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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 study[1-4]. The quadrupole coupling frequency of sodium in $NaClO_3$ has been measured at room temperature by Gutowsky and Williams[1] who report a value of 779.2 ± 4 kHz while Itoh and Kusaka[2] have reported a value of 801 ± 8 kHz. Gutwosky and Williams[1] also measured $\nu^{-1} \times (\partial\nu/\partial P)_T$ and ν^{-1} $(\partial\nu/\partial T)_P$ for the sodium at room temperature and have reported values of 7.9×10^{-6}/bar and -4.2×10^{-4}/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 Williams[1] and by Kushida, Benedek, and Bloembergen (KBB).[5]

The data were taken with a spectrometer described by Robinson[6] and modified by Dutcher and Scott.[7] The frequency measurements were conventional. The frequen-

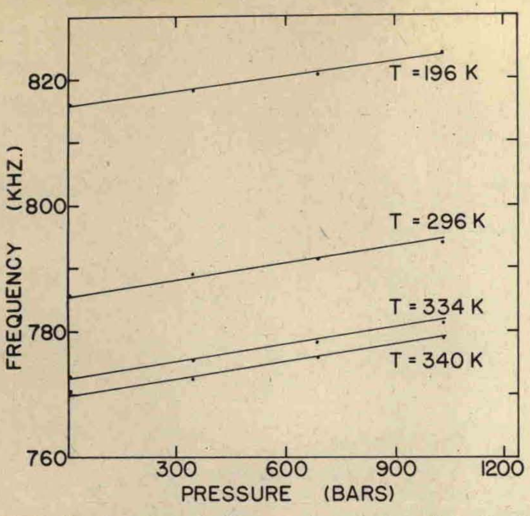

FIG. 1. Quadrupole frequency as a function of pressure at four temperatures.

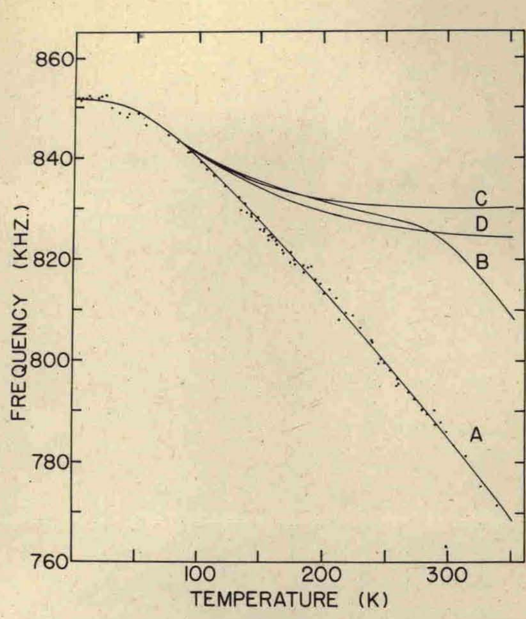

FIG. 2. Quadrupole frequency as a function of temperature for $NaClO_3$ (A) at atmospheric pressure, (B) at constant volume, V_0, with the compressibility extrapolated from the results of Mason,[9] (C) at constant volume, V_0, with the compressibility given by an equation of state, and (D) at constant volume, V_0, with a constant value for the compressibility given by Gutowsky and Williams.[1]

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 designed[8] 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 Mason[9] 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 $NaBrO_3$ 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 Williams[1] 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 10.6×10^{-6}/bar compared to 7.9×10^{-6}/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 KBB[5] (curve C), and (3) the compressibility used by Gutowsky and Williams[1] (curve D). Our computed constant-volume curve (curve B) for $NaClO_5$ exhibits the same general features found by Whidden, *et al.*[4] for $NaBrO_3$; this is consistent with the fact that two crystals are isomorphous.[12] Clearly, the shape of the 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 Bayer[13] and Kushida.[14]

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