

# **Coordination Chemistry III: Spectroscopy & Multi-Electron States**

Chapter 11

Weds, December 2, 2015

# Chem 107L Safety Training

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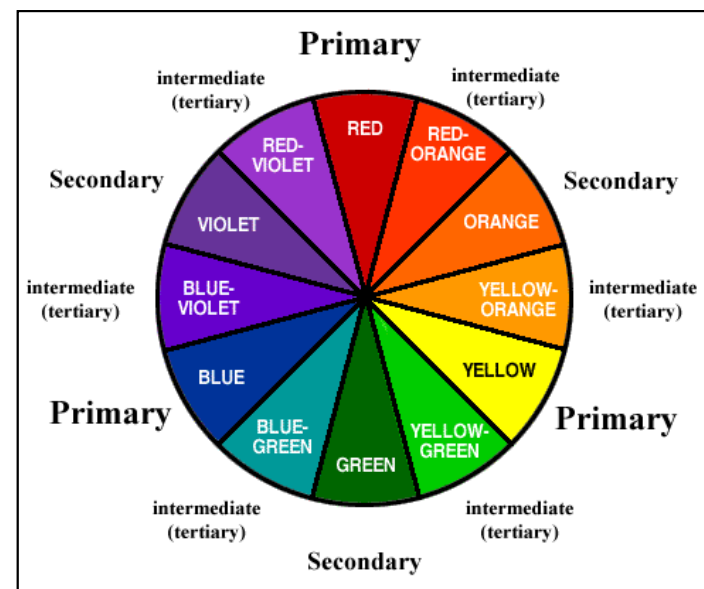
**Everyone must complete a safety training course before starting Chem 107L.**

- **Students taking Chem 107L must finish the online UCLC safety training that new graduate students take before Wednesday of week 1 in the winter quarter.**
- **Everyone should register, regardless of whether they are taking Chem 107L in the winter or spring. Only students taking the course in the winter need to do the online training by the beginning of winter quarter.**
- **Starting December 18<sup>th</sup>, you will be able to log in and complete the online portion of the safety training**
- **The hands-on portion of the safety training will be conducted during the first week of Chem 107L**
- **For more details, download the instruction sheet and general announcement from the “Readings” section of our Chem 107 website**

# Intro to Spectroscopy

The color we observe for complexes is a direct result of light absorption and its complementary transmission

Observed Color	Light Absorbed	Abs Wavelength / nm
colorless	UV	< 380
yellow	violet	380-450
orange	blue	450-490
red	green	490-550
violet	yellow	550-580
blue	orange	580-650
green	red	650-700
colorless	IR	> 700



When a compound absorbs light in the UV-vis-NIR region, an electron moves from a low energy orbital to a higher energy orbital

- UV-vis-NIR spectroscopy is a probe for electronic structure

$$\Delta E = h\nu = \frac{hc}{\lambda} = hc\bar{\nu}$$

frequency (Hz) →  $\nu$        $\lambda$  → wavelength (nm)       $\bar{\nu}$  → wavenumber (cm<sup>-1</sup>) =  $\lambda^{-1}$

# Spectroscopy Selection Rules

Transitions between orbitals with the same parity (symmetry with respect to inversion) are **FORBIDDEN!** This is the Laporte select. rule.

- $d \rightarrow d$  – both orbitals are symmetric with respect to inversion – **FORBIDDEN!**
- $p \rightarrow p$  – both orbitals are anti-symmetric with respect to inversion – **FORBIDDEN!**
- $d \rightarrow p$  –  $d$  is symmetric and  $p$  is anti-symmetric – allowed

Transitions between different spin multiplicities are **spin FORBIDDEN!**

- $^4A_2 \rightarrow ^2A_2$  – **spin FORBIDDEN!**
- $^4A_2 \rightarrow ^4T_1$  – **spin allowed**

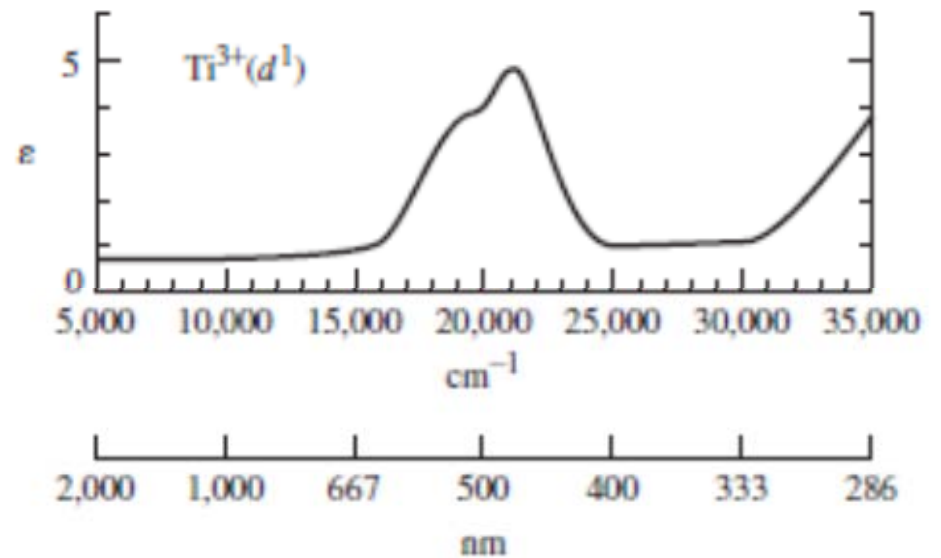
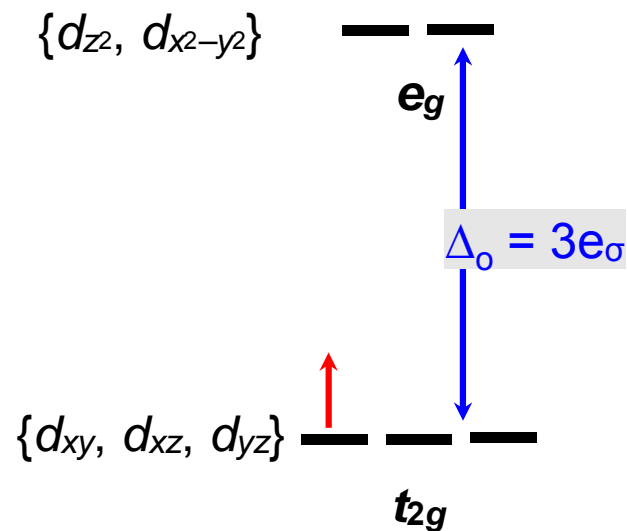
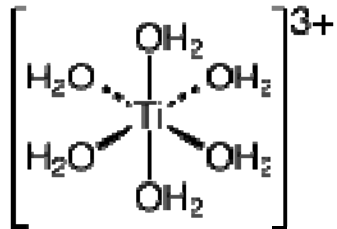
“spin multiplicity”  
means number of  
unpaired electrons  
(actually  $\#e^- + 1$ )

