The Gas-phase Raman Spectrum of Niobium(V) Oxide Trichloride

By G. A. OZIN* and D. J. REYNOLDS
(*Chemistry Department, The University, Southampton* SO9 5NH)

Summary The gas-phase spectrum differs markedly from the powder Raman spectrum.

MANY inorganic oxide-halides have different structures in the solid and gaseous states. Laser Raman spectroscopy provides a powerful tool for demonstrating these structural changes.

We are investigating a series of oxide-halides, both in the solid and gaseous states using oriented single crystal laser Raman and gas-phase laser Raman spectroscopy, respectively. We have obtained Raman data for niobium(V) oxide trichloride $NbOCl_3$, which has an infinite double chain structure in the solid state.[1]

We have obtained single-crystal Raman polarisation data for an oriented crystal of $NbOCl_3$ and the results will be presented in detail in a future publication. However, a striking change in the Raman spectrum of $NbOCl_3$ occurs on passing from the solid to the vapour phase.

We report on (Table) the Raman spectra of $NbOCl_3$ both as a powder and as a vapour. Spectra were obtained using a Spex Raman spectrometer and an argon ion laser (*ca.* 700

The Raman spectra of gaseous and solid $NbOCl_3$

$NbOCl_3$ (Powder)	$VOCl_3$*	$NbOCl_3$† (Vapour 330°)	Assignment for monomer
	1035	997 (1·8)pol *ca.* 0·05	ν_2 $\nu(M{=}O)a_1$
770vvs			
605vvvw	504	448 (0·3)dep	ν_4 $\nu(MCl_3)e$
420s			
380mw	408	395 (8·0)pol *ca.* 0·10	ν_1 $\nu(MCl_3)a_1$
347vvw			
289mw			
232vvwsh	249	225 (0·7)dep	ν_5 $\delta(MCl_3)e$
227vw			
172mw	129	110 sh (*ca.* 1·0)dep	$\nu_6\rho_r(MCl_3)e$
158w			
131m			
125wsh	165	106 (4·0)pol	ν_3 $\delta(MCl_3)a_1$
115mw			
104w			
91vw			
74vwbr			
62mw			

† Weak polarised band at *ca.* 340 cm.$^{-1}$ (*ca.* 0·1) $\nu_5 + \nu_6$ $(a_1 + a_2 + e)$.
* Reference 2.

mw at 5145 Å). The powdered sample was contained in a Pyrex ampoule, sealed off directly from the vacuum line after purification of the $NbOCl_3$. The gas-phase Raman spectrum of $NbOCl_3$ was obtained at 320° using the same sample and a gas pressure of approximately three-quarters of an atmosphere. Raman spectra were recorded using 90° illumination and collection of the incident laser light and scattered Raman light, respectively.

We found that the Raman spectrum of gaseous $NbOCl_3$ is very similar to that of $VOCl_3$[2] (frequencies given in the Table for the purposes of comparison) and is entirely consistent with the presence of a monomeric[3] molecule having pyramical (C_{3v}) symmetry.

The frequency of the niobium–oxygen stretching mode in the gaseous monomer (997 cm.$^{-1}$) is characteristic of a "double bond" whereas in the solid (Table 1), the highest niobium–oxygen stretching mode, observed at 770 cm.$^{-1}$, is characteristic of a bridging oxygen.

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