

Fig. 2. The Raman spectrum of  $\text{CCl}_4$  from  $400\text{--}500\text{ cm}^{-1}$ . Laser wavelength,  $488\text{ nm}$ . Laser power,  $200\text{ mW}$ . Slit width,  $1\text{ cm}^{-1}$ . Full scale intensity corresponds to  $2 \times 10^3$  counts. Scan speed,  $20\text{ cm}^{-1}\text{min}^{-1}$ .  
 (a). Spectrum of  $\text{CCl}_4$  contained in the high pressure cell at  $0.262\text{ kbar}$  and  $24.8^\circ\text{C}$ .  
 (b). Spectrum of  $\text{CCl}_4$  contained in a glass cuvette using  $90^\circ$  collection optics at ambient pressure and  $25.0^\circ\text{C}$ .

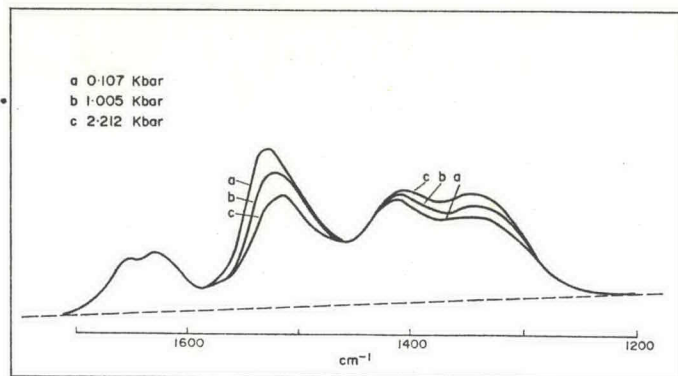


Fig. 3. The Raman spectrum of a  $1.05\text{ M}$  aqueous thorium nitrate solution,  $1200\text{--}1700\text{ cm}^{-1}$ , at various pressures. Laser power  $120\text{ mW}$ . Laser wavelength,  $488\text{ nm}$ . Slit width,  $11\text{ cm}^{-1}$ . Full scale intensity corresponds to  $5 \times 10^4$ 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

nitrate illustrates how this technique may be used to study the pressure dependence of complex equilibria. Consider the complex equilibrium involving the formation of  $\text{MX}$  from ions  $\text{M}^+$  and  $\text{X}^-$ . 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  $\text{MX}$ . Conductivity studies tabulated by HORNE support this conclusion, e.g. the ratio of the dissociation constant at  $1\text{ kbar}$  relative to the  $0.001\text{ kbar}$  value for  $\text{FeCl}_2^{2+}$  is 10, and for  $\text{MgSO}_4$  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  $1600\text{ cm}^{-1}$  may be assigned to fundamental modes of vibration of solvated and complexed nitrate ions [19, 20]. The contour between  $1200$  and  $1450\text{ cm}^{-1}$ , 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  $1527\text{ cm}^{-1}$ , 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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