**What does FORBIDDEN! mean?**

	extinction coefficient / $M^{-1} cm^{-1}$
Fully allowed	1000-100,000
Spin-allowed, Laporte forbidden	1-1000
Spin forbidden, Laporte forbidden	$\ll 1$



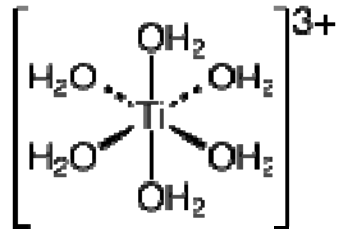
Hexaaquatitanium(III) is an octahedral  $d^1$  metal complex.



$d-d$  transition should give a single peak in the absorption spectrum.



Hexaaquatitanium(III) is an octahedral *d*<sup>1</sup> metal complex.

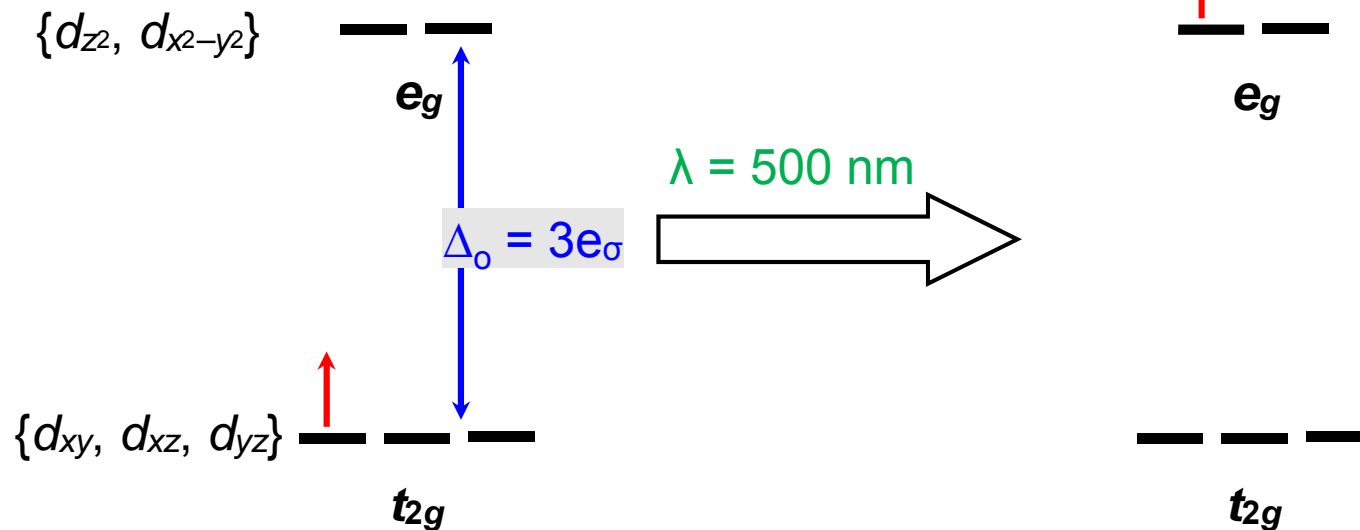


ground state  
electron configuration

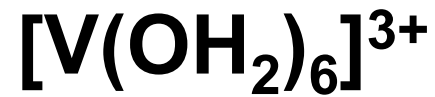
excited state  
electron configuration

**$2T_{2g}$**

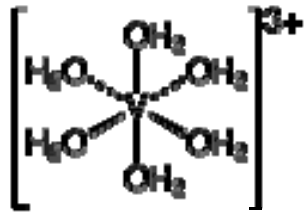
**$2E_g$**



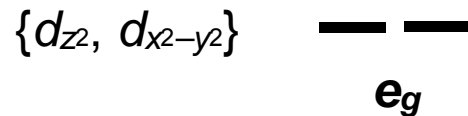
$$\begin{aligned}
 \Delta E &= \frac{hc}{\lambda} \cong \Delta_o \\
 &= \frac{(6.626 \times 10^{-34} \text{ J} \cdot \text{s})(2.998 \times 10^8 \text{ m} \cdot \text{s}^{-1})}{5.0 \times 10^{-7} \text{ m}} \\
 &= 3.97 \times 10^{-19} \text{ J} = 2.48 \cdot \text{eV} \Rightarrow 57.2 \cdot \text{kcal} \cdot \text{mol}^{-1}
 \end{aligned}$$



