Spectroscopy of atoms and molecules

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Suggested reading

- W. Demtröder, Laser spectroscopy
- A. Corney, Atomic and laser spectroscopy.
- S. Svanberg, Atomic and Molecular Spectroscopy.
- J.M. Hollas, Modern Spectroscopy.
- Ch. Chin et al., Feshbach resonances in ultracold gases,
- K. M. Jones et al.,Ultracold photoassociation spectroscopy:Long-range molecules and atomic scattering,

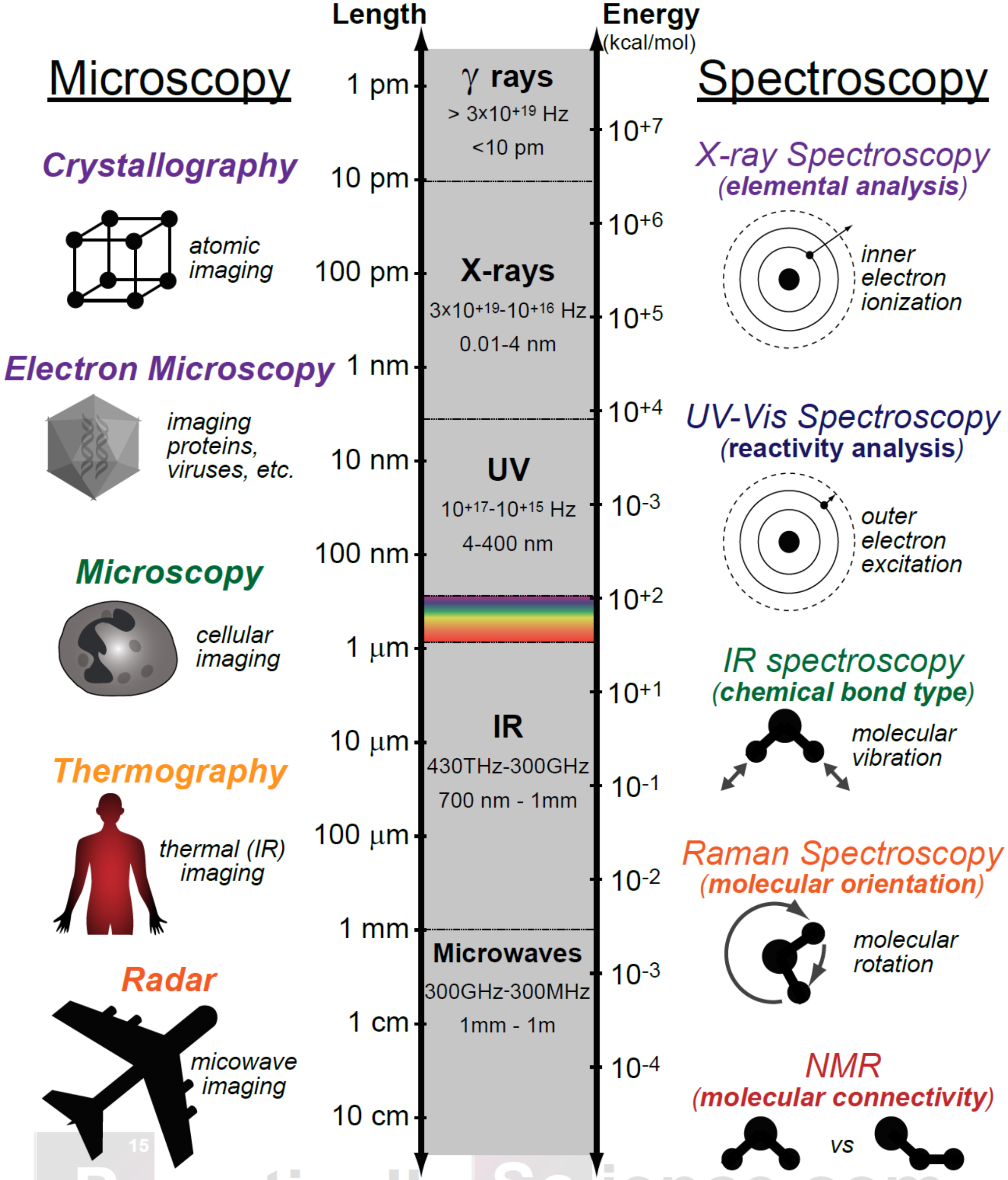
Suggested pre-reading

- „Quantum Optics, an Introduction”, M. Lewenstein, A. Sanpera, M. Pospiech
  www.matthiaspospiech.de/files/studium/skripte/QOscript.pdf
- „Statistical Optics”, Goodman
- „Quantum mechanics: non-relativistic theory”, L.D. Landau, E.M. Lifszic
- „Nonlinear Optics”, Robert W. Boyd
- „Quantum and Atom Optics”, Daniel A. Steck
  http://atomoptics-nas.uoregon.edu/~dsteck/teaching/quantum-optics/
- Quantum mechanics textbooks in general

Spectroscopy – brief history

- 1621, Willebrord Snell, law of refraction
- 1637, Rene Descartes, studies of the rainbow
- 1664, I. Newton, sun light dispersion in a prism
- 1800, discovery of infrared radiation in sunlight
- ca. 1800, T. Young, determination of wavlengths of different colors
- 1814, J. von Fraunhofer, construction of the first spectroscope
- 1859-61, G. Kirchhoff, law of thermal radiation, emission of black-body radiation, discovery of sodium, cesium and rubidium
- 1913, N. Bohr, theory of the hydrogen atom
- 1925, G. Uhlenbeck and S. Goudsmit, the idea of electron spin
- 1926, E. Schroedinger, W. Heisenberg, quantum mechanics; W. Pauli, Pauli exclusion principle

EM Limits of Microscopy and Spectroscopy



Length

Energy
(kcal/mol)

Microscopy

Crystallography
atomic imaging

Electron Microscopy
imaging proteins, viruses, etc.

Microscopy
cellular imaging

Thermography
thermal (IR) imaging

Radar
micowave imaging

γ rays
> $3\times10^{+19}$ Hz
<10 pm

X-rays
$3\times10^{+19}$-10^{+16} Hz
0.01-4 nm

UV
10^{+17}-10^{+15} Hz
4-400 nm

IR
430THz-300GHz
700 nm - 1mm

Microwaves
300GHz-300MHz
1mm - 1m

Spectroscopy

X-ray Spectroscopy
(***elemental analysis***)
inner electron ionization

UV-Vis Spectroscopy
(**reactivity analysis**)
outer electron excitation

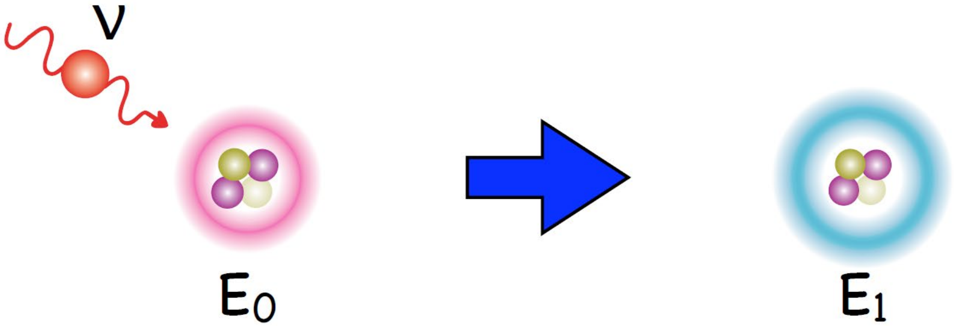
IR spectroscopy
(***chemical bond type***)
molecular vibration

Raman Spectroscopy
(***molecular orientation***)
molecular rotation

NMR
(***molecular connectivity***)
vs

A reminder: matter – field interaction

- Quantum mechanical picture of absorption tells us a photon of energy hν is absorbed by an atom or molecule which leaves the atom or molecule in a more energetic state



The Quantum picture does not tell us much about the interaction itself. Thus we consider a classical model for some insight.

A reminder: matter – field interaction

- We must model three things to describe absorption
  - Light (sinusoidal electromagnetic field)
  - Matter (simple harmonic oscillator)
  - Interaction (damped oscillator driven by periodic force)

A reminder: matter – field interaction

- Consider only the oscillating electric field (the corresponding magnetic field is implied)

$$\vec{E}(\vec{r},t) = \vec{E}_0(\vec{r})e^{i(\omega t - \vec{k}\cdot\vec{r} - \phi_0)}$$

Amplitude vector including polarization and spatial dependence (mode) information

speed of propagation
c=ω/k

“angular” frequency of the light
ω=2πf

wavevector of the light
magnitude is k=2πn/λ_0
direction defines propagation direction of the light

A reminder: matter – field interaction

For the moment we will consider the 1-dimensional description of a plane wave polarized along x, propagating along z

$$\vec{E}(z,t) = \vec{E}_0 e^{i(\omega t - kz - \phi_0)}$$

Electric field has units of Volts/meter. The intensity is the quantity more commonly measured in the laboratory. It is related to electric field by

$$I = \epsilon_0 c \left\langle E^2 \right\rangle = \frac{\epsilon_0 c}{2} E_0^2$$

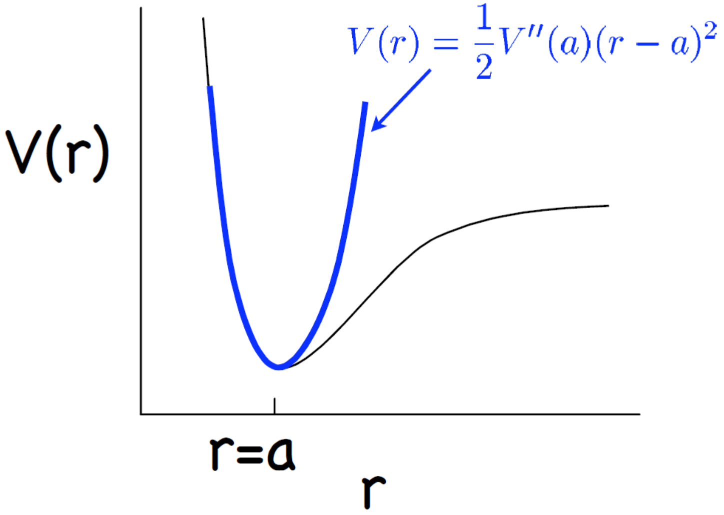
and has units of W/m^2

A reminder: matter – field interaction

Treat atoms or molecules as simple harmonic oscillators. For any molecule with an arbitrary potential

$$V(r) \approx V(a) + V'(a)(r-a) + \frac{1}{2}V''(a)(r-a)^2 + \ldots$$

at equilibrium U'=0 and potential can be modeled as a quadratic well (i.e. that of a simple harmonic oscillator)



A reminder: matter – field interaction

$$-V''(x - x_0) = m\ddot{x}$$

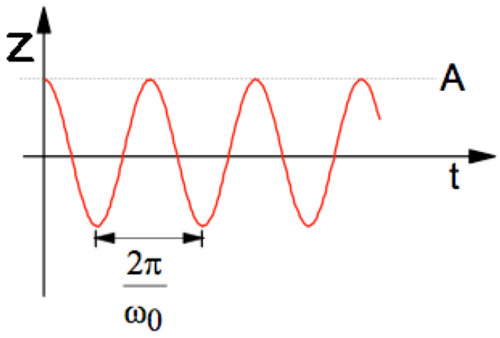
The equation of motion for the simple harmonic oscillator has solutions of the form

$$x = A\cos(\omega_0 t + \phi)$$ or $$x = Ae^{i(\omega_0 t + \phi)}$$

with

$$\omega_0 \equiv \sqrt{\frac{k}{m}}$$

natural frequency



A reminder: matter – field interaction

Now we add a velocity-dependent damping force

$$\vec{F} = (-V''(x - x_0) - \gamma m\dot{x})\hat{i}$$

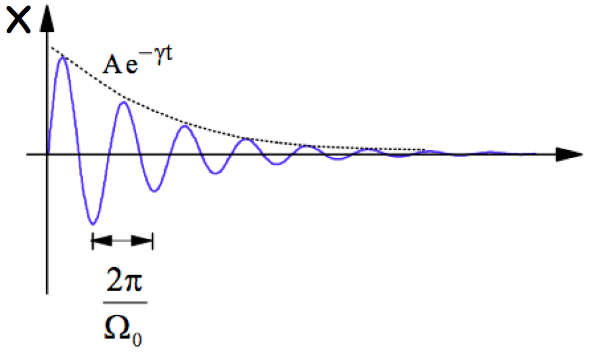
and find the solutions to

$$-V''(x - x_0) - \gamma m\dot{x} = m\ddot{x}$$

Solutions for the damped harmonic oscillator are of the form

$$x(t) = Ae^{-(\gamma/2)t}\cos(\omega' t + \phi)$$ or $$x = Ae^{-\gamma t/2}e^{i(\omega' t+\phi)}$$

with $$\omega' = \sqrt{\omega_0^2 - (\gamma/2)^2}$$



A reminder: matter – field interaction

Finally we add a the driving force of the electric field evaluated at r=0

$$\vec{F} = \left[-V''(x - x_0) - \gamma m \dot{x} + eE_0 e^{i(\omega t + \phi_0)} \right] \hat{i}$$

and find the solutions to

$$-V''(x - x_0) - \gamma m \dot{x} + eE_0 e^{i(\omega t + \phi_0)} = m \ddot{x}$$

A reminder: matter – field interaction

Solutions for the (complex) amplitude of the damped harmonic oscillator with an external driving force are of the form

$$\boxed{A = \frac{-e/m}{\omega_0^2 - \omega^2 - i\gamma\omega} E_0}$$

which means the physical displacement is

$$x(t) = \frac{(e/m)E_0}{\sqrt{\left(\omega_0^2 - \omega^2\right)^2 + \gamma^2\omega^2}} \cos\left(\omega t - \beta\right)$$

with $\tan\beta = \dfrac{\gamma\omega}{\omega_0^2 - \omega^2}$ and $E(t) = E_0 \cos\left(\omega t\right)$

A reminder: matter – field interaction

The absorbed power is

$$P = \left\langle \vec{F} \cdot \vec{v} \right\rangle$$

$$P = \left\langle -e\widetilde{E} \cdot \frac{i\omega(e/m)}{\omega_0^2 - \omega^2 - i\gamma\omega} \widetilde{E} \right\rangle$$

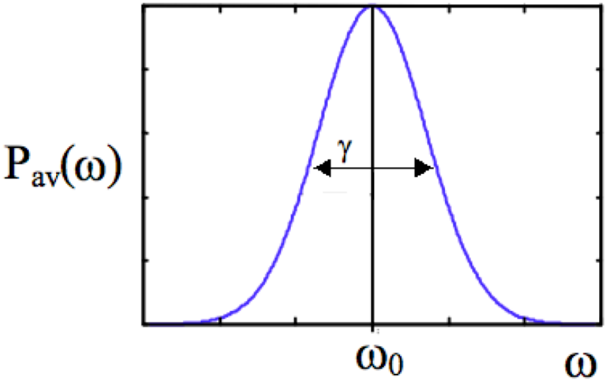
$$P = Re\left[-\frac{i\omega(e^2/m)}{\omega_0^2 - \omega^2 - i\gamma\omega} \frac{E_0^2}{2} \right]$$

$$\boxed{P = \frac{\gamma\omega^2 e^2/(2m)}{(\omega_0^2 - \omega^2)^2 + \gamma^2\omega^2} E_0^2}$$

A reminder: matter – field interaction

- Absorption is frequency dependent with a Lorentzian lineshape

LORENTZIAN LINESHAPE
peak is at $\omega = \omega_o$



At what frequency is the power absorbed reduced by ½?

