# Advanced Glass Science
## (4016101)

**Instructor: Asst.Prof.Dr. Jakrapong Kaewkhao**

## Course Outline:

**Week 13:** Judd-Ofelt Theory

- *Case studies from international publications*

**Book:** A.K., Varshneya. ***Fundamentals of inorganic glasses***
A., Paul A, ***Chemistry of glasses***
J.E. Shelby, ***Introduction to glass science and technology***

# $\Omega_2$

- Sensitive to both asymmetry and covalency at the RE site

- More affected by the asymmetry of the crystal field and by changes of the energy difference between $4f^N$ and $4f^{N-1}5d$ configuration. In other words, $\Omega_2$ increases as nephelauxetic effect increases.

- Strongly enhanced by covalent bonding.

- Relates to the structural changes of the site of RE ions. $\Omega_2$ is raised drastically by lowering the symmetry of rare earth ligand field.

- $\Omega_2$ in oxide glasses is larger than that in fluoride glasses, which is ascribed to the larger electric field gradient by divalent oxide ions than that by monovalent fluoride ions.

- Depends strongly on the ionic radius of the modifier (of glasses), which, in turn, influences the polarizability of oxygen around RE ion.

- Slightly increases as the number electron of RE ions increase.

# $\Omega_4$

- Gained by lowering the covalency of σ chemical bond between RE ion and ligand anions.

- Not directly related to the ligand symmetry of RE ions but to the electron density on the oxide ion, $\Omega_4$ decreases as the electron density on oxygen ions increases.

- Decreases as the number of electron of RE ions increases.

- It may be still risky to discuss the covalency depending on $\Omega_4$. The notable information which $\Omega_4$ provides may be the electron density around an RE ion.

# $\Omega_6$

-Shows a different type of variation related to the rigidity of the medium, and increases in the order crystalline mixed glass<glasses<viscous solutions<hydratedions<halide vapors<complexes of organic ligands.

-Not directly related to the ligand symmetry of RE ions but to the electron density on the oxide ion

- $\Omega_6$ decreases as the electron density on oxygen ions increases.

- Most sensitive to the overlap integral of the 4f and the 5d orbitals.

- Increases with a decrease in the Coulomb interaction, which can be a measure of the crystal field strength.

- $\Omega_6$ increases with an increase of the distance between RE ion and the ligands.

- $\Omega_6$ decreases with increasing covalency between ligands and RE ions due to increasing σ-electron donation of the ligands (2p orbitals of oxygen ion).
- Otherwise, $\Omega_6$ increases with the increase of π-electron donation from the ligands (such as $PO_4$ tetrahedra).

# Radiative properties

The JO parameters along with refractive index ($n$) are used to predict the radiative properties of excited states of RE ion.

The total radiative transition probability ($A_T$) for an excited state is the sum of the terms calculated over all the terminal states.

$$A_T(\Psi J) = \sum A(\Psi J, \Psi' J')$$

where $$A(\Psi J, \Psi' J') = \frac{64\pi^4 \upsilon^3}{3h(2J+1)} \frac{n(n^2+2)^2}{9} S_{ed} + \frac{64\pi^4 \upsilon^3}{3h(2J+1)} n^3 S_{md}$$

The branching ratio ($\beta_R$) corresponding to the emission from an excited level to its lower level is given by

$$\beta_R(\Psi J, \Psi' J') = \frac{A(\Psi J, \Psi' J')}{A_T(\Psi J)}$$

The branching ratios can be used to predict the relative intensities of all emission lines originating from a given excited state. The experimental branching ratios can be found from the relative areas of the emission bands.

$A_T$ is related to the radiative lifetime ($\tau_{rad}$) of an excited state by

$$\tau_{rad}(\Psi J) = \frac{1}{A_T(\Psi J)}$$

The peak stimulated emission cross-section, ($\sigma(\lambda_P)$ ( , )), between the states and having a probability of can be expressed as

$$\sigma(P)\ (\Psi J, \Psi' J') = \frac{\lambda_p{}^4}{8\pi c n^2 \Delta\lambda_{eff}} \mathrm{A}(\Psi J, \Psi' J')$$

where $\lambda_p$ is the transition peak wavelength and $\Delta\lambda_{eff}$ is its effective line width found by dividing the area of the emission band by its average height. Good laser transitions are characterized by larger cross-sections and smaller $\Delta\lambda_{eff}$ for stimulated emission.

# Parameters

(1) Oscillator strength ( $f_{exp}$) → Manual (Absorption graph)

(2) Matrix element $U_2$, $U_4$, $U_6$ → Ref. paper

(3) $\Omega_2$, $\Omega_4$, $\Omega_6$
(4) Oscillator strength ( $f_{cal}$) → Software 1 ; JO.exe

(5) Radiation transition probsability ($A_R$)
(6) Branching ratio ($\beta_{Rcal}$)
(7) Lifetime ($\tau_{Rcal}$) → Software 2 ; JORP.exe

(8) Stimulated emission cross-section ($\sigma_e$*$10^{-21}$)
(9) Branching ratio ($\beta_{Rexp}$) → Manual (Emission graph)

## (1) Oscillator strength ( $f_{exp}$)

$$f_{exp} = \frac{\left(4.318\times10^{-9}\right)\times\left(x, cm^{-2}\right)\times\left(y_{calibrate}, nm/cm\right)\times\left(Area, cm^{2}\right)}{\left(concentration, mol/L\right)\times\left(thickness, cm\right)}$$

