Basics-7

Lasers and Laser Spectroscopy

Basics of Lasers

* Principles of lasers

   "Light Amplification by Stimulated Emission of Radiation"
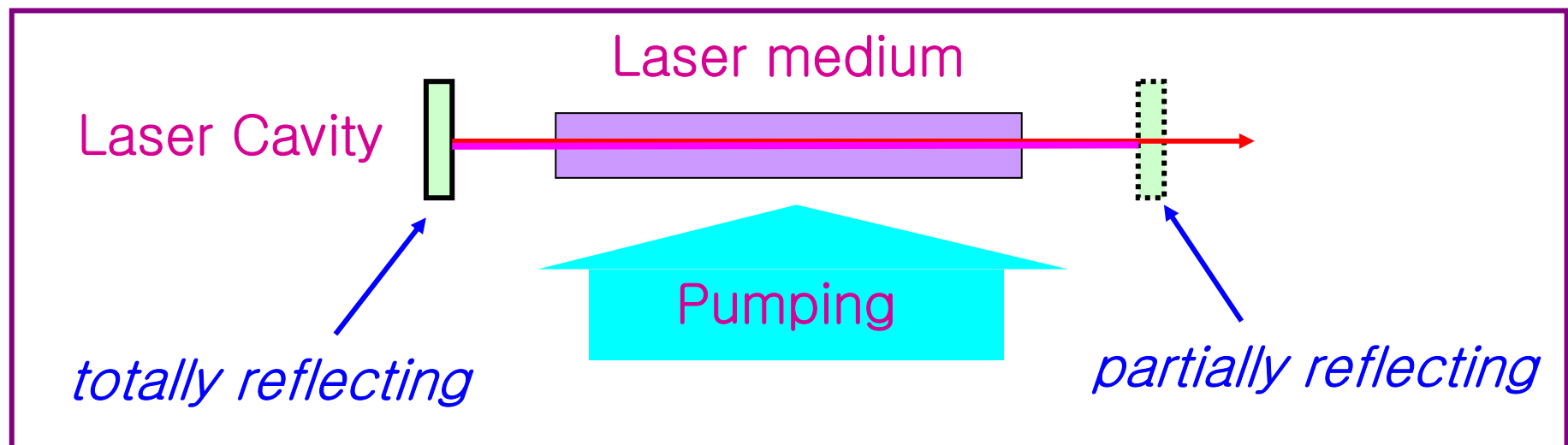
   Continuous (CW) or Pulsed Lasers

   "directionality, monochromaticity, brightness, coherence"

− Components of lasers:

   Active medium (*gas, liquid dye, solid materials*)
   Pump source (*for excitation of medium*)
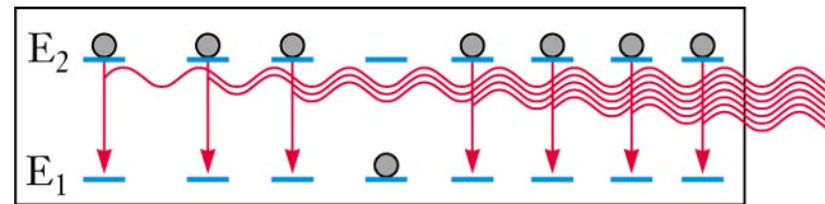   Optical resonator (*for light amplification*)

– Laser action mechanism:
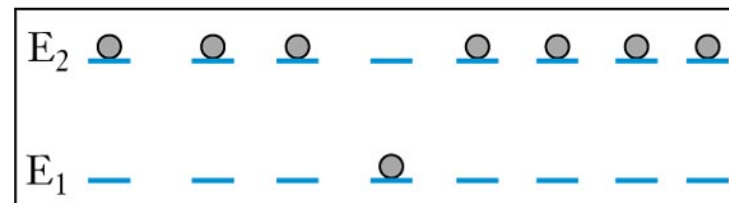
Pumping → Spontaneous Emission → Stimulated Emission

"population inversion $(N_1 > N_0)$"
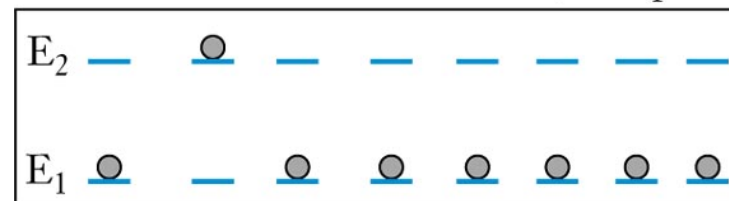
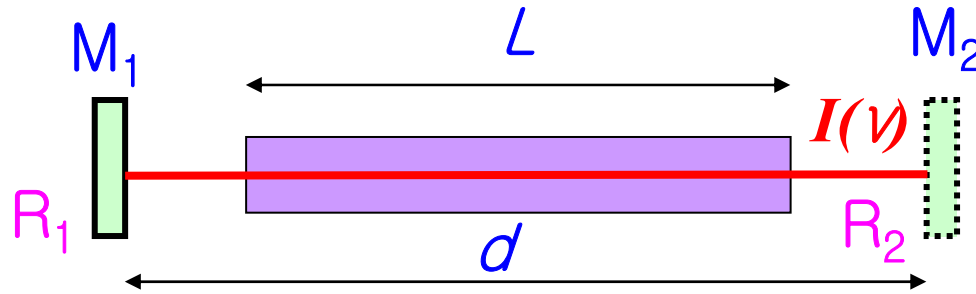"incoherent, random direction"

"coherent, light amplification"

(c) Laser action

(b) Inverted population

↑Pump

(a) Equilibrium population

$$I(\nu) = I_0(\nu)e^{-\sigma(\nu)(N_0 - N_1)l}$$

After one round trip

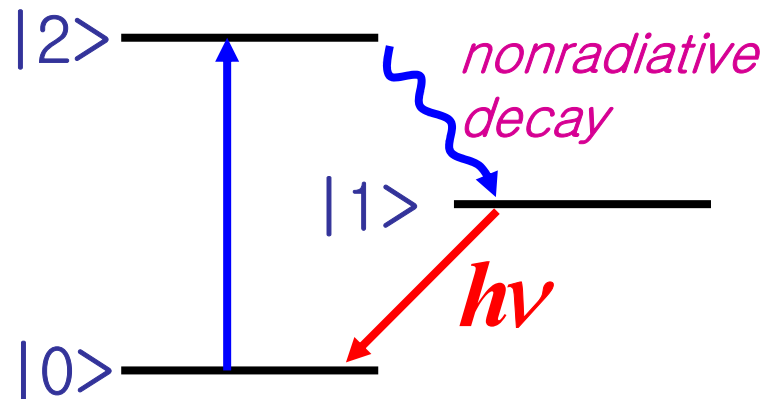$$I(\nu, 2L) = I_0(\nu)e^{2\sigma(\nu)\Delta NL} \quad \leftarrow \quad \Delta N = N_1 - N_0$$

$\leftarrow$ *loss factor* $e^{-\gamma}$ $\because$ *scattering*, *absorption by optics*, *etc*

$$\therefore I(\nu, 2L) = I_0(\nu)e^{2\sigma(\nu)\Delta NL - \gamma}$$
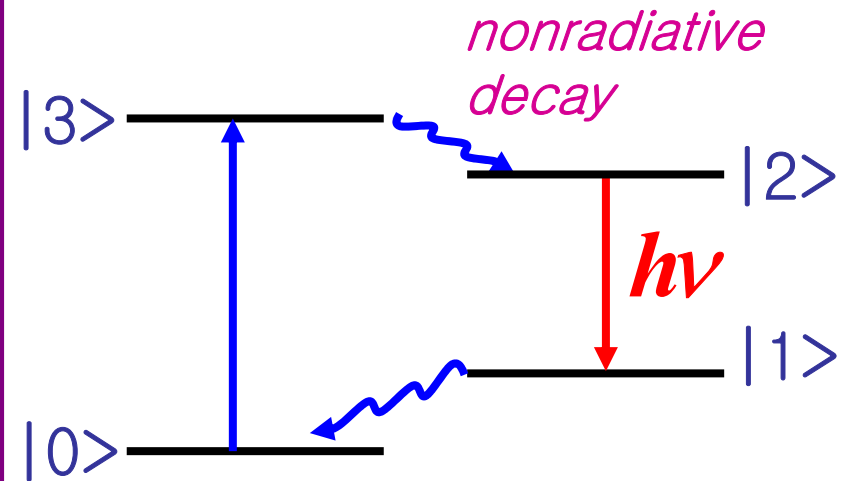
Amplification occur if $2\sigma\Delta NL > \gamma$

$\therefore$ *threshold* $\Delta N_{th} = \dfrac{\gamma}{2\sigma L}$

Three-level systems

|2>

|1>

|0>

nonradiative decay

hv

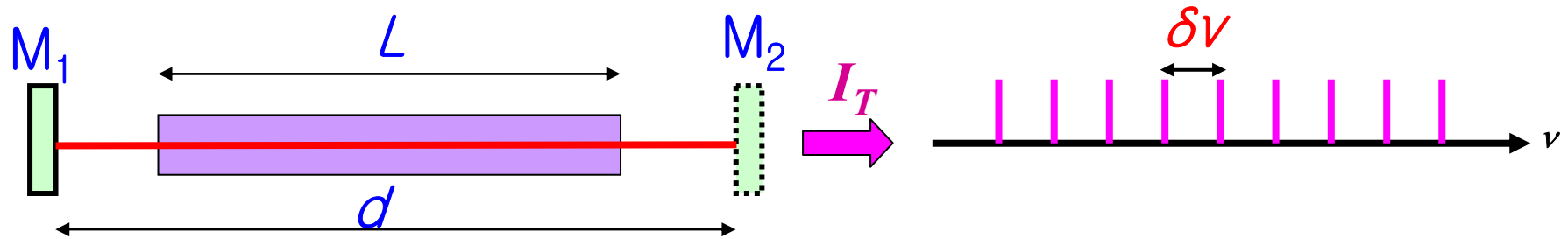"hard pumping for population inversion (PI)"

Four-level systems

|3>

|2>

|1>

|0>

nonradiative decay

hv

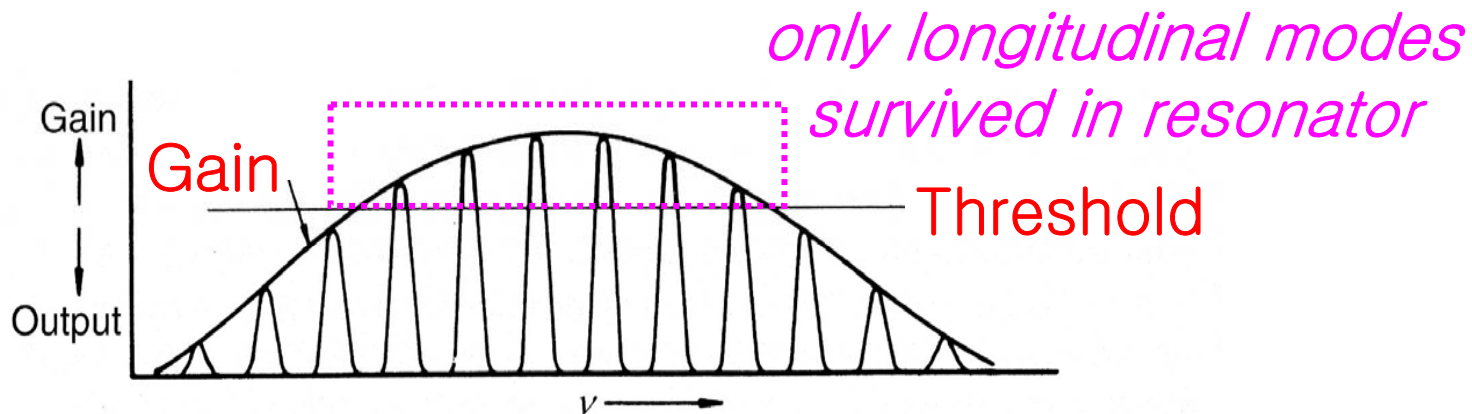"easy pumping for PI but need rapid 1→0 decay"

- Spectral characteristics: longitudinal, transverse modes

Longitudinal (or axial) modes

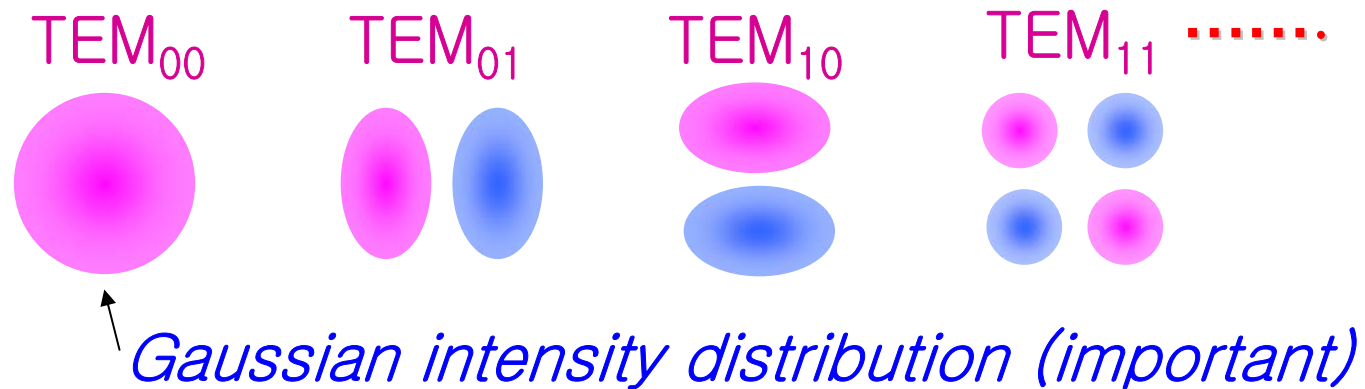$$\text{resonance condition}: d = n\left(\frac{\lambda}{2}\right), n = 1, 2, .. \rightarrow \nu = n\frac{c}{2d} \quad \text{or} \quad n = \frac{2d}{c}\nu$$

$$\rightarrow \delta\nu = \frac{c}{2d} \ (\textit{free spectral range})$$

only longitudinal modes
survived in resonator

Transverse modes (TEM$_{mn}$):

"Transverse Electric and Magnetic fields
with (m,n) nodal planes (usually use E-fields)"

TEM$_{00}$ TEM$_{01}$ TEM$_{10}$ TEM$_{11}$ ....

