Optical methods in chemistry
or
Photon tools for chemical sciences

Session 11

Course layout – contents overview and general structure

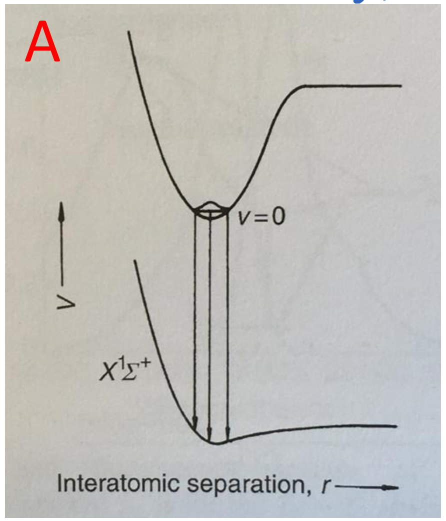
- Introduction and ray optics
- Wave optics
- Beams
- From cavities to lasers
- More lasers and optical tweezers
- From diffraction and Fourier optics
- Microscopy
- Spectroscopy
- Electromagnetic optics
- Absorption, dispersion, and non-linear optics
- Ultrafast lasers
- Introduction to x-rays
- Summary

Today:

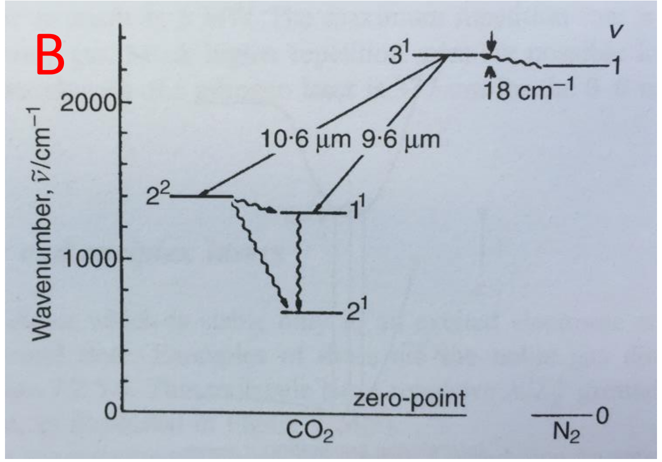
Ultrafast lasers with a bit of non-linear optics

Recall: Many different ideas and version

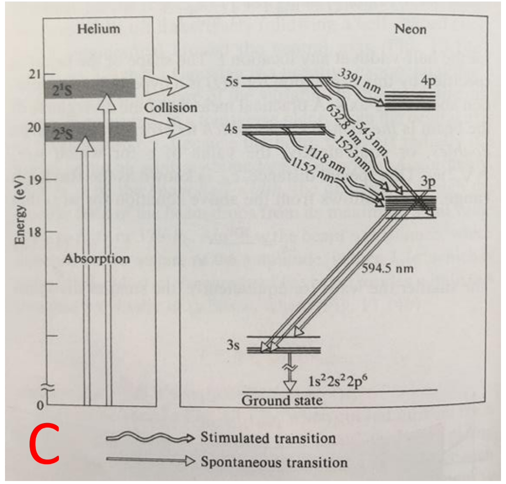
Excimer laser



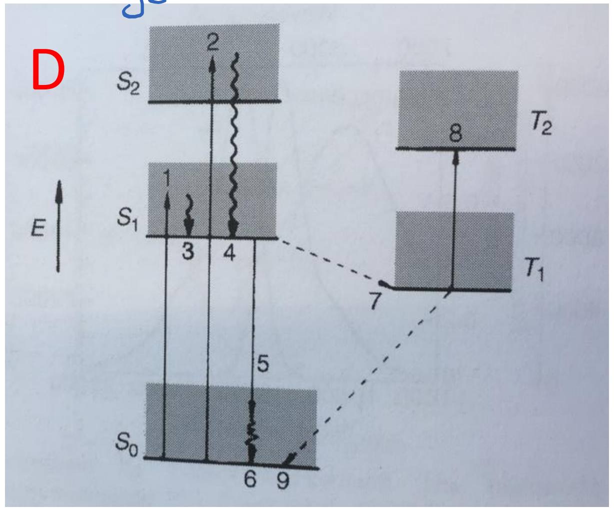
CO_2 laser – vibrational



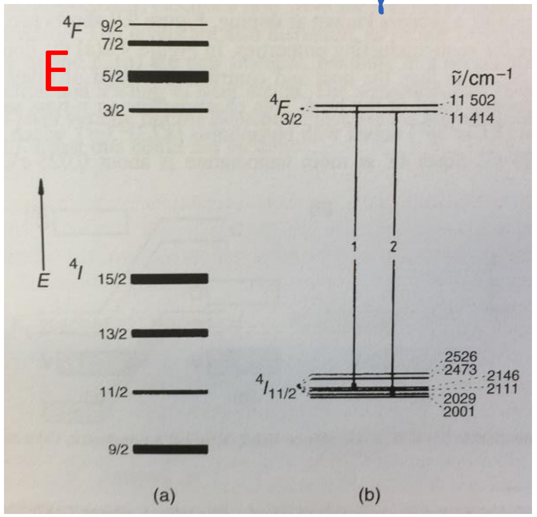
HeNe laser – electronic



Dye laser – tunable



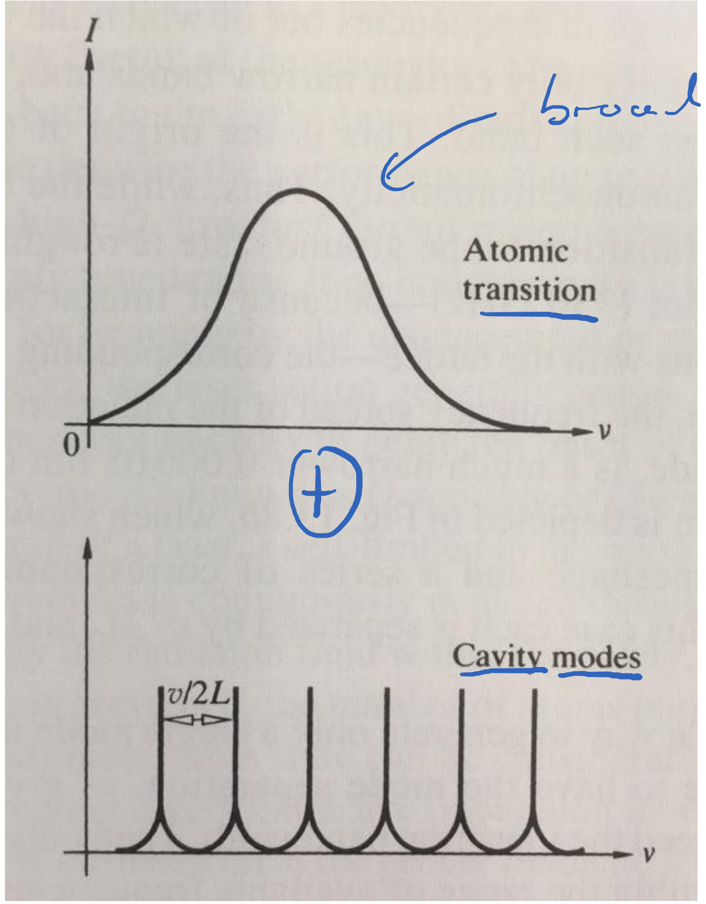
YAG laser – crystal



Recall: Lasers and laser cavities

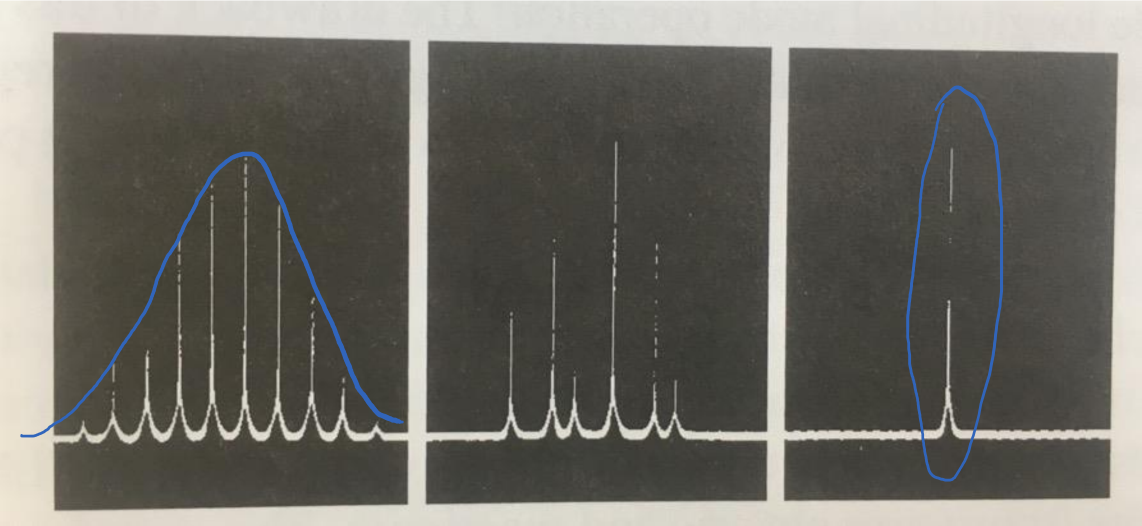
Atomic lines vs cavity modes

broad



discrete

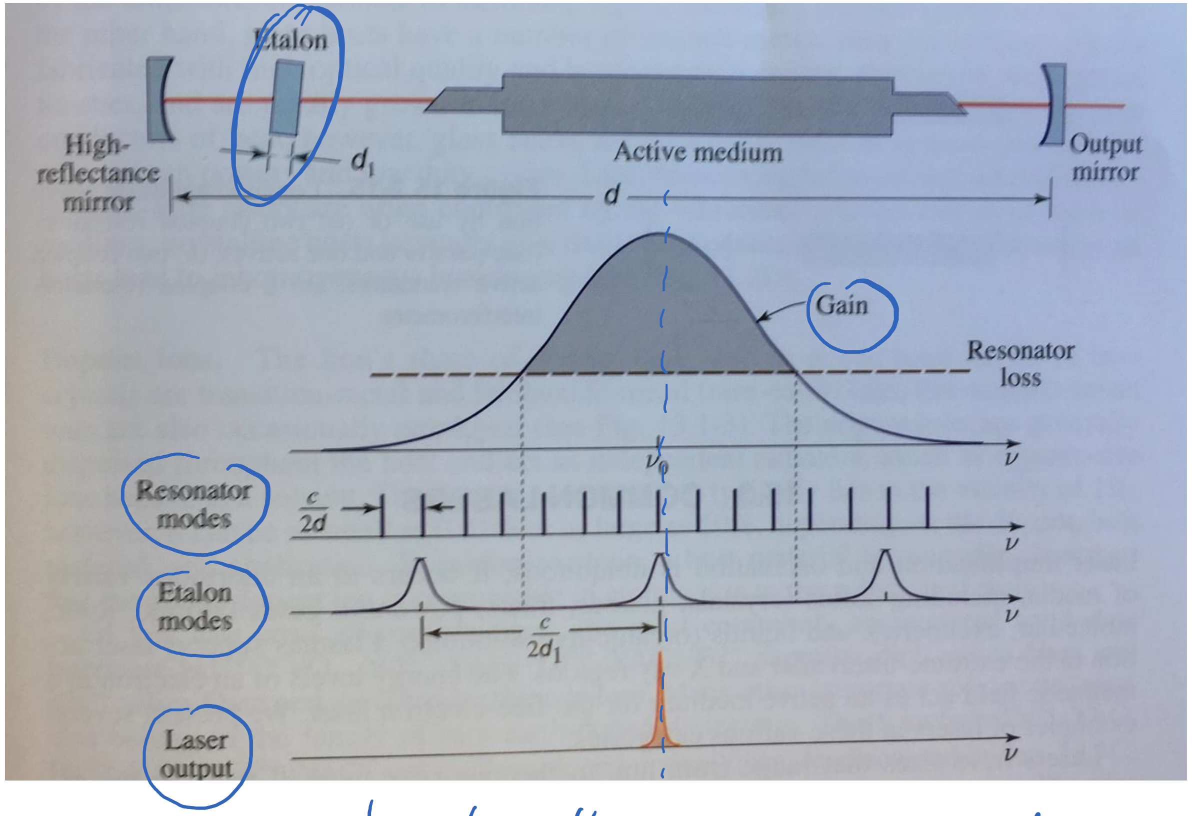
Mode selection



Laser: transition + cavity

cavity: mode selection,
only strongest survives

Recall: Mode selection with intracavity wavelength selection (here etalon)