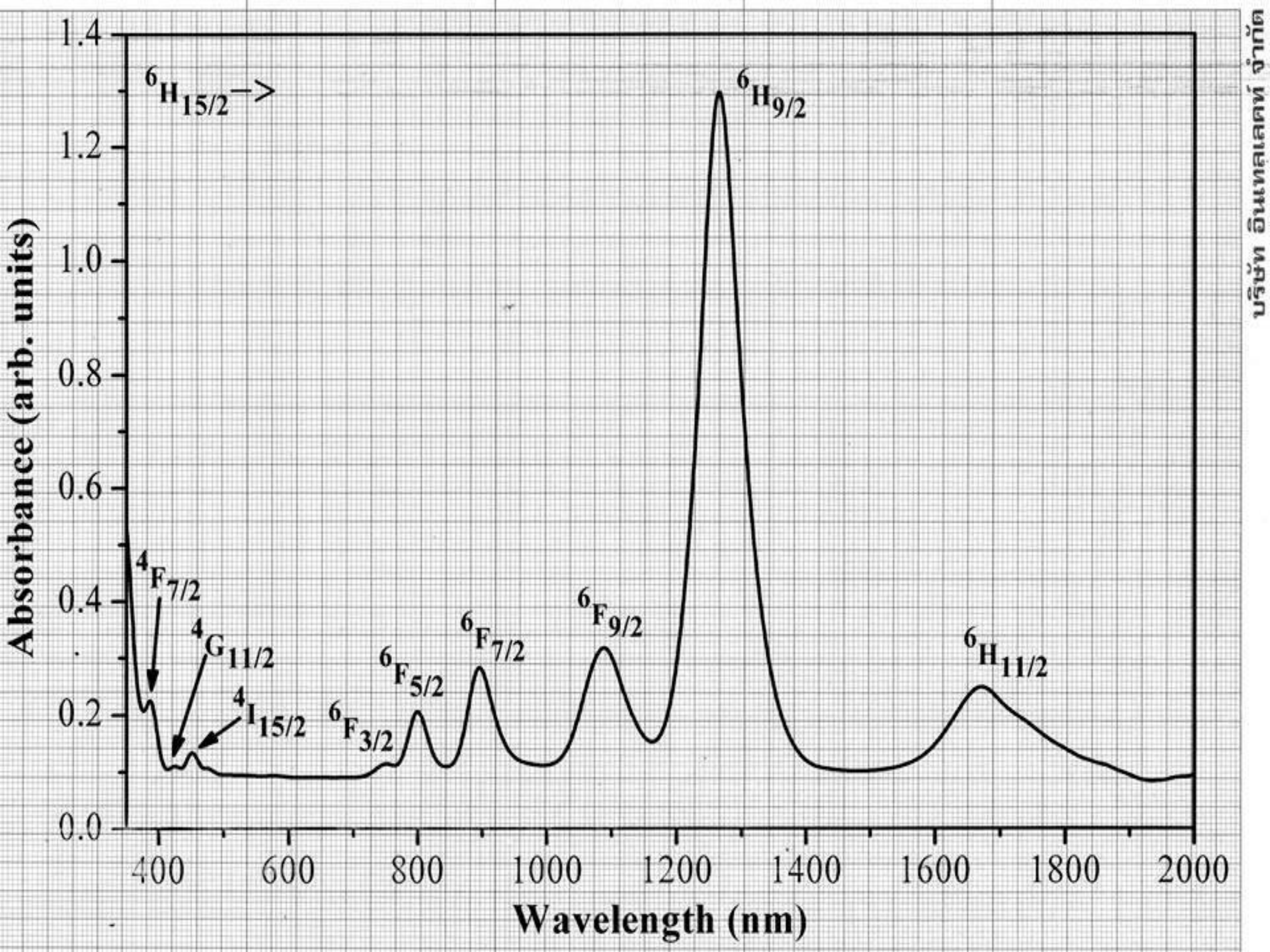
$$x, cm^{-2} = \frac{\Delta x, cm^{-1}}{w, cm}$$

$$y_{calibrate} = \frac{\left(y_{end} - y_{1,starting}\right)}{\text{length of } y\text{ - axis, cm}}$$

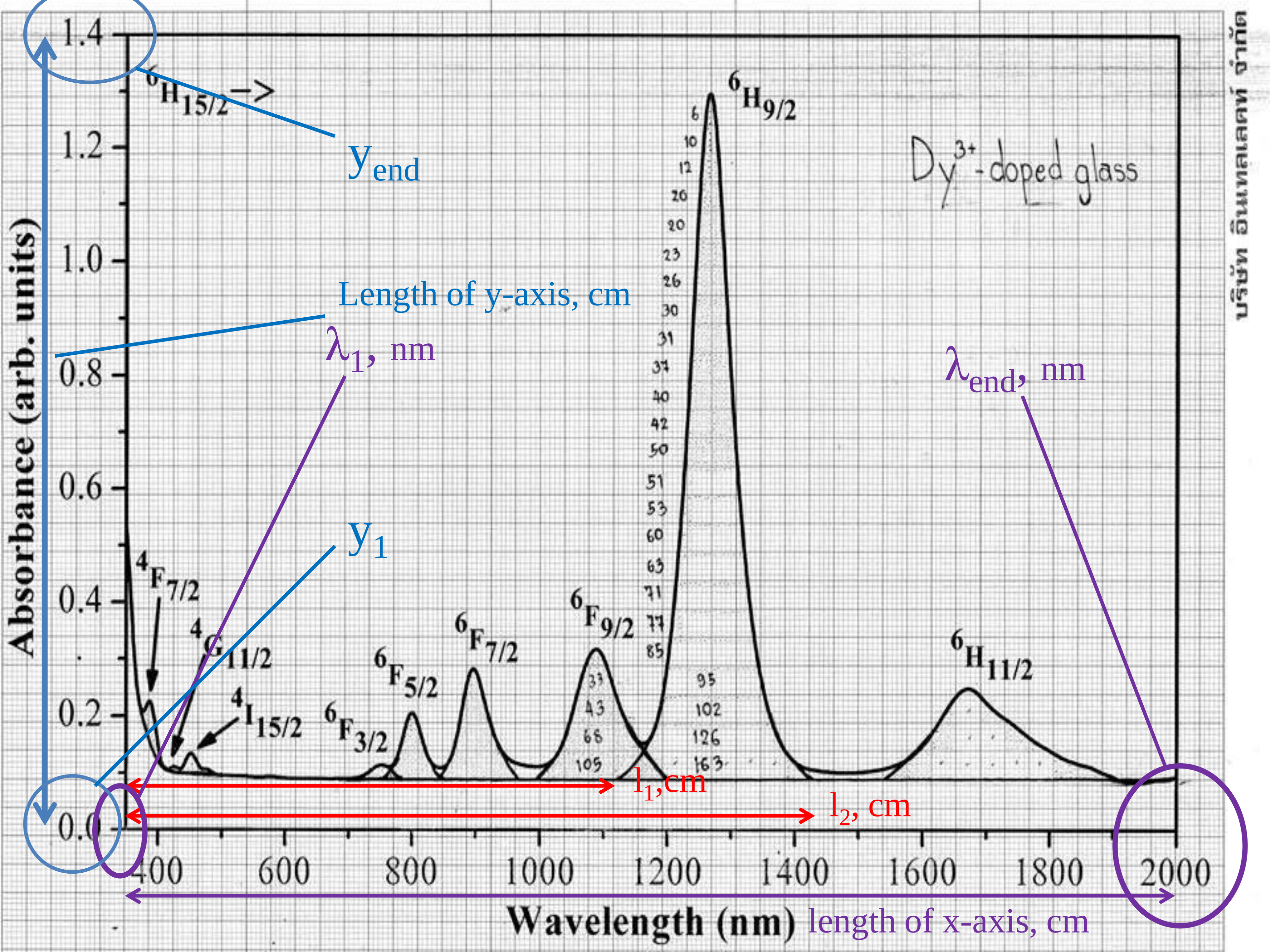
$$\Delta x, cm^{-1} = x_1, cm^{-1} - x_2, cm^{-1}$$

