

C8785 Photophysical Spectroscopic Methods

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PSM 01 Intro

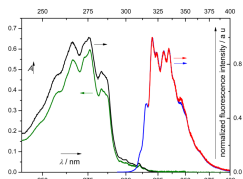
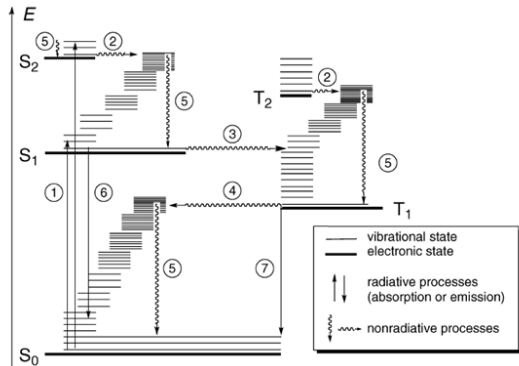


Figure 1. UV-vis absorption (green), fluorescence excitation (black; $\lambda_{exc} = 330$ nm), and emission (blue, $\lambda_{exc} = 287$ nm; red, $\lambda_{exc} = 310$ nm) spectra of naphthalene in the aqueous solutions (Fluka, 7.8×10^{-5} mol dm $^{-3}$; 10 mg L $^{-1}$) at 296 K.



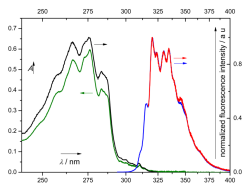
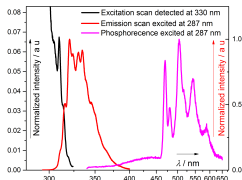
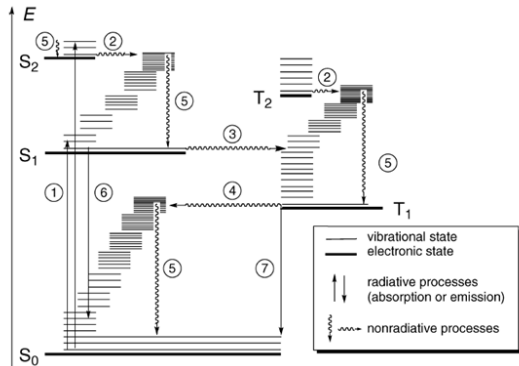
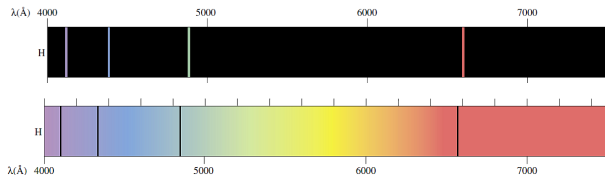


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Spectroscopy: Hydrogen emission and absorption spectra



Johann Balmer (1885, Basel, Switzerland)

Johannes Rydberg (1988, Lund, Sweden)

The goal:

- **Understand to spectroscopy, and measure well, gain self-confidence.**
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Content

- Absorption - liquid, solid.
- Luminescence - steady state, time resolved.
- Transient absorption

- 1 Spectroscopy
- 2 Photophysics
- 3 Transmittance, Reflectance, Absorptance, Absorbance
- 4 Lambert-Beer-Bouguer law
- 5 Foerster cycle

Physical quantities and their notation

Table 1.1 The SI base quantities

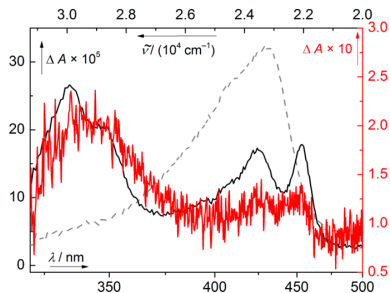
Base quantity			SI unit	
Name	Symbol for quantity	Symbol for dimension	Name	Symbol
Length	l	L	metre	m
Mass	m	M	kilogram	kg
Time	t	T	second	s
Electric current	I	I	ampere	A
Thermodynamic temperature	T	Θ	kelvin	K
Amount of substance	n	N	mole	mol
Luminous intensity	I_v	J	candela	cd