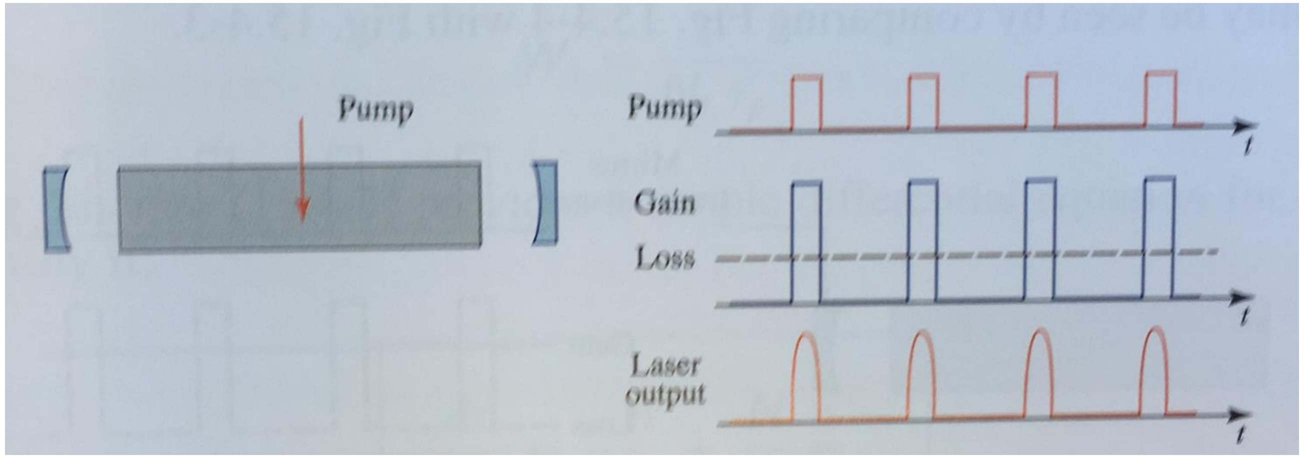


→ cavity length → # modes

→ add additional optical components (etalon)

