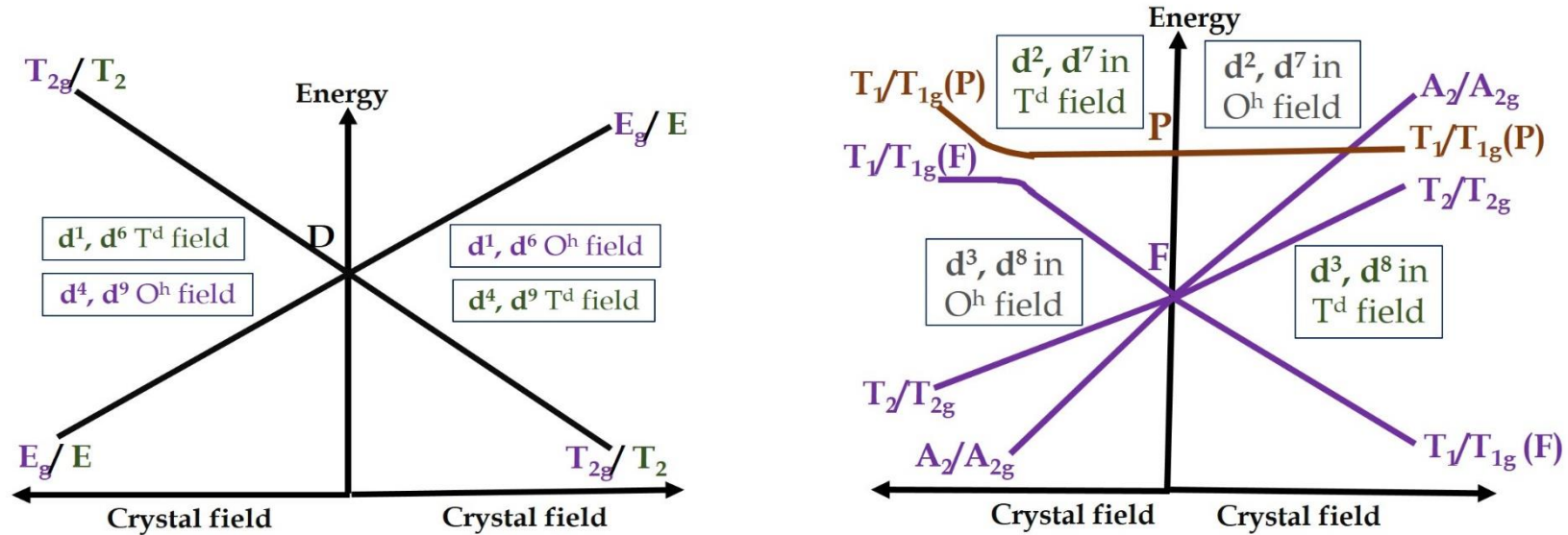# ORGEL DIAGRAM

Presented
By
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Three main steps in finding free ion Terms:

1. Resultant spin quantum number (S): Individual spin angular momenta of the electrons (m_s) combine to give resultant spin angular momentum (M_s).

2. Resultant orbital quantum number (L): Individual orbital angular momenta of the electrons (m_l) combine to give resultant orbital angular momentum (M_L).

3. Resultant spin-orbital quantum number (J): Resultant spin angular momentum (M_s) and resultant orbital angular momentum (M_L) combine to give a resultant spin-orbital angular momentum (M_J).

$$\text{Free ion Term} = {}^{(2S+1)}L$$
$$\text{Free ion Term-Symbol} = {}^{(2S+1)}L_J$$

Free ion Terms of various d^n configurations:

Configuration	No. of microstates	Terms
d^1, d^9	10	^2D
d^2, d^8	45	^3F, ^3P, ^1G, ^1D, ^1S
d^3, d^7	120	^4F, ^4P, ^2H, ^2G, ^2F, $^2D(2)$, ^2P
d^4, d^6	210	^5D, ^3H, ^3G, $^3F(2)$, ^3D, $^3P(2)$, ^1I, $^1G(2)$, ^1F, $^1D(2)$, $^1S(2)$
d^5	252	^6S, ^4G, ^4F, ^4D, ^4P, ^2I, ^2H, $^2G(2)$, $^2F(2)$, $^2D(3)$, ^2P, ^2S

Number of microstates = ^nC_r
Degeneracy of Term = (2S+1)(2L+1)
(2S+1)= Spin multiplicity
(2L+1) = Orbital multiplicity

Microstates of d^2 configuration

Degeneracy of ^3F =21
Degeneracy of ^3P =9
Degeneracy of ^1G =9
Degeneracy of ^1D =5
Degeneracy of ^1S =1

Total degeneracy = 45

Degeneracy of ^2D Term = 2 x 5 =10
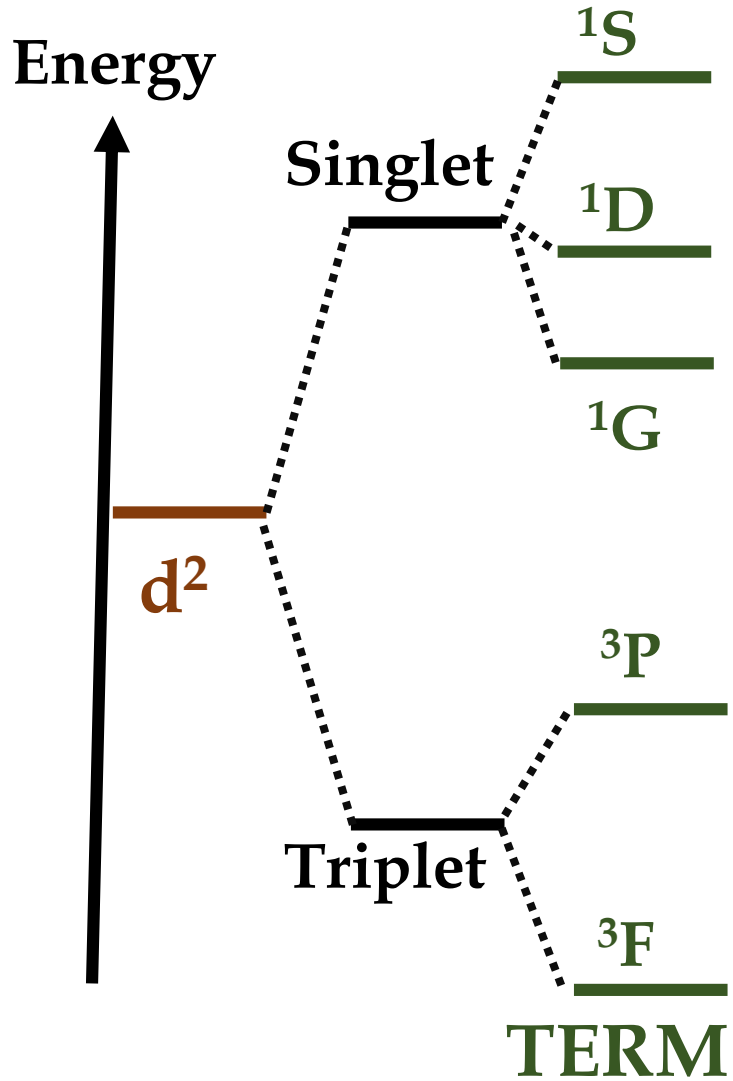
FREE ION TERMS: RUSSELL-SAUNDERS STATES

Energy

Singlet

^1S

^1D

^1G

d²

^3P

Triplet

^3F

TERM

Racah Parameters

❖ The energy separation between various 'terms' are determined by inter-electron repulsions. The inter-electron repulsions are conveniently described in terms of parameters called **Racah parameters**.

❖ The energy of each 'term' originating from a given electron configuration may be expressed as linear combination of three **Racah parameters A, B and C**.

Energy of different terms

$^1S = A + 14B + 7C$

$^1D = A – 3B + 2C$

$^1G = A + 4B + 2C$
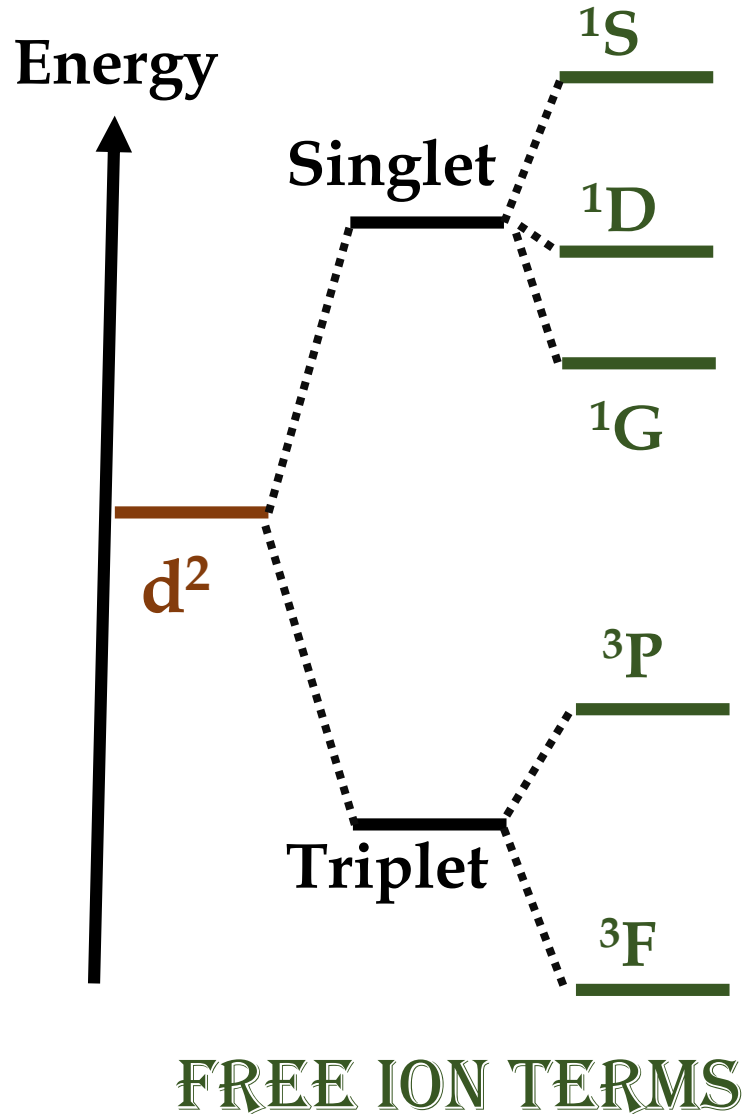
$^3P = A + 7B$

$^3F = A -8B$

The differences are given by B and C only.

Ions of first transition series have a C/B ratio of about 4, with B lying around 1000 cm^{-1}. The values of B and C in complexes are much lower than the free ion values.

Energy

^1S

Singlet

^1D

^1G

d^2

^3P

Triplet

^3F

FREE ION TERMS

How free ion terms are affected when the ion is placed in the field of ligand?

1. Weak field case:

Crystal field is smaller in comparison to inter-electron repulsion. We can first derive the terms for the free ion and then introduce the **effect of crystal field** on them. In effect, **free ion terms split into components.**

2. Strong field case:

It would be more appropriate to consider the crystal field splitting first and then to make necessary adjustments for inter-electronic repulsion.

Free ion terms split into labels by the field of ligand.

TERMS ARISING IN LIGAND FIELD

Energy

^1S

Singlet

^1D

^1G

d²

^3P

Triplet

^3F

FREE ION TERMS
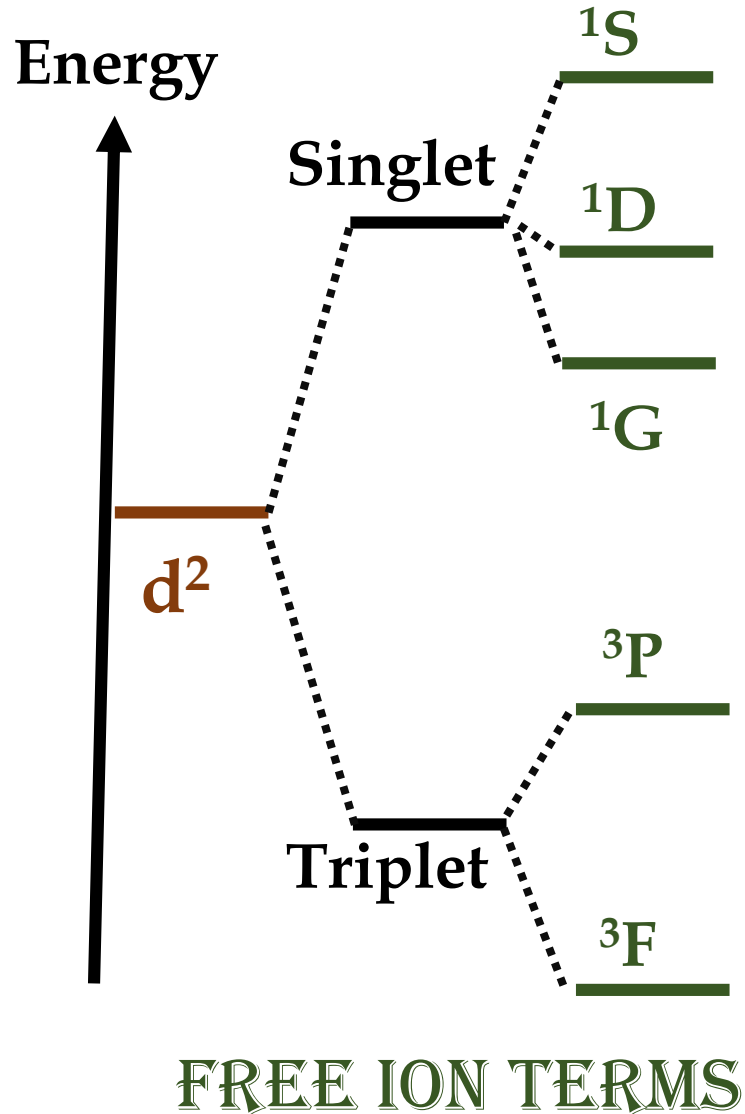
Spectroscopic labels for split components

Parent state	Degeneracy (2L+1)	Labels arising in crystal field (Irreducible representation)
S	1	A_1
P	3	T_1
D	5	$E + T_2$
F	7	$A_2 + T_1 + T_2$
G	9	$A_1 + E + T_1 + T_2$

- ➢ The labels for split components derived from group theory.
- ➢ Mulliken symbols **T**, **E** and **A**(or **B**) signify triple fold degenerate, double fold degenerate and non-degenerate states, respectively.
- ➢ The subscripts **1** and **2** denote that the wave function is symmetric or antisymmetric respectively either with respect to a 2 fold rotational axis perpendicular to the principal axis or to a plane of symmetry including principal axis.
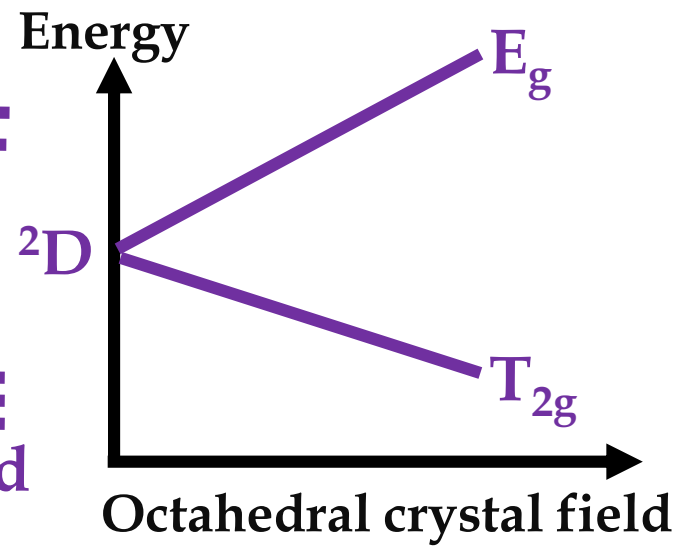
TERMS ARISING IN LIGAND FIELD

d^n	Free ion terms
d^1, d^9	^2D
d^2, d^8	^3F, ^3P, ^1G...
d^3, d^7	^4F, ^4P, ^2H...
d^4, d^6	^5D, ^3H, ^3G...
d^5	^6S, ^4G, ^4F...