Gaussian intensity distribution (important)

"...It is sometimes desirable to obtain a single longitudinal,
single transverse mode to do high resolution spectroscopy..."

Mode competition: (in multimode lasers)

Occur when $\delta\nu(\text{free spectral range}) \leq \Delta\nu^{homogeneous}$

$\rightarrow$ *needs extra wavelength selection optics*

e.g. (*i*) *He* $-$ *Ne laser* (**632.8nm**), $d = 1m$

$\delta\nu = 150MHz,\ \Delta\nu \sim 30MHz$

$\therefore$ *no mode competition*

(*ii*) Ar^+ *laser*

$\delta\nu = 150MHz,\ \Delta\nu \sim GHz$

$\therefore$ *strong mode competition*

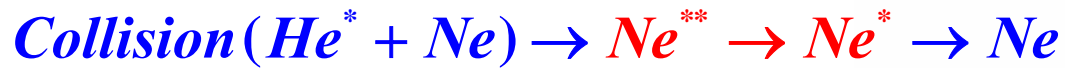(*iii*) *dye laser* : $\Delta\nu \sim 10THz$

$\therefore$ *strong mode competition*
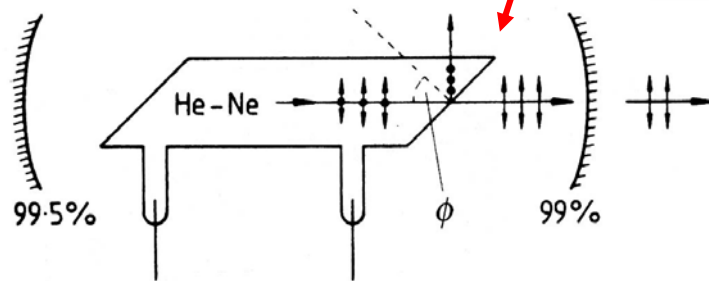
Single mode laser:

use intracavity prism, grating (Littrow) or etalon

for selecting a single mode among multi-cavity modes
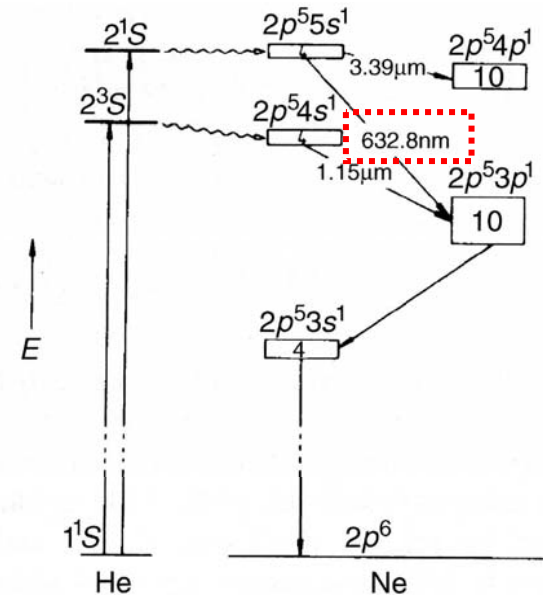
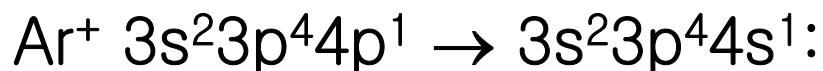* Types of lasers: Gas, liquid, solid lasers

He-Ne Laser (632.8 nm)

$$Collision\,(He^* + Ne) \rightarrow Ne^{**} \rightarrow Ne^* \rightarrow Ne$$

Brewster's angle (tanΦ=n, ~57°)

99.5%   φ   99%

discharge of 1 torr
He-Ne mixture(10:1)

Ar⁺ Laser (457.9, 488, 514.5 nm)

$$Discharge\ of\ 0.5\ torr\ Ar \rightarrow Ar^{+**} \rightarrow Ar^{+*} \rightarrow Ar^+$$

Ar^+ $3s^2 3p^4 4p^1 \rightarrow 3s^2 3p^4 4s^1$:
$^2D_{5/2} \rightarrow {}^2P_{3/2}$ (488, 514.5 nm)
$^2S_{1/2} \rightarrow {}^2P_{1/2}$ (457.9 nm)

N$_2$ Laser (337 nm)

C(v=0)−B(v=0) transition: 337 nm
Lifetimes: C(40ns), B(10µs) → ns pulsed operation

Table 9.1 Molecular orbital (MO) configurations and equilibrium bond lengths r_e of N$_2$

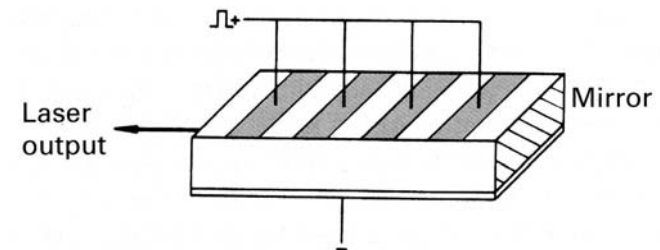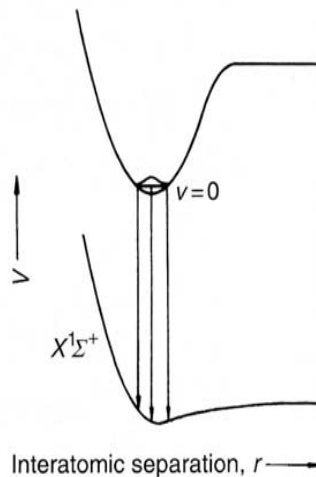| State	MO configuration	r_e/Å
$X^1\Sigma_g^+$	$\ldots(\sigma_u^*2s)^2(\pi_u2p)^4(\sigma_g2p)^2$	1.0977
$A^3\Sigma_u^+$	$\ldots(\sigma_u^*2s)^2(\pi_u2p)^3(\sigma_g2p)^2(\pi_g^*2p)^1$	1.2866
$B^3\Pi_g$	$\ldots(\sigma_u^*2s)^2(\pi_u2p)^4(\sigma_g2p)^1(\pi_g^*2p)^1$	1.2126
$C^3\Pi_u$	$\ldots(\sigma_u^*2s)^1(\pi_u2p)^4(\sigma_g2p)^2(\pi_g^*2p)^1$	1.1487

Figure 9.14 Nitrogen laser cavity
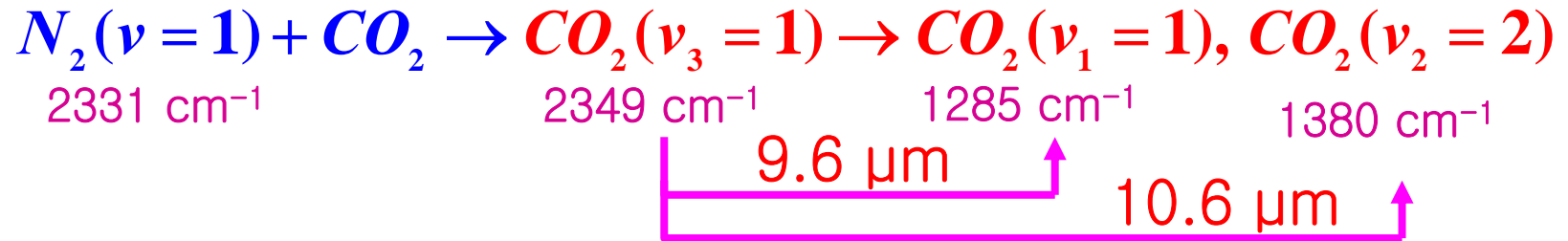
Excimer Lasers (noble gas halides)

Discharge Ar* + F$_2$ → ArF* → Ar + F
"Pulsed operation"

ArF (193 nm)
KrF (248 nm), KrCl (222 nm)
XeF (351 nm), XeCl (308 nm)

CO$_2$ Laser: infrared laser

$$N_2(v=1)+CO_2 \rightarrow CO_2(v_3=1) \rightarrow CO_2(v_1=1),\ CO_2(v_2=2)$$

2331 cm^{-1} 2349 cm^{-1} 1285 cm^{-1} 1380 cm^{-1}
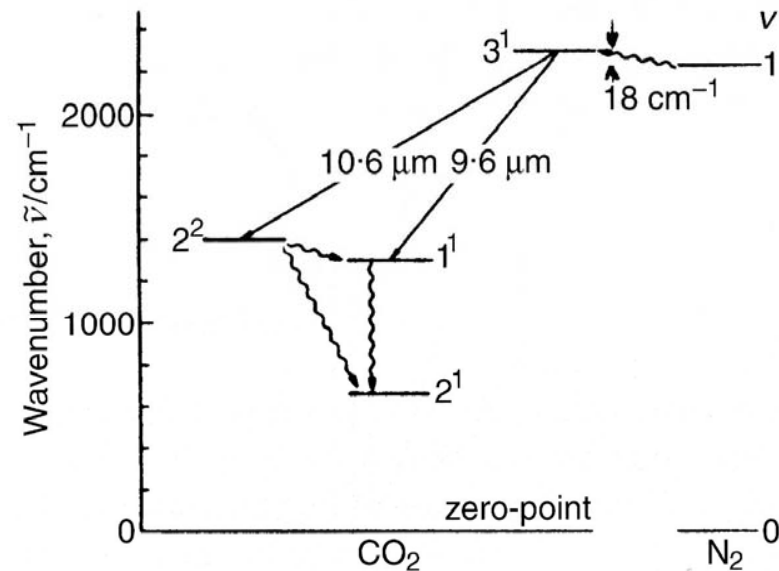
9.6 µm

10.6 µm

"Rovibrational transitions"
P, R–branches occur
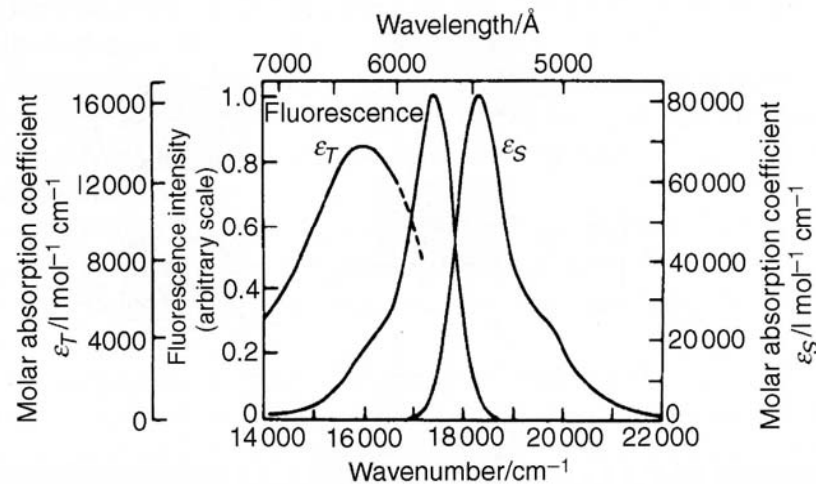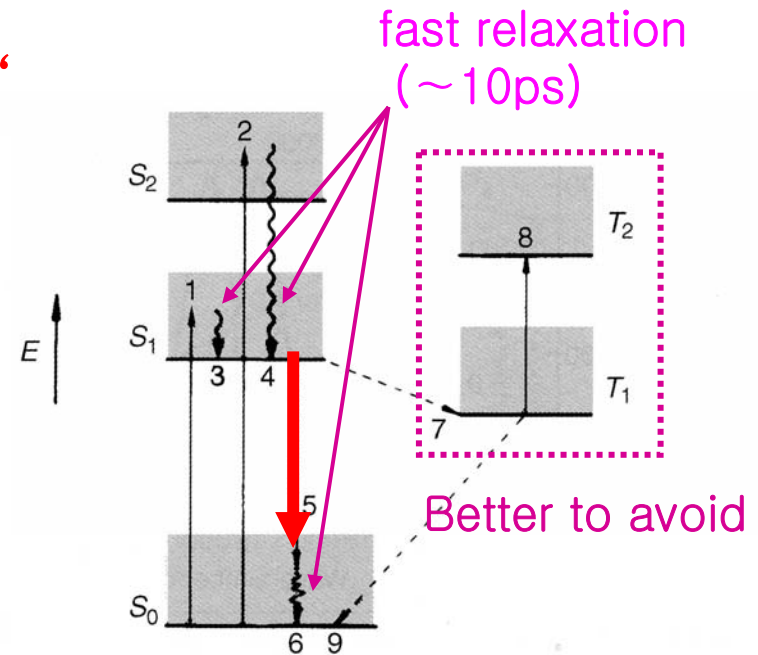→ Line–tunable