$\omega - \omega_o = \pm\gamma/2$

The full-width at half-maximum intensity (FWHM) is γ .

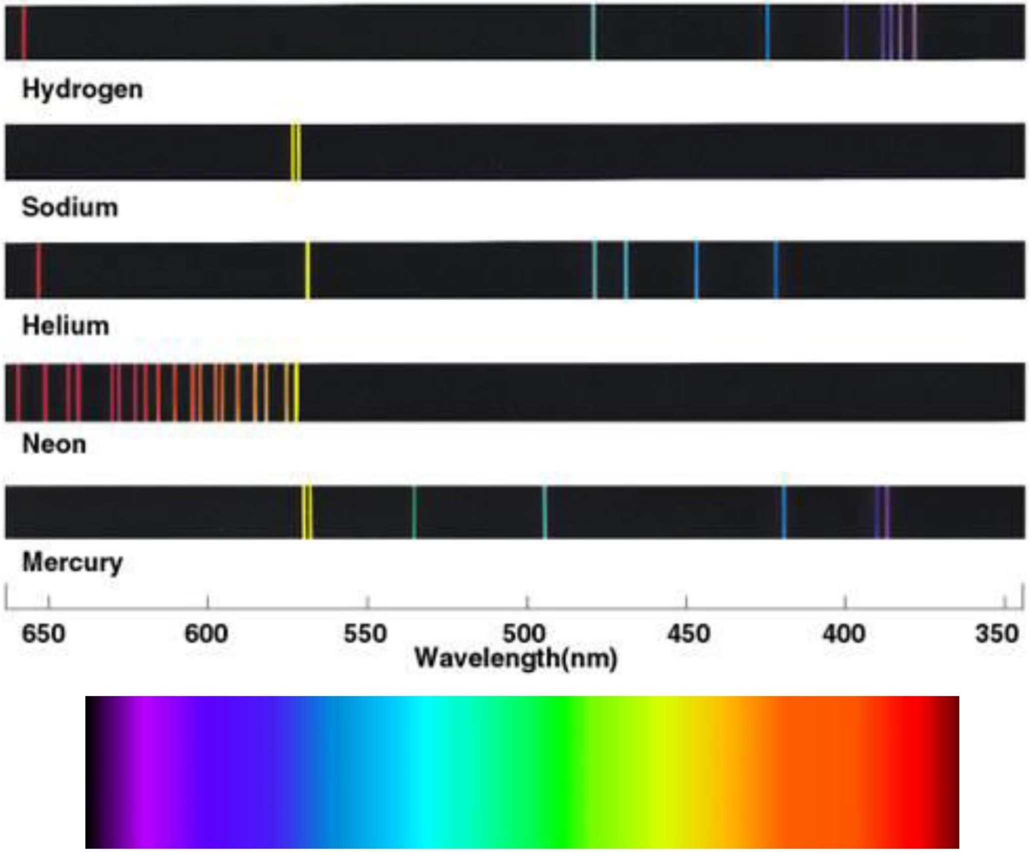
$$P = \frac{\gamma\omega^2 e^2/(2m)}{(\omega_0^2 - \omega^2)^2 + \gamma^2\omega^2} E_0^2$$

Spectral lines

- Atomic and molecular spectra: Absorption and emission of electromagnetic radiation (i.e., photons) by atoms and molecules occur only at discrete energy values.
- Classical physics would predict absorption or emission at all energies.

Spectral lines

- Every element has a DIFFERENT finger print.



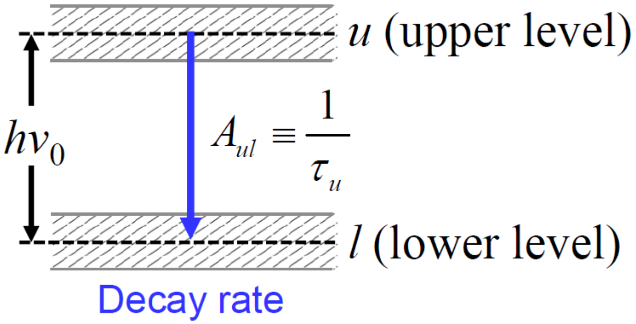
Spectral linewidth

Lorentzian Homogeneous (affects all molecules equally)	1. Natural broadening ➡ Result of finite radiative lifetime 2. Collisional/pressure broadening ➡ Finite lifetime in quantum state owing to collisions
Gaussian Inhomogeneous (affects certain class of molecule)	3. Doppler broadening ➡ Thermal motion
Lorentzian + Gaussian	4. Voigt profile ➡ Convolution of 1-3

Spectral linewidth

- Natural line broadening

1. Heisenberg uncertainty principle: $\Delta E_u \Delta t_u \geq h/2\pi$



ΔE_u = uncertainty in energy of u

$\Delta t_u = \tau$, the uncertainty in time of occupation of u

$\Delta E_u = h\Delta\nu_u = (h/2\pi)/(\Delta t = \tau_{rad})$ ➡ $\boxed{\Delta\nu_u = 1/2\pi\tau_{rad}}$ "lifetime" limited

2. In general

$$\Delta\nu_N = \Delta\nu_u + \Delta\nu_l = \frac{1}{2\pi}\left(\frac{1}{\tau_u} + \cancel{\frac{1}{\tau_l}}\right)$$

0 for ground state (natural broadening)

Spectral linewidth

- Natural line broadening

3. Typical values
    - Electronic transitions:

$$\tau_u \sim 10^{-8}\mathrm{s} \rightarrow \Delta\nu_N \sim 1.6\times10^{7}\,\mathrm{s}^{-1}$$

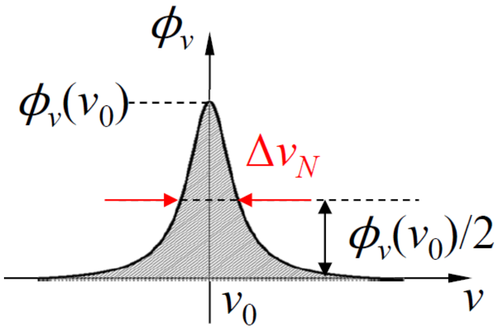
$$\Delta\omega_N,\mathrm{cm}^{-1} = \Delta\nu_N / c = 5\times10^{-4}\,\mathrm{cm}^{-1}$$

    - Vib-rot transitions

$$\tau_u \sim 10^{-2}\mathrm{s} \rightarrow \Delta\nu_N \sim 16\mathrm{s}^{-1}, \Delta\omega_N,\mathrm{cm}^{-1} = 5\times10^{-10}\,\mathrm{cm}^{-1}$$

    - These are typically much smaller than $\Delta\nu_D$ and $\Delta\nu_C$

4. Lineshape function – “Lorentzian” – follows from Fourier transform



$$\phi(\nu)_N = \frac{1}{\pi}\frac{\Delta\nu_N/2}{(\nu-\nu_0)^2+(\Delta\nu_N/2)^2}$$

Note: a) $\phi_{\max} = \phi(\nu_0) = \frac{2}{\pi}\frac{1}{\Delta\nu_N}$

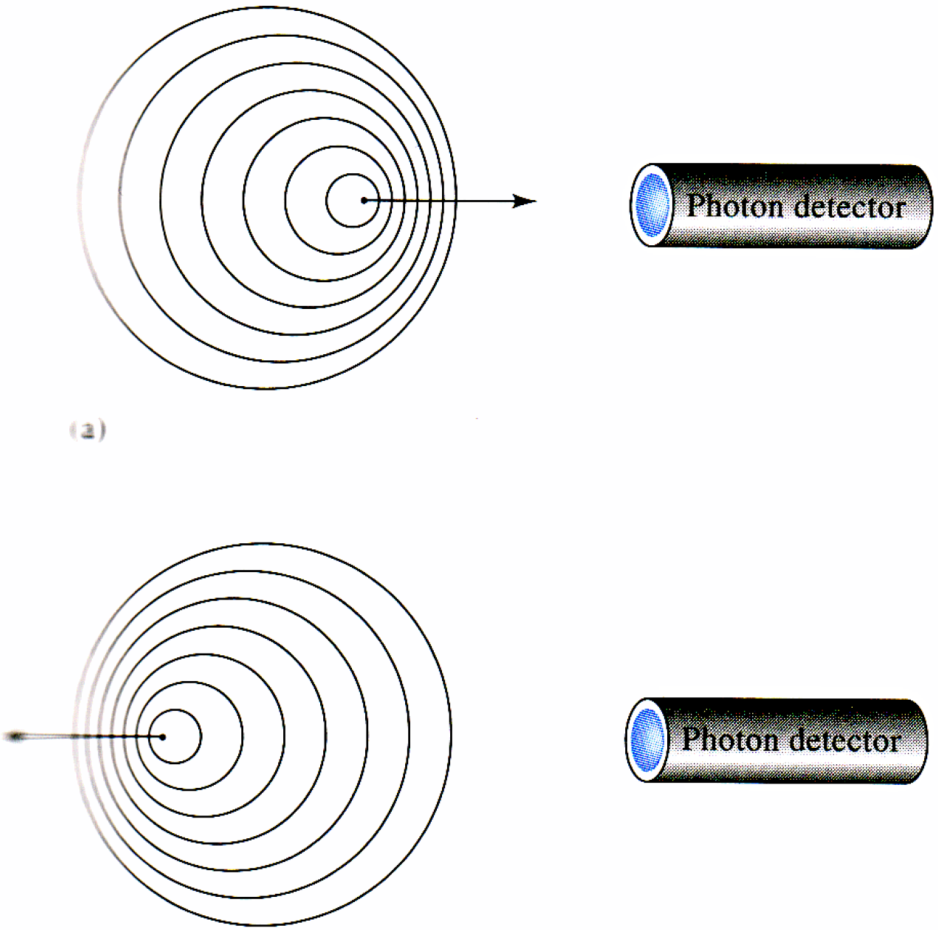
b) $\phi(\nu-\nu_0 = \Delta\nu_N/2) = \phi(\nu_0)/2$

Spectral linewidth

Line broadens due

1. **Uncertainty**
2. **Doppler effect**
3. Pressure
4. Electric and magnetic fields

