Absorption Spectra of Some Vanadium(III) Fluorides

C. J. BALLHAUSEN and FLEMMING WINTHER

Chemistry Department A, Technical University of Denmark, Copenhagen, Denmark

A number of vanadium(III) fluorides having the general formula $[VF_n(H_2O)_{6-n}]^{+(3-n)}$ were prepared and their reflection spectra measured. An identification of the various absorption bands observed is proposed based on a crystal field level scheme with spin-orbit interaction included. The presence of lower crystalline fields than O_h is deduced from the position of the first spin-forbidden band.

It is the purpose of this note briefly to study the application of the theoretical $(3d^2)$ crystalline field level scheme recently given by Liehr and Ballhausen [1] to the absorption spectra of vanadium(III) complexes. To achieve this goal we have chosen the series $[VF_n(H_2O)_{6-n}]^{+(3-n)}$, the reason for our choice being the fact that going down this series from n = 6 to n = 3 some small "spin-forbidden" bands may be seen, some of which are not easily detected otherwise. It may of course be argued that the theory as outlined by Liehr and Ballhausen [1] is not at all applicable to non-cubic complexes. While this is perfectly true in a formal way, we must nevertheless remember that F⁻ and H_2O stand very close together in the spectro-chemical series. Thus we would not expect great deviations from "cubic" hehaviour for these mixed complexes. Most important, we shall not find any kind of significant splittings of the "cubic" bands, due to the actual presence of lower symmetry. On the other hand we would expect the spin-forbidden bands to be easier to detect by comparing the spectra of the different complexes.

Furthermore, there are experimental and theoretical reasons to expect that all "cubic" V(III) complexes are distorted along the trigonal axis due to to a Jahn-Teller effect [2,3], and especially the excited states possessing E_g electronic states may be very strongly coupled to the various molecular vibrations. While this fact makes an *a priori* "exact" analysis nearly impossible, it seems nevertheless possible to understand the general features of the d^2 system assuming a pure cubic crystalline field [4-7]. For special systems it is further necessary to throw in a trigonal field component [8,9] in the Hamiltonian in order to account for specific features. This procedure was found to be necessary in the present work in order to explain the position of the first spin-forbidden band.

As the complexes in question are rather insoluble, the absorption spectra were recorded as reflection spectra taken upon the crystalline powder. This method gives quite accurate results in so far as the location of the various absorption bands are concerned, but it is completely out of the question to estimate band intensities in this way. We shall accordingly refrain from interpreting the oscillator strengths of the bands [10].

EXPERIMENTAL

The various complexes [$VF_3(H_2O)_3$], $NH_4[VF_4(H_2O)_2]$, $(NH_4)_2[VF_5H_2O]$ and $(NH_4)_3$ [VF_6] were made according to Petersen [11],[12]. $K_2[VF_5H_2O]$ was made according to Palmer [13]. An unsuccessful attempt was made to prepare the mixed complexes containing 1 and 2 fluorine atoms.

When pure all of the complexes mentioned above are quite stable in the atmosphere, the hexa- and pentafluorides being the most stable. Both the hexafluoride and the hexahydrate can be washed with alcohol without apparent structural changes, whereas this is not the case with the "mixed" complexes.

As all of the compounds mentioned have been well characterized and analyzed before [11],[12], we have only analyzed the prepared complexes for the ratio between the vanadium and fluorine contents. The analyses were carried out in a semimicro scale.

The vanadium content was found by means of potentiometry using MnO_4^- as titrating agent. This was carried out in two steps: V(III) → V(IV) and V(IV) → V(V). As the titration took place in the presence of F^-, no glass apparatus was used.

The fluorine content was found after the method of Willard and Winter [14].

The reflection spectra were recorded on a Beckman DU spectrophotometer with MgO powder used as standard.