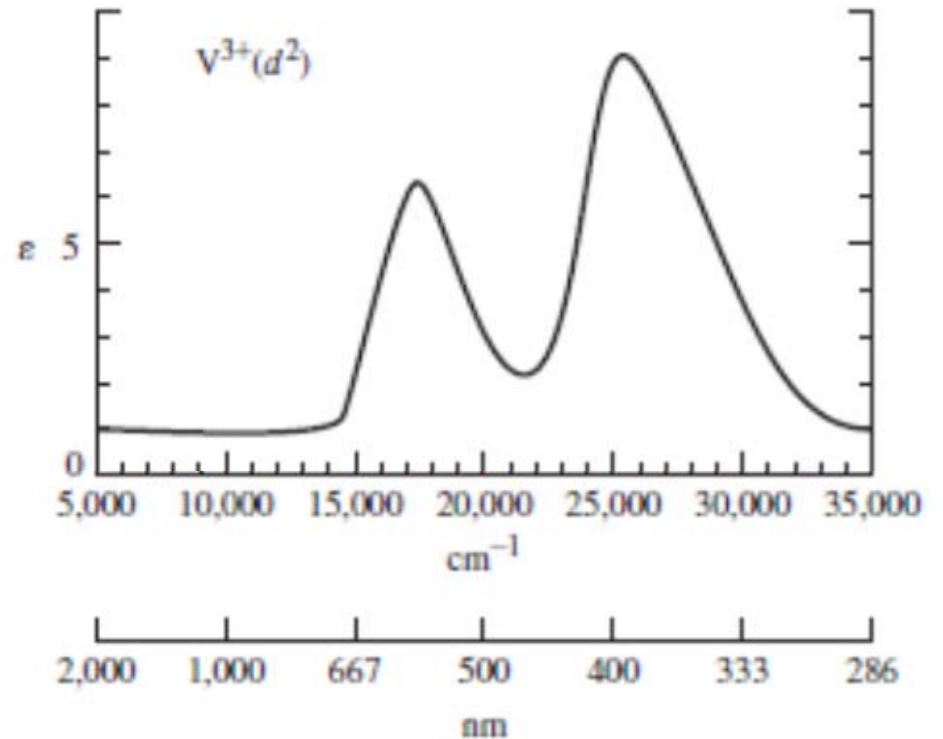
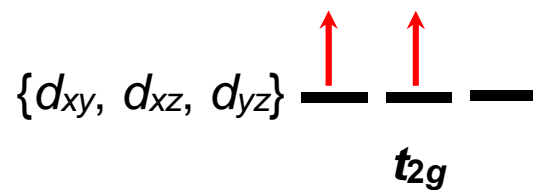
Hexaaquavanadium(III) is an octahedral  $d^2$  metal complex.

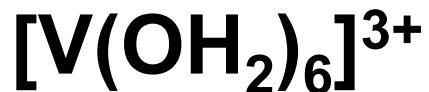


ground state  
electron configuration

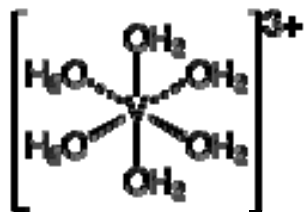


$^3T_{1g}$





Hexaaquavanadium(III) is an octahedral  $d^2$  metal complex.



ground state  
electron configuration

$\{d_{z^2}, d_{x^2-y^2}\}$

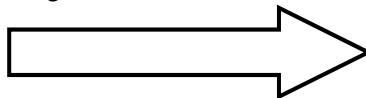


$e_g$

$\lambda_1 = 650 \text{ nm}$

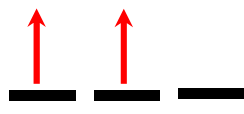
$\lambda_2 = 400 \text{ nm}$

$\lambda_3 = 250 \text{ nm}$



$^3T_{1g}$

$\{d_{xy}, d_{xz}, d_{yz}\}$



$t_{2g}$

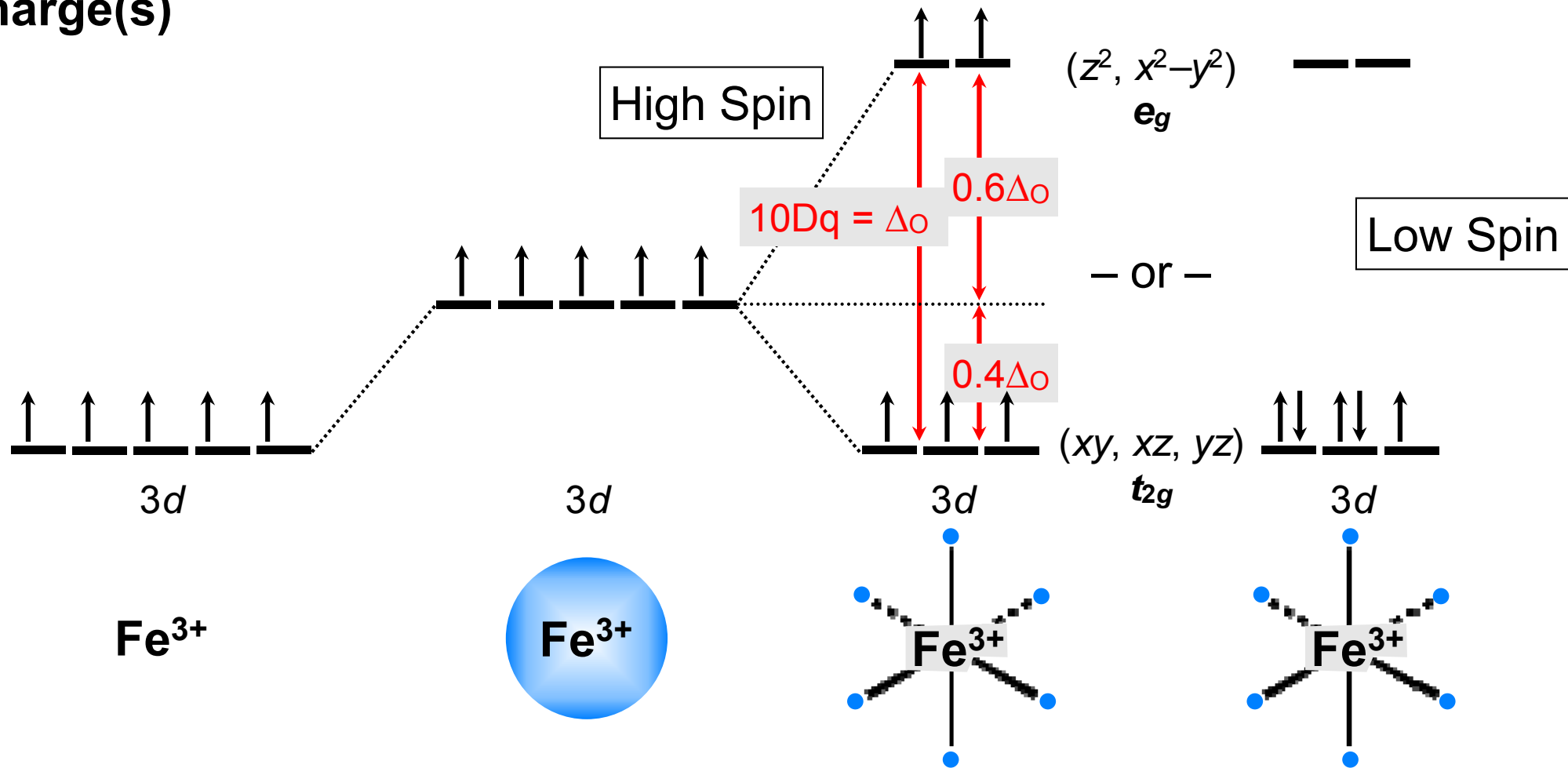
## What's going on?