$$x_1, nm = \lambda_1, nm + \left(l_1, cm \times x_{calibrate}, nm/cm\right)$$
$$x_2, nm = \lambda_1, nm + \left(l_2, cm \times x_{calibration}, nm/cm\right)$$

$$x_{calibrate}, nm/cm = \frac{\left(\lambda_{end}, nm - \lambda_{1,starting}, nm\right)}{\text{length of } x\text{ - axis, cm}}$$



$^6H_{15/2}$->
$^6H_{9/2}$
$^4F_{7/2}$
$^4G_{11/2}$
$^4I_{15/2}$
$^6F_{3/2}$
$^6F_{5/2}$
$^6F_{7/2}$
$^6F_{9/2}$
$^6H_{11/2}$
Absorbance (arb. units)
Wavelength (nm)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
400
600
800
1000
1200
1400
1600
1800
2000



Dy3+-doped glass
Absorbance (arb. units)
Wavelength (nm)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
400
600
800
1000
1200
1400
1600
1800
2000
6H15/2 ->
6H9/2
6H11/2
6F9/2
6F7/2
6F5/2
6F3/2
4I15/2
4G11/2
4F7/2
yend
y1
Length of y-axis, cm
λ1, nm
λend, nm
l1,cm
l2, cm
length of x-axis, cm

## (1) Oscillator strength ( $f_{exp}$)

$$f_{exp} = \frac{\left(4.318\times10^{-9}\right)\times(x)\times\left(y_{calibrate}\,,nm/cm\right)\times\left(Area\,,cm^{2}\right)}{\left(concentration\,,mol/L\right)\times\left(thickness\,,cm\right)}$$

$$\text{Concentration, mol/L} = \frac{(\text{Weight of RE oxide, g})\times\left(\text{Density, g/cm}^{3}\right)\times1000}{(\text{M.W. of RE oxide, g/mol})\times(\text{Total weight of glass, g})}$$

$$= \frac{0.7346\times3.1791\times1000}{372.9982\times30}$$

$$= 0.2087\ \text{mol/L}$$

# (1) Oscillator strength ( $f_{exp}$)

$$f_{exp}=\frac{\left(4.318\times10^{-9}\right)\times(x)\times\left(y_{calibrate},nm/cm\right)\times\left(Area,cm^{2}\right)}{\left(concentration,mol/L\right)\times\left(thickness,cm\right)}$$

| Transition | Wavelength λ (nm) | Wavenumber (υ = 1/λ, $cm^{-1}$) | x =Δx/w ($cm^{-2}$) | $y_{calibrate}$ (nm/cm) | Peak Area ($cm^2$) | Concentration (mol/L) | Thickness (cm) | Oscillator Strength $f_{exp}$*10^-6 |
|---|---|---|---|---|---|---|---|---|
| $^4F_{7/2}$ | 386 | 25906.74 | 5095.99 | 0.1 | 0.11 | 0.208702246 | 0.3 | **3.87** |
| $^4G_{11/2}$ | 425 | 23529.41 | 4294.15 | 0.1 | 0.01 | 0.208702246 | 0.3 | **0.30** |
| $^4I_{15/2}$ | 451 | 22172.95 | 3619.04 | 0.1 | 0.07 | 0.208702246 | 0.3 | **1.75** |
| $^6F_{3/2}$ | 750 | 13333.33 | 1384.83 | 0.1 | 0.09 | 0.208702246 | 0.3 | **0.86** |
| $^6F_{5/2}$ | 800 | 12500.00 | 1205.64 | 0.1 | 0.55 | 0.208702246 | 0.3 | **4.57** |
| $^6F_{7/2}$ | 896 | 11160.71 | 955.19 | 0.1 | 1.24 | 0.208702246 | 0.3 | **8.17** |
| $^6F_{9/2}$ | 1088 | 9191.18 | 646.104 | 0.1 | 2.49 | 0.208702246 | 0.3 | **11.10** |
| $^6H_{9/2}$ | 1266 | 7898.89 | 482.151 | 0.1 | 12.93 | 0.208702246 | 0.3 | **43.00** |
| $^6H_{11/2}$ | 1671 | 5984.44 | 261.276 | 0.1 | 3.15 | 0.208702246 | 0.3 | **5.68** |