$$\frac{\Delta\lambda}{\lambda_0} = \frac{v_{elocity}}{c}$$

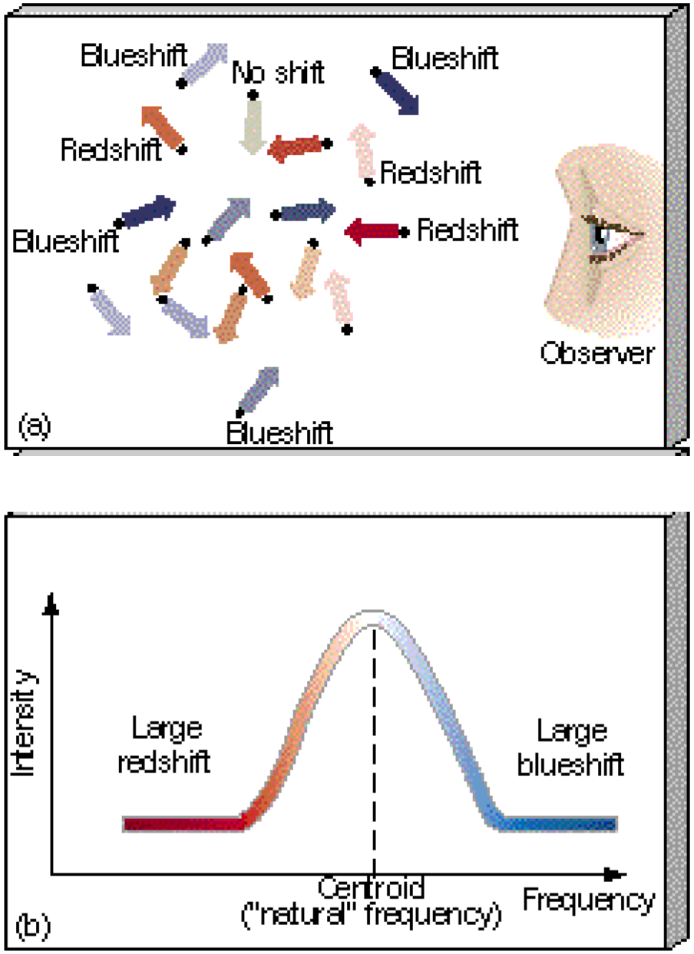


Spectral linewidth

Thermal Motion of Atoms

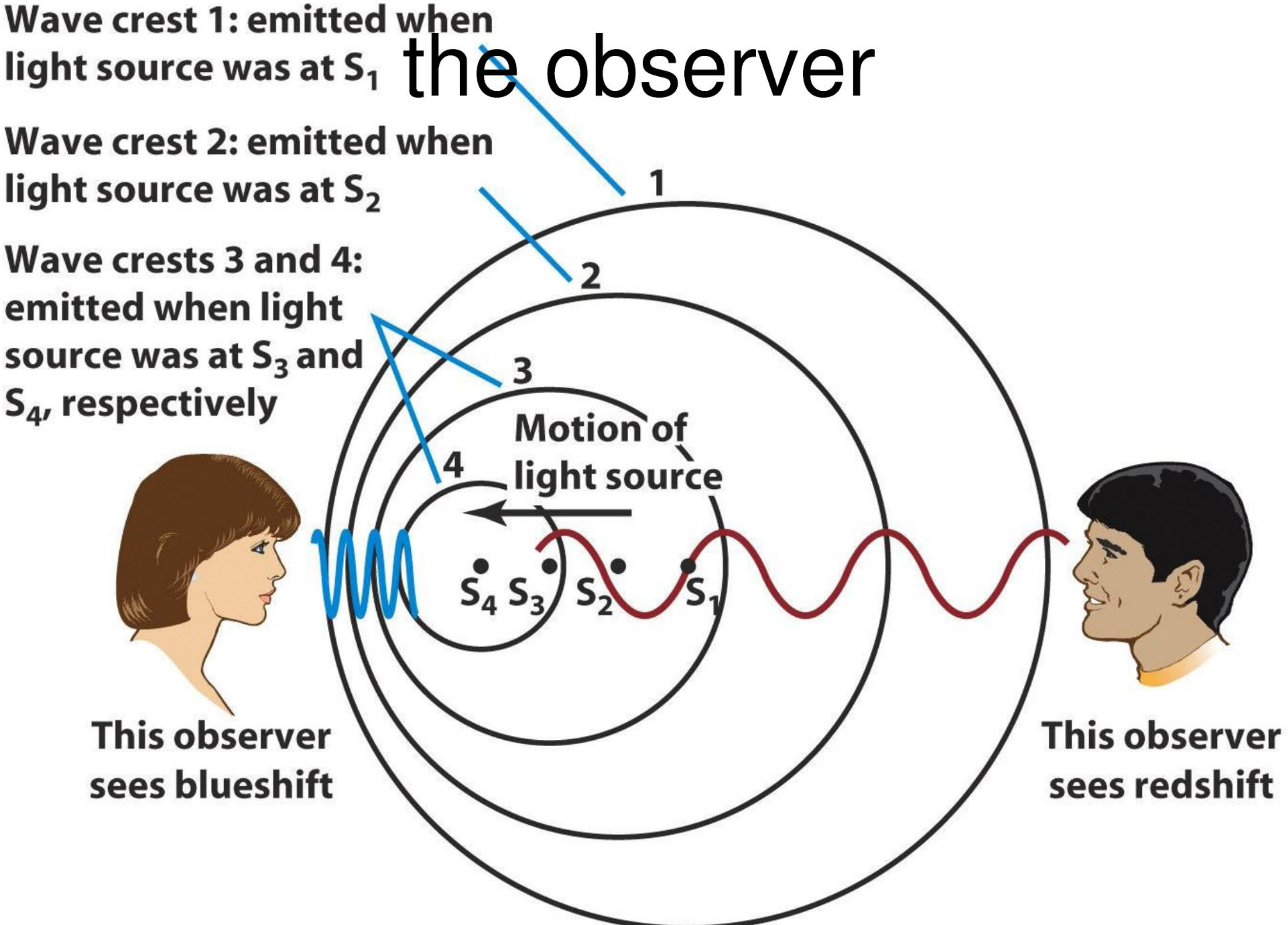
- **Atoms moving randomly.**
- **Redshifted, blueshifted, and unshifted emission lines created with respect to the observer.**
- **In the detector, individual redshifted and blueshifted emission lines merge with the unshifted lines to produce broadened spectral lines.**

$$\Delta \nu_D = \frac{\nu_0}{c}\sqrt{\frac{2kT}{m}}$$



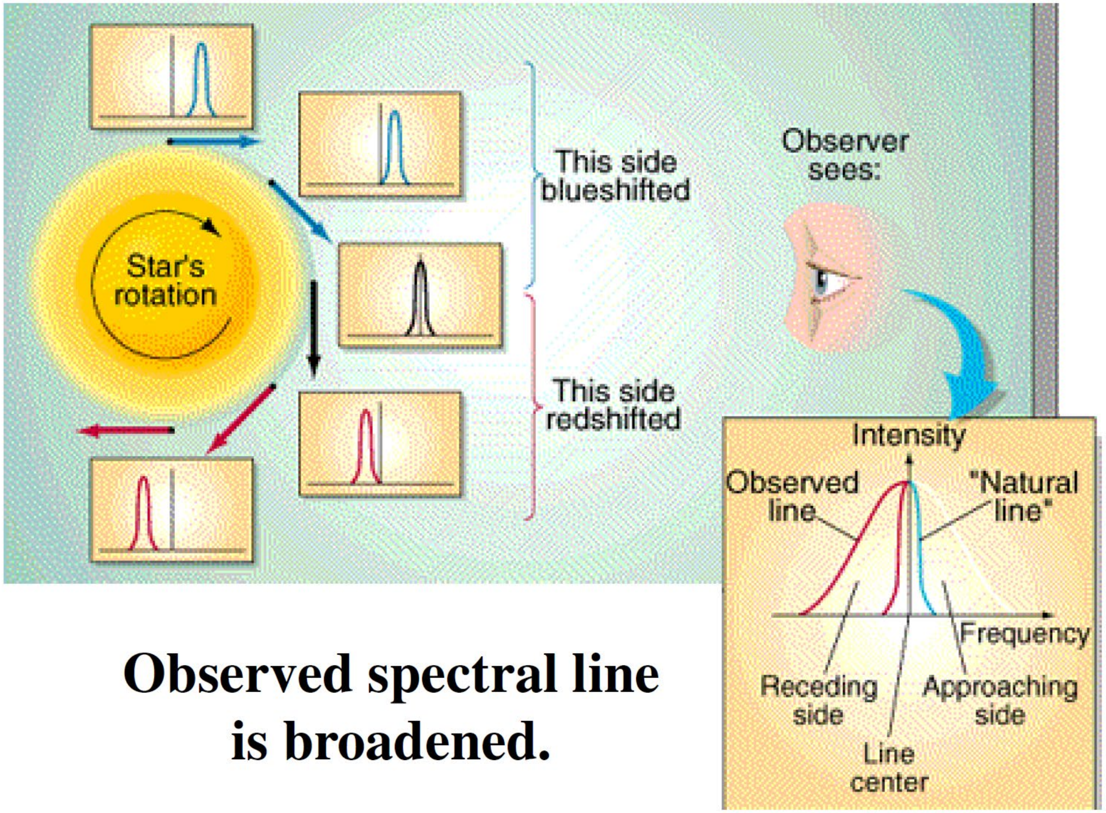
Spectral linewidth

affected by the relative motion between the source and the observer



Spectral linewidth
Doppler Effect: Rotation

- **Rotation of star/gas will produce a broadening of spectral lines.**
- **Photons emitted from side *spinning toward us*, *blueshifted*.**
- **Photons emitted from side *spinning away from us*, *redshifted*.**



Observed spectral line is broadened.

Spectral linewidth

Doppler Shifts

- **Red Shift**: The object is moving away from the observer
- **Blue Shift**: The object is moving towards the observer

$$\Delta\lambda/\lambda_o = v/c$$

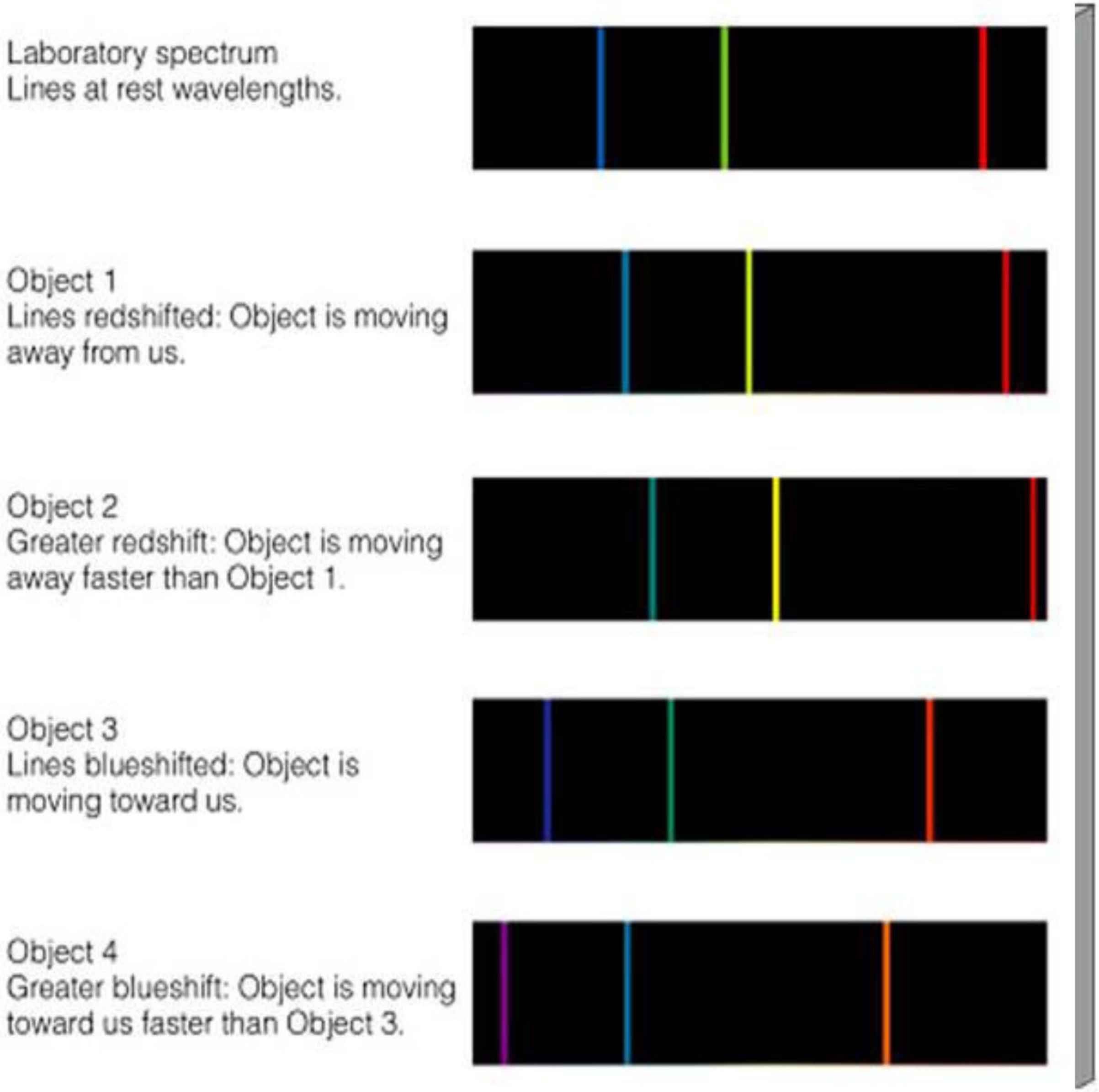
$\Delta\lambda$ = wavelength shift

λ_o = wavelength if source is not moving

v = velocity of source

c = speed of light

Spectral linewidth



Laboratory spectrum
Lines at rest wavelengths.

Object 1
Lines redshifted: Object is moving away from us.

Object 2
Greater redshift: Object is moving away faster than Object 1.

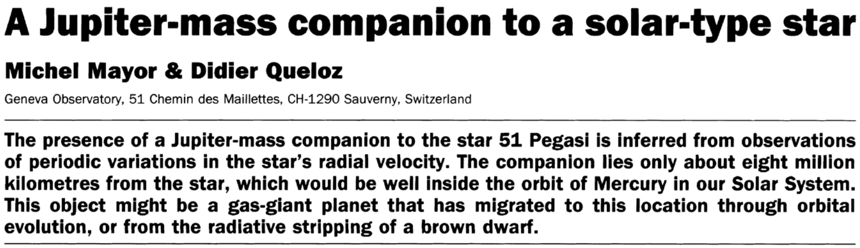
Object 3
Lines blueshifted: Object is moving toward us.

Object 4
Greater blueshift: Object is moving toward us faster than Object 3.

Doppler Shift

- The greater the velocity the greater the shift.