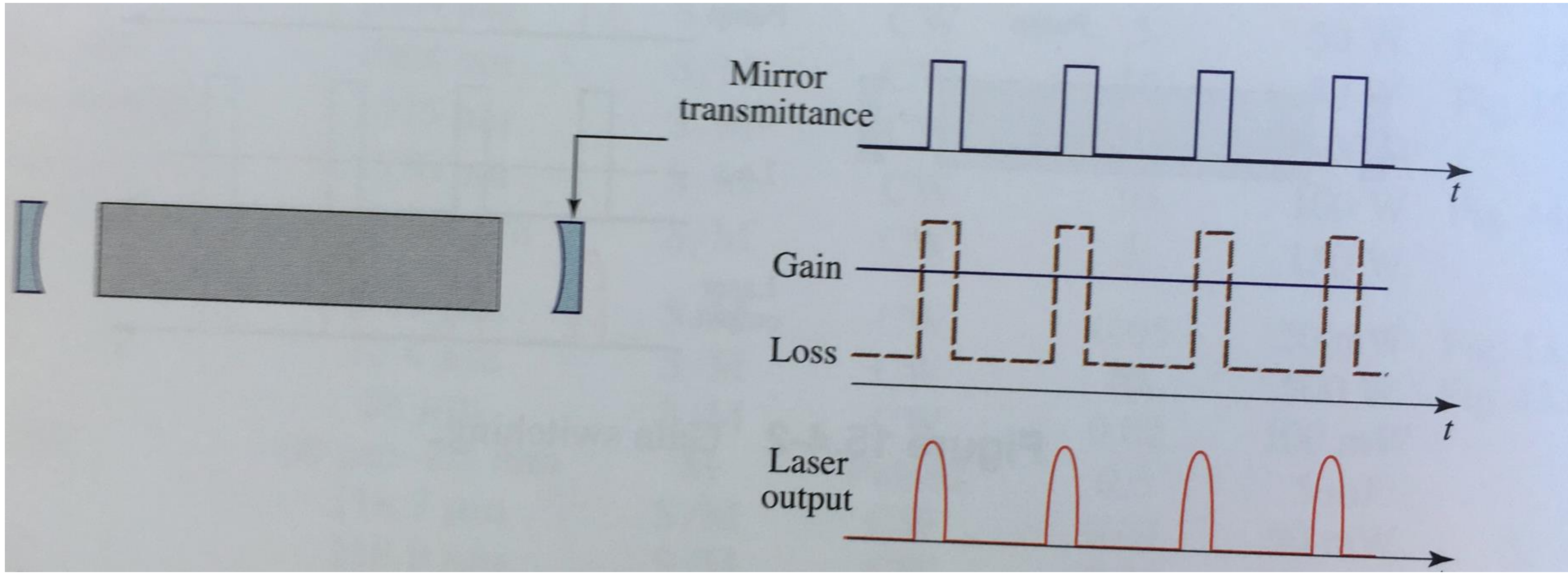
→ tune cavity properties

Pulsed lasers: Gain switching



e.g. Ruby laser

Pulsed lasers: Cavity dumping

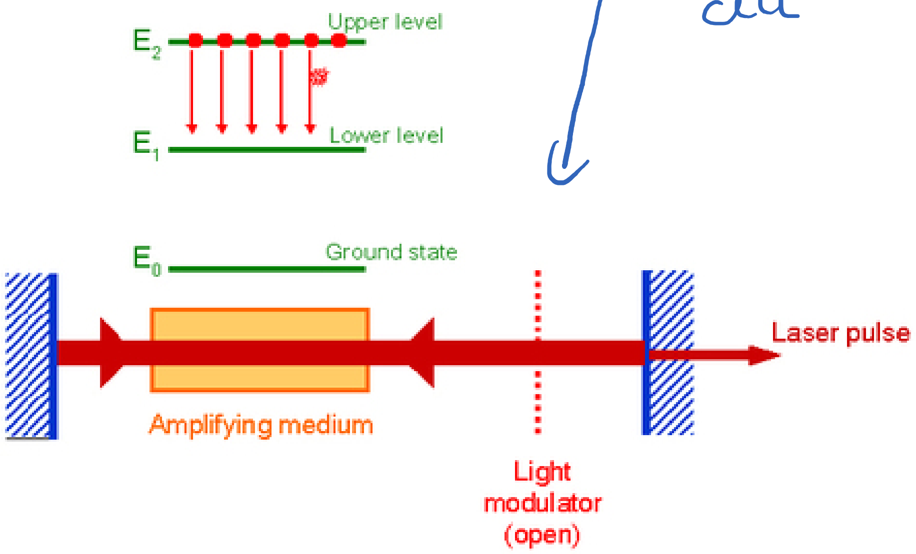


→ switch cavity on / off
with e.g. mirror

Q Switching

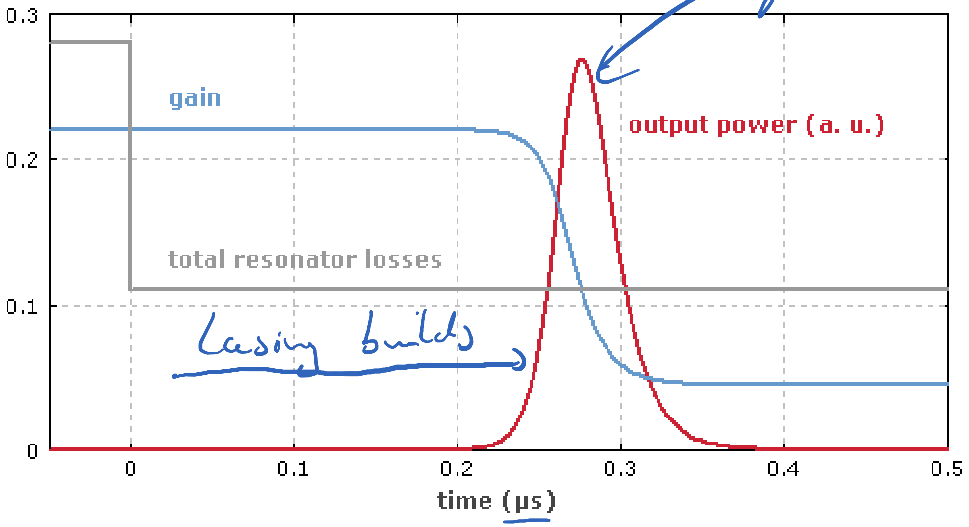
⇒ nsec lasers with mJ pulses

Pockels cell



switch

pulse



lasing builds

↑ Q-switch

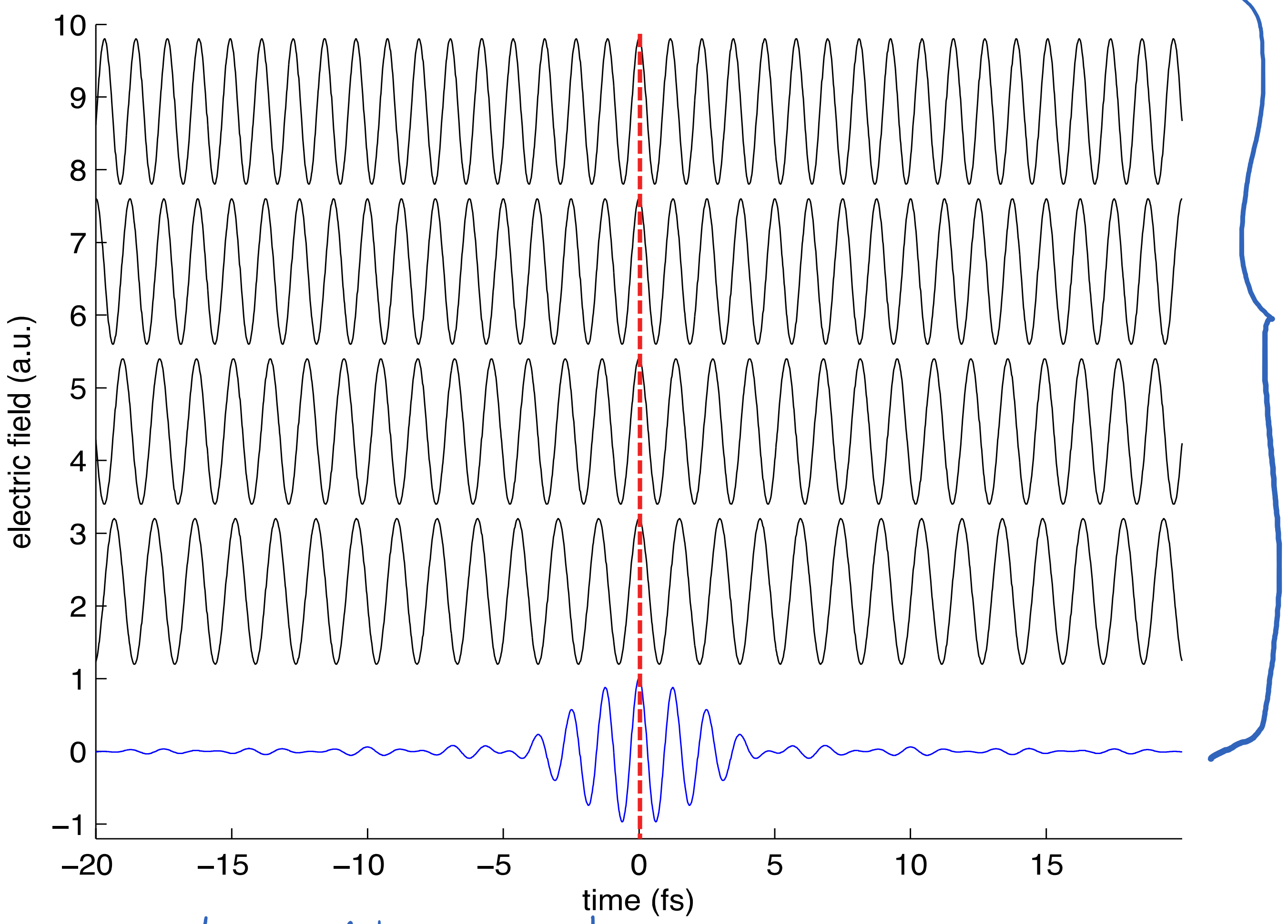
- spoil cavity properties
- pump your medium hard

⇐ suppress lasing during pumping, then open Q-switch

See video at: https://www.rp-photonics.com/q_switching.html

Now going to really short pulses:

Short pulse needs many frequencies: Shortest pulse is Fourier transform limited pulse (aka bandwidth limited pulse)



Short pulse:

Coherent superposition of plane waves

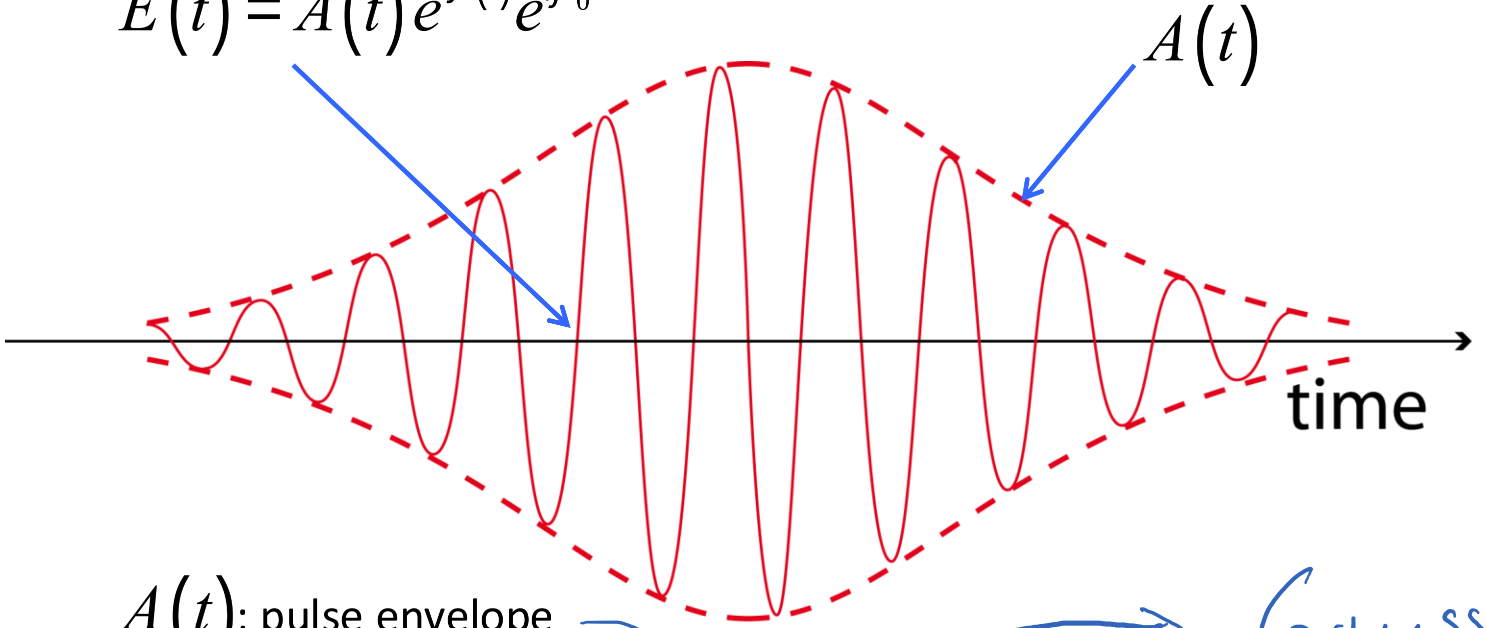
$\Downarrow$

but you also need a fixed phase relationship

Note: the shorter the pulse, the more frequencies you need

Note: Mathematical description of optical pulse

$$E(t) = A(t)e^{i\varphi(t)}e^{i\varphi_0}$$



$A(t)$; pulse envelope → Gaussian ~ $\exp-\left(\frac{t}{\tau}\right)^2$

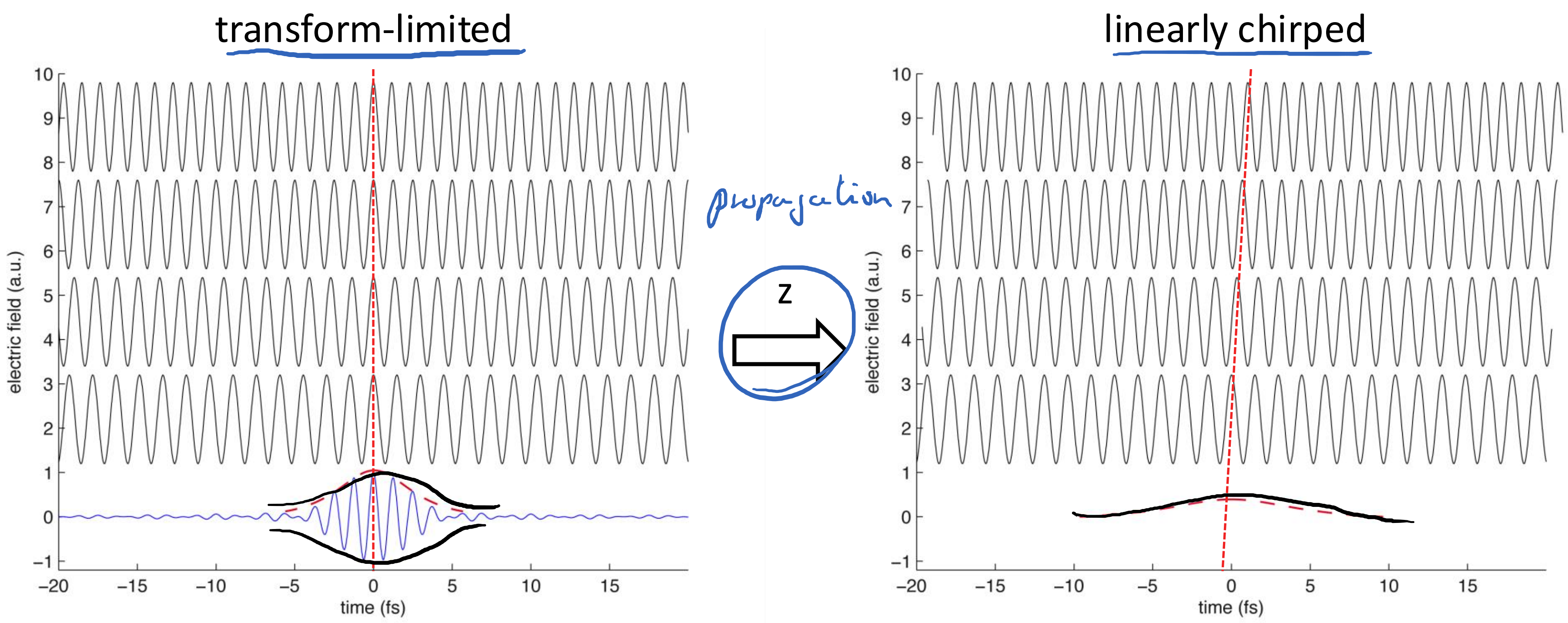
$\varphi(t)$; time dependent phase of electric field

$\omega(t) = -\frac{d\varphi(t)}{dt}$; instantaneous frequency

φ_0 ; absolute phase (typically neglected for multi-cycle pulses)

A note on “chirp”

Initially transform limited pulse becomes chirped upon propagation, ($k_2 \neq 0$, $\gamma = 0$)



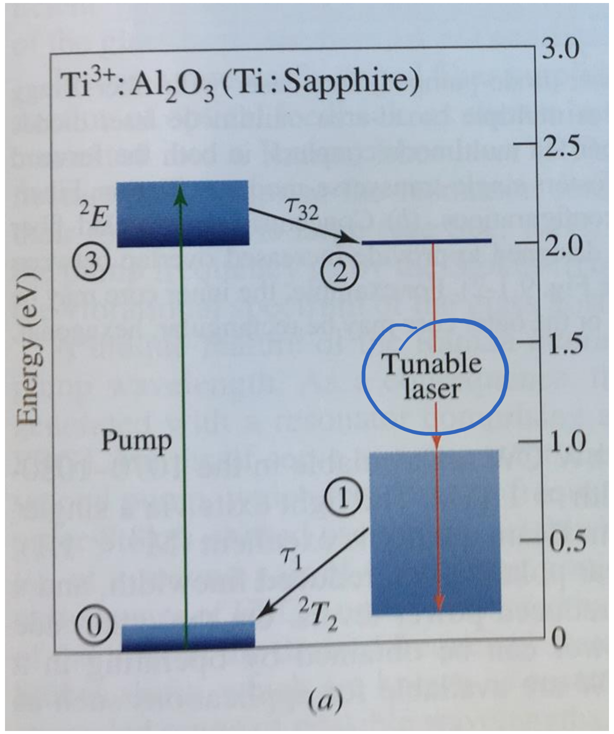
→ different velocities in dispersive media

