

system to lose lock. On the other hand, if  $C_3$  is small compared to  $C_v$  the sensitivity of the servo is reduced.

After the spectrometer has been adjusted for maximum signal-to-noise and the bucking voltage properly set, the servo is locked to the center of the resonance line. In  $\text{KClO}_3$  the signal-to-noise is about 60:1 at room temperature and the line width [9] is about 500 Hz. The phase on the lock-in detector is then adjusted for proper servo control. Depending on the signal to noise it may be necessary to readjust the gain and time constant to stabilize the servo loop gain.

In principle the servo amplifier is capable of tracking over its entire frequency range. In our experiment, however, a large sudden pressure change, corresponding to frequency increments of the order of 30 KHz, would cause the servo to become unlocked from the center of the resonance line, where as a gradual pressure change usually did not affect the lock. On the other hand, if the sample was near thermal equilibrium, the spectrometer, once locked to the resonance, would remain in the locked mode for several hours. The reason for the loss of lock is probably due to inhomogenous broadening of the resonance line associated with the temperature gradients at the sample resulting from the sudden change in pressure

$\left(\frac{\partial f}{\partial T}\right)_P = 5 \text{ KHz}/^\circ\text{C}$ . In those cases where the servo amplifier became unlocked from the resonance signal it could easily be relocked manually to the center of the resonance line after a few minutes.

#### 4. Applications

The NQR spectrometer described thus far could be adapted to any system in which perturbations on the system result in a shift of the NQR frequency. In the case where pressure is used as the perturbation many special problems must also be considered, namely, (1) a low loss feed-through, capable of withstanding high pressure is required in order to get the r-f signal inside the pressure vessel, (2) due to the small working volume, sample size must be kept to a minimum, and (3) depending on temperature sensitivity of the sample, temperature control must be strictly maintained. The latter is perhaps the most difficult problem to deal with.

We have solved some of these problems with reasonable success. The pressure vessel is a commercially available unit [15] and the r-f leads are brought out through a high pressure electrical feedthrough similar to that described by Heydemann [16]. This arrangement has worked satisfactorily for pressures up to 2 kbar. The sample chamber in this pressure vessel is about 25 mm in diameter by 75-mm long and our sample is a cylinder 5 mm in diameter and 10-mm long. By keeping the coil winding diameter small compared to the diameter of the sample chamber the decrease in inductance due to shielding is kept to a minimum.

The temperature dependence of the NQR frequency of  $^{35}\text{Cl}$  in  $\text{KClO}_3$  is considerably larger than the pressure dependence. For this reason we immersed the pressure vessel in a temperature-regulated oil bath. The temperature control was of the order of  $\pm 0.015^\circ\text{C}$ , measured in

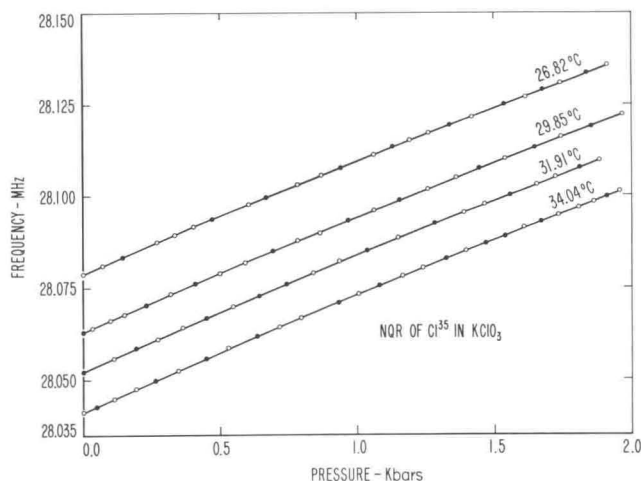


FIGURE 5. Plot of frequency-pressure-temperature data for  $^{35}\text{Cl}$  in  $\text{KClO}_3$ .

The temperature of each curve was determined by comparing the observed NQR frequency at zero pressure with the Spline fitting given by Utton [8]. Open circles indicate increasing values; solid circles, decreasing values.

the bath, over a 24-hr period corresponding to about 75 Hz or  $\pm 2.5$  bars at room temperature.

The stability of the oscillator was determined using a Systron and Donner 1037 frequency counter which was calibrated against an NBS standard frequency. After a 1-hr warm-up period the short term stability of this oscillator, when unlocked, is within  $\pm 3$  Hz; the long-term stability is of the order of  $\pm 100$  Hz. The stability of the spectrometer when locked to a resonance depends on the stability of the oscillator and on the sample temperature control. The short term stability in the locked mode, with the pressure vessel and sample immersed in the oil bath, is within  $\pm 5$  Hz where 5 Hz is the standard deviation of twenty 1-s frequency counts. The long term stability in the locked mode is of the order of  $\pm 45$  Hz, although this includes slight temperature drifts.