The value of a *physical quantity* Q can be expressed as the product of a *numerical value* $\{Q\}$ and a *unit* $[Q]$

$$Q = \{Q\}[Q]$$

Ex. $l = 5 \text{ cm}$

Scaled quantities $Q/[Q]$



pH	c (acetic acid)/ mM	k obs / s^{-1}	
		12b⁻	12c⁻
4.92	8.14	$(9.4 \pm 0.1) \times 10^6$ (2)	n.d.
4.75	1.00	$(4.35 \pm 0.50) \times 10^6$ (3)	$(4.21 \pm 0.96) \times 10^6$ (4)
4.52	0.32	$(1.41 \pm 0.17) \times 10^6$ (4)	$(1.38 \pm 0.31) \times 10^6$ (4)

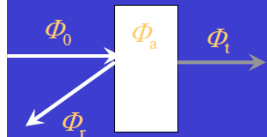
Definitions and Lambert-Beer-Bouguer law

$$-\log (\Phi_t / \Phi_0) = -\log \tau_i = \epsilon cb = A(\lambda)$$

$\tau_i = \Phi_t / \Phi_0$ internal transmittance (transmission factor)

$\rho = \Phi_r / \Phi_0$ reflectance (reflection factor)

$\alpha = \Phi_a / \Phi_0 = 1 - \tau$ absorptance (absorption faktor)



<http://old.inpac.org/reports/V/spectro/partVII.pdf>

Term	Symbol	Unit
Monochromatic radiant power	Φ	W
(decadic) internal absorbance	A	1
Molar (decadic) absorption coefficient	ϵ	$\text{L mol}^{-1} \text{cm}^{-1}$
Absorption pathlength	b	cm^{-1}
Cell pathlength	l	cm^{-1}

Extinction – sum of absorption, scattering and luminescence.

Lambert-Beer-Bouguer law

Lambert-Beer

```
> restart;with( DEtools );with( plots );with( linalg):  
> ode:=diff(F(z),z)=-m(z)*F(z);
```

$$\text{ode} := \frac{d}{dz} F(z) = -m(z) F(z) \quad (2.1)$$

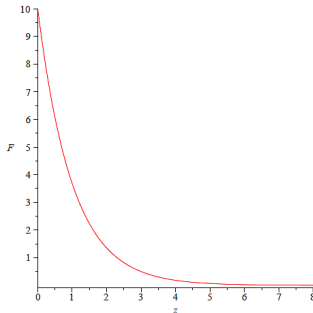
```
> dsolve({ode,F(0)=F0},F(z));
```

$$F(z) = F_0 e^{\int_0^z (-m(z)) dz} \quad (2.2)$$

```
> m:=1.0;nsol:=dsolve({ode,F(0)=10},type=numeric, output=  
listprocedure);
```

$$\text{nsol} := [z = \text{proc}(z) \dots \text{end proc}, F(z) = \text{proc}(z) \dots \text{end proc}] \quad (2.3)$$

```
> odeplot(nsol,[z,F(z)],0..8);
```



Limits of Lambert-Beer-Bouguer law

Conditions for validity of linear relation $A = \epsilon * c * l$

- Independence of attenuators
- Homogenous distribution
- No turbidity
- Parallel rays
- Radiation being monochromatic
- Incident flux must not influence the atoms of molecules - should be non-invasive probe (far from saturation or total absorption)

Spectra

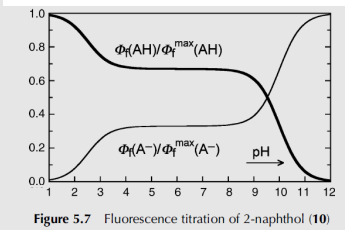
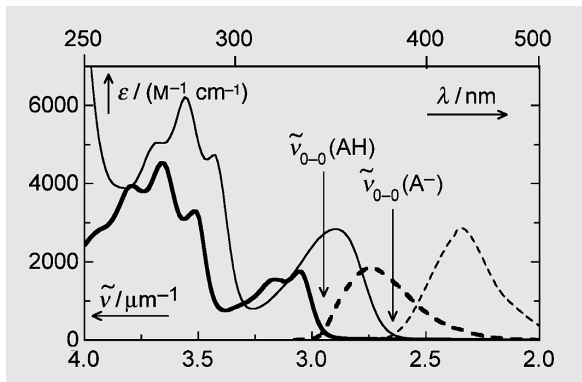
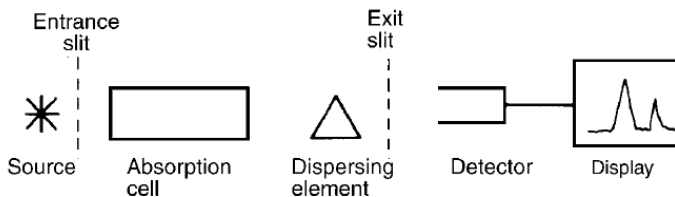