State	Labels
S	A_1
P	T_1
D	$E + T_2$
F	$A_2 + T_1 + T_2$

d^1 Octahedral weak field

	Ground state	Excited state
	Degeneracy = 3 **Label =T**	Degeneracy = 2 **Label = E**

Ground state

Free ion ground state term = ^2D
$D = E + T_2$
Total degeneracy = 2+3 = 5

Excited state

Energy

E_g

^2D

T_{2g}

Octahedral crystal field

TERMS ARISING IN LIGAND FIELD

d^n	Free ion terms
d^1, d^9	^2D
d^2, d^8	^3F, ^3P, ^1G…
d^3, d^7	^4F, ^4P, ^2H…
d^4, d^6	^5D, ^3H, ^3G…
d^5	^6S, ^4G, ^4F…

d^1 Octahedral weak field

Ground state	Excited state
Degeneracy = 3 **Label =T**	Degeneracy = 2 **Label = E**

Free ion ground state term = ^2D
$D = E + T_2$
Total degeneracy = 2+3 = 5

Ground state

Excited state

Energy

^2D

E_g

T_{2g}

Octahedral crystal field
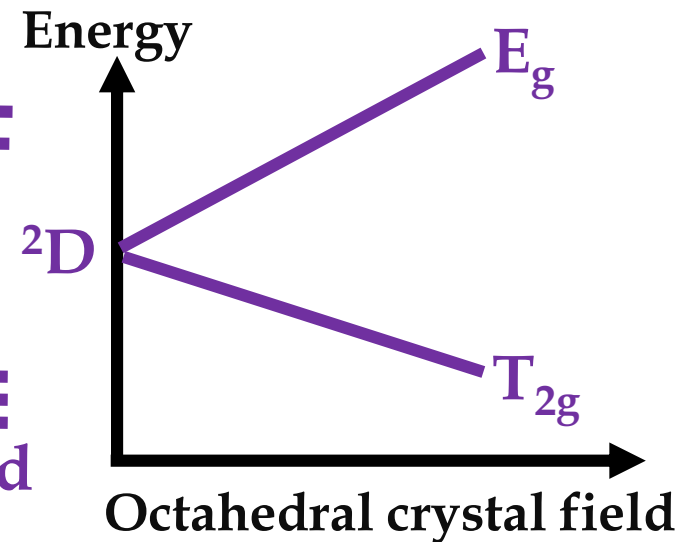
State	Labels
S	A_1
P	T_1
D	$E + T_2$
F	$A_2 + T_1 + T_2$

d^1 Tetrahedral field

Ground state	Excited state
Degeneracy = 2 **Label =E**	Degeneracy = 3 **Label = T**

Free ion ground state term = ^2D
$D = E + T_2$
Total degeneracy = 2+3 = 5

Ground state

Excited state

Energy

^2D

T_2

E

Tetrahedral crystal field

TERMS ARISING IN LIGAND FIELD

d¹ system in ligand field

d^n	Free ion terms
d^1, d^9	^2D
d^2, d^8	^3F, ^3P, ^1G…
d^3, d^7	^4F, ^4P, ^2H…
d^4, d^6	^5D, ^3H, ^3G…
d^5	^6S, ^4G, ^4F…

State	Labels
S	A_1
P	T_1
D	$E + T_2$
F	$A_2 + T_1 + T_2$

d^1 system in tetrahedral ligand field

d^1 system in octahedral ligand field

T_2

E_g

^2D

E

T_{2g}

Energy

Crystal field

Crystal field

Octahedral crystal field

Energy

^2D E_g

T_{2g}

Tetrahedral crystal field

Energy

^2D T_2

E

TERMS ARISING IN LIGAND FIELD

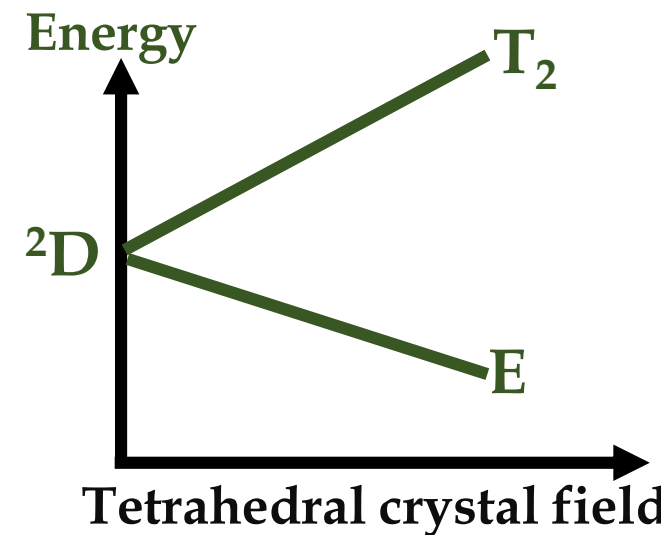| d^n	Free ion terms
d^1, d^9	^2D
d^2, d^8	^3F, ^3P, ^1G…
d^3, d^7	^4F, ^4P, ^2H…
d^4, d^6	^5D, ^3H, ^3G…
d^5	^6S, ^4G, ^4F…

d^6 Octahedral weak field
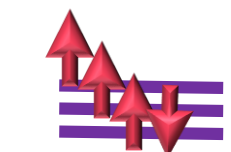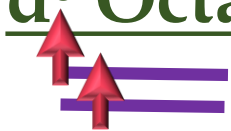
Ground state	Excited state
Degeneracy = 3 **Label =T**	Degeneracy = 2 **Label = E**

Ground state

Free ion ground state term = ^5D
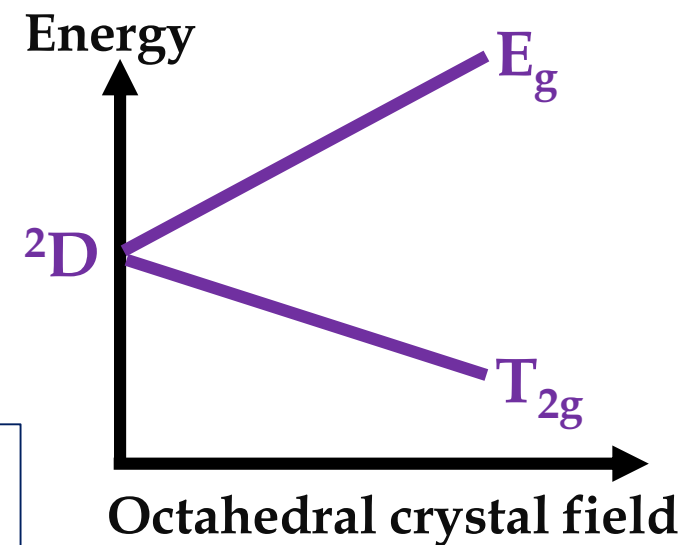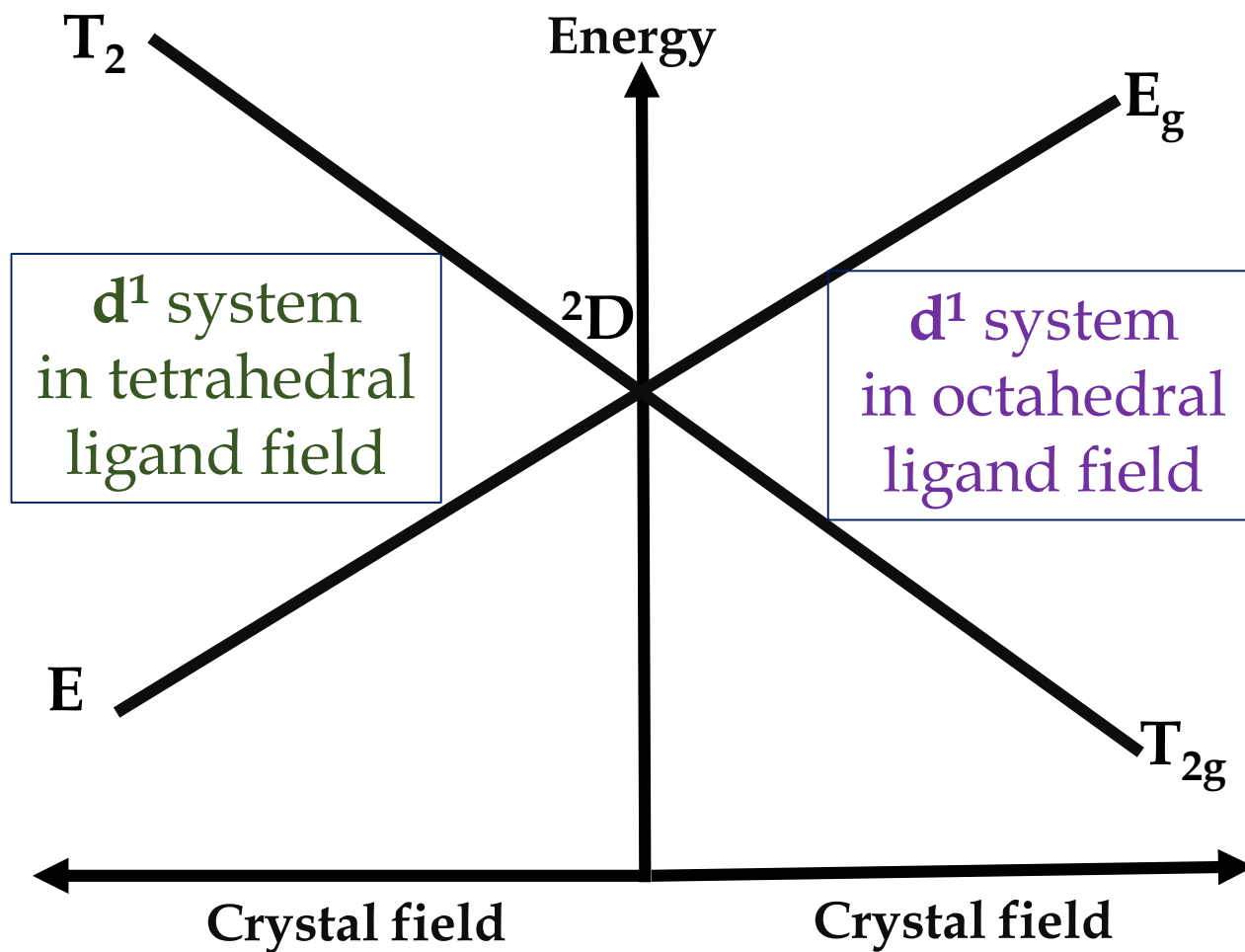$D = E + T_2$
Total degeneracy = 2+3 = 5
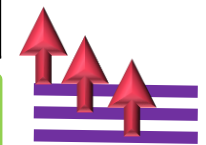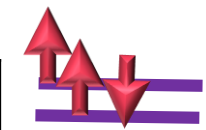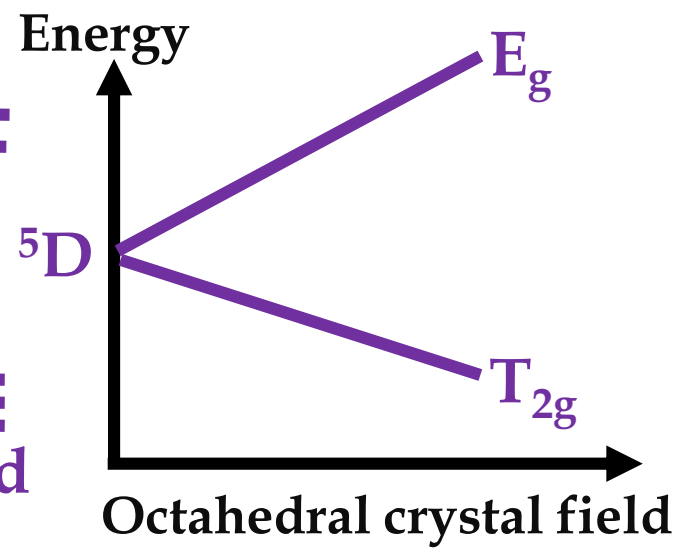
Excited state

State	Labels
S	A_1
P	T_1
D	$E + T_2$
F	$A_2 + T_1 + T_2$

d^6 Tetrahedral field

Ground state	Excited state
Degeneracy = 2 **Label =E**	Degeneracy = 3 **Label = T**

Ground state

Free ion ground state term = ^5D
$D = E + T_2$
Total degeneracy = 2+3 = 5
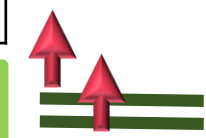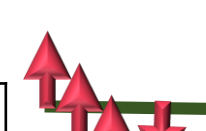
Excited state
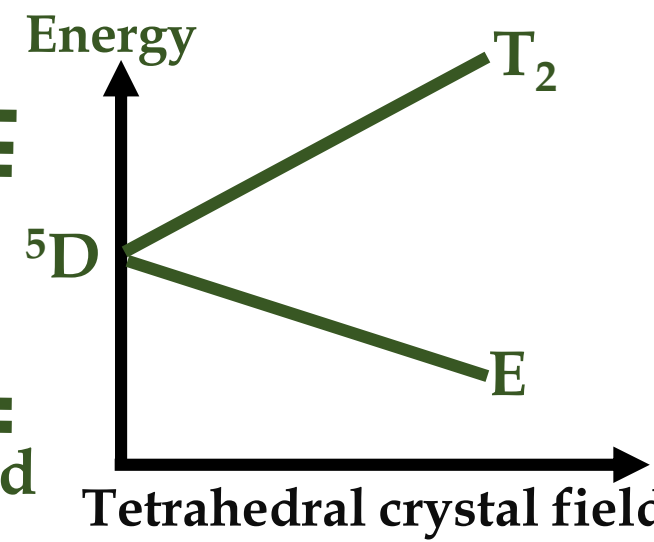
d^6 system in ligand field

d^n	Free ion terms
d^1, d^9	^2D
d^2, d^8	^3F, ^3P, $^1G\ldots$
d^3, d^7	^4F, ^4P, $^2H\ldots$
d^4, d^6	^5D, ^3H, $^3G\ldots$
d^5	^6S, ^4G, $^4F\ldots$

State	Labels
S	A_1
P	T_1
D	$E + T_2$
F	$A_2 + T_1 + T_2$

d^6 system in tetrahedral ligand field
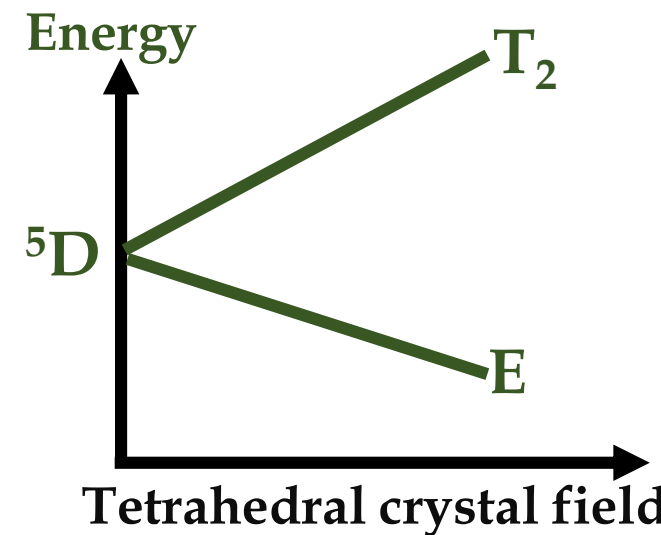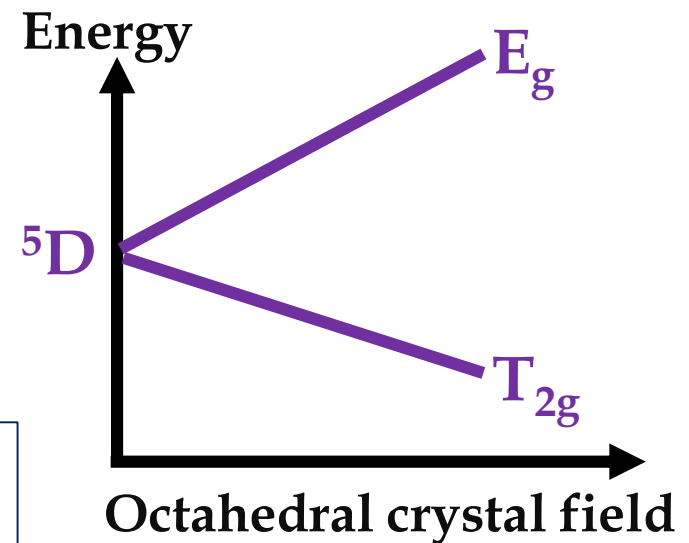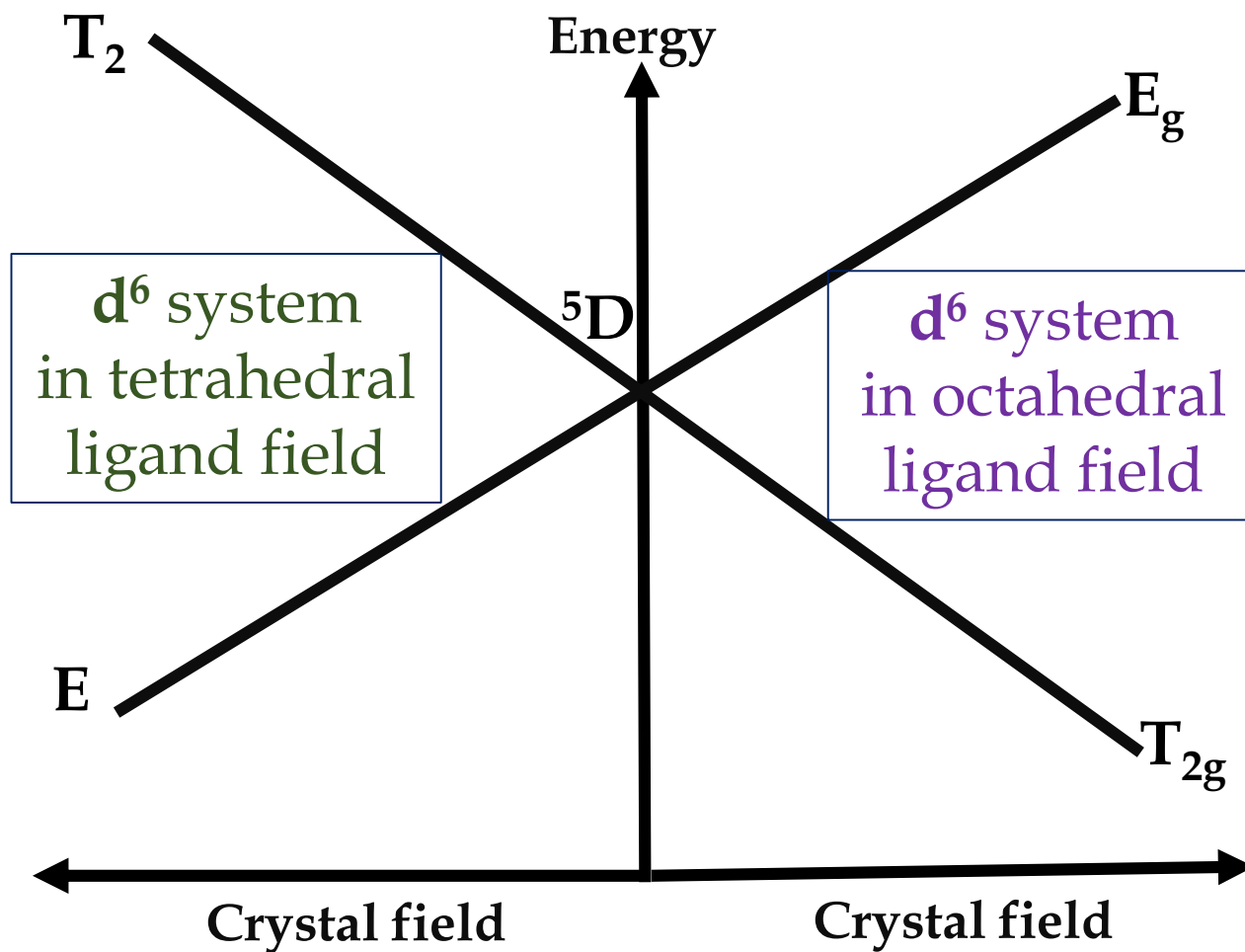
d^6 system in octahedral ligand field

Energy

T_2

E_g

^5D

E

T_{2g}

Crystal field   Crystal field

Energy

E_g

^5D

T_{2g}

Octahedral crystal field

Energy

T_2

^5D

E

Tetrahedral crystal field

TERMS ARISING IN LIGAND FIELD

d^n	Free ion terms
d^1, d^9	^2D
d^2, d^8	^3F, ^3P, ^1G…
d^3, d^7	^4F, ^4P, ^2H…
d^4, d^6	^5D, ^3H, ^3G…
d^5	^6S, ^4G, ^4F…

d^4 Octahedral weak field

Ground state	Excited state
Degeneracy = 2 **Label =E**	Degeneracy = 3 **Label = T**

