

Fig. 2. The Raman spectrum of CCl_4 from $400\text{--}500\text{ cm}^{-1}$. Laser wavelength, 488 nm . Laser power, 200 mW . Slit width, 1 cm^{-1} . Full scale intensity corresponds to 2×10^3 counts. Scan speed, $20\text{ cm}^{-1}\text{min}^{-1}$.

(a). Spectrum of CCl_4 contained in the high pressure cell at 0.262 kbar and 24.8°C .
 (b). Spectrum of CCl_4 contained in a glass cuvette using 90° collection optics at ambient pressure and 25.0°C .

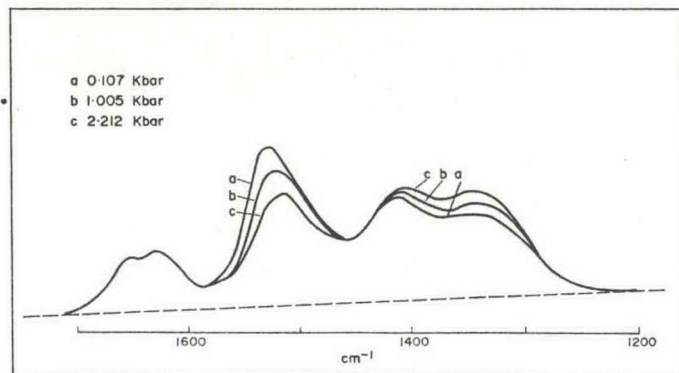


Fig. 3. The Raman spectrum of a 1.05 M aqueous thorium nitrate solution, $1200\text{--}1700\text{ cm}^{-1}$, at various pressures. Laser power 120 mW . Laser wavelength, 488 nm . Slit width, 11 cm^{-1} . Full scale intensity corresponds to 5×10^4 counts/sec. Scan speed, $20\text{ cm}^{-1}\text{min}^{-1}$. Temperature, 25.2°C .

nitrate illustrates how this technique may be used to study the pressure dependence of complex equilibria. Consider the complex equilibrium involving the formation of MX from ions M^+ and X^- . Electrostriction effects will in general lead one to conclude that the sum of the partial molar volumes of the ions will be less than the partial molar volume of the complex species [17]. Therefore, an increase in pressure will favour the dissociation of the complex MX . Conductivity studies tabulated by HORNE support this conclusion, e.g. the ratio of the dissociation constant at 1 kbar relative to the 0.001 kbar value for FeCl_2^{2+} is 10, and for MgSO_4 is 1.5 [18]. The variation of spectral intensity of part of the Raman spectrum of thorium nitrate is shown in Fig. 3. The region between 1200 and 1600 cm^{-1} may be assigned to fundamental modes of vibration of solvated and complexed nitrate ions [19, 20]. The contour between 1200 and 1450 cm^{-1} , which may be ascribed to solvated nitrate ion, increases in intensity with increase in pressure. This effect may be contrasted with the decrease in intensity of the band at 1527 cm^{-1} , ascribed to complexed nitrate ion, with increase in pressure. These observations are interpreted in terms of the dissociation of complex nitrate-thorium species with increase of pressure. Consistent intensity variations are obtained for both rising and falling pressure.

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