Doppler effect and 2019 Nobel Prize

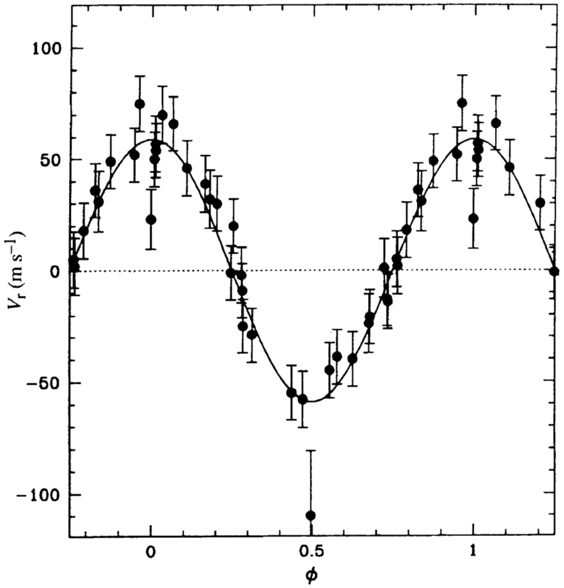


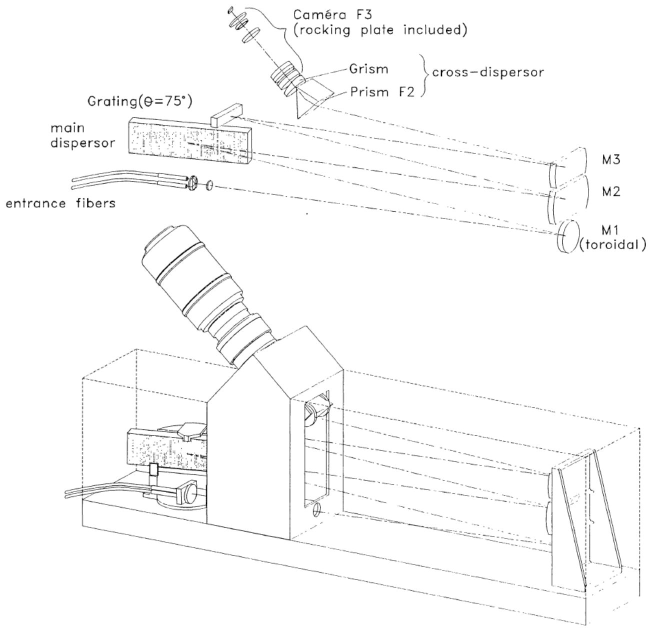
A Jupiter-mass companion to a solar-type star

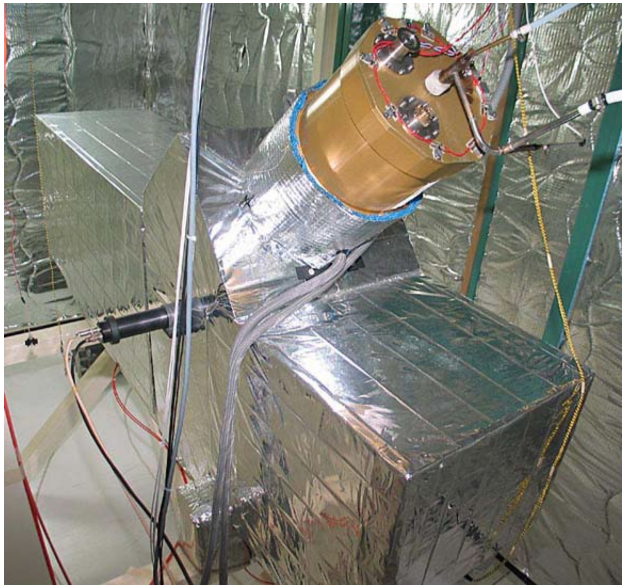
Michel Mayor & Didier Queloz

Geneva Observatory, 51 Chemin des Maillettes, CH-1290 Sauverny, Switzerland

The presence of a Jupiter-mass companion to the star 51 Pegasi is inferred from observations of periodic variations in the star's radial velocity. The companion lies only about eight million kilometres from the star, which would be well inside the orbit of Mercury in our Solar System. This object might be a gas-giant planet that has migrated to this location through orbital evolution, or from the radiative stripping of a brown dwarf.



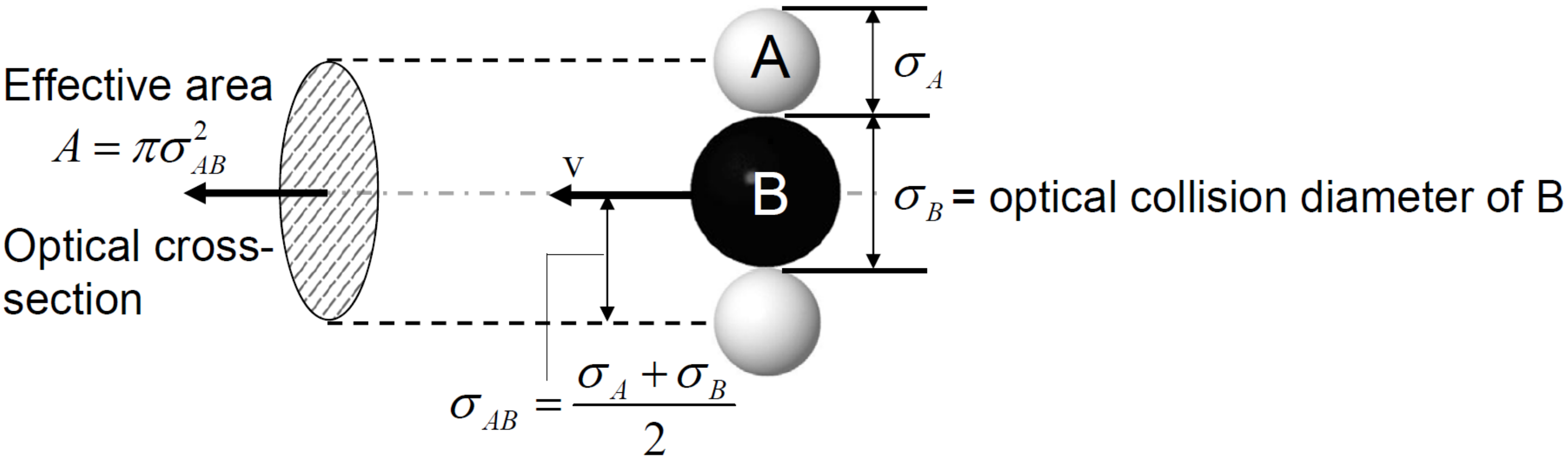




Title: ELODIE: A spectrograph for accurate radial velocity measurements.
Authors: Baranne, A., Queloz, D., Mayor, M., Adrianzyk, G., Knispel, G., Kohler, D., ,
Journal: Astronomy and Astrophysics Supplement, v.119, p.373-390

Spectral linewidth

- Collision broadening
  1. Also lifetime limited – time set by collision time interval



Effective area

$A = \pi\sigma_{AB}^2$

Optical cross-section

σ_B = optical collision diameter of B

$$\sigma_{AB} = \frac{\sigma_A + \sigma_B}{2}$$

$$Z_{BA} = \#\,\text{collision/s of a single B with all A}$$

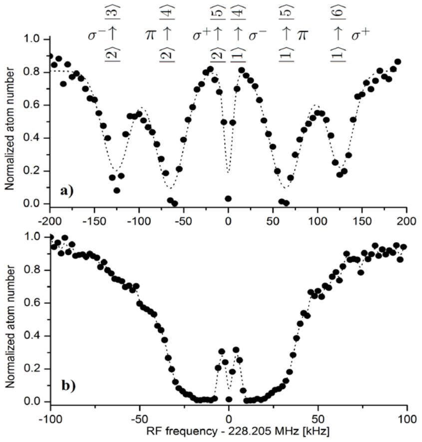
$$= \overset{\text{\#/cc}}{n_A} \cdot \pi\sigma_{AB}^2 \cdot \left(\bar{c} = \sqrt{\frac{8kT}{\pi\mu_{AB}}}\right)$$

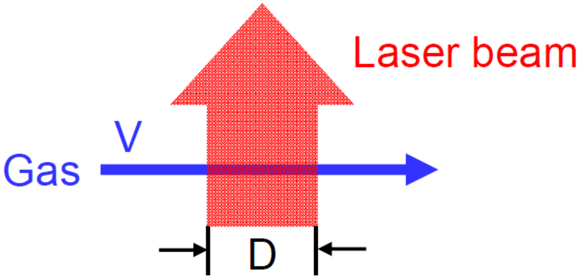
$$\mu_{AB} = \frac{m_A m_B}{m_A + m_B}$$

Lineshape function – Lorentzian $\phi(\nu)_{coll} = \dfrac{1}{\pi}\dfrac{\Delta\nu_C/2}{(\nu-\nu_0)^2 + (\Delta\nu_C/2)^2}$

Spectral linewidth

- Stark broadening
  - Important in charged gases, i.e., plasmas.
  - Coulomb forces perturb energy levels
- Types of instrument broadening
  - Instruments have insufficient resolution
  - Powerful lasers can perturb populations away from equilibrium (saturation effect)
  - Transit-time broadening
- Another type of lifetime-limited broadening is transit-time broadening





$$\text{Transit time} \approx D/V$$

$$\therefore \Delta\nu_{transit} \approx V/D$$

for apparent broadening of an abs. line

Reference: Demtröder p.85-p.88

$$A(\omega) = \frac{1}{\sqrt{2\pi}} \int_0^T X_0 \cos(\omega_0 t) e^{-i\omega t} dt$$

$$I(\omega) = C \frac{\sin^2[(\omega - \omega_0)T/2]}{(\omega - \omega_0)^2}$$

Spectral linewidth

Intensity of spectral lines

- The transition probability between the two states (selection rules)

Transition dipole moment

$$\mu_{fi} = \int \Psi_f \hat{\mu} \Psi_i \, d\tau = \left\langle \Psi_f \left| \hat{\mu} \right| \Psi_i \right\rangle$$

Only if this integral is non-zero, the transition is allowed

Spectral linewidth

Selections rules
Electric dipole moment operator

- The probability for a vibrational transition to occur, i.e. the intensity of the different lines in the IR spectrum, is given by the transition dipole moment μ_{fi} between an initial vibrational state υ_i and a vibrational final state υ_f :

$$\mu_{fi} = \int \upsilon_f \hat{\mu} \upsilon_i \, d\tau = \langle \upsilon_f | \hat{\mu} | \upsilon_i \rangle$$

$$\mu(x) = \mu_0 + \left(\frac{\partial \mu}{\partial x} \right)_0 x + \frac{1}{2} \left(\frac{\partial^2 \mu}{\partial x^2} \right)_0 x^2 + \ldots$$

The electric dipole moment operator depends on the location of all electrons and nuclei, so its varies with the modification in the intermolecular distance “x”. $\mu 0$ is the permanent dipole moment for the molecule in the equilibrium position Re

Spectral linewidth

$$\mu_{fi} = \mu_0 \underset{\substack{\shortparallel \\ 0}}{\cancel{\int \upsilon_f}\, \upsilon_i \, d\tau} + \left(\frac{\partial \mu}{\partial x}\right)_0 \int \upsilon_f \, x \upsilon_i \, d\tau + \frac{1}{2}\left(\cancel{\frac{\partial^2 \mu}{\partial x^2}}\right)_0 \int \upsilon_f \, x^2 \upsilon_i \, d\tau + \ldots$$

The two states υ_i and υ_f are orthogonal.
Because they are solutions of the operator H which is Hermitian

The higher terms can be neglected for small displacements of the nuclei

Spectral linewidth

$$\mu_{fi} = \underbrace{\left(\frac{\partial \mu}{\partial x}\right)_0} \int \underbrace{\upsilon_f \, x \upsilon_i \, d\tau}$$

First condition: $\mu_{fi} = 0$, if $\boxed{\partial\mu / \partial x = 0}$

In order to have a vibrational transition visible in IR spectroscopy: the electric dipole moment of the molecule must change when the atoms are displaced relative to one another. Such vibrations are " infrared active". It is valid for polyatomic molecules.

Second condition: $\int \upsilon_f \, x \upsilon_i \, d\tau \neq 0$

By introducing the wavefunctions of the initial state υ_i and final state υ_f , which are the solutions of the SE for an harmonic oscillator, the following selection rules is obtained:

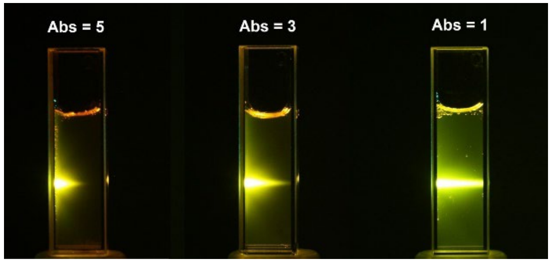
$\boxed{\Delta\upsilon = \pm 1}$

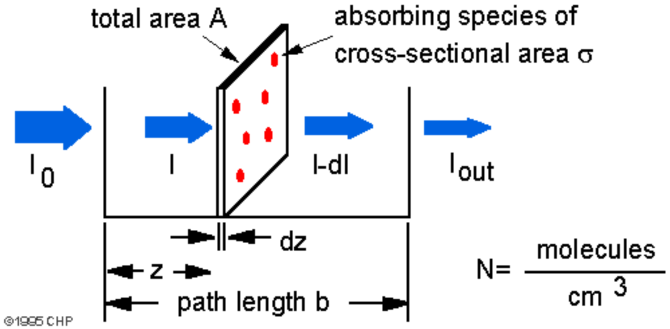
Spectral linewidth

Note 1: Vibrations in homonuclear diatomic molecules do not create a variation of μ ➔ not possible to study them with IR spectroscopy.

Note 2: A molecule without a permanent dipole moment can be studied, because what is required is a variation of μ with the displacement. This variation can start from 0.

