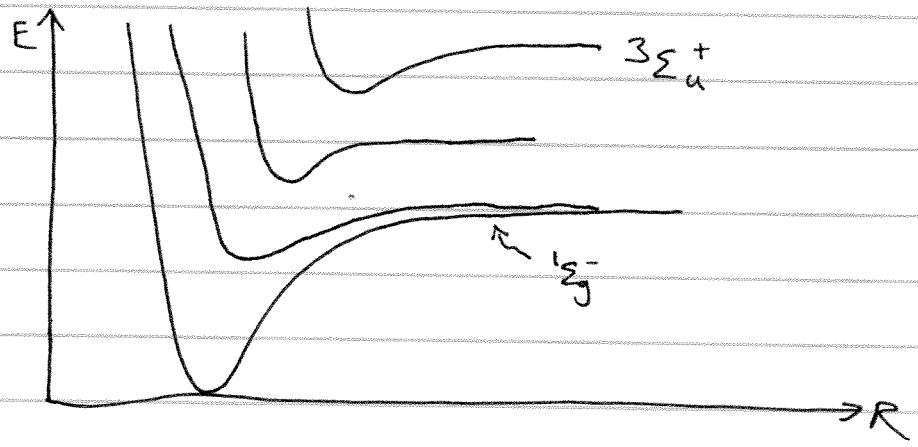
Electronic (UV & visible) spectroscopy

Exciting electrons into higher-lying states (MOs) usually takes light in the UV or visible portion of the spectrum. Here are the first few electronic states of the O_2 molecule:



Each of the electronic surfaces has a different potential energy for the nuclei.

The term symbols are a way of describing the electronic configuration:

$^{2M_S+1}|M_L|$

$|M_L|$: symmetry due to reflection (+ or −); symmetry under inversion (g or u)

Spin multiplicity M_S = Σ over all $+\frac{1}{2}$ & $-\frac{1}{2}$ contributions due to electrons

$|M_L|$ = total orbital angular momentum of electron orbitals

Consider H_2 with both electrons in $\sigma = 1s_A + 1s_B$

$$\Psi = \frac{1}{\sqrt{2}} \begin{vmatrix} \sigma_{1s}(1)\alpha(1) & \sigma_{1s}(1)\beta(1) \\ \sigma_{1s}(2)\beta(2) & \sigma_{1s}(2)\beta(2) \end{vmatrix} = \frac{1}{\sqrt{2}} \sigma_{1s}(1)\,\sigma_{1s}(2)\left(\alpha(1)\beta(2) - \alpha(2)\beta(1)\right)$$

$\sigma_{1s} = 1s_A + 1s_B \Rightarrow M_L = 0 \Rightarrow {}^1\Sigma$

(π orbitals have $m_\ell = \pm 1$)

$M_S = \left(\frac{1}{2} + \frac{-1}{2}\right) - \left(\frac{1}{2} - \frac{1}{2}\right) \Rightarrow M_S = 0 \Rightarrow$ singlet $= {}^1\Sigma$

$\underline{1\downarrow} = \underline{\downarrow\uparrow}$ only one observed line in magnetic field

He_2^+

$1\ \sigma_u$ — $\overline{1s}$

$\underline{1\downarrow}\ \sigma_g$ — $\overline{1s}$

$M_L = 0$ (both σ)

$M_S = \pm\frac{1}{2}$ ← 2 possibilities for upper spin

doublet $= {}^2\Sigma$

Ground state for B_2

$$(1\sigma_g)^2 (1\sigma_u)^2 (2\sigma_g)^2 (2\sigma_u)^2 (1\pi_u)^1 (1\pi_u)^1$$

$\underline{1}\ \underline{1}\ \pi_u$ ← 3 ways of arranging SpMS in this MO:

$\underline{1\downarrow}\ 2\sigma_u$

$\underline{1\downarrow}\ 2\sigma_g$

$\underline{1\downarrow}\ 1\sigma_u$

$\underline{1\downarrow}\ 1\sigma_g$

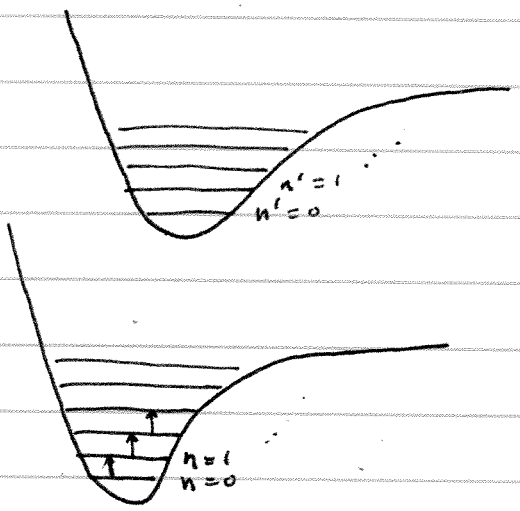
$\downarrow\ \downarrow$

$1\downarrow \Leftrightarrow \downarrow\uparrow$

this is a <u>triplet</u> state

${}^3\Sigma$

On <u>each</u> surface, there is a manifold of vibrational levels



Transitions between <u>vibrational</u> levels happen in the <u>IR</u> and have selection rules

$\Delta n = \pm 1$ $\quad$ ν = directly related to spring constant k

$\Delta E = h\nu = \hbar\omega = \hbar\sqrt{\frac{k}{\mu}}$

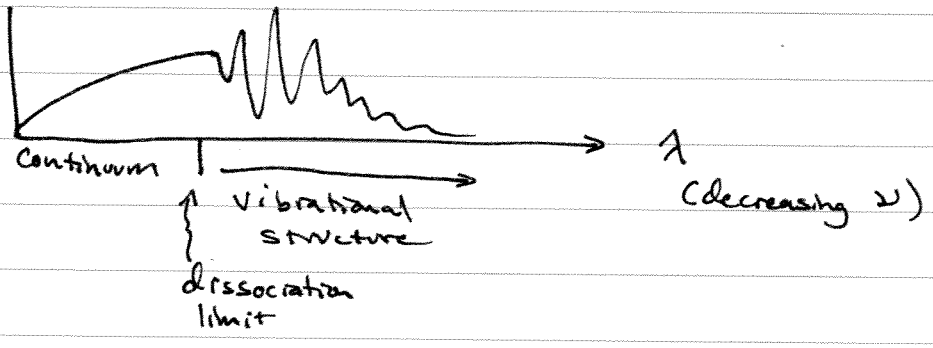
Each vibrational level also has a manifold of <u>rotational</u> states

