Optical spectroscopy in materials science 9. Symmetry and selection rules in vibrational spectroscopy

Kamarás Katalin
MTA Wigner FK
kamaras.katalin@wigner.mta.hu

Vibrational degrees of freedom

For a molecule with N atoms: 3N – 6 (3N- 3 translations– 3 rotations)
For linear molecules: 3N – 5 (rotation around axis does not cause atomic displacement)

Selection rules:

IR $\frac{\partial \mu}{\partial Q} \neq 0$ Raman $\frac{\partial \alpha}{\partial Q} \neq 0$

Q normal coordinate, also for more complicated vibrations

Example: CS_2

normal vibrations

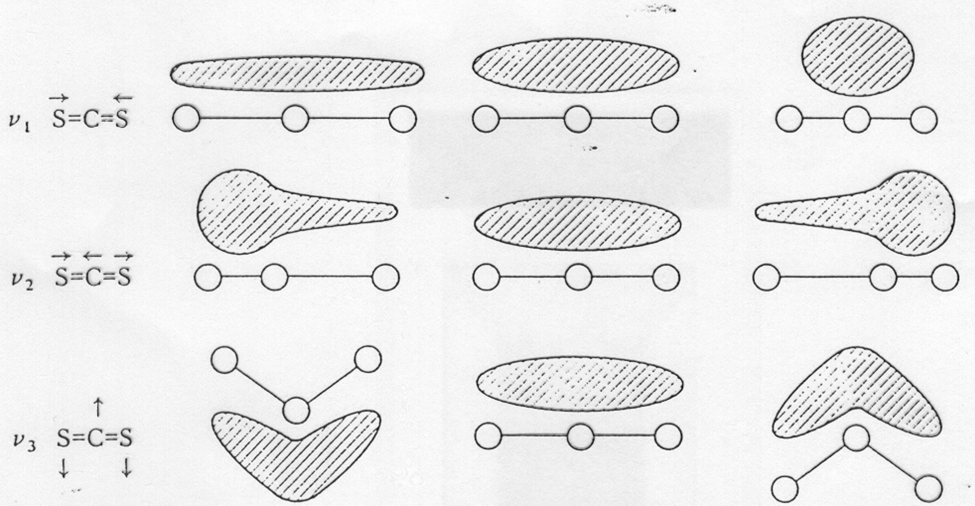


Fig. 5.2 Vibrations of carbon disulfide and accompanying changes in polarizability. Bending vibration ν_3 is degenerate, the other ν_4 being perpendicular to the paper plane.

symmetric stretch

asymmetric stretch

bend

Basic concepts - symmetry

Symmetry operations:

- identity
- rotations
- reflections

Symmetry point group: *all* symmetry operations which leave at least one point in the object fixed

Symmetry elements and operations: (Schoenflies' notation)

- C_n^m axis of rotation: rotation by $2\pi/n$ m times
- σ: mirror plane
  - σ_v: vertical
  - σ_h: horizontal
  - σ_d: diagonal (vertical, bisects two C_2 axes perpendicular to principal axis)
- S_n^m : improper rotation (C_n^m , then σ_h) rotation-reflection
- *i*: inversion center

Basic concepts - groups

Symmetry operations form a group

Group multiplication: subsequent application of operations

Group:

$AB \in G$	closed
$A(BC) = (AB)C$	associative
$E \in G$	contains identity element
$A^{-1}A = E, A \in G, A^{-1} \in G$	contains inverse element

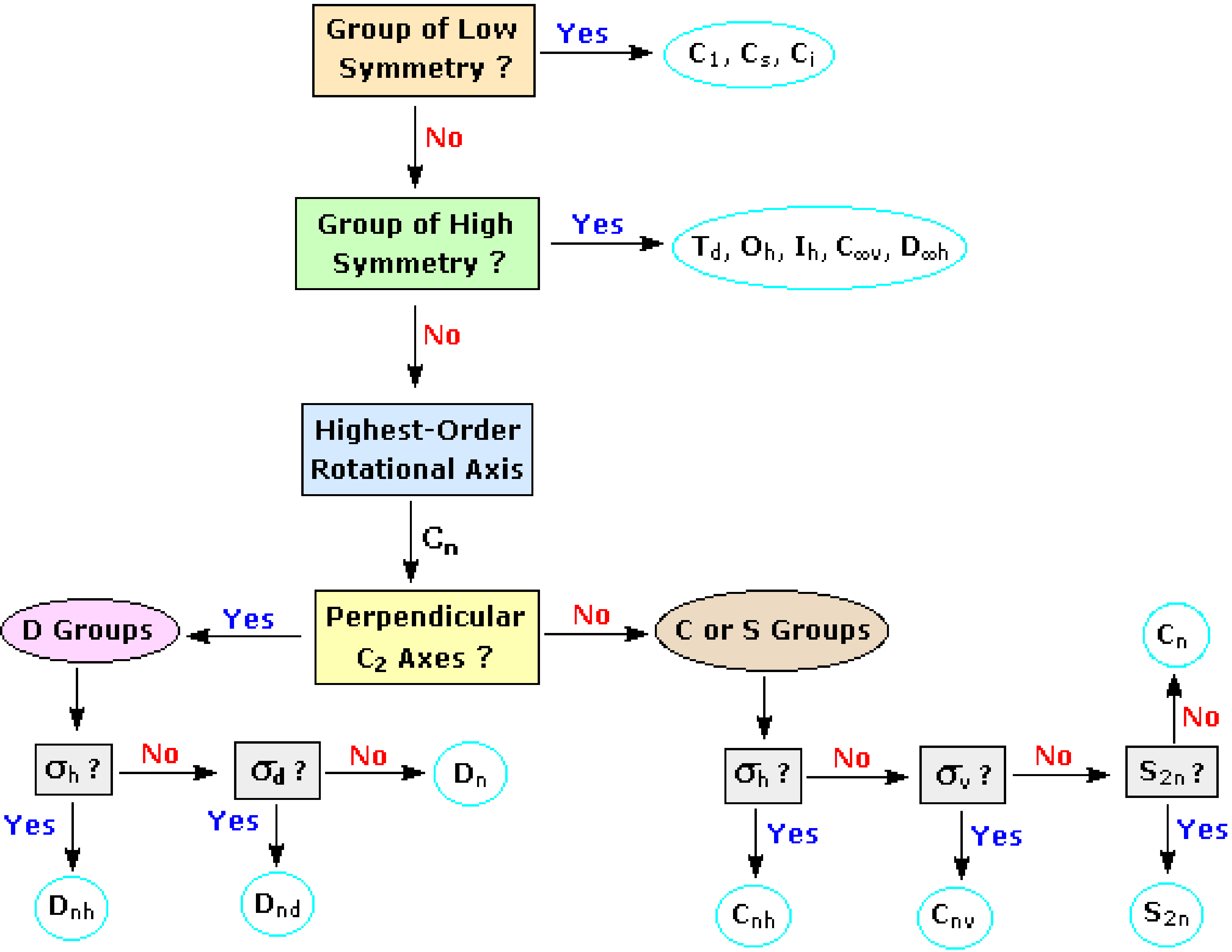
Crystallographic point groups

	notation	n	number
Rotation	C_n	1,2,3,4,6	5
$C_n + \sigma_h$	C_{nh}	1,2,3,4,6	5
$C_n + \sigma_v$	C_{nv}	2,3,4,6	4
$C_n + S_n$	S_n	2,4,6	3
$C_n + C_2'$	D_n	2,3,4,6	4
$C_{nh} + C_2'$	D_{nh}	2,3,4,6	4
$S_n + C_2'$	D_{nd}	2,3	2
Cubic	no principal axis	$4C_3$	5

For molecules: any n (5,7,10...)

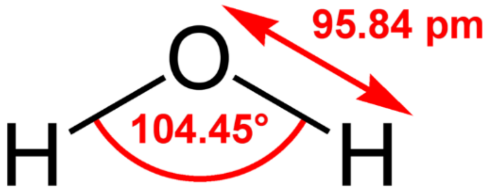
$C_{\infty v}$ (HCl), $D_{\infty h}$ (Cl_2), I_h (C_{60})

Point group determination

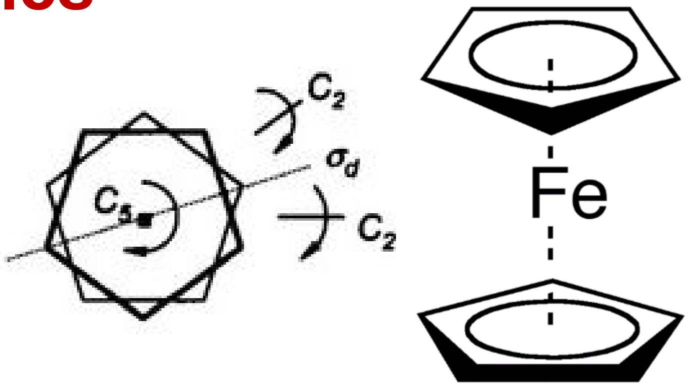


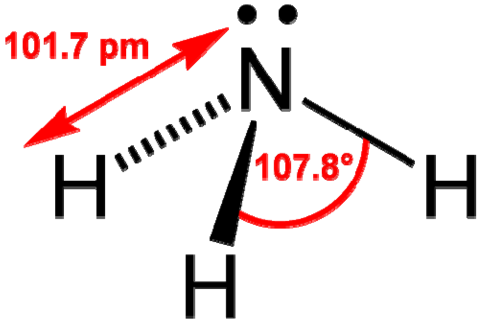
http://www.cem.msu.edu/~reusch/VirtualText/symmetry/symmtry.htm

Examples



Water
C_{2v}



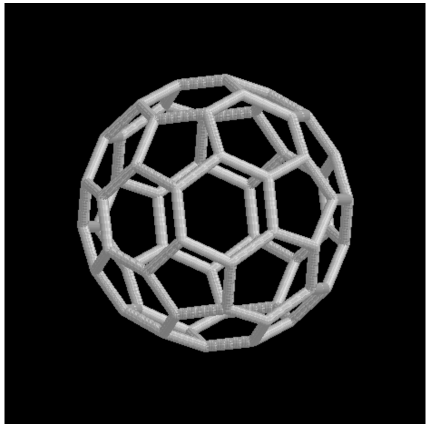


Ammonia
C_{3v}

Ferrocene
D_{5d}

Source: Wikipedia

Fullerene C_{60}
I_h



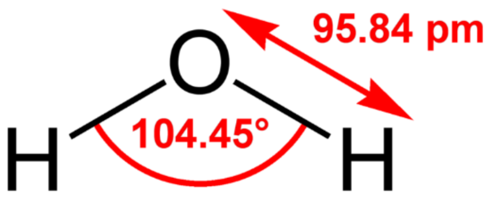
Multiplication tables

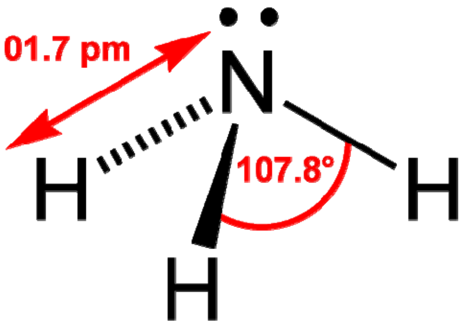
C_{2v}

C_{2v}	E	C_2	σ_v	σ_v'
E	E	C_2	σ_v	σ_v'
C_2	C_2	E	σ_v'	σ_v
σ_v	σ_v	σ_v'	E	C_2
σ_v'	σ_v'	σ_v	C_2	E

C_{3v}

C_{3v}	E	C_3	C_3^2	σ_v	σ_v'	σ_v''
E	E	C_3	C_3^2	σ_v	σ_v'	σ_v''
C_3	C_3	C_3^2	E	σ_v'	σ_v''	σ_v
C_3^2	C_3^2	E	C_3	σ_v''	σ_v	σ_v'
σ_v	σ_v	σ_v''	σ_v'	E	C_3^2	C_3
σ_v'	σ_v'	σ_v	σ_v''	C_3	E	C_3^2
σ_v''	σ_v''	σ_v'	σ_v	C_3^2	C_3	E





Representations

- Symmetry operations can be represented by matrices

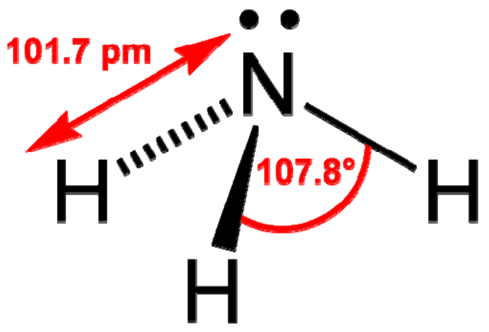
- The trace of the matrices (*the character*) is invariant with respect to similarity transformations

- *Reducible representation:* matrices attain *block format* on a suitably chosen basis

- *Irreducible representation:* cannot be simplified (reduced) further

- *Character table:* characters of irreducible representations (*irreps*) by symmetry operation for individual point groups

Representations - example: NH_3



Representation on Cartesian basis:

$$E=\begin{pmatrix}1&0&0\\0&1&0\\0&0&1\end{pmatrix} C_3=\begin{pmatrix}-\frac{1}{2}&-\frac{\sqrt{3}}{2}&0\\\frac{\sqrt{3}}{2}&-\frac{1}{2}&0\\0&0&1\end{pmatrix} C_3^2=\begin{pmatrix}-\frac{1}{2}&\frac{\sqrt{3}}{2}&0\\-\frac{\sqrt{3}}{2}&-\frac{1}{2}&0\\0&0&1\end{pmatrix}$$

$$\sigma_v'=\begin{pmatrix}1&0&0\\0&-1&0\\0&0&1\end{pmatrix} \sigma_v''=\begin{pmatrix}-\frac{1}{2}&-\frac{\sqrt{3}}{2}&0\\-\frac{\sqrt{3}}{2}&\frac{1}{2}&0\\0&0&1\end{pmatrix} \sigma_v'''=\begin{pmatrix}-\frac{1}{2}&\frac{\sqrt{3}}{2}&0\\\frac{\sqrt{3}}{2}&\frac{1}{2}&0\\0&0&1\end{pmatrix}$$

Representation on r_1, r_2, r_3 basis:

$$E=\begin{pmatrix}1&0&0\\0&1&0\\0&0&1\end{pmatrix} C_3=\begin{pmatrix}0&0&1\\1&0&0\\0&1&0\end{pmatrix} C_3^2=\begin{pmatrix}0&1&0\\0&0&1\\1&0&0\end{pmatrix}$$

$$\sigma_v'=\begin{pmatrix}1&0&0\\0&0&1\\0&1&0\end{pmatrix} \sigma_v''=\begin{pmatrix}0&0&1\\0&1&0\\1&0&0\end{pmatrix} \sigma_v'''=\begin{pmatrix}0&1&0\\1&0&0\\0&0&1\end{pmatrix}$$