- It turns out not all electron configurations are equal.
- To understand the absorbance spectrum of  $[\text{V}(\text{OH}_2)_6]^{3+}$  (or any other multi-electron species), we need to do a little work...



# Crystal Field Theory

CFT aims to explain electronic spectra of crystalline materials by treating the metal ion and its valence electrons in a field of negative charge(s)



CFSE is the energy difference for the given electron distribution in the crystal field compared to the free ion.

$$CFSE = \left( \# e_{t_{2g}} \right) (-0.4\Delta_o) + \left( \# e_{e_g} \right) (0.6\Delta_o)$$

# Tackling the Multi-Electron Problem

## Start by taking a step back

- first we must treat the  $V^{3+}$  ‘free ion’ with no ligands in a spherically symmetric environment
- since  $V^{3+}$  is  $d^2$ , we must consider  $e^-e^-$  interactions, spin-spin interactions, and spin-orbital interactions

## Define a few terms

- microstate – a specific valence electron configuration for a multi-electron free ion

$$\# \text{microstates} = \frac{\overset{\# \text{spaces}}{i!}}{\underset{\# e^-}{j!(i-j)!}} = \frac{10!}{2!(10-2)!} = 45$$

- atomic state – a collection of microstates with the same energy
- term symbol – the label for a free ion atomic state



L	term symbol label
0	S
1	P
2	D
3	F
4	G

# Multi-Electron Quantum Numbers

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When we learn about atoms and electron configurations, we learn the one-electron quantum numbers ( $n, l, m_l, m_s$ )

Multi-electron ions need multi-electron quantum numbers

- $L$  gives the total orbital angular momentum of an atomic state (equal to the maximum value of  $M_L$ )
  - $M_L$  is the z-component of the orbital angular momentum of a microstate

$$M_L = \sum m_l$$

$$M_L \Rightarrow -L, -L + 1, \dots, -1, 0, +1, \dots, L - 1, L$$

- $S$  gives the total spin angular momentum of an atomic state (equal to the maximum value of  $M_S$  (for a given  $L$  value))
  - $M_S$  is the z-component of the spin angular momentum of a microstate

$$M_S = \sum m_s$$

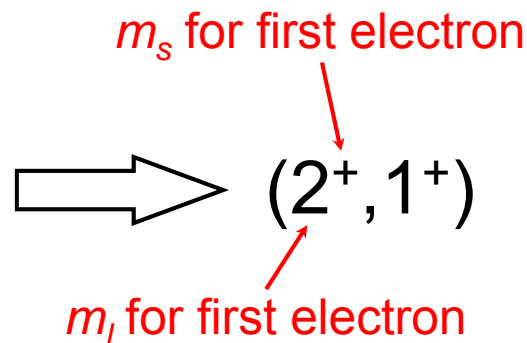
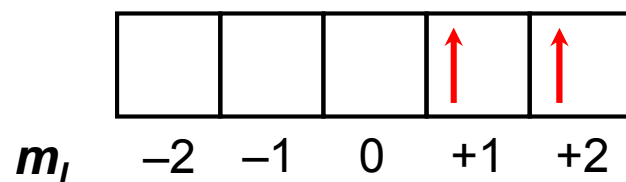
$$M_S \Rightarrow -S, -S + 1, \dots, -1, 0, +1, \dots, S - 1, S$$

# The $V^{3+}$ Free Ion

$V^{3+}$  has a valence electron configuration of  $[Ar]3d^2$

- $n = 3, l = 2$
- $m_l = -2, -1, 0, +1, +2$
- $m_s = -1/2, +1/2$
- $m_l$  and  $m_s$  interact such that certain combinations are lower in energy and others are higher in energy (Russell-Saunders Coupling)

Determining a microstate of  $V^{3+}$



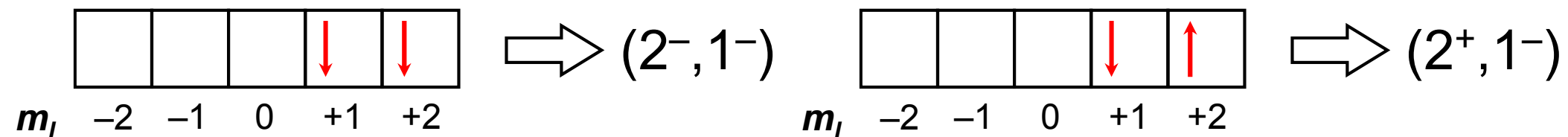
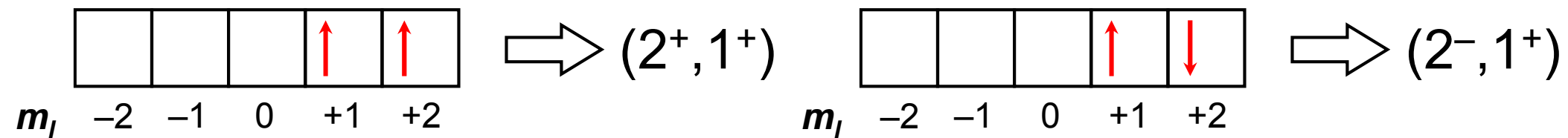
$$M_L = \sum m_l = 2 + 1 = 3$$

$$M_S = \sum m_s = \frac{1}{2} + \frac{1}{2} = 1$$

We only need to find 44 more!