$\Delta J = \pm 1$ ← sequence of lines with $2\hat{B}$ spacing =

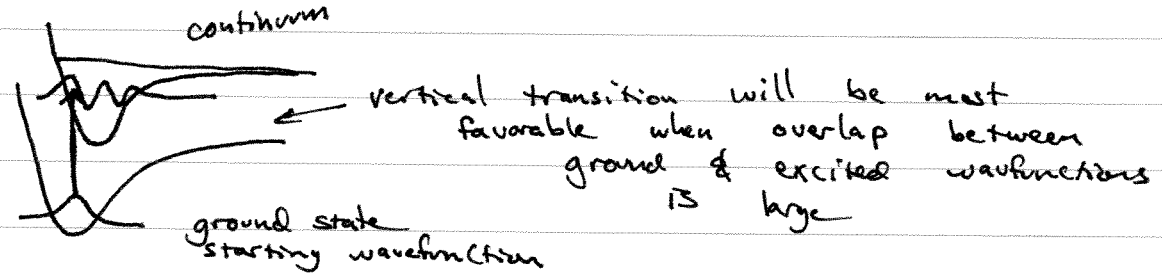
The selection rules were a side effect of the requirement that μ <u>must change</u> during a transition for us to be able to interact with the molecule with light.

For electronic transitions, the electronic degrees of freedom automatically make μ change, so there's no selection rule. However, some electronic transitions are more <u>likely</u> to be observed than others.

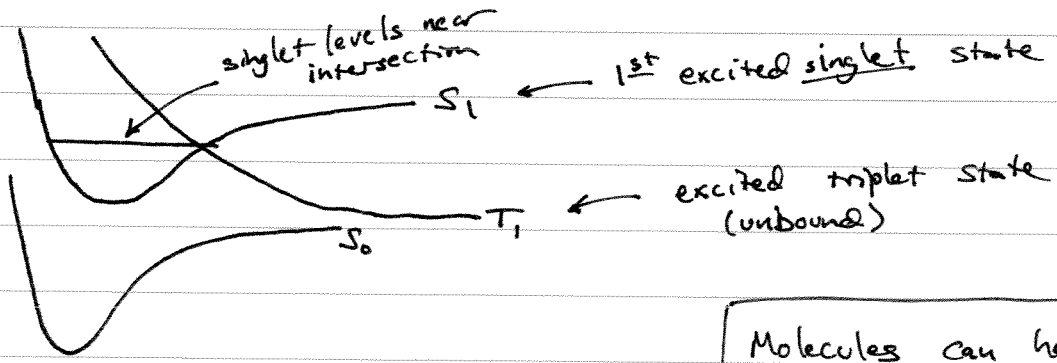
What do electronic spectra look like?

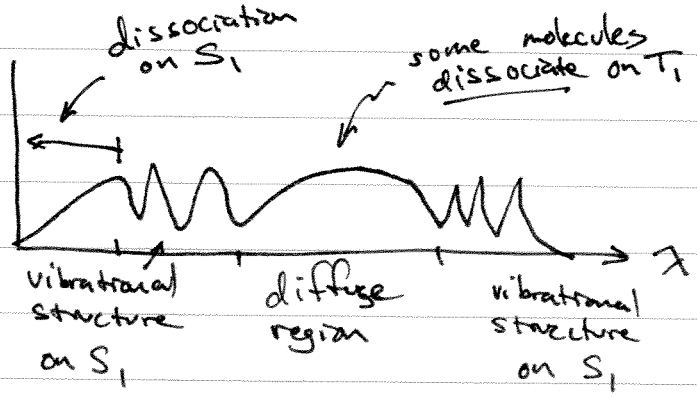


How we understand these:



Pre-dissociation & inter-system crossing



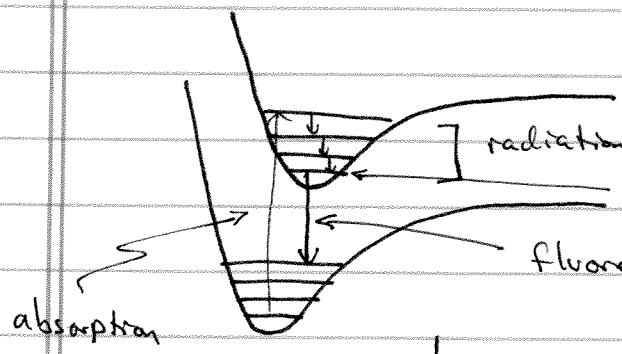


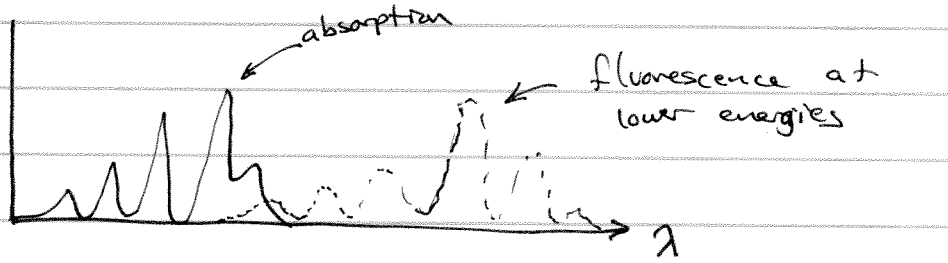
Molecules can have an internal conversion of energy between electronic states. Here, vibrational energy on S_1 converts to electronic excitation.

Internal conversion or intersystem crossing usually happens when electronic states have a "curve crossing"

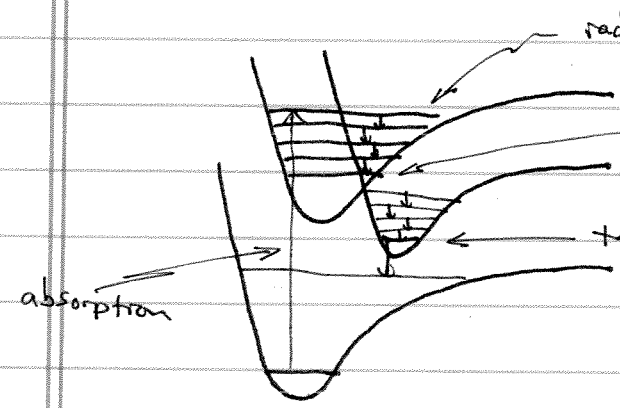
Singlet → Singlet conversion is fast!

