The frequencies of the transitions between adjacent energy levels can therefore be written

[3] $\qquad v_i = r_i(\eta)(eqQ)/24h$

where $r_i(\eta)$ is the difference between two adjacent roots of eq. 2. In the following, $i = 1$ refers to the $\pm 1/2 \leftrightarrow \pm 3/2$ transition and $i = 2$ refers to the $\pm 3/2 \leftrightarrow \pm 5/2$ transition; in BiCl$_3$ these transitions occur near 31.8 and 25.1 MHz, respectively (2), and are the transitions which were measured as a function of temperature and pressure. The frequencies were found to be linear functions of the temperature and pressure over the ranges investigated, and the subsequent analysis was therefore carried out in terms of the derivatives $(\partial v_i/\partial T)_P$ and $(\partial v_i/\partial P)_T$. Using eq. 3 these derivatives can be written

[4] $\qquad \left(\dfrac{\partial v_i}{\partial T}\right)_P = \dfrac{r_i(\eta)}{24h}\left(\dfrac{\partial eqQ}{\partial T}\right)_P + \dfrac{dr_i}{d\eta}\left(\dfrac{\partial \eta}{\partial T}\right)_P \dfrac{eqQ}{24h}$

[5] $\qquad \left(\dfrac{\partial v_i}{\partial P}\right)_T = \dfrac{r_i(\eta)}{24h}\left(\dfrac{\partial eqQ}{\partial P}\right)_T + \dfrac{dr_i}{d\eta}\left(\dfrac{\partial \eta}{\partial P}\right)_T \dfrac{eqQ}{24h}$

The derivatives $dr_i/d\eta$ are calculated from differences of the derivatives $dx/d\eta$, which are obtained from setting the total derivative of $f(x, \eta)$ equal to zero.

[6] $\qquad \dfrac{dx}{d\eta} = -\left(\dfrac{\partial f}{\partial \eta}\right) \bigg/ \left(\dfrac{\partial f}{\partial x}\right)$

In evaluating r_i and its derivatives, the value of η at room temperature was used. When $(\partial v_i/\partial T)_P$ is known for two resonances, eq. 4 may be solved simultaneously for $(\partial eqQ/\partial T)_P$ and $(\partial \eta/\partial T)_P$, and similarly for the pressure derivatives. It is advantageous to measure the $\pm 1/2 \rightarrow \pm 3/2$ transition no matter which of the other three transitions is measured, for the frequency of this transition varies strongly with the value of η; the frequencies of the other transitions are less sensitive to the value of η and reflect changes in the coupling constant more directly.

Experimental

Spectra were recorded with a self-quenched superregenerative spectrometer similar to that described by Dean (7); for frequency measurements it was found advantageous to remove the coherence feedback control function in order to allow quick manual change in the quench conditions. Frequency modulation and lock-in detection were used to record the resonances on a chart recorder; the shape of the resonances recorded was complex but was not affected by changes of temperature or pressure so that shifts in the resonance frequency could be measured consistently.

Frequency measurement was performed as follows. The unquenched, unmodulated oscillator was driven slowly in frequency by a synchronous motor, and its frequency as measured by a frequency counter was recorded regularly on the chart record; as the frequency of the oscillator approached the resonance the quench and modulation were switched on, and the resonance was recorded. After the resonance had been passed, further frequency measurements on the unquenched, unmodulated oscillator were recorded. The recorded frequency was fitted to a least squares parabolic function of displacement along the record, and the resonance frequency calculated from this function. A correction for the shift in oscillator frequency with grid time constant was applied by also recording the zero beat of the quenched modulated oscillator with an appropriate harmonic of 100 kHz derived from the frequency counter, either before or after the resonance was recorded; the correction was generally less than 10 kHz. Individual frequency measurements made by this technique appear to be repeatable to within several kHz.

The bomb used for the high pressure measurements was of conventional design, with an O-ring seal which was satisfactory up to a pressure of about 275 MNm^{-2}. The coned electrical seal was insulated with epoxy resin. The pressure coefficients of the resonances were large enough that it was not necessary to carry the measurements to very high pressures, the highest pressure used being about 140 MNm^{-2}; vacuum pump oil was used as a hydraulic medium. The powdered sample was mixed with oil and placed inside a short section of drinking straw with the ends sealed with wax, in order to prevent contact with the stainless steel bomb. The coil of the oscillator was a close fit around the sample. The bomb was thermally insulated, and its temperature was recorded; some temperature drift occurred during the measurements and the frequencies were corrected to 25.0 °C later using the measured temperature dependence.

The temperature dependence was measured using a sample sealed under vacuum. The temperature was varied between 0 and 50 °C using a refrigerated thermostat; the temperature was measured with a mercury thermometer which was compared with a calibrated thermometer in a separate experiment.

Bismuth trichloride from the Matheson, Coleman and Bell Company was dried *in vacuo* at 100 °C over phosphorus pentoxide, before being sealed in an evacuated sample tube, or mixed with oil in a dry atmosphere.