Most intense line:
P(22), 10.6 µm

Dye Lasers: Liquid Lasers

Active medium: fluorescent dyes (Rhodamine, Coumarine, etc) in solvents (e.g. EtOH)

" Wide tuning range (UV ~ IR) "

Rhodamine B

fast relaxation (~10ps)

Better to avoid

Pumping Sources:
(CW operation) Ar+ laser (usually longitudinal pumping)
(Pulsed) flash lamps, pulsed lasers (Nd-YAG, excimer, N_2, etc)
(longitudinal or side pumping)

Ruby and Alexandrite Lasers:

Ruby crystal: Cr_2O_3 in Al_2O_3 (693.4, 694.3 nm); three-level
Alexandrite: Cr_2O_3 in $BeAl_2O_4$ (720-800 nm); four level

Cr^{3+} in O_h field

693.4nm

694.3nm

720-800nm
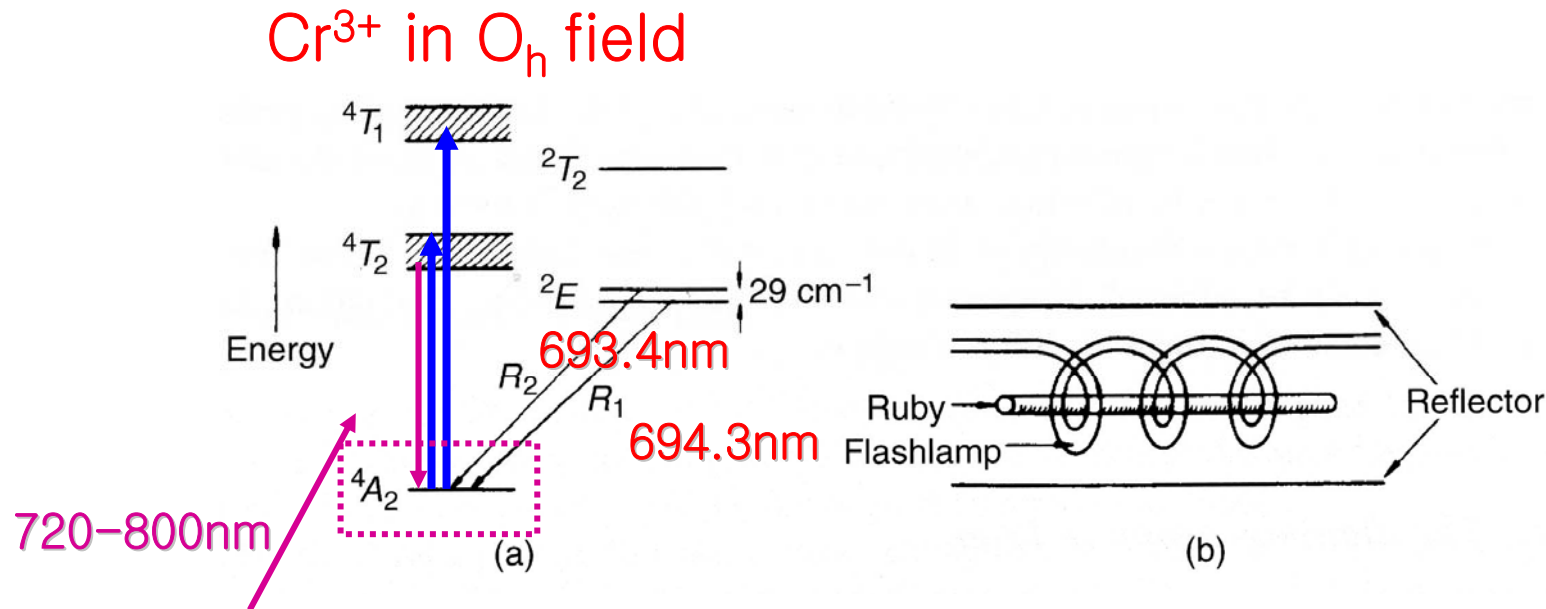
Broadens in Alexandrite $\rightarrow$ Four-level laser
($^4T_2$ vibronic, $^4T_2$ zero-level, $^4A_2$ vibronic, $^4A_2$ zero-level)

Ti-Sapphire Laser:

Active medium: 0.1% Ti_2O_3 in Al_2O_3
"...lasing occur between energy levels (t_2,e) of Ti^{3+} ($3s^2 3p^6 3d^1$)
In O_h field coupled to lattice vibrations resulting in band broadening..."
- Tunable in 670 – 1100 nm wavelength range
- Pumping: (CW, fs pulse laser) Ar^+ laser
 (ns pulse) Nd-YAG laser

Nd-YAG Laser: neodymium-yttrium aluminium garnet laser

Active medium: Nd^{3+} ($4d^{10} 4f^3 5s^2 5p^6$) in $Y_3Al_5O_{12}$ matrix
"...lasing occur between $^4F_{3/2}$ and $^4I_{11/2}$ levels allowed by Crystal field splittings around 1.06µm (1.0648, 1.0612)···"
- Pumping: flash lamp
- High power ns laser (used as a pump laser for dye laser and fs, ps Ti-sapphire lasers)

Diode or semiconductor Laser:

0V ▶|— 0V

CB

Fermi level

VB

p-type   n-type

pn junction

+V ▶|— −V

CB

VB

⊖

$h\nu$

Polished

Junction
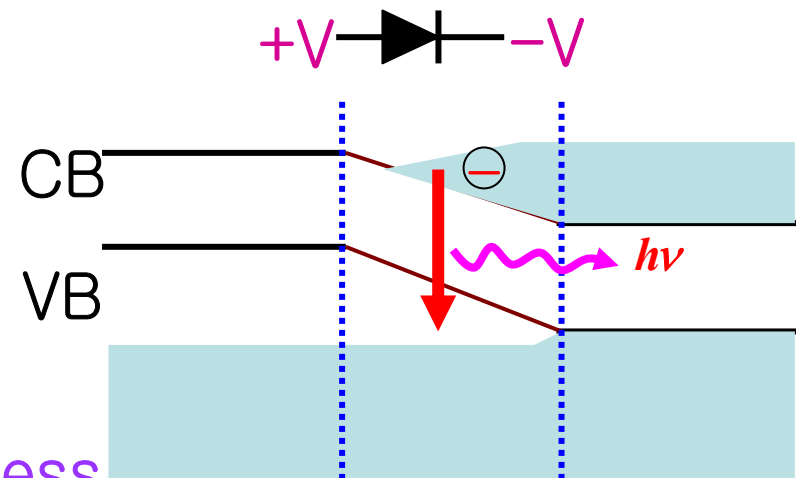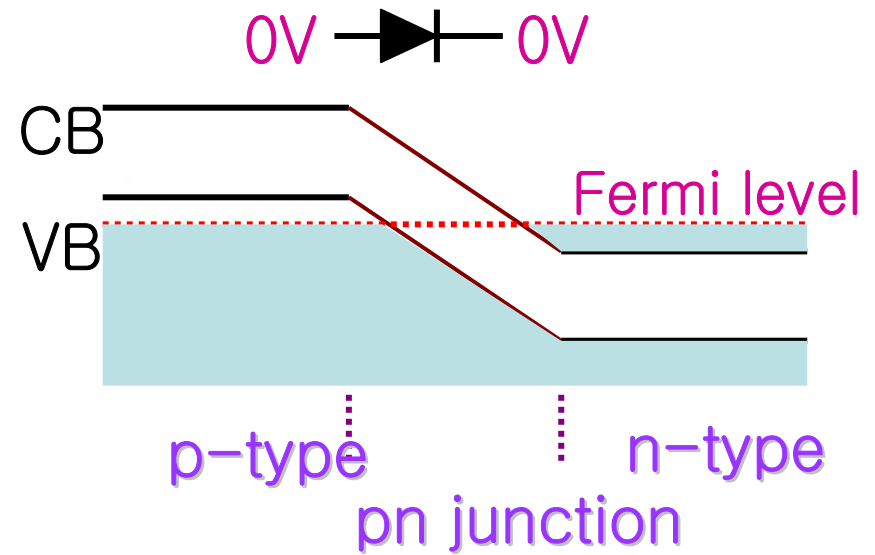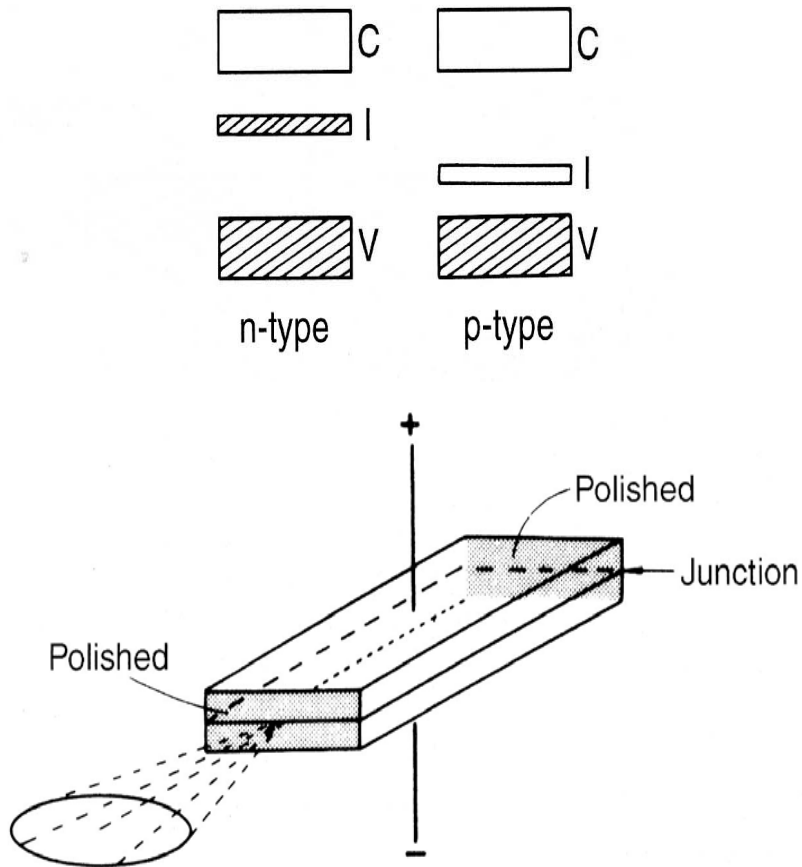
Polished

* ~mm length and ~μm thickness
* multiple reflections by two polished faces
* temperature-controlled
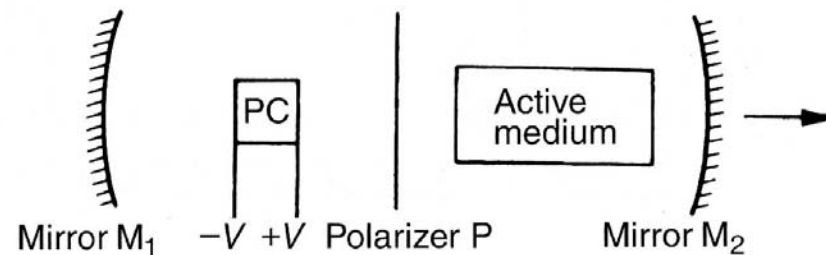e.g. InGaP, PbCdSe, PbSnTe, InGaAs, PbSSe, etc.

* Pulsed operations

– Q-switching (for ns laser)

"… maintain cavity in nonresonant condition with population inversion building up, then allow resonant condition only for a short period of time producing a short laser pulse…"
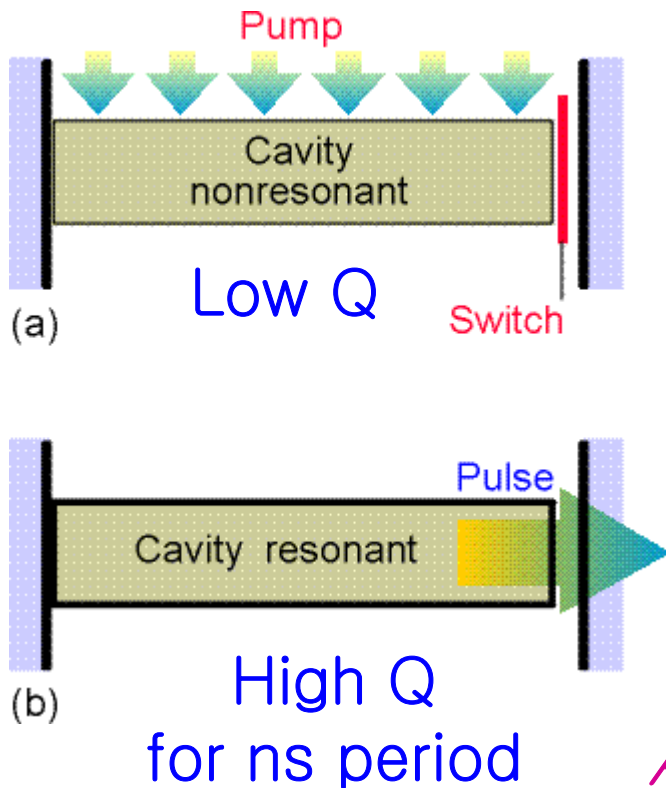
e.g. Pockels Cell as Q-switch

Electro-optical materials:
Ammonium dihydrogen phosphate (ADP)
Potassium dihydrogen phosphate (KDP)
*etc.*

– Mode–Locking (for ps, fs lasers)

"... lock phases of multiple longitudinal modes by optical modulators operated at the frequency of mode separation f=2d/c..."

$$\nu = \nu_0 \xrightarrow{f} v = \nu_0,\ \nu_0 \pm f \xrightarrow{f} \nu_0,\ \nu_0 \pm f,\ \nu_0 \pm 2f \ldots \xrightarrow{f} \nu_0 \pm mf$$

Active ML (AO, EO modulators), Passive ML (saturable absorber), Kerr lens ML (KLM), regenerative ML...