Fluorescence





Phosphorescence

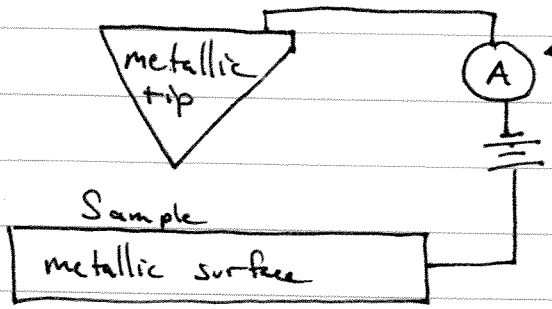


$T_1 \rightarrow S_0$ transitions are "spin forbidden"

it requires a heavy atom to make this happen

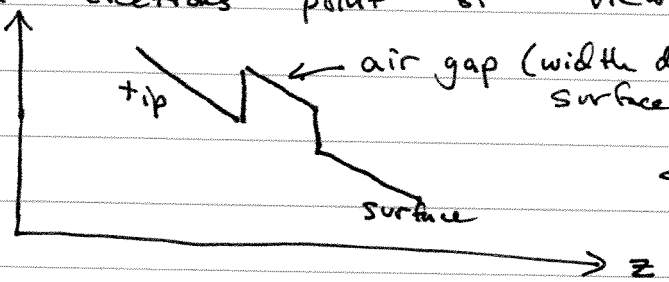
Process	Transition	Change in Spin Multiplicity	Time Scale
Fluorescence	Radiative $S_1 \rightarrow S_0$	0	10^{-9} s
Internal Conversion	$S_1 \rightarrow S_0$ collisional	0	$10^{-7} - 10^{-12}$ s
Relaxation	collisional	0	10^{-14} s
ISC	$S_1 \rightarrow T_1$	1	$10^{-12} - 10^{-6}$ s
Phosphorescence	$T_1 \rightarrow S_0$	1	$10^{-7} - 10^{-5}$ s (sometimes longer)

Tunnelling



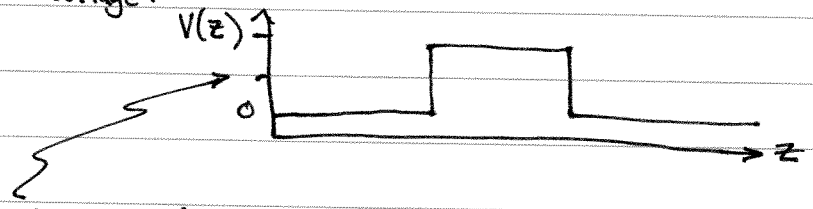
← An STM device stripped to most essential portion

From an electron's point of view:



← These lines are slanted because there is a driving voltage

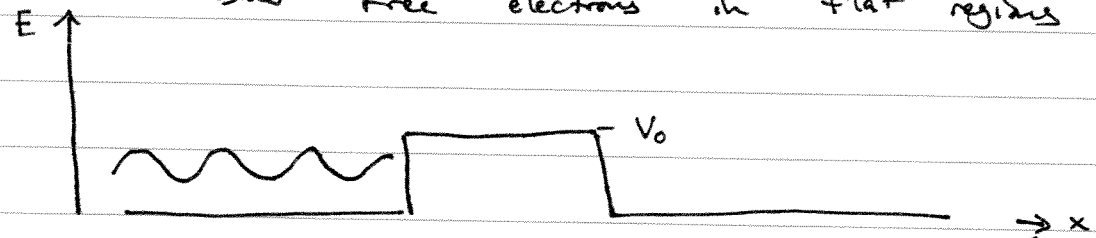
What voltage:



what would the classical behavior be in this case?

The electron would not have enough energy to overcome the potential barrier of the air gap. It would reflect (bounce) back.

Consider free electrons in flat regions



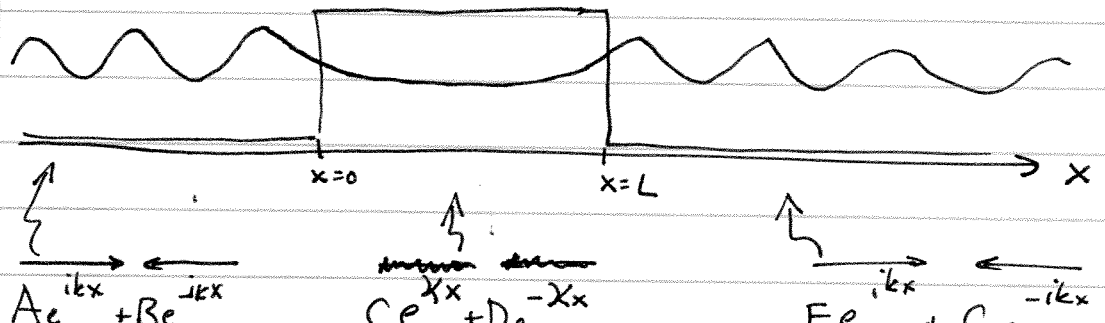
In a flat region with particle energy above local potential energy: $\psi(x) = Ae^{ikx} + Be^{-ikx}$ ← moving backwards

with $k = \frac{\sqrt{2m(E-V)}}{\hbar}$ ← k is real

In a flat region with energy below the local potential:

$$\psi(x) = Ce^{\chi x} + De^{-\chi x}$$

with $\chi = \frac{\sqrt{2m(V-E)}}{\hbar}$ ← χ real



oscillatory | decaying/growing | oscillatory

Boundary conditions:

at $x=0$: $A+B = C+D$ ← wavefunction must be continuous

$ikA - ikB = \chi C - \chi D$ ← 1st derivative must be continuous

at $x=L$: $Ce^{\chi L} + De^{-\chi L} = Fe^{ikL} + Ge^{-ikL}$ ← $\psi(L)$ continuous

$\chi Ce^{\chi L} - \chi De^{-\chi L} = ikFe^{ikL} - ikGe^{ikL}$ ← $\psi'(L)$ continuous

The probability that the electron is moving to the right on the left side: $|A|^2$

The probability that the electron is moving to the right on the right side $= |F|^2$

Transmission probability $= \frac{|F|^2}{|A|^2}$

(classically $T = 1$ above the barrier, 0, below)

How might we solve this?