→ short pulse becomes chirped upon propagation and thus, also stretched

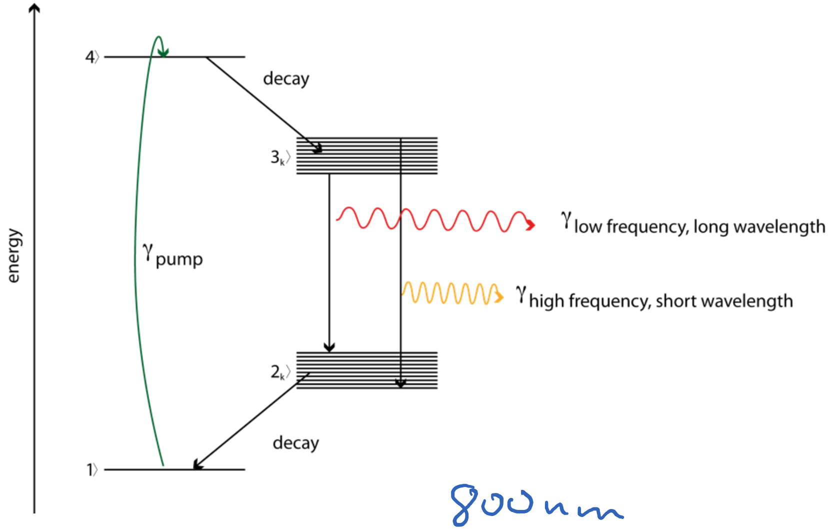
→ need dispersion control

Important laser: TiSa

- Ti^{3+} ions in Al_2O_3 (Saphire) → optically active
- Tunable, broad bandwidth ✓
- Can provide ultrashort pulses ✓
- Workhorse laser for ultrafast sciences

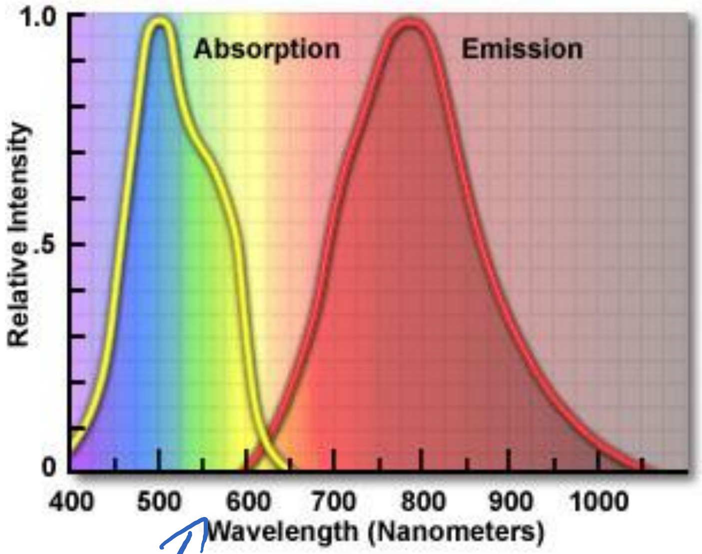


(a)



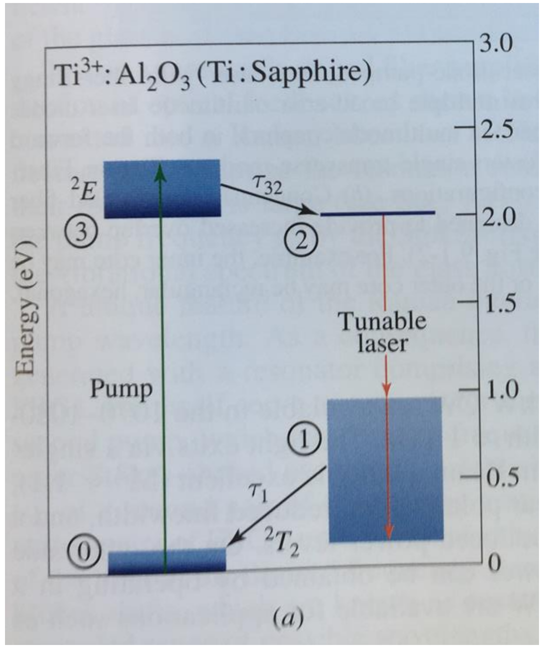
Note
typically pumped
with YAG laser

800nm

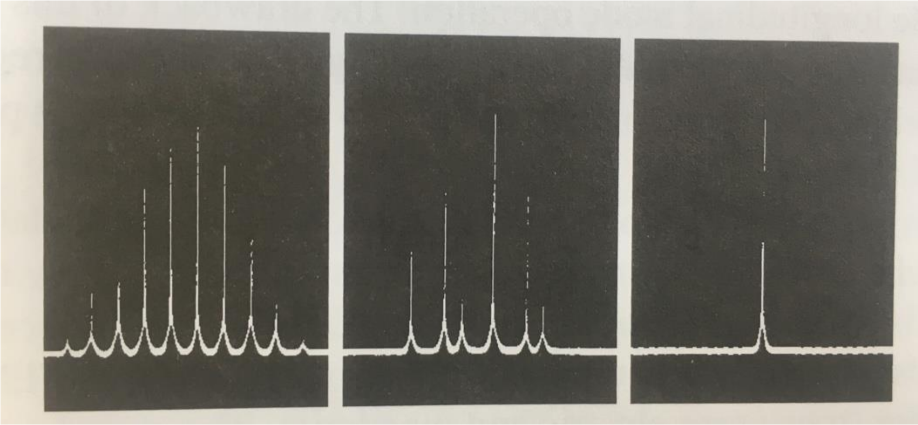


YAG

Short pulses and cavities – how do they go together?



how do both go together



We introduced switching methods

- Gain switching
- Cavity dumping
- Q-switching

but we need to do better…

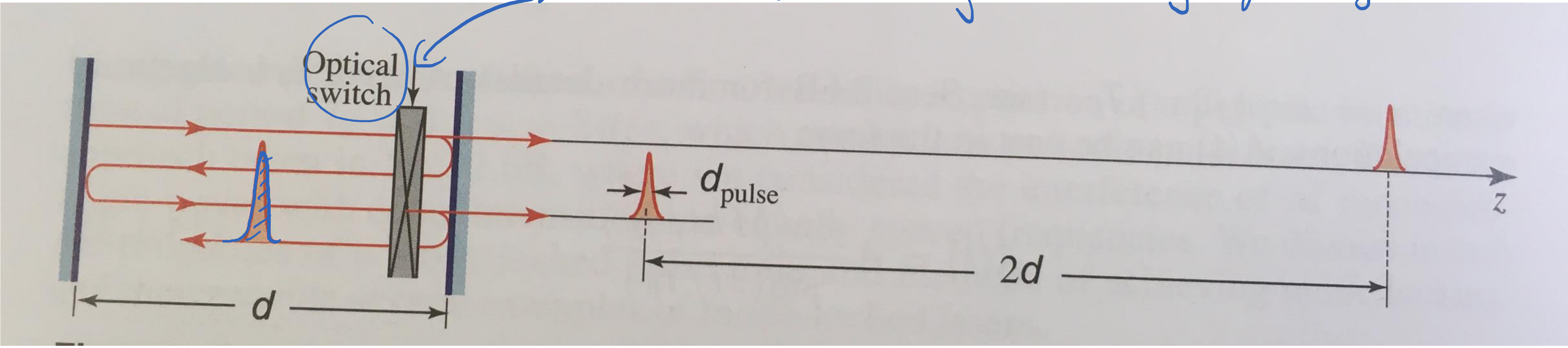
For short pulse we need
→ many frequencies
→ fixed phase relationship

In principle long cavity helps → supports many modes

$\lambda = \frac{2L}{d} \rightarrow \nu_n = n\left(\frac{c}{2L}\right)$ but phase?!

Mode locking

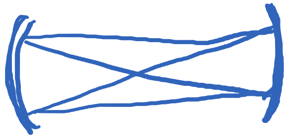
→ we need something that only opens for duration of pulse!



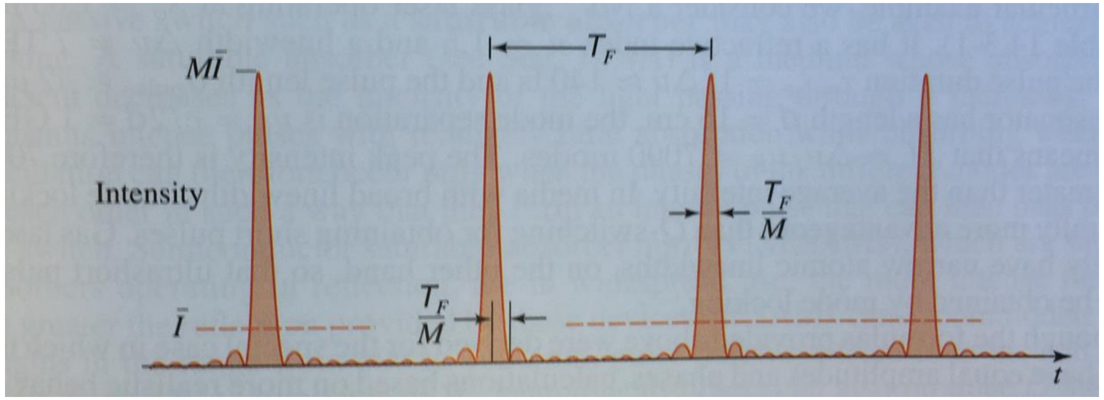
travelling pulse

→ output is a periodic pulse train

Remember cavity geometries



→ fits Gaussian beam well



Expanded description of relationship between Polarization density P and Electric field E

Generally $\quad P = \varepsilon_0 \chi E \quad$ $\chi \rightarrow$ lets say details unknown

Solution $\quad$ Taylor expansion

$$P = \varepsilon_0 \left(\chi E + \chi^2 E^2 + \chi^3 E^3 + \dots \right)$$

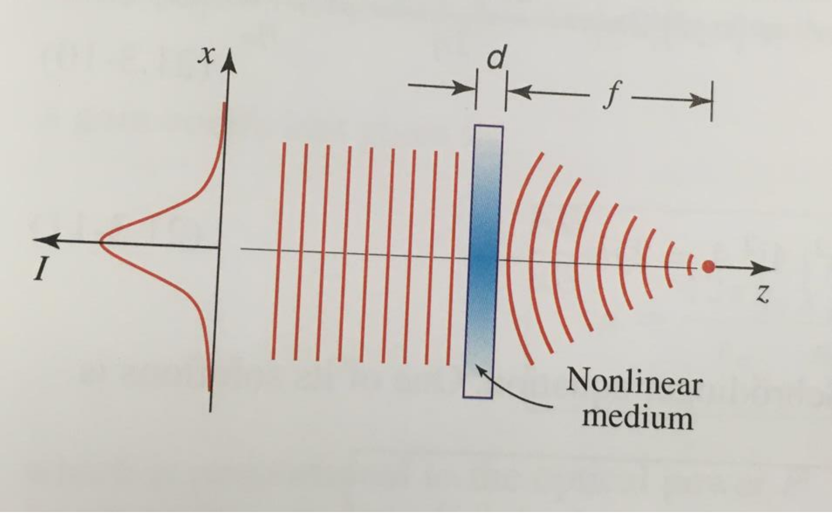
linear $\qquad$ 2nd order non-linearity $\qquad$ 3rd order non-linearity