"Pulse duration becomes narrower as number of phase–locked modes increases, eventually by spectral bandwidth of gain profile"

$t_r = 2d/c$

1ps
1ns

Output power

t_r

Δt

Time, t
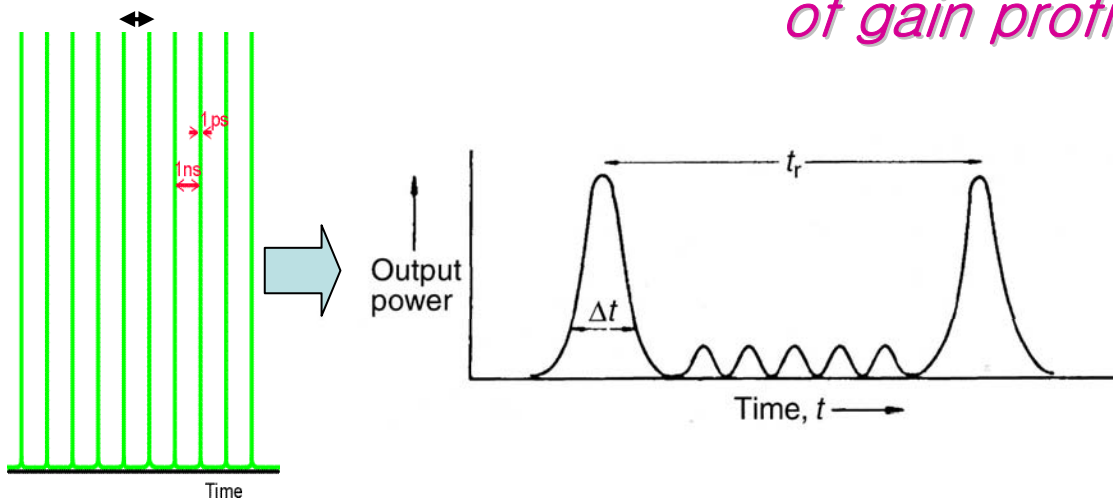
$$\Delta t = \frac{2\pi}{(2m+1)\Delta \nu} = \frac{2\pi}{N \Delta \nu} = \frac{1}{\delta \nu}$$

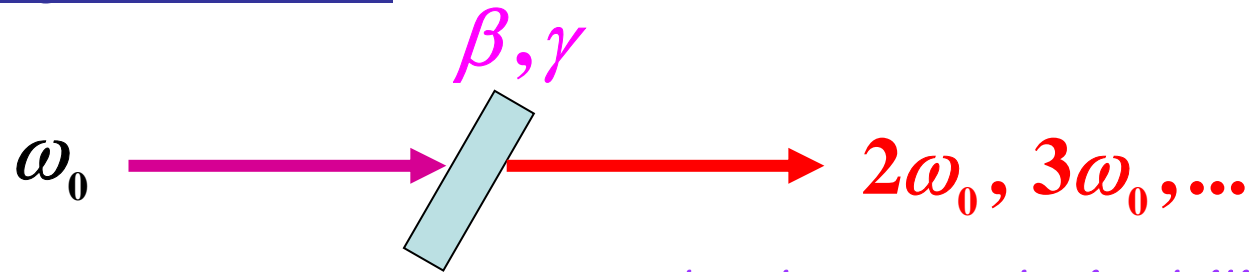$\leftarrow$ m: no. of longitudinal modes

N: # of phase-locked modes

δv: bandwidth of gain profile

– Extension of wavelength range

Use of nonlinear crystals: KDP, BBO, $LiNbO_3$, $AgGaS_2$, etc.

Harmonic generations:

β, γ

ω_0 $\longrightarrow$ $2\omega_0, 3\omega_0, ...$

1st hyperpolarizability ($\chi^{(2)}$)

$$\mu = \mu^{(1)} + \mu^{(2)} + \mu^{(3)} + ... = \alpha E + \frac{1}{2}\beta E^2 + \frac{1}{6}\gamma E^3 + ...$$

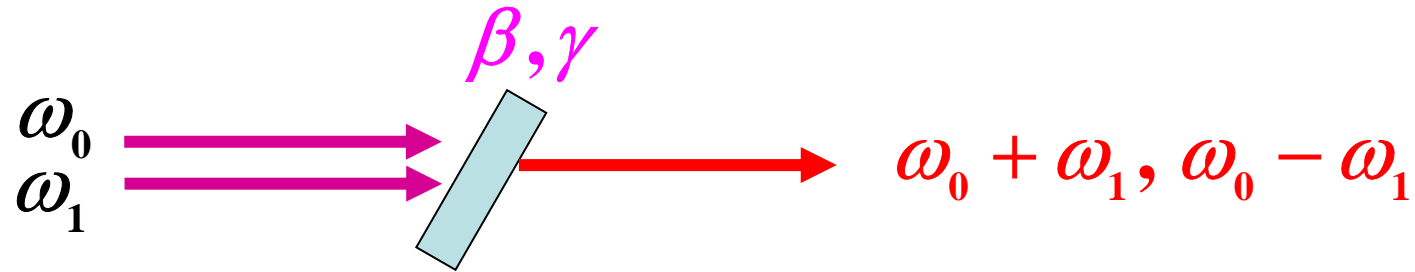$$E = A\sin\omega t$$

2nd hyperpolarizability ($\chi^{(3)}$)

$$E^2 \ term \propto A^2\sin^2\omega t = \frac{1}{2}A^2(1-\cos 2\omega t) \ "second \ harmonic"$$

$$E^3 \ term \propto A^3\sin^3\omega t = A^3(\frac{3}{4}\sin\omega t - \frac{1}{4}\sin 3\omega t) \ "third \ harmonic"$$

$$phase \ matching \ condition: \vec{k}_2(2\omega) = \vec{k}_1(\omega) + \vec{k}_1(\omega)$$

$$\vec{k}_3(3\omega) = \vec{k}_1(\omega) + \vec{k}_1(\omega) + \vec{k}_1(\omega)$$

Sum and difference frequency generations:

$$\mu = ... + \frac{1}{2}\beta_{12}E_1E_2 + ...$$

$$E_1 = A_1\sin\omega_1 t, \quad E_2 = A_2\sin\omega_2 t$$

$$E^2 \; term \propto A_1A_2\sin\omega_1 t\sin\omega_2 t = \frac{1}{2}A_1A_2\{\cos(\omega_1-\omega_2)t - \cos(\omega_1+\omega_2)t\}$$

$$\rightarrow (\omega_1-\omega_2): difference \; frequency; \; (\omega_1+\omega_2): sum \; frequency$$

$$phase \; matching \; condition: \vec{k}_3(\omega_1\pm\omega_2) = \vec{k}_1(\omega_1)\pm\vec{k}_2(\omega_2)$$

Applications of Lasers: Laser Spectroscopy

* Hyper Raman Spectroscopy

$2\tilde{\nu}_0$ ⟿ $\boxed{hyperpolarizability\ \beta}$ ⟿ $2\tilde{\nu}_0$ $2\tilde{\nu}_0 \pm \tilde{\nu}_{HR}$

$2\tilde{\nu}_0$: *Hyper Rayleigh scattering*

     (allowed only for molecules

      with no inversion symmetry)

$2\tilde{\nu}_0 \pm \tilde{\nu}_{HR}$: *Hyper Raman Scattering*

$\nu_s = \nu_L - \nu_M$

$\nu_{aS} = \nu_L + \nu_M$

$\nu_{HS} = 2\nu_L - \nu_M$

$\nu_{HaS} = 2\nu_L + \nu_M$

$$\Gamma(v') \times \Gamma(\beta_{ijk}) \times \Gamma(v'') \supset A_1$$

$$if\ \Gamma(v'') = A_1, \Gamma(v') = \Gamma(\beta_{ijk})$$

- *IR active modes: HR active*
- *Molecules w/ inversion symmetry:*
  only u modes are HR active

HR Spectrum of C_2H_6
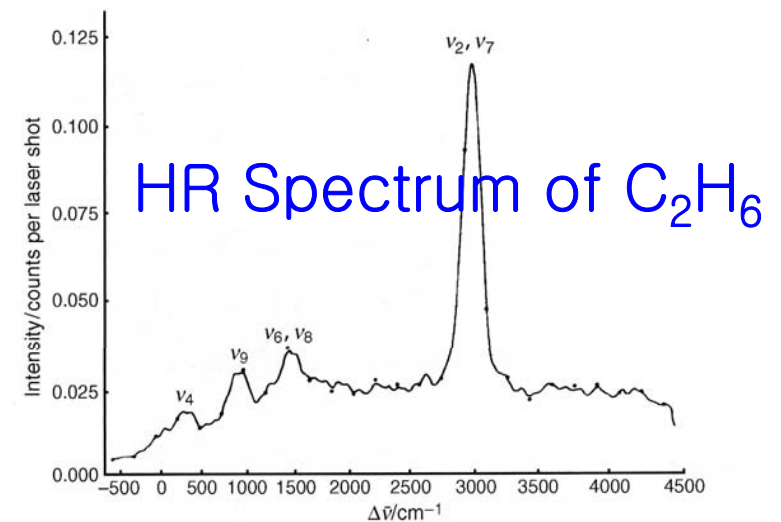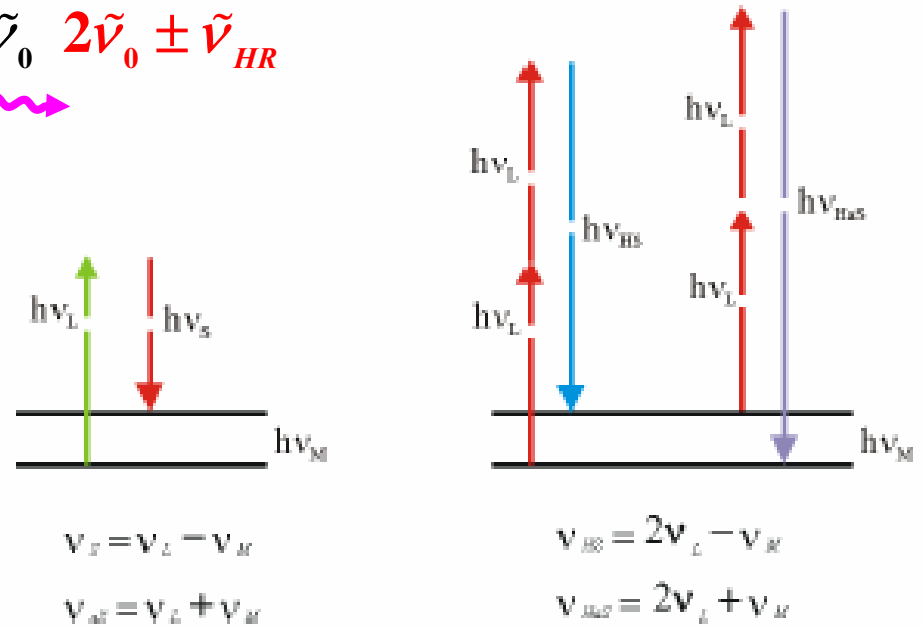
* Stimulated Raman Spectroscopy