# J-O Analysis method

Part 2 : Software analysis

Part 3 : Emission spectrum analysis

# System requirement for run software

System and Security ▸ System

View basic information about your computer

Windows edition

Windows 7 Ultimate

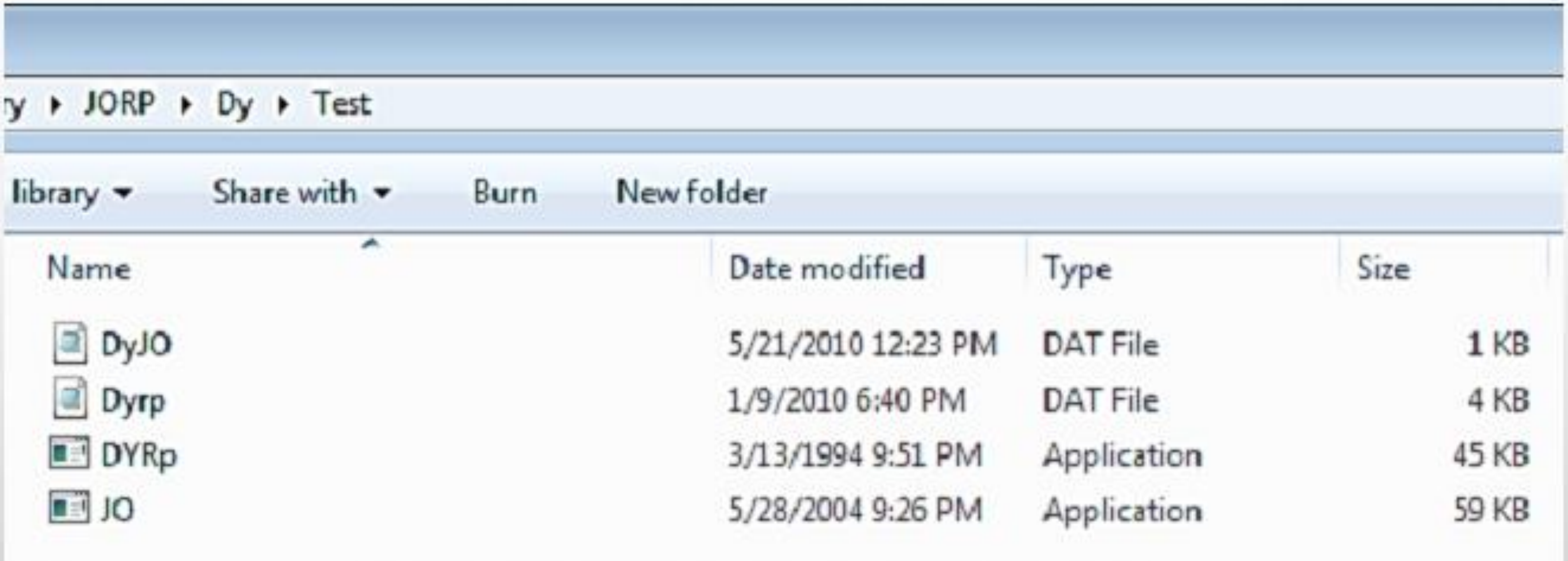


Service Pack 1

System

| | |
|---|---|
| Rating: | System rating is not available |
| Processor: | Intel(R) Core(TM) i5-3230M CPU @ 2.60GHz 2.60 GHz |
| Installed memory (RAM): | 8.00 GB (2.91 GB usable) |
| System type: | 32-bit Operating System |
| Pen and Touch: | No Pen or Touch Input is available for this Display |

# Software files




| Name | Date modified | Type | Size |
|---|---|---|---|
| DyJO | 5/21/2010 12:23 PM | DAT File | 1 KB |
| Dyrp | 1/9/2010 6:40 PM | DAT File | 4 KB |
| DYRp | 3/13/1994 9:51 PM | Application | 45 KB |
| JO | 5/28/2004 9:26 PM | Application | 59 KB |

Take all file to drive c:

# J-O calculating process

$$f_{exp} = 4.318 \times 10^{-9} \cdot \frac{\hat{x} y_{cal} A}{ct}$$

$$\boxed{\text{Absorption spectrum}} \xrightarrow{f_{exp} = 4.318 \times 10^{-9} \cdot \frac{\hat{x} y_{cal} A}{ct}} \boxed{f_{exp}} \xrightarrow{\text{1st Software: JO}} \boxed{\Omega_{2,4,6} \; f_{cal}}$$

# $1^{st}$ Software: JO

## 1.1. Go into DyJO.dat (by notepad) for set parameter

| Transition $^6H_{15/2} \rightarrow$ | Wavenumber ($\upsilon = 1/\lambda$, $cm^{-1}$) | Oscillator Strength $f_{exp}$ *10^-6 |
|---|---|---|
| $^4F_{7/2}$ | 25906.74 | 3.87E-06 |
| $^4G_{11/2}$ | 23529.41 | 2.96E-07 |
| $^4I_{15/2}$ | 22172.95 | 1.75E-06 |
| $^6F_{3/2}$ | 13333.33 | 8.6E-07 |
| $^6F_{5/2}$ | 12500.00 | 4.57E-06 |
| $^6F_{7/2}$ | 11160.71 | 8.17E-06 |
| $^6F_{9/2}$ | 9191.18 | 1.11E-05 |
| $^6F_{11/2}$ | 7898.89 | 4.3E-05 |
| $^6H_{11/2}$ | 5984.44 | 5.68E-06 |