Convention $\quad P = \varepsilon_0 \chi E + 2 d E^2 + 4 \chi^{(3)} E^3 + \dots$

Third order non-linear optics example: Optical Kerr Effect and Self-Focusing

For 3rd order non-linearities you can get an intensity-dependent refractive index

$$\boxed{n(I) = n + n_2 \bar{I} \quad \text{optical Kerr effect}}$$

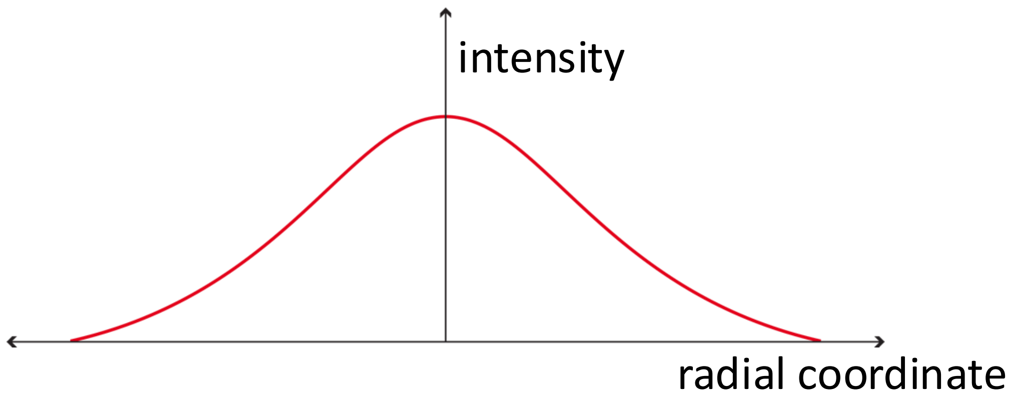


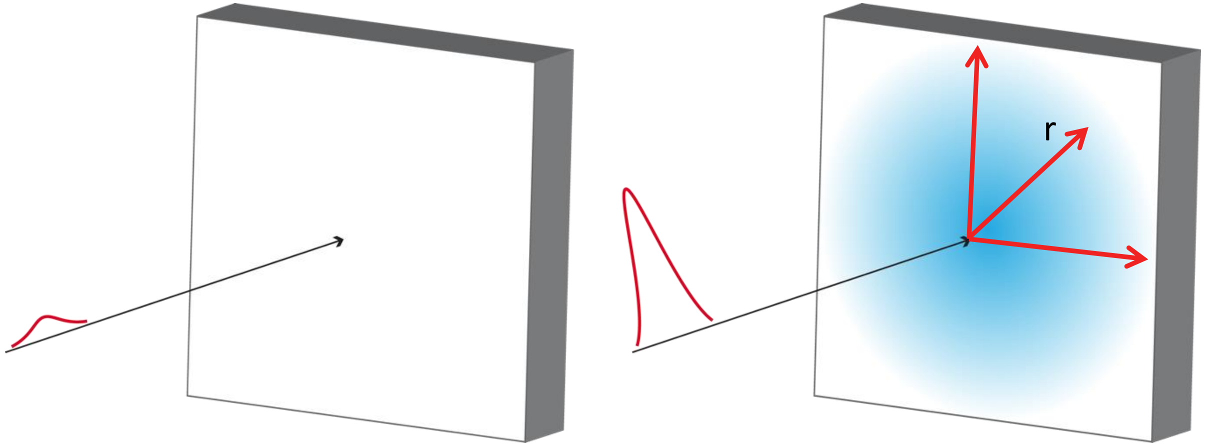
→ use light pulse to change optical properties

→ with Gaussian beam → intensity dependent lens

Kerr lens from non-linear refractive index

spatial profile:



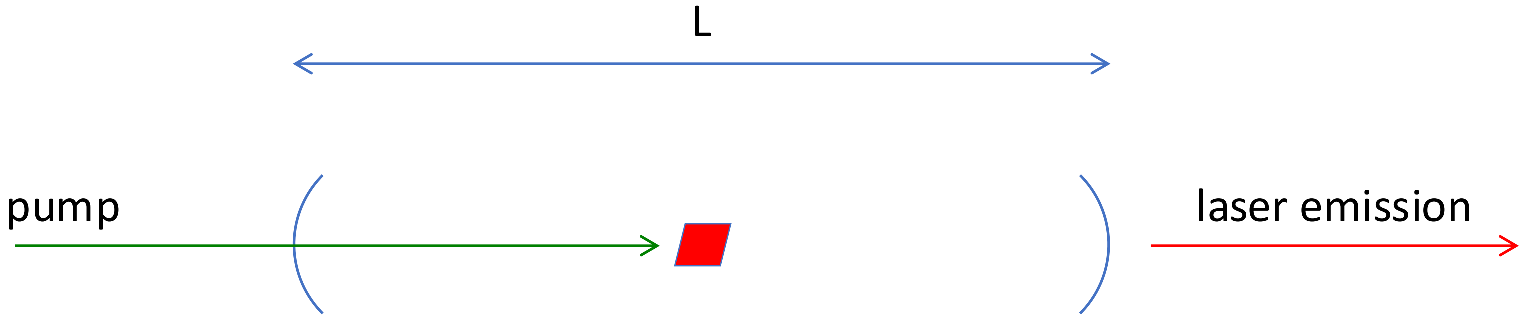


material behaves transparent

material behaves as a lens

active optical element as a fct of I

Resonant laser cavity

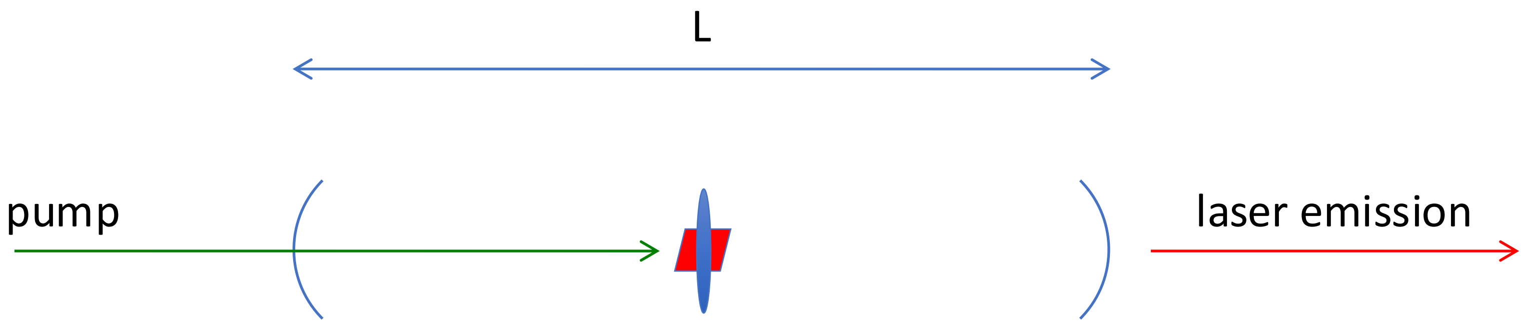


Resonant modes have nodes at cavity end mirrors

Resonant wavelengths and possible frequency modes given by:

$$\lambda_n = \frac{2L}{n} \qquad \nu_n = n\left(\frac{c}{2L}\right)$$

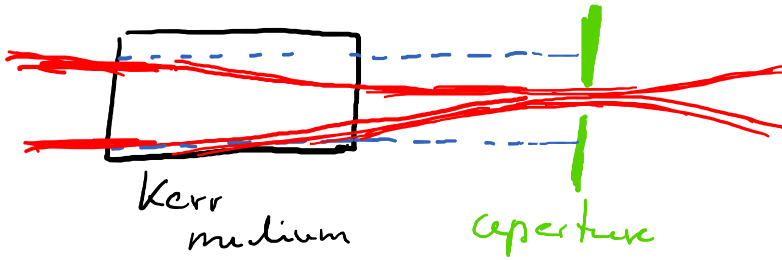
Self mode locking



- Kerr Lens Effect, due to nonlinear index of refraction
- At high intensities, the gain crystal acts like a lens
- Cavity tuned so that is most efficient with the crystal behaving as a lens
- Many modes lase and automatically arrange phases for pulsed high-intensity operation
- Intra-cavity dispersion tuned to support pulsed operation
- nJ pulse energies as short as 4 fs FWHM
- Output ~100MHz repetition rate pulse train