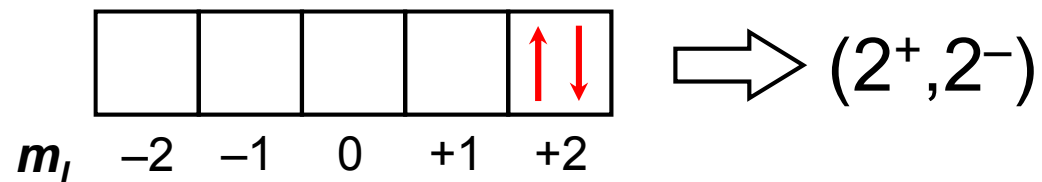
# V<sup>3+</sup> Microstate Table

		$M_L$								
		-4	-3	-2	-1	0	+1	+2	+3	+4
$M_S$	-1								(2 <sup>-</sup> ,1 <sup>-</sup> )	
	0								(2 <sup>+</sup> ,1 <sup>-</sup> ) (2 <sup>-</sup> ,1 <sup>+</sup> )	
	+1								(2 <sup>+</sup> ,1 <sup>+</sup> )	



# V<sup>3+</sup> Microstate Table

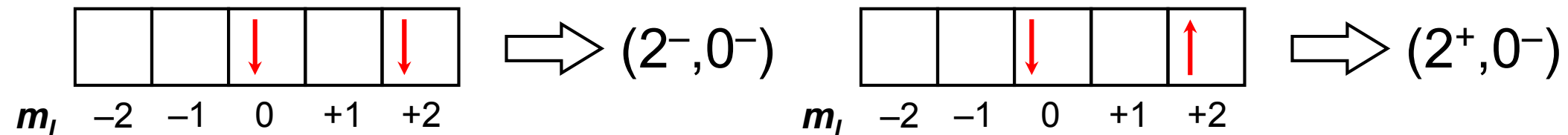
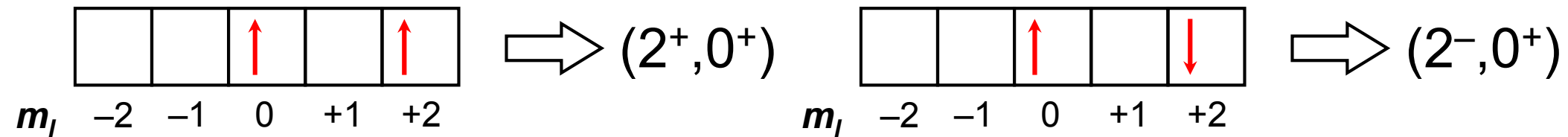
		$M_L$								
		-4	-3	-2	-1	0	+1	+2	+3	+4
$M_S$	-1								(2 <sup>-</sup> ,1 <sup>-</sup> )	
	0								(2 <sup>+</sup> ,1 <sup>-</sup> ) (2 <sup>-</sup> ,1 <sup>+</sup> )	(2 <sup>+</sup> ,2 <sup>-</sup> )
	+1								(2 <sup>+</sup> ,1 <sup>+</sup> )	



Pauli exclusion principle says there are no other possibilities for  $M_L = 4$ .

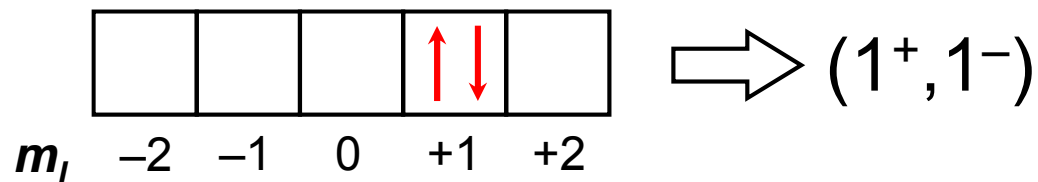
# V<sup>3+</sup> Microstate Table

		$M_L$								
		-4	-3	-2	-1	0	+1	+2	+3	+4
$M_S$	-1							(2 <sup>-</sup> ,0 <sup>-</sup> )	(2 <sup>-</sup> ,1 <sup>-</sup> )	
	0							(2 <sup>+</sup> ,0 <sup>-</sup> ) (2 <sup>-</sup> ,0 <sup>+</sup> )	(2 <sup>+</sup> ,1 <sup>-</sup> ) (2 <sup>-</sup> ,1 <sup>+</sup> )	(2 <sup>+</sup> ,2 <sup>-</sup> )
	+1							(2 <sup>+</sup> ,0 <sup>+</sup> )	(2 <sup>+</sup> ,1 <sup>+</sup> )	



# V<sup>3+</sup> Microstate Table

		$M_L$								
		-4	-3	-2	-1	0	+1	+2	+3	+4
$M_S$	-1							(2 <sup>-</sup> ,0 <sup>-</sup> )	(2 <sup>-</sup> ,1 <sup>-</sup> )	
	0							(2 <sup>+</sup> ,0 <sup>-</sup> ) (2 <sup>-</sup> ,0 <sup>+</sup> ) (1 <sup>+</sup> ,1 <sup>-</sup> )	(2 <sup>+</sup> ,1 <sup>-</sup> ) (2 <sup>-</sup> ,1 <sup>+</sup> )	(2 <sup>+</sup> ,2 <sup>-</sup> )
	+1							(2 <sup>+</sup> ,0 <sup>+</sup> )	(2 <sup>+</sup> ,1 <sup>+</sup> )	





# V<sup>3+</sup> Microstate Table

		$M_L$								
		-4	-3	-2	-1	0	+1	+2	+3	+4
$M_S$	-1		(-2 <sup>-</sup> , -1 <sup>-</sup> )	(-2 <sup>-</sup> , 0 <sup>-</sup> )	(-1 <sup>-</sup> , 0 <sup>-</sup> ) (-2 <sup>-</sup> , 1 <sup>-</sup> )	(1 <sup>-</sup> , -1 <sup>-</sup> ) (2 <sup>-</sup> , -2 <sup>-</sup> )	(1 <sup>-</sup> , 0 <sup>-</sup> ) (2 <sup>-</sup> , -1 <sup>-</sup> )	(2 <sup>-</sup> , 0 <sup>-</sup> )	(2 <sup>-</sup> , 1 <sup>-</sup> )	
	0	(-2 <sup>+</sup> , -2 <sup>-</sup> )	(-2 <sup>+</sup> , -1 <sup>-</sup> ) (-2 <sup>-</sup> , -1 <sup>+</sup> )	(-2 <sup>+</sup> , 0 <sup>-</sup> ) (-2 <sup>-</sup> , 0 <sup>+</sup> ) (-1 <sup>+</sup> , -1 <sup>-</sup> )	(-1 <sup>+</sup> , 0 <sup>-</sup> ) (-1 <sup>-</sup> , 0 <sup>+</sup> ) (-2 <sup>+</sup> , 1 <sup>-</sup> ) (-2 <sup>-</sup> , 1 <sup>+</sup> )	(2 <sup>-</sup> , -2 <sup>+</sup> ) (2 <sup>+</sup> , -2 <sup>-</sup> ) (1 <sup>-</sup> , -1 <sup>+</sup> ) (1 <sup>+</sup> , -1 <sup>-</sup> ) (0 <sup>+</sup> , 0 <sup>-</sup> )	(1 <sup>+</sup> , 0 <sup>-</sup> ) (1 <sup>-</sup> , 0 <sup>+</sup> ) (2 <sup>+</sup> , -1 <sup>-</sup> ) (2 <sup>-</sup> , -1 <sup>+</sup> )	(2 <sup>+</sup> , 0 <sup>-</sup> ) (2 <sup>-</sup> , 0 <sup>+</sup> ) (1 <sup>+</sup> , 1 <sup>-</sup> )	(2 <sup>+</sup> , 1 <sup>-</sup> ) (2 <sup>-</sup> , 1 <sup>+</sup> )	(2 <sup>+</sup> , 2 <sup>-</sup> )
	+1		(-2 <sup>+</sup> , -1 <sup>+</sup> )	(-2 <sup>+</sup> , 0 <sup>+</sup> )	(-1 <sup>+</sup> , 0 <sup>+</sup> ) (-2 <sup>+</sup> , 1 <sup>+</sup> )	(1 <sup>+</sup> , -1 <sup>+</sup> ) (2 <sup>+</sup> , -2 <sup>+</sup> )	(1 <sup>+</sup> , 0 <sup>+</sup> ) (2 <sup>+</sup> , -1 <sup>+</sup> )	(2 <sup>+</sup> , 0 <sup>+</sup> )	(2 <sup>+</sup> , 1 <sup>+</sup> )	

