

seven expected isotopic components for the symmetric Si-Cl stretching mode³³². The Raman spectrum of Re_2O_7 is consistent with the presence of a monomeric species in the gaseous and liquid states, whilst the completely different solid state spectrum is indicative of the polymeric nature of the solid³³³ (Fig. 6). The solid state spectra of several dichromate salts²⁴⁸ show evidence of site and factor group splitting.

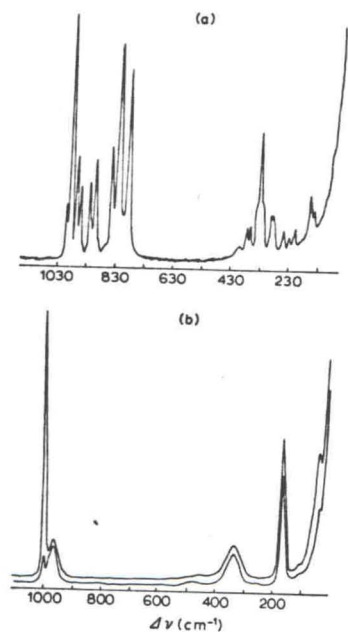


Fig. 6. (a) The Raman spectrum of solid Re_2O_7 . (b) The Raman spectrum of liquid Re_2O_7 at 350 °C. (Reproduced from I. R. Beattie and G. A. Ozin, *J. Chem. Soc., A*, (1969) 2615.)

The vibrational spectra^{334,335} of several eight coordinate ions such as $\text{Mo}(\text{CN})_8^{4-}$ and $\text{W}(\text{CN})_8^{4-}$ are consistent with a square antiprismatic structure (D_{4d}) in solution, and with a dodecahedral structure (D_{2d}) in the solid state.

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H. Compounds of phosphorus(V), selenium(IV) and tellurium(IV)

Halide compounds of P(V), Se(IV) and Te(IV) are discussed separately since they show similar properties to those of phosphorus pentachloride, viz. whilst it has the covalent structure in non-polar solvents it exists in the ionic form, $\text{PCl}_4^+ \text{PCl}_6^-$, in the solid state.

The gas phase Raman spectrum of PCl_5 is consistent with the presence of the trigonal bipyramidal D_{3h} species. With increasing temperature new bands appear in the spectrum due to the $\text{PCl}_5 \rightleftharpoons \text{PCl}_3 + \text{Cl}_2$ dissociation²⁸¹.

The vibrational spectra of benzene and methylene chloride solutions of PCl_5 are consistent with the presence of the covalent form³³⁶. The covalent form can also be trapped in the solid by deposition of the vapour onto a cold window at -185 °C. As the temperature is allowed to increase the spectrum changes as disproportionation from the covalent PCl_5 to the ionic form occurs³³⁷. The single crystal Raman spectrum of PCl_5 exhibits splittings of the degenerate bands due to the low site symmetry of the PCl_4^+ and PCl_6^- ions³³⁸.

The vibrational spectra of CH_3PCl_4 suggest the ionic formulation $\text{CH}_3\text{PCl}_3^+ \text{Cl}^-$ in the solid state, whilst in non-ionizing solvents the compound is monomeric³³⁹. Vibrational spectra also suggest ionic formulations for the following compounds: $\text{PBr}_4(\text{PBr}_4^- \text{Br}^-)$ ³⁴⁰; $\text{PBr}_7(\text{PBr}_4^- \text{Br}_3^-)$ ³⁴⁰; $\text{P}_2\text{Br}_4\text{F}_6(\text{PBr}_4^- \text{PF}_6^-)$ ³⁴⁰ and for the addition compounds formed between PCl_5 and MCl_3 , MCl_4 and MCl_5 species³⁴¹.

The solid state vibrational spectra of the tetrahalides of Se(IV) and Te(IV) have been interpreted in terms of an ionic $\text{MX}_3^+ \text{X}^-$ formulation³⁴²⁻³⁴⁴, although one paper favours the covalent structure for the solid state³⁴⁵. The solution vibrational spectra differ from the solid state spectra and they suggest that the tetrahalides exist as the monomeric C_2v species at low concentrations³⁴⁶⁻³⁴⁸. The vapour phase Raman spectrum of TeCl_4 is consistent with the presence of the monomeric C_2v species³⁴⁹, but the gas phase Raman spectrum of SeCl_4 indicates complete dissociation³⁵⁰ to SeCl_2 and Cl_2 (Fig. 7).

I. Miscellaneous studies

(i) Benzene, substituted benzenes and condensed aromatics

The Raman spectra of crystalline benzene and benzene- d_6 have been reported (refs. 351, 352). Splittings are observed for all the Raman active degenerate vibrations but for none of the non-degenerate vibrations³⁵⁴. The low frequency Raman bands have been assigned to rotational lattice modes³⁵³, whereas the low frequency infrared bands are due to translational lattice modes³⁵⁵. The infrared spectra of $\text{C}_6\text{H}_6/\text{C}_6\text{D}_6$ mixed crystals³⁵⁶⁻³⁵⁸, and polarised infrared spectra³⁵⁹ of C_6H_6 and C_6D_6 have also been reported.

Solid state vibrational spectra have been reported for a variety of phenols (refs. 360-363), for a series of monosubstituted benzenes^{364,365}, and for benzoyl

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