No. of transition Refractive index

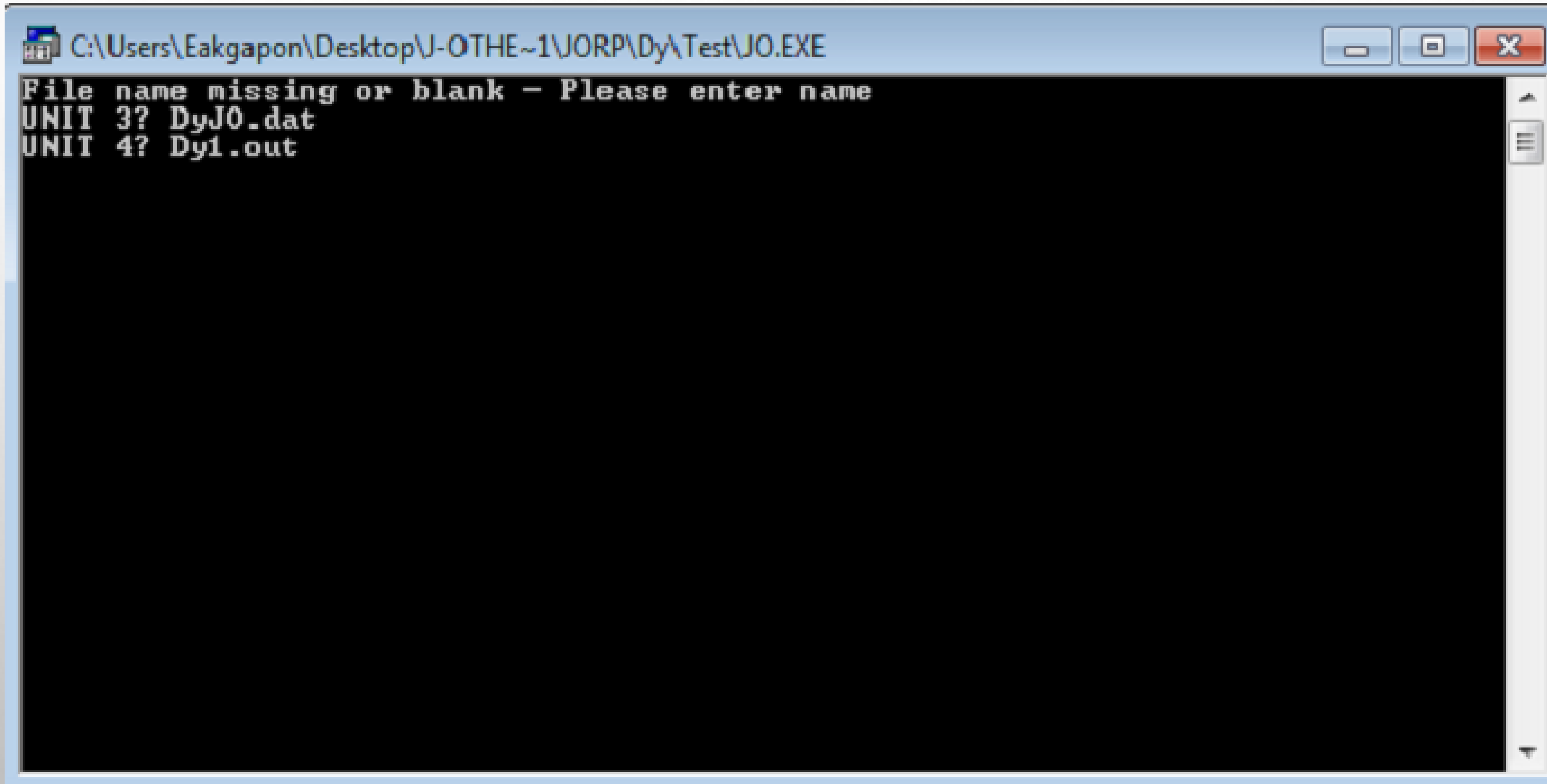
DyJO - Notepad

File Edit Format View Help

```
9,1.6500
7.5,5984,5.68E-6,0.0923,0.0366,0.6410
7.5,7899,4.30E-5,0.9387,0.8292,0.2048
7.5,9191,1.11E-5,0.0000,0.5736,0.7213
7.5,11160,8.17E-6,0.0000,0.1360,0.7146
7.5,12500,4.57E-6,0.0000,0.0000,0.3452
7.5,13333,8.60E-7,0.0000,0.0000,0.0610
7.5,22173,1.75E-6,0.0073,0.0003,0.0654
7.5,23529,2.96E-7,0.0004,0.0145,0.0003
7.5,25906,3.87E-6,0.0000,0.0768,0.0263
```

J of ground state $\upsilon$ $f_{Exp}$ $U_2, U_4, U_6$

# 1.2. Run JO.exe resulting to DOS windows



# 1.3. Analyze Dy1.out file

DY1 - Notepad

File Edit Format View Help

$\Omega_2$ $\Omega_4$ $\Omega_6$

K = 9 RI = 1.65000 W2 = .45619E-18 W4 = .10800E-18 W6 = .79800E-19 ($cm^2$)

| I | GJ | ENEXPT | U2SQR | U4SQR | U6SQR | FEXPX6 | FCALX6 | DELTA |
|---|---|---|---|---|---|---|---|---|
| 1 | 7.50 | 5984.0 | .09230 | .03660 | .64100 | 5.6800 | 5.9243 | -.2443 |
| 2 | 7.50 | 7899.0 | .93870 | .82920 | .20480 | 43.0000 | 42.9678 | .0322 |
| 3 | 7.50 | 9191.0 | .00000 | .57360 | .72130 | 11.1000 | 11.1864 | -.0864 |
| 4 | 7.50 | 11160.0 | .00000 | .13600 | .71460 | 8.1700 | 8.1506 | .0194 |
| 5 | 7.50 | 12500.0 | .00000 | .00000 | .34520 | 4.5700 | 3.5068 | 1.0632 |
| 6 | 7.50 | 13333.0 | .00000 | .00000 | .06100 | .8600 | .6610 | .1990 |
| 7 | 7.50 | 22173.0 | .00730 | .00030 | .06540 | 1.7500 | 1.9378 | -.1878 |
| 8 | 7.50 | 23529.0 | .00040 | .01450 | .00030 | .2960 | .4247 | -.1287 |
| 9 | 7.50 | 25906.0 | .00000 | .07680 | .02630 | 3.8700 | 2.7420 | 1.1280 |

NO.OF EQU.(M) = 9 DELSQSU = 2.56271 RMS = .534

# J-O calculating process

$$f_{exp} = 4.318 \times 10^{-9} \cdot \frac{\hat{x} y_{cal} A}{ct}$$

$$\boxed{\text{Absorption spectrum}} \longrightarrow \boxed{f_{exp}} \xrightarrow{\text{1st Software: JO}} \boxed{\begin{matrix}\Omega_{2,4,6}\\ f_{cal}\end{matrix}}$$

$$\boxed{\begin{matrix}\Omega_{2,4,6}\\ f_{cal}\end{matrix}} \xrightarrow{\text{2st Software: DyRP}} \boxed{\begin{matrix}S_{ED,MD}\\ \beta_{R\_cal}\\ A_R\\ \tau_R\end{matrix}}$$

