

Theoretical and experimental investigations of vanadium (III) oxychloride[†]

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An attempt has been made to produce vanadium (III) oxychloride, (OVCl) by an on-line process for the first time using vanadium oxytrichloride, VOCl₃ as a precursor passed over heated silver wool at about 930°C. The vapour products have been characterised by their infrared spectra; values for ν_3 of 1010 cm⁻¹ (O=V stretch) and for ν_2 of 420 cm⁻¹ (V-Cl stretch) were obtained. *Ab initio* self-consistent-field molecular orbital calculations were performed to determine the geometry, total energy and the vibrational frequencies of OVCl.

Keywords: vanadium(III) oxychloride

Following our gas phase infrared and photoelectron spectroscopic detection of thiazyl halides, NSX (where X=Br and I)^{1,2}, the work was extended to record the gas phase infrared spectra and perform theoretical calculations of OPX where X= F, Cl, Br and I.^{3,4} Zidan and Allaf have reported the gas-phase on-line production of vanadium oxytrihalides, OVX₃ (X= F, Cl, Br and I) and their identification by infrared spectroscopy.⁵ In comparison with the existence of gas phase OPCI³ and SPCI⁶ species, the asymmetric top OVCl molecule in the gas phase is expected to be a bent triatomic species with C_s symmetry and possesses three normal infrared active modes of vibrations. To our knowledge, there are neither experimental nor theoretical investigations on OVCl; this paper describes the first initial attempt of gas phase production and the assignment of two fundamental vibration modes using a very high temperature gas/solid reaction process. The remaining band and some other properties were determined using *ab initio* quantum chemical calculations.

Experimental

The first step was to optimise the production conditions of OVCl₃. These conditions were as used in ref.⁵ Both OVCl₃ and silver wool were obtained from Fluka and Merck, respectively with a purity of 99.9%. The on-line production process of OVCl involves obtaining enough vapor pressure of OVCl₃ passed directly over heated silver at 930°C by fast flow reaction under about 0.4 torr pressure; the resulting vapor reaction products were passed directly via the vacuum line into the infrared cell which is fitted with two KBr windows. In order to avoid any disproportionation or polymerisation, the IR cell was heated to about 180°C with heating tape. The vacuum system was pumped out via a liquid nitrogen trap with a rotary pump (RV8, Edwards) displacing 8.5 m³ h⁻¹. The infrared spectrum was recorded on a JASCO 300E FTIR spectrometer with a resolution of 2 cm⁻¹.

Computational details

In order to facilitate the interpretation of the infrared spectrum of OVCl, *ab initio* self-consistent-field (SCF) molecular orbital (MO) calculations were performed to estimate the vibrational frequencies of OVCl. The eigenvalues for the optimized geometry were computed using a 6-311G + (d, p) and the Gaussian 98 program⁷ which gave a molecular energy of -1477.25280016 E_h. Table 1 shows the optimised calculated geometry of OVCl where Scheme 1 shows the theoretical predicted structure of OVCl. The preferred stoichiometry of OVCl is ClOV where the oxygen is centered. The experimental and theoretical vibrational frequencies and assignments of OVCl are listed in Table 2. This is the first initial experimental and theoretical investigations of OVCl and calculations of this kind normally give vibrational frequencies within ±10–15% of the experimental values.

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† This is a Short Paper, there is therefore no corresponding material in *J. Chem. Research (M)*.

Table 1 Optimised bond length (Å) and angles (°) of OVCl as calculated by the Gaussian 98 package using the 6-311G+ (d, p) basis set

Band	Calculated
O=V	1.56
V-Cl	2.33
∠OVCl	179.97

Table 2 Observed and calculated frequencies (cm⁻¹) of OVCl

Mode	Symmetry	Band	Observed	Calculated
ν_3	\hat{A}	O=V Stretch.	1010	1157.30
ν_2	\hat{A}	V-Cl- Stretch.	420	376.08
ν_1	\hat{A}	OVCl Bend	–	37.37



Scheme 1 The optimised structure of OVCl as calculated with a 6-311G+(d,p) basis set using the Gaussian 98 package where the angle of OVCl is about 179.97°.