Beer-Lambert law





$$\frac{dI}{I_z} = -\sigma N\,dz$$

$$\ln(I) - \ln(I_0) = -\sigma N b$$

$$-\ln\left(\frac{I}{I_0}\right) = -\sigma N b$$

Beer-Lambert law

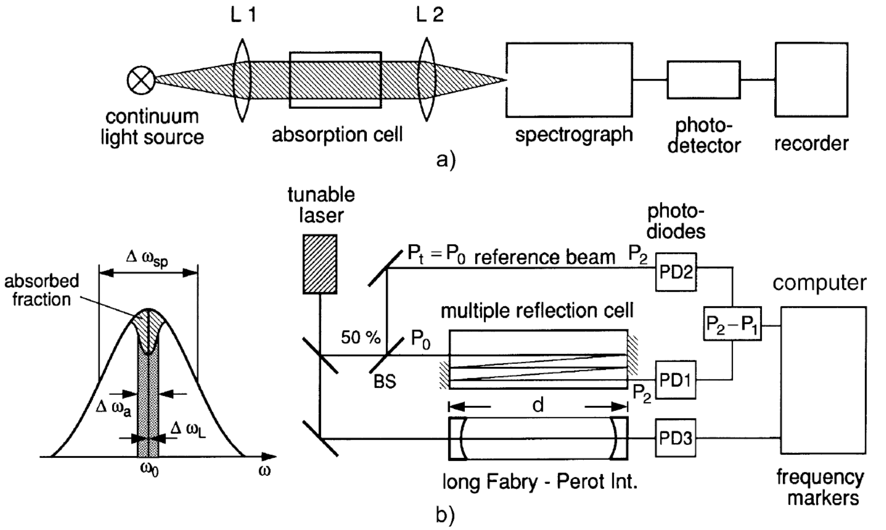


Fig. 1.1 Comparison between absorption spectroscopy with a broadband incoherent source (**a**) and with a tunable single-mode laser (**b**)

$$P_T = P_0 \cdot e^{-\alpha L} \approx P_0(1 - \alpha L)$$

$$\Delta P = P_0 - P_T = P_0 \alpha L$$

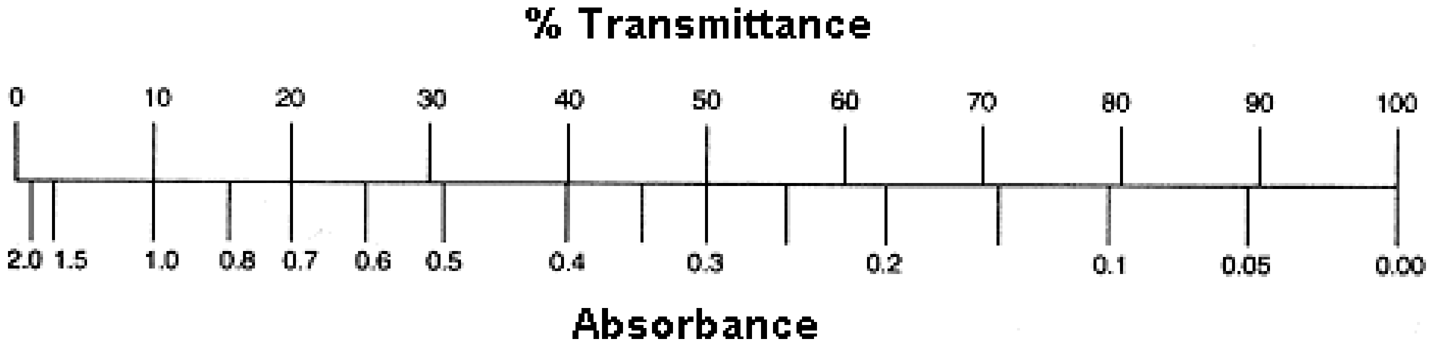
$$P_A(\lambda) = a\left[P_0(\lambda) - P_T(\lambda)\right] = a\left[b P_R(\lambda) - P_T(\lambda)\right]$$

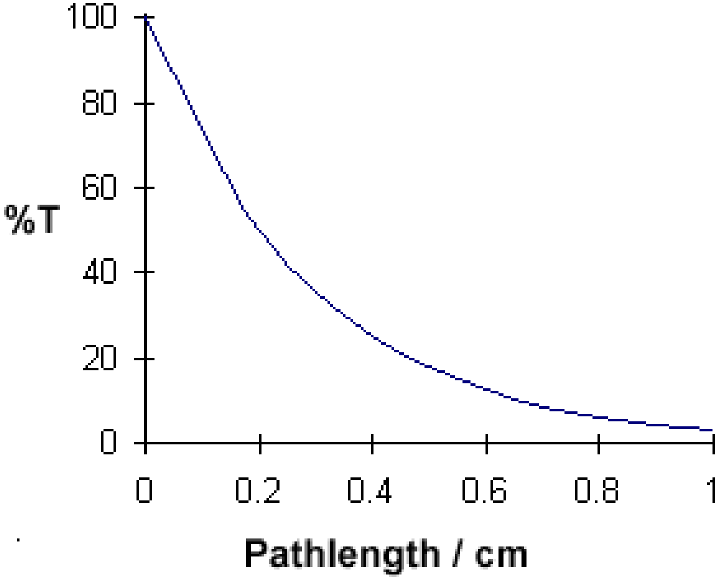
$$P_A(\omega)\,d\omega = a\left[b P_R(\omega) - P_T(\omega)\right] d\omega$$

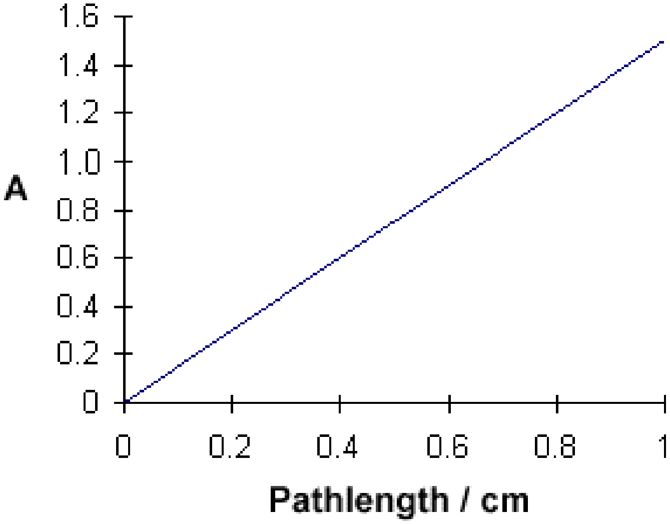
$$\alpha(\lambda) = N_i \cdot \sigma_{ik}(\lambda)$$

$$S = a \Delta P = a \cdot P_0 \cdot N_i \cdot \sigma_{ik} \cdot L$$

Transmittance, Absorbance, and Cell Pathlength

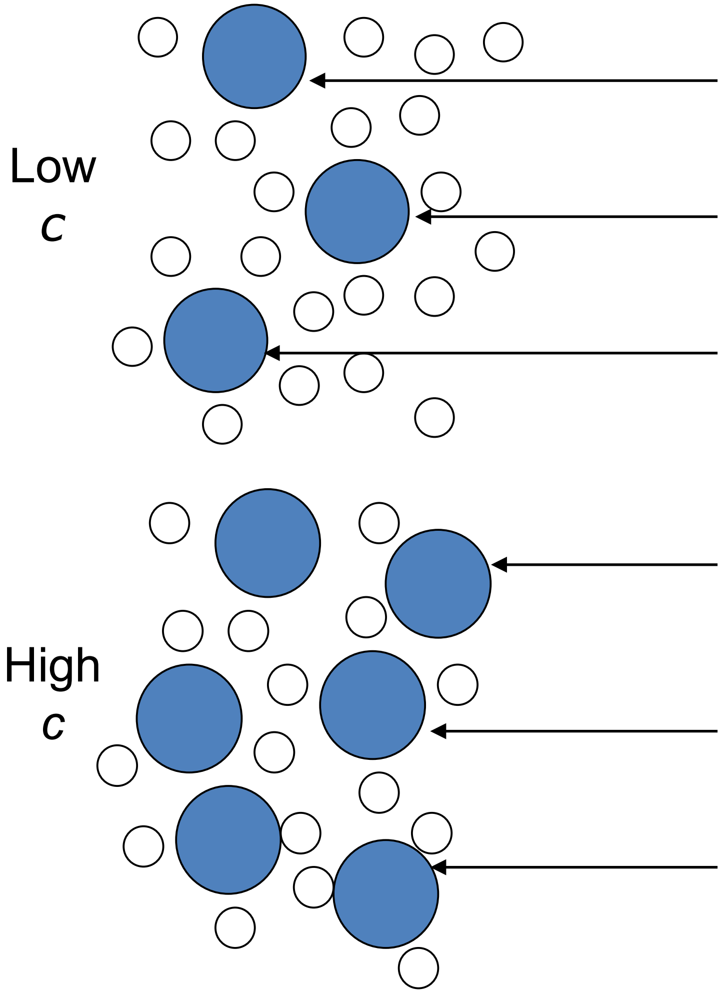


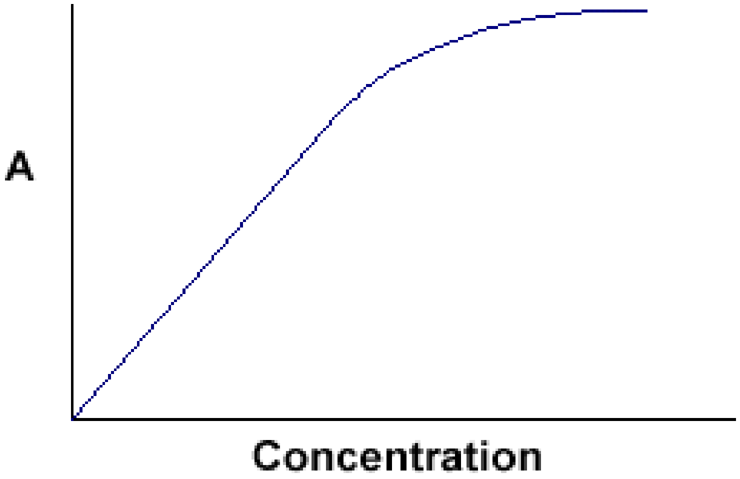




http://www.shu.ac.uk/schools/sci/chem/tutorials/molspec/beers1.htm

Deviations from the Beer-Lambert Law

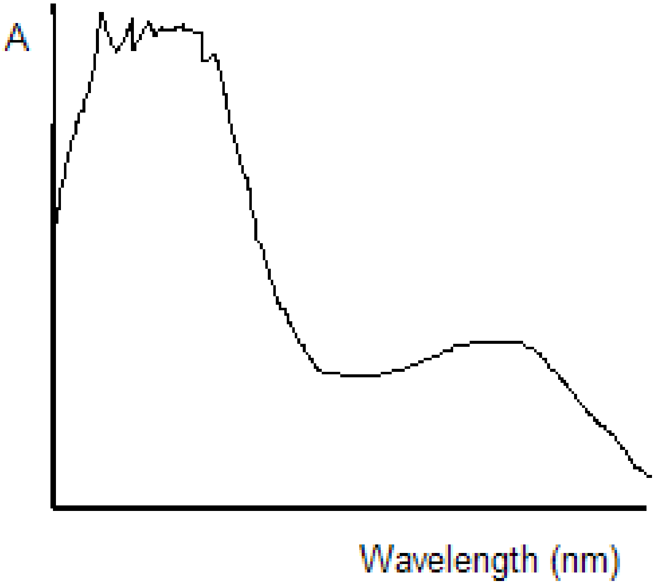




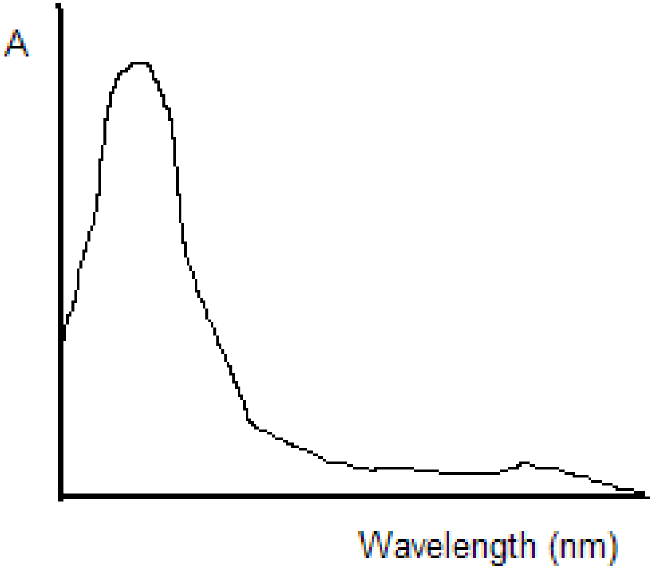
The Beer-Lambert law assumes that all molecules contribute to the absorption and that no absorbing molecule is in the shadow of another

http://www.shu.ac.uk/schools/sci/chem/tutorials/molspec/beers1.htm

Sample Concentrations

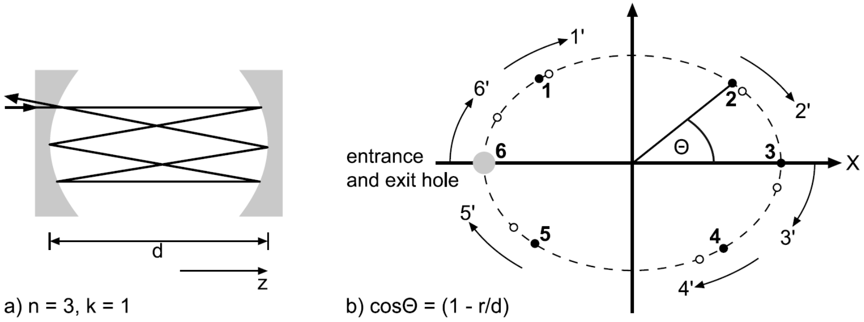


Solution too concentrated



Diluted five-fold

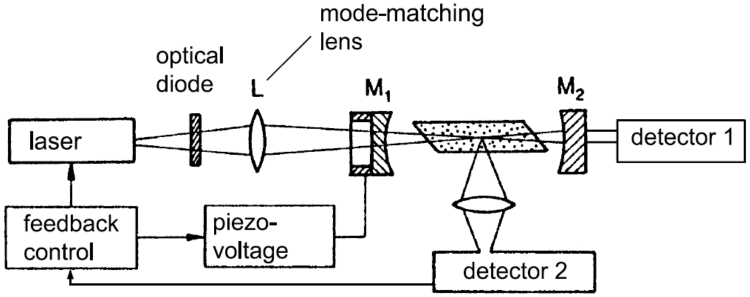
Enhancement of absorption with cavities

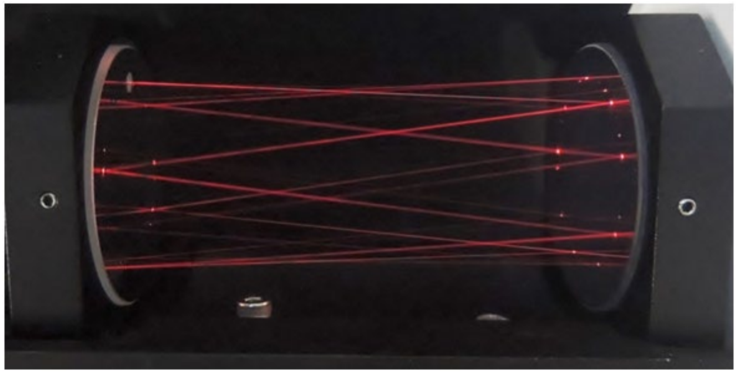


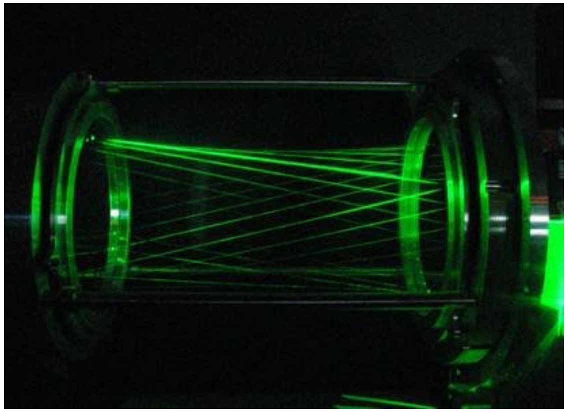
a) n = 3, k = 1

b) cosΘ = (1 - r/d)