Free ion ground state term = ^5D
$D = E + T_2$
Total degeneracy = 2+3 = 5

Ground state

Excited state

Energy

^5D

T_{2g}

E_g

Octahedral crystal field
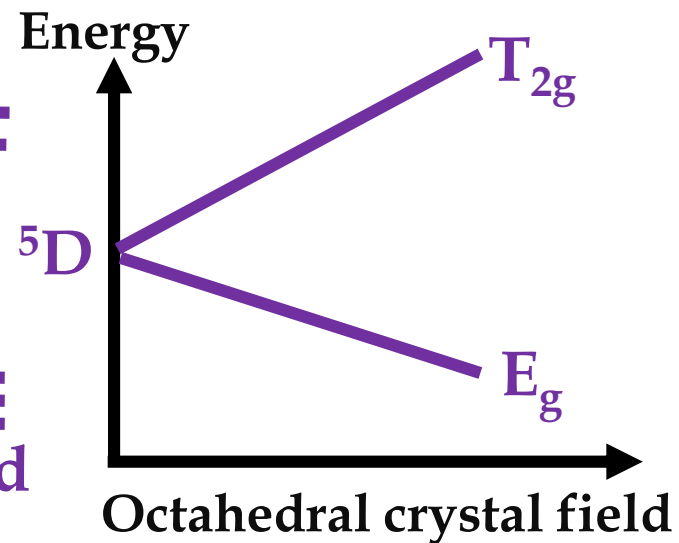
State	Labels
S	A_1
P	T_1
D	$E + T_2$
F	$A_2 + T_1 + T_2$

d^4 Tetrahedral field

Ground state	Excited state
Degeneracy = 3 **Label =T**	Degeneracy = 2 **Label = E**

Free ion ground state term = ^5D
$D = E + T_2$
Total degeneracy = 2+3 = 5

Ground state

Excited state

Energy

^5D

E

T_2

Tetrahedral crystal field
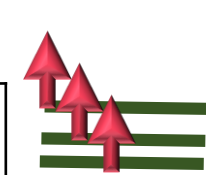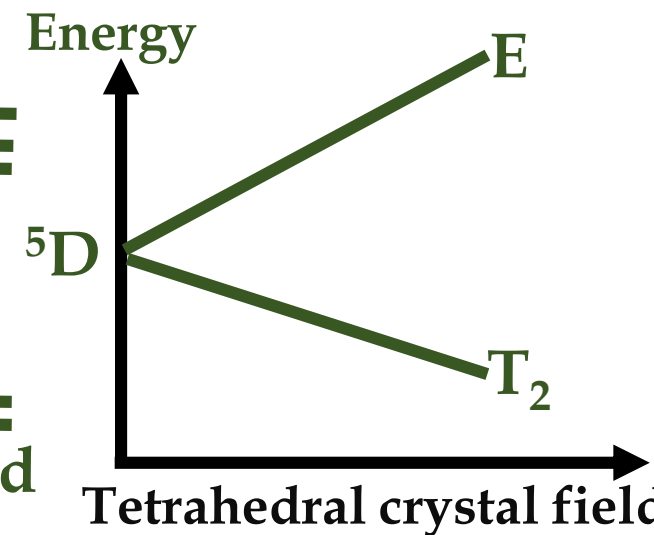
TERMS ARISING IN LIGAND FIELD

d^n	Free ion terms
d^1, d^9	^2D
d^2, d^8	^3F, ^3P, ^1G…
d^3, d^7	^4F, ^4P, ^2H…
d^4, d^6	^5D, ^3H, ^3G…
d^5	^6S, ^4G, ^4F…

State	Labels
S	A_1
P	T_1
D	$E + T_2$
F	$A_2 + T_1 + T_2$

d^4 system in ligand field
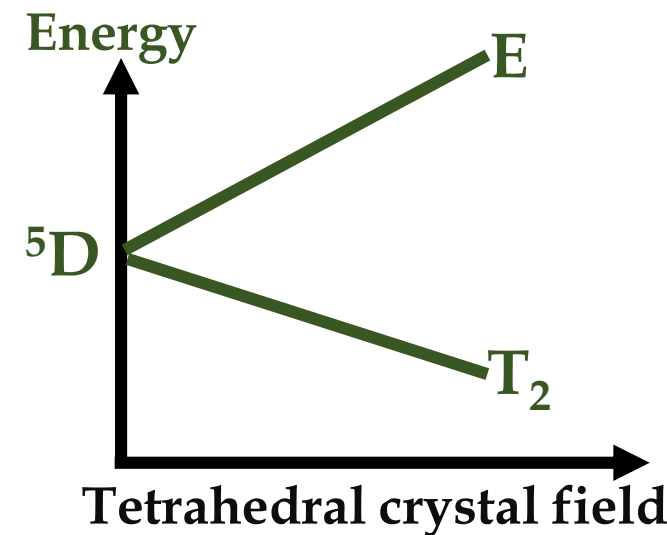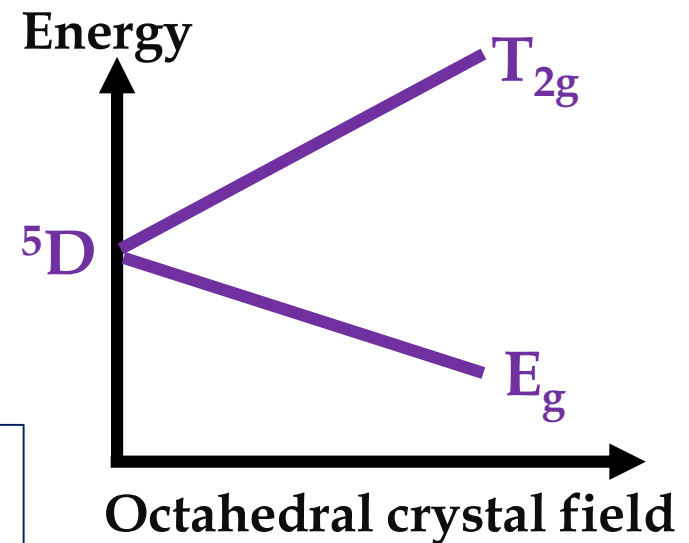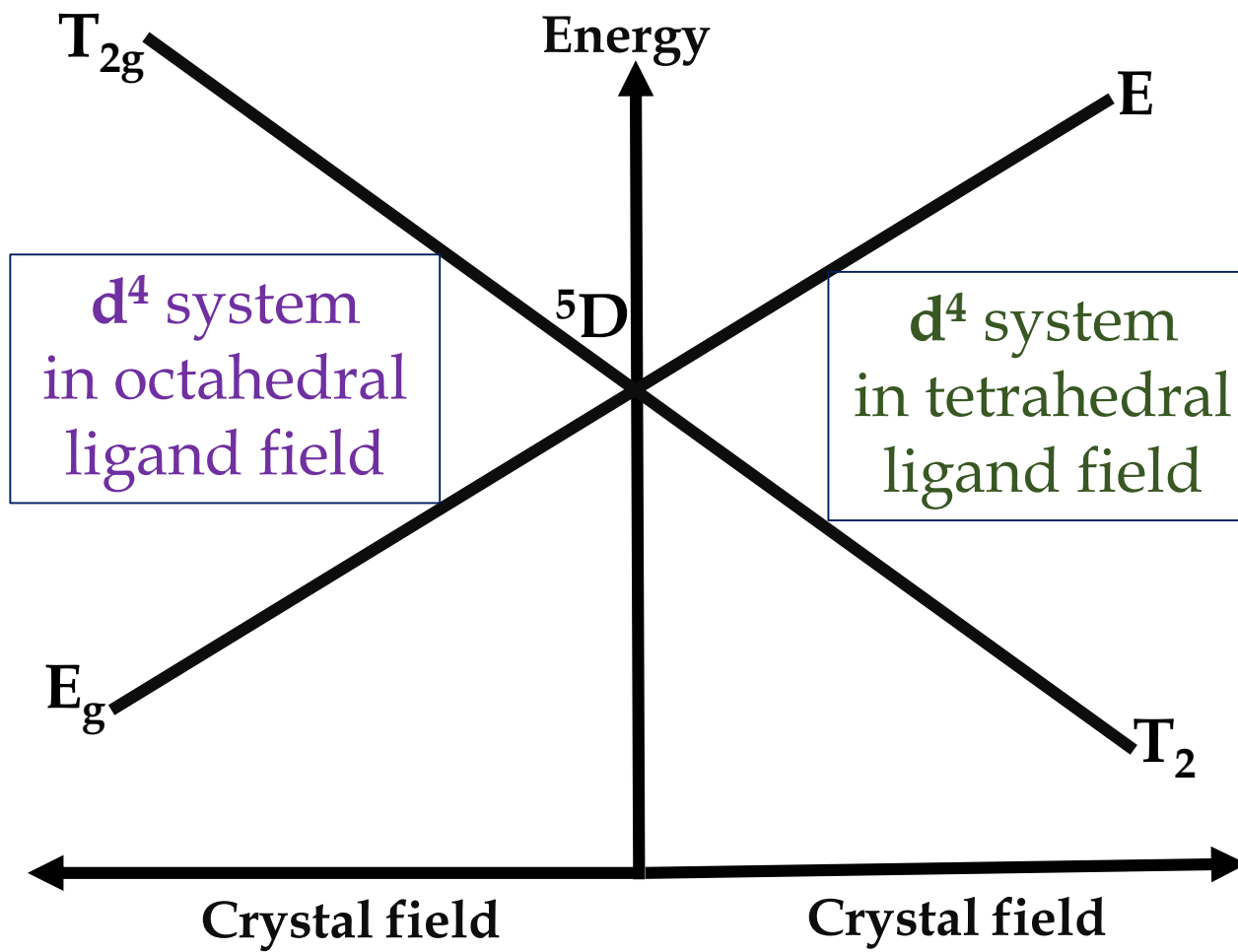
d⁴ system in octahedral ligand field

d⁴ system in tetrahedral ligand field

T_{2g}

^5D

E

E_g

T_2

Crystal field

Crystal field

Energy

Octahedral crystal field

T_{2g}

^5D

E_g

Tetrahedral crystal field

Energy

^5D

E

T_2

TERMS ARISING IN LIGAND FIELD

d^n	Free ion terms
d^1, d^9	^2D
d^2, d^8	^3F, ^3P, $^1G...$
d^3, d^7	^4F, ^4P, $^2H...$
d^4, d^6	^5D, ^3H, $^3G...$
d^5	^6S, ^4G, $^4F...$

d^9 Octahedral weak field

Ground state	Excited state
Degeneracy = 2 **Label = E**	Degeneracy = 3 **Label = T**

Free ion ground state term = ^2D
D = E + T_2
Total degeneracy = 2+3 = 5

Ground state

Excited state

Energy

^2D

T_{2g}

E_g

Octahedral crystal field
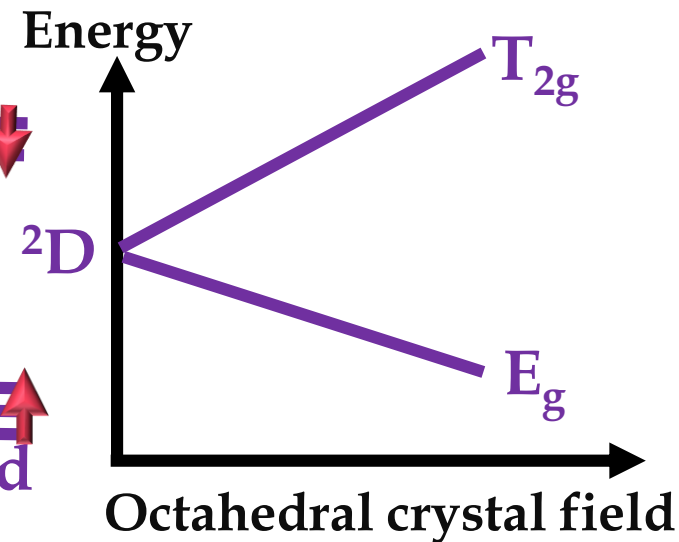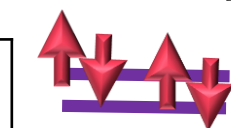
State	Labels
S	A_1
P	T_1
D	$E + T_2$
F	$A_2 + T_1 + T_2$

d^9 Tetrahedral field
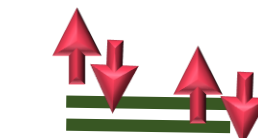
Ground state	Excited state
Degeneracy = 3 **Label = T**	Degeneracy = 2 **Label = E**

Free ion ground state term = ^2D
D = E + T_2
Total degeneracy = 2+3 = 5

Ground state

Excited state

Energy

^2D

E

T_2

Tetrahedral crystal field

TERMS ARISING IN LIGAND FIELD

d⁹ system in ligand field
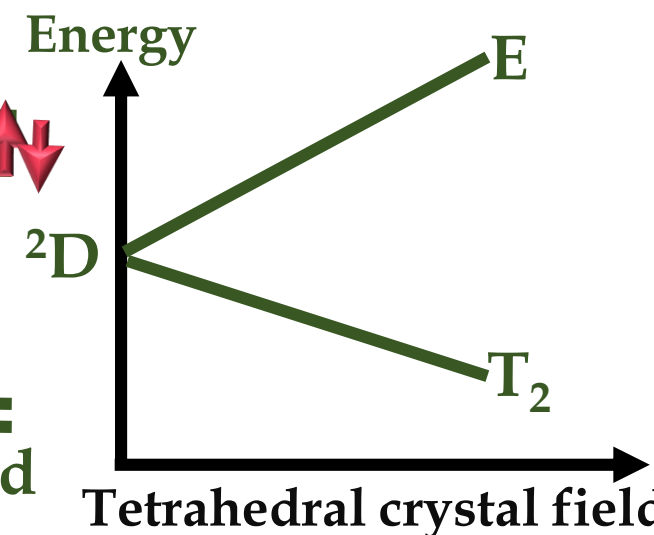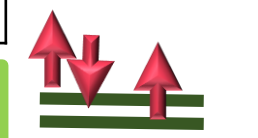
d^9 system in ligand field

d^n	Free ion terms
d^1, d^9	^2D
d^2, d^8	^3F, ^3P, ^1G…
d^3, d^7	^4F, ^4P, ^2H…
d^4, d^6	^5D, ^3H, ^3G…
d^5	^6S, ^4G, ^4F…

State	Labels
S	A_1
P	T_1
D	$E + T_2$
F	$A_2 + T_1 + T_2$

d^9 system in octahedral ligand field

d^9 system in tetrahedral ligand field

T_{2g}

Energy

^2D

E

E_g

T_2

Crystal field

Crystal field

Energy

T_{2g}

^2D

E_g

Octahedral crystal field

Energy

E

^2D

T_2

Tetrahedral crystal field

TERMS ARISING IN LIGAND FIELD

T_{2} Energy E_g

d¹ in Td. field ^2D **d¹ in Oct. field**

E T_{2g}

Crystal field   Crystal field

T_{2} Energy E_g

d⁶ in Td field ^5D **d⁶ in Oct field**

E T_{2g}

Crystal field   Crystal field

T_{2g} Energy   E

d⁴ in Oct field ^5D **d⁴ in Td field**

E_g T_{2}

Crystal field   Crystal field

T_{2g} Energy   E

d⁹ in Oct field ^2D **d⁹ in Td field**

E_g T_{2}

Crystal field   Crystal field

T_{2g}/T_{2} Energy E_g/E

d¹, d⁶ Tᵈ field   D   **d¹, d⁶ Oʰ field**

d⁴, d⁹ Oʰ field   **d⁴, d⁹ Tᵈ field**

E_g/E T_{2g}/T_{2}

Crystal field   Crystal field

Combine energy level diagram for free ion ground term D

Orgel diagram

Orgel diagram:

The energy separation between the ground state terms for various d^n configuration in ligand field with the increasing ligand field is termed as Orgel diagram after its originator.