Samples were prepared by slow recrystallization to improve the sample purity as described by Utton [17]. A plot of the  $^{35}\text{Cl}$  NQR frequency as a function of pressure is shown in figure 5. The data shown here are the results of preliminary experiments for the purpose of determining the feasibility of using NQR as a pressure measuring device. The choice of  $\text{KClO}_3$  as a possible material for pressures less than 6 kbar stems from the good signal-to-noise ratio and narrow line width of the  $^{35}\text{Cl}$  resonance, as well as a lack of frequency hysteresis with temperature [8].  $\text{KClO}_3$  would not be an acceptable material for a larger pressure range due to a phase transition at 6 kbar [18] at room temperature. The values used for pressure were recorded from a 0-40,000 psi bourdon tube gage [19] and are believed to be accurate to  $\pm 40$  psi. The accuracy to which the NQR frequency can be recorded is  $\pm 5$  Hz. However, due to the large temperature coefficient in  $\text{KClO}_3$ , and the regulation of the oil bath, ( $\pm 0.015^\circ\text{C}$ ), the estimated uncertainty due to temperature instability is  $\pm 75$  Hz. Hence the total estimated uncertainty in the frequency for a given pressure and temperature is 160 Hz or 5.3 bars. The value of tempera-



ture assigned to each curve was determined by comparing the NQR frequency at zero pressure to the temperature data given by Utton [8]. As previously mentioned this type of temperature measurement is accurate to  $\pm 0.001$  °C. Since we were interested in small temperature changes, a thermopile consisting of four junctions was used. Fluctuations in temperature were then monitored based on the changes in thermopile EMF. At any temperature the data points, plotted in figure 5, are from both increasing and decreasing pressures. The increasing pressure points are denoted by open circles and the decreasing points by solid circles. For each data point the value of the NQR frequency, pressure, and thermopile EMF, was recorded. The data points shown on the isotherms of figure 4 are normalized to the given temperature which means that although the real data points included small temperature variations, corrections of 4.90 KHz/°C were applied for adjustment; deviations between the line drawn and these values did not exceed 50 Hz. Along the lines of constant pressure the temperature coefficient calculated from the data was found to be 4.93 KHz/°C below 6000 psi and 4.86 KHz/°C at the 2 kbar limit. Qualitatively, this difference agrees with the change in the temperature coefficient with pressure indicated by Benedek et al. [3]. Furthermore, the data shown here demonstrate that  $\text{KClO}_3$  exhibit no detectable hysteresis in this pressure range.

The results of our preliminary investigation clearly indicate that nuclear quadrupole resonance can be used as a pressure measuring technique. However, substantial progress towards establishing temperature-pressure-frequency curves will depend on more accurate pressure measurements and on controlling temperature more carefully. Experiments are presently in progress towards improving the temperature regulation of the oil bath to  $\pm 0.001$  °C. We are also considering other materials which have a much smaller temperature coefficient than

$\text{KClO}_3$ . Improving the accuracy of the pressure measurement can only be accomplished by using a more accurate pressure standard such as a piston gage.

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## 5. References

- [1] Bayer, H., *Z. Physik* **130**, 227 (1951).
- [2] Kushida, T., Benedek, G., and Bloembergen, N., *Phys. Rev.* **104**, 1364 (1956).
- [2a] Livingston, R., and Beldes, *Mol. Phys.* **3**, 501-524, D. Williams, Ed. (1962).
- [3] Benedek, G., and Kushida, T., *Rev. Sci. Instr.* **28**, 92, (1957).
- [4] Dean, C., and Pound, R. V., *J. Chem. Phys.* **20**, 195 (1952).
- [5] Vanier, J., *Can. J. Phys.* **38**, 1397 (1960).
- [6] Vanier, J., *Metrologia* **1**, 135 (1965).
- [7] Volpicelli, R. J., Nageswara Rao, B. D., and Baldeschwieler, J. D., *Rev. Sci. Instr.* **36**, 150 (1965).
- [8] Utton, D. B., *International Journal of Scientific Metrology* **3**, No. 4, 98 (1967).
- [9] Heydemann, Peter L. M., Private communication.
- [10] Watkins, G., Thesis Howard University, 1952, Pound, R. V., and Knight, W. D., *Rev. Sci. Instr.* **21**, 219 (1959).
- [11] Robinson, F. N. H., *J. Sci. Instr.* **36**, 481 (1959).
- [12] Valley, G. E., Jr., Wallman, H., M.I.T. Radiation Laboratory Series **18**, 166 (1964).
- [13] Systron-Donner SD-1037B4D1F.
- [14] Honeywell Amplifier #361925.
- [15] The pressure vessel was on loan from Dr. P. L. M. Heydemann.
- [16] Heydemann, P. L. M., *Rev. Sci. Instr.* **38**, 558 (1967).
- [17] Utton, D. B., *J. Res. Nat. Bur. Stand. (U.S.)*, 71A (Phys. and Chem.), No. 2, 125 (March-Apr. 1967).
- [18] Bridgman, P. W., *Proc. Am. Acad. Sci.* **51**, 55 (1915).
- [19] Heise Bourdon Tube Co. Inc., Newtown, Conn.

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