$$A + B - C - D = 0$$

$$ikA - ikB - \chi C + \chi D = 0$$

$$Ce^{\chi L} + De^{-\chi L} - Fe^{ikL} - Ge^{-ikL} = 0$$

$$\chi Ce^{\chi L} - \chi De^{-\chi L} - ikFe^{ikL} + ikGe^{-ikL} = 0$$

no way to get G; if there's nothing to reflect back → $G = 0$ ← no reflection

Assume unit incoming flux → $A = 1$ ← unit flux

6 equations, 6 unknowns

$$\begin{pmatrix} 1 & 1 & -1 & -1 & 0 & 0 \\ ik & -ik & -\chi & +\chi & 0 & 0 \\ 0 & 0 & e^{\chi L} & e^{-\chi L} & -e^{ikL} & -e^{ikL} \\ 0 & 0 & \chi e^{\chi L} & -\chi e^{-\chi L} & -ike^{ikL} & ike^{-ikL} \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} A \\ B \\ C \\ D \\ F \\ G \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 1 \end{pmatrix}$$

Matrix → $\underline{\underline{A}} \cdot \vec{x} = \vec{b}$

$\vec{x}$: vector of unknowns; $\vec{b}$: vector of knowns

$$\underline{\underline{A}}^{-1} \cdot \underline{\underline{A}} \cdot \vec{x} = \underline{\underline{A}}^{-1} \cdot \vec{b}$$

$\underline{\underline{A}}^{-1} \cdot \underline{\underline{A}} = \underline{\underline{I}}$

$$\vec{x} = \underline{\underline{A}}^{-1} \cdot \vec{b}$$

When we solve the matrix inverse:

T = transmission probability $= \left|\frac{F}{A}\right|^2$

$$= \left(1 + \frac{\sinh^2\left(\sqrt{V_0}\ (1-r)^{1/2}\right)}{4r\ (1-r)}\right)^{-1}$$

$$r = \frac{E}{V_0} \qquad V_0 = \frac{2mL^2V_0}{\hbar^2}$$

In atomic units $m = 1$, $\hbar = 1$ and we'll set $L = 2$ a.u (approximately 1.06 Å)

(And arbitrarily set $V_0 = 5$ hartree).

In[1]:=
```
v0 = 2 m L^2 V0 / hbar^2
```

Out[1]=
$$\frac{2\,L^2\,m\,V0}{hbar^2}$$

In[2]:=
```
r = Energy / V0
```

Out[2]=
$$\frac{Energy}{V0}$$

In[3]:=
```
m = 1
```

Out[3]= 1

In[4]:=
```
m = .
```

In[5]:=
```
T = (1 + Sinh[Sqrt[v0] Sqrt[1 - r]]^2 / (4 r (1 - r)))^(-1)
```

Out[5]=
$$\frac{1}{1+\frac{V0\,\text{Sinh}\left[\sqrt{2}\,\sqrt{1-\frac{Energy}{V0}}\,\sqrt{\frac{L^2\,m\,V0}{hbar^2}}\right]^2}{4\,Energy\left(1-\frac{Energy}{V0}\right)}}$$

In[6]:=
```
m = 1
```

Out[6]= 1

In[7]:=
```
hbar = 1
```

Out[7]= 1

In[8]:=
```
V0 = 5
```

Out[8]= 5

In[9]:=
```
T
```

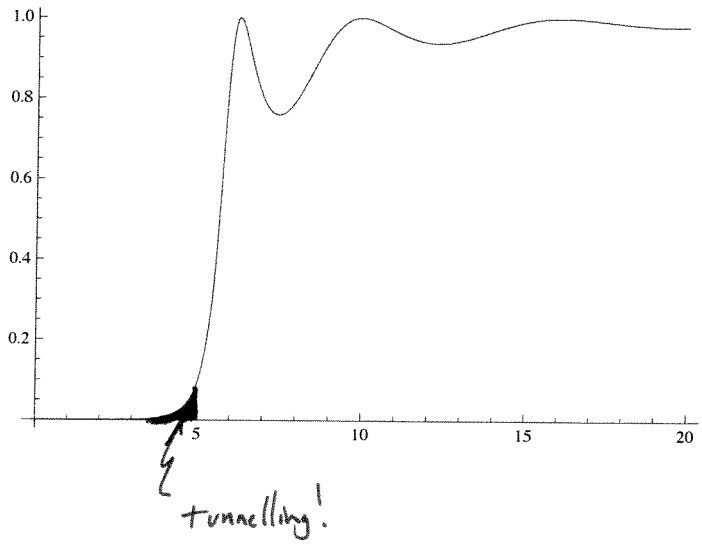
Out[9]=
$$\frac{1}{1+\frac{5\,\text{Sinh}\left[\sqrt{10}\,\sqrt{1-\frac{Energy}{5}}\,\sqrt{L^2}\right]^2}{4\left(1-\frac{Energy}{5}\right)Energy}}$$

In[11]:=
```
L = 2
```

Out[11]= 2

In[14]:=
```
Plot[T, {Energy, 0, 20}, PlotRange → Full]
```

Out[14]=



Symmetry

Symmetric objects:  sphere  cube

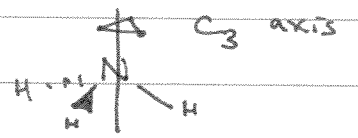
they are both "symmetric" objects, but in different ways.

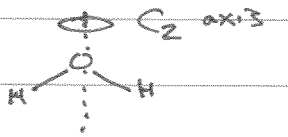
→ Group theory: Lets us classify objects by using all of the "operations" that leave the object the same

— Symmetry operations:
- Rotation around a line or axis
- Reflection through a plane
- Inversion through a point
- "Improper Rotation" (rotation followed by a reflection)

Once we decide which operations leave a molecule alone, we can classify them into Symmetry groups.

Some examples of symmetry operations:

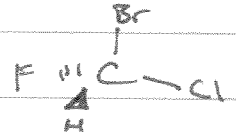




C_n = rotation around $\frac{360^\circ}{n}$ gives identical structure

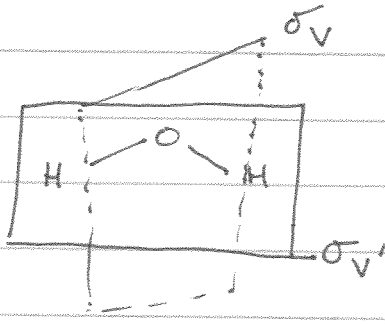
How many and what kind of axes:

C_6 + 3 C_2 axes (+ 3 C_2' axes)



← only identity ($\hat{E}$) operation

Reflection



Water has 2 reflection planes

NH_3? (there are 3 σ_v reflection planes in NH_3)