$$\nu_{rep-rate} = \left(\frac{c}{2L} \right)$$

hard aperture



Low intensity, no change in $n \rightarrow$ no/low transmission

high intensity

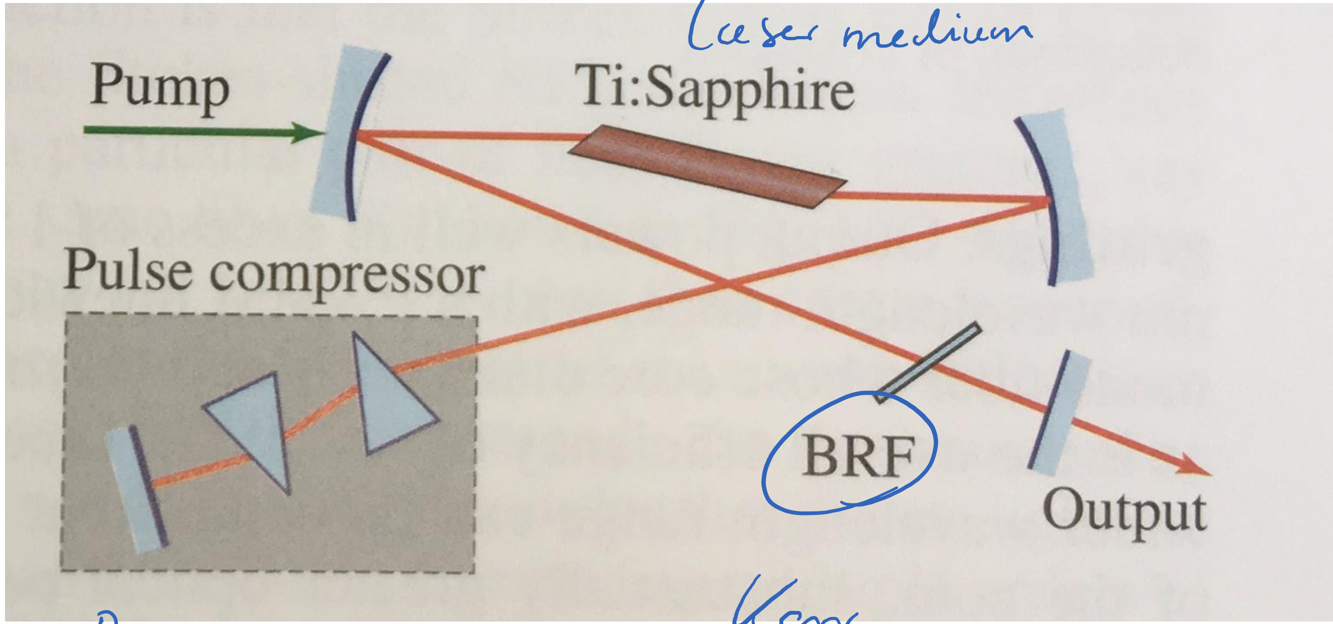
$\Downarrow$

pulse with proper phase relationship survives

Soft aperture

pump only small region

TiSaphire oscillator setup → femtosecond lasers

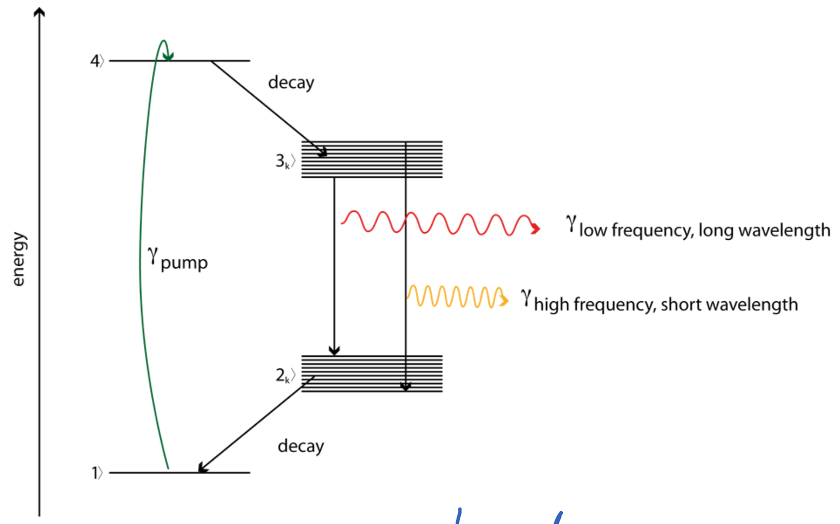


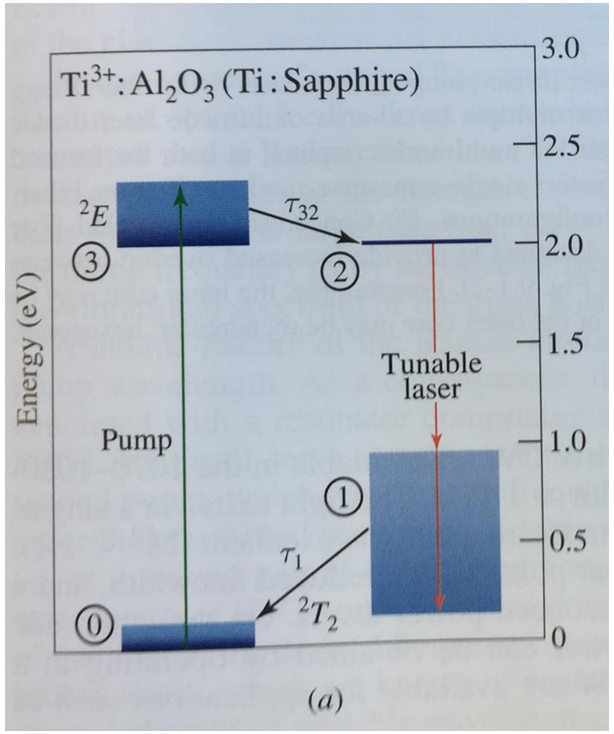
Dispersion control

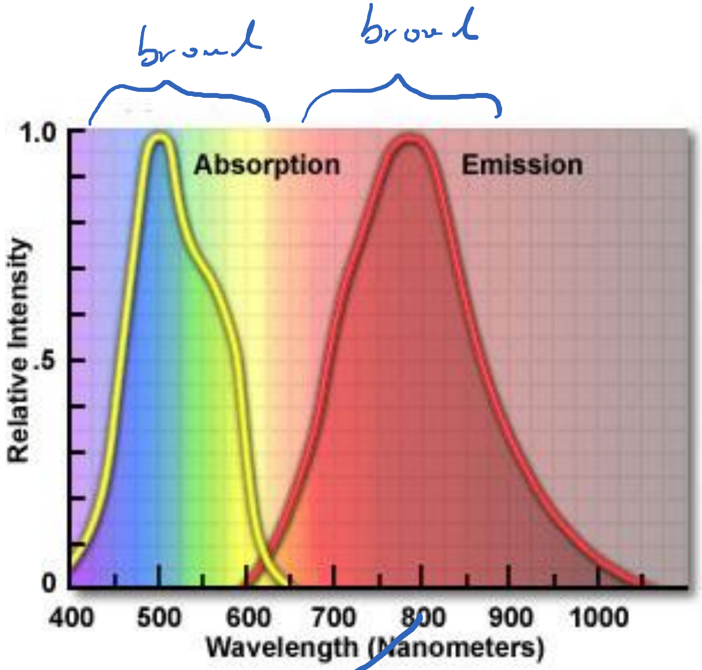
Kerr lens

Important laser: TiSa

- Ti^{3+} ions in Al_2O_3 (Saphire)
- Tunable, broad bandwidth
- Can provide ultrashort pulses
- Workhorse laser for ultrafast sciences



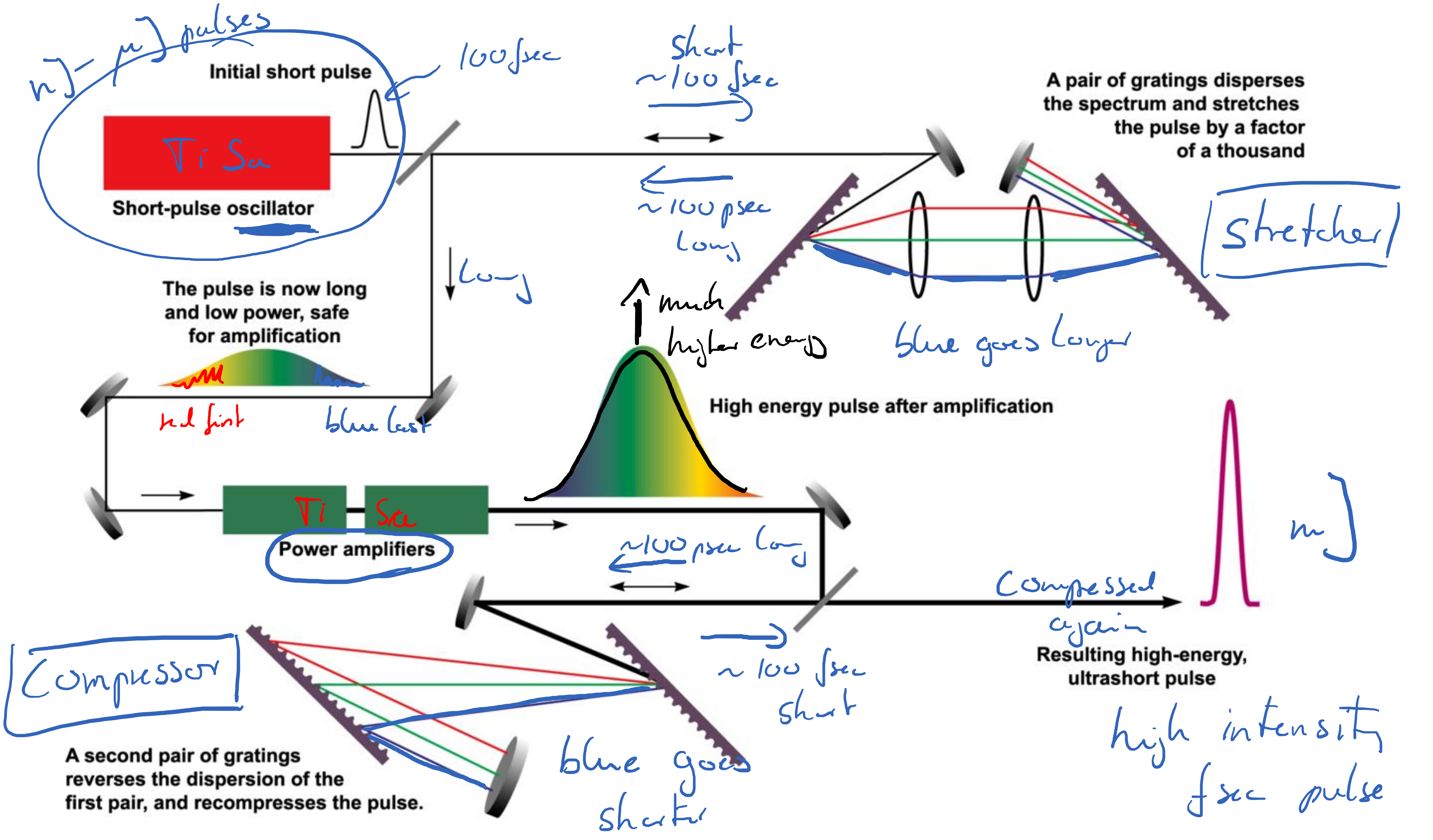




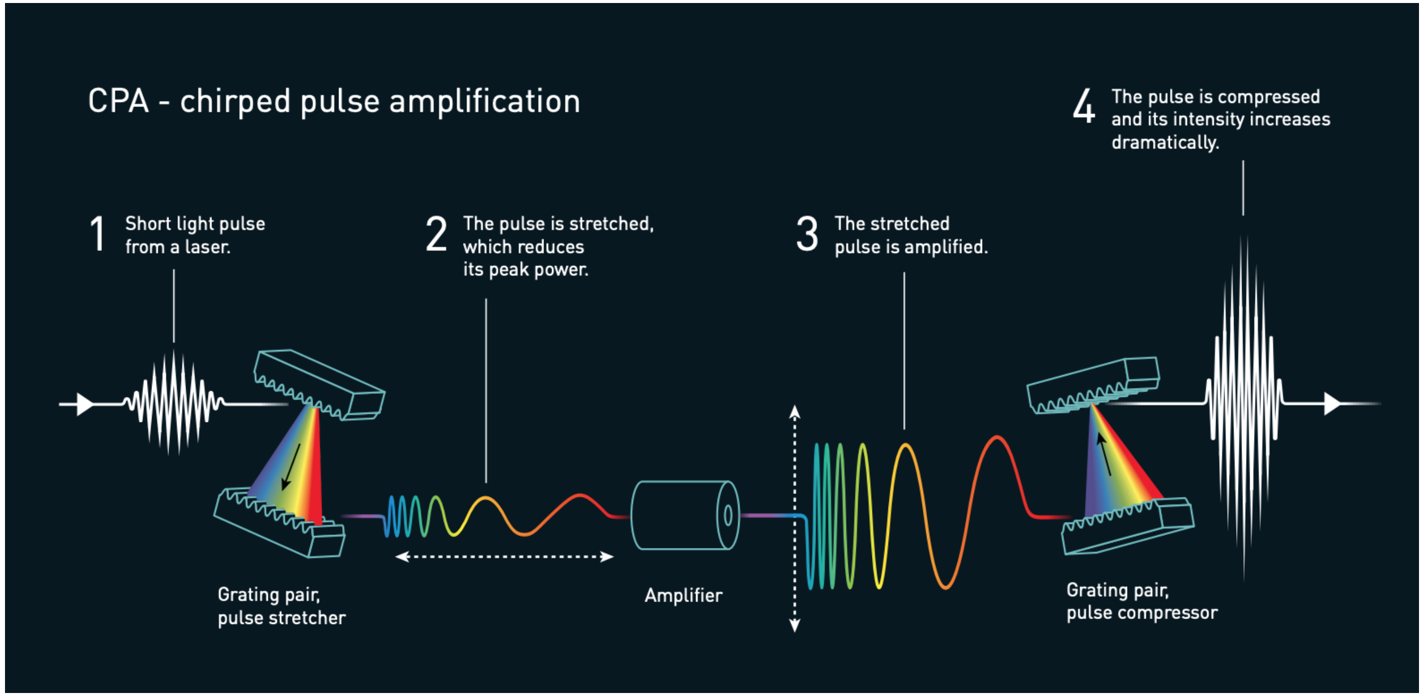
Spectral width that determines the minimal pulse length

Chirped pulse amplification

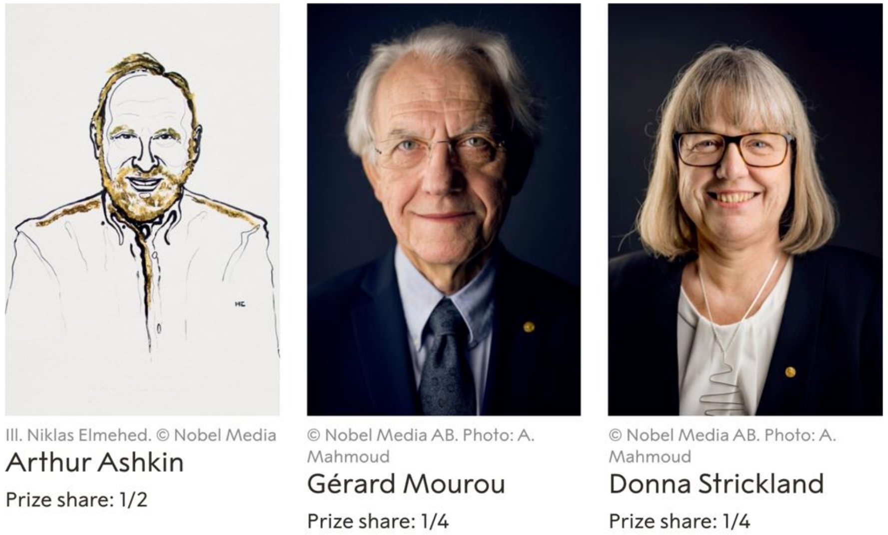
→ how to make intense fsec pulses ?