T_{2g}/T_2

Energy

E_g/E

d¹, d⁶ Tᵈ field

D

d¹, d⁶ Oʰ field

d⁴, d⁹ Oʰ field

d⁴, d⁹ Tᵈ field

E_g/E

T_{2g}/T_2

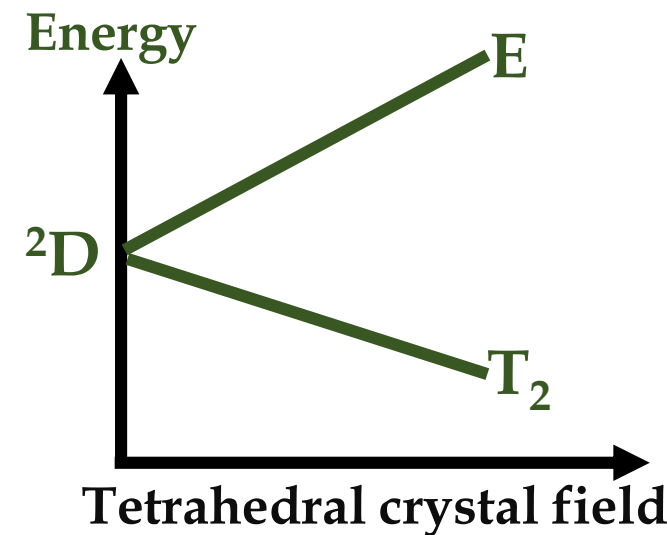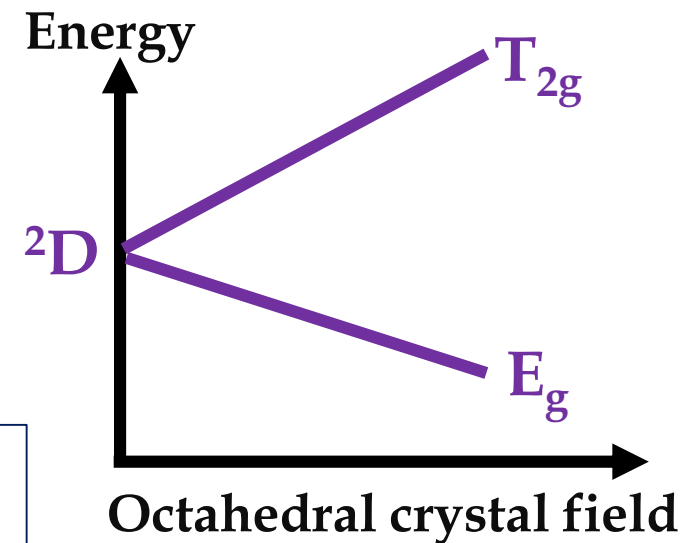Crystal field   Crystal field
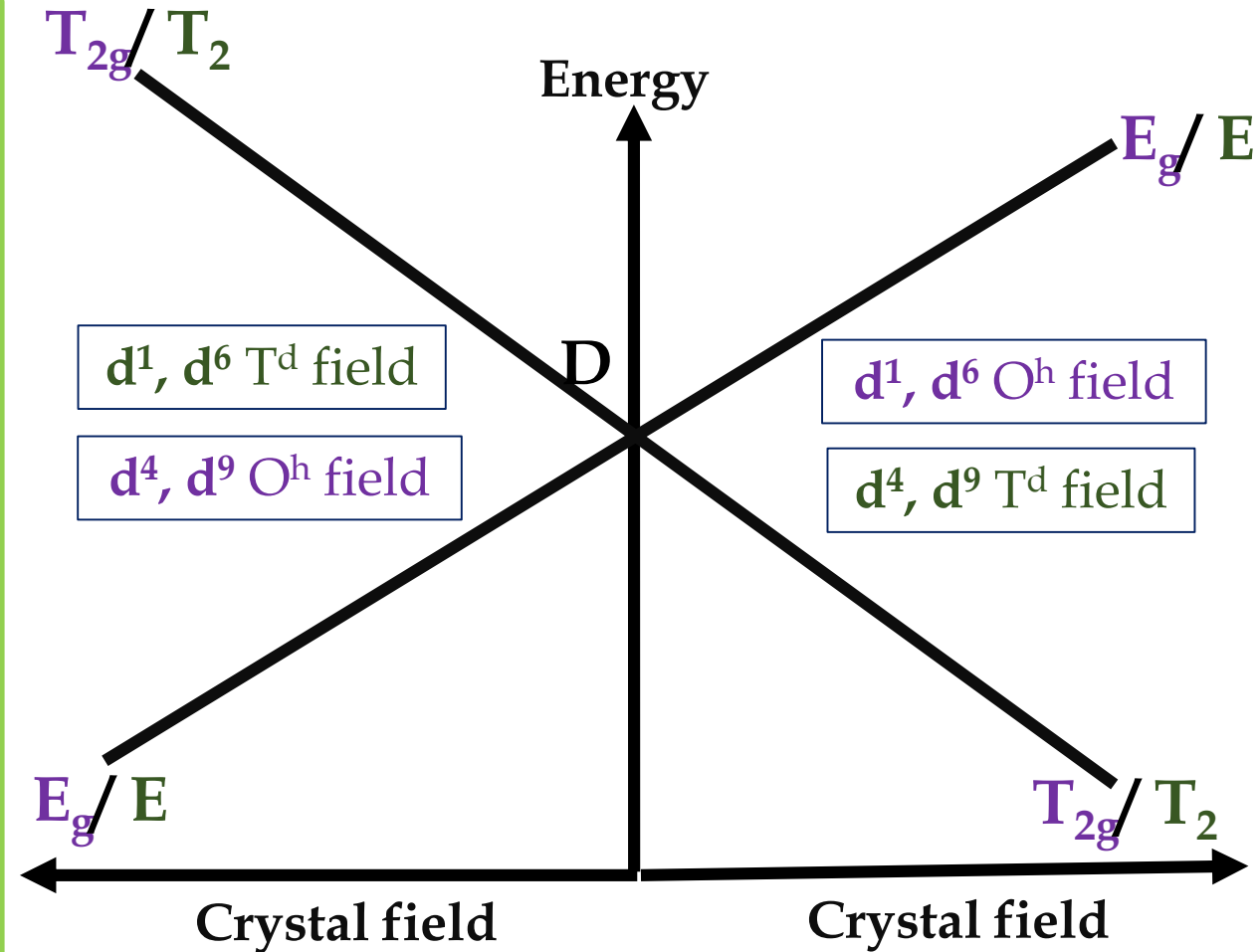
Combine energy level diagram for free ion ground term D

Orgel diagram

TERMS ARISING IN LIGAND FIELD

d^n	Free ion terms
d^1, d^9	^2D
d^2, d^8	$^3F, ^3P, ^1G\ldots$
d^3, d^7	$^4F, ^4P, ^2H\ldots$
d^4, d^6	$^5D, ^3H, ^3G\ldots$
d^5	$^6S, ^4G, ^4F\ldots$

State	Labels
S	A_1
P	T_1
D	$E + T_2$
F	$A_2 + T_1 + T_2$

d^2 Octahedral weak field

Ground state
Degeneracy = 3

Excited state-I
Degeneracy = 3 x 2 = 6

Excited state-II
Degeneracy = 1

Total degeneracy = 3+6+1 = 10

Free ion ground state term = $^3F, ^3P$

$$F = A_2 + T_1 + T_2$$
$$P = T_1$$

Total degeneracy = 1+3+3+3 = 10

Energy

A_{2g}

^3P T_{1g} (P)

T_{2g}

^3F

T_{1g} (F)

Octahedral crystal field

TERMS ARISING IN LIGAND FIELD

d^n	Free ion terms
d^1, d^9	^2D
d^2, d^8	^3F, ^3P, ^1G…
d^3, d^7	^4F, ^4P, ^2H…
d^4, d^6	^5D, ^3H, ^3G…
d^5	^6S, ^4G, ^4F…

State	Labels
S	A_1
P	T_1
D	$E + T_2$
F	$A_2 + T_1 + T_2$

d^2 Tetrahedral field

Ground state

Degeneracy = 1

Excited state-I

Degeneracy = 2 x 3 = 6

Excited state-II

Degeneracy = 3

Total degeneracy = 1+6+3 = 10
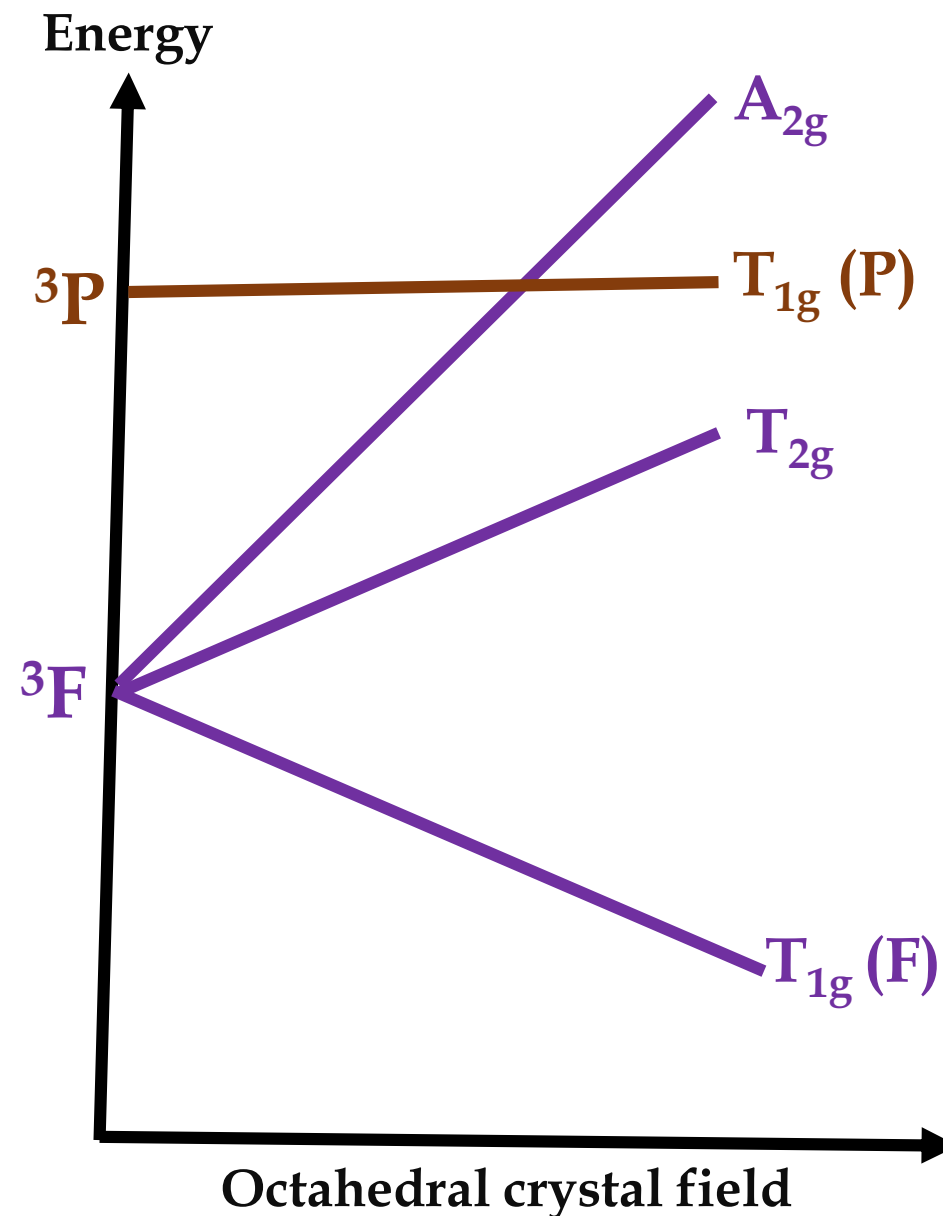
Free ion ground state term = ^3F, ^3P

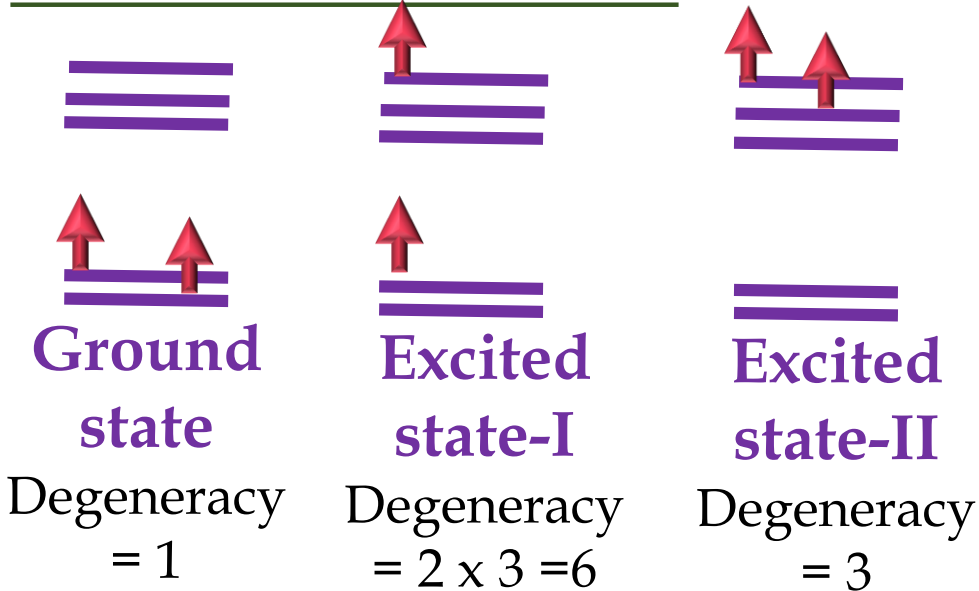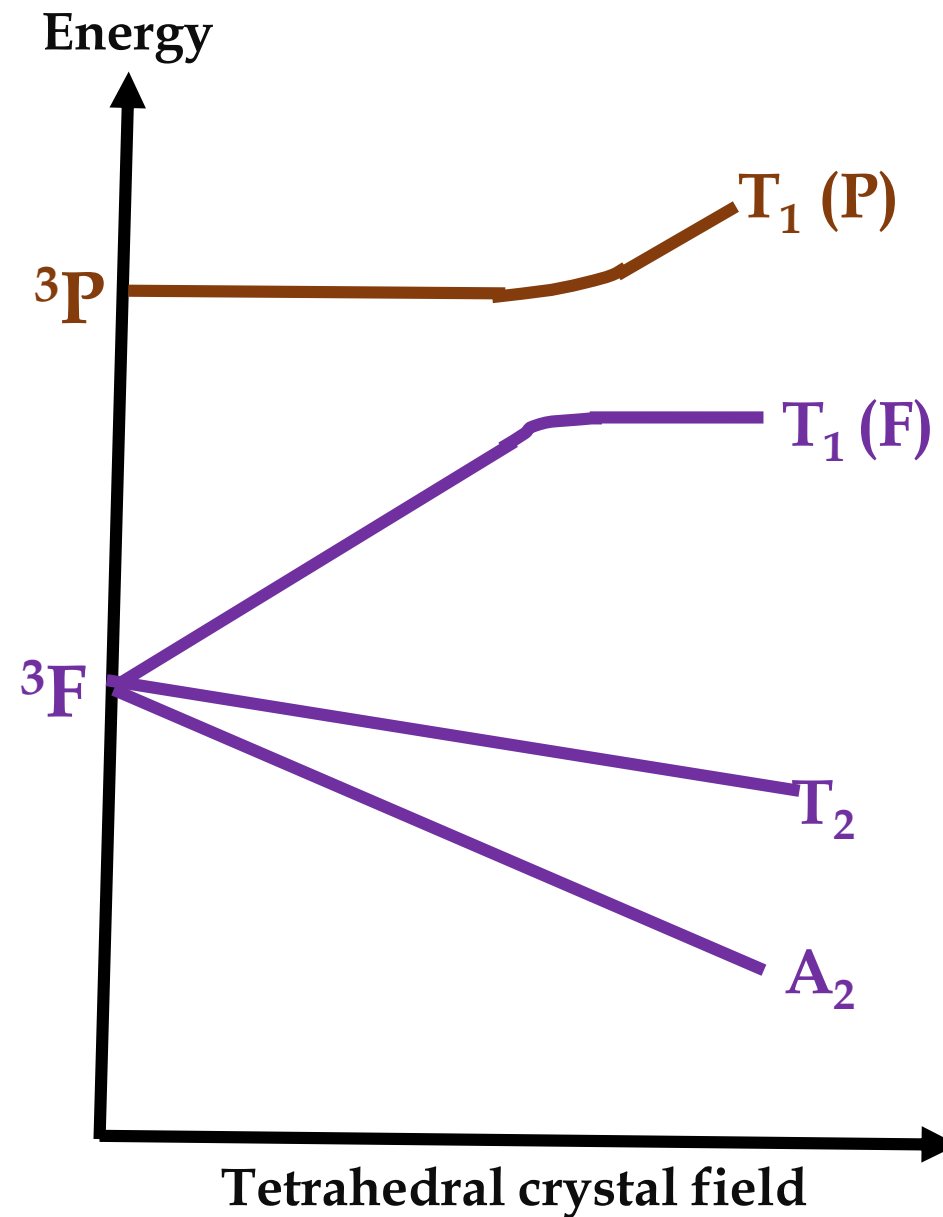$$F = A_2 + T_1 + T_2$$
$$P = T_1$$

Total degeneracy = 1+3+3+3 = 10

Energy

^3P → T_1 (P)

^3F → T_1 (F), T_2, A_2

Tetrahedral crystal field

TERMS ARISING IN LIGAND FIELD

d^n	Free ion terms
d^1, d^9	^2D
d^2, d^8	^3F, ^3P, ^1G…
d^3, d^7	^4F, ^4P, ^2H…
d^4, d^6	^5D, ^3H, ^3G…
d^5	^6S, ^4G, ^4F…

State	Labels
S	A_1
P	T_1
D	$E + T_2$
F	$A_2 + T_1 + T_2$

d^2 Tetrahedral field

Ground state   **Excited state-I**   **Excited state-II**

Non-crossing rule

It states that if two states of the same symmetry approach each other as a parameter is changed (here the increasing ligand field) , they do not cross each other but band from one another.

Because of this with increasing crystal field, $T_1(F)$ and $T_1(P)$ diverge from each other.