CONCLUSIONS

The spectra recorded all show broad maxima at $\sim$15 000 cm^{-1} and $\sim$23 000 cm^{-1}. These we attributed to the assignments [7]

$$15\ 000\ \text{cm}^{-1} \text{ due to } {}^3T_{1g} \rightarrow {}^3T_{2g} \text{ and}$$
$$23\ 000\ \text{cm}^{-1} \text{ due to } {}^3T_{1g} \rightarrow {}^3T_{1g}.$$

More exactly for $VF_6^{\equiv}$ we get ${}^3T_{1g} \rightarrow {}^3T_{2g}$ 14 800 cm^{-1}, from which we calculate [1],[7] $Dq = 1\ 585$ cm^{-1} taking $F_2 = 14\ F_4$ with $F_4 = 70$ cm^{-1} as in Liehr and Ballhausen [1].

Table 1. Calculated [1] and observed band maxima for V(III) complexes.

Calculated wavenumbers for d^2 cubic configuration $F_4 = 70$ cm^{-1} and $F_2 = 14\ F_4$ $Dq = 1\ 585$ cm^{-1} and $\lambda = 65$ cm^{-1} Transitions from ${}^3T_{1g}$ to:		Observed wavenumbers			
		$VF_6^{\equiv}$	$VF_5(H_2O)^=$	$VF_4(H_2O)_2^-$	$VF_3(H_2O)_3$
${}^1E_g,\ {}^1T_{2g}$	9 200 cm^{-1}	10 200	10 500	12 000	11 500
${}^3T_{2g}$	14 800 cm^{-1}	14 800	15 500	16 000	16 200
${}^1A_{1g}$	19 600 cm^{-1}				
${}^3T_{1g}$	23 200 cm^{-1}	23 000	23 500	23 800	24 500
${}^1T_{2g}$	25 200 cm^{-1}				
${}^1T_{1g}$	27 300 cm^{-1}			28 200	
${}^3A_{2g}$	31 200 cm^{-1}				

The calculated and the experimental absorption peaks are collected in Table 1.

The agreement between the calculated and observed absorption bands is seen to be fairly good with the single exception of the first "spin-forbidden" band $^3T_{1g} \rightarrow {}^1E_g$, $^1T_{2g}$. Assuming a pure cubic crystallinen field, the two levels ^1E_g and $^1T_{2g}$ are nearly degenerate. However, by superimposing a trigonal field upon the octahedral field the $^1T_{2g}$ level will split into a ^1E_g and $^1A_{1g}$ level, whereas ^1E_g is not split. Thus we would expect a strong repulsion to take place between the two ^1E_g levels by going down in symmetry, and this fact can explain why the "first" spin-forbidden band is pushed upwards about 1 000 cm^{-1}. For details see the appendix.

All in all it may thus be concluded that a slightly modified theoretical level scheme [1] is sufficient to explain the experimental facts.

APPENDIX

The d-electrons in a cubic field are usually quantized along the four-fold axis, and are described as $t_{2g} = (xz)$, (yz) and (xy) and $e_g = (z^2)$ and (x^2-y^2). If instead we quantize along the three-fold axis of the octahedron, the following linear combinations of d-orbitals transform correctly as zero-order wave-functions

$$t_{2g}^+ = \sqrt{\tfrac{2}{3}}\ (x^2-y^2) - \sqrt{\tfrac{1}{3}}\ (xz)$$
$$t_{2g}^- = \sqrt{\tfrac{2}{3}}\ (xy) + \sqrt{\tfrac{1}{3}}\ (yz)$$
$$t_{2g}^0 = (z^2) \qquad\qquad \text{and}$$
$$e_g^+ = \sqrt{\tfrac{1}{3}}\ (x^2-y^2) + \sqrt{\tfrac{2}{3}}\ (xz)$$
$$e_g^- = \sqrt{\tfrac{1}{3}}\ (xy) - \sqrt{\tfrac{2}{3}}\ (yz)$$

Now choosing the most general trigonal perturbation as

$V_\tau = A_2^0 Y_2^0 + A_4^0 Y_4^0 + A_4^3 (Y_4^3 - Y_4^{-3})$, we obtain by taking a suitable reference energy

$$(t_{2g}^\pm \mid V_\tau \mid t_{2g}^\pm) = D\tau$$
$$(t_{2g}^0 \mid V_\tau \mid t_{2g}^0) = -2\ D\tau.$$

