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Theory of the Structure of Vanadyl Ion

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ABSTRACT

This Paper describes how the degeneracy of a d^1 transition metal ion is split in octahedral crystal field, resulting in T_{2g} to E_g absorption transitions. The energy levels of vanadyl ion water complex have further been explained on the basis of ligand-field theory, which considers the formation of hybrid molecular orbitals between metal orbitals and ligand orbitals. It has been explained how the electrons fill the different Mo energy levels, leading to an unpaired electron in the non-bonding b_z level with observance of EPR by such a complex and also explaining the optical absorption in such systems due to $b_2 \rightarrow e_\pi^* \text{ and } b_2 \rightarrow b_1^*$ transitions.

VO^{2+} as a d^1 ion

A vanadium ion has the electronic configuration of $3d^3 4s^{1.}$ In vanadyl ion VO^{2+}, V^{2+} shares its two electrons with the oxygen, the resulting electronic configuration is therefore of $3d^1$ type and the VO^{2+} ion is equivalent to a V^{4+} ion.

d^1 ion in an octahedral field

The vanadyl ion usually occurs in octahedral coordination with its surrounding atoms or ligands. The situation thus represents a configuration where a $3d^1$ ion is perturbed by a crystal field of O_h symmetry.

The five d-orbitals involved are given below:

$$d_{xy} = \frac{1}{\sqrt{2}}\left(\phi_{22} - \phi_{2-2}\right)$$

$$= R_{3d}(r).\frac{\sqrt{15}}{2}\sqrt{\pi}\, xy$$

$$d_{xz} = \frac{1}{\sqrt{2}}\left(\phi_{21} + \phi_{2-1}\right)$$

$$= R_{3d}(r).\frac{\sqrt{15}}{2}\sqrt{\pi}\, xz$$

$$d_{yz} = \frac{1}{\sqrt{2}}\left(\phi_{21} - \phi_{2-1}\right)$$

$$= R_{3d}(r).\frac{\sqrt{15}}{2}\sqrt{\pi}\, yz$$

$$d_{x^2-y^2} = \frac{1}{\sqrt{2}}\left(\phi_{22} + \phi_{2-2}\right)$$

$$= R_{3d}(r).\frac{\sqrt{15}}{4}\sqrt{\pi}\left(x^2 - y^2\right)$$

$$d_{z^2} = \phi_{20}$$

$$= R_{3d}(r)\frac{\sqrt{15}}{4}\sqrt{\pi}\left(2z^2 - x^2 - y^2\right)$$

where R_{3d}(r) is the radial wave function for a 3d electron; and $\square_{2m}$ (m= 2, 1, 0, –1, -2) are the spherical harmonics.

The unperturbed Hamiltonian H_0 relating to the free ion has complete spherical symmetry. If an entity as above is placed in an electric field of O_h symmetry, then from the character table of O_h point group[1], given in Table 1, the $3d_{z^2}$ and $3d_{x^2-y^2}$ orbitals transform according to E_g. Representation and the trio d_{xy}, d_{yz} and d_{zx}, accordingly to the T_{2g} representation. The d_{z^2} and $d_{x^2-y^2}$ orbitals point along the axes, while d_{xy}, d_{yz} and d_{zx} are directed between the axes. If the field of ligands is due to point negative charges, then an electron in the d_{xy}, d_{yz} and d_{zx} orbitals will have a lower energy than one in d_{z^2} and $d_{x^2-y^2}$ .The five d-orbitals which were degenerate before application of crystalline electric field as above are now split in an O_h symmetry.

Henderson and Imbusch[2] have given the quantum mechanical treatment for energy splitting of 3d electrons under O_h field, using point ion model. They also obtain a splitting arrangement as above with

$$D = \frac{1}{4\pi\varepsilon_0}\frac{35ze^2}{4a^5}$$

and $$q = \frac{2}{105} < r^4 >_{3d}$$

'a' being the identical distance of six point charge neighbors from the 3d electron site. The parameters D and q always occur as a product.

The crystal field transitions $T_{2g} \rightarrow E_g$ can now occur, if all the five d-orbitals are not filled. This is a very common phenomenon among the hexa-coordinated transition metal complexes.

The agreement between experimental value of Dq and that calculated, as per formulae given, are however not very good. The lack of agreement reflects the crudeness_of point ion model and a more rigorous model involving extended ligands has to be worked out. Nevertheless, the point ion model correctly describes the symmetry of the crystal field.

The three p-orbitals p_x, p_y and p_z, however remain degenerate under O_h field and belong to the T_{1u} representation, because they have exactly equivalent positions with respect to legends. Hence, the crystal field transitions involving p-orbitals in a complex of O_h symmetry cannot be observed.