With High power pulse lasers, parametric conversions between incident light and Stokes or anti-Stokes lines occur
→ Incident and SR or ASR intensities are comparable
→ used for wavelength extension "Raman laser"
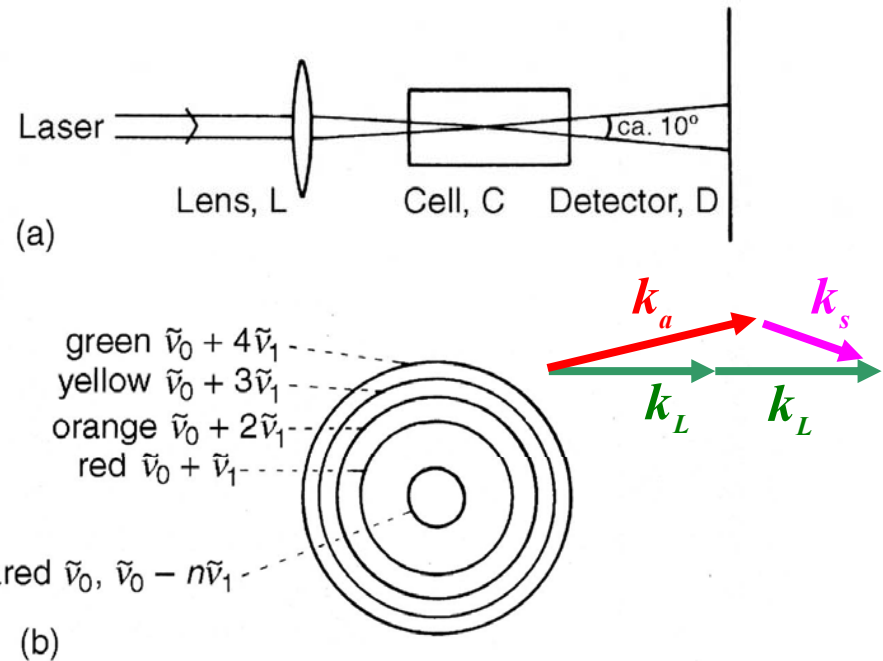*observed only for strongest Raman bands*

$$\nu = \nu_0 \pm n\nu \quad (-: stokes; +: antistokes\ shift),$$

$$four-wave\ mixing: \omega_4 = \omega_1 + \omega_2 \pm \omega_3$$

$$(SSR)\ \vec{k}_L + \vec{k}_S = \vec{k}_L + \vec{k}_S(automatic); (SASR)\ 2\vec{k}_L = \vec{k}_a + \vec{k}_s$$
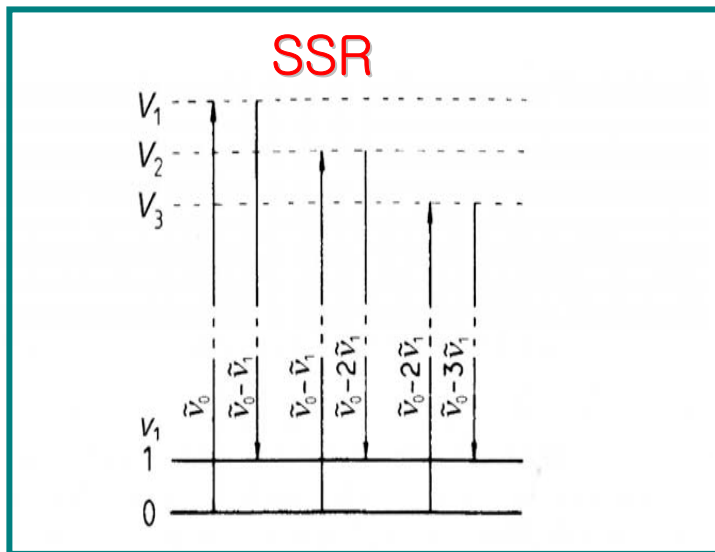
* Coherent Anti-Stokes Raman Scattering (CARS)

High sensitivity, high spatial resolution spectroscopic technique

"four-wave mixing"

$$\nu_{3,as} = 2\nu_1 - \nu_2 = \nu_1 + (\nu_1 - \nu_2) \ @ \ \nu_1 - \nu_2 = \nu_{i,mol} \quad "CARS"$$
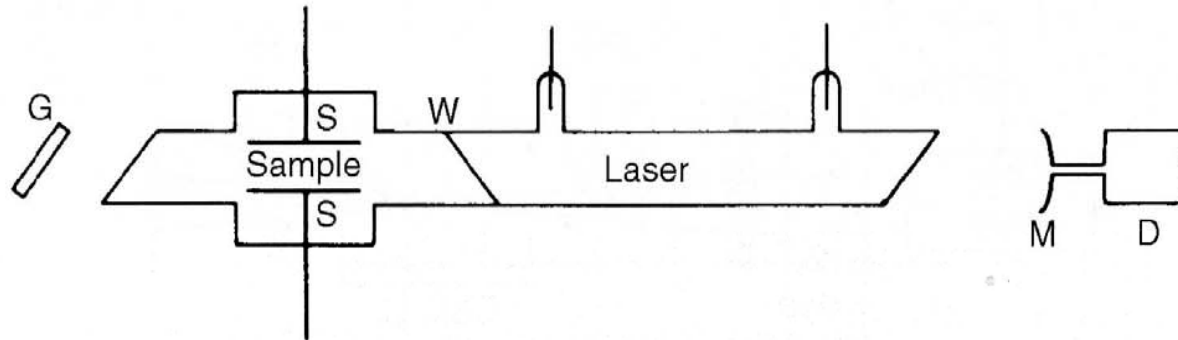
$$2\vec{k}_L(\nu_1) = \vec{k}(\nu_3) + \vec{k}(\nu_2)$$

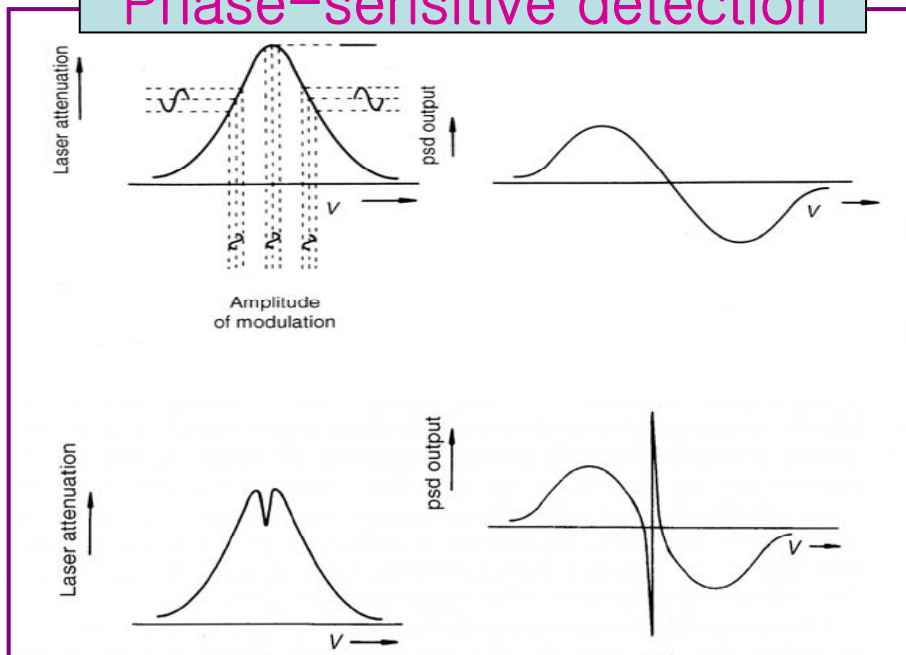$$cf. \ \nu_{3,s} = 2\nu_2 - \nu_1 = \nu_2 - (\nu_1 - \nu_2) \ @ \ \nu_1 - \nu_2 = \nu_{i,mol} \quad "CSRS"$$
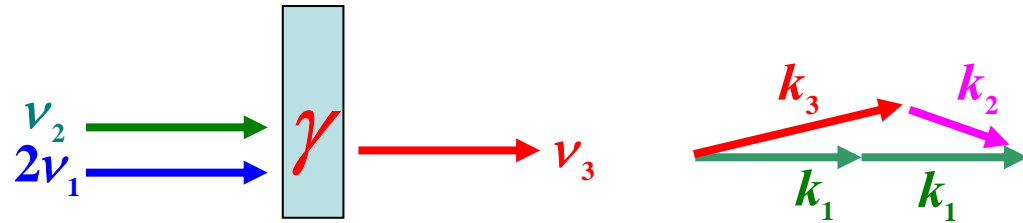
ν_1 : *fixed / ν_2 : variable to match $\nu_1 - \nu_2 = \nu_{vib-rot}$*

$$\nu_{as} = 2\nu_L - \nu_s$$
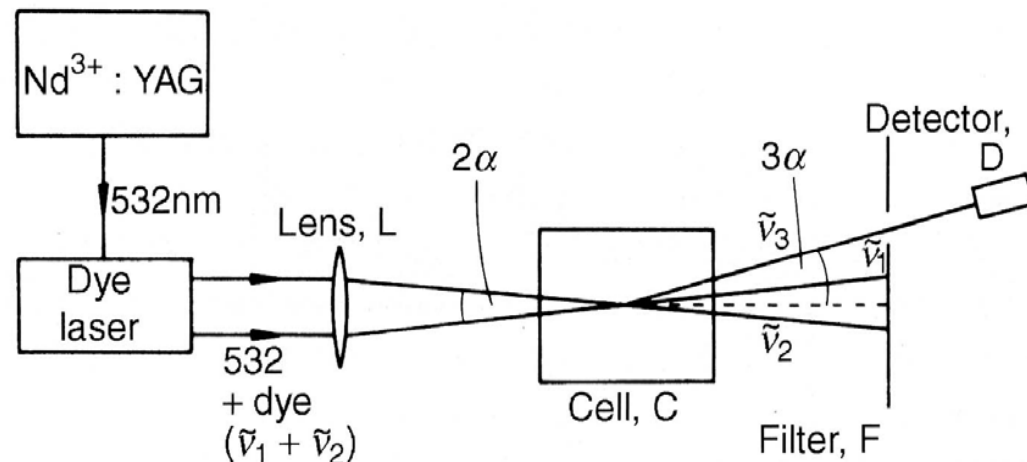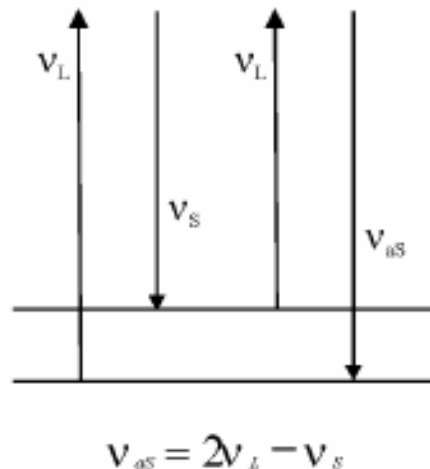
* Laser Stark Spectroscopy: "Stark effect"

Stark effect splits rotational levels according to their $|M_J|$ values and applied voltages

$$E_{stark} = \mu^2 E^2 (c_1 - c_2 M_J^2)$$
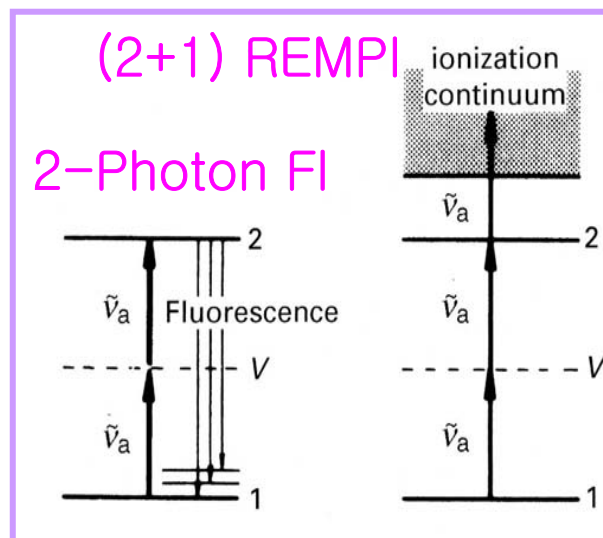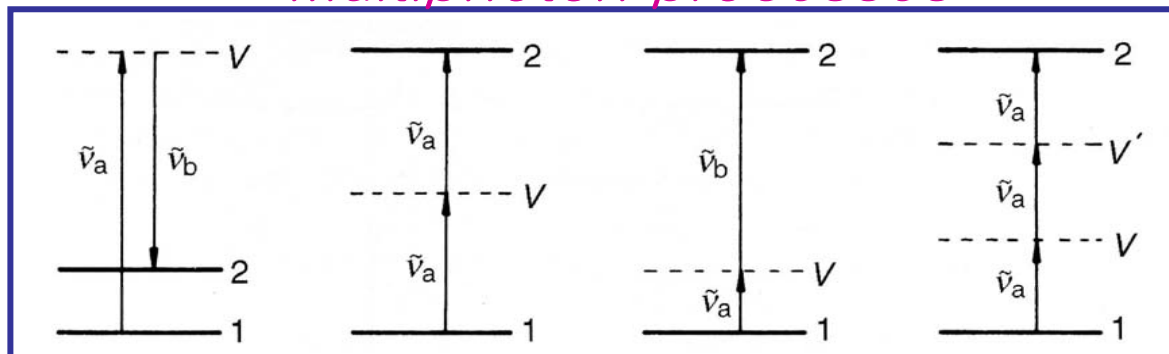

Voltage modulation and Phase-sensitive detection

Example: FNO, $^qP_7(8)$ of ν_1
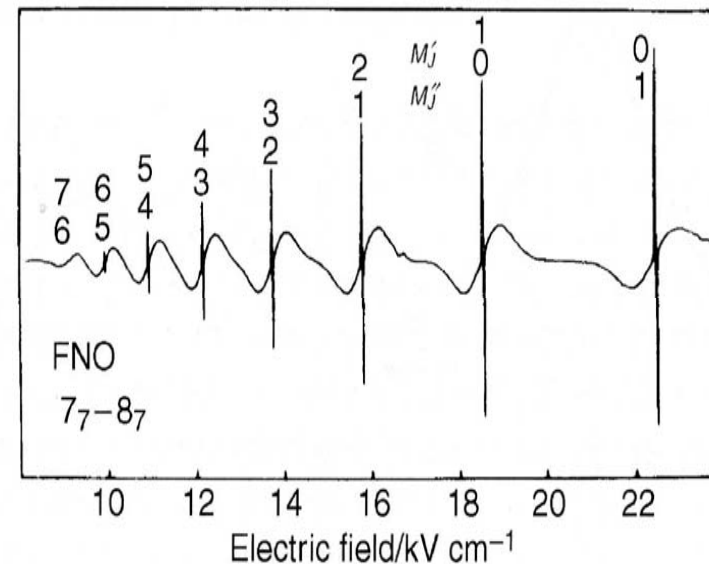
* Two-photon and multiphoton absorption

