and the temperature variation of the lattice frequencies has been plotted as shown in figures 3 and 4. The results obtained are shown in table 3.

5. Discussion

From figures 1 and 2, there is no indication of any phase transition in these systems. Negative temperature coefficients have been observed in all the cases. The lattice

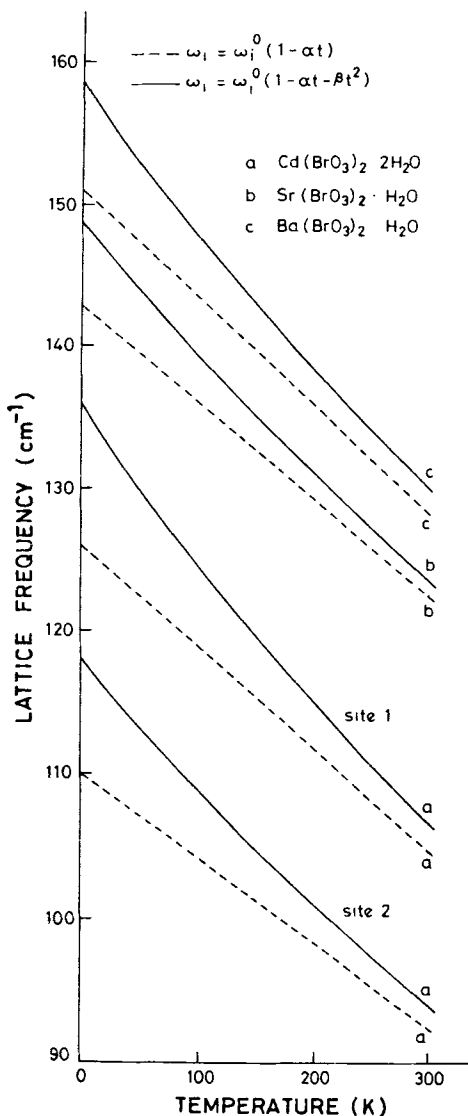


Figure 3. Variation of lattice frequency with temperature in $\text{Cd}(\text{BrO}_3)_2 \cdot 2\text{H}_2\text{O}$, $\text{Sr}(\text{BrO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Ba}(\text{BrO}_3)_2 \cdot \text{H}_2\text{O}$.