Character table:

C_{3v}	E	$2C_3$	$3\sigma_v$
Γ_1	1	1	1
Γ_2	1	1	-1
Γ_3	2	-1	0

Great Orthogonality Theorem (GOT)
(Fundamentális ortogonalitási tétel (FOT))

$$\sum_R \Gamma_i(R)^*_{mn}\Gamma_j(R)_{op} = \frac{h}{l_i}\delta_{ij}\delta_{mo}\delta_{np}$$

where:

Γ_i, Γ_j are two non-equivalent irreducible representations

h is the order of the group (number of elements)

l_i is the dimension of the matrices

These relations for the characters follow from the GOT: $(\chi_R = \sum_k \Gamma_i(R)_{kk}):$

$$\sum_R \chi_i(R)^* \chi_j(R) = h\delta_{ij}$$

$$\sum_i l_i^2 = h$$

Reduction

Reduction of reducible representations: $\chi(R) = \sum_i n_i \chi_i(R)$

$\chi(R)$ being the character of the reducible representation, n_i the coefficient of the *i*th irrep

$$n_j = \frac{1}{h} \sum_R \chi_j(R)^* \chi(R)$$

$$C_3 = \begin{pmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix} \longrightarrow C_3 = \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

(r_1, r_2, r_3) (x, y, z)

C_{3v}	E	$2C_3$	$3\sigma_v$
Γ_1	1	1	1
Γ_2	1	1	-1
Γ_3	2	-1	0
Γ	3	0	1

$$\Gamma = \Gamma_1 \oplus \Gamma_3$$

Vibrational modes

Vibrational Hamiltonian:

$$H_{vib} = \sum_i H_i = \frac{1}{2}(-\hbar^2 \frac{\partial}{\partial q_i^2}) + \omega_i q_i^2)$$

q_i normal coordinates → ω_i eigenfrequencies

$$V = \frac{1}{2}\sum_i \omega_i^2 q_i^2$$

Neumann principle: V and ω_i show the symmetry of the point group

- non-degenerate case: $V \sim q_i^2, \qquad Rq_i = \pm q_i$

•degenerate case: $V \sim (q_j^2 + q_k^2 + q_l^2) \qquad R\left|q_j, q_k, q_l\right| \Rightarrow \left|\pm q_j, \pm q_k, \pm q_l\right|$

The normal coordinates form bases of the irreps of the point group; the dimension of the representation equals the degeneracy

Selection rules

IR: $$\frac{\partial \mu}{\partial q} \neq 0$$

$\mu_x \sim x$, $\mu_y \sim y$, $\mu_z \sim z$ are always basis functions for an irrep of the point group

Since basis functions of inequivalent representations are orthogonal, this selection rule means:
those vibrations are IR active, whose normal coordinate belongs to the same irrep as one of the x,y,z coordinates

Raman: $$\frac{\partial \alpha}{\partial q} \neq 0$$

$\alpha_{xx} \sim x^2$, $\alpha_{xy} \sim xy$,...and the products of the coordinates are also always basis functions for an irrep of the point group, this selection rule means:
those vibrations are Raman active whose normal coordinate belongs to the same irrep as one of the binary products of the x,y,z coordinates

Notation of irreps

A, B	1-dimensional
E	2-dimensional
T (F)	3-dimensional
G	4-dimensional
H	5-dimensional

In point groups containing inversion:

Subscript g (gerade = even) or u (ungerade = odd)

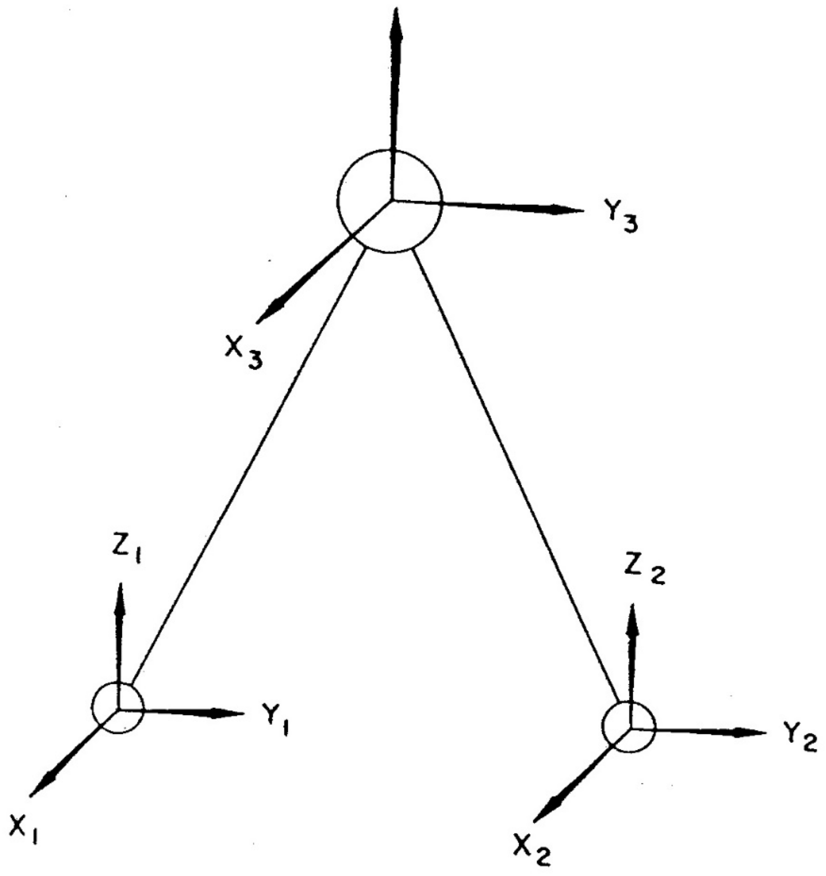
refers to the character of *i* in the given irrep:

$\chi(i) > 0 \ \mathbf{g}, \ \chi(i) < 0 \ \mathbf{u}$

number in subscript is just a “serial number”

"Counting" of vibrational modes

H_2O



C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v(yz)$	
A_1	1	1	1	1	z, x^2, y^2, z^2
A_2	1	1	-1	-1	R_x, xy
B_1	1	-1	1	-1	x, R_x, xz
B_2	1	-1	-1	1	y, R_z, yz

Representation on a 3N-dimensional basis

$$C_2\begin{pmatrix} x_1 \\ y_1 \\ z_1 \\ x_2 \\ y_2 \\ z_2 \\ x_3 \\ y_3 \\ z_3 \end{pmatrix} = \begin{pmatrix} 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix}\begin{pmatrix} x_1 \\ y_1 \\ z_1 \\ x_2 \\ y_2 \\ z_2 \\ x_3 \\ y_3 \\ z_3 \end{pmatrix}$$

$$\sigma_v(yz)\begin{pmatrix} x_1 \\ y_1 \\ z_1 \\ x_2 \\ y_2 \\ z_2 \\ x_3 \\ y_3 \\ z_3 \end{pmatrix} = \begin{pmatrix} -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix}\begin{pmatrix} x_1 \\ y_1 \\ z_1 \\ x_2 \\ y_2 \\ z_2 \\ x_3 \\ y_3 \\ z_3 \end{pmatrix}$$

Character contributions of atoms situated on symmetry elements

R	$\chi(R)$	R	$\chi(R)$
C_n^k	$1+2\cos(2\pi k/n)$	S_n^k	$-1+2\cos(2\pi k/n)$
$E=C_1^k$	3	$\sigma=S_1^1$	1
C_2^1	-1	$i=S_2^1$	-3
C_3^1, C_3^2	0	S_3^1, S_3^5	-2
C_4^1, C_4^3	1	S_4^1, S_4^3	-1
C_6^1, C_6^5	2	S_6^1, S_6^5	0

Reduction

$$n_j = \frac{1}{h}\sum_R \chi_j(R)^* \chi(R)$$

For water, $\chi_r(E) = 9$, $\chi_r(C_2) = -1$, $\chi_r(\sigma_{xz}) = 1$, $\chi_r(\sigma_{yz}) = 3$.
Applying the reduction formula and using the character table:

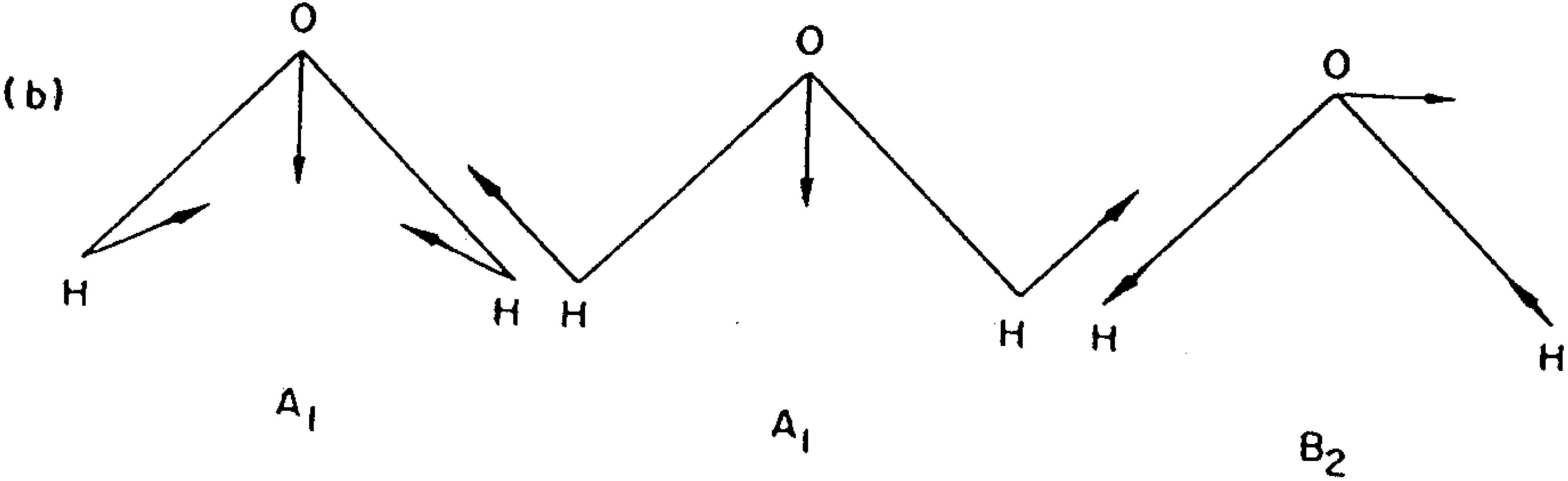
$n(A_1) = 3$, $n(A_2) = 1$, $n(B_1) = 2$, $n(B_2) = 3$

C_{2v}	**E**	**C_2**	**$\sigma_v(xz)$**	**$\sigma_v(yz)$**	
A_1	1	1	1	1	z, x^2, y^2, z^2
A_2	1	1	-1	-1	R_z, xy
B_1	1	-1	1	-1	x, R_y, xz
B_2	1	-1	-1	1	y, R_x, yz

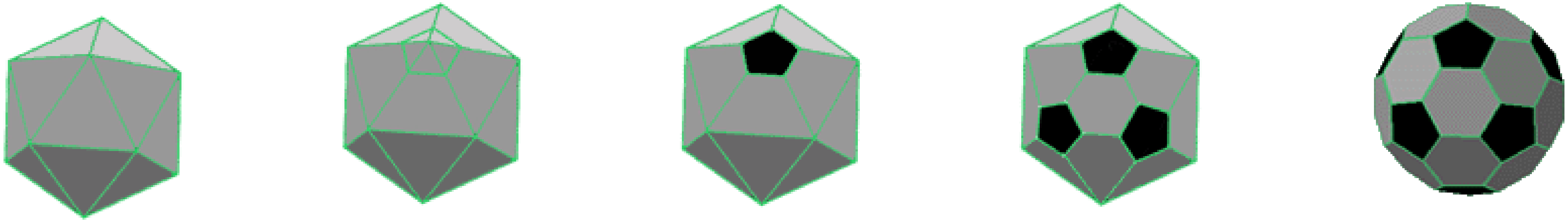
	E	C_2	$\sigma_v(xz)$	$\sigma_v(yz)$
n	3	1	1	3
Γ	9	-1	1	3

Vibrational modes: $\Gamma = 2A_1 \oplus B_2$

Normal vibrations of the water molecule

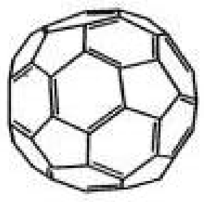


C_{60}, the truncated icosahedron



http://www.seed.slb.com/en/scictr/watch/fullerenes2/saved.htm

Vibrational modes of C_{60}



C_{60}

Character table:

I_h	E	$12C_5$	$12C_5^2$	$20C_3$	$15C_2$	i	$12S_{10}$	$12S_{10}^3$	$20S_6$	$15\sigma_d$	
A_g	1	1	1	1	1	1	1	1	1	1	Raman
A_u	1	1	1	1	1	-1	-1	-1	-1	-1	
F_{1g}	3	$\frac{(1+\sqrt{5})}{2}$	$\frac{(1-\sqrt{5})}{2}$	0	-1	3	$\frac{(1-\sqrt{5})}{2}$	$\frac{(1+\sqrt{5})}{2}$	0	-1	rot
F_{1u}	3	$\frac{(1+\sqrt{5})}{2}$	$\frac{(1-\sqrt{5})}{2}$	0	-1	-3	$-\frac{(1-\sqrt{5})}{2}$	$-\frac{(1+\sqrt{5})}{2}$	0	1	IR
F_{2g}	3	$\frac{(1-\sqrt{5})}{2}$	$\frac{(1+\sqrt{5})}{2}$	0	-1	3	$\frac{(1+\sqrt{5})}{2}$	$\frac{(1-\sqrt{5})}{2}$	0	-1	
F_{2u}	3	$\frac{(1-\sqrt{5})}{2}$	$\frac{(1+\sqrt{5})}{2}$	0	-1	-3	$-\frac{(1+\sqrt{5})}{2}$	$-\frac{(1-\sqrt{5})}{2}$	0	1	
G_{1g}	4	-1	-1	1	0	4	-1	-1	1	0	
G_{1u}	4	-1	-1	1	0	-4	1	1	-1	0	
H_g	5	0	0	-1	1	5	0	0	-1	1	Raman
H_u	5	0	0	-1	1	-5	0	0	1	-1	

Characters and reduction of 3N dimensional representation

Counting of C_{60} vibrational modes:

Characters of representation defined by Cartesian unit vectors on atoms:

I_h	E	$12C_5$	$12C_5^2$	$20C_3$	$15C_2$	i	$12S_{10}$	$12S_{10}^3$	$20S_6$	$15\sigma_d$
$\chi_\Gamma(R)$	180	0	0	0	0	0	0	0	0	4

From here, using the reduction formula, we get for the A_g mode:

$n(A_g) = 1/120(1*180) – 12(1*0) +12(1*0)+20(1*0)+15(1*0)+1*0+12(1*0)+20(1*0)+15(1*4) = 2$

The final result of the reduction is:

$$\Gamma = 2A_g \oplus 4T_{1g} \oplus 4T_{2g} \oplus 6G_g \oplus 8H_g \oplus 1A_u \oplus 5T_{1u} \oplus 5T_{2u} \oplus 6G_u \oplus 7H_u$$

Estimation of the number of vibrations

IR $\frac{\partial \mu}{\partial Q} \neq 0$ Raman $\frac{\partial \alpha}{\partial Q} \neq 0$

3N – 6 degrees of freedom

↓

degeneration

↓

selection rules → IR / Raman / silent

Principle of mutual exclusion:
if the molecule possesses an inversion center, IR-active modes are not Raman active and vice versa

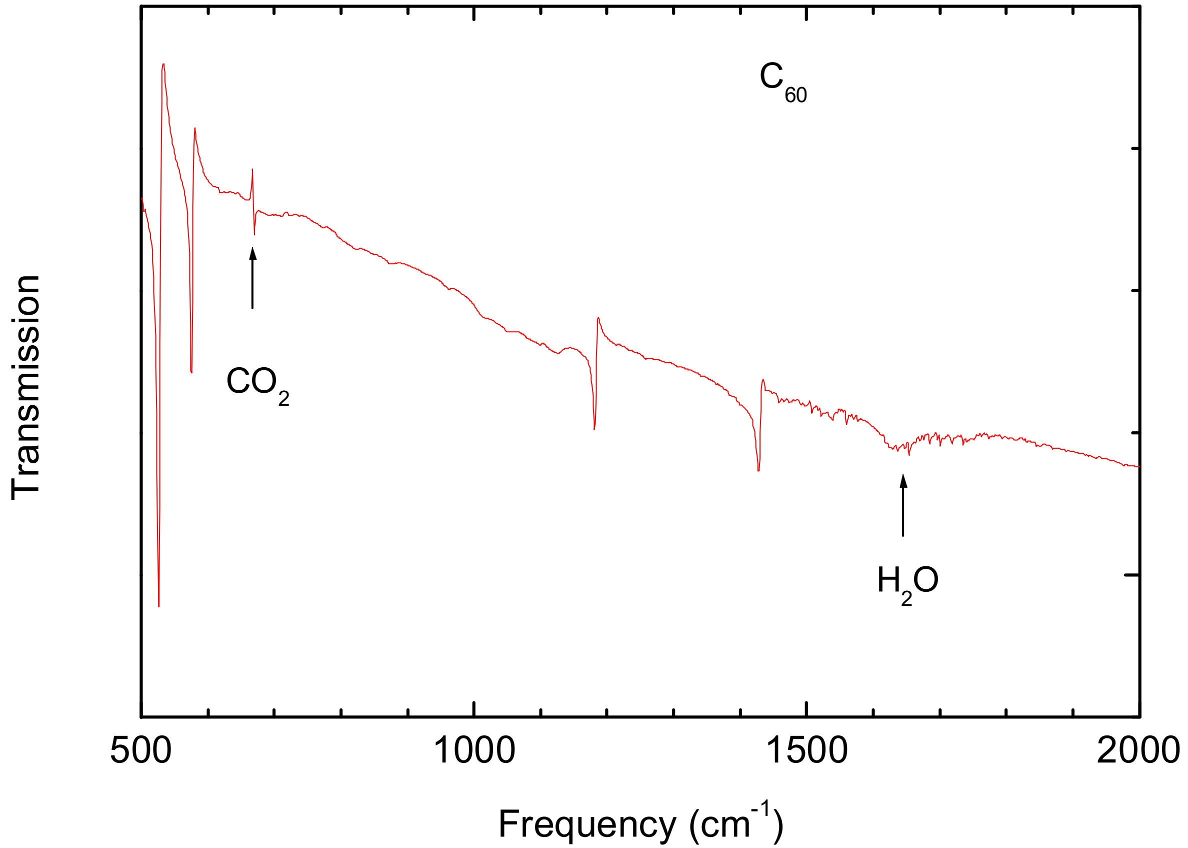
i: $\mu \rightarrow -\mu$ (u)

$\alpha \rightarrow \alpha$ (g)

odd *(ungerade)* and even *(gerade)* modes are orthogonal

Symmetry analysis gives the maximum number of spectral lines
(it can decrease by incidental degeneration, intensity below detection threshold)

Infrared spectrum of C_{60}



Take-home message

- Point group: set of symmetry operations leaving at least one point in the object fixed
- Symmetry operations form a group in the mathematical sense
- Matrix representations – reducible, irreducible
- Starting from the molecular structure, using the character tables and the reduction formula, the number of vibrational modes can be predicted
- IR and Raman activity:

  symmetry analysis – selection rules – principle of mutual exclusion

Összefoglalás

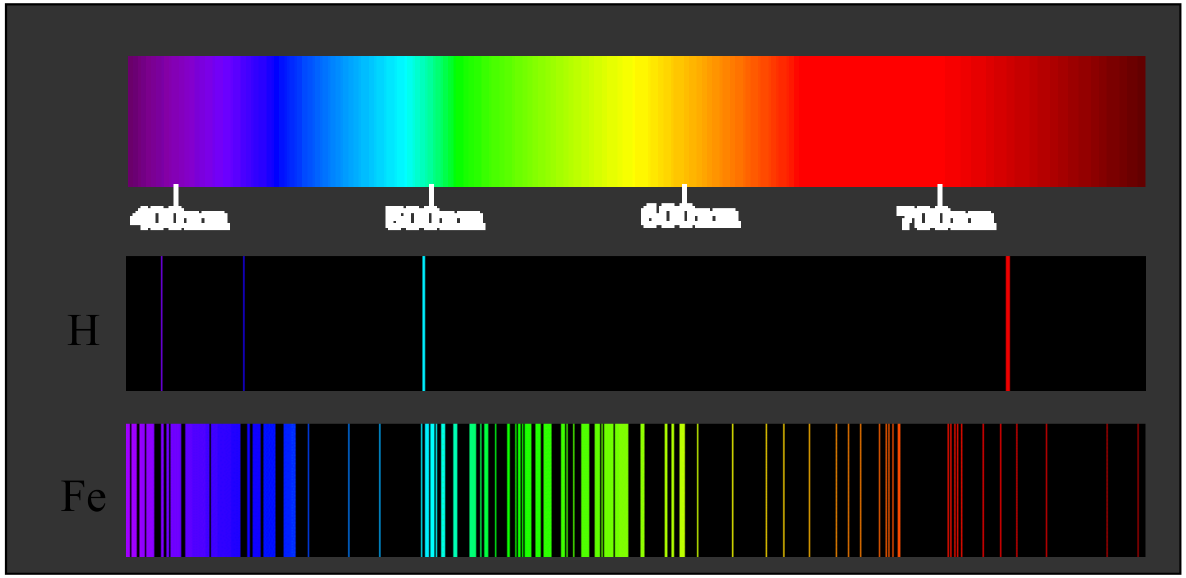
- Pontcsoport: azon szimmetriaműveletek halmaza, amik egy objektumban legalább egy pontot mozdulatlanul hagynak
- A szimmetriaműveletek matematikai értelemben csoportot alkotnak
- A szimmetriaműveletek mátrixokkal ábrázolhatók – reducibilis, irreducibilis
- A szerkezetből kiindulva, a karaktertáblák és a redukciós formula alkalmazásával a rezgési módusok száma meghatározható
- IR és Raman-aktív módusok:

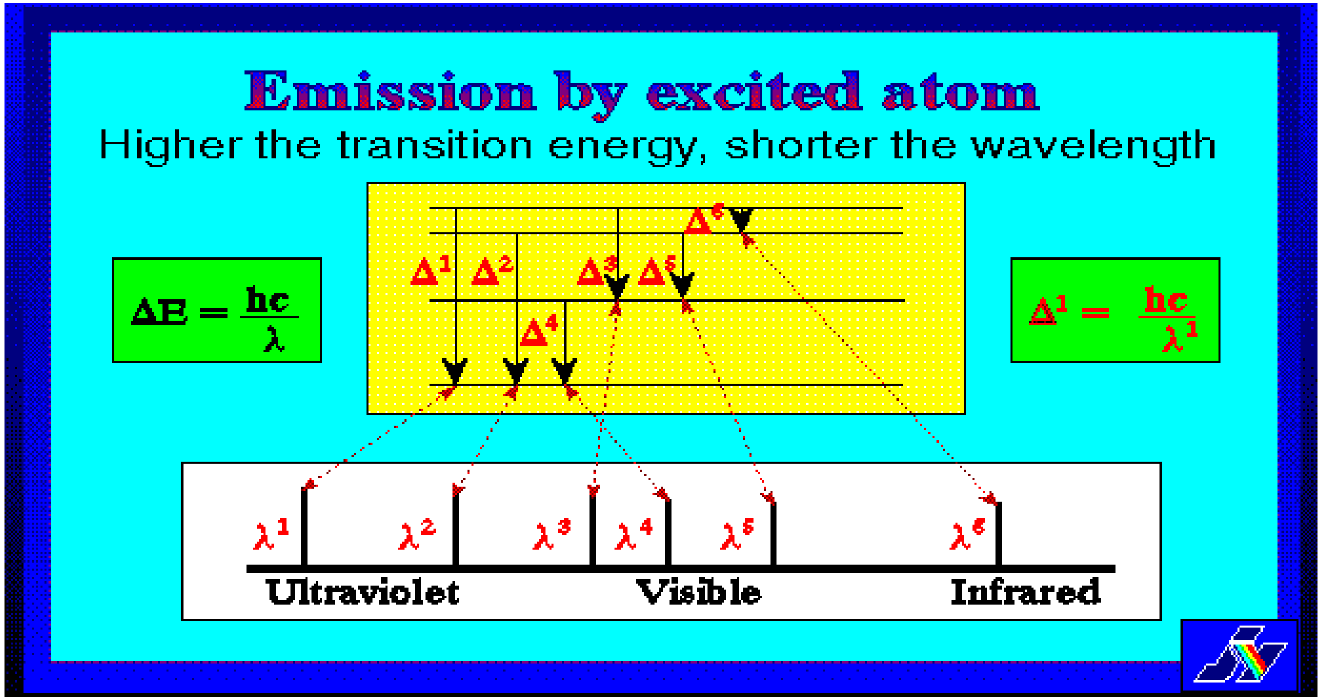
  szimmetria-analízis – kiválasztási szabályok – kölcsönös kizárás elve

Emission spectroscopy

- **Atomic emission spectroscopy (AES)**
  - Flame test
  - Flame emission photometry
  - Atomic absorption spectrophotometry
  - Inductively coupled plasma
- Molecular spectroscopy
  - IR emission spectroscopy
  - Luminescence

Emission spectroscopy





Emission by excited atom

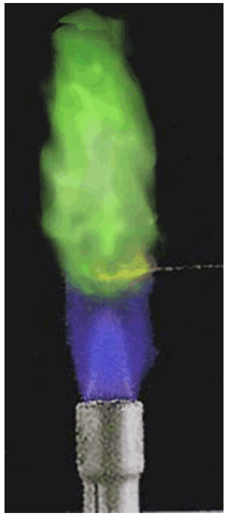
Higher the transition energy, shorter the wavelength

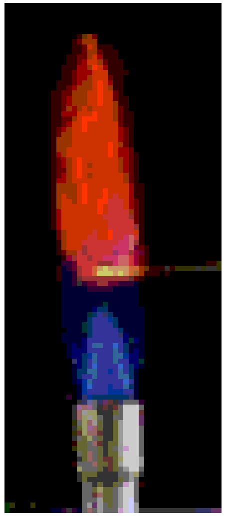
$$\Delta E = \frac{hc}{\lambda}$$

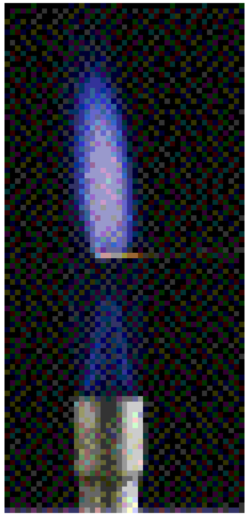
$$\Delta^1 = \frac{hc}{\lambda^1}$$

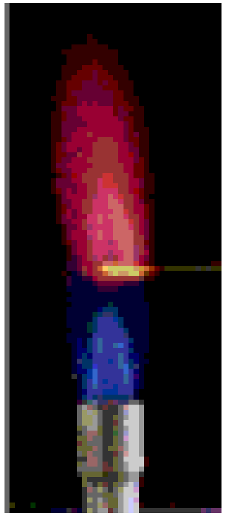
Atomic emission spectroscopy - Flame test

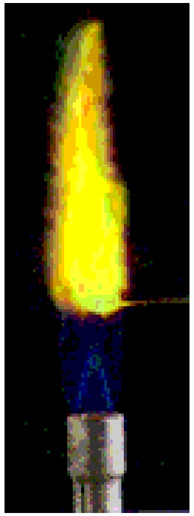
Walt Wolland, Bellevue Community College
http://www.800mainstreet.com/s/s.html


Ba


Ca


K


Li

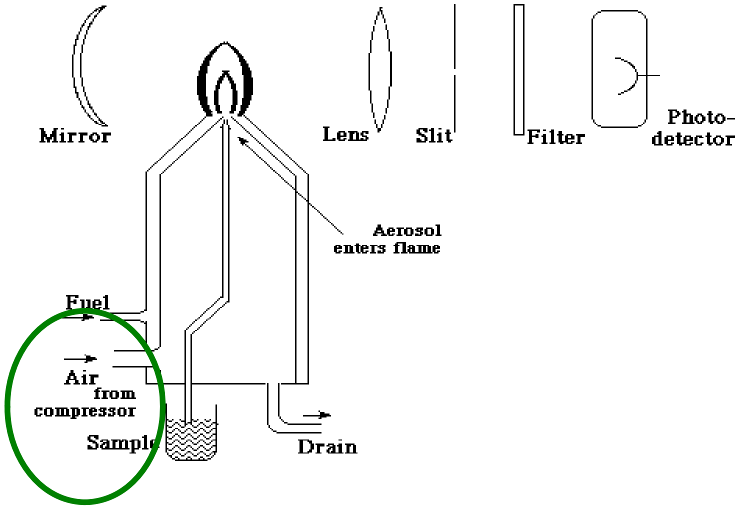

Na


Rb

Quantitative methods: flame photometry, atomic absorption spectroscopy (AAS)

Atomic emission spectroscopy

Flame Emission Photometry (FEP)