Fig. 1.2 Multipass absorption cell. (**a**) Beam geometry, (**b**) laser beam spots on a mirror surface







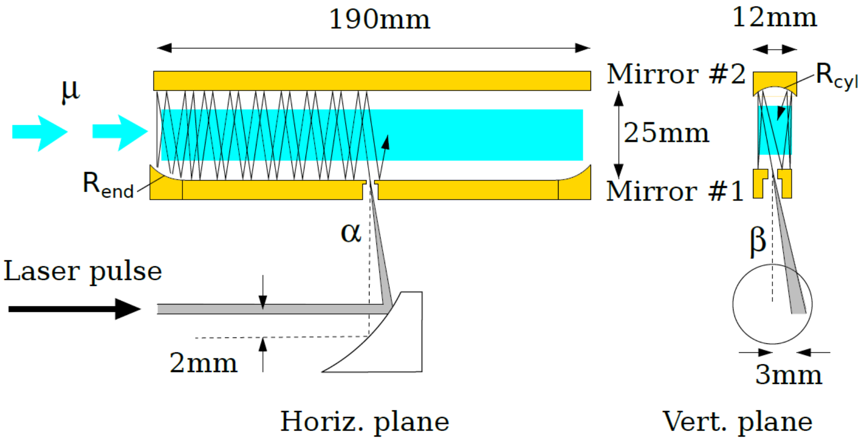
Increase length

$$\exp[-2(1-R)].$$

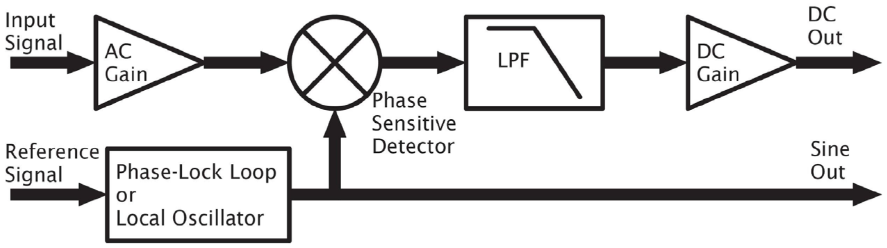
$$I_0 \exp[-2q(1-R)-2q\alpha L]$$

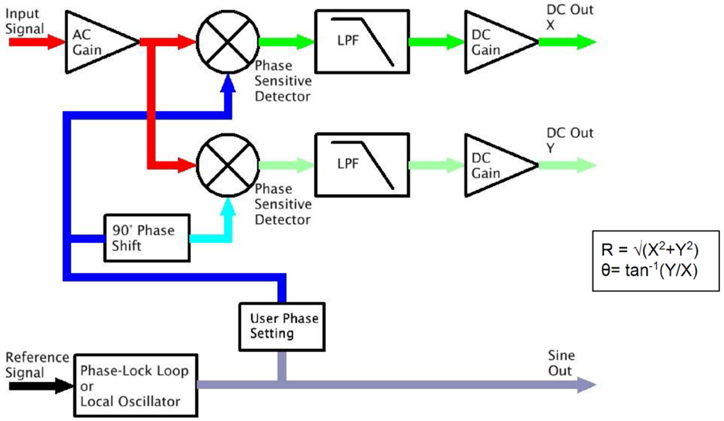
Increase power: resonant cavities

$$P_{\mathrm{i}} = P_0/(1-R)$$



Lock-in detection





$$\mathbf{\sin(a)\,\sin(b) = [\,\cos(a-b) - \cos(a+b)\,] / 2}$$

$$\mathbf{\sin(a)\,\cos(b) = [\,\sin(a-b) + \sin(a+b)\,] / 2}$$

input signal $s(t)=\sqrt{2}\,V_{sig}\sin(2\pi f_{sig}t + \theta_{sig})$ where V_{sig} is the *RMS* signal

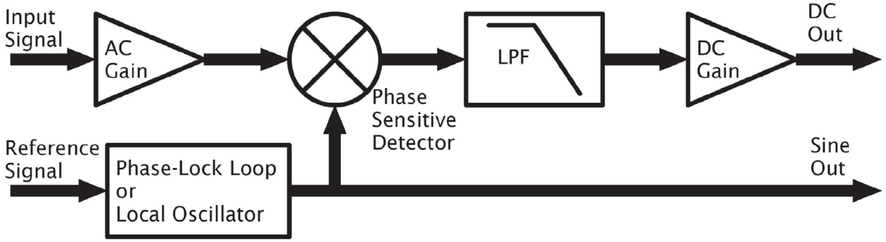
ref. oscillators $r_X(t)=\sin(2\pi f_{ref}t+\theta_{ref})$; $r_Y(t)=\sin(2\pi f_{ref}t+\theta_{ref}+\pi/2) =\cos(2\pi f_{ref}t+\theta_{ref})$

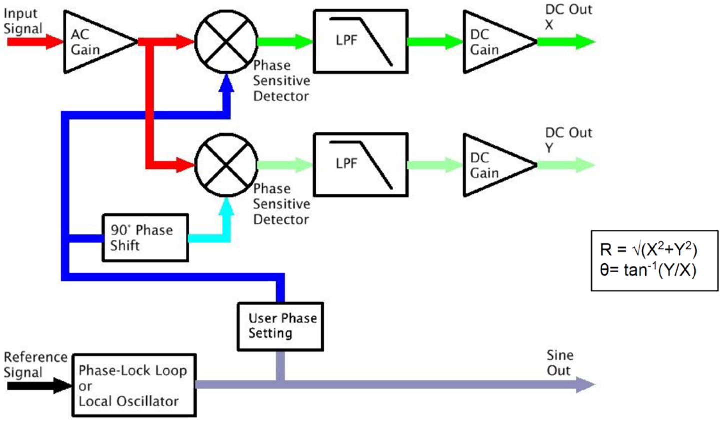
PSD outputs: $V_{psd\text{-}X}= s(t)\,r_X(t)$; $V_{psd\text{-}Y}= s(t)\,r_Y(t)$

$$V_{psd\text{-}X} = (V_{sig}/\sqrt{2})\left\{\cos(2\pi[f_{sig}-f_{ref}]t + \theta_{sig} - \theta_{ref}) - \cos(2\pi[f_{sig}+f_{ref}]t + \theta_{sig} + \theta_{ref})\right\}$$

$$V_{psd\text{-}Y} = (V_{sig}/\sqrt{2})\left\{\sin(2\pi[f_{sig}-f_{ref}]t + \theta_{sig} - \theta_{ref}) + \sin(2\pi[f_{sig}+f_{ref}]t + \theta_{sig} + \theta_{ref})\right\}$$

Lock-in detection





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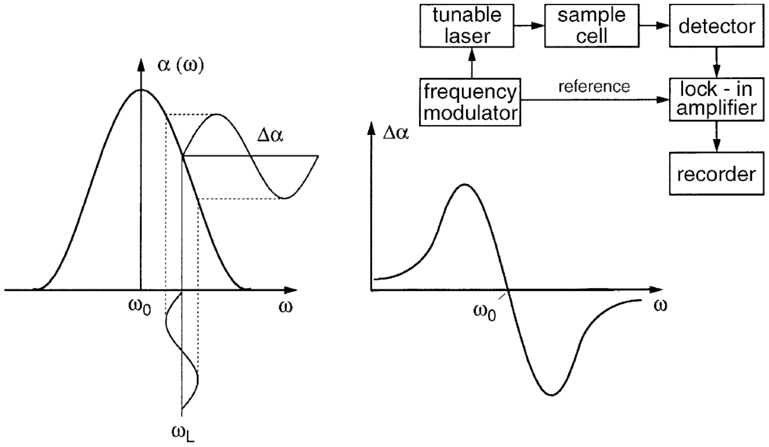
$$V_{psd\text{-}Y} = (V_{sig}/\sqrt{2})\,\{\sin(2\pi[f_{sig}-f_{ref}]t+\theta_{sig}-\theta_{ref}) + \sin(2\pi[f_{sig}+f_{ref}]t+\theta_{sig}+\theta_{ref})\}$$

The “DC” term

The “2f” term

Frequency modulation



When laser is tuned through the absorption spectrum

$$\Delta P_{\mathrm{T}} = P_{\mathrm{T}}(\omega_{\mathrm{L}} - \Delta\omega_{\mathrm{L}}/2) - P_{\mathrm{T}}(\omega_{\mathrm{L}} + \Delta\omega_{\mathrm{L}}/2)$$

$$\frac{\mathrm{d}\alpha(\omega)}{\mathrm{d}\omega} = -\frac{1}{P_{\mathrm{R}}L}\frac{\mathrm{d}P_{\mathrm{T}}}{\mathrm{d}\omega}$$

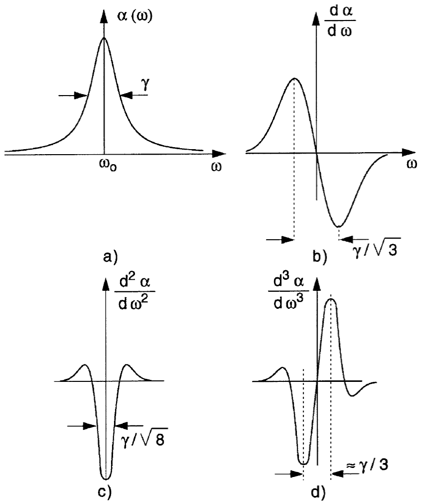
For sinusoidal frequency modulation

$$\omega_{\mathrm{L}}(t) = \omega_0 + a\sin\Omega t$$

$$P_{\mathrm{T}}(\omega_{\mathrm{L}}) = P_{\mathrm{T}}(\omega_0) + \sum_n \frac{a^n}{n!}\sin^n \Omega t\left(\frac{\mathrm{d}^n P_{\mathrm{T}}}{\mathrm{d}\omega^n}\right)_{\omega_0}$$

$$\left(\frac{\mathrm{d}^n P_{\mathrm{T}}}{\mathrm{d}\omega^n}\right)_{\omega_0} = -P_0 x\left(\frac{\mathrm{d}^n \alpha(\omega)}{\mathrm{d}\omega^n}\right)_{\omega_0}$$

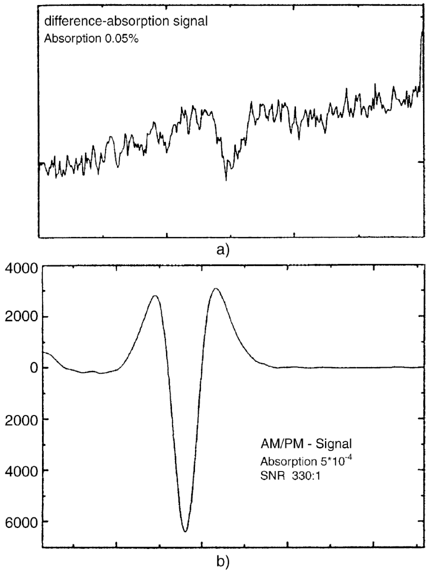
Frequency modulation



$$\begin{aligned}\frac{\Delta P_{\mathrm{T}}}{P_0} = -aL\Bigg\{&\left[\frac{a}{4}\left(\frac{\mathrm{d}^2\alpha}{\mathrm{d}\omega^2}\right)_{\omega_0} + \frac{a^3}{64}\left(\frac{\mathrm{d}^4\alpha}{\mathrm{d}\omega^4}\right)_{\omega_0} + \dots\right]\\
&+\left[\left(\frac{\mathrm{d}\alpha}{\mathrm{d}\omega}\right)_{\omega_0} + \frac{a^2}{8}\left(\frac{\mathrm{d}^3\alpha}{\mathrm{d}\omega^3}\right)_{\omega_0} + \dots\right]\sin(\Omega t)\\
&+\left[-\frac{a}{4}\left(\frac{\mathrm{d}^2\alpha}{\mathrm{d}\omega^2}\right)_{\omega_0} + \frac{a^3}{48}\left(\frac{\mathrm{d}^4\alpha}{\mathrm{d}\omega^4}\right)_{\omega_0} + \dots\right]\cos(2\Omega t)\\
&+\left[-\frac{a^2}{24}\left(\frac{\mathrm{d}^3\alpha}{\mathrm{d}\omega^3}\right)_{\omega_0} + \frac{a^4}{384}\left(\frac{\mathrm{d}^5\alpha}{\mathrm{d}\omega^5}\right)_{\omega_0} + \dots\right]\sin(3\Omega t)\\
&+\dots\Bigg\}.\end{aligned}$$

For small modulation amplitudes, the first terms in brackets are dominant.