Results and discussion

Due to the absence of any published results on OVCl, the assignment of this elusive species has been made with the help of OVCl₃⁵ and also with the comparison experimental shifts observed between OPCI₃⁸ and OPCI³ and between SPCI₃⁹ and SPCI⁶, respectively. Figure 1 shows the gas phase infrared spectrum of OVCl which was the result of passing OVCl₃ gas over heated silver at 930°C. Two of three bands of OVCl centred at 1010 and 420 cm⁻¹ were observed within the spectrometer range used (400–4000 cm⁻¹).

The first band centered at 1010 cm⁻¹, assigned to ν_3 , is the O=V stretching mode of OVCl and appears to the low energy side of the precursor. It is well known from the literature, that

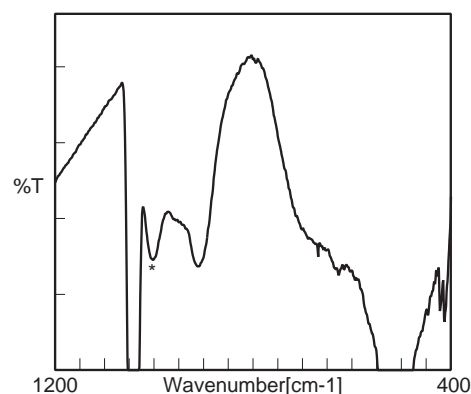


Fig. 1 Gas phase infrared spectrum of OVCl species marked with an asterisk (400–1200 cm⁻¹).

the O=V stretching frequency lies in the range of 1000–1100 cm^{-1} .^{5,10} Therefore, the reported O=V frequency at 1010 cm^{-1} lies within an acceptable range. It is worth noting that the O=V stretching frequency of OVCl_3 was observed at 1035 cm^{-1} .⁵ The O=V stretching frequency in OVCl can be compared with the gas phase O=P stretching frequency observed in OPCl_3 and OPCl , which have values of 1312⁸ and 1272³ cm^{-1} , respectively. Also, the O=V stretching frequency in OVCl can be compared with the gas phase S=P stretching frequency observed in SPCl_3 and SPCl , which have values of 762⁹ and 716.1⁶ cm^{-1} , respectively.

Finally in the gas phase, the structure of the O=V stretching band in OVCl is expected to be of the PQR type, therefore, better resolution is needed in order to resolve this structure.

The second band centred at 420 cm^{-1} is assigned to ν_2 and corresponds to the V-Cl stretching mode and has a PR-type structure. The third expected band of OVCl corresponds to a bend mode, ν_1 lies out of the range spectrometer used (400–4000 cm^{-1}).

The remaining bands at 1040, 910 and 504 cm^{-1} in Fig. 1 are assigned as follows. The band centred at 1040 cm^{-1} , is assigned to the $\nu_1(a_1)$, the O=V stretching mode of VOCl_3 .⁵ The band at 910 cm^{-1} could be due to a combination band $\nu_2(a_1) + \nu_4(e)$ of VOCl_3 which has a value of 912 cm^{-1} . The last band observed in Fig. 1 centred at 504 cm^{-1} is assigned to the $\nu_4(e)$ mode of VOCl_3 .⁵

From the theoretical point of view, the three calculated frequencies ν_3 , ν_2 and ν_1 of OVCl are at 1157.30, 376.08 and 37.37 cm^{-1} , respectively. The optimised calculated geometry of OVCl gives that; this species is almost linear (see Table 1) which is inconsistent with exceptions since the species was generated in the gas phase; the expected structure is a bent one. The shift between the calculated and the observed frequencies concerning the O=V and V-Cl stretching modes of OVCl is 147.3 and 43.92 cm^{-1} , respectively, and lies within the above theoretical prediction (± 10 –15%).

Conclusion

It is concluded that the present work reports the gas phase infrared spectrum of OVCl using an on-line production and detection using the FTIR technique. The calculations give vibrational frequencies within ± 10 –15% of the experimental values.

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