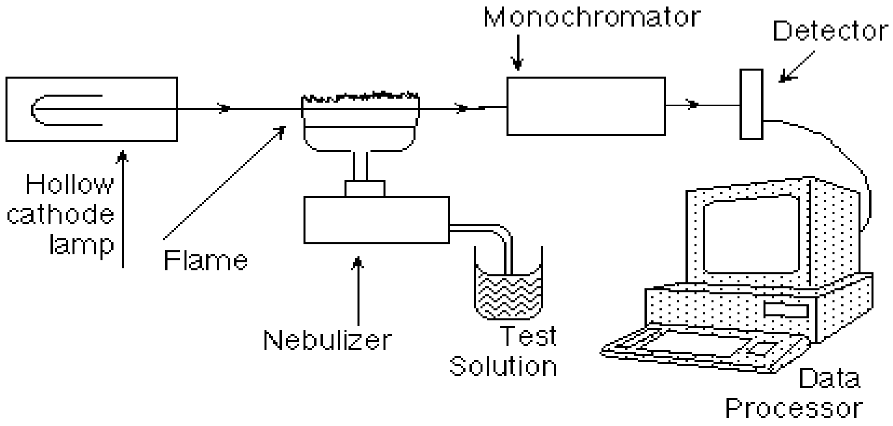


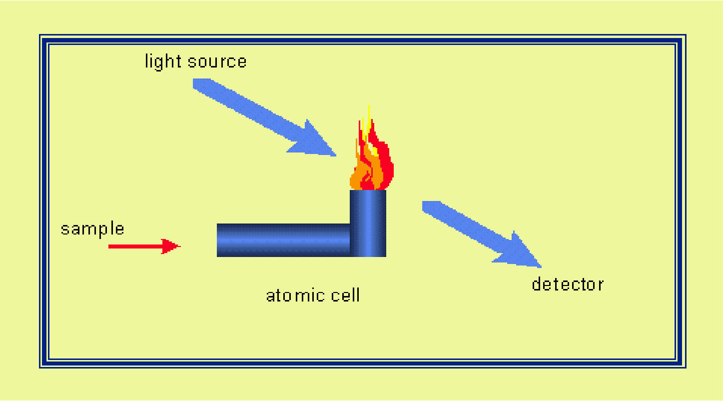
- **Excitation:** thermal energy of the flame
- **Flame:** - most frequent: acetylene and air

  - vaporization → homogeneous atomic cloud

  - excitation, but not ionization, of atoms
- **Vaporizer** → sample solution
- **Temperature:** 2000 – 3000 ˚C
- **Requirement**: constant composition, temperature and structure of the flame

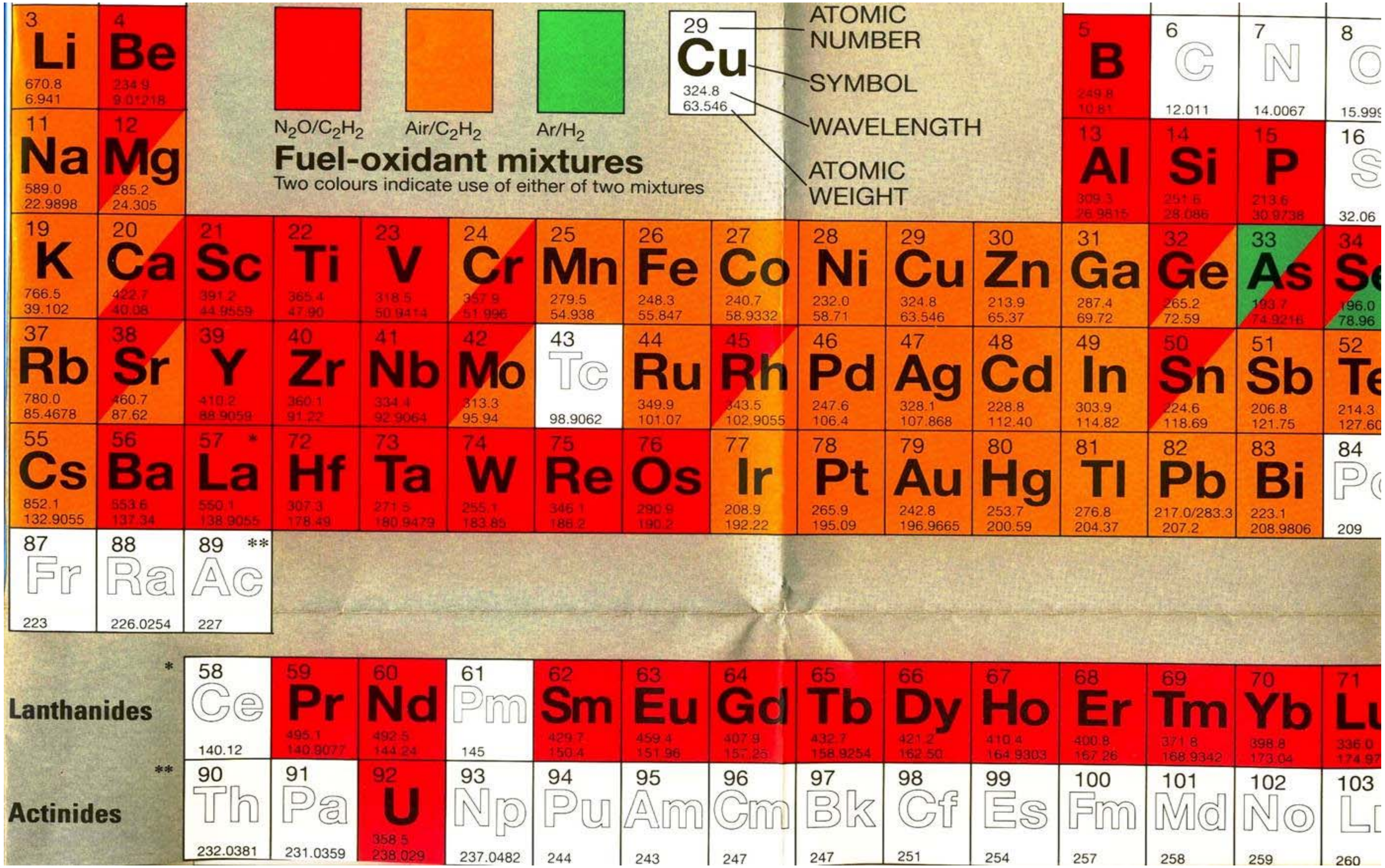
Atomic Absorption Spectroscopy (AAS)





http://www.cee.vt.edu/ewr/environmental/teach/smprimer/aa/aa.html
http://www.resonancepub.com/atomicspec.htm

Detectable elements



🟥 N_2O/C_2H_2

🟧 Air/C_2H_2

🟩 Ar/H_2

Fuel-oxidant mixtures

Two colours indicate use of either of two mixtures

29
Cu
324.8
63.546

ATOMIC NUMBER
SYMBOL
WAVELENGTH
ATOMIC WEIGHT

ATOMIC NUMBER	SYMBOL	WAVELENGTH	ATOMIC WEIGHT	
3	Li	670.8	6.941	🟧
4	Be	234.9	9.01218	🟥
5	B	249.8	10.81	🟥
6	C		12.011	
7	N		14.0067	
8	O		15.999	
11	Na	589.0	22.9898	🟧
12	Mg	285.2	24.305	🟥🟧
13	Al	309.3	26.9815	🟥
14	Si	251.6	28.086	🟥
15	P	213.6	30.9738	🟥
16	S		32.06	
19	K	766.5	39.102	🟧
20	Ca	422.7	40.08	🟧🟥
21	Sc	391.2	44.9559	🟥
22	Ti	365.4	47.90	🟥
23	V	318.5	50.9414	🟥
24	Cr	357.9	51.996	🟧🟥
25	Mn	279.5	54.938	🟧
26	Fe	248.3	55.847	🟧
27	Co	240.7	58.9332	🟧
28	Ni	232.0	58.71	🟧
29	Cu	324.8	63.546	🟧
30	Zn	213.9	65.37	🟧
31	Ga	287.4	69.72	🟧
32	Ge	265.2	72.59	🟥🟧
33	As	193.7	74.9216	🟩🟥
34	Se	196.0	78.96	🟥🟩
37	Rb	780.0	85.4678	🟧
38	Sr	460.7	87.62	🟥🟧
39	Y	410.2	88.9059	🟥
40	Zr	360.1	91.22	🟥
41	Nb	334.4	92.9064	🟥
42	Mo	313.3	95.94	🟥🟧
43	Tc		98.9062	
44	Ru	349.9	101.07	🟧
45	Rh	343.5	102.9055	🟥🟧
46	Pd	247.6	106.4	🟧
47	Ag	328.1	107.868	🟧
48	Cd	228.8	112.40	🟧
49	In	303.9	114.82	🟧
50	Sn	224.6	118.69	🟥🟧
51	Sb	206.8	121.75	🟧
52	Te	214.3	127.60	🟧
55	Cs	852.1	132.9055	🟧
56	Ba	553.6	137.34	🟥
57 *	La	550.1	138.9055	🟥
72	Hf	307.3	178.49	🟥
73	Ta	271.5	180.9479	🟥
74	W	255.1	183.85	🟥
75	Re	346.1	186.2	🟥
76	Os	290.9	190.2	🟥
77	Ir	208.9	192.22	🟧
78	Pt	265.9	195.09	🟧
79	Au	242.8	196.9665	🟧
80	Hg	253.7	200.59	🟧
81	Tl	276.8	204.37	🟧
82	Pb	217.0/283.3	207.2	🟧
83	Bi	223.1	208.9806	🟧
84	Po		209	
87	Fr		223	
88	Ra		226.0254	
89 **	Ac		227	

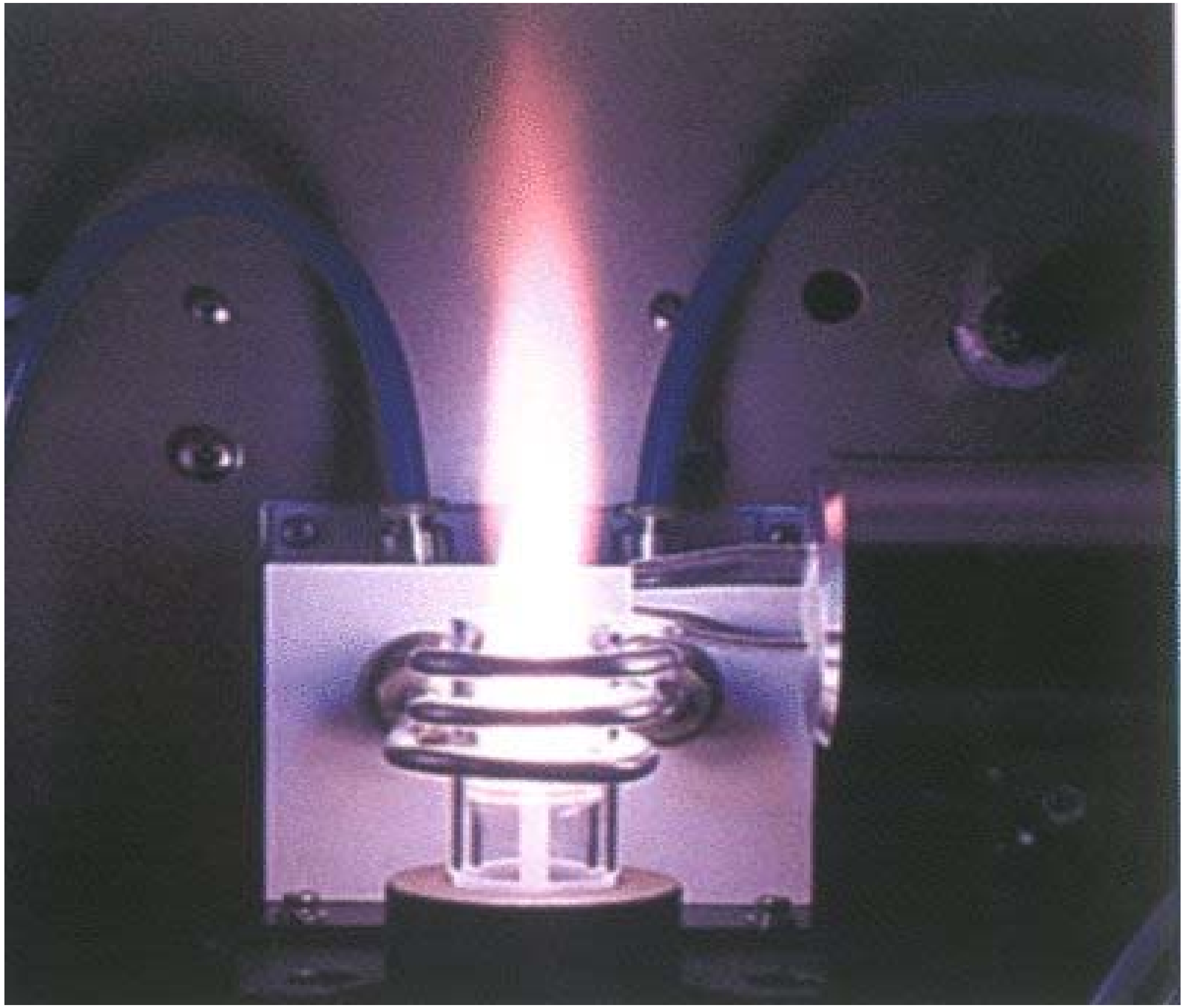
Lanthanides *

ATOMIC NUMBER	SYMBOL	WAVELENGTH	ATOMIC WEIGHT	
58	Ce		140.12	
59	Pr	495.1	140.9077	🟥
60	Nd	492.5	144.24	🟥
61	Pm		145	
62	Sm	429.7	150.4	🟥
63	Eu	459.4	151.96	🟥
64	Gd	407.9	157.25	🟥
65	Tb	432.7	158.9254	🟥
66	Dy	421.2	162.50	🟥
67	Ho	410.4	164.9303	🟥
68	Er	400.8	167.26	🟥
69	Tm	371.8	168.9342	🟥
70	Yb	398.8	173.04	🟥
71	Lu	336.0	174.97	🟥

