Pressure Dependence of Chlorine NQR in Strontium Chlorate and Barium Chlorate Monohydrate*

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The pressure dependence of the ^{35}Cl-NQR frequencies in barium chlorate monohydrate and strontium chlorate, has been investigated up to 7000 kg cm^{-2}. $Ba(ClO_3)_2 \cdot H_2O$ shows a single ^{35}Cl-NQR line at 29.337 MHz ($T = 297$ K, $p = 1$ bar). $\nu(^{35}Cl)$ increases linearly with pressure in the range studied, with $(1/\nu)(\partial\nu/\partial p)_T = +0.409 \times 10^{-6}$ kg^{-1} cm^2 which is much smaller than observed in $NaClO_3$ and $KClO_3$. $Sr(ClO_3)_2$ also gave a single ^{35}Cl-NQR frequency at 20.105 MHz ($T = 297$ K, $p = 1$ bar). The pressure dependence is very small and negative in this case. The data in both cases have been analysed to obtain the volume dependence of the torsional frequency. It is pointed out that explicit pressure effects on the electric field gradient have to be taken into account to provide an explanation for the observed pressure dependence of $\nu(^{35}Cl)$.

Introduction

Chlorates are interesting in that they contain a partially covalent ClO_3 group within an ionic lattice. In an effort to understand the effect or pressure on metal chlorates, we have taken up an NQR investigation. The ^{35}Cl NQR frequency in chlorates generally lies in the frequency range 28–31 MHz. The grouping of the frequencies within a narrow range indicates that the electric field gradient, EFG, at the chlorine site is mainly due to the chlorate group.

We report here the pressure dependence at room temperature of ^{35}Cl NQR in $Ba(ClO_3)_2 \cdot H_2O$ and $Sr(ClO_3)_2$.

A home-made super-regenerative spectrometer operating in the range 20–40 MHz was used to record the signals. The frequency was measured using a BC 221 frequency meter. Hydrostatic pressure was generated using a lock-nut type piston cylinder device [1] and the teflon cell technique [2]. Liquid paraffin was used as the pressure transmitting medium. Pelletized powder samples were used.

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Results

a) Barium Chlorate Monohydrate

The ^{35}Cl NQR frequency in $Ba(ClO_3)_2 \cdot H_2O$ was measured at room temperature as a function of pressure up to a maximum pressure of 7 kbar. The frequency increases linearly with pressure; the pressure coefficient $1/\nu(\partial\nu/\partial p)_T$ is 0.409×10^{-6} kg^{-1} cm^2. This value is more than a factor of two smaller than those reported [3, 4] for sodium chlorate (0.95×10^{-6} kg^{-6} cm^2) and potassium chlorate (1.01×10^{-6} kg^{-1} cm^2).

The temperature derivatives of the NQR frequency at constant volume and constant pressure are related to the pressure derivative at constant temperature by the equation [4]

$$\left(\frac{\partial\nu}{\partial T}\right)_p = \left(\frac{\partial\nu}{\partial T}\right)_V - \frac{\alpha}{\beta}\left(\frac{\partial\nu}{\partial p}\right)_T . \quad (1)$$

The torsional oscillations of te ClO_3 group about the principal axes of the EFG tensor are simple harmonic and the torsional frequencies about the principal x and y axes are essentially equal, as the moments of inertia about the axes differ only by 2% [5]. We then obtain the high temperature limit [6].

$$\left(\frac{\partial\nu}{\partial T}\right)_V = \frac{-3\nu_0 k}{4\pi^2 I f_{rot}^2} , \quad (2)$$

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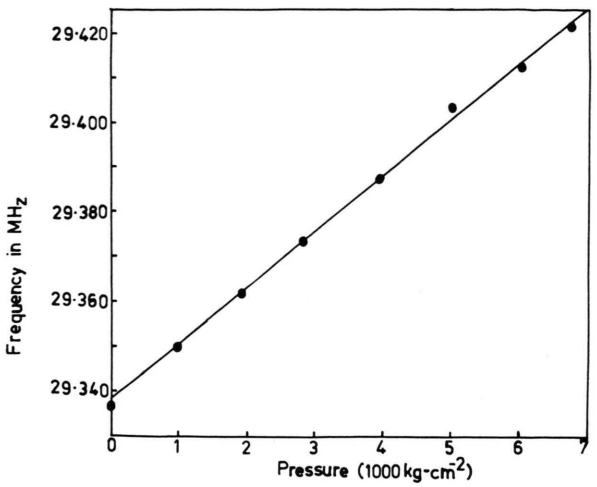

Fig. 1. Pressure dependence of ^{35}Cl NQR in $Ba(ClO_3)_2 \cdot H_2O$ at 297 K.