Energy

^3P ⟶ T_1 (P)

T_1 (F)

^3F

T_2

A_2

Tetrahedral crystal field

d² in Oₕ and Tₐ field

dⁿ	Free ion terms
d¹, d⁹	²D
d², d⁸	³F, ³P, ¹G…
d³, d⁷	⁴F, ⁴P, ²H…
d⁴, d⁶	⁵D, ³H, ³G…
d⁵	⁶S, ⁴G, ⁴F…

State	Labels
S	A₁
P	T₁
D	E + T₂
F	A₂ + T₁ + T₂

TERMS ARISING IN LIGAND FIELD

d^n	Free ion terms
d^1, d^9	^2D
d^2, d^8	^3F, ^3P, ^1G…
d^3, d^7	^4F, ^4P, ^2H…
d^4, d^6	^5D, ^3H, ^3G…
d^5	^6S, ^4G, ^4F…

State	Labels
S	A_1
P	T_1
D	$E + T_2$
F	$A_2 + T_1 + T_2$

d^7 Octahedral weak field

Ground state
Degeneracy = 3 x 1=3

Excited state-I
Degeneracy = 3 x 2 =6

Excited state-II
Degeneracy = 1 x 1=1

Total degeneracy = 3+6+1 = 10

Free ion ground state term = ^4F, ^4P

$$F = A_2 + T_1 + T_2$$
$$P = T_1$$

Total degeneracy = 1+3+3+3 = 10

Energy

A_{2g}

^4P ——— T_{1g} (P)

T_{2g}

^4F

T_{1g} (F)

Octahedral crystal field

TERMS ARISING IN LIGAND FIELD

d^n	Free ion terms
d^1, d^9	^2D
d^2, d^8	$^3F, ^3P, ^1G\ldots$
d^3, d^7	$^4F, ^4P, ^2H\ldots$
d^4, d^6	$^5D, ^3H, ^3G\ldots$
d^5	$^6S, ^4G, ^4F\ldots$

State	Labels
S	A_1
P	T_1
D	$E + T_2$
F	$A_2 + T_1 + T_2$

d^7 Tetrahedral field

Ground state

Degeneracy = 1 x 1 = 1

Excited state-I

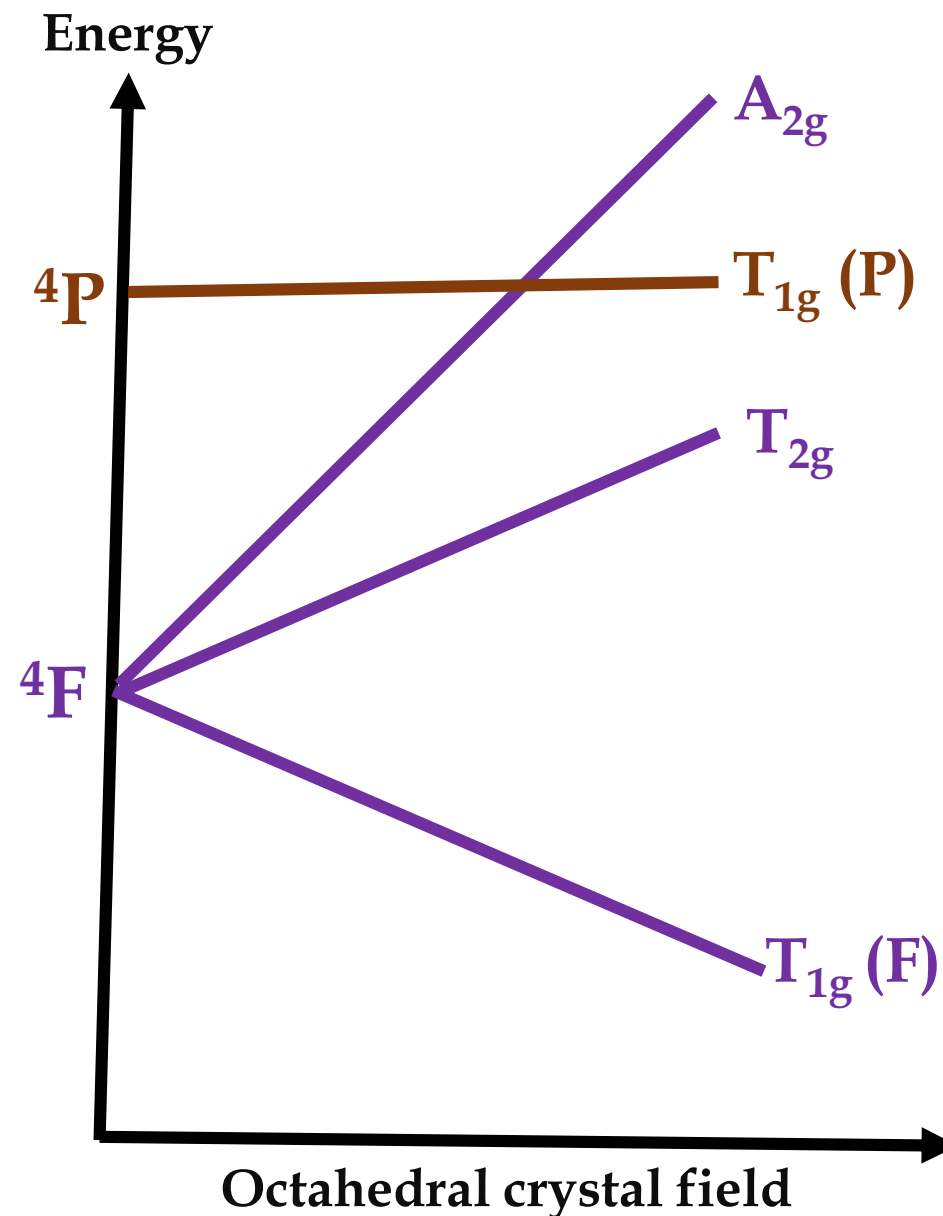Degeneracy = 2 x 3 = 6

Excited state-II

Degeneracy = 1 x 3 = 3

Total degeneracy = 1+6+3 = 10

Free ion ground state term = $^4F, ^4P$

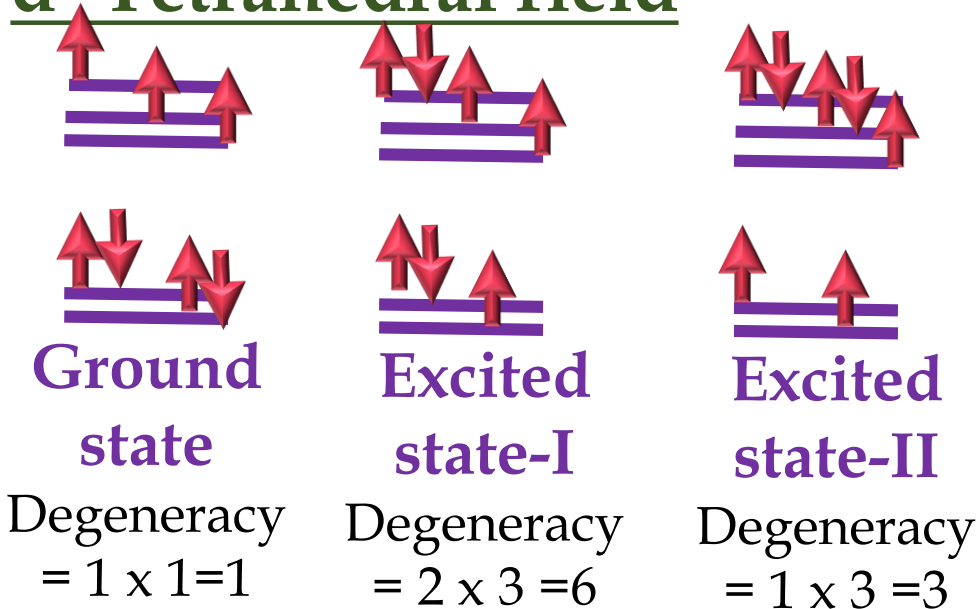$$F = A_2 + T_1 + T_2$$
$$P = T_1$$

Total degeneracy = 1+3+3+3 = 10

Energy

^4P — T_1 (P)

^4F — T_1 (F), T_2, A_2

Tetrahedral crystal field

d^7 in O^h and T^d field

d^n	Free ion terms
d^1, d^9	^2D
d^2, d^8	^3F, ^3P, ^1G…
d^3, d^7	^4F, ^4P,^2H…
d^4, d^6	^5D, ^3H, ^3G…
d^5	^6S, ^4G, ^4F…

State	Labels
S	A_1
P	T_1
D	$E + T_2$
F	$A_2 + T_1 + T_2$

TERMS ARISING IN LIGAND FIELD

d^n	Free ion terms
d^1, d^9	^2D
d^2, d^8	^3F, ^3P, ^1G…
d^3, d^7	^4F, ^4P, ^2H…
d^4, d^6	^5D, ^3H, ^3G…
d^5	^6S, ^4G, ^4F…

State	Labels
S	A_1
P	T_1
D	$E + T_2$
F	$A_2 + T_1 + T_2$

d^3 Octahedral weak field

Ground state
Degeneracy = 1

Excited state-I
Degeneracy = 3 x 2 = 6

Excited state-II
Degeneracy = 1 x 3 = 3

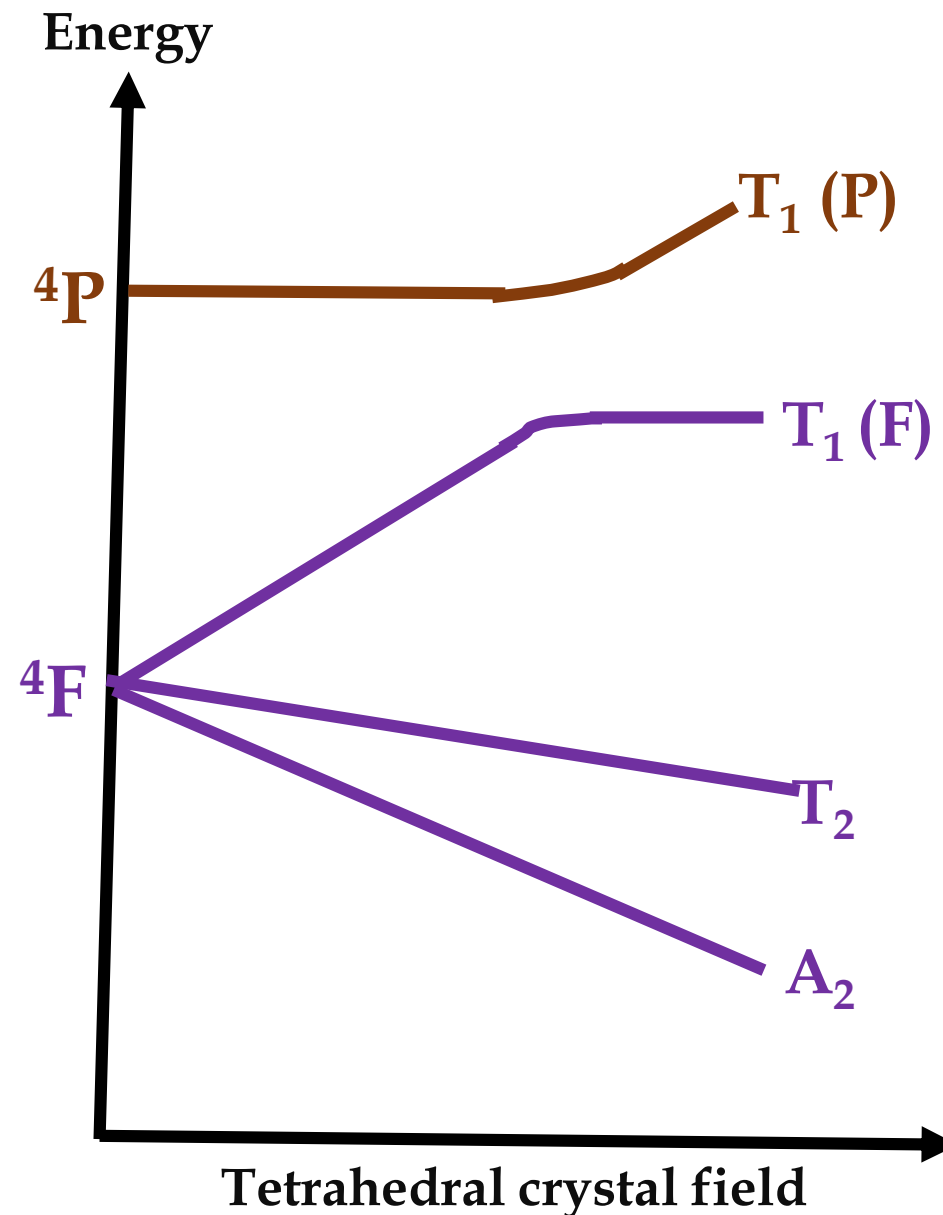Total degeneracy = 1+6+3 = 10

Free ion ground state term = ^4F, ^4P

$$F = A_2 + T_1 + T_2$$
$$P = T_1$$

Total degeneracy = 1+3+3+3 = 10

Energy

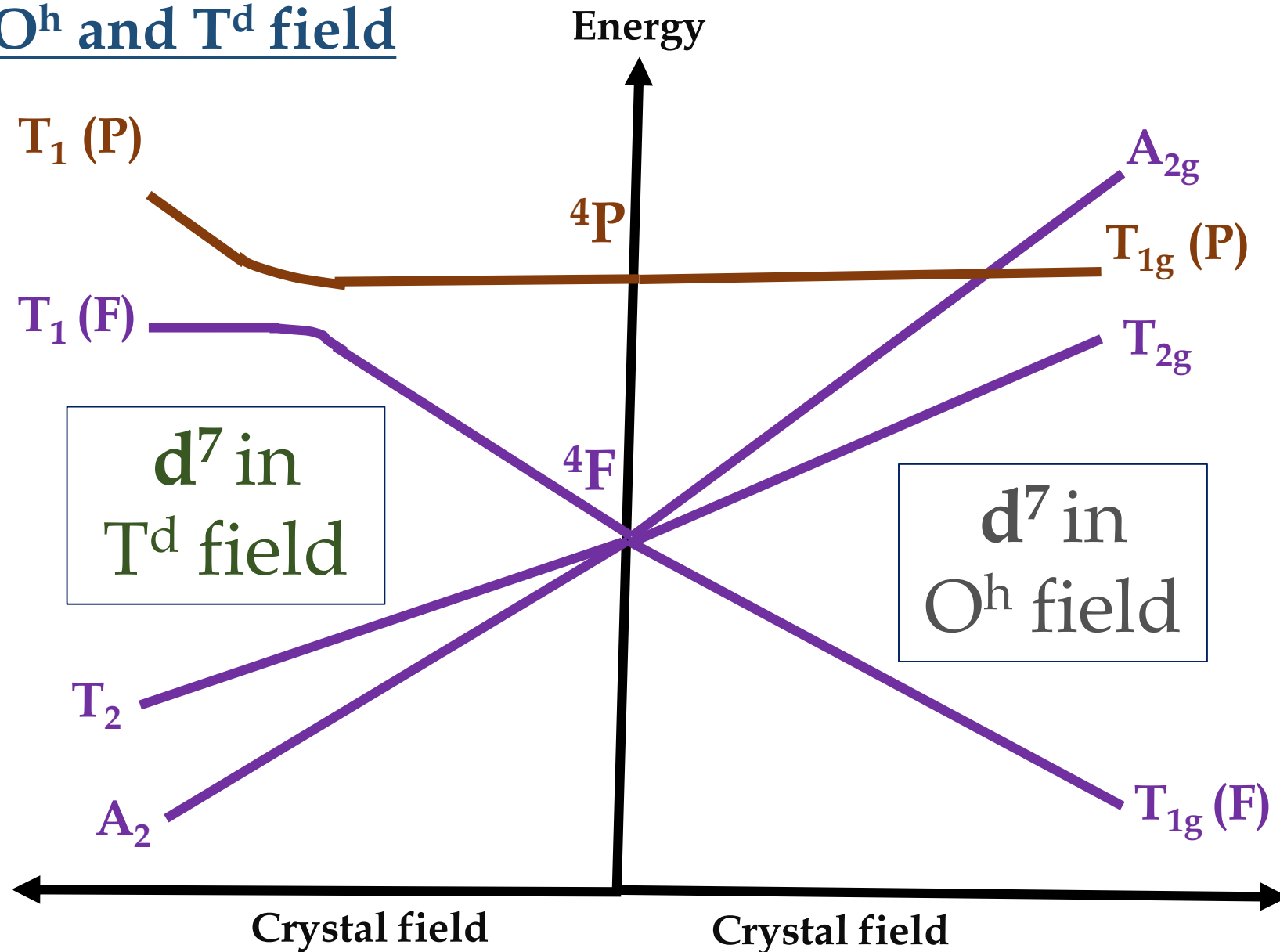^4P

^4F

T_{1g} (P)

T_{1g} (F)

T_{2g}

A_{2g}

Octahedral crystal field

TERMS ARISING IN LIGAND FIELD

d^n	Free ion terms
d^1, d^9	^2D
d^2, d^8	$^3F, ^3P, ^1G\ldots$
d^3, d^7	$^4F, ^4P, ^2H\ldots$
d^4, d^6	$^5D, ^3H, ^3G\ldots$
d^5	$^6S, ^4G, ^4F\ldots$

State	Labels
S	A_1
P	T_1
D	$E + T_2$
F	$A_2 + T_1 + T_2$

d^3 Tetrahedral field

Ground state
Degeneracy = 1 x 3 = 3

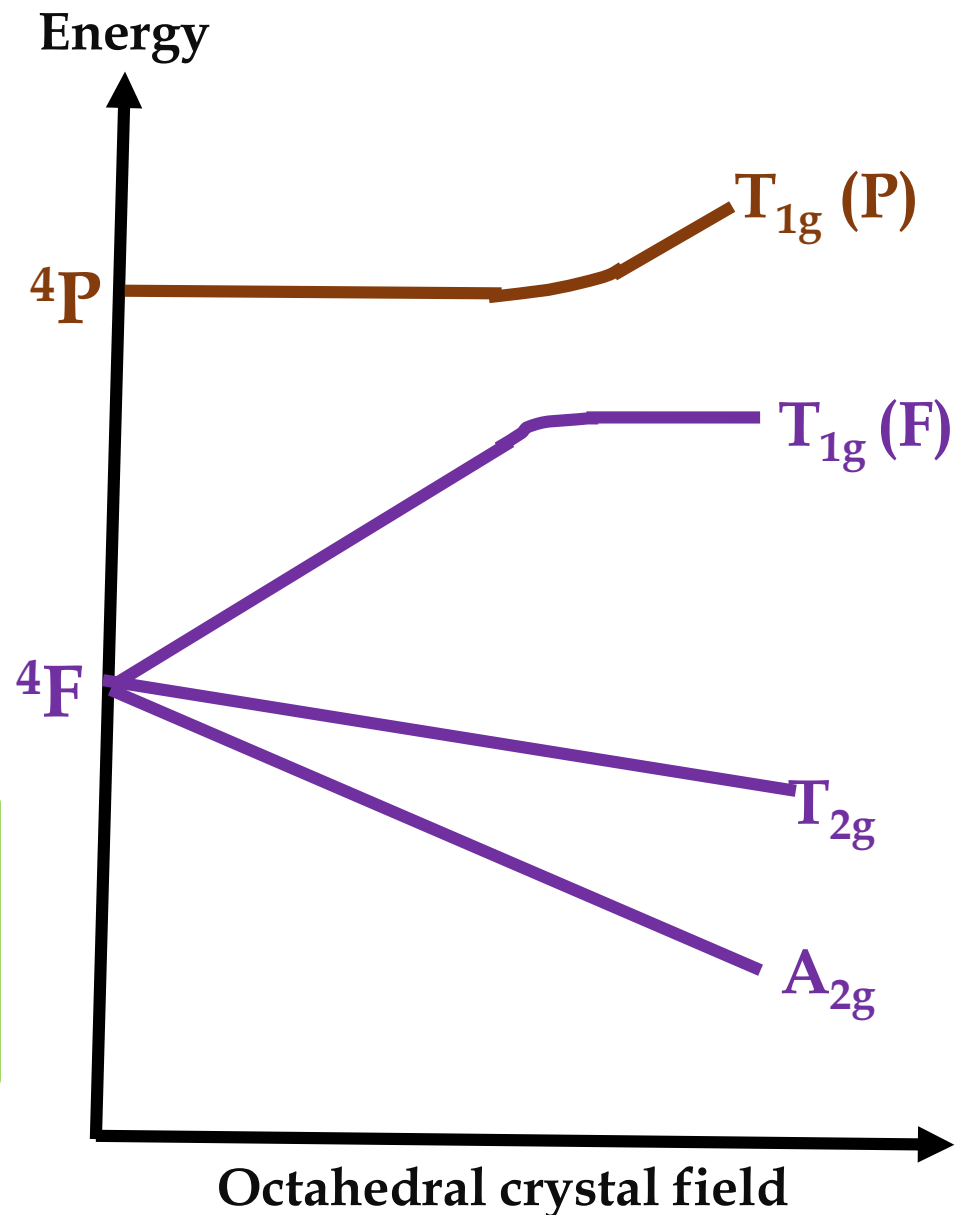**Excited state-I**
Degeneracy = 2 x 3 = 6