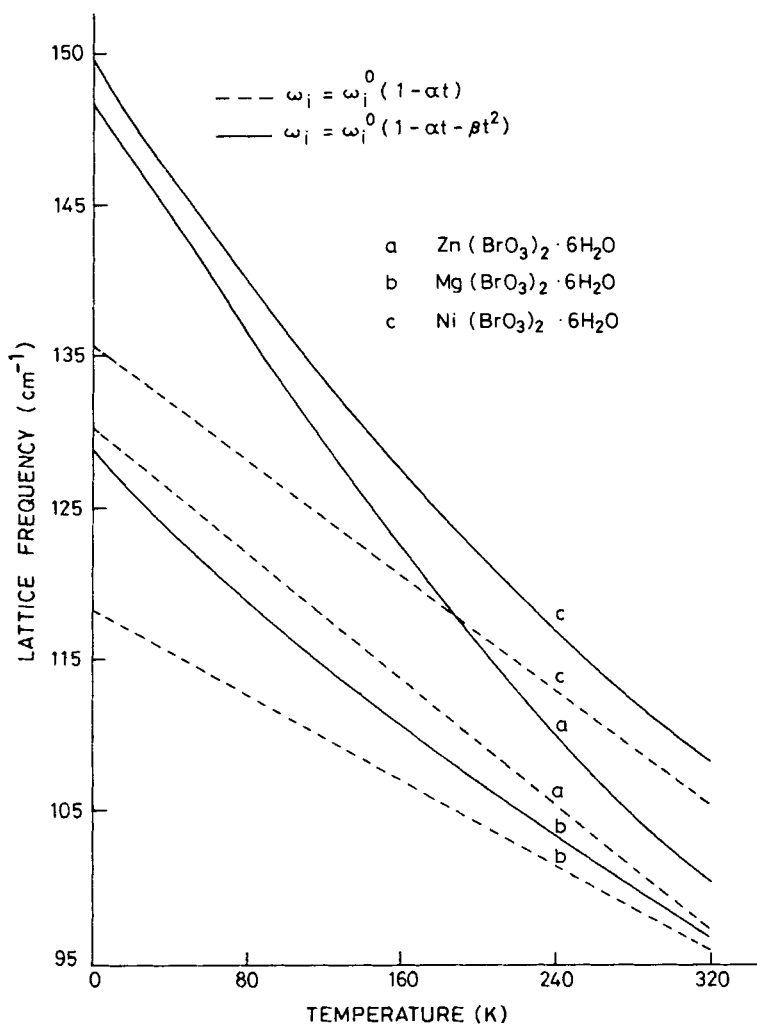


Figure 4. Variation of lattice frequency with temperature in $\text{Zn}(\text{BrO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Mg}(\text{BrO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Ni}(\text{BrO}_3)_2 \cdot 6\text{H}_2\text{O}$.

Table 3. Values of the lattice frequencies and the coefficients of their temperature variation in bromates.

System	Site	$A_i^{-1} \times 10^{40*}$ (g cm^2)	$\omega_i^{0\dagger}$ (cm^{-1})	ω_i^{0***} (cm^{-1})	$\alpha \times 10^{3\dagger}$ (MHz/deg)	$\alpha \times 10^{3**}$ (MHz/deg)	$\beta \times 10^{6***}$ (MHz/deg^2)
$\text{Cd}(\text{BrO}_3)_2 \cdot 2\text{H}_2\text{O}$	Br(1)	75	104.47	106.01	0.684	0.75	-0.590
	Br(2)	77	92.07	93.35	0.646	0.71	-0.536
$\text{Sr}(\text{BrO}_3)_2 \cdot \text{H}_2\text{O}$		76	124.05	125.14	0.553	0.59	-0.315
$\text{Ba}(\text{BrO}_3)_2 \cdot \text{H}_2\text{O}$		100	128.17	129.45	0.589	0.64	-0.369
$\text{Zn}(\text{BrO}_3)_2 \cdot 6\text{H}_2\text{O}$		111.63	99.36	102.19	1.040	1.20	-1.500
$\text{Mg}(\text{BrO}_3)_2 \cdot 6\text{H}_2\text{O}$		113.62	97.19	98.53	0.715	0.78	-0.680
$\text{Ni}(\text{BrO}_3)_2 \cdot 6\text{H}_2\text{O}$		110.01	107.55	110.01	0.883	1.00	-1.070

* Calculated from geometry; † Linear equation assumed for the variation of lattice frequency with temperature; ** Parabolic equation assumed for the variation of lattice frequency with temperature.

frequencies obtained for these systems are in the range 90–130 cm^{-1} . From the temperature study on ^{35}Cl resonance in $\text{Ca}(\text{ClO}_3)_2 \cdot 2\text{H}_2\text{O}$, $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$ and $\text{Sr}(\text{ClO}_3)_2$, Ramamohan and Sobhanadri (1971) have calculated the lattice frequencies of the chlorate group in the range 125–140 cm^{-1} . This suggests that the lattice frequencies of the chlorates and bromates lie almost in the same range.

Raman spectra of these bromates have been taken using Argon (488 nm) laser as the source (Valli 1981; Ramaprabhu 1983). Several low frequency modes are seen below 130 cm^{-1} probably corresponding to the torsional modes of the bromate group. However, the Raman lines have not been characterized to identify these precisely.

Both linear and parabolic temperature dependence of the lattice frequencies has been used to explain the volume effects that may accompany with temperature. However, there is no remarkable change in the results obtained.

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