Back to start



The Nobel Prize in Physics 2018



The inventions being honoured this year have revolutionised laser physics. Extremely small objects and incredibly fast processes now appear in a new light. Not only physics, but also chemistry, biology and medicine have gained precision instruments for use in basic research and practical applications. Arthur Ashkin invented optical tweezers that grab particles, atoms and molecules with their laser beam fingers. Viruses, bacteria and other living cells can be held too, and examined and manipulated without being damaged. Ashkin's optical tweezers have created entirely new opportunities for observing and controlling the machinery of life. Gérard Mourou and Donna Strickland paved the way towards the shortest and most intense laser pulses created by mankind. The technique they developed has opened up new areas of research and led to broad industrial and medical applications; for example, millions of eye operations are performed every year with the sharpest of laser beams.

Ultrafast lasers in chemistry

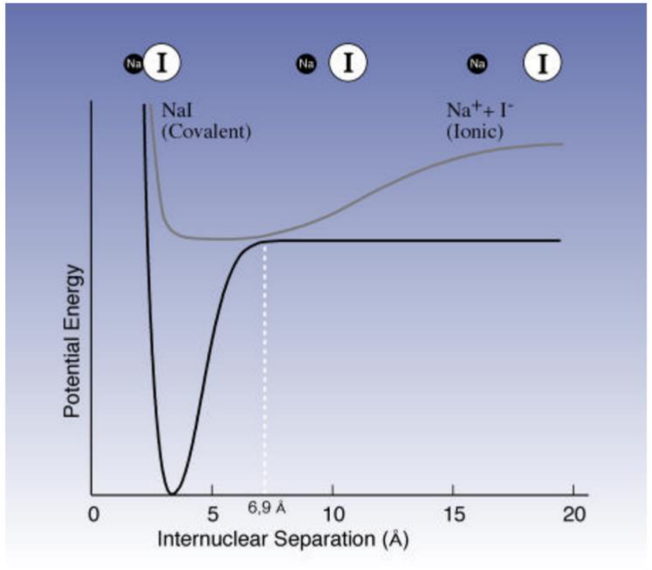


Fig. 1a) Potential energy curves showing the energies of ground state (bottom curve with deep minimum) and excited state (top curve) for NaI as function of the distance between the nuclei.

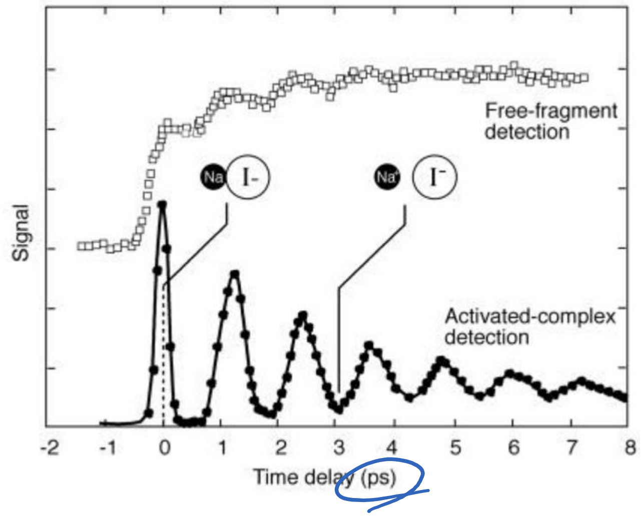


Fig. 1b) Experimental observations of coherent vibrations (so-called wave-packet motion) in femtosecond-excited NaI, on one hand manifested in terms of amount of activated complex [Na-I] at covalent (short) distance, on the other*

Photo from the Nobel Foundation archive.

Ahmed H. Zewail

Prize share: 1/1

→ pump/probe spectroscopy

This year's Nobel Laureate, Professor Ahmed Zewail, is rewarded for his pioneering investigations of chemical reactions on the time-scale they really occur. This is the same timescale on which the atoms in the molecules vibrate, namely femtoseconds (1 fs = 10-15 seconds). Only recently have developments in laser technology enabled us to study such rapid processes, using ultra-short laser flashes. Professor Zewail's contributions have brought about a revolution in chemistry, with consequences for many other fields of science, since this type of investigation allows us to understand and predict important processes.

↳ PChem !

Third order non-linear optics example: Self-phase modulation

Gaussian pulse

$I_{(t)} = I_0 \exp(-\frac{t^2}{T^2})$

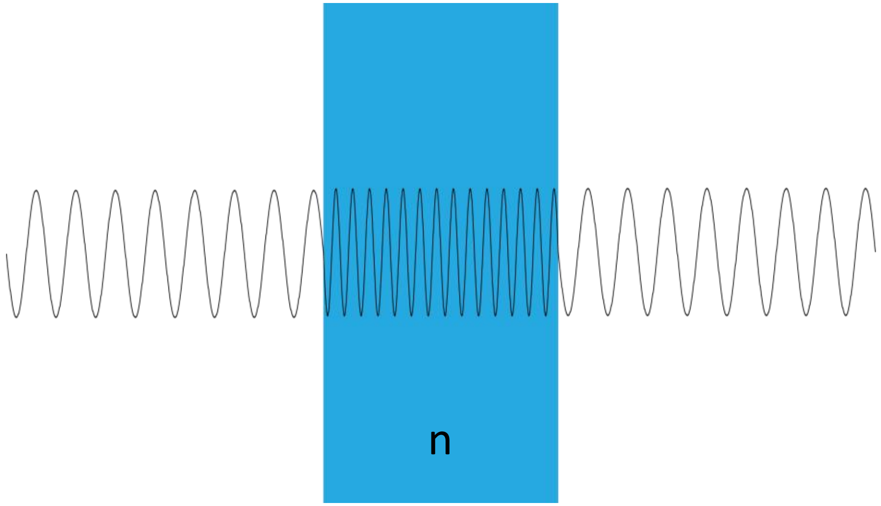
$n_{(I)} = n_0 + n_2 I$

pulse travels → time-dependent

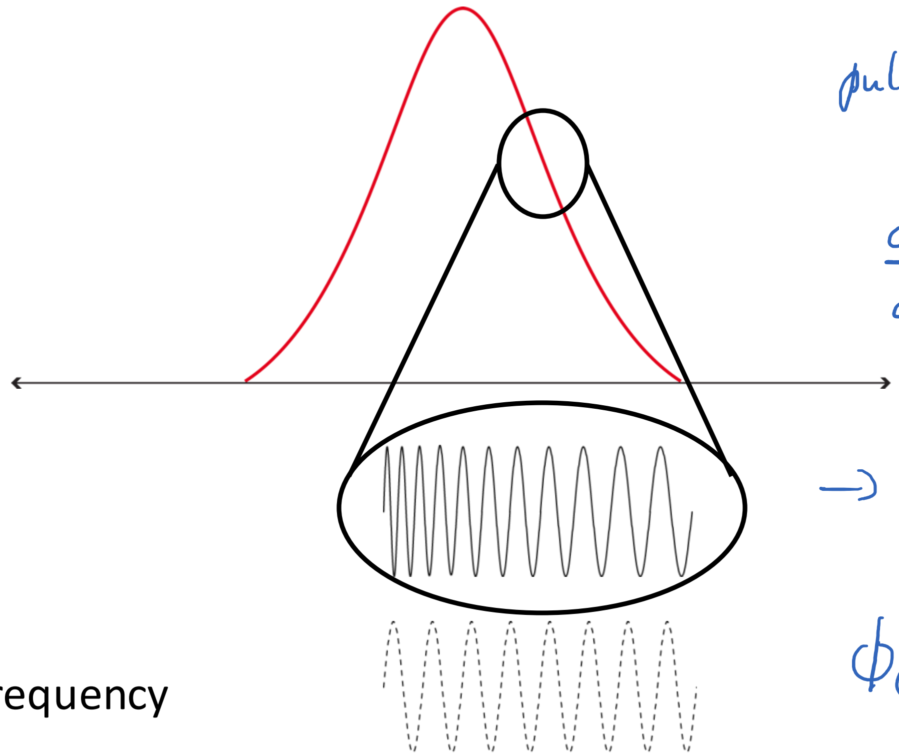
$\frac{dn}{dt} = n_2 \frac{dI}{dt}$

$= n_2 I_0 \frac{-2t}{T} \exp()$

normal refractive index



time-dependent refractive index



→ variation produces shift in phase

$\phi_{(t)} = \omega_0 t - kz$ opt path length

$= \omega_0 t - \frac{2\pi}{\lambda_0} n_{(I)} L$

$$w(t) = -\frac{dj(t)}{dt}$$; instantaneous frequency

- Conceptually – consider a plane monochromatic wave
- Time-dependent index leads to time-dependent frequency
- New frequency components are generated

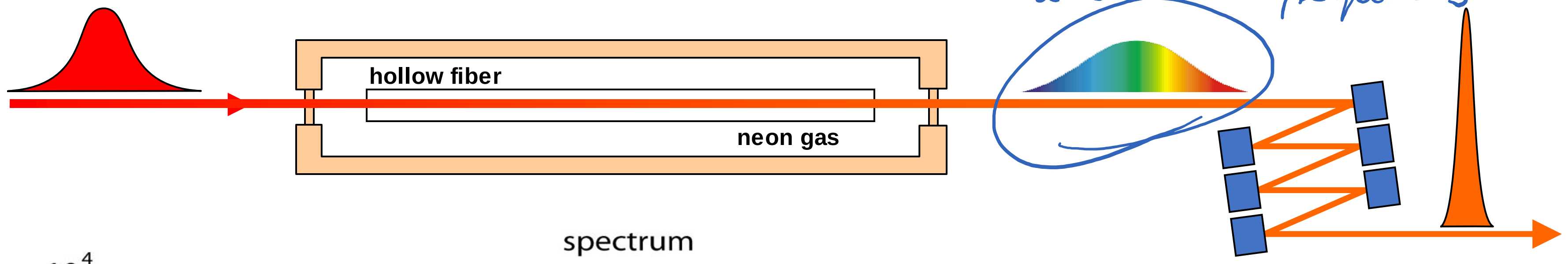
instant frequency

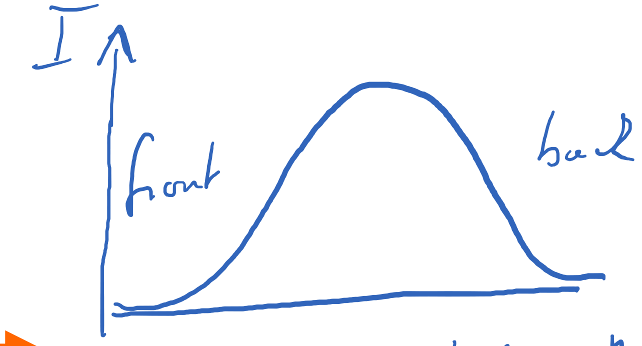
$\omega_{(t)} = \frac{d\phi}{dt}$ .....