Actinides **

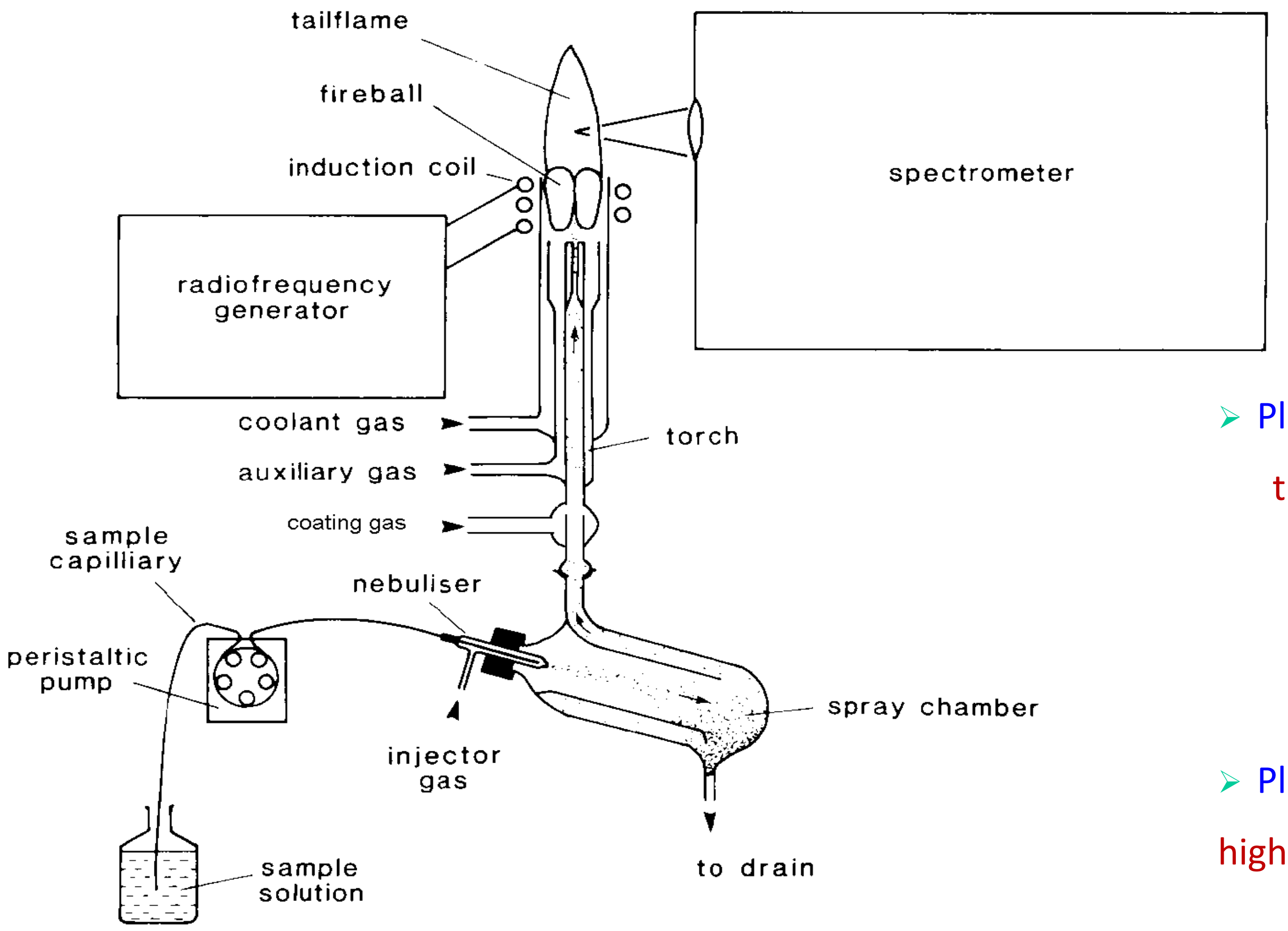
ATOMIC NUMBER	SYMBOL	WAVELENGTH	ATOMIC WEIGHT	
90	Th		232.0381	
91	Pa		231.0359	
92	U	358.5	238.029	🟥
93	Np		237.0482	
94	Pu		244	
95	Am		243	
96	Cm		247	
97	Bk		247	
98	Cf		251	
99	Es		254	
100	Fm		257	
101	Md		258	
102	No		259	
103	Lr		260	

Inductively coupled plasma (ICP)



ISA JOBIN YVON - SPEX
Groupe HORIBA

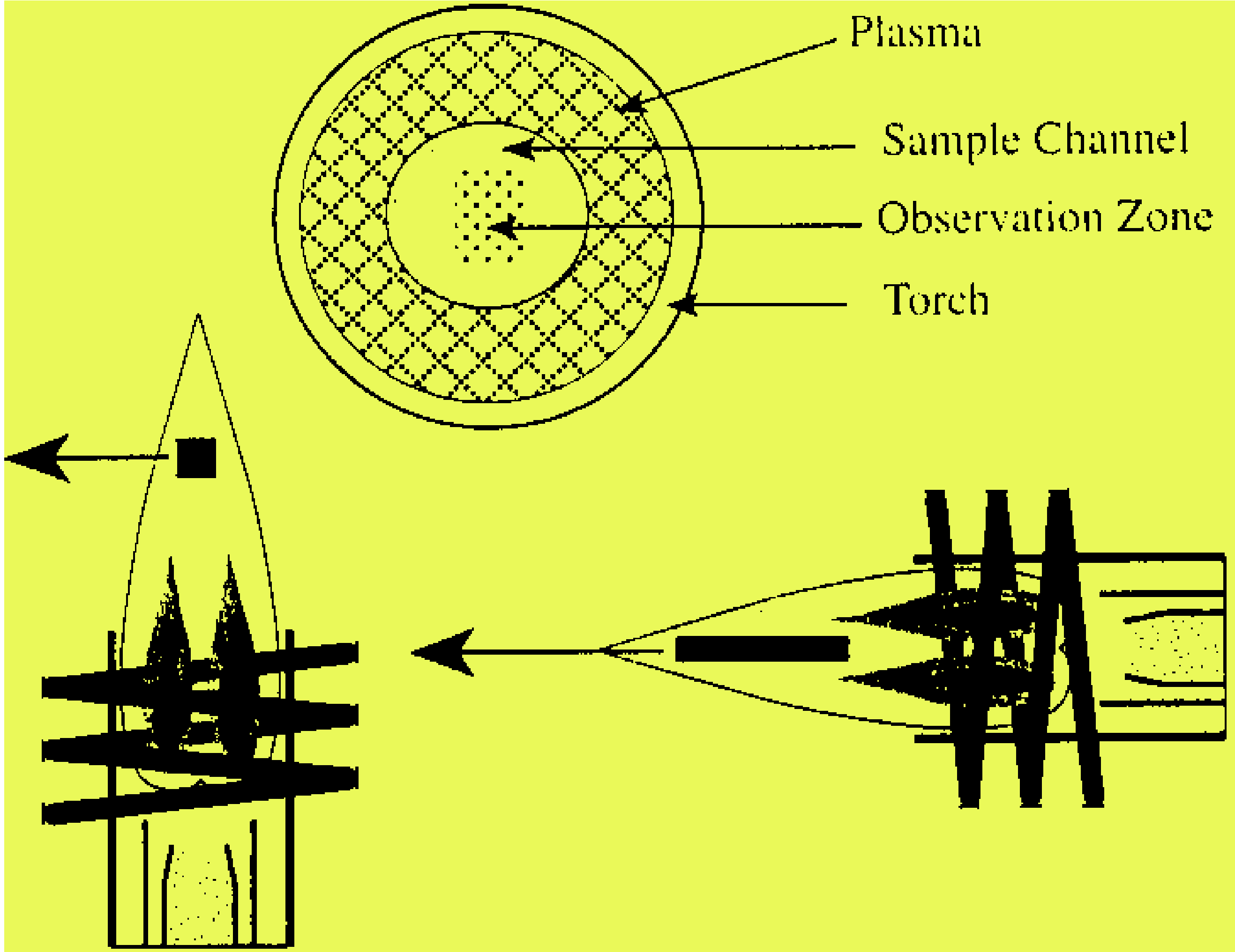
ICP Kitchen area



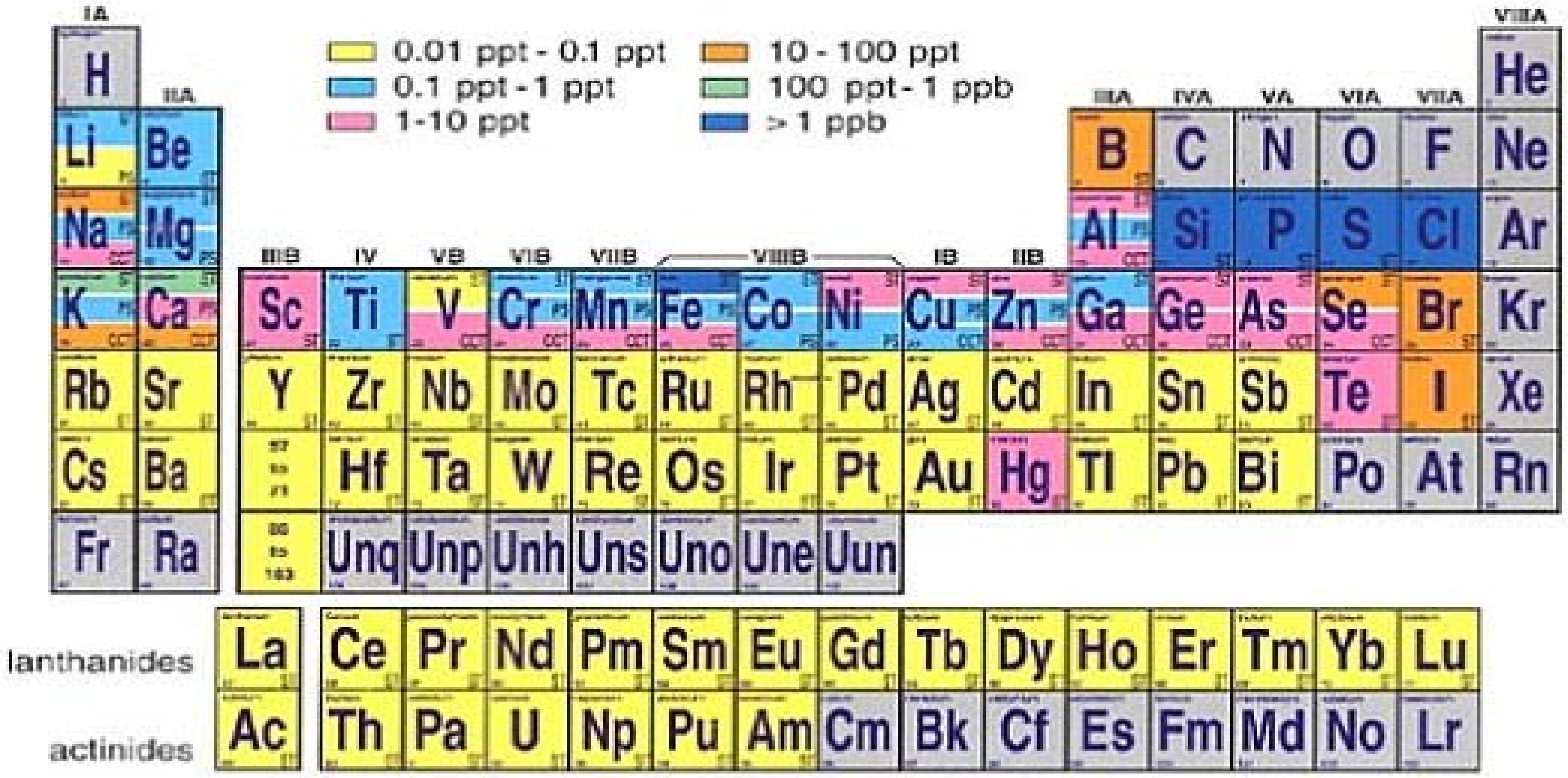
- Ar gas excited at radio frequency
- Temperature up to 8000̊ C
- Low concentration

- Plasma torch: 3 concentric quartz tubes, streaming Ar
  - Outside→ cooling
  - Central→ plasma
  - Inside→ carrier gas for sample
- Plasma state: electric excitation→ high temperature fireball

ICP plasma



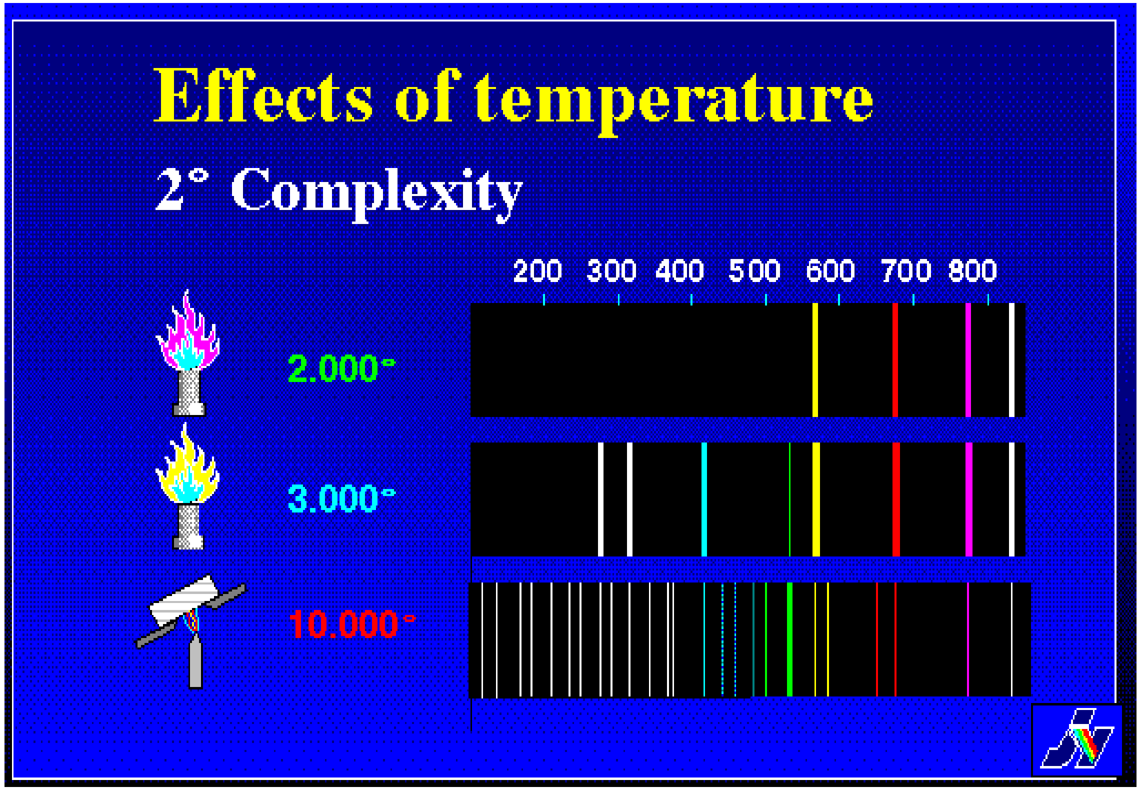
ICP-AES – Detection limits



3 sigma detection limits in de-ionized water

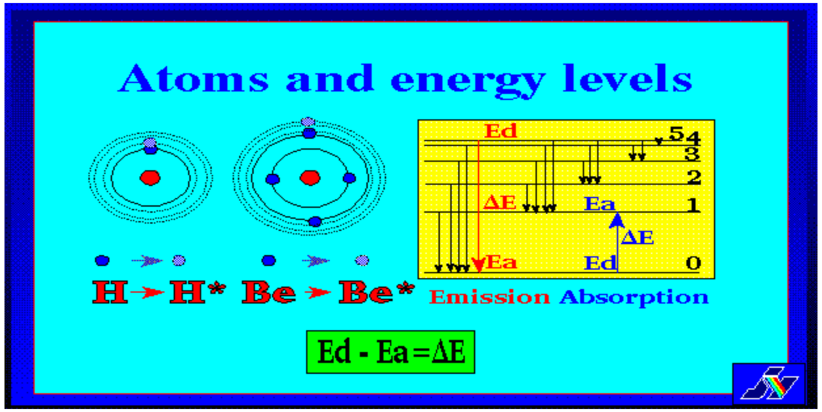
ST = Standard PS = PlasmaScreen CCT = Collision Cell