"Multiphoton processes"

(2+1) REMPI

2-Photon Fl

Selection rule:
  "two-photon absorption"

$$\Gamma(\psi'_{ev}) \times \Gamma(S_{ij=xx,xy,...}) \times \Gamma(\psi''_{ev}) \supset A_1$$
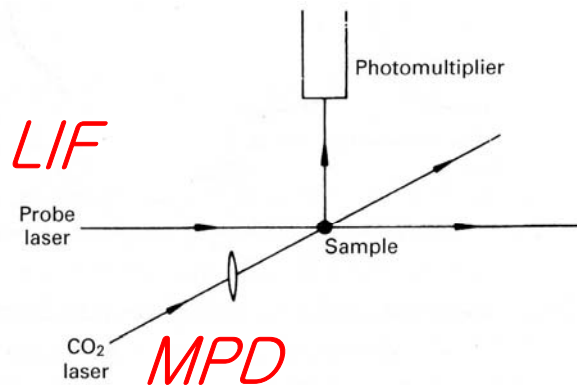
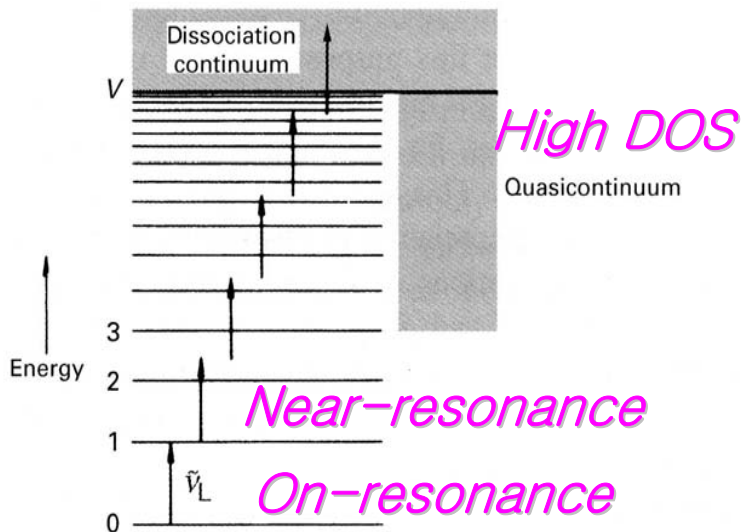$$\textbf{if } \Gamma(\psi''_{ev}) = A_1,$$

$$\Gamma(\psi'_{ev}) = \Gamma(S_{ij=xx,xy,...}) = \Gamma(\alpha_{ij})$$

$$\textbf{or } \Gamma(\psi'_e) \times \Gamma(\psi'_v) = \Gamma(\alpha_{ij})$$
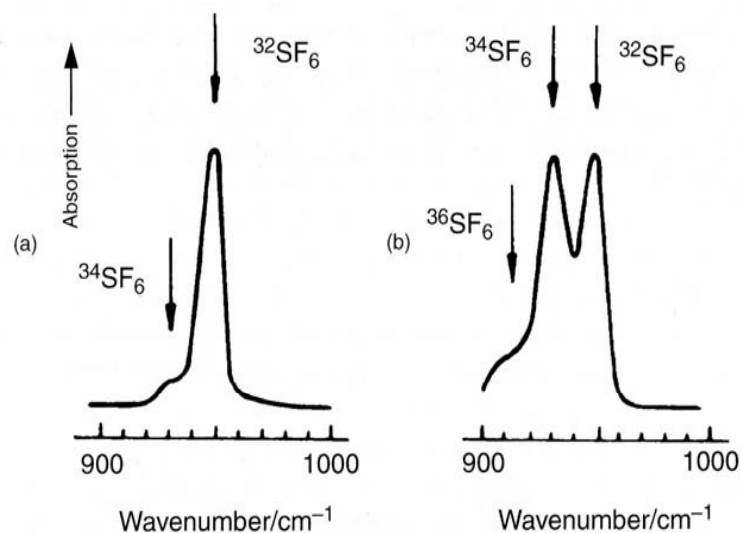
Two-photon fluorescence excitation

Two-photon energy/cm⁻¹

$$\tilde{A}\,^1B_{2u} \leftarrow \tilde{X}\,^1A_g$$
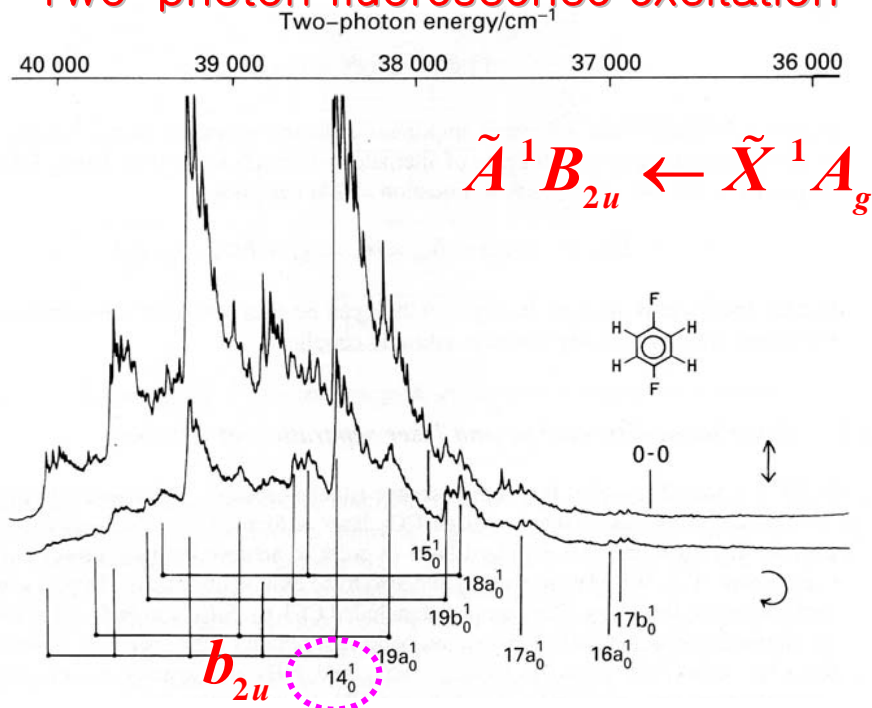
* Multiphoton dissociation (MPD) and isotope separation

High DOS

Near-resonance

On-resonance

LIF

MPD

MPD of $^{32}SF_6$ – depletion

– Isotope separation
MPD of single isotope
by using isotope shift
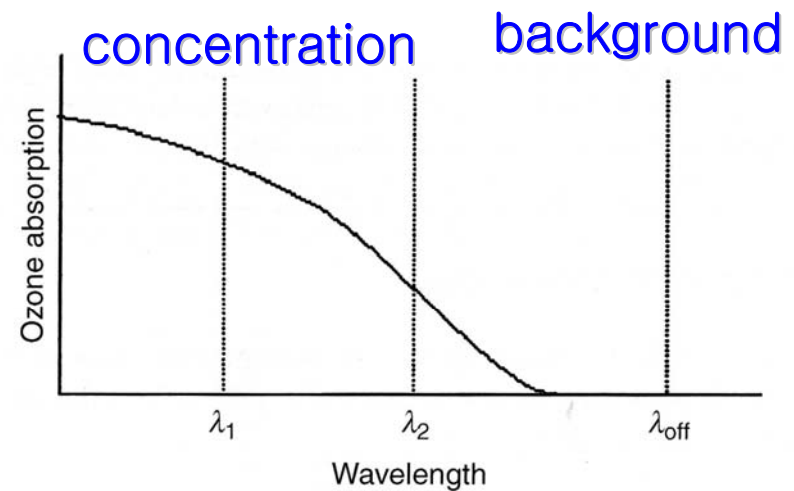of vibrational frequency

* Light Detection and Ranging (LIDAR)

With pulse laser, determine the concentrations of objects (aerosols, atmospheric molecules, etc) as a function of distance in tropo- and strato-spheres by measuring return times

LIDAR

e.g. Ozone Monitoring

concentration   background
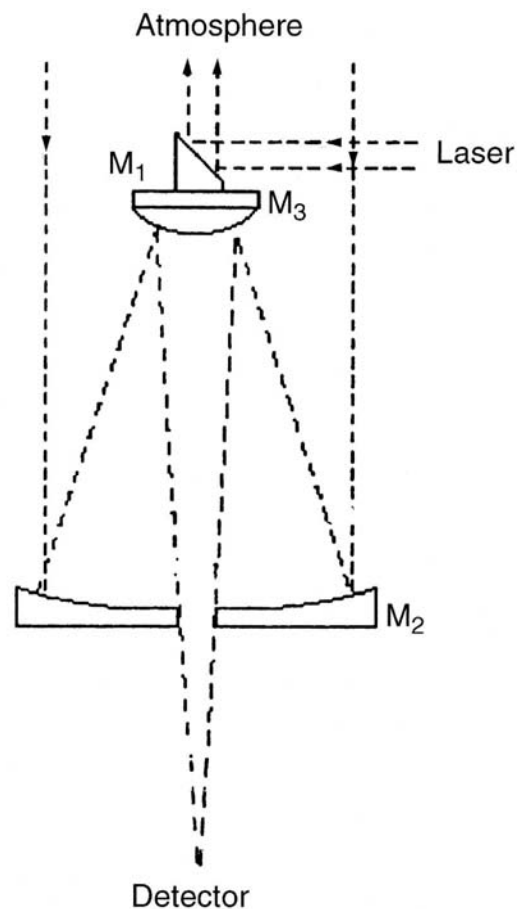
* Cavity Ring−Down Spectroscopy (CRDS)

"High sensitivity absorption technique: enhance sample length by multiple passes and measure the transmitted intensity as a function of time..."

Good for measuring spectra of reaction intermediates

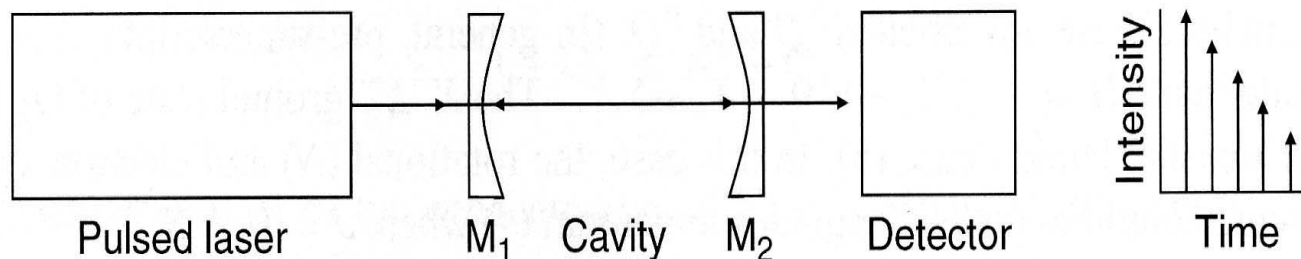$Beer - Lambert\ law: A = \log_{10}(I_0/I) = \varepsilon cl$

$\rightarrow \ln(I_0/I) = \alpha l \ (\alpha: absorption\ coefficient)$

$\therefore\ I/I_0 = \exp(-\alpha l) = \exp(-\alpha c t_l)$

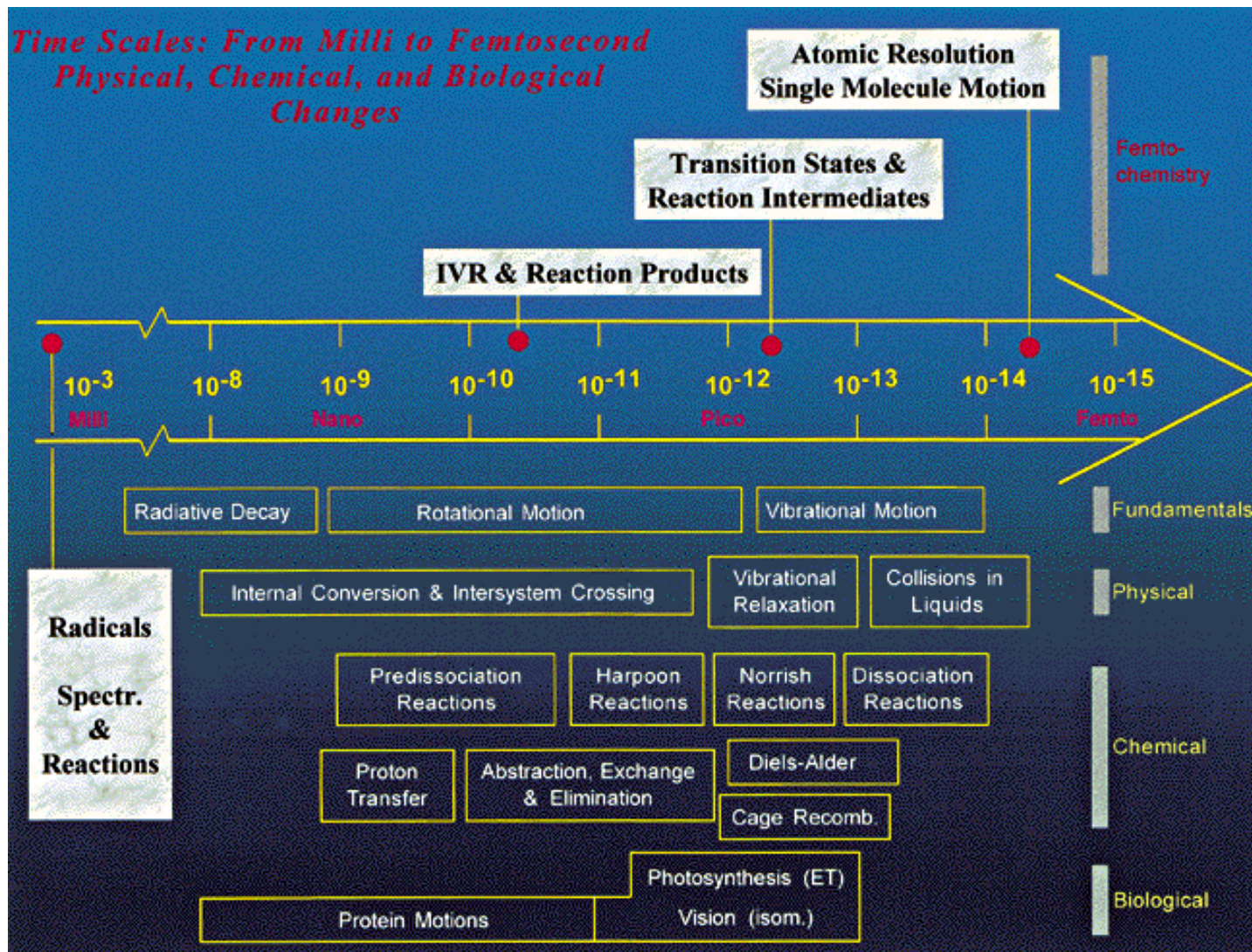*"light intensity decays exponentially as cell length l or travel time t"*