# $2^{st}$ Software: DyRP

## 1.1. Go into DyRP.dat (by notepad) for set parameter

| Transition | Wavenumber ($\upsilon = 1/\lambda$, $cm^{-1}$) | Oscillator Strength $f_{exp}$*10^-6 |
|---|---|---|
| $^4F_{7/2}$ | 25906.74 | 3.87E-06 |
| $^4G_{11/2}$ | 23529.41 | 2.96E-07 |
| $^4I_{15/2}$ | 22172.95 | 1.75E-06 |
| $^6F_{3/2}$ | 13333.33 | 8.6E-07 |
| $^6F_{5/2}$ | 12500.00 | 4.57E-06 |
| $^6F_{7/2}$ | 11160.71 | 8.17E-06 |
| $^6F_{9/2}$ | 9191.18 | 1.11E-05 |
| $^6F_{11/2}$ | 7898.89 | 4.3E-05 |
| $^6H_{11/2}$ | 5984.44 | 5.68E-06 |

$\Omega_2$, $\Omega_4$, $\Omega_6$ (x$10^{-22}$)

Refractive index

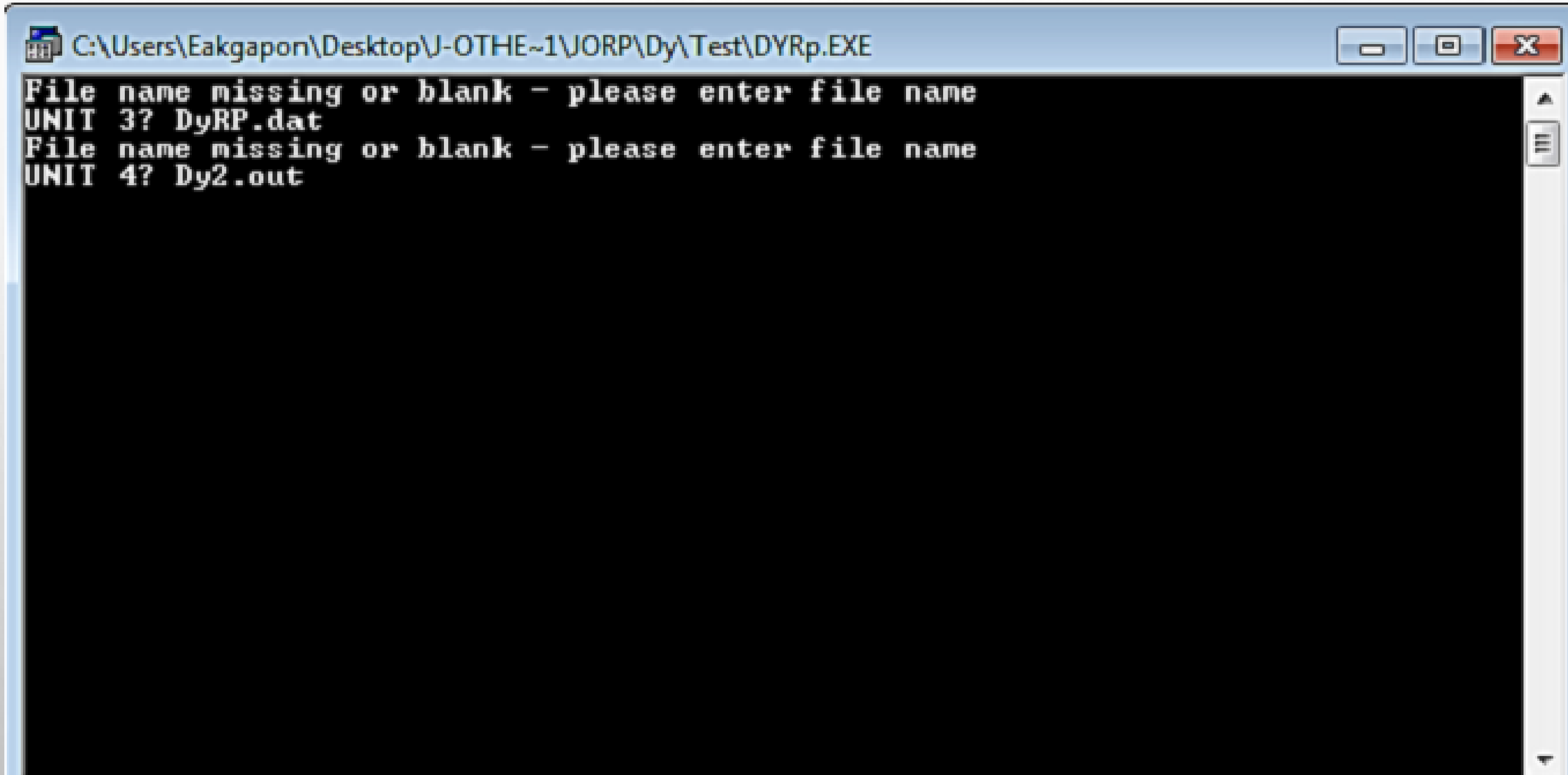
DyRP - Notepad

File Edit Format View Help

```
4561.9,1080.0,798.0,1.650
26455,25907,25858,25840,25199,23529,22172,21142,13891,13333
12500,11161,10282,9219,9191,7898,7784,5984,3665,0
0.0,0.00042823,0.0
0.0,0.000021043,0.0002703
0.00651783,0.000807,0.0004203
0.0002118,0.00430762,0.0031676
0.00000354,0.00370896,0.00123109
0.0008562,0.00815237,0.0071580
0.00078624,0.0057323,0.0005259
0.0023066,0.0024272,0.0033848
0.00345900,0.00337769,0.0026597
0.0096466,0.00188719,0.0034771
0.0511916,0.0172161,0.0572554
```

modify just υ that relate with you data and leave the rest

# 1.2. Run DyRP.exe resulting to DOS windows



# 1.3. Analyze Dy2.out file

Find transition from excited state that you want

BR : calculated Branching ratio
A : radiative transition possibility
SMDXE+22 : line strength of MD
SEDXE+22 : line strength of ED
Life of 4G5/2 : $\tau_R$