The complex of vanadyl ion with water

In $VO(H_2O)_5$ complex of vanadyl ion with water, the V^{4+} is surrounded by oxygen of vanadyl itself and five other oxygen's of water groups. Such a complex has C_{4v} site symmetry. The corresponding character table[1] is shown in Table 1. Out of the six V-O bonds, five are almost equal in the range 1.3 to 1.4 Å. The sixth V-O bond is however quite short with value around 1.67 Å.

The transformation scheme under $O_h \rightarrow C_{4v}$ transformation for various metal and ligand orbitals[5] is given in Table 3. The two hybrid combinations of $3d_{z^2}$ and 4s orbitals and p_z behave like a_1-representation of C_{4v} point group. The d_{xz}, d_{yz} and p_x, p_y behave like e-representation. The $d_{x^2-y^2}$ behaves like b_1-representation and d_{xy} is of b_2-type. Among the orbitals of ligands the different combination with required symmetry are also given in Table 3. Four different combinations of $\sigma_1, \sigma_2, \sigma_3$ *and* σ_4 are used. Further p_x, p_y orbitals of oxygens show up a □-type orbital.

In view of sufficiently long V to O (water) bond lengths (~ 1.3 Å) and further considering the alignment of water orbitals, the □-bonding involving the vanadium orbitals and water oxygens seems unlikely and is ignored. The □-bonding however exists between the oxide-oxygen and d_{xz}, d_{yz} orbitals.

It is seen that metal and ligand orbitals of like symmetry (□ □ or □ □ type) overlap to yield two linear combinations represented as bonding and anti-bonding (indicated by an asterisk *) orbitals. The bonding orbitals have lower energy compared to corresponding anti-bonding orbitals of higher energy. The non-degenerate orbitals a_1, b_1 and b_2 can occupy upto two electrons and degenerate e-orbitals up to four electrons.

we have finally three a_1-type bonding molecular orbitals (MOs) and consequently three anti-bonding MOs too. Coming to other representations, we have one set of b_1-type bonding and anti-bonding orbitals, one set of e-type bonding and anti-bonding orbitals. Ultimately the b_2-type metal orbital remains uncombined and is thus called a non-bonding MO.

It is the electron, which is responsible for the observed EPR spectrum of vanadyl ion complex and also for the optical absorption spectrum, originating by the shift of an electron from b_2 to e_π^* and b_1^* levels.

TABLE1

Character table for O_h point group

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$	i	$6S_4$	$8S_6$	3□$_h$	6□$_d$	
A_{1g}	1	1	1	1	1	1	1	1	1	1	$x^2 + y^2 + z^2$
A_{2g}	1	1	–1	–1	1	1	–1	1	1	–1	–
A_{1u}	1	1	1	1	1	–1	–1	–1	–1	–1	–
A_{2u}	1	1	–1	–1	1	–1	1	–1	–1	1	–
E_g	2	–1	0	0	2	2	0	–1	2	0	$3x^2–r^2, x^2–y^2$
E_u	2	–1	0	0	2	–2	0	1	–2	0	–
T_{1g}	3	0	–1	1	–1	3	1	0	–1	–1	R_x, R_y, R_z
T_{1u}	3	0	–1	1	–1	–3	–1	0	1	1	x, y, z
T_{2g}	3	0	1	–1	–1	3	–1	0	–1	1	xy, yz, zx
T_{2u}	3	0	1	–1	–1	–3	1	0	1	–1	–

TABLE-2

Character table of C_{4v} point group

C_{4v}	E	$2C_4(z)$	C_2	2□$_v$	2□$_d$		
A_1	1	1	1	1	1	z	$x^2 + y^2, z^2$
A_2	1	1	1	–1	–1	R_z	–
B_1	1	–1	1	1	–1	–	$x^2 – y^2$
B_2	1	–1	1	–1	1	–	xy
E	2	0	–2	0	0	x, y, R_x, R_y	xz, yz

TABLE-3
Representations of metal and ligand orbitals in C_{4v} symmetry

Representation	Vanadium orbitals	Ligand orbitals
a_1	$3d_{z^2} + 4s$ $4s - 3d_{z^2}$ $4p_z$	$\square_5$ $(\square_1 + \square\ \square_2 + \square\ \square_3 + \square\ \square_4)/2$ $\square_6$
e	$3d_{xz}$, $3d_{yz}$ $4p_x$, $4p_y$	$\square_5(2p_x, 2p_y)$ $(\square_1 - \square\ \square_3)/\sqrt{2}$, $(\square_2 - \square\ \square_4)/\sqrt{2}$,
b_1	$3d_{x^2-y^2}$	$(\square_1 - \square\ \square_2 + \square\ \square_3 + \square\ \square_4)/2$
b_2	$3d_{xy}$	–

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