- Proceeding in the same way we can generate the microstates corresponding to  $M_L = +1$  and 0
- To generate the  $M_L = -4, -3, -2, -1$  microstates, just multiply the  $m_l$  values we already have by -1
- Microstates with the same energy now must be collected into atomic states.

# Determining Atomic States

$M_L$

	-4	-3	-2	-1	0	+1	+2	+3	+4
-1		(-2 <sup>-</sup> , -1 <sup>-</sup> )	(-2 <sup>-</sup> , 0 <sup>-</sup> )	(-1 <sup>-</sup> , 0 <sup>-</sup> ) (-2 <sup>-</sup> , 1 <sup>-</sup> )	(1 <sup>-</sup> , -1 <sup>-</sup> ) (2 <sup>-</sup> , -2 <sup>-</sup> )	(1 <sup>-</sup> , 0 <sup>-</sup> ) (2 <sup>-</sup> , -1 <sup>-</sup> )	(2 <sup>-</sup> , 0 <sup>-</sup> )	(2 <sup>-</sup> , 1 <sup>-</sup> )	
0	(-2 <sup>+</sup> , -2 <sup>-</sup> )	(-2 <sup>+</sup> , -1 <sup>-</sup> ) (-2 <sup>-</sup> , -1 <sup>+</sup> )	(-2 <sup>+</sup> , 0 <sup>-</sup> ) (-2 <sup>-</sup> , 0 <sup>+</sup> ) (-1 <sup>+</sup> , -1 <sup>-</sup> )	(-1 <sup>+</sup> , 0 <sup>-</sup> ) (-1 <sup>-</sup> , 0 <sup>+</sup> ) (-2 <sup>+</sup> , 1 <sup>-</sup> ) (-2 <sup>-</sup> , 1 <sup>+</sup> )	(2 <sup>-</sup> , -2 <sup>+</sup> ) (2 <sup>+</sup> , -2 <sup>-</sup> ) (1 <sup>-</sup> , -1 <sup>+</sup> ) (1 <sup>+</sup> , -1 <sup>-</sup> ) (0 <sup>+</sup> , 0 <sup>-</sup> )	(1 <sup>+</sup> , 0 <sup>-</sup> ) (1 <sup>-</sup> , 0 <sup>+</sup> ) (2 <sup>+</sup> , -1 <sup>-</sup> ) (2 <sup>-</sup> , -1 <sup>+</sup> )	(2 <sup>+</sup> , 0 <sup>-</sup> ) (2 <sup>-</sup> , 0 <sup>+</sup> ) (1 <sup>+</sup> , 1 <sup>-</sup> )	(2 <sup>+</sup> , 1 <sup>-</sup> ) (2 <sup>-</sup> , 1 <sup>+</sup> )	(2 <sup>+</sup> , 2 <sup>-</sup> )
+1		(-2 <sup>+</sup> , -1 <sup>+</sup> )	(-2 <sup>+</sup> , 0 <sup>+</sup> )	(-1 <sup>+</sup> , 0 <sup>+</sup> ) (-2 <sup>+</sup> , 1 <sup>+</sup> )	(1 <sup>+</sup> , -1 <sup>+</sup> ) (2 <sup>+</sup> , -2 <sup>+</sup> )	(1 <sup>+</sup> , 0 <sup>+</sup> ) (2 <sup>+</sup> , -1 <sup>+</sup> )	(2 <sup>+</sup> , 0 <sup>+</sup> )	(2 <sup>+</sup> , 1 <sup>+</sup> )	

$M_S$

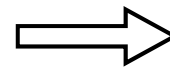
- An atomic state, summarized by a term symbol  $^{2S+1}L$ , includes microstates of the same energy.
- $L$  is the maximum value of  $M_L$  for the collection of microstates
  - we start with  $L = 4$  because that is the largest  $M_L$  on the table
- $S$  is the maximum value of  $M_S$ , given a value for  $L$ 
  - for  $L = 4$  the maximum (and only)  $M_S$  value is 0, which is also the value for  $S$

