# The Raman Spectra of Tungsten(VI) Chloride and the Hexachlorotungstate(IV) Ion in Solution

By J. A. CREIGHTON
(*University Chemical Laboratories, Canterbury, Kent*)

THE Raman spectrum of tungsten(VI) chloride has been measured by laser excitation;[1] with laser light-sources and double monochromators it is often easier to study crystalline samples than solutions.[2] Caution must be exercised, however, in applying the frequencies so obtained to species in solution. We have measured the Raman spectrum of tungsten(VI) chloride dissolved in liquid chlorine, and find three bands of wavenumbers 409vs, pol, 317m, and 209m, which are assigned to $\nu_1$, $\nu_2$, and $\nu_5$ respectively of the $WCl_6$ molecule. With the exception of $\nu_1$, these frequencies are considerably lower than those (410, 377, and 266 cm.$^{-1}$) reported[1] for the crystalline substance, but are in good agreement with the frequencies (408, 312, and 206 cm.$^{-1}$) calculated[3] from studies of i.r. combination bands of tungsten(VI) chloride in solution in carbon disulphide, carbon tetrachloride, and benzene. They also appear more consistent than the solid-state data with the frequencies of the isoelectronic ions $HfCl^{2-}$ and $TaCl_6^{2-}$.[1]

The solution of tungsten(VI) chloride was prepared by vacuum transfer and was examined in a sealed ampoule at room temperature, by use of a 150 mw He–Ne laser and a Coderg Raman spectrometer. The solution, like the vapour, was dark red.

Measurements have also been made on the $TiCl_6^{2-}$ ion in solutions of its tetrabutylammonium salt in nitromethane. Two Raman bands (316vs, pol and 171m cm.$^{-1}$) are assigned to $\nu_1$ and $\nu_5$ respectively, but $\nu_2$, though evidently weak, was obscured by a band of the cation at 259 cm.$^{-1}$. These frequencies are in good agreement with wavenumbers measured from crystalline salts of this anion with large cations ($Et_4N^+$: 319 and 173; $Me_4N^+$: 319 and 179; $Cs^+$: 320 and 185; $K^+$: 334 and 186; $NH_4^+$: 331 and 194†) as has also been observed previously for salts of other hexachloro-anions.[4] Comparison of the frequencies from the nitromethane solution with those[5,6] observed from aqueous hydrochloric acid solutions of titanium(IV) chloride confirms the view[6] that the latter solutions do not contain appreciable quantities of $TiCl_6^{2-}$ anions.

(*Received, December 5th*, 1968; *Com.* 1666.)

† See ref. 5.

[1] R. A. Walton, *Chem. Comm.*, 1968, 1385.
[2] P. J. Hendra, *Ann. Reports* (*A*), 1967, **64**, 189.
[3] J. C. Evans and G. Y. S. Lo, *J. Mol. Spectroscopy*, 1968, **23**, 147.
[4] D. M. Adams and D. M. Morris, *J. Chem. Soc.* (*A*), 1967, 1666, 1669.
[5] D. M. Adams and D. C. Newton, *J. Chem. Soc.* (*A*), 1968, 2262.
[6] J. E. D. Davies and D. A. Long, *J. Chem. Soc.* (*A*), 1968, 2560.