Excited state-II
Degeneracy = 1

Total degeneracy = 3+6+1 = 10

Free ion ground state term = $^4F, ^4P$
$$F = A_2 + T_1 + T_2$$
$$P = T_1$$
Total degeneracy = 1+3+3+3 = 10

Energy

A_2

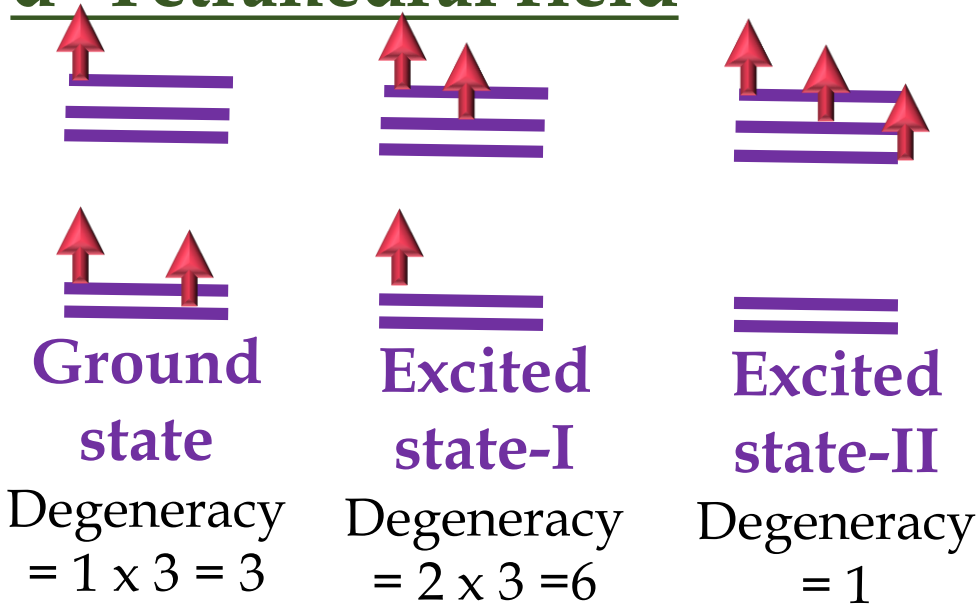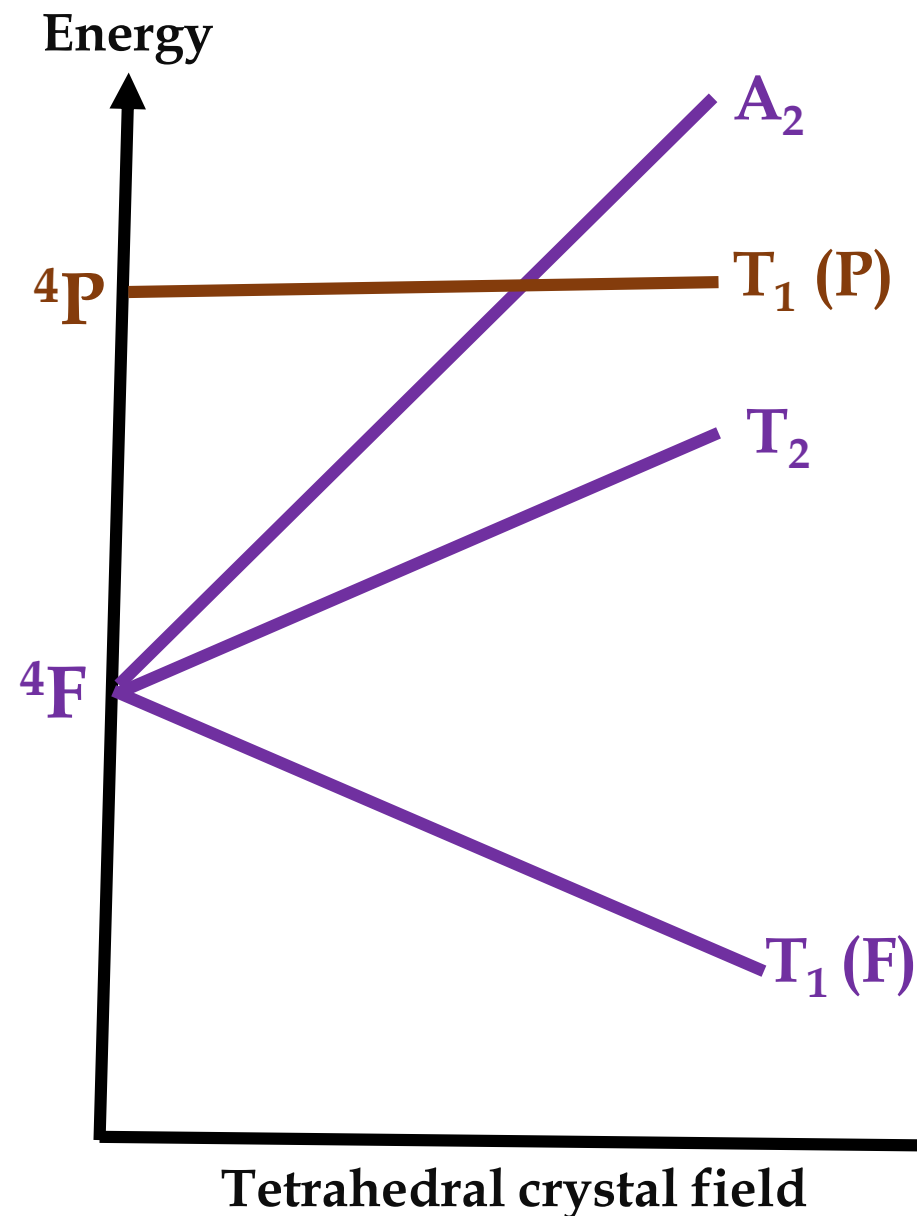^4P ———— $T_1 (P)$

T_2

^4F

$T_1 (F)$

Tetrahedral crystal field

TERMS ARISING IN LIGAND FIELD

d^n	Free ion terms
d^1, d^9	^2D
d^2, d^8	$^3F, ^3P, ^1G...$
d^3, d^7	$^4F, ^4P, ^2H...$
d^4, d^6	$^5D, ^3H, ^3G...$
d^5	$^6S, ^4G, ^4F...$

State	Labels
S	A_1
P	T_1
D	$E + T_2$
F	$A_2 + T_1 + T_2$

d^3 in O^h and T^d field

d^3 in O^h field

d^3 in T^d field

TERMS ARISING IN LIGAND FIELD

d^n	Free ion terms
d^1, d^9	^2D
d^2, d^8	^3F, ^3P, $^1G...$
d^3, d^7	^4F, ^4P, $^2H...$
d^4, d^6	^5D, ^3H, $^3G...$
d^5	^6S, ^4G, $^4F...$

State	Labels
S	A_1
P	T_1
D	$E + T_2$
F	$A_2 + T_1 + T_2$

d^8 Octahedral weak field

Ground state — Degeneracy = 1

Excited state-I — Degeneracy = 3 x 2 = 6

Excited state-II — Degeneracy = 3 x 1 = 3

Total degeneracy = 1+6+3 = 10

Free ion ground state term = ^3F, ^3P

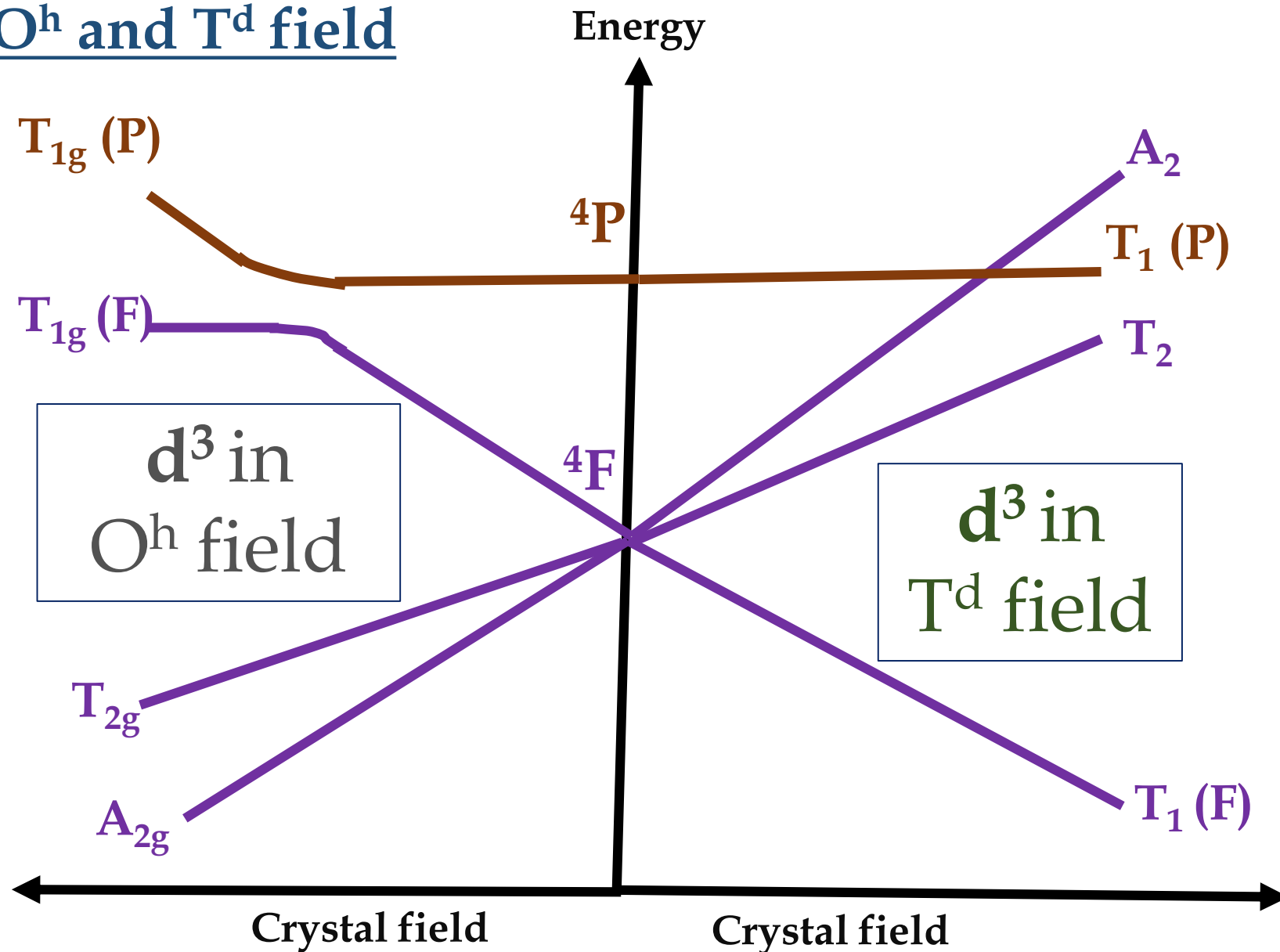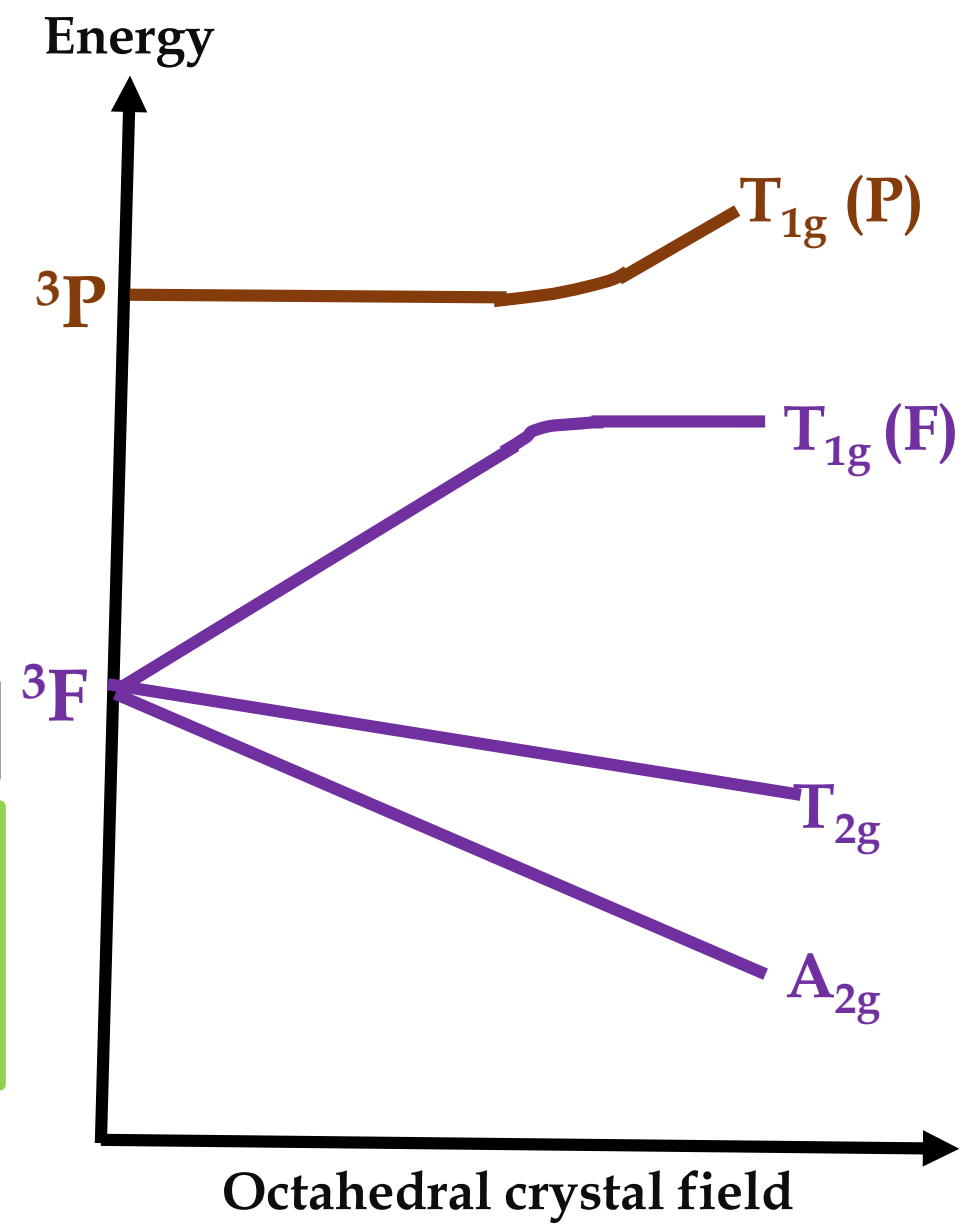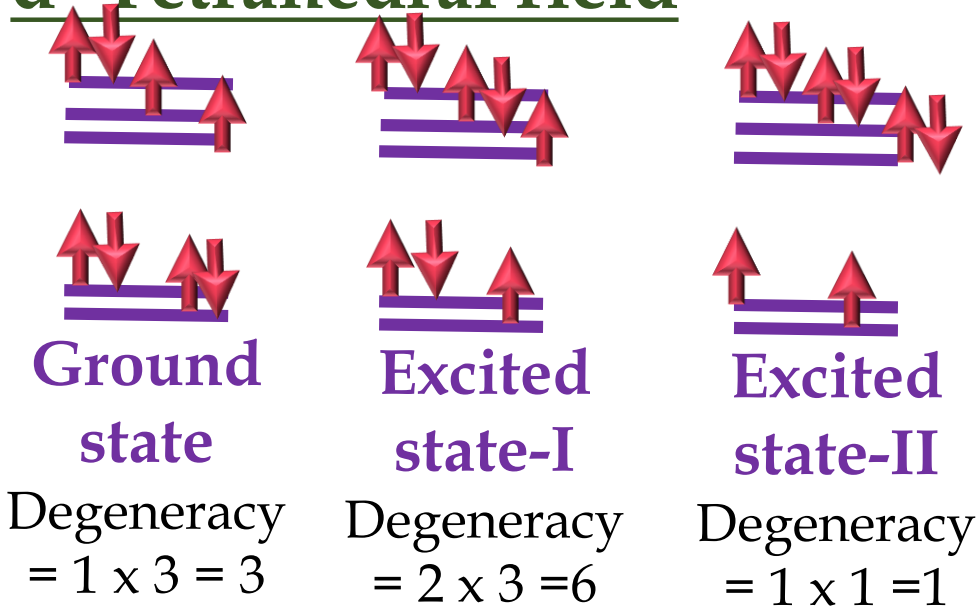$F = A_2 + T_1 + T_2$

$P = T_1$

Total degeneracy = 1+3+3+3 = 10

Energy

T_{1g} (P)

^3P

T_{1g} (F)

^3F

T_{2g}

A_{2g}

Octahedral crystal field

TERMS ARISING IN LIGAND FIELD

d^n	Free ion terms
d^1, d^9	^2D
d^2, d^8	^3F, ^3P, ^1G…
d^3, d^7	^4F, ^4P, ^2H…
d^4, d^6	^5D, ^3H, ^3G…
d^5	^6S, ^4G, ^4F…