σ_v = parallel to principal axis of symmetry

σ_h = perpendicular to principal axis of symmetry

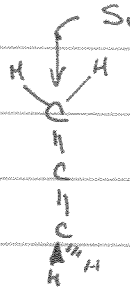
σ_d = bisects 2 C_2 axes that are perpendicular to principal C_2 axis's but also S_4

Improper rotation:

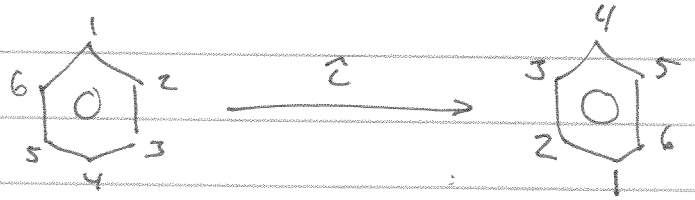
CH_4:

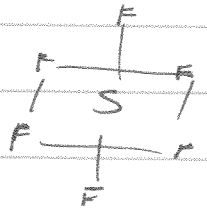
S_4 means rotate 90° and reflect through a plane perpendicular to the axis

Allene:



Inversion:

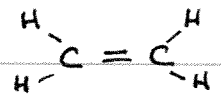




$\hat{i}$ → also returns structure (what others does SF_6 have)

Molecules can be grouped by what kinds of symmetry operations they have. The first step is to catalog all of the operations:

C_2H_2



$C_2 \times 3$

$\sigma_v \times 3$

$\hat{i}$

$\hat{E}$

Benzene

$C_6 \times 1$

$C_2 \times 3$

$\sigma_v \times 3$

$\sigma_h \times 1$

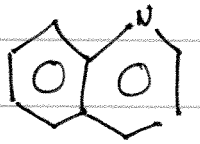
$\sigma_d \times 3$

E

$\hat{i}$

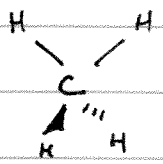
S_6

Quinoline



E, σ

Methane



C_4

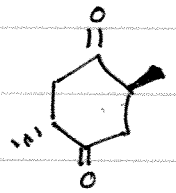
$4 \times C_3$

$3 \times C_2$

$3 \times S_4$

$6 \times \sigma_d$

Symmetry groups are then classified by all of the symmetry operations that work on that set of molecules:

Group	operations	example
C_1	only E	CBrClFI
C_i or S_2	only E & i	
C_s	E & σ	
C_n, C_{nv} groups	C_n symmetry axis	
C_{2v}	E, C_2, $2\sigma_v$	H_2O, 

D_n ← n-fold axis & n C_2 axes perpendicular to it

D_{nh} ← D_n + mirror plane (σ_h) ⊥ to C_n axis

D_{nd} ← D_n + n dihedral (σ_d) planes

D_{2h} : C_2, $+2C_2$, i, E, $3\sigma_v$ 

D_{6h} : C_6, $3C_2$, $3C_2'$, i, S_6, σ_h, $3\sigma_v$, $3\sigma_d$ 

T_d : tetrahedral group
E, $4C_3$, $3C_2$, $3S_4$, $6\sigma_d$ CH_4

Operations

1. We can combine symmetry operations.

$\hat{C}_2 \hat{i}$ = inversion followed by C_2 rotation

2. Symmetry ops are associative.

$$\hat{A}(\hat{B}\hat{C}) = (\hat{A}\hat{B})\hat{C}$$

3. Identity must always work.

$$EA = AE$$

4. Operations can have inverses.

$$AA^{-1} = A^{-1}A = E \qquad \text{for all operators } A$$

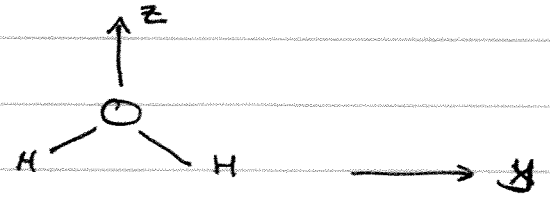
$\hat{C}_3^2$ = rotation by 240°

$\hat{C}_3^{-1}$ = rotation by −120°

$\hat{C}_3 \hat{C}_3^{-1}$ = rotation by −120° followed by rotation by 120°

More on symmetry

Consider H_2O



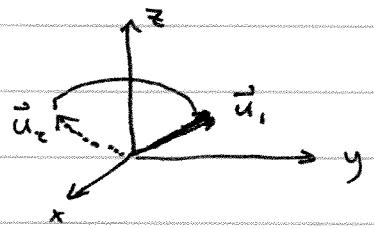
Water has these symmetry elements: C_2, σ_v, σ_v', E

These form a group called the C_{2v} group.

Since the molecule is symmetric, the electronic wavefunctions also have symmetry:

$\psi(\vec{u}_1) = \psi(\vec{u}_2)$ when $\vec{u}_1$ & $\vec{u}_2$ are related by a symmetry operation:

Suppose $\vec{u}_1 = \begin{pmatrix} u_x \\ u_y \\ u_z \end{pmatrix}$



$$\hat{C}_2 = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$ ← matrix representation of one operation of the C_2 symmetry element

$$\hat{C}_2 \vec{u}_1 = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} u_{1x} \\ u_{1y} \\ u_{1z} \end{pmatrix} = \begin{pmatrix} -u_{1x} \\ -u_{1y} \\ u_{1z} \end{pmatrix} = \vec{u}_2$$

