Spectroscopic Studies on Molecular Vanadium Pentafluoride isolated in Inert Gas Matrices

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Matrix-isolation studies have been carried out on vanadium pentafluoride. In a nitrogen matrix prominent i.r. bands at 806 and 769 cm^{-1} are assigned to V–F stretching modes of monomeric VF_5 (D_{3h}). Corresponding u.v.–visible spectra were obtained and assigned on the basis of trigonal bipyramidal geometry.

Following the recent successes in the spectroscopic characterisation of transition metal hexafluorides in inert gas matrices,[1–3] attention has been turned to the transition-metal pentafluorides. However, CrF_5[4] and PtF_5[5] disproportionate when heated under high vacuum whilst the other platinum metal pentafluorides afford complex matrix-isolated i.r. spectra due to the presence of oligomers in the gas phase.[5] Following a brief report on the i.r. spectrum of vanadium pentafluoride isolated in an argon matrix,[6] it was apparent that VF_5 could be a model compound to aid the interpretation of the more complex platinum metal pentafluoride spectra. Gaseous VF_5 has been extensively studied by i.r. and Raman spectroscopy and electron diffraction.[7,8] It was shown to be a D_{3h} monomer and Blinova *et al.*[6] postulated that it had the same symmetry in an argon matrix. However, recent work on transition-metal pentachlorides[9] has indicated discrepancies between gas-phase data (i.r., Raman, electron diffraction) and matrix-isolated i.r. spectra, *viz.* molecular $MoCl_5$ appears to have D_{3h} symmetry from gas-phase studies but C_{4v} symmetry from matrix-isolated experiments.

Therefore in this paper spectroscopic studies on matrix-isolated vanadium pentafluoride are reported with three aims: (*i*) to investigate a model transition-metal pentafluoride as an aid to the interpretation of the spectra of other matrix-isolated transition-metal pentafluorides, (*ii*) to investigate whether VF_5 has the same symmetry in the gas phase and isolated in a matrix, and (*iii*) to record the electronic spectrum of VF_5.

Experimental

Vanadium pentafluoride was prepared by the static fluorination of vanadium metal. In a typical preparation, vanadium powder (0.3 g, 5.9 mmol) was charged into a passivated stainless-steel autoclave (150 cm^3) in a dry-box. After evacuation on a metal line, fluorine [300 cm^3, 2 atm (202 650 Pa)] was admitted and the autoclave heated to 250 °C for 2 h. After cooling to room temperature, the excess of fluorine was removed at −78 °C, and the vanadium pentafluoride purified by sublimation under static vacuum. Yields typically 60—70%.

Details of the matrix-isolation apparatus have been reported elsewhere.[4] Samples of sublimed VF_5 in F.E.P. tubes were connected *via* a poly(tetrafluoroethylene) (ptfe) tap (Production Techniques STD/VC-4/P) to the high-vacuum apparatus, and held at −63 °C during co-deposition with nitrogen or argon (BOC 99.999%) as matrix materials. Matrix gas ratios of >1 000:1 were routinely employed. I.r. spectra were recorded on a P.E. 983G spectrometer fitted with CsI optics, electronic spectra on a P.E. 554 instrument fitted with LiF optics.