State	Labels
S	A_1
P	T_1
D	$E + T_2$
F	$A_2 + T_1 + T_2$

d^8 Tetrahedral field

Ground state
Degeneracy = 1 x 3 = 3

Excited state-I
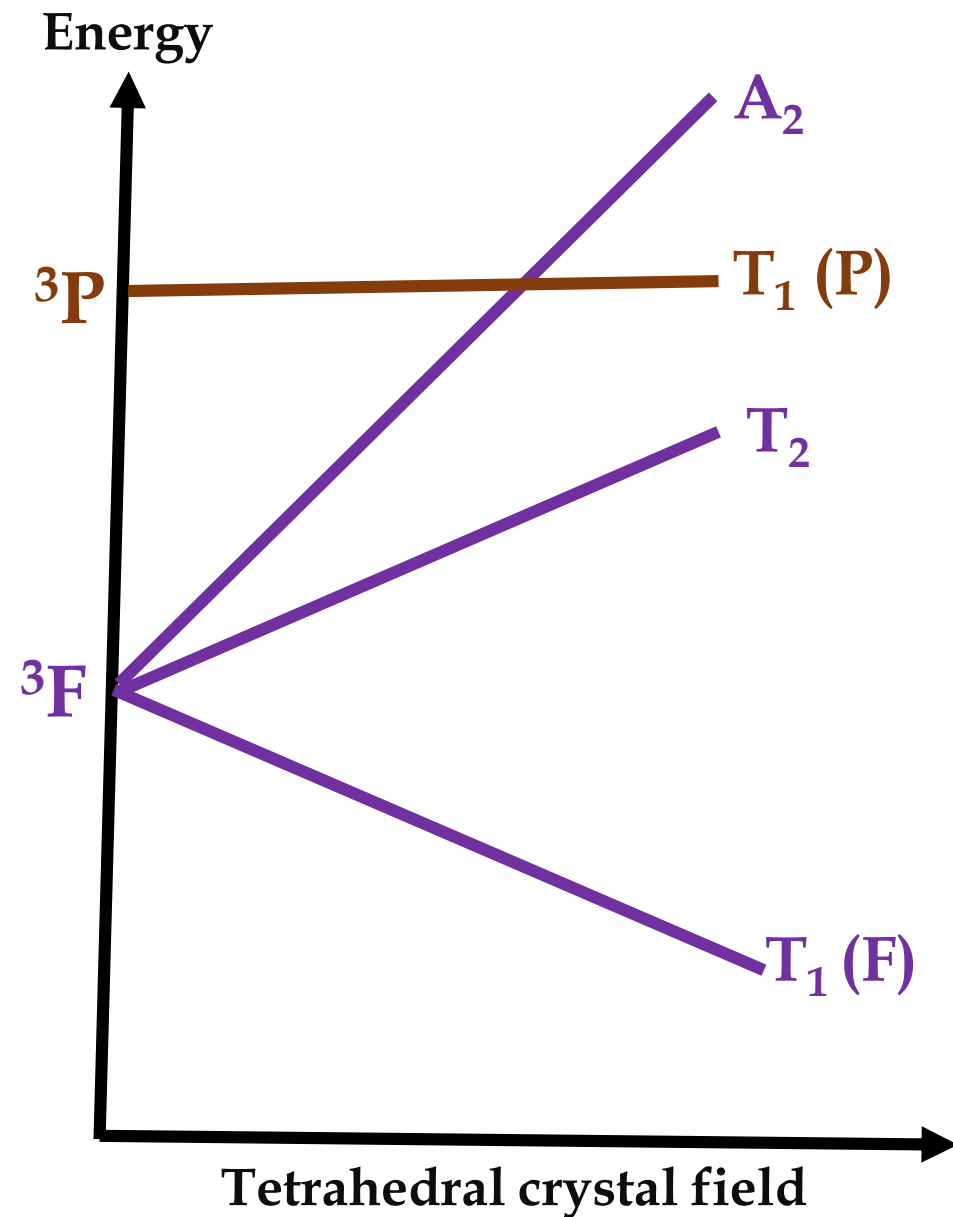Degeneracy = 2 x 3 = 6

Excited state-II
Degeneracy = 1 x 1 = 1

Total degeneracy = 3+6+1 = 10

Free ion ground state term = ^3F, ^3P
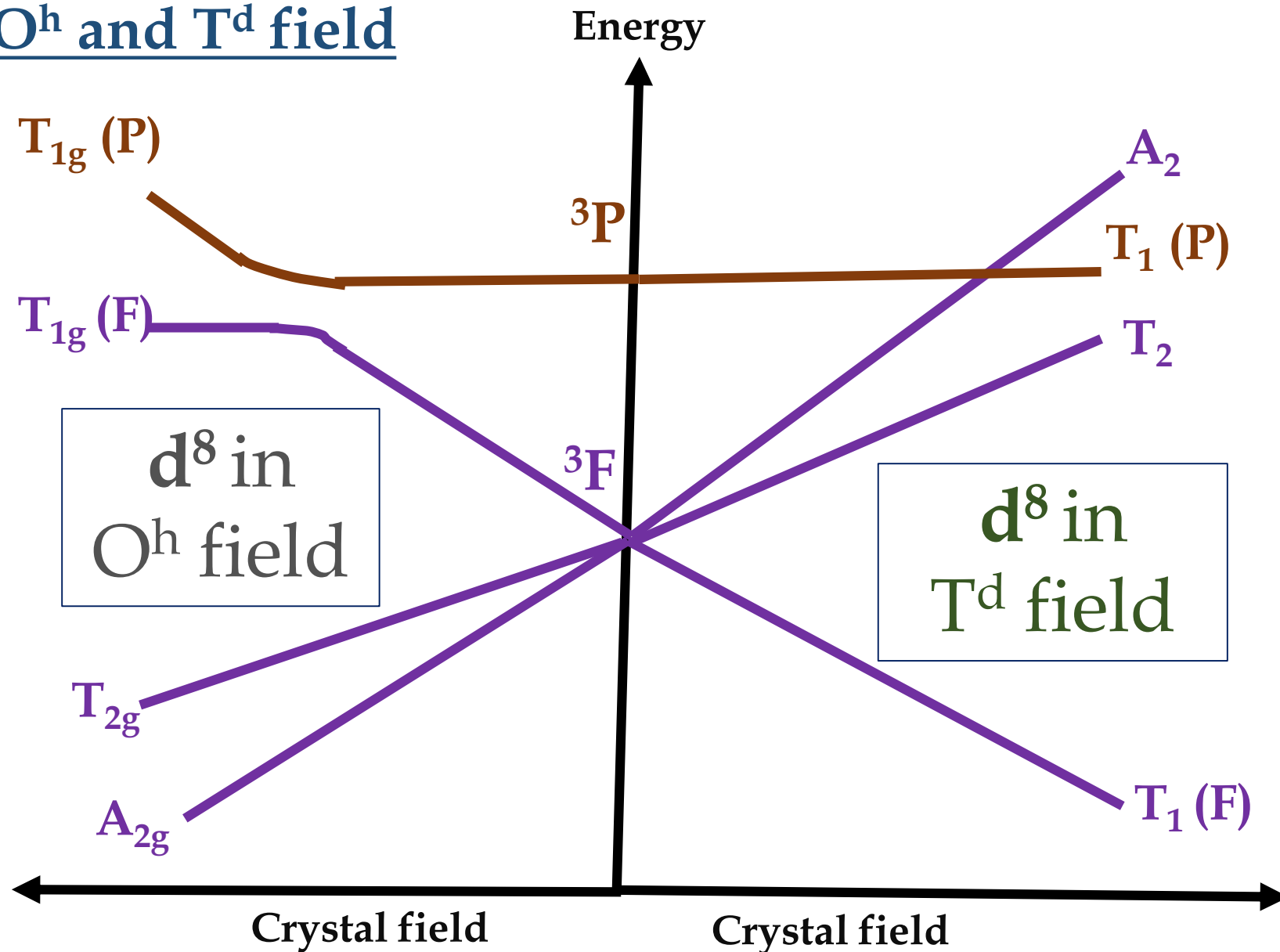$$F = A_2 + T_1 + T_2$$
$$P = T_1$$
Total degeneracy = 1+3+3 = 10

Energy

A_2

^3P — $T_1 (P)$

T_2

^3F

$T_1 (F)$

Tetrahedral crystal field

TERMS ARISING IN LIGAND FIELD

d⁸ in Oʰ and Tᵈ field

d^n	Free ion terms
d^1, d^9	^2D
d^2, d^8	$^3F, ^3P, ^1G...$
d^3, d^7	$^4F, ^4P, ^2H...$
d^4, d^6	$^5D, ^3H, ^3G...$
d^5	$^6S, ^4G, ^4F...$

State	Labels
S	A_1
P	T_1
D	$E + T_2$
F	$A_2 + T_1 + T_2$

Energy

T_{1g} (P)

^3P

T_1 (P)

A_2

T_{1g} (F)

T_2

^3F

d⁸ in Oʰ field

d⁸ in Tᵈ field

T_{2g}

A_{2g}

T_1 (F)

Crystal field   **Crystal field**

Terms Arising in Ligand Field
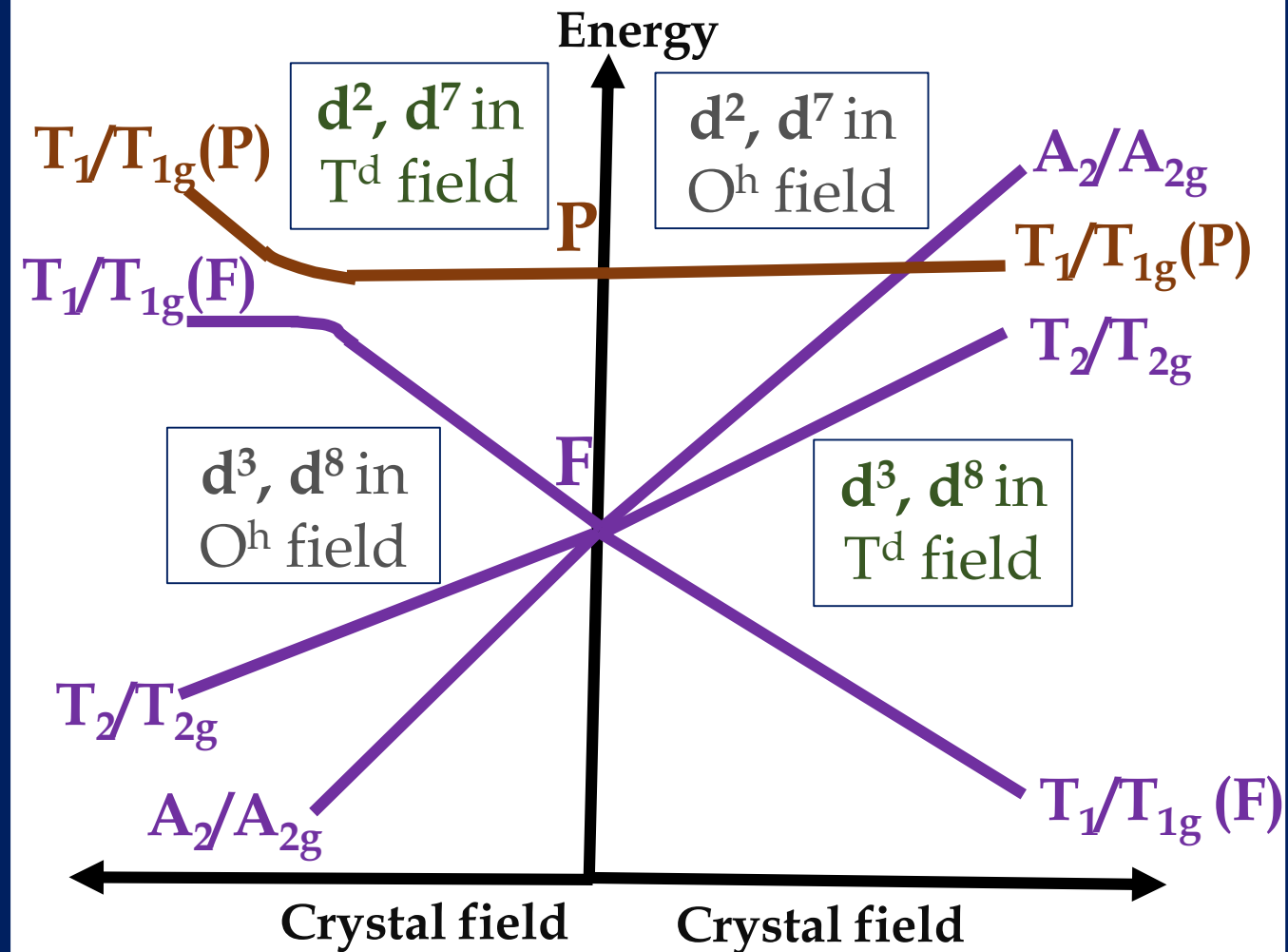

Orgel diagram for d^2, d^3, d^7 and d^8 systems.

TERMS ARISING IN LIGAND FIELD

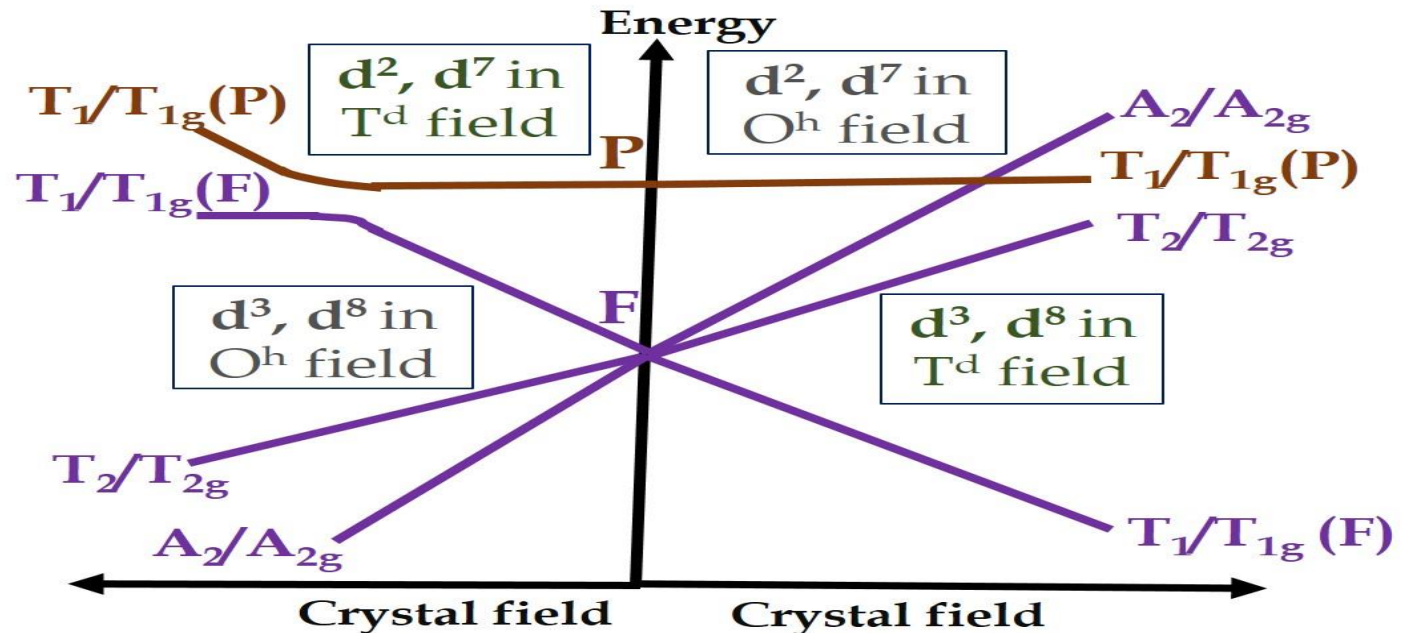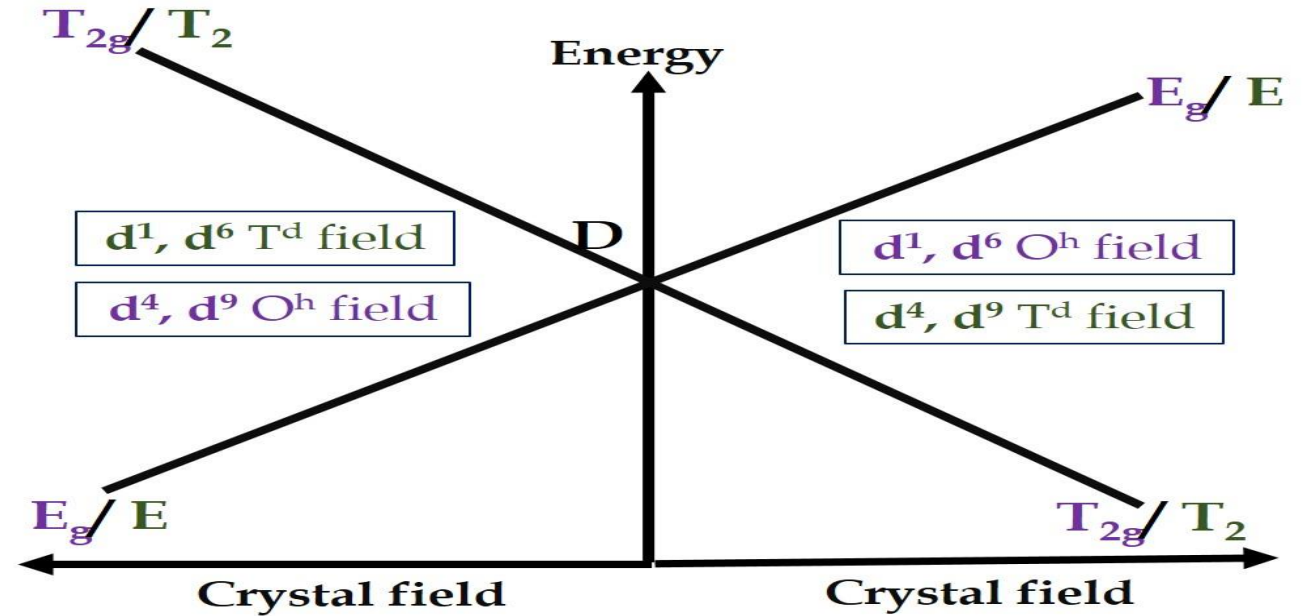Orgel diagram for d^1, d^4, d^6 and d^9 systems.

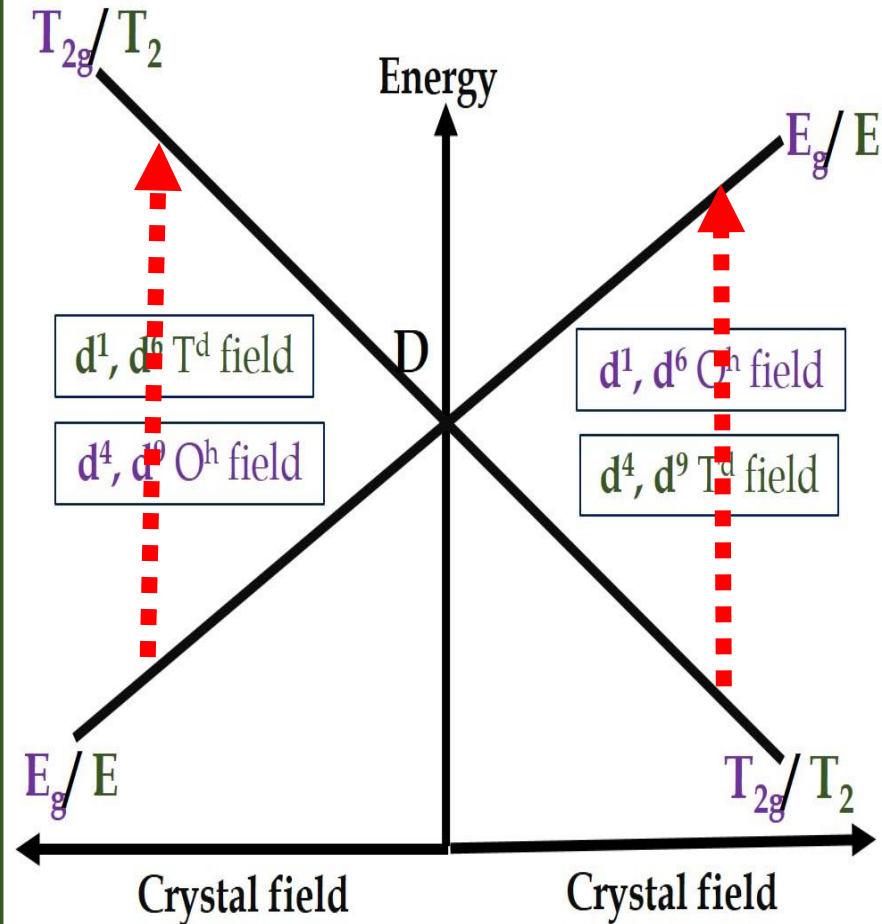Orgel diagram for d^2, d^3, d^7 and d^8 systems.