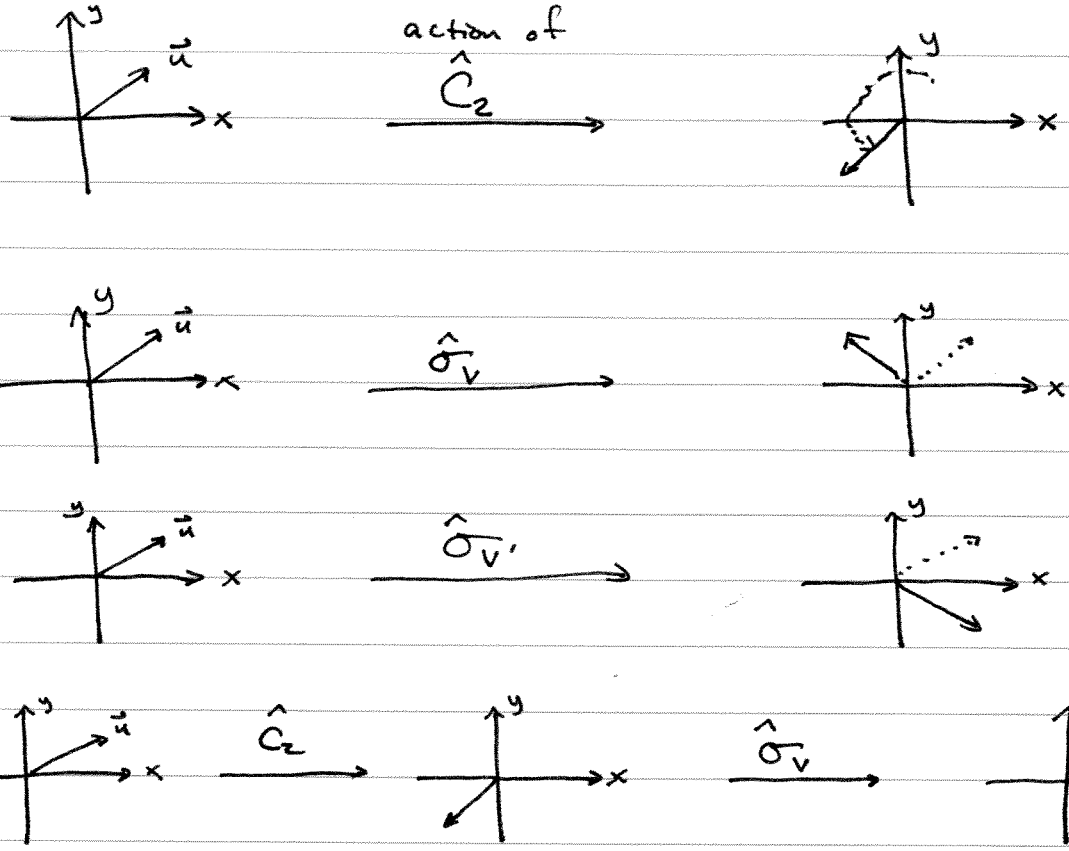
What does the matrix representation of $\hat{\sigma}_v$ look like?

$$\hat{\sigma}_v = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \qquad \hat{\sigma}_{v'} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$\hat{E} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

Once we know all of these, we can look at multiple operations.

Looking down the z-axis



$$\hat{\sigma}_v \hat{C}_2 \vec{u} = \hat{\sigma}_{v'} \vec{u}$$

multiple operations are equivalent to a single operation of one of the other operators!

2nd op ↓ / First operator: →	$\hat{E}$	$\hat{C}_2$	$\hat{\sigma}_v$	$\hat{\sigma}_{v'}$
$\hat{E}$	E	C_2	σ_v	$\sigma_{v'}$
$\hat{C}_2$	C_2	E	$\sigma_{v'}$	σ_v
$\hat{\sigma}_v$	σ_v	$\sigma_{v'}$	E	C_2
$\hat{\sigma}_{v'}$	$\sigma_{v'}$	σ_v	C_2	E

CH_3Cl is in a group called C_{3v}

C_{3v} has 5 symmetry elements: $E, C_3, \sigma_v, \sigma_{v'}, \sigma_{v''}$

but 6 symmetry operations: $\hat{E}, \hat{C}_3, \hat{C}_3^2, \hat{\sigma}_v, \hat{\sigma}_{v'}, \hat{\sigma}_{v''}$ ← rotate by 240°

	E	C_3	C_3^2	σ_v	$\sigma_{v'}$	$\sigma_{v''}$
E	E	C_3	C_3^2	σ_v	$\sigma_{v'}$	$\sigma_{v''}$
C_3	C_3	C_3^2	E			
C_3^2	C_3^2	E				
σ_v	σ_v					
$\sigma_{v'}$	$\sigma_{v'}$					
$\sigma_{v''}$	$\sigma_{v''}$					

← can you fill in the rest?

It is good practice!

Irreducible Representations

Back to the C_{2v} group

$$\hat{E} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \qquad \hat{C}_2 = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$\hat{\sigma}_v = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \qquad \hat{\sigma}_{v'} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

These represent the actual operations

What other matrices have the same multiplication table?

~~We could leave out the 3rd row & column.~~

$$E = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \qquad C_2 = \begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}$$

$$\sigma_v = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \qquad \sigma_{v'} = \begin{pmatrix} 0 & -1 \\ -1 & 0 \end{pmatrix}$$

Here $\sigma_v \sigma_{v'} = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} 0 & -1 \\ -1 & 0 \end{pmatrix} = \begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix} = C_2$

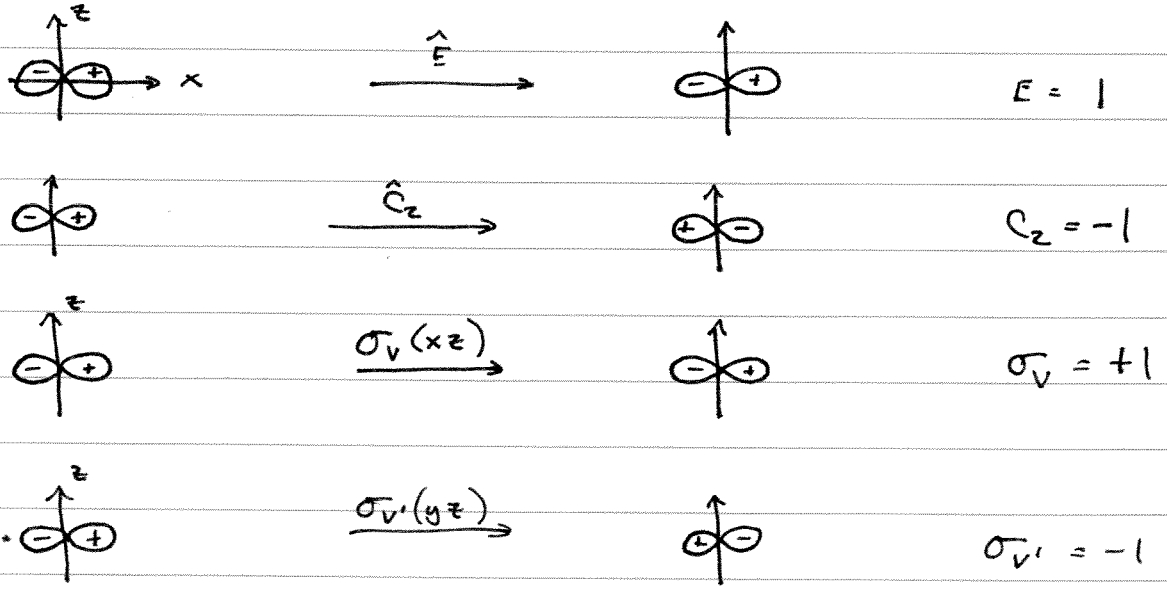
Even simpler reductions to numbers:

A_1:	$E = 1$	$C_2 = 1$	$\sigma_v = 1$	$\sigma_{v'} = 1$
A_2:	$E = 1$	$C_2 = 1$	$\sigma_v = -1$	$\sigma_{v'} = -1$
B_1:	$E = 1$	$C_2 = -1$	$\sigma_v = 1$	$\sigma_{v'} = -1$
B_2:	$E = 1$	$C_2 = -1$	$\sigma_v = -1$	$\sigma_{v'} = 1$

A_1, A_2, B_1, B are called irreducible representations for the symmetry group C_{2v}. They are 4 sets of numbers that have the same multiplication table as the actual symmetry operations.