With lock-in detection:



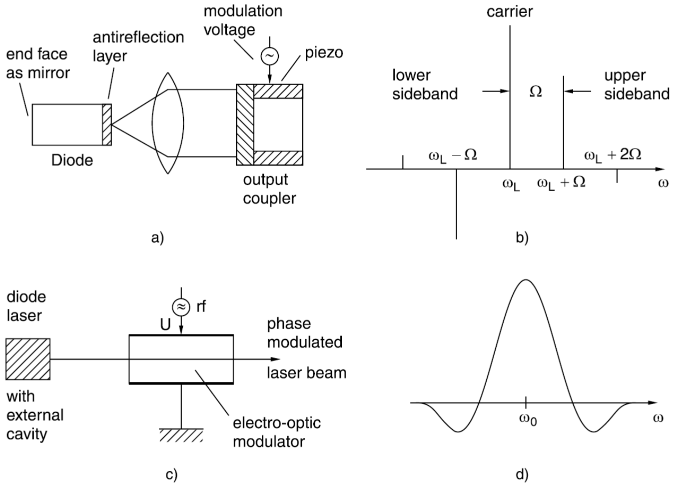
$$S(n\Omega) = \left(\frac{\Delta P_{\mathrm{T}}}{P_0}\right)_{n\Omega} = aL\begin{cases} b_n \sin(n\Omega t), & \text{for } n = 2m+1\\ c_n \cos(n\Omega t), & \text{for } n = 2m.\end{cases}$$

$$S(\Omega) = -aL\frac{\mathrm{d}\alpha}{\mathrm{d}\omega}\sin(\Omega t),$$

$$S(2\Omega) = +\frac{a^2 L}{4}\frac{\mathrm{d}^2\alpha}{\mathrm{d}\omega^2}\cos(2\Omega t),$$

$$S(3\Omega) = +\frac{a^3 L}{24}\frac{\mathrm{d}^3\alpha}{\mathrm{d}\omega^3}\sin(3\Omega t).$$

Frequency modulation



Cavity length modulation

$$\nu = q \cdot (c/2d).$$

$$\Delta\nu = -q\left(c/2d^2\right)\Delta d$$

Electro-optic modulation

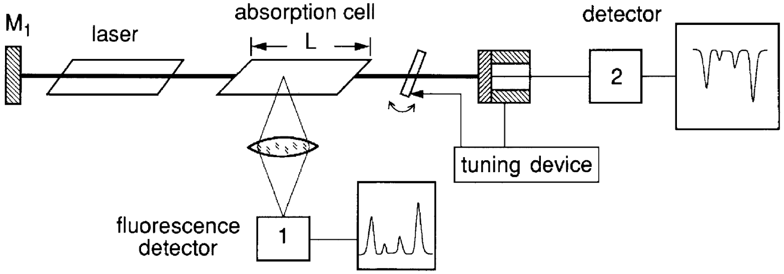
$$\Delta\phi = \frac{\pi n_0^3 rV}{\lambda} \cdot \frac{l}{d}$$

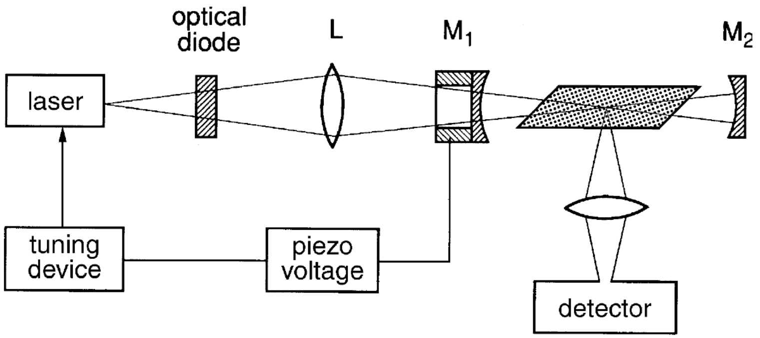
$$2\pi f\left(t\right) \equiv \frac{d\phi\left(t\right)}{dt} = \omega + \frac{d\phi\left(t\right)}{dt}$$

$$E_{pm} = E_0 e^i\left[\omega t + m\sin\Omega t\right] \equiv E_0\left\{\sum_{k=0}^{\infty} J_k\left(m\right)e^{ik\Omega t} + \sum_{k=0}^{\infty}\left(-1\right)^k J_k\left(m\right)e^{-ik\Omega t}\right\}e^{i\omega t}$$

$$E_{pm} = E_0\left[1 + im\sin\Omega t\right]e^{i\omega t}.$$

Intracavity/external resonator laser absorption spectroscopy





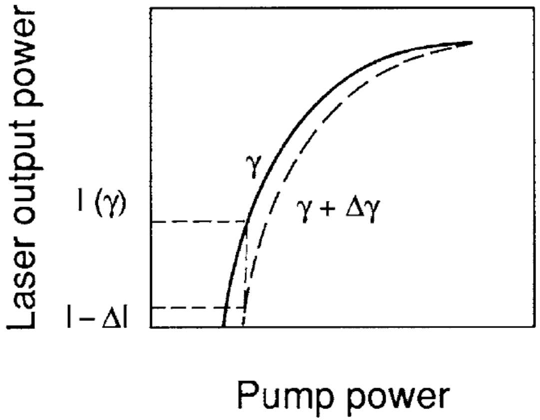
1 $$R_2 = 1 - T_2 \quad q = 1/T_2 \quad \alpha L \ll 1$$

$$P_{\text{int}} = q\,P_{\text{out}}$$

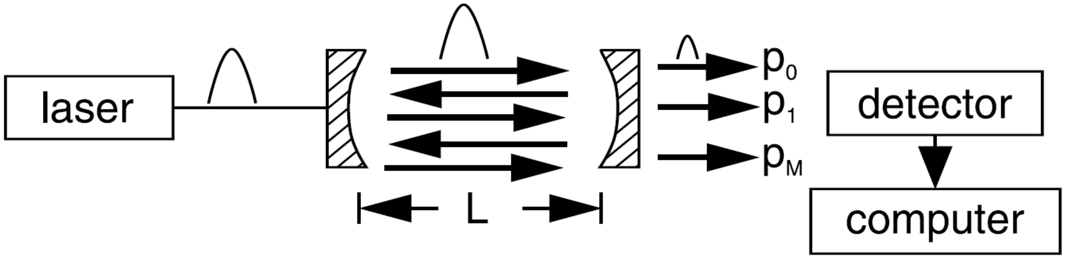
power absorbed at the frequency ω in the absorption cell (length L)

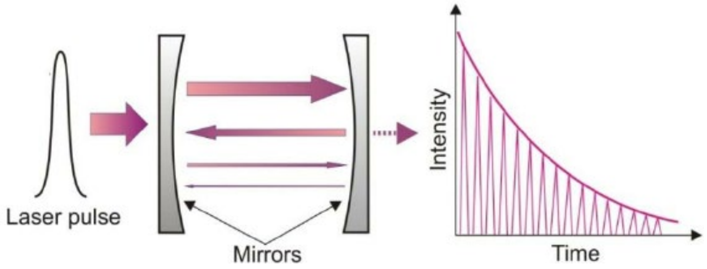
$$\Delta P(\omega) = \alpha(\omega) L P_{\text{int}} = q\alpha(\omega) L P_{\text{out}}$$

2 $$\Delta P/P = \frac{g_0}{g_0 - \gamma}\frac{\Delta\gamma}{\gamma + \Delta\gamma} \simeq \frac{g_0}{\gamma}\frac{\Delta\gamma}{g_0 - \gamma}, \quad \text{for } \Delta\gamma \ll \gamma$$



Cavity Ring Down Spectroscopy





Input power P_0 , T=1-R-A

$$P_1 = T^2 e^{-\alpha L} \cdot P_0$$

$$R^2 \cdot \exp(-2\alpha L)$$

$$P_n = \left[R \cdot e^{-\alpha L}\right]^{2n} P_1 = \left[(1 - T - A)e^{-\alpha L}\right]^{2n} P_1$$

$$P_n = P_1 \cdot e^{+2n(\ln R - \alpha \cdot L)}$$

Or for high reflectivity mirrors lnR ≈ R – 1 = -(T+A)

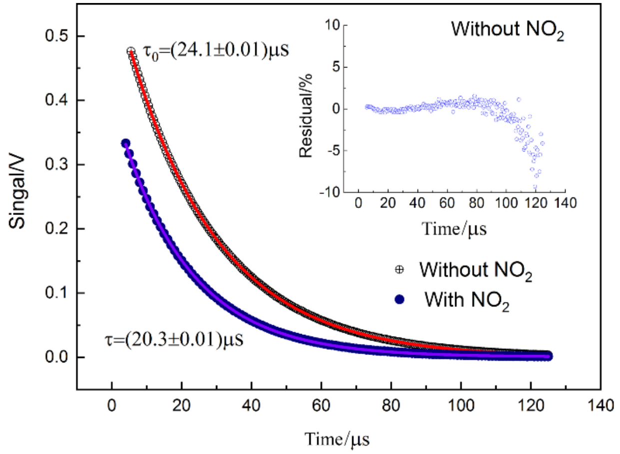
$$P_n = P_1 \cdot e^{-2n(T + A + \alpha L)}$$

Cavity Ring Down Spectroscopy

$$T_R = 2L/c$$

$$t = 2nL/c$$

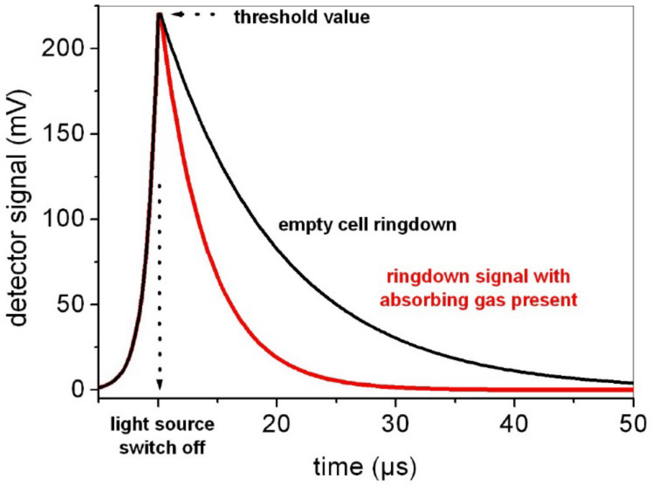
$$P(t) = P_1 \cdot e^{-t/\tau_1}$$



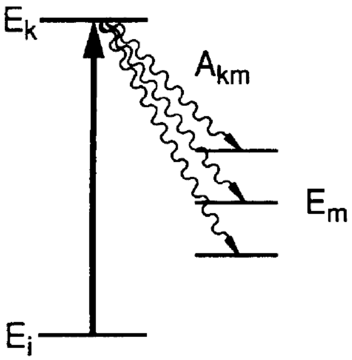
$$\tau_1 = \frac{L/c}{T + A + \alpha \cdot L}$$

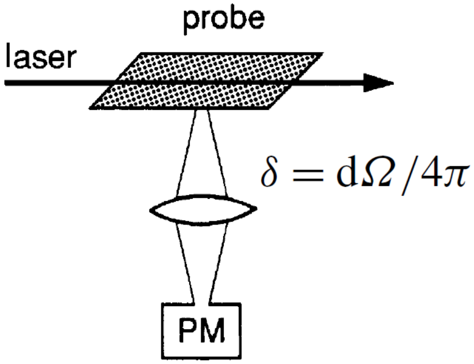
$$\tau_2 = \frac{L/c}{T + A} \approx \frac{L/c}{1 - R} \qquad (\alpha = 0)$$

$$1/\tau_1 - 1/\tau_2 = c \cdot \alpha$$

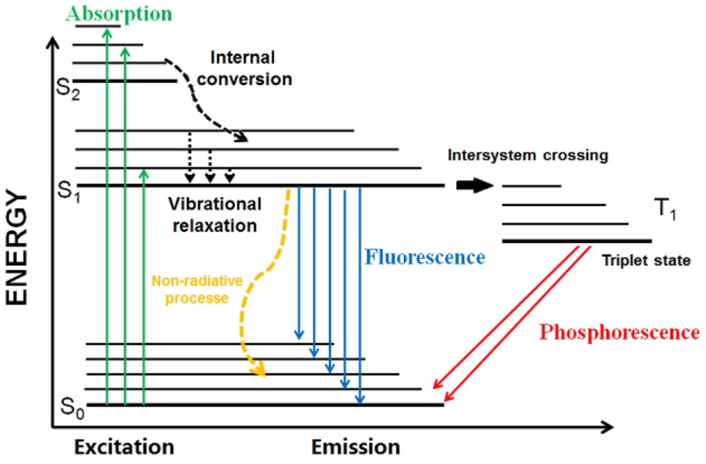


Fluorescence Excitation Spectroscopy





$$\delta = \mathrm{d}\Omega/4\pi$$



number of photons absorbed per second along the path length Δx

$$n_{\mathrm{a}} = N_i n_{\mathrm{L}} \sigma_{ik} \Delta x$$

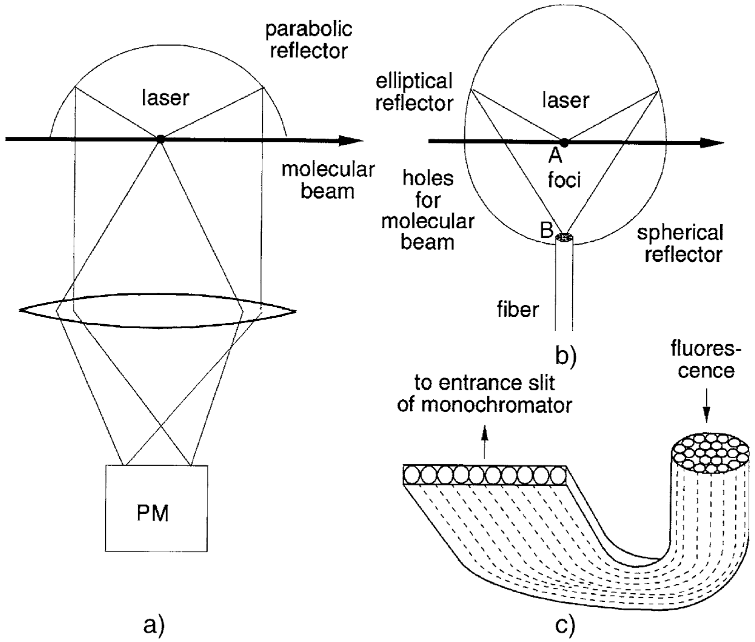
where n_{L} is the number of incident laser photons per second, σ_{ik} the absorption cross section per molecule, and N_i the density of molecules in the absorbing state $|i\rangle$.