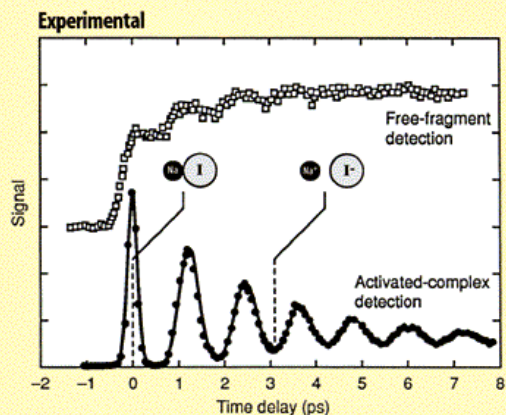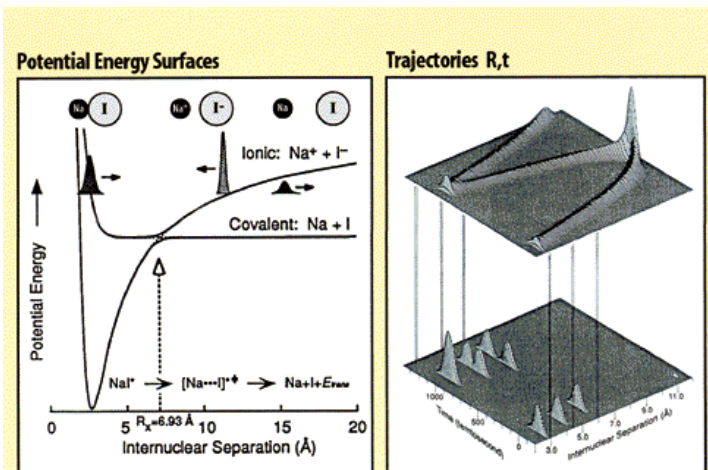$\therefore from\ decay\ rates \rightarrow determine\ \alpha(\nu)\ "absorption\ spectrum"$

99.93% reflectivity

Pulsed laser   M₁   Cavity   M₂   Detector   Intensity / Time

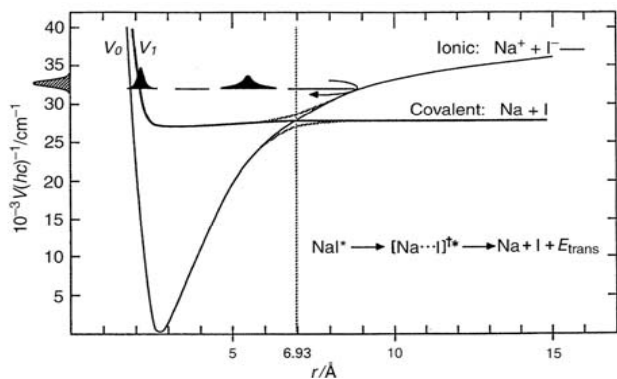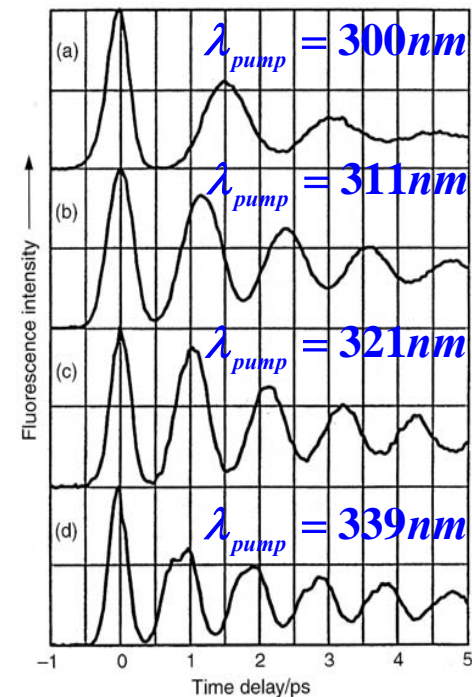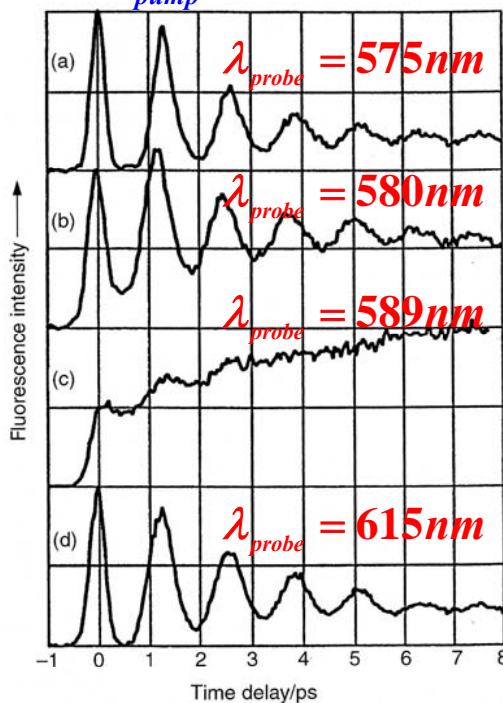## * Femtosecond Spectroscopy

"...With fs pump-probe pulses, ultrafast molecular motions and transient reaction intermediates can be directly monitored..."
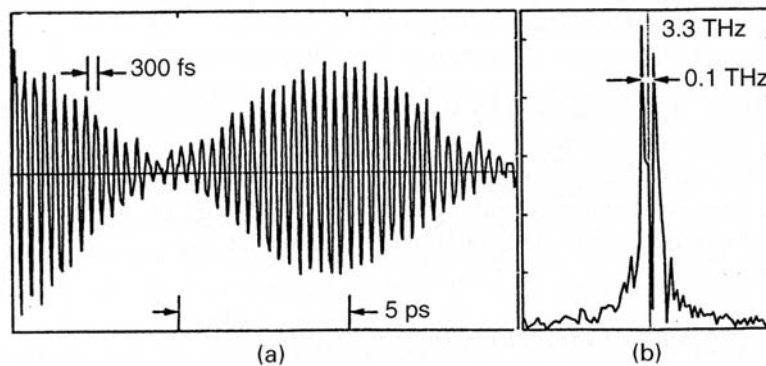
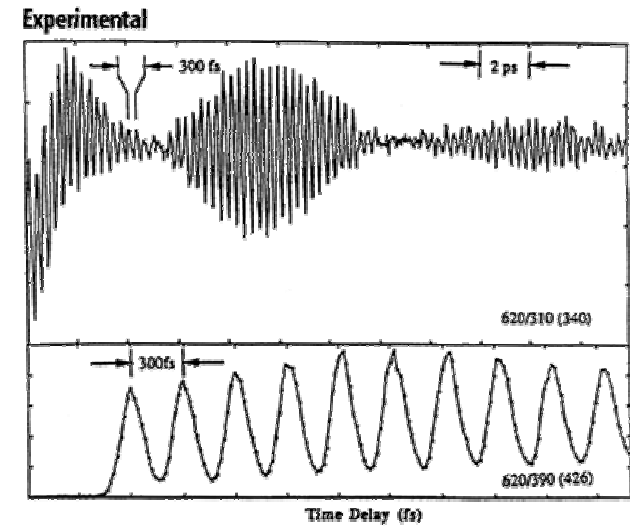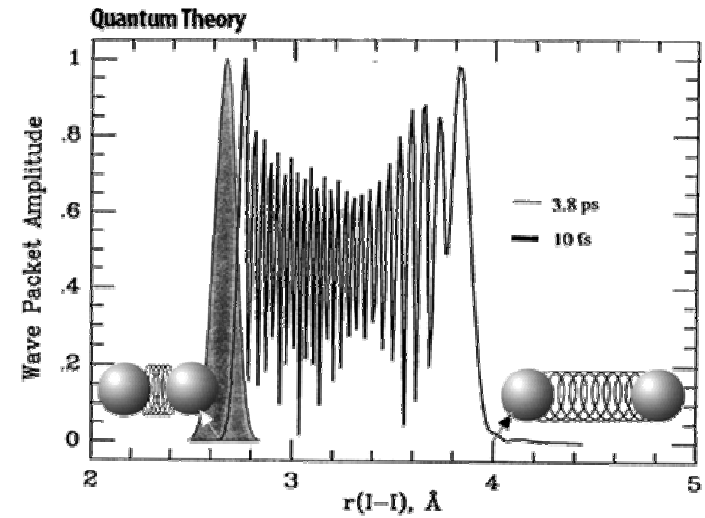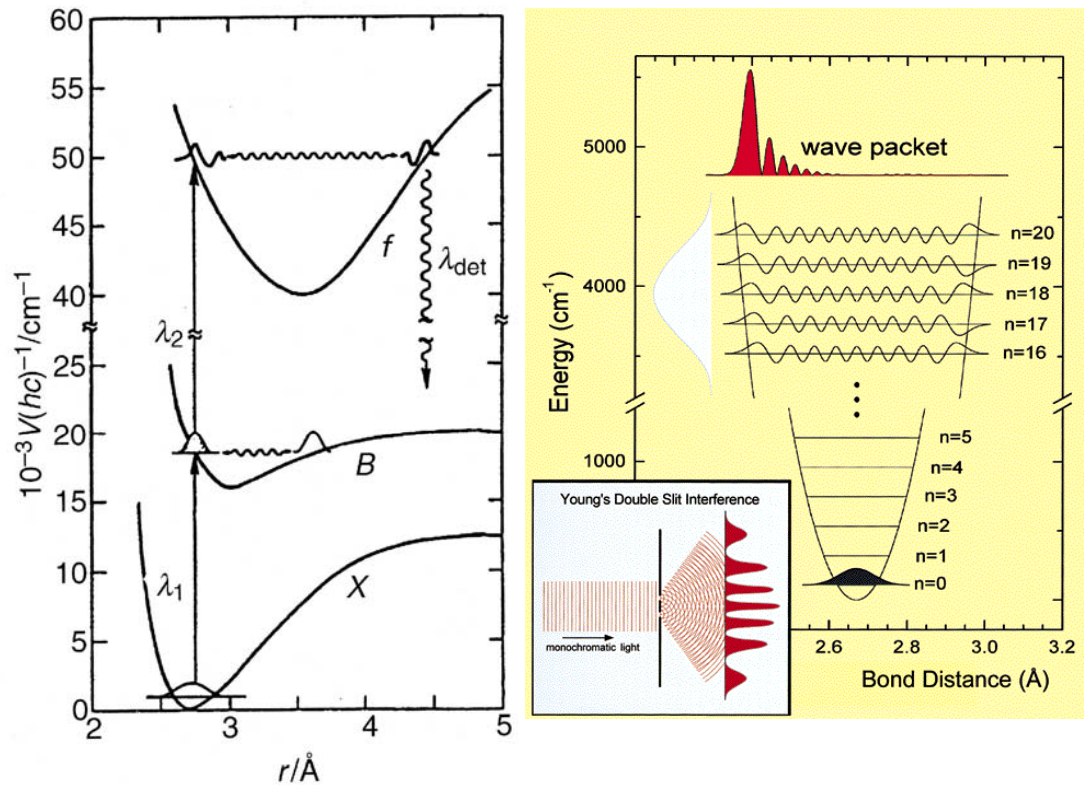# Example 1: $NaI \xrightarrow{\text{fs pump}} NaI^* \rightarrow [Na\cdots I]^* \rightarrow Na(^2P_{3/2}) + I(^2P_{3/2}, {}^2P_{1/2})$

$$\xrightarrow{\text{fs probe}} Na^* \rightarrow Na + h\nu$$

$\lambda_{pump} = 307\,nm$

$\lambda_{probe} =\sim 600\,nm$

$\lambda_{probe} = 575\,nm$

$\lambda_{probe} = 580\,nm$

$\lambda_{probe} = 589\,nm$

$\lambda_{probe} = 615\,nm$

$\lambda_{pump} = 300\,nm$

$\lambda_{pump} = 311\,nm$

$\lambda_{pump} = 321\,nm$

$\lambda_{pump} = 339\,nm$

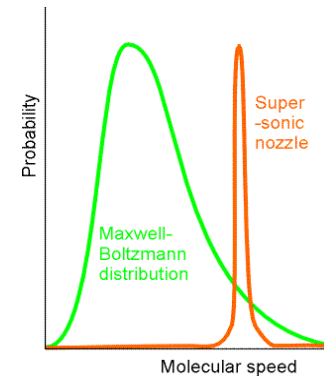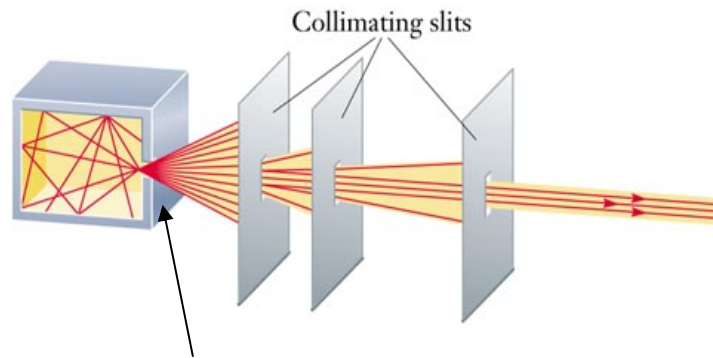*Directly monitor the wavepacket motions along dissociation path*