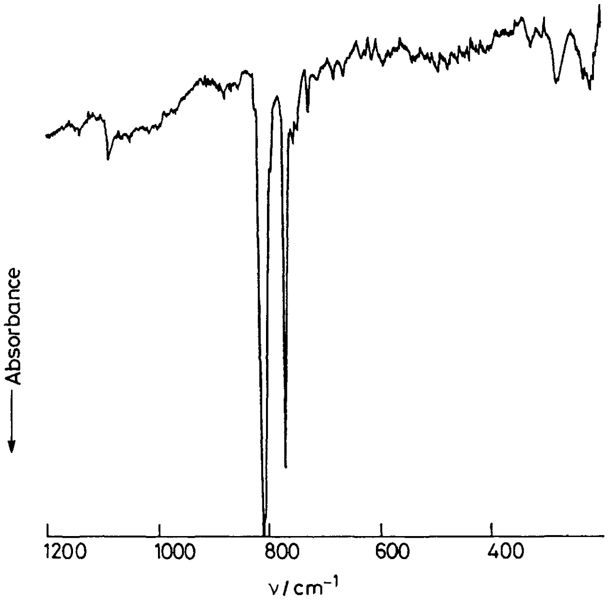

Figure 1. I.r. spectrum of vanadium pentafluoride isolated in a nitrogen matrix

Table. Vibrational spectroscopic data for vanadium pentafluoride

Gas phase[a]		Nitrogen matrix[b]	Argon matrix		
I.r.	Raman	I.r.	I.r.[b]	I.r.[c]	Assignment
	719				a_1' (ν_1)
	608				a_1' (ν_2)
784		769	771	774	a_2'' (ν_3)
331		325	321	322	a_2'' (ν_4)
810		809, 804	802	804	e' (ν_5)
282	282	280	278	278	e' (ν_6)
(≈200)	(≈200)				e' (ν_7)
	350				e'' (ν_8)

[a] Ref. 10. [b] This work; frequency accuracy ±0.5 cm^{-1}. [c] Ref. 6.

Results and Discussion

I.R. Spectroscopic Studies.—Figure 1 shows a typical i.r. spectrum of vanadium pentafluoride isolated in a nitrogen matrix and the Table compares the i.r. spectrum with the previous matrix-isolated i.r. spectra and the gas-phase i.r. and Raman spectra of Claassen and Selig.[10] There are no signs of

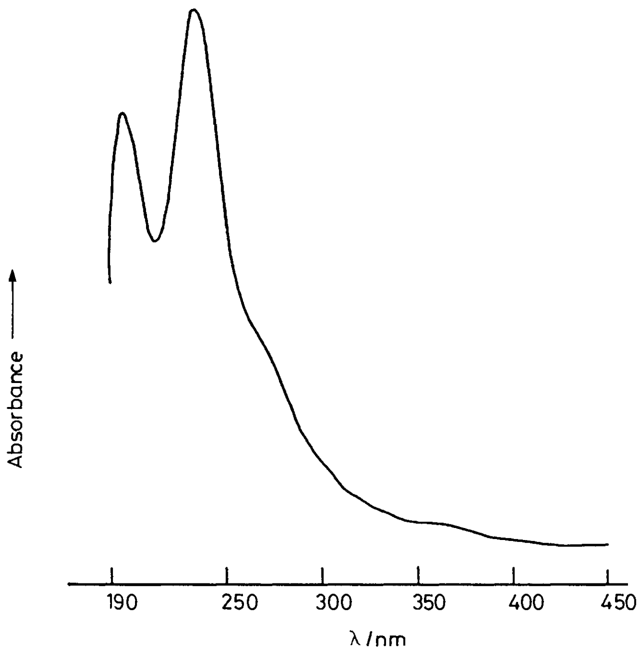

Figure 2. Electronic spectrum of vanadium pentafluoride isolated in a nitrogen matrix

oligomers and the very close agreement of the three sets of data and the ratios of intensity of the two ν(V–F) stretches indicate conclusively that vanadium pentafluoride has the same symmetry in the gas phase as in argon and nitrogen matrices. Under very high resolution the E mode of VF_5 in a nitrogen matrix shows a slight splitting, but this is an effect often encountered in nitrogen matrix-isolated species,[11] and the D_{3h} symmetry of monomeric VF_5 suggested in previous studies is supported.

This contrasts with the results on molecular $MoCl_5$ which has D_{3h} symmetry in the gas phase and C_{4v} symmetry when isolated in nitrogen and argon matrices. However, this may just be a subtle electronic effect since the energy barrier for square pyramidal to trigonal bipyramidal inversion would be expected to be low, and further work on other five-co-ordinated molecules is in progress.