By descending in symmetry from O_h to C_{3v} we get $^1T_{2g} \rightarrow {}^1E_g + {}^1A_{1g}$ and $^1E_g \rightarrow {}^1E_g$. Writing down zero-order determinental single-electronic wave-functions which transform correctly both under O_h and C_{3v}, we obtain

$$^1E_g[^1E_g^-(t_{2g})^2] = -\sqrt{\tfrac{1}{6}}\mid \overset{+}{t_{2g}^+}\ \overset{-}{t_{2g}^-}\mid + \sqrt{\tfrac{1}{6}}\mid \overset{-}{t_{2g}^+}\ \overset{+}{t_{2g}^-}\mid + \sqrt{\tfrac{2}{6}}\mid \overset{+}{t_{2g}^-}\ \overset{-}{t_{2g}^0}\mid - \sqrt{\tfrac{2}{6}}\mid \overset{-}{t_{2g}^-}\ \overset{+}{t_{2g}^0}\mid$$

$$^1T_{2g}[^1E_g^-(t_{2g})^2] = \sqrt{\tfrac{2}{6}}\mid \overset{+}{t_{2g}^+}\ \overset{-}{t_{2g}^-}\mid - \sqrt{\tfrac{2}{6}}\mid \overset{-}{t_{2g}^+}\ \overset{+}{t_{2g}^-}\mid + \sqrt{\tfrac{1}{6}}\mid \overset{+}{t_{2g}^-}\ \overset{-}{t_{2g}^0}\mid - \sqrt{\tfrac{1}{6}}\mid \overset{-}{t_{2g}^-}\ \overset{+}{t_{2g}^0}\mid$$

where $|\cdots|$ designates an antisymmetrized, normalized wavefunction and the plus or minus sign above the single orbitals means α or β spin.

For the interaction of the two ^1E_g levels in C_{3V} we get:

$$\begin{vmatrix} -E & -\sqrt{2}\,D\tau \\ -\sqrt{2}\,D\tau & D\tau - E \end{vmatrix} = 0$$

with $E = 2D\tau$ and $-D\tau$.

Taking $D\tau$ to be 500 cm^{-1}, we find that the accidental degeneracy in O_h of ^1E_g and $^1T_{2g}$ at 9 200 cm^{-1} is done away with, and that instead we have three levels located at 10 200 cm^{-1}, 9 200 cm^{-1} and 8 700 cm^{-1}. This value of $D\tau$ is in close agreement with the results of Pryce and Runciman [9]. Due to experimental difficulties the two expected bands at $\sim 9\,000$ cm^{-1} have not yet been found.

REFERENCES

1. Liehr, A. D. and Ballhausen, C. J. *Ann. of Phys.* (N.Y.) **6** (1959) 134.
2. Öpik, U. and Pryce, M. H. L. *Proc. Roy. Soc. London* **A238** (1957) 425.
3. Liehr, A. D. and Ballhausen, C. J. *Ann. of Physics* (N.Y.) **3** (1958) 304.
4. Ilse, F. E. and Hartmann, H. *Z. Naturforsch.* **6a** (1951) 751.
5. Hartmann, H., Furlani, C. and Bürger, A. *Z. physik. Chem.* (N.F.) **9** (1956) 62.
6. Orgel, L. E. *J. Chem. Phys.* **23** (1955) 1004.
7. Ballhausen, C. J. *Z. physik. Chem.* (N.F.) **11** (1957) 205.
8. Ballhausen, C. J. *Z. physik. Chem.* (N.F.) **17** (1958) 246.
9. Pryce, M. H. L. and Runciman, W. A. *Discussions Faraday Soc.* **26** (1958) 34.
10. Ballhausen, C. J. and Liehr, A. D. *Mol. Physics* **2** (1959) 123.
11. Petersen, E. *Vanadinet og dets nærmeste Analoger.* Thesis. København 1888.
12. Petersen, E. *J. prakt. Chem.* **40** (1889) 44.
13. Palmer, W. G. *Experimental Inorganic Chemistry.* Cambridge University Press 1954.
14. Fresenius, W. and Jander, G. *Handbuch der analytischen Chemie.* 3. Vol. 7 p. 200 f.f. Springer 1950.