# Determining Atomic States

		$M_L$								
		-4	-3	-2	-1	0	+1	+2	+3	+4
$M_S$	-1		(-2 <sup>-</sup> , -1 <sup>-</sup> )	(-2 <sup>-</sup> , 0 <sup>-</sup> )	(-1 <sup>-</sup> , 0 <sup>-</sup> ) (-2 <sup>-</sup> , 1 <sup>-</sup> )	(1 <sup>-</sup> , -1 <sup>-</sup> ) (2 <sup>-</sup> , -2 <sup>-</sup> )	(1 <sup>-</sup> , 0 <sup>-</sup> ) (2 <sup>-</sup> , -1 <sup>-</sup> )	(2 <sup>-</sup> , 0 <sup>-</sup> )	(2 <sup>-</sup> , 1 <sup>-</sup> )	
	0	(-2 <sup>+</sup> , -2 <sup>-</sup> )	(-2 <sup>+</sup> , -1 <sup>-</sup> ) (-2 <sup>-</sup> , -1 <sup>+</sup> )	(-2 <sup>+</sup> , 0 <sup>-</sup> ) (-2 <sup>-</sup> , 0 <sup>+</sup> ) (-1 <sup>+</sup> , -1 <sup>-</sup> )	(-1 <sup>+</sup> , 0 <sup>-</sup> ) (-1 <sup>-</sup> , 0 <sup>+</sup> ) (-2 <sup>+</sup> , 1 <sup>-</sup> ) (-2 <sup>-</sup> , 1 <sup>+</sup> )	(2 <sup>-</sup> , -2 <sup>+</sup> ) (2 <sup>+</sup> , -2 <sup>-</sup> ) (1 <sup>-</sup> , -1 <sup>+</sup> ) (1 <sup>+</sup> , -1 <sup>-</sup> ) (0 <sup>+</sup> , 0 <sup>-</sup> )	(1 <sup>+</sup> , 0 <sup>-</sup> ) (1 <sup>-</sup> , 0 <sup>+</sup> ) (2 <sup>+</sup> , -1 <sup>-</sup> ) (2 <sup>-</sup> , -1 <sup>+</sup> )	(2 <sup>+</sup> , 0 <sup>-</sup> ) (2 <sup>-</sup> , 0 <sup>+</sup> ) (1 <sup>+</sup> , 1 <sup>-</sup> )	(2 <sup>+</sup> , 1 <sup>-</sup> ) (2 <sup>-</sup> , 1 <sup>+</sup> )	(2 <sup>+</sup> , 2 <sup>-</sup> )
	+1		(-2 <sup>+</sup> , -1 <sup>+</sup> )	(-2 <sup>+</sup> , 0 <sup>+</sup> )	(-1 <sup>+</sup> , 0 <sup>+</sup> ) (-2 <sup>+</sup> , 1 <sup>+</sup> )	(1 <sup>+</sup> , -1 <sup>+</sup> ) (2 <sup>+</sup> , -2 <sup>+</sup> )	(1 <sup>+</sup> , 0 <sup>+</sup> ) (2 <sup>+</sup> , -1 <sup>+</sup> )	(2 <sup>+</sup> , 0 <sup>+</sup> )	(2 <sup>+</sup> , 1 <sup>+</sup> )	

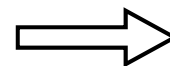
- For  $L = 4$  and  $S = 0$  we have the free ion term symbol  $^1G$
- To determine which microstates are in the  $^1G$  atomic state, we need to remember:

$$M_L \Rightarrow -L, -L + 1, \dots, -1, 0, +1, \dots, L - 1, L$$



since  $L = 4$ ,  $^1G$  will include  $M_L$  values from +4 to -4

$$M_S \Rightarrow -S, -S + 1, \dots, -1, 0, +1, \dots, S - 1, S$$



since  $S = 0$ ,  $^1G$  will only include  $M_S = 0$

# Determining Atomic States

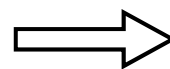
$M_L$

	-4	-3	-2	-1	0	+1	+2	+3	+4
-1		(-2 <sup>-</sup> , -1 <sup>-</sup> )	(-2 <sup>-</sup> , 0 <sup>-</sup> )	(-1 <sup>-</sup> , 0 <sup>-</sup> ) (-2 <sup>-</sup> , 1 <sup>-</sup> )	(1 <sup>-</sup> , -1 <sup>-</sup> ) (2 <sup>-</sup> , -2 <sup>-</sup> )	(1 <sup>-</sup> , 0 <sup>-</sup> ) (2 <sup>-</sup> , -1 <sup>-</sup> )	(2 <sup>-</sup> , 0 <sup>-</sup> )	(2 <sup>-</sup> , 1 <sup>-</sup> )	
0		(-2 <sup>+</sup> , -1 <sup>-</sup> )	(-2 <sup>+</sup> , 0 <sup>-</sup> ) (-2 <sup>-</sup> , 0 <sup>+</sup> )	(-1 <sup>+</sup> , 0 <sup>-</sup> ) (-1 <sup>-</sup> , 0 <sup>+</sup> ) (-2 <sup>+</sup> , 1 <sup>-</sup> )	(2 <sup>-</sup> , -2 <sup>+</sup> ) (2 <sup>+</sup> , -2 <sup>-</sup> ) (1 <sup>-</sup> , -1 <sup>+</sup> ) (1 <sup>+</sup> , -1 <sup>-</sup> )	(1 <sup>+</sup> , 0 <sup>-</sup> ) (1 <sup>-</sup> , 0 <sup>+</sup> ) (2 <sup>+</sup> , -1 <sup>-</sup> )	(2 <sup>+</sup> , 0 <sup>-</sup> ) (2 <sup>-</sup> , 0 <sup>+</sup> )	(2 <sup>+</sup> , 1 <sup>-</sup> )	
+1		(-2 <sup>+</sup> , -1 <sup>+</sup> )	(-2 <sup>+</sup> , 0 <sup>+</sup> )	(-1 <sup>+</sup> , 0 <sup>+</sup> ) (-2 <sup>+</sup> , 1 <sup>+</sup> )	(1 <sup>+</sup> , -1 <sup>+</sup> ) (2 <sup>+</sup> , -2 <sup>+</sup> )	(1 <sup>+</sup> , 0 <sup>+</sup> ) (2 <sup>+</sup> , -1 <sup>+</sup> )	(2 <sup>+</sup> , 0 <sup>+</sup> )	(2 <sup>+</sup> , 1 <sup>+</sup> )	

$M_S$

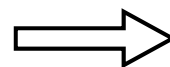
- The next atomic state will have  $L = 3$  and  $S = 1$ , so the term symbol is  ${}^3F$
- The microstates in the  ${}^3F$  atomic state are:

$$M_L \Rightarrow -L, -L + 1, \dots, -1, 0, +1, \dots, L - 1, L$$



since  $L = 3$ ,  ${}^3F$  will include  $M_L$  values from +3 to -3

$$M_S \Rightarrow -S, -S + 1, \dots, -1, 0, +1, \dots, S - 1, S$$



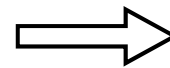
since  $S = 1$ ,  ${}^3F$  will include  $M_S$  values from +1 to -1