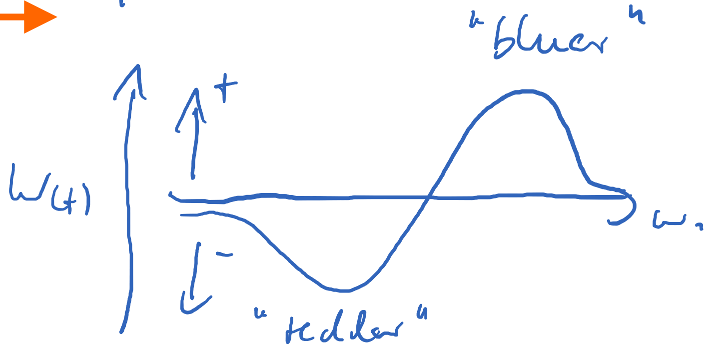
$\sim \omega_0 + \frac{n_2 I_0}{\lambda_0 T} t \exp(\frac{t^2}{\tau^2})$

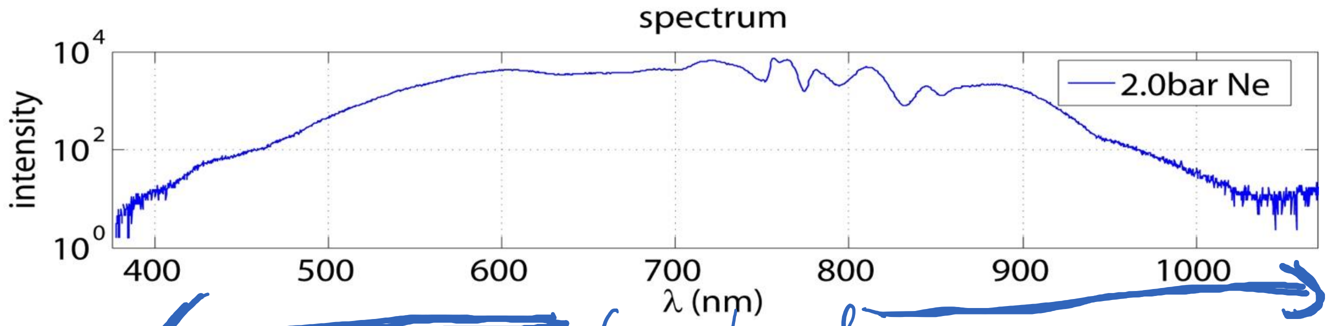
Post Compression by SPM & Chirped Mirror Compressor

additional frequencies

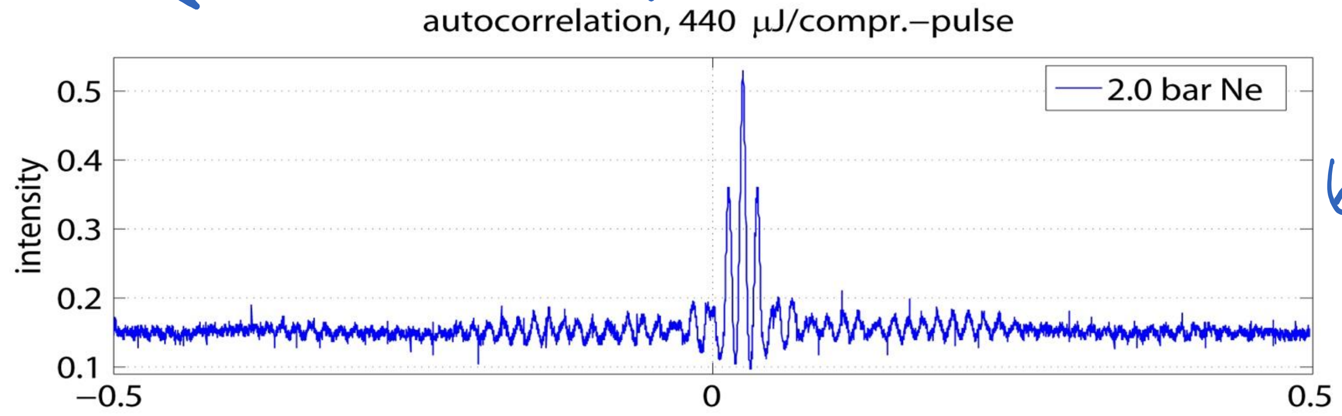




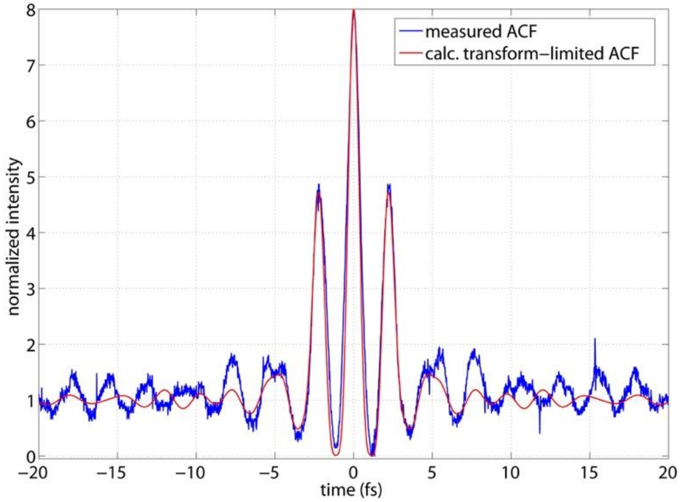




Super broad



Super short



C.f. optical cycle for 800nm → 2.3fs

(Adrian Cavalieri *et. al.*, *NJP* **9**, 242 (2007))

The end.

Kerr lensing needs to be analyzed in wave / beam picture! It is about accumulated phase.

From https://ocw.mit.edu/courses/electrical-engineering-and-computer-science/6-977-ultrafast-optics-spring-2005/lecture-notes/chapter7.pdf

7.1.4 The Kerr Lensing Effects

At high intensities, the refractive index in the gain medium becomes intensity dependent

$$n = n_0 + n_2 I. \tag{7.59}$$

The Gaussian intensity profile of the beam creates an intensity dependent index profile

$$I(r) = \frac{2P}{\pi w^2} \exp\left[-2\left(\frac{r}{w}\right)^2\right]. \tag{7.60}$$

In the center of the beam the index can be appoximated by a parabola

$$n(r) = n_0' \left(1 - \frac{1}{2}\gamma^2 r^2\right), \text{ where} \tag{7.61}$$

$$n_0' = n_0 + n_2 \frac{2P}{\pi w^2}, \; \gamma = \frac{1}{w^2}\sqrt{\frac{8 n_2 P}{n_0' \pi}}. \tag{7.62}$$

A thin slice of a parabolic index medium is equivalent to a thin lens. If the parabolic index medium has a thickness t, then the ABCD matrix describing the ray propagation through the medium at normal incidence is [16]

$$M_K = \begin{pmatrix} \cos\gamma t & \frac{1}{n_0'\gamma}\sin\gamma t \\ -n_0'\gamma\sin\gamma t & \cos\gamma t \end{pmatrix}. \tag{7.63}$$

Note that, for small t, we recover the thin lens formula ($t \to 0$, but $n_0'\gamma^2 t = 1/f$ =const.). If the Kerr medium is placed under Brewster's angle, we again have to differentiate between the sagittal and tangential planes. For the sagittal plane, the beam size entering the medium remains the same, but for the tangential plane, it opens up by a factor n_0'

$$\begin{aligned} w_s &= w \\ w_t &= w \cdot n_0' \end{aligned} \tag{7.64}$$

The spotsize propotional to w^2 has to be replaced by $w^2 = w_s w_t$.Therefore, under Brewster angle incidence, the two planes start to interact during propagation as the gamma parameters are coupled together by

$$\gamma_s = \frac{1}{w_s w_t}\sqrt{\frac{8 n_2 P}{n_0' \pi}} \tag{7.65}$$

$$\gamma_t = \frac{1}{w_s w_t}\sqrt{\frac{8 n_2 P}{n_0' \pi}} \tag{7.66}$$

Without proof (see [12]), we obtain the matrices listed in Table 7.2. For low

Optical Element	ABCD-Matrix
Kerr Medium Normal Incidence	$M_K = \begin{pmatrix} \cos\gamma t & \frac{1}{n_0'\gamma}\sin\gamma t \\ -n_0'\gamma\sin\gamma t & \cos\gamma t \end{pmatrix}$
Kerr Medium Sagittal Plane	$M_{Ks} = \begin{pmatrix} \cos\gamma_s t & \frac{1}{n_0'\gamma_s}\sin\gamma_s t \\ -n_0'\gamma_s\sin\gamma_s t & \cos\gamma_s t \end{pmatrix}$
Kerr Medium Tangential Plane	$M_{Kt} = \begin{pmatrix} \cos\gamma_t t & \frac{1}{n_0'^3\gamma_t}\sin\gamma_t t \\ -n_0'^3\gamma_t\sin\gamma_t t & \cos\gamma_t t \end{pmatrix}$

Table 7.2: ABCD matrices for Kerr media, modelled with a parabolic index profile $n(r) = n_0'\left(1 - \frac{1}{2}\gamma^2 r^2\right)$.

peak power P, the Kerr lensing effect can be neglected and the matrices in Table 7.2 converge towards those for linear propagation. When the laser is mode-locked, the peak power P rises by many orders of magnitude, roughly the ratio of cavity round-trip time to the final pulse width, assuming a constant pulse energy. For a 100 MHz, 10 fs laser, this is a factor of 10^6. With the help of the matrix formulation of the Kerr effect, one can iteratively find the steady state beam waists in the laser. Starting with the values for the linear cavity, one can obtain a new resonator mode, which gives improved values for the beam waists by calculating a new cavity round-trip propagation matrix based on a given peak power P. This scheme can be iterated until there is only a negligible change from iteration to iteration. Using such a simulation, one can find the change in beam waist at a certain position in the resonator between cw-operation and mode-locked operation, which can be expressed in terms of the delta parameter

$$\delta_{s,t} = \frac{1}{p}\frac{w_{s,t}(P,z) - w_{s,t}(P=0,z)}{w_{s,t}(P=0,z)} \tag{7.67}$$

where p is the ratio between the peak power and the critical power for self-focusing

$$p = P/P_{crit}, \text{ with } P_{crit} = \lambda_L^2 / \left(2\pi n_2 n_0^2\right). \tag{7.68}$$

To gain insight into the sensitivity of a certain cavity configuration for KLM, it is interesting to compute the normalized beam size variations $\delta_{s,t}$ as a function of the most critical cavity parameters. For the four-mirror cavity, the natural parameters to choose are the distance between the crystal and the pump mirror position, x, and the mirror distance L, see Figure 7.12. Figure 7.15 shows such a plot for the following cavity parameters $R_1 = R_2 = 10$ cm, $L_1 = 104$ cm, $L_2 = 86$ cm, $t = 2$ mm, $n = 1.76$ and $P = 200$ kW.

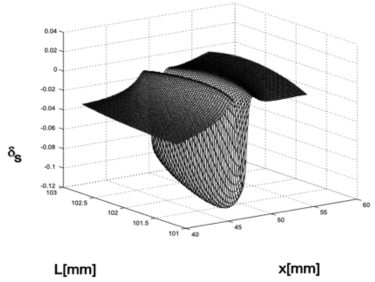


Figure 7.15: Beam narrowing ratio δ_s, for cavity parameters $R_1 = R_2 = 10$ cm, $L_1 = 104$ cm, $L_2 = 86$ cm, $t = 2$ mm, $n = 1.76$ and $P = 200$ kW