Example 2: Direct Observation of Vibrational Motions of I_2

$$I_2(X\,^1\Sigma_g^+) \xrightarrow{\ fs\ pump\ } I_2(B\,^3\Pi_{0_u^+})\ (wavepcket) \xrightarrow{\ fs\ probe\ } I_2(f\,0_g^+) \Rightarrow h\nu$$

* Spectroscopy of molecules in supersonic jets

− Supersonic jet: expansion from high to low pressure regions

hole diameter >> mean free path
→ directional flow
→ collision−less molecular flow

cold molecular beam
(T_{trans}∼1K, T_{rot}∼10K, T_{vib}∼50K)

High Mach number: $M = \dfrac{mass\ flow\ speed(u)}{speed\ of\ sound(a)}$, $a = \left(\dfrac{\gamma k T_{trans}}{m} \right)^{1/2}$
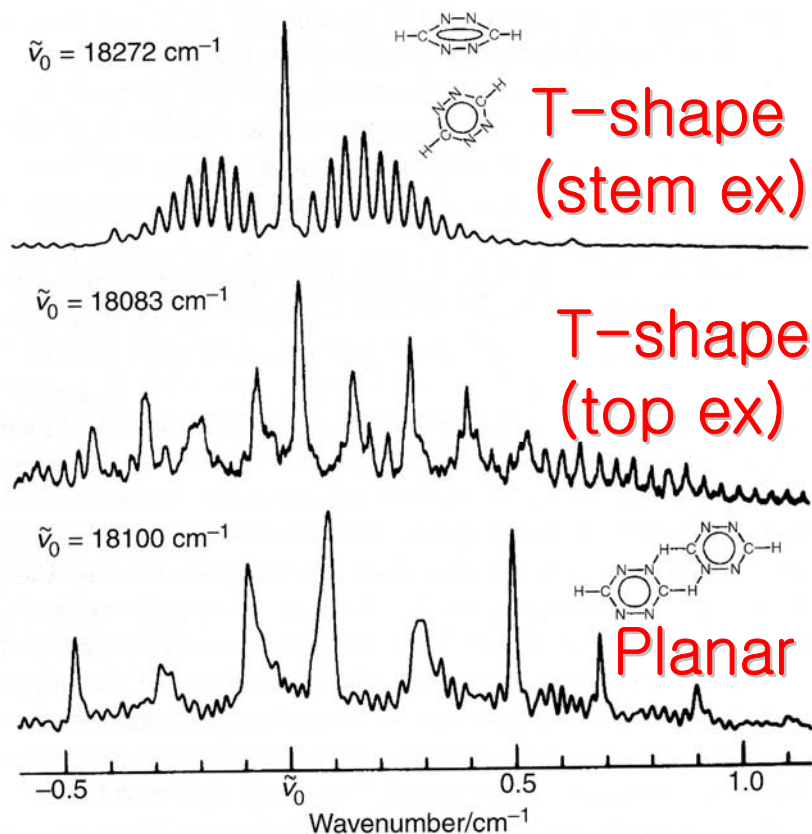
$\gamma = C_p / C_v$

"Due to adiabatic cooling, weakly bound clusters are formed"

- Fluorescence excitation spectroscopy: on clusters

"... perform high resolution spectroscopy on individual cluster isomers by measuring fluorescence as a function of excitation wavelength..."
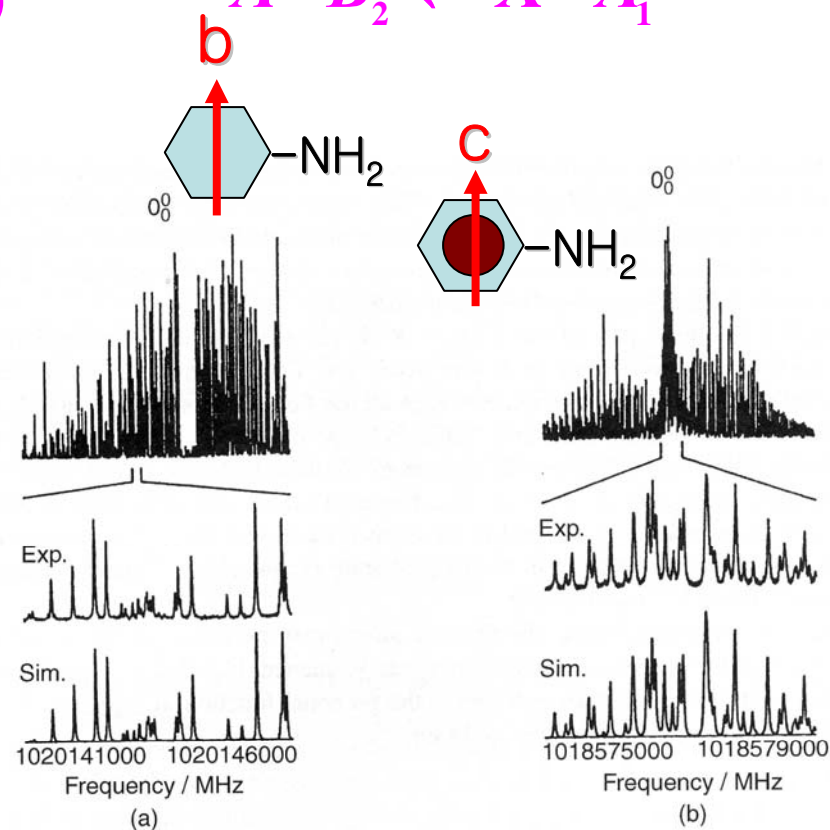
s-tetrazine dimer (two isomers)

$$\tilde{A}\ ^1B_{3u} \leftarrow \tilde{X}\ ^1A_g\ (n-to-\pi^* \ transition)$$

aniline–Ar cluster

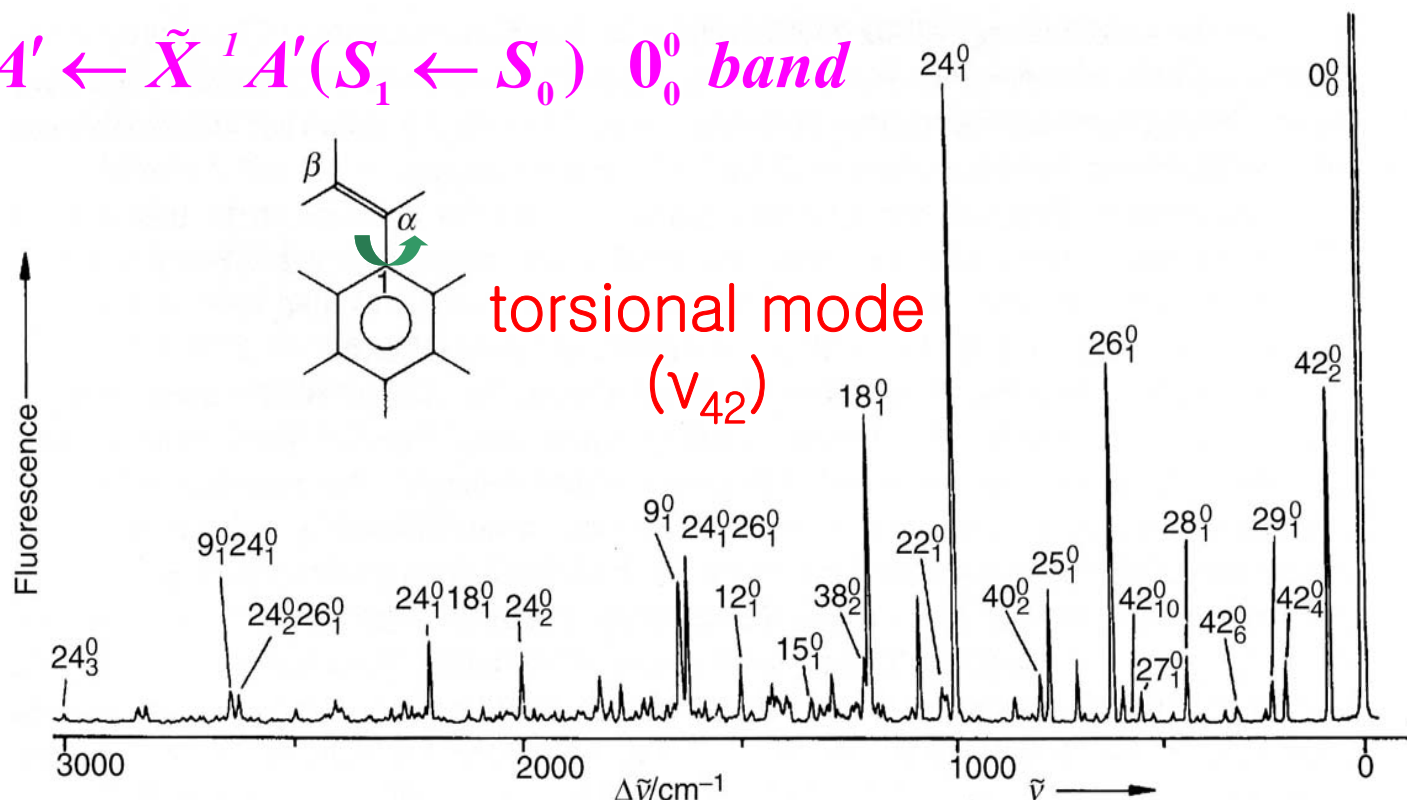$$\tilde{A}\ ^1B_2 \leftarrow \tilde{X}\ ^1A_1$$

– Single vibronic level fluorescence spectroscopy

Excite uncongested, single vibronic level and detect its pure fluorescence in collision-free conditions
$\rightarrow$ *determine PES of ground state very accurately*

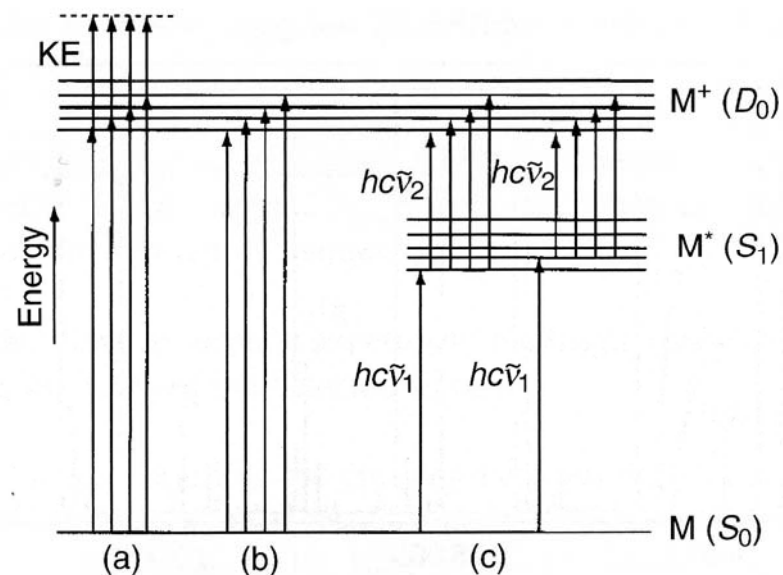$\tilde{A}\ ^1A' \leftarrow \tilde{X}\ ^1A'(S_1 \leftarrow S_0)\ 0_0^0\ band$

torsional mode
(ν_{42})

$Torsional\ PES: V(\phi) = \left[1070(1-\cos 2\phi) - 275(1-\cos 4\phi) + 7(1-\cos 6\phi)\right]$

$\rightarrow$ *Minimum Energy @ $\phi = 0°$ "planar due to conjugation"*

– Zero kinetic energy (ZEKE) photoelectron spectroscopy

Detect only zero–kinetic Energy photoelectrons via state–selective ionization and delayed pulsed field extraction

"High resolution spectroscopy on excited neutral and cationic states"

ZEKE spectrum of 1,4–difluorobenzene