Emission spectra: effect of temperature



Effects of temperature

2° Complexity



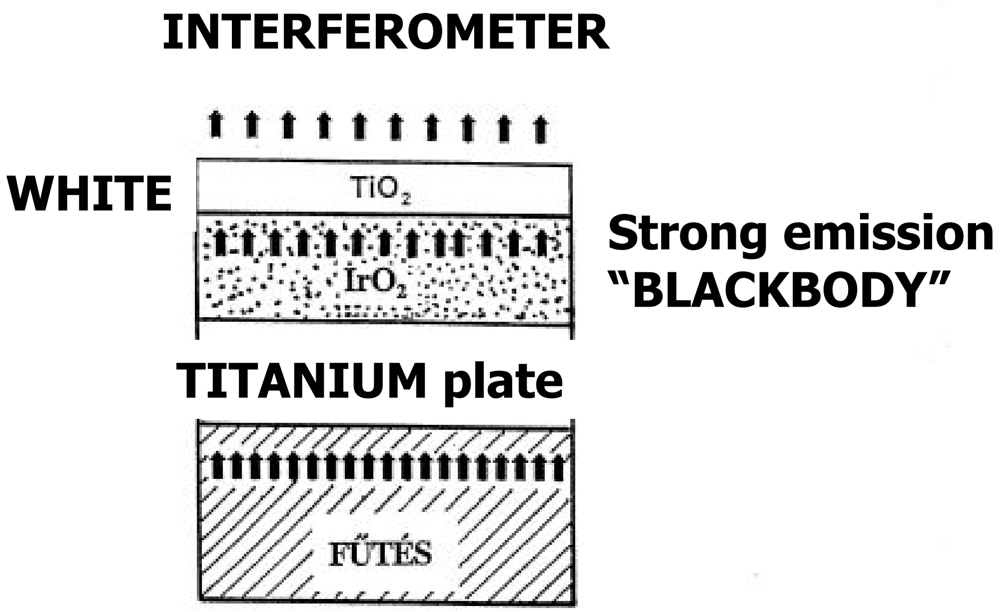
Atoms and energy levels

Ed - Ea = ΔE

Infrared emission spectroscopy

Temperature: 100 – 200 °C

Keresztury Gábor, Mink János,
Kristóf János
MTA Kémiai Kutatóközpont,
Veszprémi Egyetem



INTERFEROMETER

WHITE

Strong emission
“BLACKBODY”

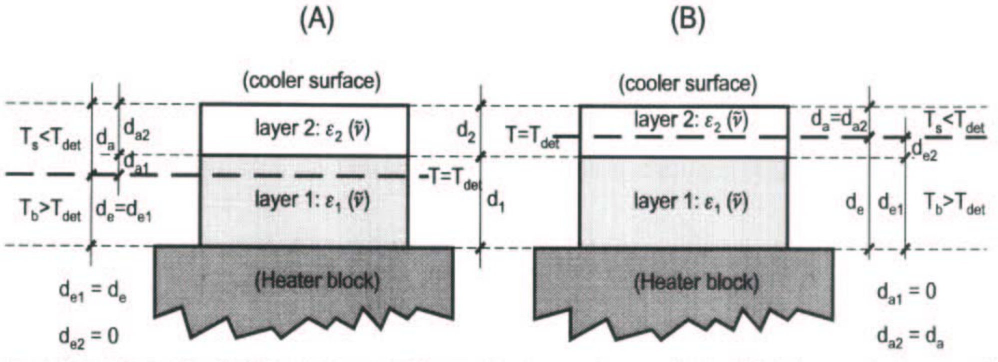
TITANIUM plate

The model of layer structure

Self-absorption

The spectral shape depends on:

- effective thickness of the layers (d_1, d_2)
- thickness of emitting, absorbing layers (d_e, d_a)



G. Keresztury, J. Mink, J. Kristóf:
Anal. Chem. **67**, 3782 (1995)

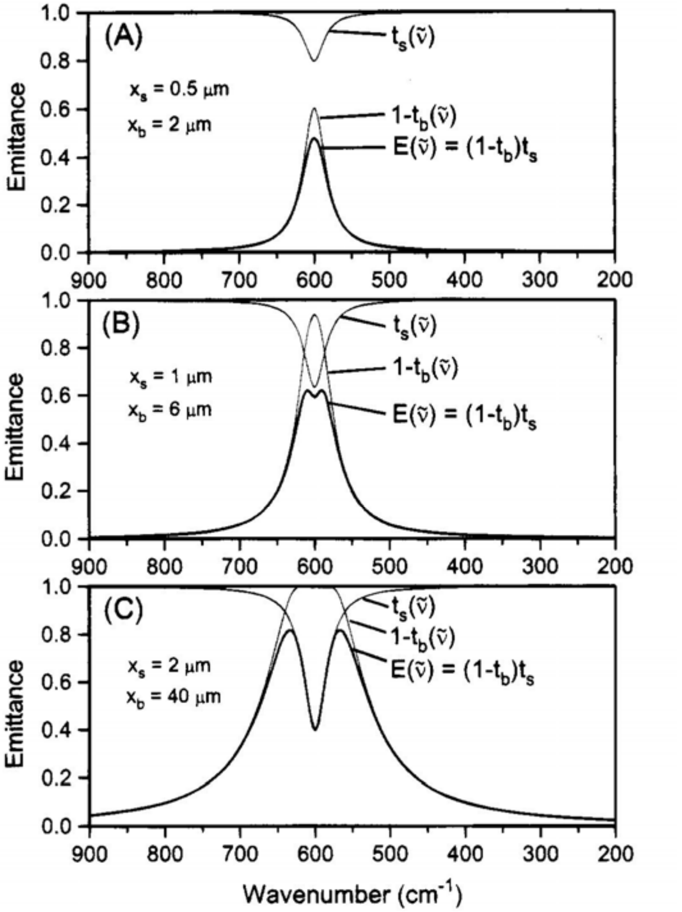


Figure 2. Simulation of the effect of self-absorption using eq 12 for different effective thicknesses of emitting bulk (x_b) and absorbing surface layer (x_s). (Lorentzian band shapes with $\tilde{\nu}_0 = 600$, $I_0 = 2000$, and $w = 30$ cm^{-1}.)

t_b – transmittance of the bulk

t_s – transmittance of the surface

E - emittance

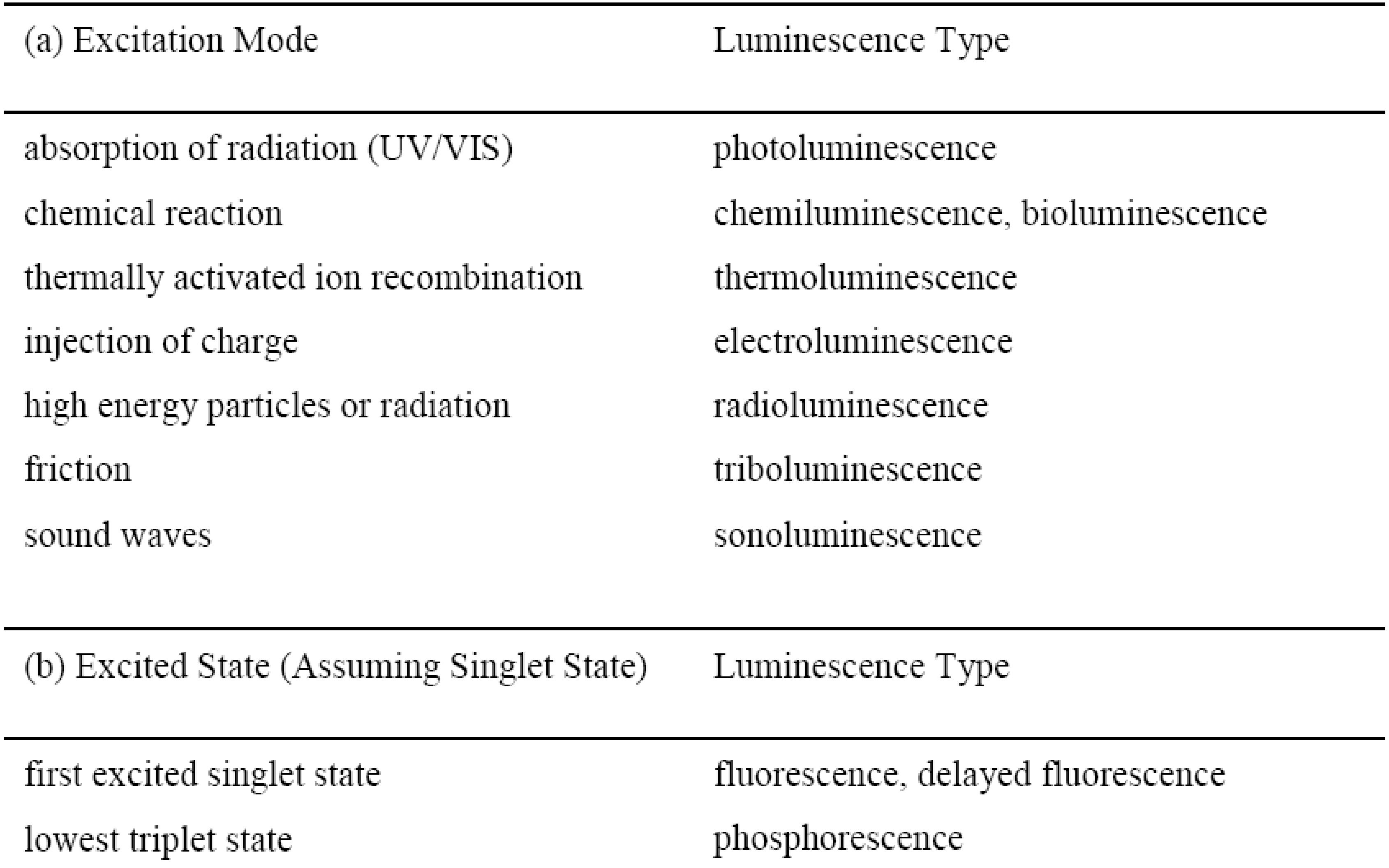
Molecular spectroscopy – Luminescence

Light emission by excited molecules

Fluorescence of different sized CdSe quantum dots

Joseph R. Lakowicz – Principles of fluorescence spectroscopy, 3rd edition

Types of luminescence



(a) Excitation Mode	Luminescence Type
absorption of radiation (UV/VIS)	photoluminescence
chemical reaction	chemiluminescence, bioluminescence
thermally activated ion recombination	thermoluminescence
injection of charge	electroluminescence
high energy particles or radiation	radioluminescence
friction	triboluminescence
sound waves	sonoluminescence

(b) Excited State (Assuming Singlet State)	Luminescence Type
first excited singlet state	fluorescence, delayed fluorescence
lowest triplet state	phosphorescence

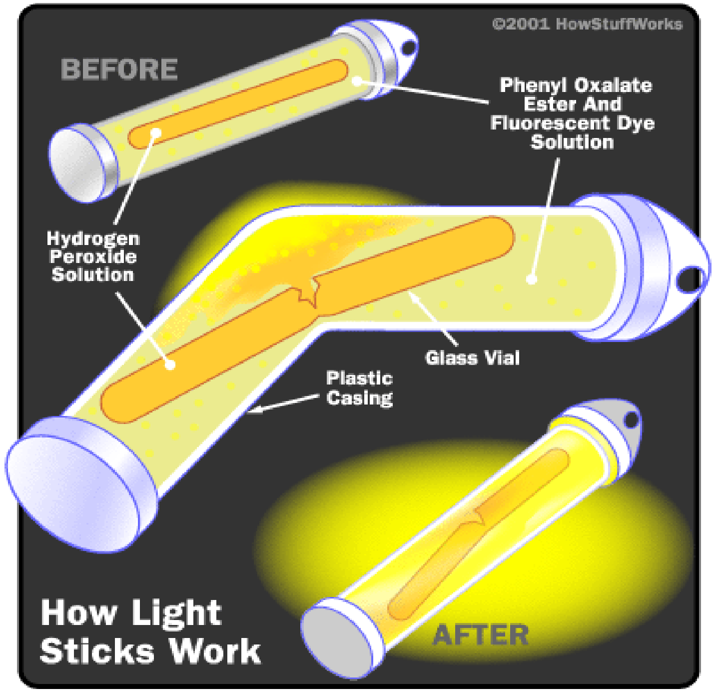
Chemiluminescence/bioluminescence

Chemiluminescence – is the emission of light as the result of a chemical reaction

↓

Bioluminescence – one type of chemiluminescence; the light is produced and emitted by a living organism

e.g. firefly, deep-sea fish, jellyfish, squids, bacteria, planktons, mushrooms



Luminescence

	Fluorescence	Phosphorescence
➢ Emission:	From excited singlet state	From excited triplet state
➢ Transition:	Allowed	„Forbidden”
➢ Emission rate:	Fast: $10^8\ s^{-1}$	Slow: $10^3 – 10^0\ s^{-1}$
➢ Average lifetime:	1 – 10 ns	ms – s

- Example:

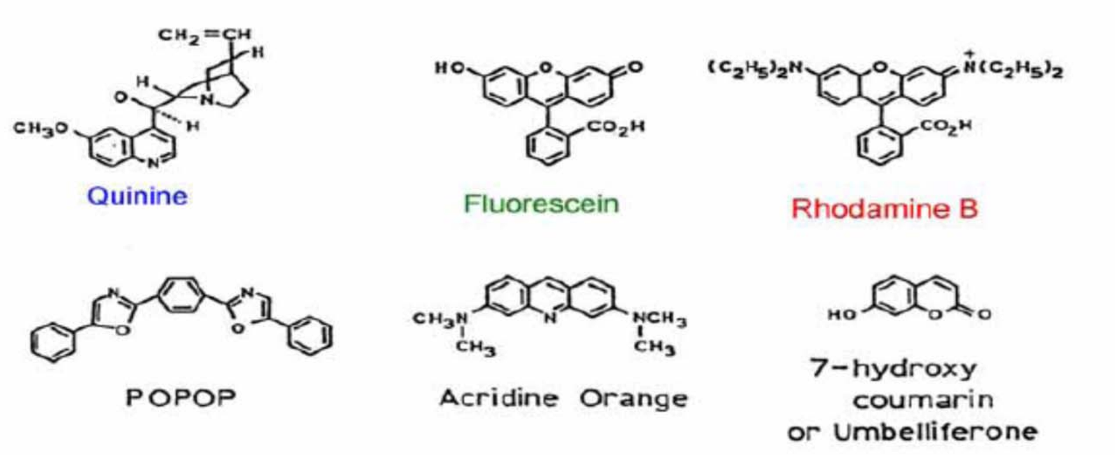

0 sec 1 sec 640 sec

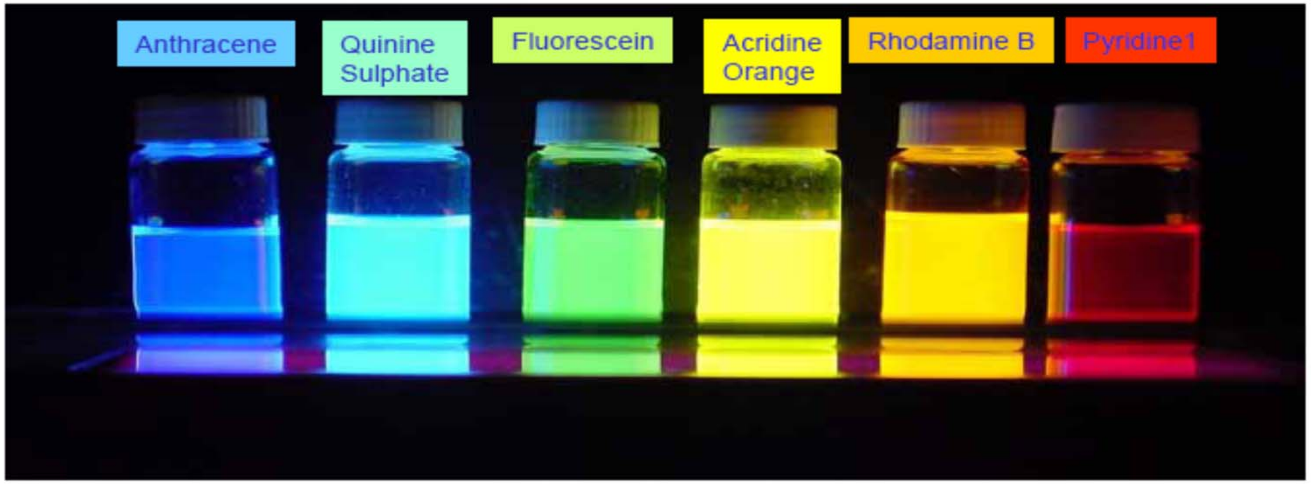
Molecular spectroscopy

Fluorescence – Typical fluorophores

- Typically aromatic molecules
- Usually no fluorescence

in condensed state



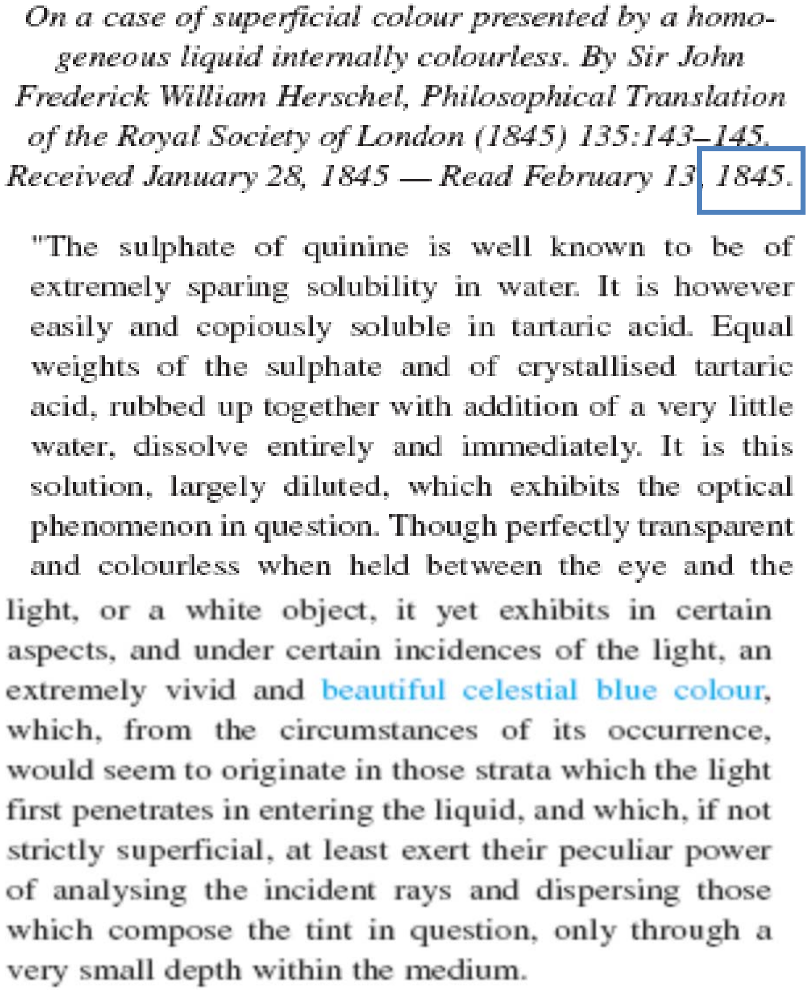


Molecular spectroscopy

Fluorescence – the beginning

Sir John Fredrich William Herschel

1792 – 1871



On a case of superficial colour presented by a homogeneous liquid internally colourless. By Sir John Frederick William Herschel, Philosophical Translation of the Royal Society of London (1845) 135:143–145. Received January 28, 1845 — Read February 13, 1845.

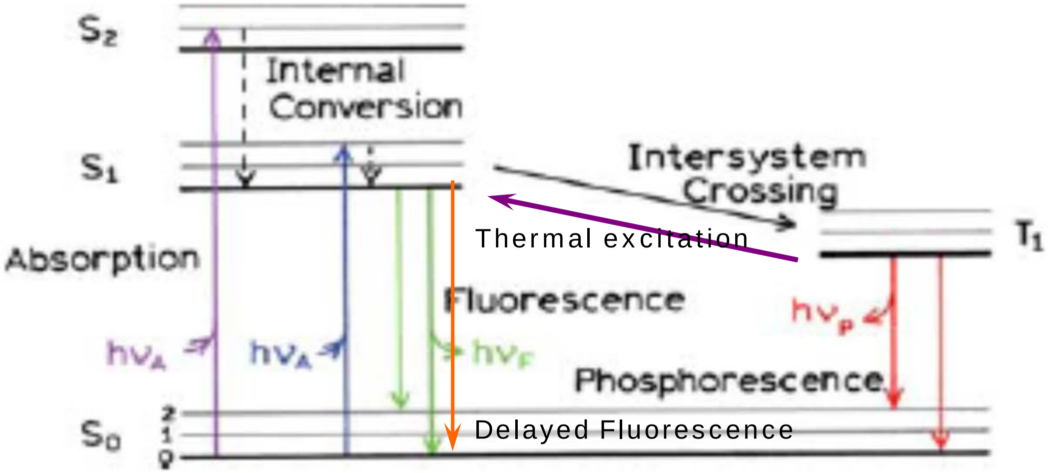
"The sulphate of quinine is well known to be of extremely sparing solubility in water. It is however easily and copiously soluble in tartaric acid. Equal weights of the sulphate and of crystallised tartaric acid, rubbed up together with addition of a very little water, dissolve entirely and immediately. It is this solution, largely diluted, which exhibits the optical phenomenon in question. Though perfectly transparent and colourless when held between the eye and the light, or a white object, it yet exhibits in certain aspects, and under certain incidences of the light, an extremely vivid and beautiful celestial blue colour, which, from the circumstances of its occurrence, would seem to originate in those strata which the light first penetrates in entering the liquid, and which, if not strictly superficial, at least exert their peculiar power of analysing the incident rays and dispersing those which compose the tint in question, only through a very small depth within the medium.

Fluorescence of quinine is the most widely used example up to now

Luminescence – Jablonski diagram

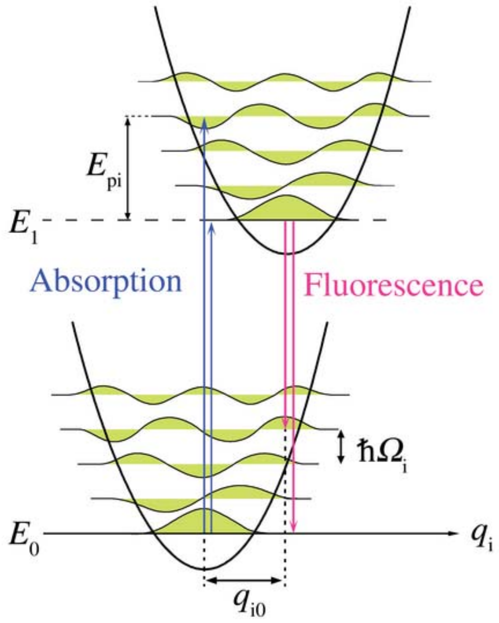
Professor Alexander Jablonski

1898 – 1980



One form of a Jablonski diagram.

Luminescence in molecules



Franck-Condon principle
R: configuration coordinate

absorption (vertical)

↓

relaxation

↓

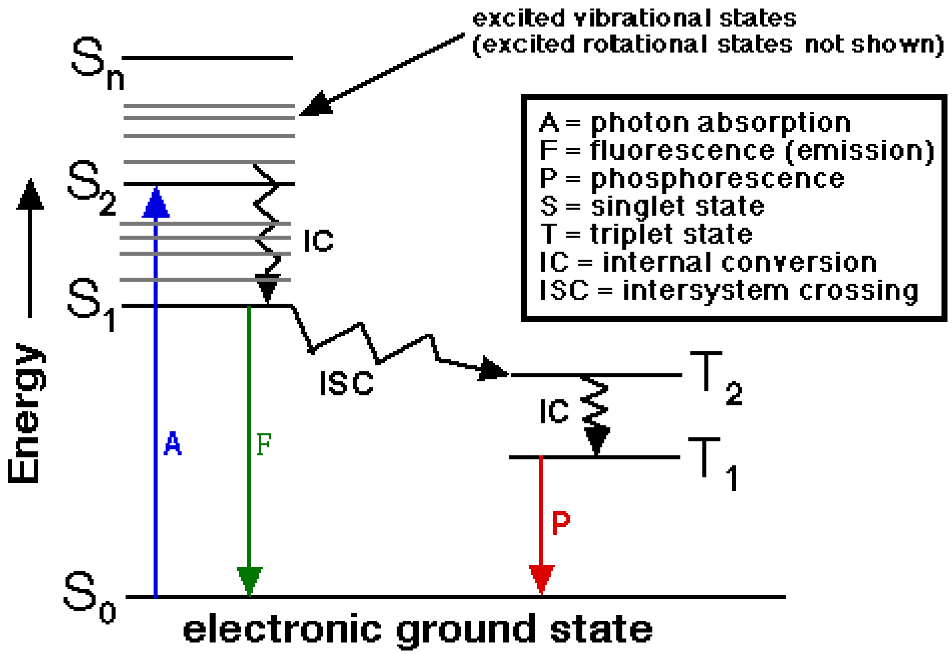
emission (vertical)

↓

relaxation

http://en.wikipedia.org/wiki/Franck-Condon_principle

http://www.shsu.edu/~chemistry/chemiluminescence/JABLONSKI.html

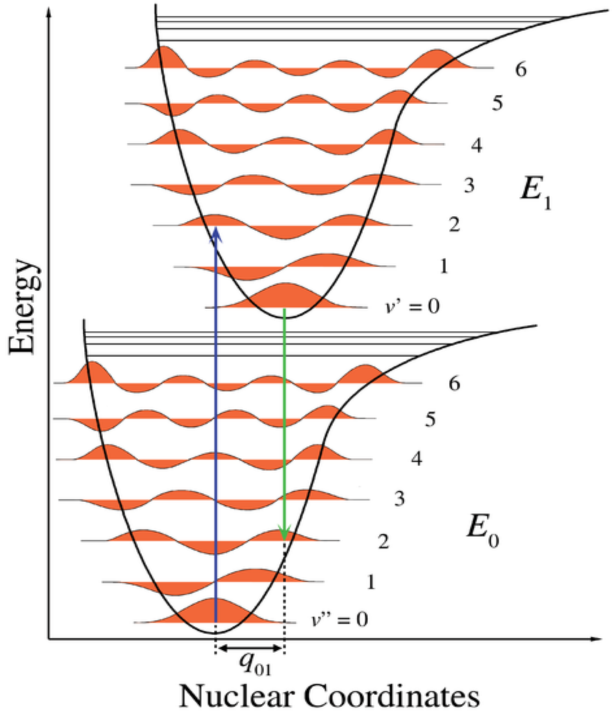


Jablonski diagram

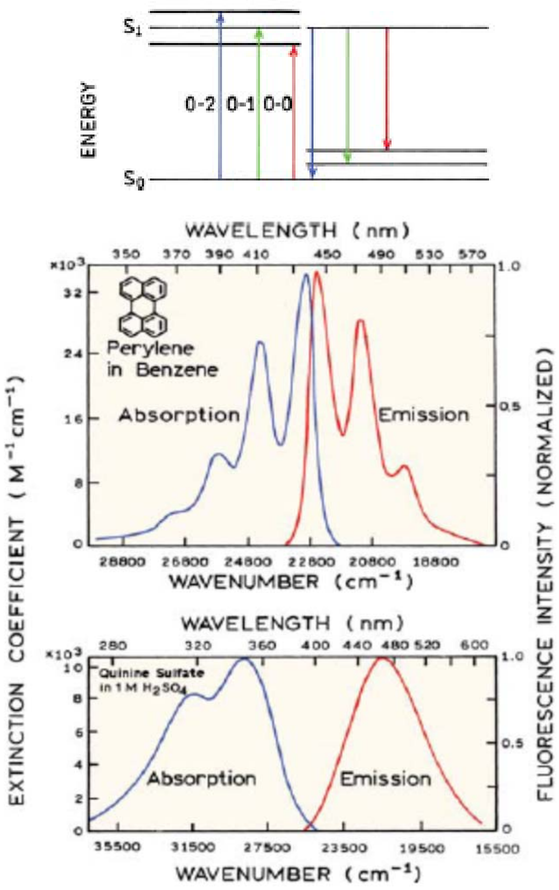
Intersystem crossing: singlet– triplet
Internal conversion: into vibrationally excited state of higher singlet
Fluorescence: singlet - singlet
Phosphorescence: singlet – triplet (delayed)