Some features:

➤ Octahedral d^n and tetrahedral d^{10-n} give rise to similar type of splitting.

➤ Octahedral d^n has inverse splitting of octahedral d^{10-n}.

T_{2g}/T_2

Energy

E_g/E

| d^1, d^6 T^d field |
| d^4, d^9 O^h field |

D

| d^1, d^6 O^h field |
| d^4, d^9 T^d field |

E_g/E

T_{2g}/T_2

Crystal field   Crystal field

Energy

$T_1/T_{1g}(P)$

| d^2, d^7 in T^d field |

| d^2, d^7 in O^h field |

A_2/A_{2g}

P

$T_1/T_{1g}(P)$

$T_1/T_{1g}(F)$

T_2/T_{2g}

| d^3, d^8 in O^h field |

F

| d^3, d^8 in T^d field |

T_2/T_{2g}

A_2/A_{2g}

$T_1/T_{1g}(F)$

Crystal field   Crystal field

Some features:

➤ In case of d^1, d^4, d^6 and d^9, there exists only one state above the ground state. So we expect only one transition.

➤ $[Ti(H_2O)_6]^{3+}$ shows a broad band with a peak around 20100 cm^{-1} ($T_{2g} \rightarrow E_g$ transition). Broad band is due to pronounced JT effect in the excited state.

➤ Octahedral Cu(II) complexes may be expected to produce a single absorption ($T_{2g} \rightarrow E_g$ transition). Here JT distortion is greater. Because of this, $[Cu(H_2O)_6]^{2+}$ has broad band with long tail near infrared.
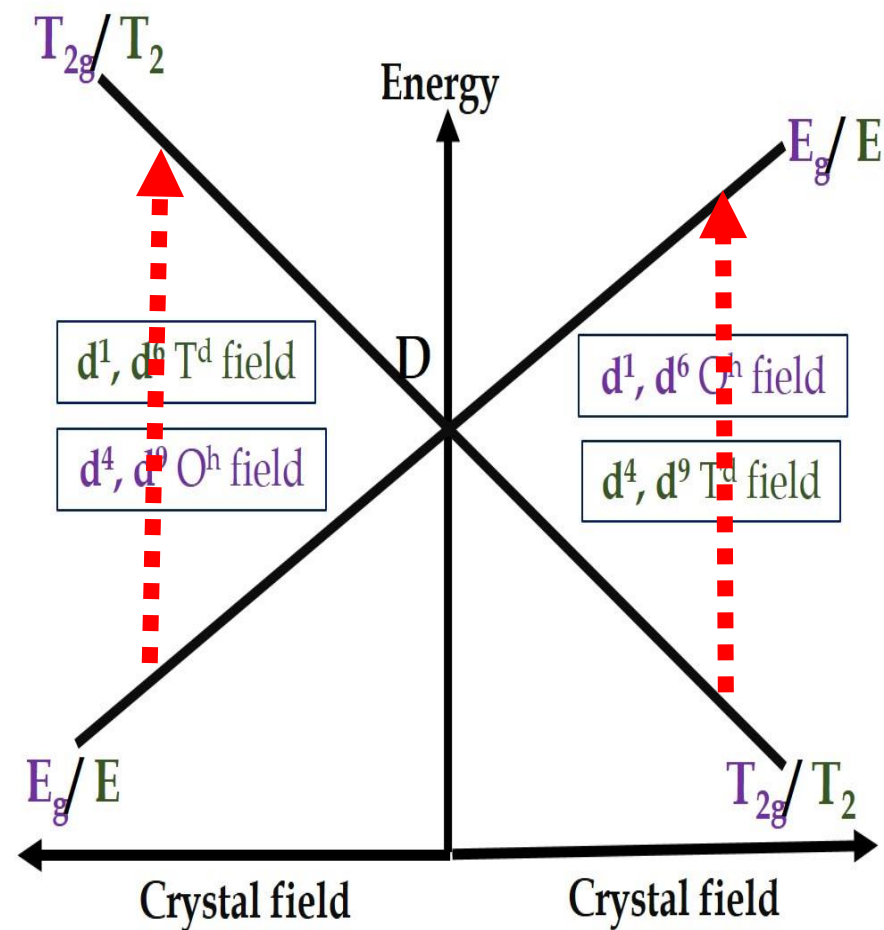
T_{2g}/T_2

Energy

E_g/E

| d^1, d^6 T^d field | D | d^1, d^6 O^h field |
| d^4, d^9 O^h field | | d^4, d^9 T^d field |

E_g/E

T_{2g}/T_2

Crystal field   Crystal field

Orgel diagram for d^1, d^4, d^6 and d^9 systems.

Jorgensen's rule of average environment:
The position of the peak in a complex $[TiX_3L_3]$ will be midway between that for $[TiL_6]^{3+}$ and $[TiX_6]^{3-}$ provided all three complexes have the same symmetry.

Problem. Calculate the Δ_o for $[Ti(CH_3COCH_3)_6]^{3+}$ from the following absorption peaks. $[TiCl_3(CH_3COCH_3)_3]$ at 15400 cm^{-1} and $[TiCl_6]^{3-}$ at 12750 cm^{-1}.
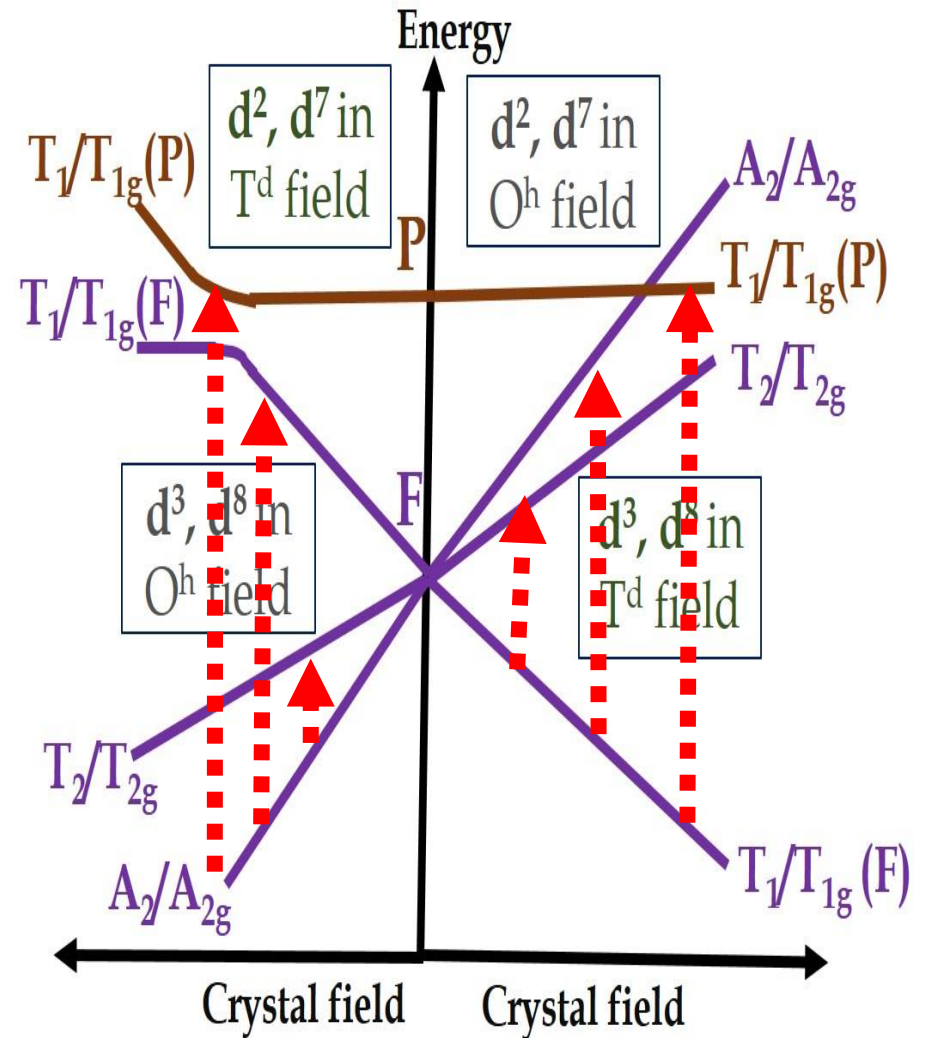(Ans. 18000 cm^{-1}.)

T_{2g}/T_2 Energy E_g/E

| d^1, d^6 T^d field | D | d^1, d^6 O^h field |
| d^4, d^9 O^h field | | d^4, d^9 T^d field |

E_g/E T_{2g}/T_2

Crystal field   Crystal field

Orgel diagram for d^1, d^4, d^6 and d^9 systems.

Some features:

➢ In case of d^2, d^3, d^7 and d^8, there exists three states above the ground state. So we expect three transitions.

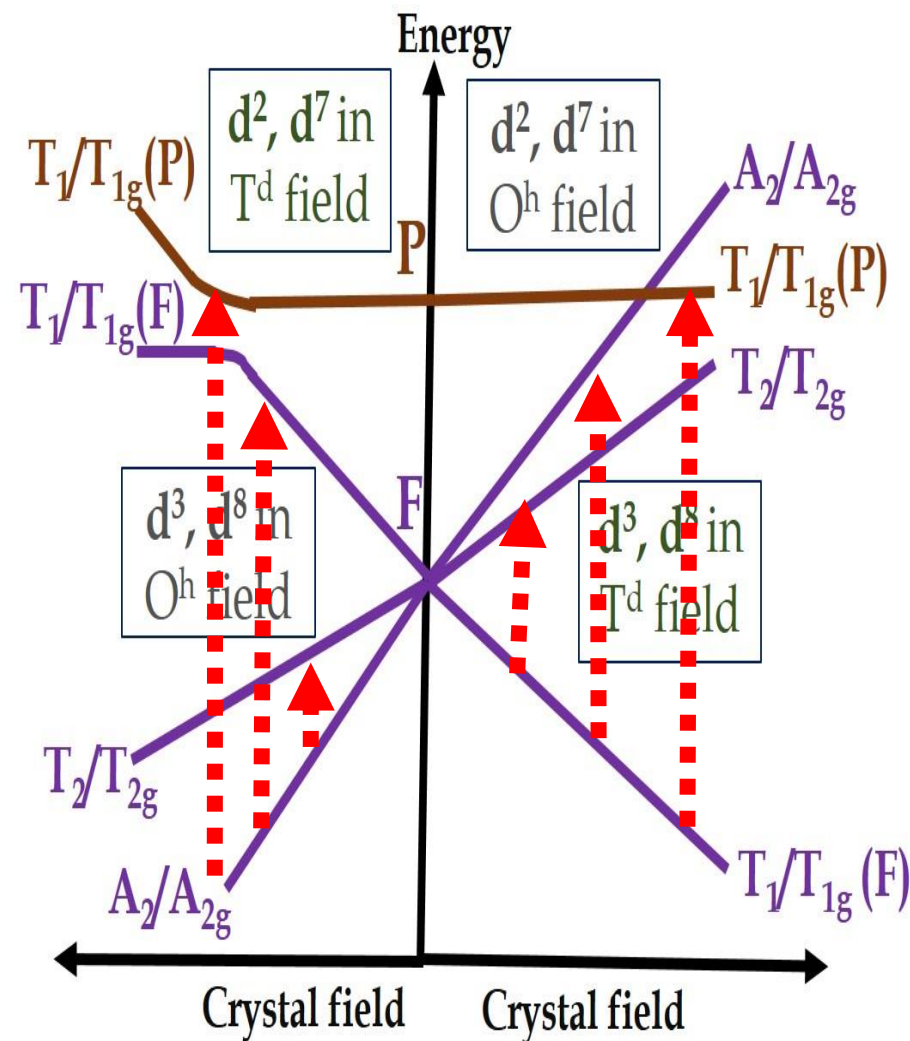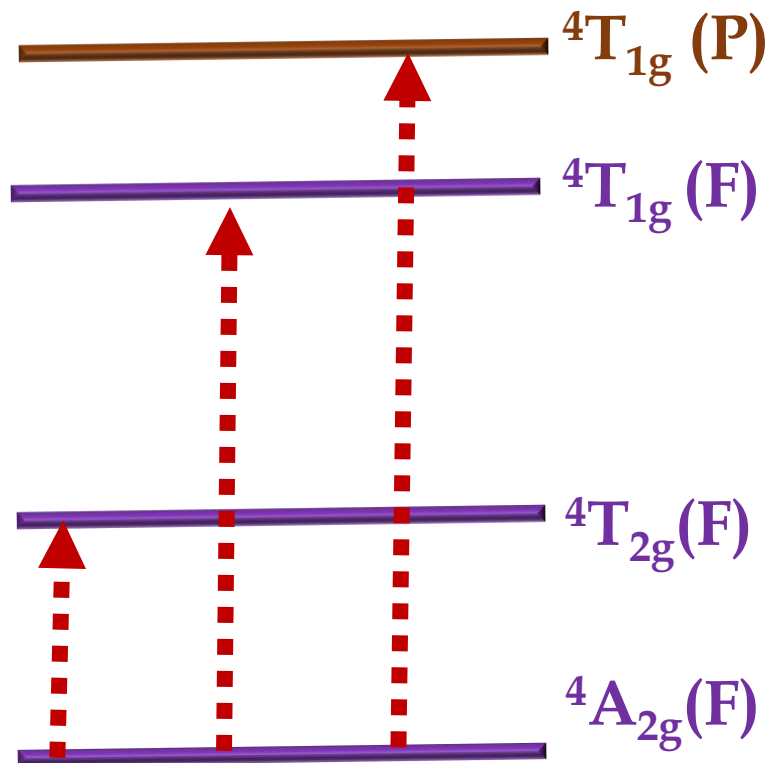Orgel diagram for d^2, d^3, d^7 and d^8 systems.

Some features:
➢ In case of d^2, d^3, d^7 and d^8, there exists three states above the ground state. So we expect three transitions.

d³ in Oʰ field

Possible transitions
(i) $^4A_{2g} \rightarrow {}^4T_{2g}$
(ii) $^4A_{2g} \rightarrow {}^4T_{1g}(F)$
(iii) $^4A_{2g} \rightarrow {}^4T_{1g}(P)$

$^4T_{1g}$ (P)

$^4T_{1g}$ (F)

$^4T_{2g}$(F)

$^4A_{2g}$(F)

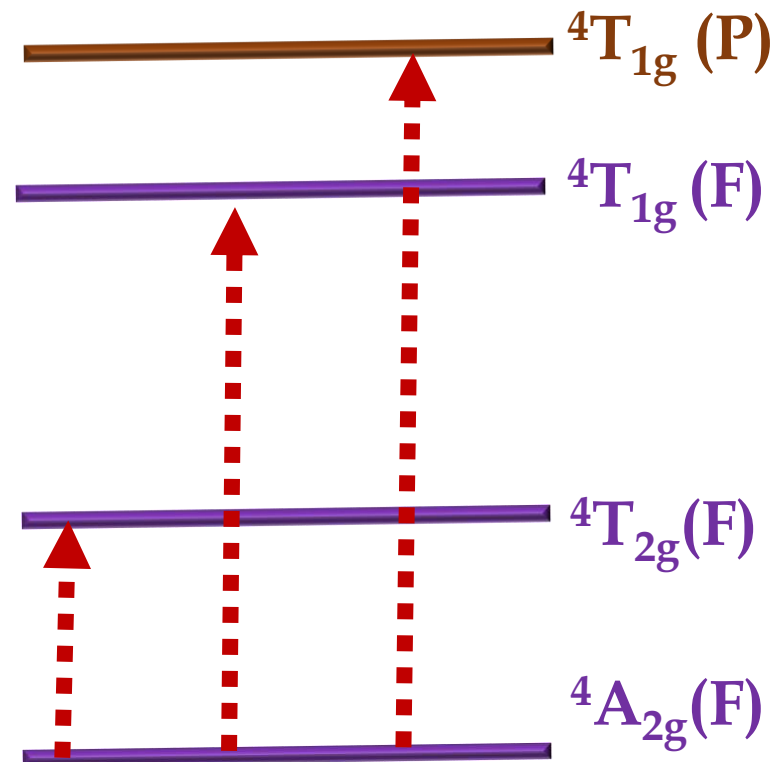**Orgel diagram for d², d³, d⁷ and d⁸ systems.**

Some features:
➤ In case of d^2, d^3, d^7 and d^8, there exists three states above the ground state. So we expect three transitions.

d³ in Oʰ field

Possible transitions
(i) $^4A_{2g} \rightarrow {}^4T_{2g}$
(ii) $^4A_{2g} \rightarrow {}^4T_{1g}(F)$
(iii) $^4A_{2g} \rightarrow {}^4T_{1g}(P)$

$^4T_{1g}$ **(P)**

$^4T_{1g}$ **(F)**

$^4T_{2g}$**(F)**

$^4A_{2g}$**(F)**

Ruby Laser
➤ Ruby contains Cr^{3+} ions embedded in α-Al_2O_3 where oxide ions provide a nearly distorted octahedral field. It produce pulses of coherent visible light (deep red color) at 694.3 nm.
➤ When a large single crystal of ruby is exposed to light of appropriate frequency to excite Cr^{3+} to the $^4T_{2g}$(F) state, it does not return to the ground state. Instead, energy is lost to crystal lattice by vibrational modes.