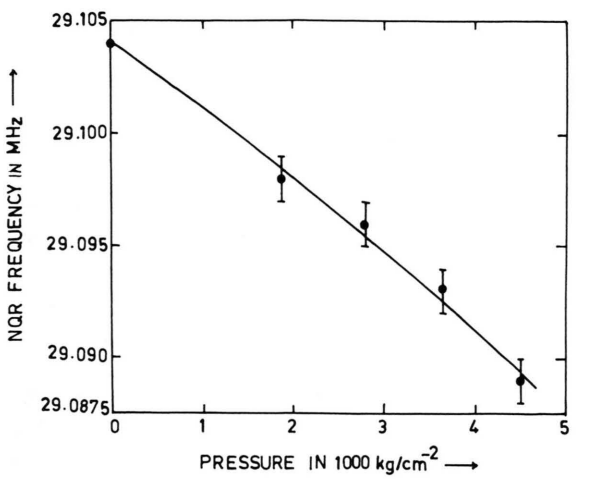

Fig. 2. Pressure dependence of ^{35}Cl NQR frequency in $Sr(ClO_3)_2$ at 297 K.

where ν_0 is the static NQR frequency, f_{rot} is the rotary mode frequency, and I is the moment of inertia about the x and y axis. α and β are the coefficients of thermal expansion and isothermal compressibility. Using (1) and (2), f_{rot} can be calculated if α/β is known. The ratio α/β falls in the range of 20 to 30 kg cm^{-2} K^{-1} for potassium and sodium chlorate [7, 8]. Assuming the ratio α/β to be of the same order in $Ba(ClO_3)_2 \cdot H_2O$, f_{rot} is found to be about 115 cm^{-1}. This value is in reasonable agreement with the value of 124 cm^{-1} obtained from the temperature variation of the NQR frequency [9].

In general, the shift in the NQR frequency with pressure arises primarily due to dynamic effects (i.e., due to changes in the amplitudes of the torsional modes). Static effects due to the molecules coming closer together are usually small at room temperature. In the high temperature approximation ($h\nu/kT \ll 1$), the NQR frequency can be written [3] as

$$\nu = a(V/V_0)^n [1 + b(V/V_0)^{2\gamma} T], \quad (3)$$

where the exponents n and γ represent the volume dependence of the static and dynamic contributions to the NQR frequency. Assuming the values of n and β in $Ba(ClO_3)_2 \cdot H_2O$ to be of the same order as those in $KClO_3$, the value of γ was found to be about half of that in $KClO_3$.

b) Strontium Chlorate

NQR experiments show a single line spectrum and a recent Zeeman NQR study indicates that the crystal is monoclinic with two molecules per unit cell and the asymmetry parameter is 0.176 ± 0.005 [3].

The ^{35}Cl NQR frequency of $Sr(ClO_3)$ was measured at room temperature as a function of pressure up to 4.5 kbar. The frequency decreases approximately linearly with pressure in contrast to the behaviour in other chlorates. The pressure coefficient is -0.1086×10^{-6} kg^{-1} cm^2, much smaller than those reported for other chlorates.

Using the procedure outlined earlier, f_{rot} has been calculated to be about 115 cm^{-1}, which compares well with the value of 118.8 cm^{-1} reported [9] for this compound. From the present study one can only infer that the dynamical effects which result in a positive pressure coefficient of the NQR frequency are overcome by more dominant static effects, indicating that intermolecular effects are important in strontium chlorate. Such a conclusion draws support from the observation that the asymmetry parameter in this compound deviates considerably from zero.

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