

The complex formed between niobium tetrafluoride and pyridine is a black compound, whose Raman spectrum has been obtained using He/Ne excitation⁴³⁷. Comparison of the low frequency infrared and Raman spectra suggests that the complex has the *trans*-NbF₄ · 2py structure.

The Raman spectra of single crystals of graphite and other graphite materials have been obtained using blue Ar⁺ 4880 Å excitation⁴³⁸ (Fig. 9). Single crystals of graphite show a single band at 1575 cm⁻¹. Other materials like stress-annealed pyrolytic graphite, commercial graphites, activated charcoal, lampblack and vitreous carbon, give an additional band at 1355 cm⁻¹. The intensity of the additional band is inversely proportional to the crystallite size and can be used to estimate the crystallite size in the surface layer of any carbon sample.

The compounds Re₂(O₂CCH₃)₂Cl₄ · 2H₂O and Re₂(O₂CCH₃)₂Br₄ · 2H₂O are extremely dark blue and dark green, respectively, so much so that in bulk they appear to be black compounds. The Raman spectra have been obtained using Kr 6471 Å excitation⁴³⁹. The spectra contain a strong band at 280 cm⁻¹, which is possibly due to the vibrational mode of the Re-Re bond, which is thought to have a bond order of the order of four.

3. PRESSURE CHANGES

Lippincott et al.⁴⁴⁰ first described a high-pressure diamond anvil cell for use in infrared spectroscopy in 1959. During the period under review, this type of cell has been adapted for use in Raman and far-infrared spectroscopy and a number of interesting pressure-induced changes have been reported.

Several publications have appeared concerned with the effect of pressure on far-infrared spectra. It has been shown that the internal modes of vibration of a polyatomic species show only small minor shifts under high pressure, while lattice modes show much larger shifts¹². Thus the ν₄(f₂) band of Na₂SO₄ at 622 cm⁻¹ is displaced to 625 cm⁻¹ on increasing the pressure to 35,000 atm, while the lattice mode at 183 cm⁻¹ shifts to 235 cm⁻¹. It has also been observed that changes in band shapes and intensities occur; in general, bands become broader with increasing pressure^{441,442}.

Pressure effects (up to 50,000 atm) upon the symmetric and antisymmetric metal halogen stretching modes of coordination compounds have been measured (ref. 443) (Fig. 10). The frequencies are relatively insensitive to pressure, but the intensities of the symmetric bands decrease to a much greater extent than the intensities of the antisymmetric bands. This technique has thus been proposed as a method of distinguishing symmetric and antisymmetric metal-halogen stretching modes.

The red → yellow phase transition in mercuric iodide can be induced at a pressure of 13 kilobars. This transition has been followed using Raman spectroscopy.

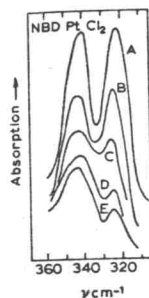


Fig. 10. Pt-Cl stretching bands as a function of pressure in (NBD)PtCl₂, a square-planar structure. (NBD = norbornadiene) Curves are displaced vertically: (A) atmospheric pressure (341.322 cm⁻¹); (B) 6000 atm (345.325 cm⁻¹); (C) 12,000 atm (343.326 cm⁻¹); (D) 18,000 atm (343.326 cm⁻¹); (E) 24,000 atm (345.325 cm⁻¹). (Reproduced from C. Postmus, K. Nakamoto and J. R. Ferraro, *Inorg. Chem.*, 6 (1967) 2194.)

copy^{444,445} and the spectral changes are similar to those observed during the temperature-induced⁷⁸ red → yellow phase transition at 126 °C. The effect of pressure on the Raman spectrum of α-quartz has been reported⁴⁴⁶, together with the pressure-induced phase transition in thallos iodide⁴⁴⁷.

The effect of pressure on the infrared spectra of coordination^{448,449} complexes containing (CH₃)₂S, pyrazine and 2,2'-bipyridyl have been observed. It is found that certain molecular vibrations of the ligands are much more pressure sensitive than others. The frequencies of the lattice modes of square planar and octahedral platinum and palladium compounds have been found to be much more pressure dependent than the frequencies of the internal modes⁴⁵⁰. A high-pressure spectroscopic study of hydrogen-bonded compounds has shown that increasing pressure shortens the hydrogen bond^{451,452}.

Pressure studies on calcium carbonate indicate that a new polymorph is produced at pressures greater than 50 kilobars having a vaterite-type structure⁴⁵³. Trioxane is thought to undergo a change in molecular conformation from C_{3v} to D_{3h} at high pressure⁴⁵⁴.

The liquid and solid phase Raman spectra of Br₂ and CS₂ have been obtained at high pressure⁴⁵⁵. Single crystals of three polymorphs of CH₃CN and CD₃CN have been studied at high pressure and the data have been used to predict likely crystal structures for the three crystalline phases⁴⁵⁶. The effect of pressure on the Fermi resonance doublet in the infrared spectrum of NH₄⁺ isolated in CsBr has been reported⁴⁵⁷.