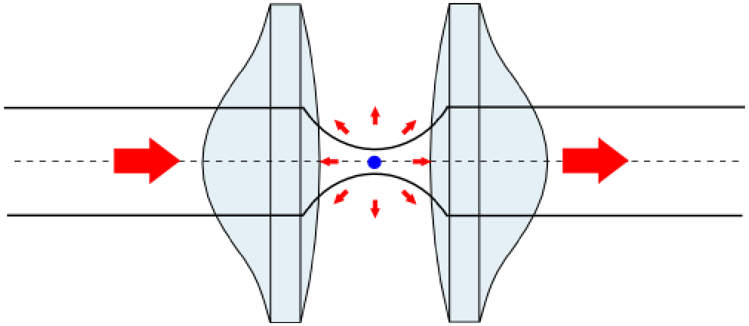
$$n_{\mathrm{Fl}} = N_k A_k = n_{\mathrm{a}} \eta_k \qquad A_k = \sum_m A_{km}$$

$$\eta_k = A_k/(A_k + R_k)$$

photoelectrons counted per second $\quad n_{\mathrm{pe}} = n_{\mathrm{a}} \eta_k \eta_{\mathrm{ph}} \delta = (N_i \sigma_{ik} n_{\mathrm{L}} \Delta x) \eta_k \eta_{\mathrm{ph}} \delta$

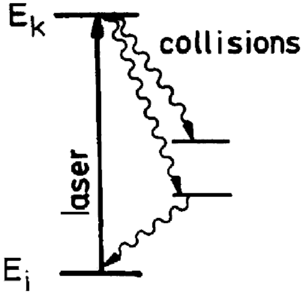
Fluorescence Excitation Spectroscopy

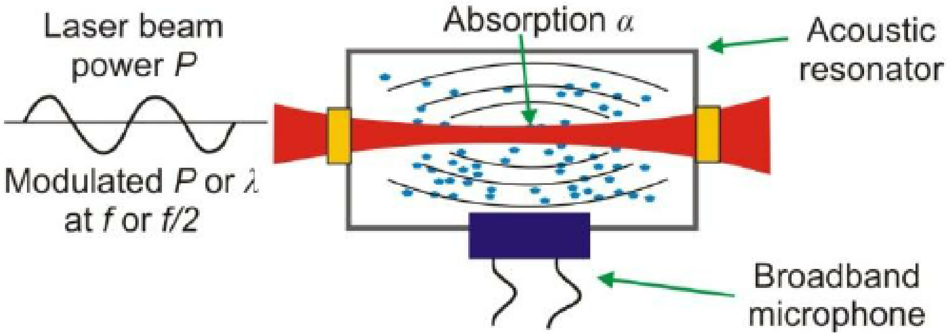




Excitation spectroscopy has its highest sensitivity in the visible, ultraviolet, and near-infrared regions.

Photoacoustic spectroscopy





absorbed energy per cycle

$$\Delta W = N_i \sigma_{ik} \Delta x (1 - \eta_K) P_L \Delta t,$$

is proportional to the density N_i [cm^{-3}] of the absorbing molecules in level $|i\rangle$, the absorption cross section σ_{ik} [cm^2], the absorption pathlength Δx, the cycle period Δt, and the incident laser power P_L.

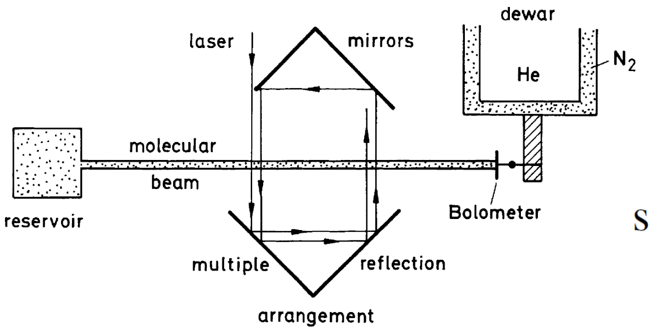
$$\Delta W = \frac{1}{2} f V N k \Delta T$$

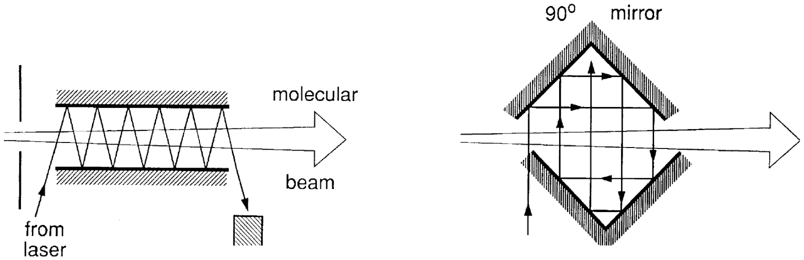
$$pV = NVkT,$$

$$\Delta p = N k \Delta T = \frac{2 \Delta W}{f V}$$

$$S = \Delta p S_m = \frac{2 N_i \sigma_{ik}}{f V} \Delta x (1 - \eta_k) P_L \Delta t S_m$$

Optothermal spectroscopy





spectroscopy of vibrational–rotational transitions in molecules

If N excited molecules hit the bolometer per second, the additional rate of heat transfer is

$$\frac{\mathrm{d}Q}{\mathrm{d}t} = N\Delta E = Nh\nu$$

With the heat capacity C of the bolometer and a heat conduction $G(T - T_0)$ the temperature T is determined by

$$Nh\nu = C\frac{\mathrm{d}T}{\mathrm{d}t} + G(T - T_0).$$

Under stationary conditions ($\mathrm{d}T/\mathrm{d}t = 0$), we obtain from (1.42) the temperature rise

$$\Delta T = T - T_0 = \frac{Nh\nu}{G}.$$

$$\Delta R = \frac{\mathrm{d}R}{\mathrm{d}T}\Delta T$$

Ionization spectroscopy

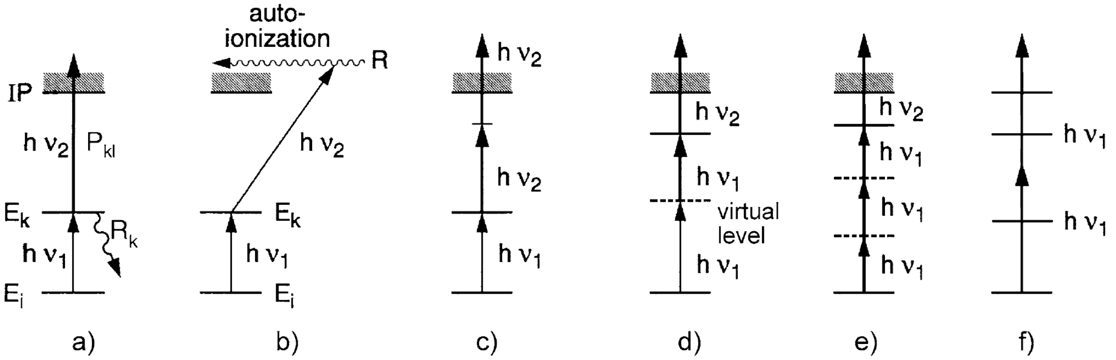


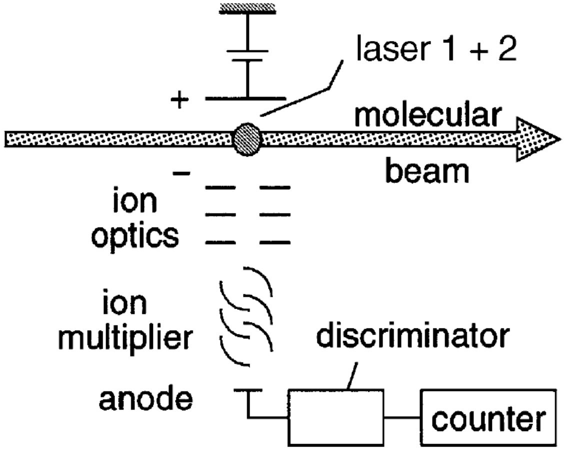
Fig. 1.36 Level schemes of ionization spectroscopy: (**a**) photoionization; (**b**) excitation of autoionizing Rydberg levels; (**c**) two-photon ionization of excited molecules; (**d**) one-photon ionization of a high lying level, excited by non-resonant two-photon process; (**e**) three-photon excitation of a level which is ionized by a fourth photon; (**f**) non-resonant two-photon ionization

Photoionization

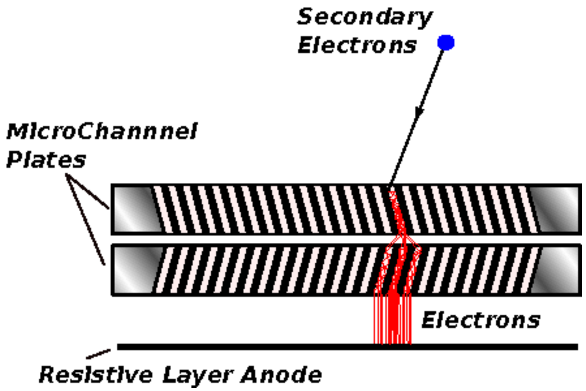
$$M^*(E_k) + h\nu_2 \longrightarrow M^+ + e^- + E_{\text{kin}}.$$

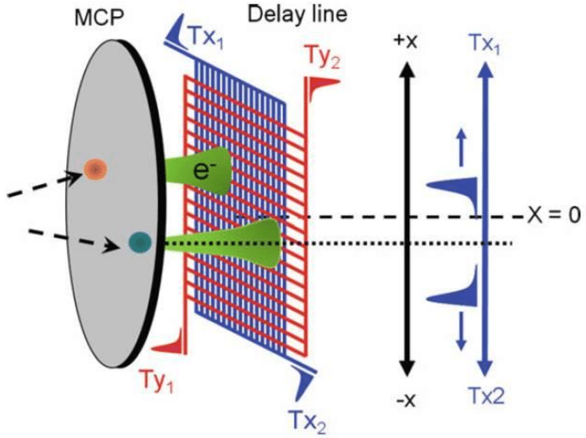
$$n_a = N_i n_L \sigma_{ik} \Delta x$$

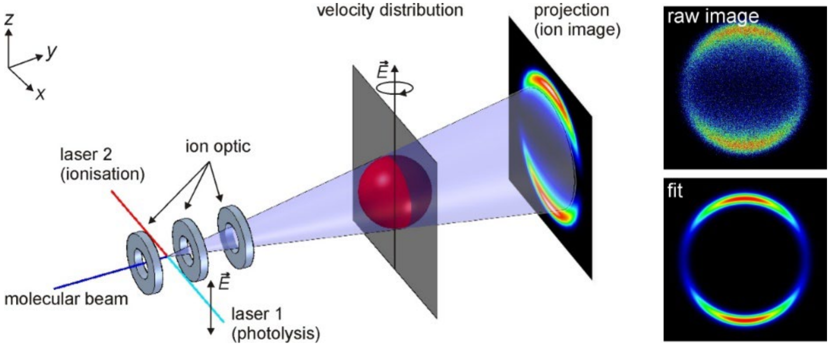
$$S_I = N_k P_{kI} \delta \cdot \eta = n_a \frac{P_{kI}}{P_{kI} + R_k} \delta \cdot \eta = N_i n_L \sigma_{ik} \Delta x \frac{P_{kI}}{P_{kI} + R_k} \delta \cdot \eta$$

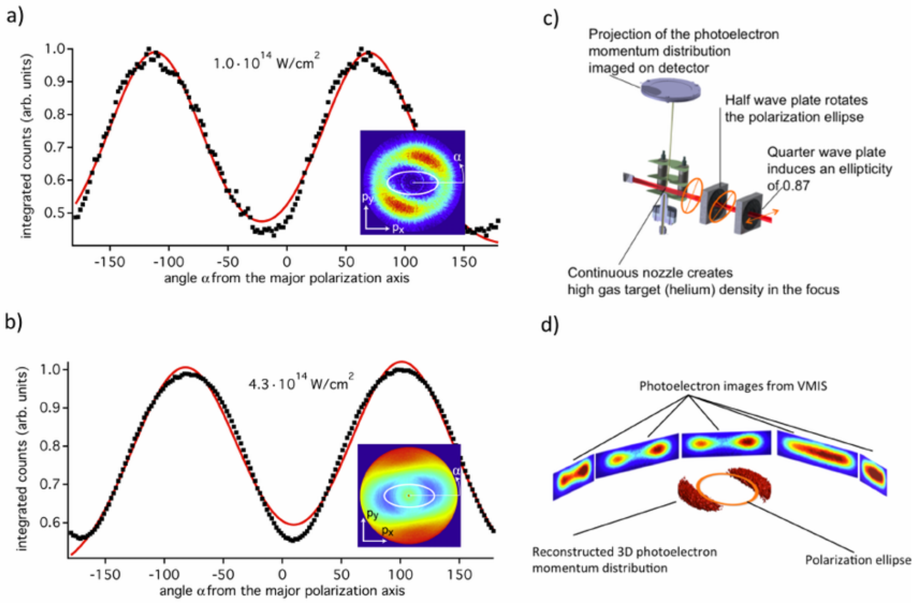


Ionization spectroscopy

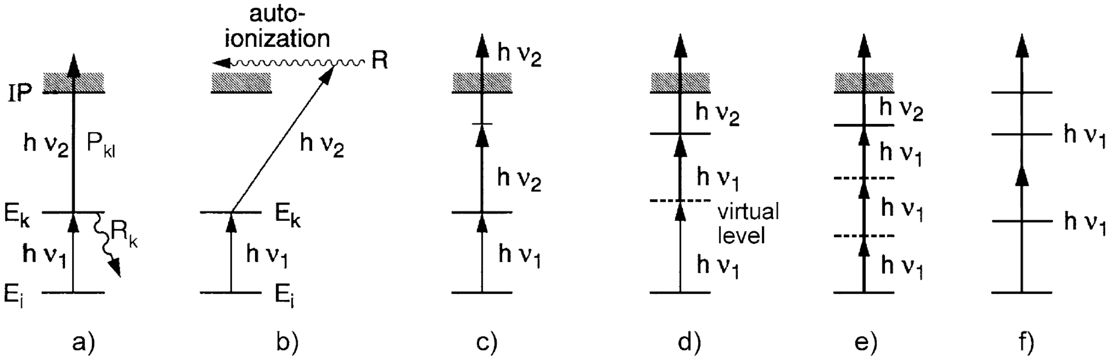








Ionization spectroscopy



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Resonant Multiphoton Ionization REMPI

Collision-Induced Ionization

$$M^*(E_k) + e^- \longrightarrow M^+ + 2e^-$$

$$M^*(E_k) + A \longrightarrow M + A^+ + e^-$$

Penning ionization

Field Ionization