Fluorescence basics

Franck-Condon principle



Mirror image

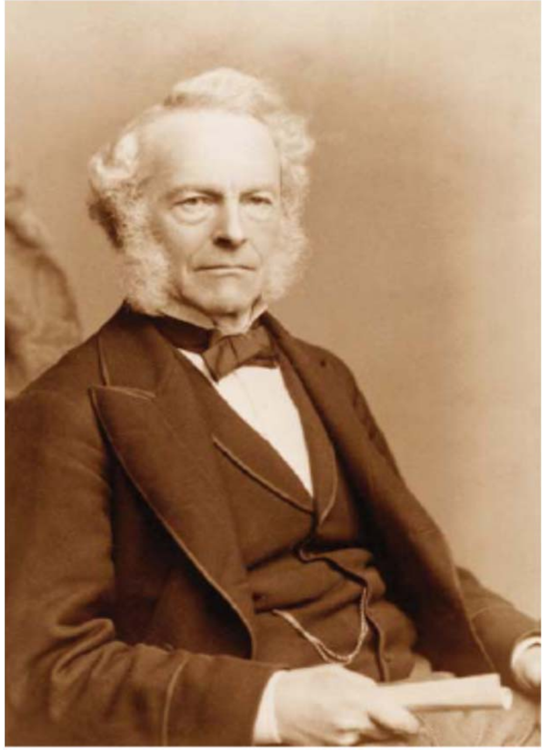


During an electronic transition a change from one vibrational energy level to another will be more likely to happen if the two vibrational wavefunctions overlap more significantly

Electronic excitation does not greatly alter the nuclear geometry

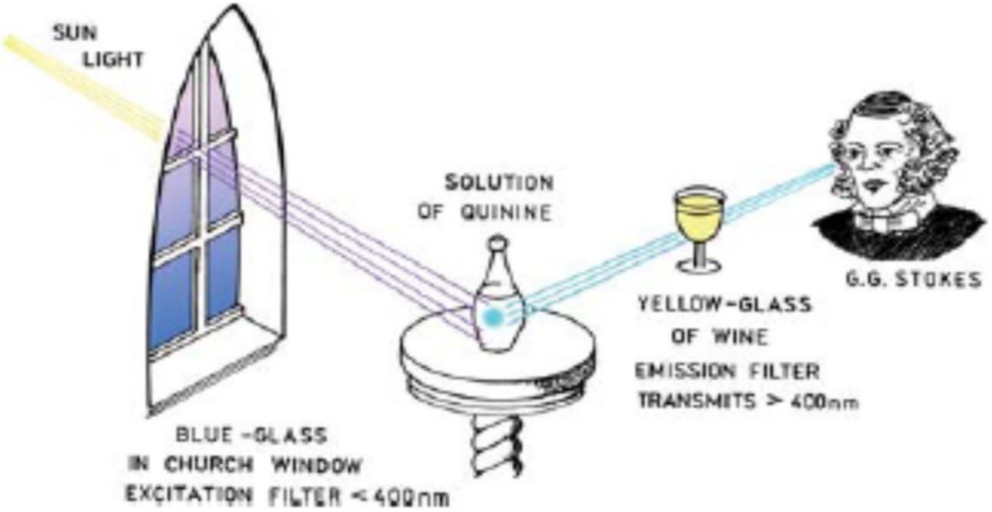
Molecular spectroscopy

Fluorescence – Stokes shift



Sir George Gabriel Stokes

1819 – 1903



Experimental schematic for detection of the Stokes shift.

Visual observation of Stokes shift

Molecular spectroscopy

Fluorescence – Lifetime (τ) and quantum yield (Q)

- These are the two most important characteristics

$$\text{quantum yield} = Q = \frac{number\ of\ emitted\ photons}{number\ of\ absorbed\ photons} = \frac{\Gamma}{\Gamma + k_{nr}}$$

where Γ – emission rate of fluorophores

k_{nr} – number of non-radiative transitions to ground state S_0

if there is Stokes shift, $Q < 1$

Lifetime: average time between excitation and emission

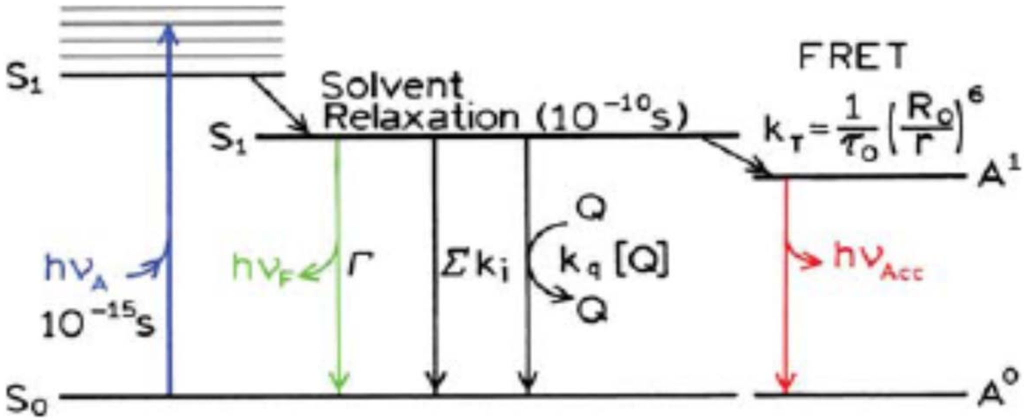
$$\tau = \frac{1}{\Gamma + k_{nr}}$$

if $k_{nr} = 0$, *intrinsic* lifetime

Molecular spectroscopy

Fluorescence – Quenching

Quenching – intensity of fluorescence decreases



Jablonski diagram with collisional quenching and fluorescence resonance energy transfer (FRET). The term Σk_i is used to represent non-radiative paths to the ground state aside from quenching and FRET.

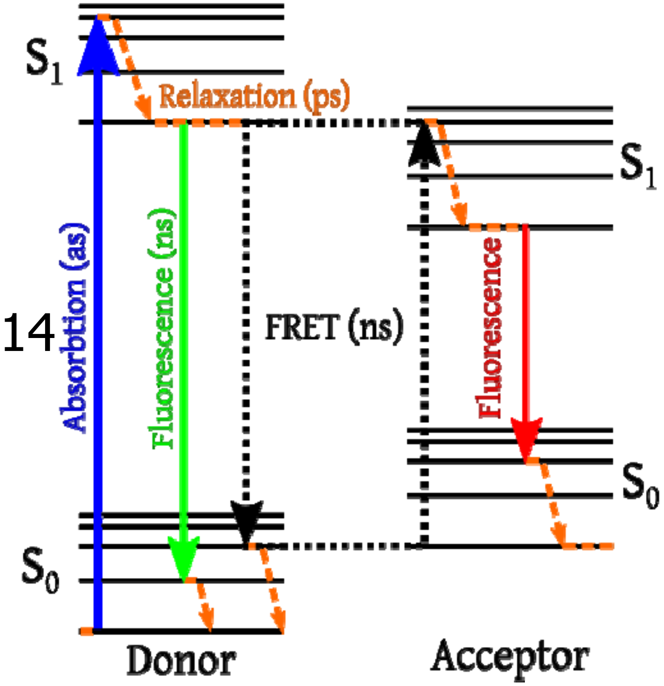
Reasons:

- collision with other molecules (quenchers)
- formation of non-fluorescent complexes
- resonance energy transfer (RET)

Molecular spectroscopy

Fluorescence – Resonance energy transfer

- emission spectrum of donor overlaps with absorption spectrum of acceptor
- no intermediate photon
- dipole-dipole interaction between donor and acceptor



By Alex M Mooney - Own work, CC BY-SA 3.0,
https://commons.wikimedia.org/w/index.php?curid=23197114

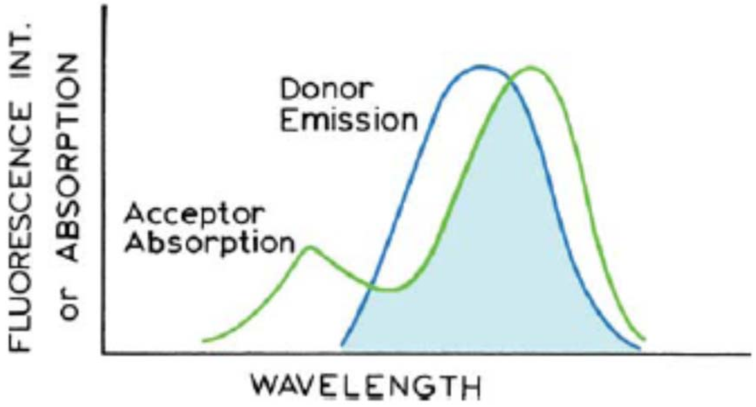


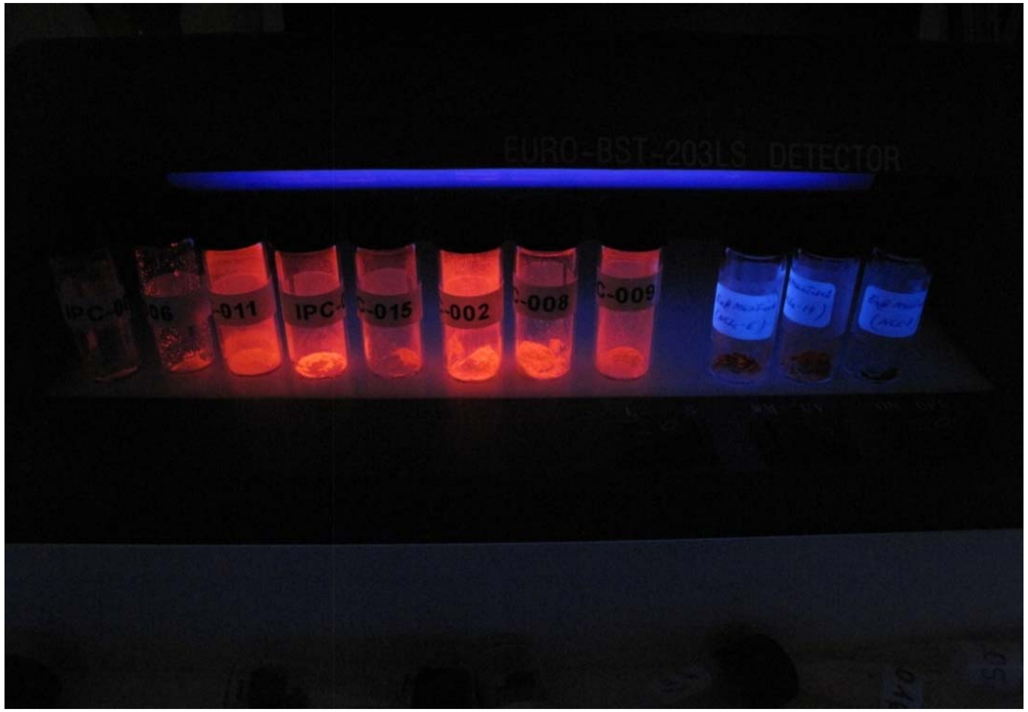
Figure 1.16. Spectral overlap for fluorescence resonance energy transfer (RET).

Molecular spectroscopy

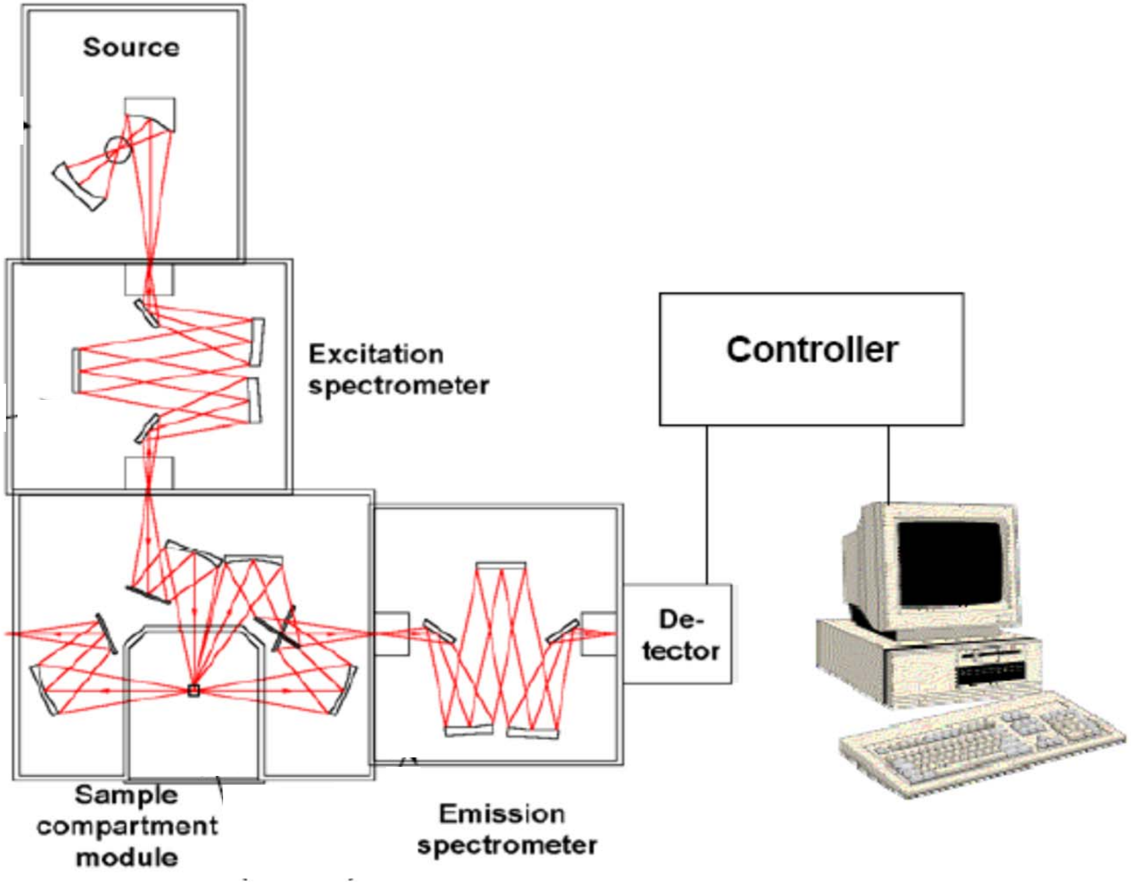
Fluorescence – Eu-based fluorophores

White llight illumination

UV light (365 nm)



Spectrofluorimeter – Fluorolog 3



Take-home message

- Atomic emission spectroscopy: flame test, flame emission photometry, atomic absorption spectroscopy, inductive coupled plasma
- Infrared emission spectroscopy: vibrational levels, self-absorption
- Molecular spectroscopy: types of luminescence
- Jablonski diagram: absorption, fluorescence, phosphorescence, internal conversion, intersystem crossing
- Quantum yield and lifetime
- Resonance energy transfer

Összefoglalás

- Atomi emissziós spektroszkópia: lángfestés, lángfotometria, atomabszorpciós spektroszkópia
- Infravörös emissziós spektroszkópia: rezgési szintek, önabszorpció
- Molekulaspektroszkópia: lumineszcencia típusok
- Jablonski-diagram: abszorpció, fluoreszcencia, foszforeszcencia, belső konverzió, intersystem crossing
- Kvantumhatásfok és élettartam
- Rezonáns energiatranszfer