The Laser Raman Spectrum of Crystalline Tungsten(VI) Chloride

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TUNGSTEN(VI) chloride is the most readily available and best characterised of the few known transition-metal hexachlorides.[1] Its octahedral structure in the vapour[2] and solid state[3] have been reported and its chemical reactivity and spectral properties have been of continuing interest.[1] However, its dark-blue colour has in the past precluded the successful measurement of its Raman spectrum because of the absence of a suitable exciting source, although such data is desirable for a detailed interpretation of its electronic spectrum.

Evans and Lo[4] have attempted to overcome this problem by studying the i.r.-active fundamental modes and the combination bands of solutions of tungsten(VI) chloride in carbon disulphide, carbon tetrachloride, and benzene. From these combination bands, values for ν_1, ν_2, and ν_5, the Raman-active fundamentals of an octahedral MX_6 species,[5] were calculated (408, 312, and 206 cm.$^{-1}$). Attempts to record the Raman spectrum of tungsten(VI) chloride using helium–neon laser and mercury-arc excitation were unsuccessful, other than revealing "a doubtful indication of a band near 400 cm.$^{-1}$". Two important points are relevant concerning this work. Firstly, these workers were unable to obtain a sample of hexachloride free from small amounts of the oxytetrachloride $WOCl_4$, and secondly, it is now clear that in organic solvents, particularly carbon tetrachloride and benzene, tungsten(VI) chloride may be reduced to the pentachloride.[6] The latter observation emphasises the care which must be taken in interpreting the solution data unless the presence of tungsten(V) chloride can be ruled out.*

The Raman spectrum of pure crystalline tungsten(VI) chloride† has now been successfully recorded using a Cary 81 Raman spectrophotometer in conjunction with a Spectra Physics Model 140 argon-ion laser. With the 4880 Å excitation (emitting 1·9 w), Raman lines were observed at 410s, 377m br, and 266m br cm.$^{-1}$, which are assigned to ν_1, ν_2, and ν_5 (Table). This result was further confirmed when the 4765 Å excitation was used, although in this case ν_2 was partially obscured by a spurious line at 360 cm.$^{-1}$. Support for the present assignment comes from a comparison with Raman data for isoelectronic d^0 $HfCl_6^{2-}$ and $TaCl_6^-$ (see Table). The usual increase in vibration frequencies with increase in oxidation state ($Hf^{IV} \rightarrow Ta^{V} \rightarrow W^{VI}$) is observed.

Raman-active fundamentals of isoelectronic $HfCl_6^{2-}$, $TaCl_6^-$, *and* WCl_6

	ν_1	ν_2	ν_5
$HfCl_6^{2-}$ [a]	328	264	158
$TaCl_6^-$ [b]	380	300	181
WCl_6	410	377	266

[a] B. J. Brisdon, G. A. Ozin, and R. A. Walton, to be published.

[b] I. R. Beattie, T. Gilson, and G. A. Ozin, *J. Chem. Soc. (A)*, 1968, in the press.

For crystalline tungsten(VI) chloride ν_1 is clearly in good agreement with that calculated from i.r. solution-measurements,[4] but the lack of agreement for ν_2 and ν_5 is disappointing. It should be noted that ν_5 is located at the rather high frequency of 266 cm.$^{-1}$; from a comparison with the related data for $HfCl_6^{2-}$ and $TaCl_6^-$ (see Table), a frequency of *ca.* 210 cm.$^{-1}$ might have been anticipated for ν_5. However, an alternative assignment for this mode is ruled out since in the region 300—160 cm.$^{-1}$, no additional lines attributable to the hexachloride were observed.

The present Raman results are the first obtained for a transition-metal hexachloride and are encouraging for the future recording of the Raman spectra of other highly coloured blue or green transition-metal compounds.

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* A recent report [P. M. Boorman, N. N. Greenwood, M. A. Hildon, and R. V. Parish, *J. Chem. Soc. (A)*, 1968, 2002], indicates that in benzene at least significant reduction does not occur below *ca.* 30°.

† The halide was sealed under nitrogen in a Pyrex tube. The absence of any $WOCl_4$ impurity was confirmed by recording the i.r. spectrum (2000—400 cm.$^{-1}$) of this sample; the oxytetrachloride has a strong band at *ca.* 880 cm.$^{-1}$ which was not present in the spectrum of this sample of hexachloride.

[1] See for example, J. E. Fergusson, "Halogen Chemistry," ed. V. Gutmann, Academic Press, London, 1967, vol. **3**, p. 227.
[2] R. V. G. Ewens and M. W. Lister, *Trans. Faraday Soc.*, 1938, **34**, 1358.
[3] J. A. A. Ketelaan and G. W. Oosterhaut, *Rec. Trav. chim.*, 1943, **62**, 167.
[4] J. C. Evans and G. Y. S. Lo, *J. Mol. Spectroscopy*, 1968, **23**, 147.
[5] K. Nakamoto, "Infrared Spectra of Inorganic and Co-ordination Compounds", Wiley, New York, 1963, p. 118.
[6] Reference 1, p. 278.