DY2 - Notepad

File Edit Format View Help

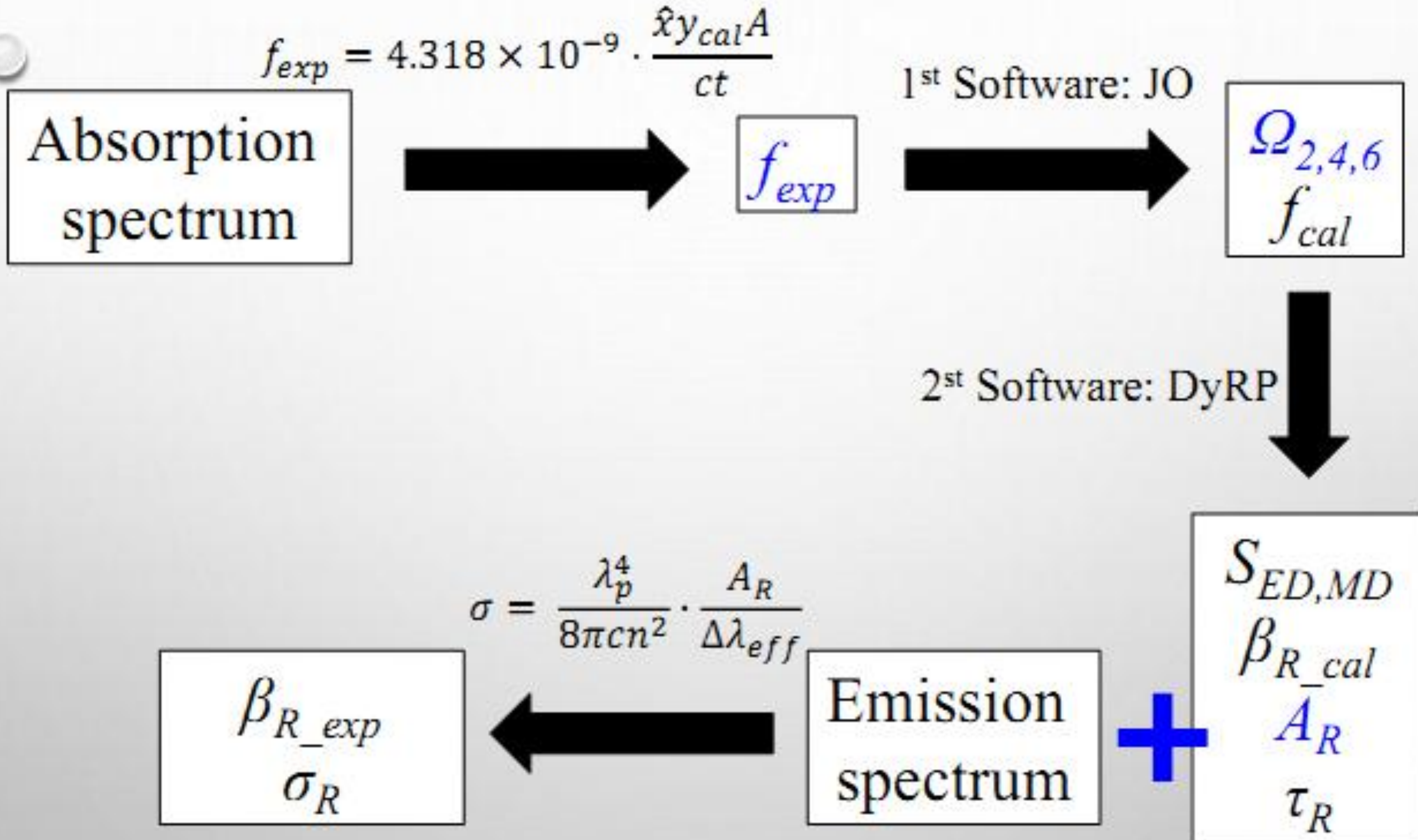
I;ENEDIF;U2SQ;U4SQ;U6SQ;SEDXE+22;SMDXE+22;A;BR;SI