Figure 5.7 Fluorescence titration of 2-naphthol (10)

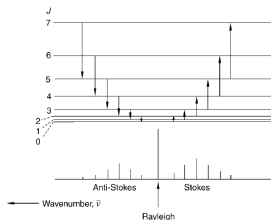
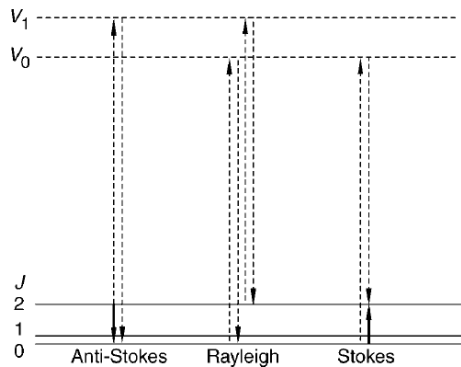
General Scheme of Spectrometer



J. Michael Hollas: Modern Spectroscopy

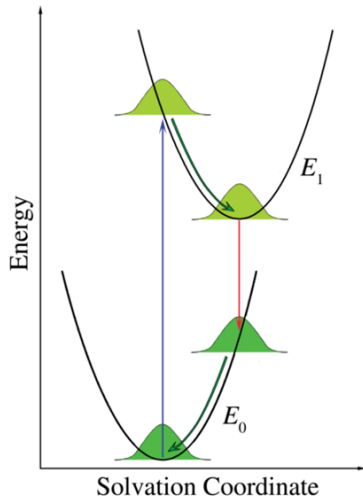
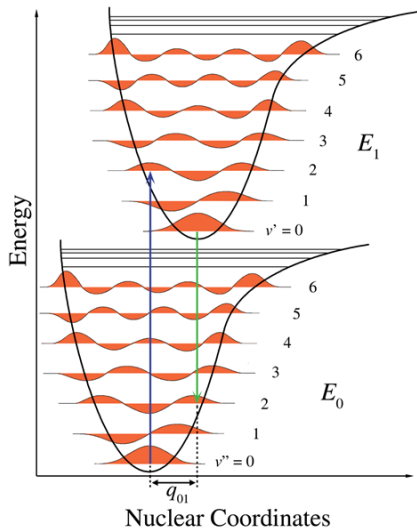
Klán, Wirz: Photochemistry of Organic Compounds, From Concepts to Practice

Stokes shift

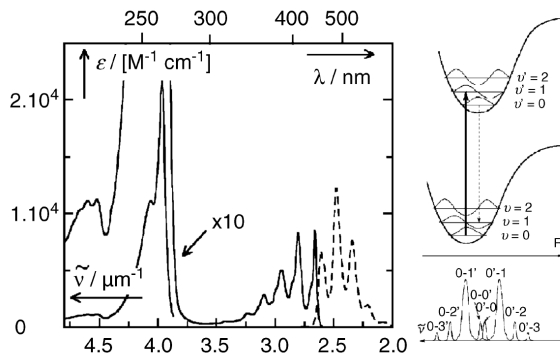


J. Michael Hollas: Modern Spectroscopy

Franck-Condon Principle; Vertical excitation



Stokes shift



The spectral positions of the $0-0'$ bands of absorption and fluorescence usually do not coincide exactly. The difference is called the *Stokes shift*. The excited state is generally more polarizable and often more polar than the ground state. Solvent relaxation then stabilizes the excited state following Franck–Condon excitation, so that the $0-0'$ band of absorption is usually at higher frequency than that of emission. When the excited state is much less polar than the ground state, the $0-0'$ band of fluorescence may appear at higher frequency than that of absorption (*anti-Stokes shift*). Unfortunately, the term Stokes shift is also used to refer to the gap between the band maxima of absorption and emission (see the footnote to fluorescence in Section 2.1.1), which may be much larger than the shift between the $0-0$ bands.

Klán, Wirz:

Photochemistry of Organic Compounds