

Temperature and pressure dependence of the nuclear quadrupole interaction of ^{23}Na in NaClO_3 *

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Several investigations of the temperature and pressure dependence of the nuclear electric quadrupole interaction of ^{23}Na are particularly pertinent to the present study¹⁻⁴. The quadrupole coupling frequency of sodium in NaClO_3 has been measured at room temperature by Gutowsky and Williams¹ who report a value of 779.2 ± 4 kHz while Itoh and Kusaka² have reported a value of 801 ± 8 kHz. Gutowsky and Williams¹ also measured $\nu^{-1} \times (\partial\nu/\partial P)_T$ and $\nu^{-1} (\partial\nu/\partial T)_P$ for the sodium at room temperature and have reported values of $7.9 \times 10^{-6}/\text{bar}$ and $-4.2 \times 10^{-4}/\text{K}$, respectively. The purpose of this Note is

to present the results of recent measurements of the ^{23}Na quadrupole coupling frequency in NaClO_3 at atmospheric pressure from 4.2 to 340 K and at temperatures of 196, 296, 334, and 340 K from atmospheric pressure to 15 kpsi. and to analyze these measurements in the context of the work done by Gutowsky and Williams¹ and by Kushida, Benedek, and Bloembergen (KBB).⁵

The data were taken with a spectrometer described by Robinson⁶ and modified by Dutcher and Scott.⁷ The frequency measurements were conventional. The frequen-

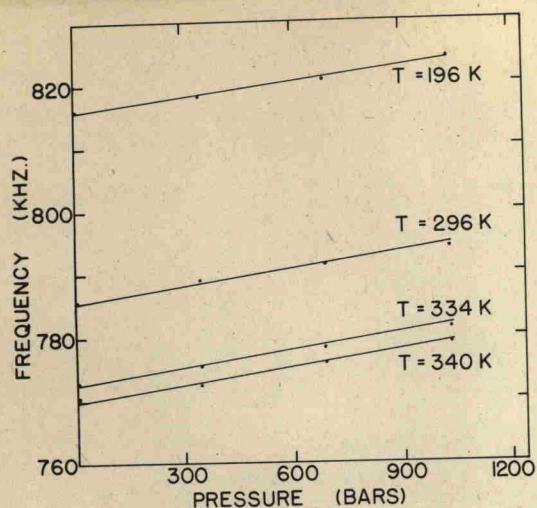


FIG. 1. Quadrupole frequency as a function of pressure at four temperatures.

cy vs temperature data were obtained in the manner described by Whidden, *et al.*⁴ The frequency versus pressure data were obtained utilizing a conventionally designed⁸ pressure bomb made of Be-Cu alloy and conventional pressure generation techniques.⁴ Our data gave a value of the quadrupole coupling frequency at room temperature and atmospheric pressure of 783 ± 0.8 kHz.

The thermal expansion coefficient and compressibilities required for the analysis have been extrapolated from the results of several workers.⁹⁻¹¹ From our pressure data, shown in Fig. 1, and the Mason⁹ data, $(V/\nu)(\partial\nu/\partial V)_T$ has been computed to yield -2.928 at 196 K, -2.805 at 296 K, -2.706 at 334 K, and -2.734 at 340 K. The different values result from using a temperature-dependent compressibility. These results are in much better agreement with the value of -2.5 found for NaBrO₃ by Whidden, *et al.*⁴ than the -1.9 reported by Gutowsky and Williams.¹ The large deviation of our result from that of Gutowsky and Williams¹ is due in part to the determination of the compressibility. Also, our data indicate a constant but larger value for $\nu^{-1}(\partial\nu/\partial P)_T$ of $10.6 \times 10^{-6}/\text{bar}$ compared to $7.9 \times 10^{-6}/\text{bar}$ previously reported.¹

The constant pressure data, shown by curve A in Fig. 2, were converted to constant volume using (1) compressibilities and expansion coefficient extrapolated from the results of Mason,⁹ Sharma,¹⁰ and Ganeson,¹¹ (2) an equation of state for the compressibility as suggested by KBB⁵ (curve C), and (3) the compressibility used by Gutowsky and Williams¹ (curve D). Our computed constant-volume curve (curve B) for NaClO₅ exhibits the same general features found by Whidden, *et al.*⁴ for NaBrO₃; this is consistent with the fact that two crystals are isomorphous.¹² Clearly, the shape of the

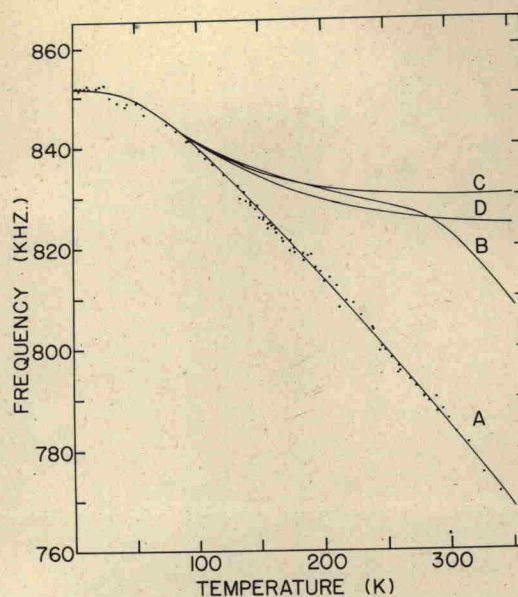


FIG. 2. Quadrupole frequency as a function of temperature for NaClO₅ (A) at atmospheric pressure, (B) at constant volume, V_0 , with the compressibility extrapolated from the results of Mason,⁹ (C) at constant volume, V_0 , with the compressibility given by an equation of state, and (D) at constant volume, V_0 , with a constant value for the compressibility given by Gutowsky and Williams.¹

constant-volume curve is very sensitive to the values chosen for the compressibility. Because of the unusual shapes of the constant-volume curves shown in Fig. 2, no attempt was made to fit them to the theoretical results of Bayer¹³ and Kushida.¹⁴

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