TRANSITIONS FROM 4F9/2 LEVEL

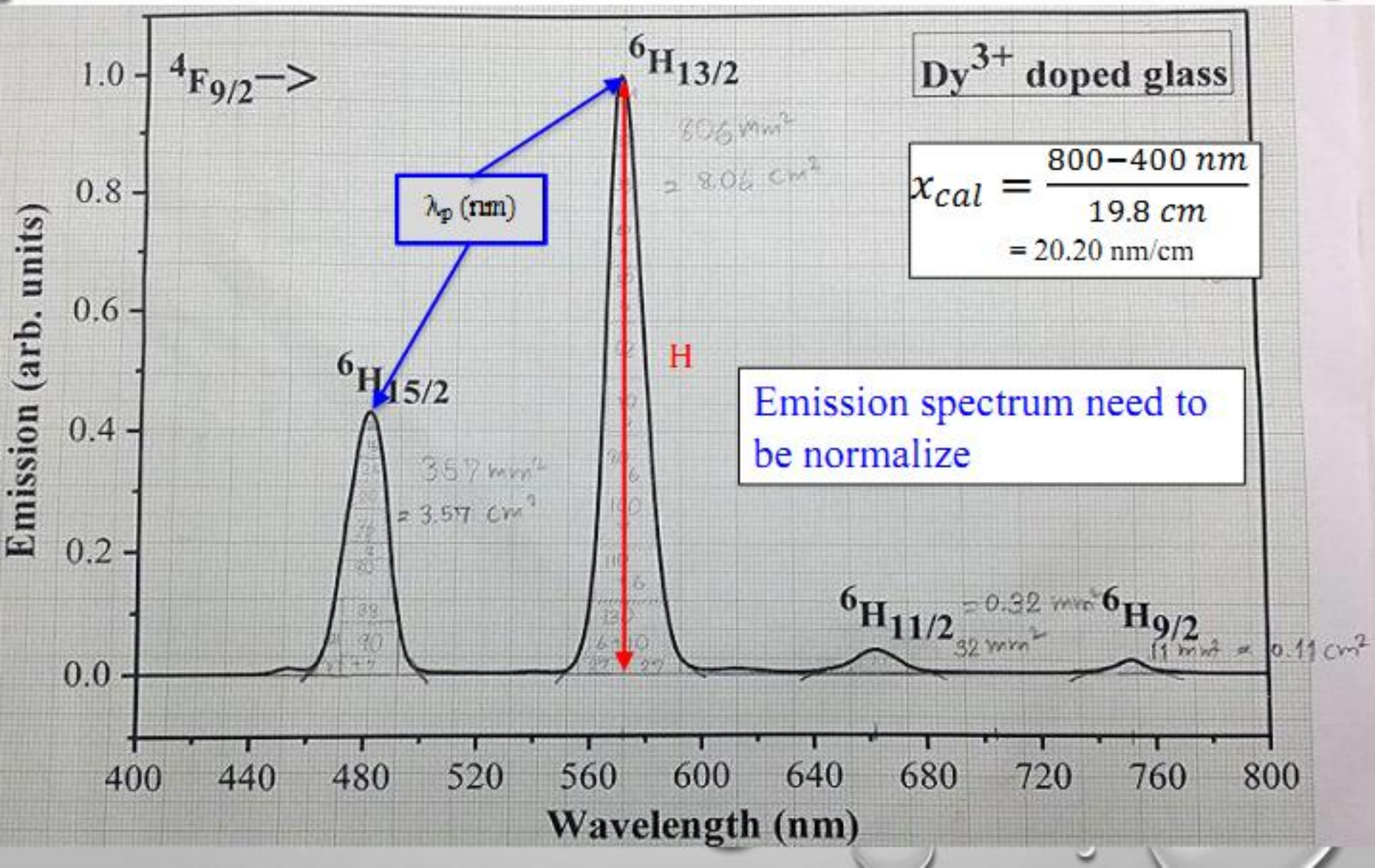
| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 9 | 7251.0 | .0000 | .0004 | .0000 | .462 | .000 | .52 | .0001 | .005 |
| 10 | 7809.0 | .0000 | .0000 | .0003 | .238 | .000 | .34 | .0001 | .003 |
| 11 | 8642.0 | .0065 | .0008 | .0004 | 30.941 | .000 | 59.10 | .0089 | .386 |
| 12 | 9981.0 | .0002 | .0043 | .0032 | 8.146 | 1.930 | 30.21 | .0046 | .148 |
| 13 | 10860.0 | .0000 | .0037 | .0012 | 5.004 | .000 | 18.97 | .0029 | .078 |
| 14 | 11923.0 | .0009 | .0082 | .0072 | 18.423 | .656 | 96.03 | .0145 | .329 |
| 15 | 11951.0 | .0008 | .0057 | .0005 | 10.197 | 1.139 | 57.84 | .0087 | .197 |
| 16 | 13244.0 | .0023 | .0024 | .0034 | 15.845 | .434 | 112.22 | .0169 | .312 |
| 17 | 13358.0 | .0035 | .0034 | .0027 | 21.550 | 7.582 | 210.79 | .0318 | .576 |
| 18 | 15158.0 | .0096 | .0019 | .0035 | 48.820 | 1.157 | 516.34 | .0778 | 1.095 |
| 19 | 17477.0 | .0512 | .0172 | .0573 | 297.814 | .000 | 4705.40 | .7094 | 7.507 |
| 20 | 21142.0 | .0000 | .0049 | .0303 | 29.506 | .000 | 825.27 | .1244 | .900 |

ATOT OF 4F9 = 6633.04 LIFE OF 4F9 = 150

# J-O calculating process



# Emission spectrum Analysis



| Transition $^4F_{5/2} \rightarrow$ | $\lambda_p$ (nm) | $\upsilon = 1/\lambda$ | Peak area (A) | Height of Peak (H) | $\Delta l = A/H$ | $\Delta\lambda_{eff} = \Delta l \cdot x_{cal}$ | $A_R$ from J-O | $\sigma_e$ | $\beta_R$ | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | ($cm^{-1}$) | ($cm^2$) | (cm) | (cm) | (nm) | ($s^{-1}$) | ($cm^2$) | Exp = PA/TA | Cal from J-O |
| $^6H_{15/2}$ | 479 | 20876.83 | 3.57 | 4.20 | 0.8500 | 17.1700 | 825.27 | 1.3109E-21 | 0.2960 | 0.1244 |
| $^6H_{13/2}$ | 572 | 17482.52 | 8.06 | 10.80 | 0.7463 | 15.0752 | 4705.4 | 1.7311E-20 | 0.6683 | 0.7094 |
| $^6H_{11/2}$ | 661 | 15128.59 | 0.32 | 0.40 | 0.8000 | 16.1600 | 516.34 | 3.1601E-21 | 0.0265 | 0.0778 |
| $^6H_{9/2}$ | 753 | 13280.21 | 0.11 | 0.30 | 0.3667 | 7.4067 | 210.79 | 4.7403E-21 | 0.0091 | 0.0169 |

```
I;ENEDIF;U2SQ;U4SQ;U6SQ;SEDXE+22;SMDXE+22;A;BR;SI

 TRANSITIONS FROM 4F9/2 LEVEL

9   7251.0 .0000 .0004 .0000    .462   .000     .52  .0001    .005
10  7809.0 .0000 .0000 .0003    .238   .000     .34  .0001    .003
17 13358.0 .0035 .0034 .0027  21.550  7.582  210.79  .0318    .576
18 15158.0 .0096 .0019 .0035  48.820  1.157  516.34  .0778   1.095
19 17477.0 .0512 .0172 .0573 297.814   .000 4705.40  .7094   7.507
20 21142.0 .0000 .0049 .0303  29.506   .000  825.27  .1244    .900

ATOT OF 4F9 =   6633.04  LIFE OF 4F9 =  150
```

$$\sigma = \frac{\lambda_p^4}{8\pi c n^2} \cdot \frac{A_R}{\Delta\lambda_{eff}}$$

$$\eta = \frac{\tau_{exp}}{\tau_R}$$

All unit: nm → cm

# Next week

**Course Outline:**

**Week 14:** Inokuti Hirayama (IH) Model

- *Case studies from international publications*