Another way of thinking about this:

Consider the p_x orbital:



This is the "B_1" representation.

We can do the same for p_y

Character tables

symmetry ops

group → C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$	
A_1	1	1	1	1	z, z^2, x^2, y^2
A_2	1	1	−1	−1	xy
B_1	1	−1	1	−1	x, xz
B_2	1	−1	−1	1	y, yz

irreducible representation

behavior of irreducible rep under symmetry operation

which orbitals (p & d) give you this irreducible rep

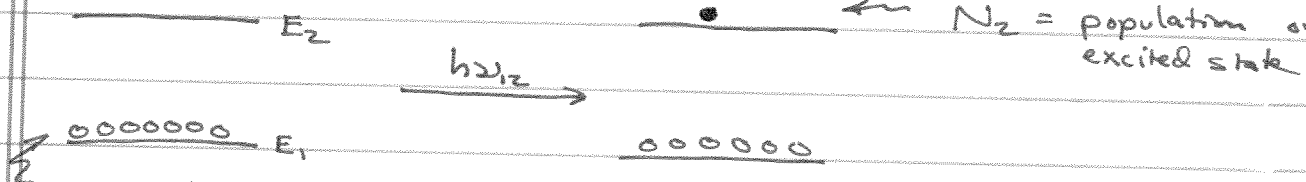
Absorption & Emission & Lasers

Last week, we talked about the kinds of electronic transitions that happen spectroscopically

Excitation	$S_0 \rightarrow S_1$	← rate
Fluorescence	$S_1 \rightarrow S_0$	fast
Inter System Crossing	$S_1 \rightarrow T_1$	slow
Phosphorescence	$T_1 \rightarrow S_0$	very slow

These transitions are governed by a set of rate equations when we have populations of identical molecules.

Absorption:



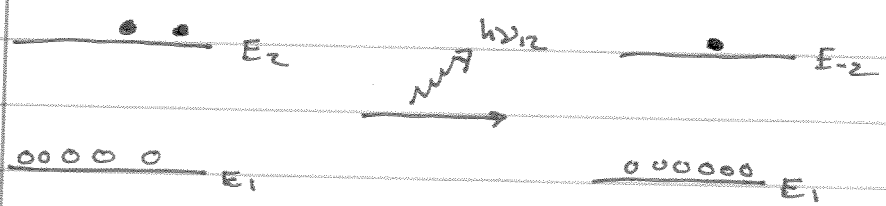
← N_2 = population on excited state

N_1 = population on ground state

Rate of Absorption: $\frac{-dN_1}{dt} = \frac{dN_2}{dt} = B_{12}\,\rho(\nu_{12})\,N_1$

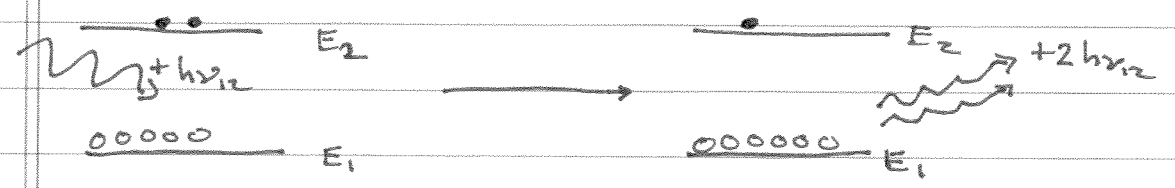
"Einstein" coefficient; $\rho(\nu_{12})$: spectral density at frequency ν_{12}

Spontaneous Emission



$$\frac{-dN_2}{dt} = A_{21}\,N_2$$

Stimulated Emission



$$-\frac{dN_2}{dt} = B_{21}\rho(\nu_{12})N_2$$

All 3 processes together:

$$-\frac{dN_1}{dt} = \frac{dN_2}{dt} = B_{12}\rho(\nu_{12})N_1(t) - A_{21}N_2(t) - B_{21}\rho(\nu_{12})N_2(t)$$

If we're in the steady state, $\frac{dN_1}{dt} = 0$, so we can solve for ρ:

$$\rho(\nu_{12}) = \frac{A_{21}}{(N_1/N_2)B_{12} - B_{21}}$$

One thing you'll learn next semester is that at equilibrium the populations are proportional to the Boltzmann factors:

$$N_1 = Ce^{-E_1/kT} \qquad N_2 = Ce^{-E_2/kT}$$

$$N_1/N_2 = e^{-(E_2-E_1)/k_BT} = e^{-h\nu_{12}/k_BT}$$

$$\therefore \quad \rho(\nu_{12}) = \frac{A_{21}}{B_{12}e^{h\nu_{12}/kT} - B_{21}}$$

Blackbody radiation:

$$\rho(\nu_{12}) = \frac{8\pi h}{c^3}\frac{\nu_{12}^3}{e^{h\nu_{12}/kT} - 1} \quad \Rightarrow \quad B_{12} = B_{21}$$

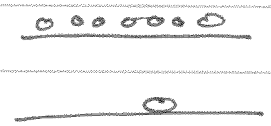
$$A_{21} = \frac{8h\pi\nu_{12}^3}{c^3}B_{21}$$

Lasers

To make a laser, we need to create a situation when the population in an excited state is bigger than in a lower state. This will allow a cascade of stimulated emission to create a beam of coherent light:

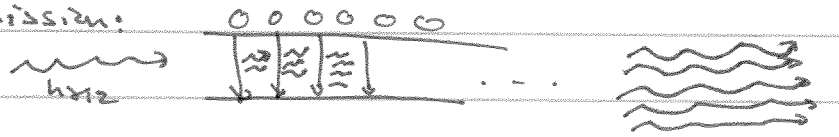
Normally we can't do this at equilibrium since $N_2 = e^{-E_2/kT}$ ← is always smaller than $N_1 = e^{-E_1/kT}$

We need a population inversion



This situation is inherently unstable or non-equilibrium.