U.V.–Visible Spectroscopic Studies.—Figure 2 shows the electronic spectrum of molecular VF_5 in a nitrogen matrix. There are two principal bands (42 400 and 50 000 cm^{-1}) with a weaker low-energy band (36 000 cm^{-1}). This is considerably different from the only other report of the electronic spectrum of vanadium pentafluoride reported in conference proceedings.[12] Four maxima are claimed in the 200—400 nm region, 29 000, 33 800, 36 000, and 46 000 cm^{-1}, but only one of these bands correlates with the spectrum reported here. The i.r. studies on their samples suggested at least a 5% VOF_3 impurity; VOF_3 has a low volatility and could arise from hydrolysis during the experiments. It has been shown[13] that the intense absorptions of some transition-metal oxide and oxide fluoride impurities can completely obscure the electronic spectrum of the molecule under investigation. Hence their spectrum could easily arise from their VOF_3 impurity. The i.r. studies in this work indicate $\leqslant 1\%$ VOF_3 impurity, and there is no evidence for any bands lower than 36 000 cm^{-1} in the electronic spectra of vanadium pentafluoride.

There has been very little work carried out on the electronic spectra of neutral five-co-ordinate molecules, and so any assignments of the electronic spectra must remain tentative. The position of the lowest-energy charge-transfer band, $E_{obs.}$, may be estimated using the optical electronegativity formula (1).[14]

$$E_{obs.} = 30\,000[\chi_{opt.}(F) - \chi_{opt.}(V^V)] \qquad (1)$$

Taking $\chi_{opt.}(F) = 3.9$ and $\chi_{opt.}(V^V) = 2.7$, the lowest-energy charge-transfer band ($E_{obs.}$) is predicted to lie at $36\,000 \pm 3\,000$ cm^{-1} which is in good agreement with the observed transition at 36 000 cm^{-1}. There is no literature value for the optical electronegativity of V^V in a trigonal bipyramidal environment. However, previous studies[11,15] have indicated that the values for the same oxidation state of the metal differ little between five- and six-co-ordinate environments and the estimated value of $\chi_{opt.}$ has been taken from the electronic spectrum of octahedral $[VOF_5]^{2-}$.[16]

The exact nature of the fluorine-to-metal charge-transfer transition is difficult to assign. The vanadium $3d$ orbitals split in D_{3h} symmetry to e'', e', and a_1' in order of increasing energy. Under D_{3h} symmetry the fluorine π orbitals are A_2', $2E'$, A_2'', and $2E''$ but it is impossible to predict the ordering of these levels. Therefore under this symmetry $13\pi(F) \longrightarrow d(V)$ charge-transfer transitions are theoretically possible. There have been no estimates on the e'' to a_1' separation in VF_5, but it is likely to be at least 23 000 cm^{-1} when one considers similar fluoride complexes for which 10 Dq is known, *i.e.* VF_6^{2-} 21 200, CrF_6^{2-} 21 250, and $(CrF_5)_n$ 24 000 cm^{-1}.[14] Therefore, the lowest $\pi(F) \longrightarrow a_1'(V)$ transition would be at $\geqslant 60\,000$ cm^{-1}, outside the range of the spectrometer.

The e'' to e' separation would be considerably smaller than the e'' to a_1' separation and a comparable band gap in the slightly distorted trigonal bipyramidal VCl_5^- has been reported at 6 200 cm^{-1}.[17] Obviously this would be larger for fluoride complexes (unfortunately VF_5^- salts have not been isolated), but since 10 Dq for VCl_5^- is 16 000 cm^{-1} and my estimate of 10 Dq for VF_5 is 23 000 cm^{-1}, the e'' to e' separation in VF_5 would be at least 9 000 cm^{-1}. Therefore, the bands at 36 000 and 42 400 cm^{-1} may tentatively be assigned as $\pi(F) \longrightarrow e''(V)$ transitions and the band at 50 000 cm^{-1} as the lowest $\pi(F) \longrightarrow e'(V)$ transition.

Conclusion

Monomeric vanadium pentafluoride has D_{3h} symmetry in the gas phase and in inert-gas matrices. The u.v.–visible spectrum has been recorded for the first time on a pure sample and assigned on the basis of D_{3h} symmetry.

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