# Determining Atomic States

		$M_L$								
		-4	-3	-2	-1	0	+1	+2	+3	+4
$M_S$	-1				(-2 <sup>-</sup> ,1 <sup>-</sup> )	(2 <sup>-</sup> ,2 <sup>-</sup> )	(2 <sup>-</sup> ,1 <sup>-</sup> )			
	0			(-2 <sup>-</sup> ,0 <sup>+</sup> )	(-1 <sup>-</sup> ,0 <sup>+</sup> ) (-2 <sup>+</sup> ,1 <sup>-</sup> )	(2 <sup>+</sup> ,2 <sup>-</sup> ) (1 <sup>-</sup> ,1 <sup>+</sup> ) (1 <sup>+</sup> ,1 <sup>-</sup> )	(1 <sup>-</sup> ,0 <sup>+</sup> ) (2 <sup>+</sup> ,1 <sup>-</sup> )	(2 <sup>-</sup> ,0 <sup>+</sup> )		
	+1				(-1 <sup>+</sup> ,0 <sup>+</sup> )	(1 <sup>+</sup> ,1 <sup>+</sup> )	(1 <sup>+</sup> ,0 <sup>+</sup> )			

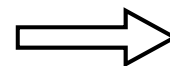
- Now we have a maximum  $M_L$  of 2, so  $L = 2$  and  $S = 0$  and the term symbol is  $^1D$
- The microstates in the  $^1D$  atomic state are:

$$M_L \Rightarrow -L, -L + 1, \dots, -1, 0, +1, \dots, L - 1, L$$



since  $L = 2$ ,  $^1D$  will include  $M_L$  values from +2 to -2

$$M_S \Rightarrow -S, -S + 1, \dots, -1, 0, +1, \dots, S - 1, S$$



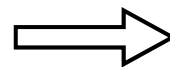
since  $S = 0$ ,  $^1D$  will only include  $M_S = 0$

# Determining Atomic States

		$M_L$								
		-4	-3	-2	-1	0	+1	+2	+3	+4
$M_S$	-1				(-2-,1-)	(2-,2-)	(2-,1-)			
	0				(-1-,0+)	(2+,-2-) (1-,1+)	(1-,0+)			
	+1				(-1+,0+)	(1+,-1+)	(1+,0+)			

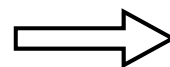
- Next we have  $L = 1$  and  $S = 1$  for a term symbol is  ${}^3P$
- The microstates in the  ${}^3P$  atomic state are:

$$M_L \Rightarrow -L, -L + 1, \dots, -1, 0, +1, \dots, L - 1, L$$



since  $L = 1$ ,  ${}^3P$  will include  $M_L$  values from +1 to -1

$$M_S \Rightarrow -S, -S + 1, \dots, -1, 0, +1, \dots, S - 1, S$$



since  $S = 1$ ,  ${}^3P$  will include  $M_S$  values from +1 to -1

# Determining Atomic States

		$M_L$									
		-4	-3	-2	-1	0	+1	+2	+3	+4	
$M_S$	-1										
	0					(1 <sup>-</sup> , -1 <sup>+</sup> )					
	+1										

- We have only one microstate left with  $L = 0$  and  $S = 0$  for a term symbol is  $^1S$
- So now we have the 45 microstates for the  $d^2 V^{3+}$  ion separated into five atomic states:

$$^1G, ^3F, ^1D, ^3P, ^1S$$

# Determining the Ground State

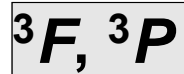
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The  $d^2 V^{3+}$  free ion has five atomic states:



The lowest energy state of the free ion is determined by Hund's rules:

1. The ground state has the highest spin multiplicity (to maximize  $\Pi_e$  and minimize  $\Pi_c$ )



2. For the same spin multiplicity, the ground state is the one with the largest value of  $L$  (i.e., the atomic state with the largest number of microstates)



So the ground state electron configuration for the  $V^{3+}$  **free ion** (or any other  $d^2$  free ion) is  $^3F$ , the other four atomic states are excited state electron configurations



# Free-Ion Terms

Table 11.5 in your text lists the atomic states of ions with various  $d$  electron counts.

**TABLE 11.5** Free-Ion Terms for  $d^n$  Configurations

Configuration	Free-Ion Terms						
$d^1$	$^2D$						
$d^2$		$^1S^1D^1G$	$^3P^3F$				
$d^3$	$^2D$		$^4P^4F$	$^2P^2D^2F^2G^2H$			
$d^4$	$^5D$	$^1S^1D^1G$	$^3P^3F$	$^3P^3D^3F^3G^3H$	$^1S^1D^1F^1G^1I$		
$d^5$	$^2D$		$^4P^4F$	$^2P^2D^2F^2G^2H$	$^2S^2D^2F^2G^2I$	$^4D^4G$	$^6S$
$d^6$	Same as $d^4$						
$d^7$	Same as $d^3$						
$d^8$	Same as $d^2$						
$d^9$	Same as $d^1$						
$d^{10}$	$^1S$						

NOTE: For any configuration, the free-ion terms are the sum of those listed; for example, for the  $d^2$  configuration, the free-ion terms are  $^1S + ^1D + ^1G + ^3P + ^3F$ .

# Spin-Orbit Coupling

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So far we've considered only  $e^-e^-$  (orbital angular momentum) and spin-spin (spin angular momentum) interactions.

Orbitals and spins can also interact giving rise to spin-orbit coupling

- $J$  is the total angular momentum

$$J \Rightarrow L + S, L + S - 1, L + S - 2, \dots, |L - S|$$

So for the  ${}^3F$  ground state of a  $d^2$  free ion, we have

$$\begin{aligned} J &\Rightarrow L + S = 4 \\ &\Rightarrow |L - S| = 2 \\ \text{so } J &= 4, 3, 2 \end{aligned}$$

So the  ${}^3F$  ground state electron configuration of a  $d^2$  free ion splits into  ${}^3F_4$ ,  ${}^3F_3$ , and  ${}^3F_2$ .

To determine the lowest energy spin-orbit coupled state:

1. For less than half-filled shells, the lowest  $J$  is the lowest energy
2. For more than half-filled shells, the highest  $J$  is the lowest energy
3. For half-filled shells, only one  $J$  is possible