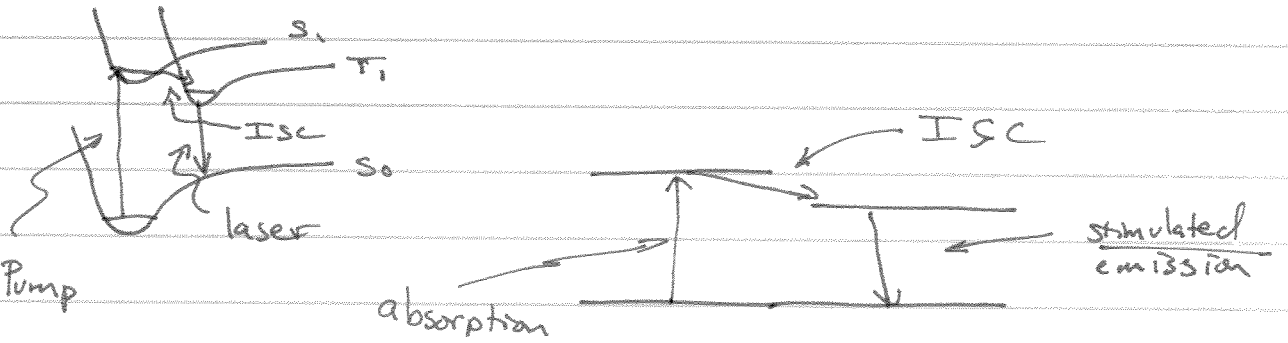
Once we have a population inversion, we can get stimulated emission:



lots of "coherent" photons all at exactly the same frequency.

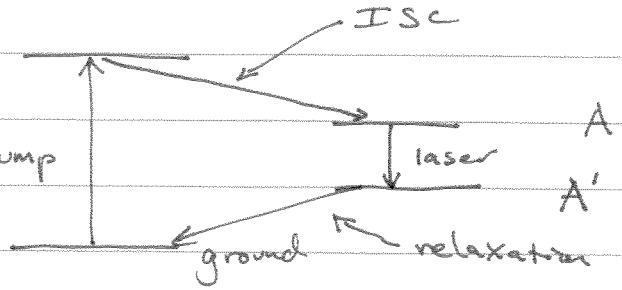
So, how do we do it?

3-level laser



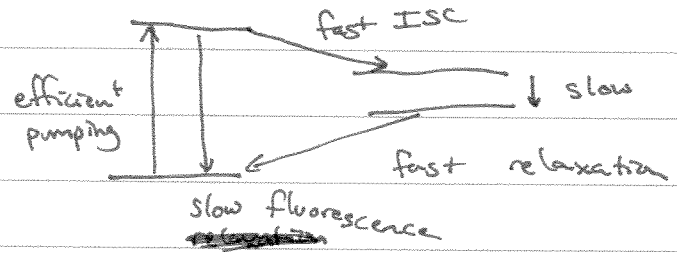
More common:

4 level lasers



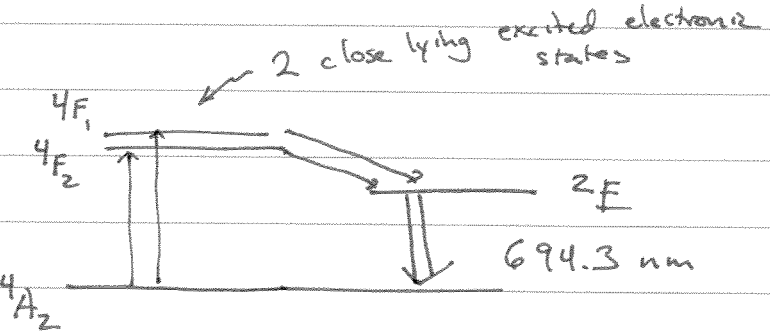
Why is this easier? The population in A' is already quite low (as it is an excited state) so creating a population inversion is quite easy!

What makes a good laser:



Common lasers:

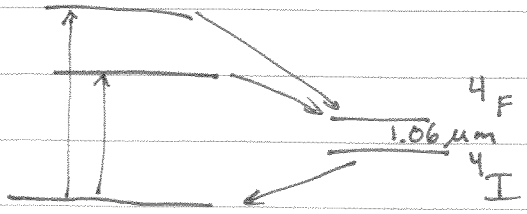
Cr^{3+} ions in a ruby:

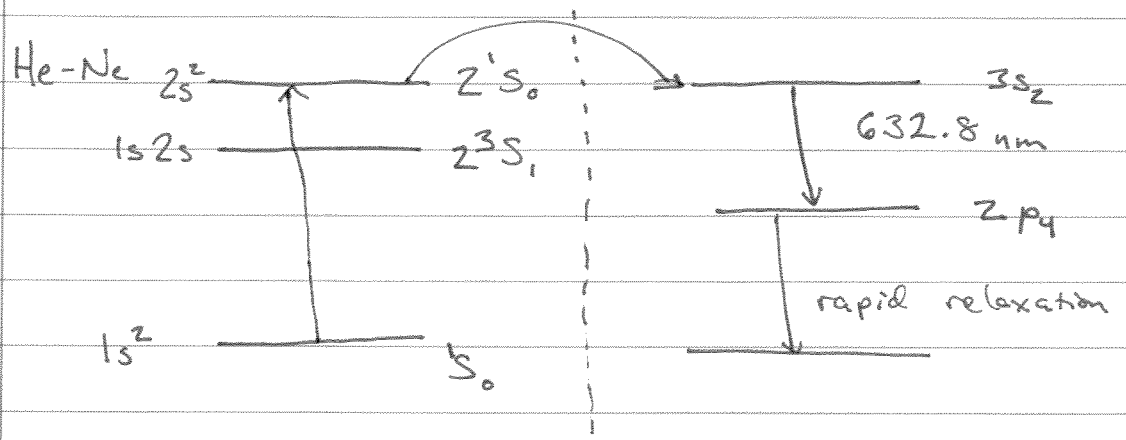


Nd^{3+} in $Y_3Al_3O_{12}$

Neodymium - Yttrium Aluminum Garnet

Nd-YAG





An <u>excimer laser</u> involves a <u>chemical reaction</u> that creates a molecule in an excited state:

$$Cl + h\nu \longrightarrow Cl^*$$

$$Xe + Cl^* \longrightarrow XeCl^*$$