Results and Discussion

The frequencies of both resonances varied linearly with both pressure and temperature over the restricted ranges investigated, with the following coefficients. For the 31.8 MHz resonance,

$$\left(\frac{\partial v_1}{\partial T}\right)_P = -10.42 \pm 0.06 \text{ kHz K}^{-1}$$

$$\left(\frac{\partial v_1}{\partial P}\right)_T = +1.36 \pm 0.02 \text{ kHz (MN m}^{-2})^{-1}$$

and for the 25.1 MHz resonance

$$\left(\frac{\partial v_2}{\partial T}\right)_P = -4.46 \pm 0.03 \text{ kHz K}^{-1}$$

$$\left(\frac{\partial v_2}{\partial P}\right)_T = -1.720 \pm 0.008 \text{ kHz (MN m}^{-2})^{-1}$$

The pressure coefficients refer to a temperature of 25 °C. The extrapolated zero pressure frequencies measured for the sample in the high pressure bomb were $31\ 878.3 \pm 1.1$ and $25\ 137.3 \pm 0.7$ kHz, respectively, while the measurements on the larger sample *in vacuo* at the same temperature (25 °C) were $31\ 893.8 \pm 2.0$ and $25\ 136.6 \pm 0.9$ kHz, respectively; the value of η derived from these measurements is 0.5544 ± 0.0002, and the quadrupole coupling constant is 318.70 ± 0.15 MHz. The two measurements of the lower frequency resonance are in good agreement, but there is a discrepancy of about 15 kHz in the results for the higher frequency; the latter line was weaker than the former, and the assignment of the central point of the resonance pattern for the sample in the bomb may have been in error, without affecting the value of the derivatives. Substituting these values into eqs. 4 and 5 and solving, the temperature and pressure derivatives of the coupling constant and asymmetry parameter are found to be

$$\frac{1}{h}\left(\frac{\partial eqQ}{\partial T}\right)_P = -40.6 \pm 0.7 \text{ kHz K}^{-1}$$

$$\frac{1}{h}\left(\frac{\partial eqQ}{\partial P}\right)_T = -33.6 \pm 0.2 \text{ kHz (MN m}^{-2})^{-1}$$

$$\left(\frac{\partial \eta}{\partial T}\right)_P = -(1.54 \pm 0.03) \times 10^{-4} \text{ K}^{-1}$$

$$\left(\frac{\partial \eta}{\partial P}\right)_T = +(1.15 \pm 0.07)$$
$$\times 10^{-4} \text{ (MN m}^{-2})^{-1}$$

These results may be combined in an analysis following the method of Kushida *et al.* (1); the parameters q and η of the electric field gradient tensor are assumed to depend explicitly upon the volume V of a fixed amount of solid, as well as the temperature:

[7]
$$q = q(T, V)$$
$$\eta = \eta(T, V)$$

These are fairly drastic assumptions, for it is implied that the effects of thermal expansion and hydrostatic pressure upon the electric field gradient tensor are functions of a single variable, the volume; in a rigorous analysis of a complex crystal, changes of shape and atomic positions within the unit cell must be included as well as the volume, but it is not practical to carry out such an analysis at present. Within the approximations implied by eq. 7, it is found that

[8]
$$\left(\frac{\partial q}{\partial T}\right)_P = -\frac{\alpha}{\beta}\left(\frac{\partial q}{\partial P}\right)_T + \left(\frac{\partial q}{\partial T}\right)_V$$

[9]
$$\left(\frac{\partial \eta}{\partial T}\right)_P = -\frac{\alpha}{\beta}\left(\frac{\partial \eta}{\partial P}\right)_T + \left(\frac{\partial \eta}{\partial T}\right)_V$$

where $\alpha = (1/V)(\partial V/\partial T)_P$ is the coefficient of bulk thermal expansion, and $\beta = -(1/V)(\partial V/\partial P)_T$ is the isothermal compressibility. The value of α has been reported (6) as 2.8×10^{-4} K^{-1}, but the compressibility does not appear to have been measured, and so an approximate value of α/β based upon the Gruneisen–Mie equation of state for solids (8) will be used

[10]
$$\alpha/\beta = \gamma \bar{C}_V/\bar{V}$$

where γ is the Gruneisen constant, generally between 1 and 2, $\bar{C}_V$ is the molar specific heat at constant volume, and $\bar{V}$ is the molar volume. Since $\bar{C}_V$ is not available experimentally, $\bar{C}_p$ may be used together with $\gamma = 2$ to calculate an estimated upper limit for α/β. For BiCl$_3$, $\bar{C}_p = 109$ J K^{-1} mol^{-1} (9) and $\bar{V} = 66 \times 10^{-6}$ m^3 (4), yielding a value $\alpha/\beta \lesssim 3.3$ MNm^{-2} K^{-1}. The compressibility derived from this estimate and the measured value of the thermal expansion coefficient is $\beta \gtrsim 0.8 \times 10^{-4}$ (MNm^{-2})$^{-1}$.

The temperature derivatives of the electric field gradient parameters at constant volume can now be estimated from eqs. 8 and 9

$$\frac{1}{h}\left(\frac{\partial eqQ}{\partial T}\right)_V \cong -150 \text{ kHz K}^{-1}$$

$$\left(\frac{\partial \eta}{\partial T}\right)_V \cong +2 \times 10^{-4} \text{ K}^{-1}$$

The value of $(\partial\eta/\partial T)_V$ is very uncertain, since two terms of opposite sign and comparable magnitude are added together and the uncertainty in the value of α/β is consequently magnified; no further quantitative analysis of the data on the asymmetry parameter is justified.