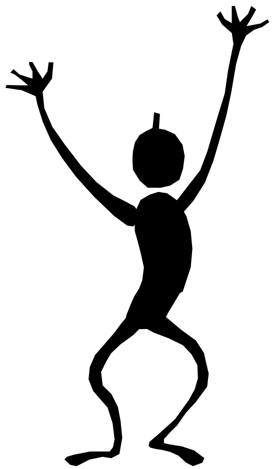
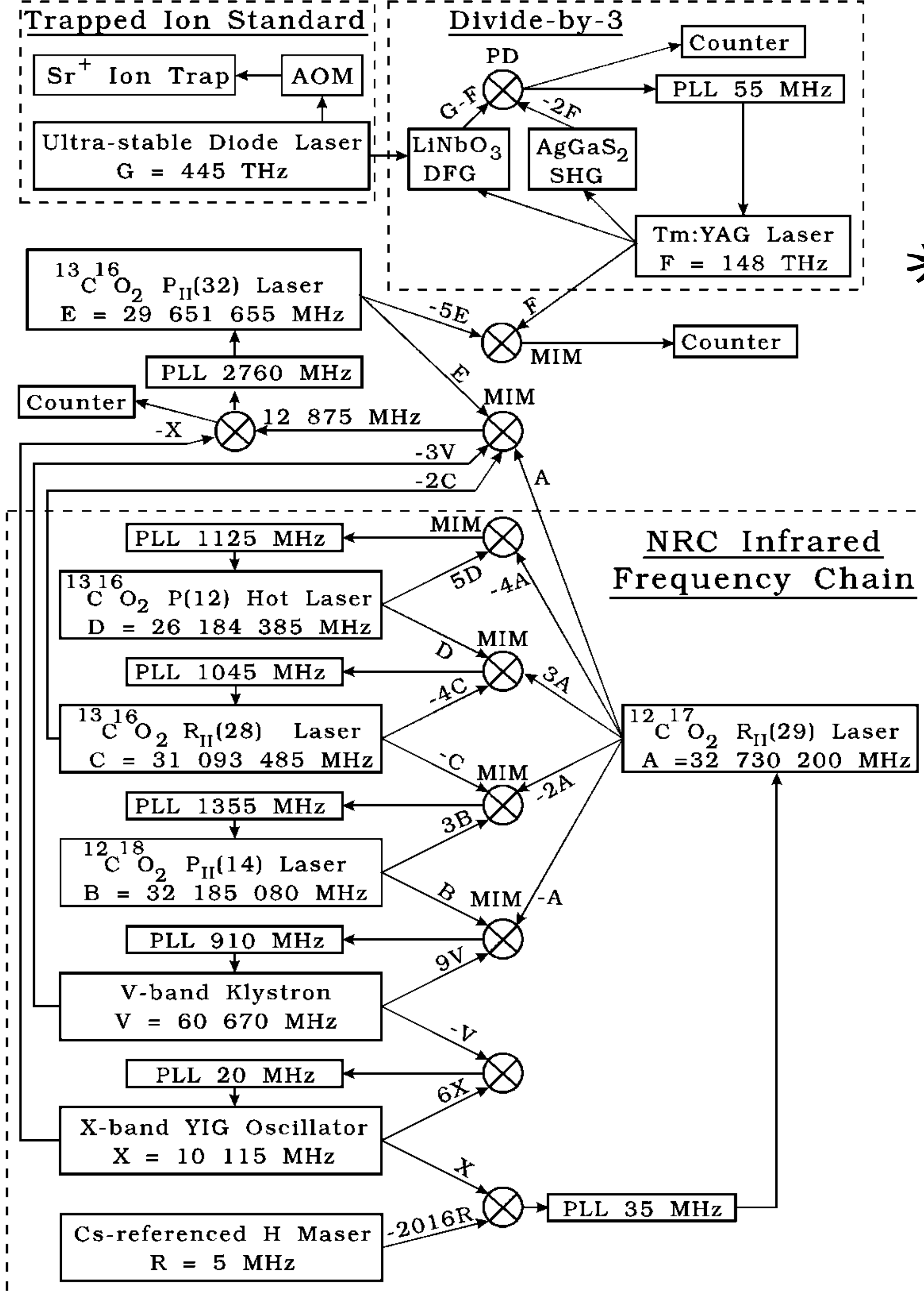
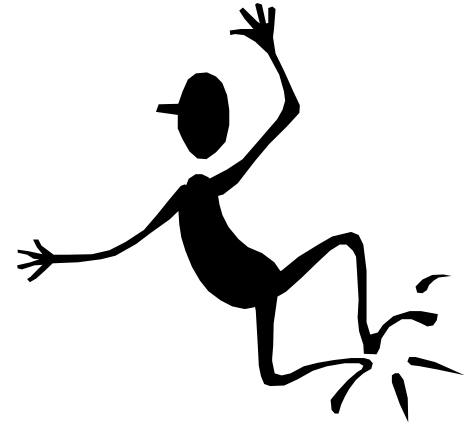
Until a few years ago only two chains in the world:

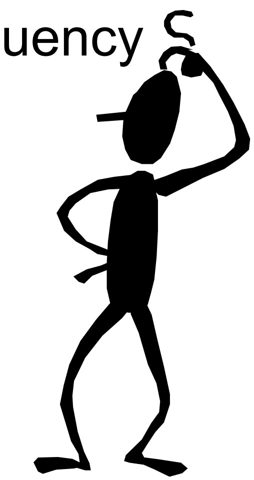
PTB and NRC







Needs about one year and four people to do one measurement at a new frequency



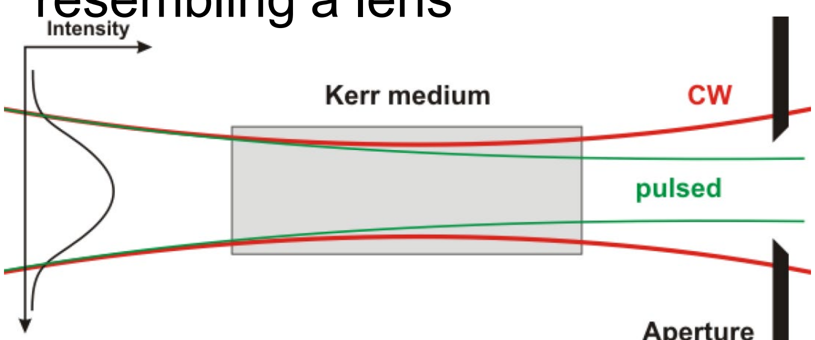
Spectroscopy with frequency combs

Mode locking a laser:

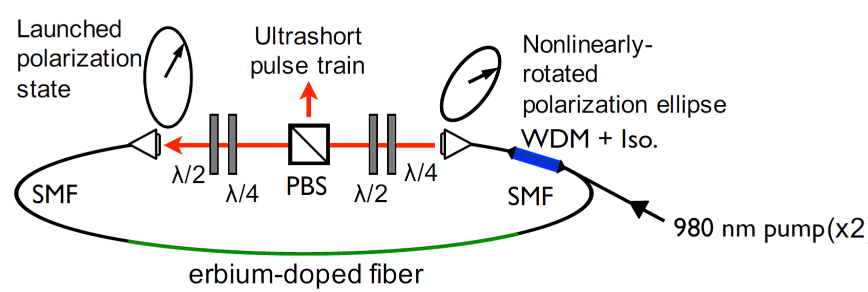
Build a laser cavity that is low-loss for intense pulses, but high-loss for low-intensity continuous beam.

Solution: Intracavity saturable absorber, or Kerr lensing (passive mode-locking)

- Intensity-dependent refractive index: $n = n_0 + n_{Kerr}I$
- Gaussian transverse intensity profile leads to a refractive indexgradient, resembling a lens

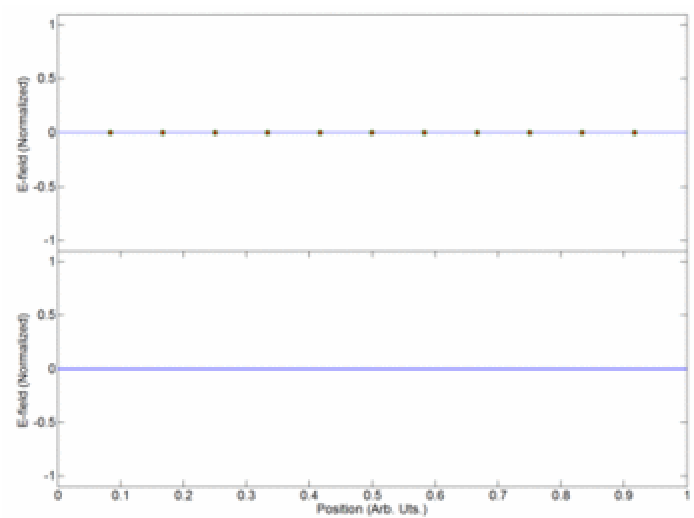


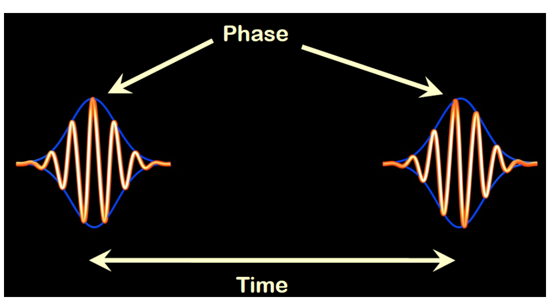
→ mode-locking based on nonlinear polarization rotation

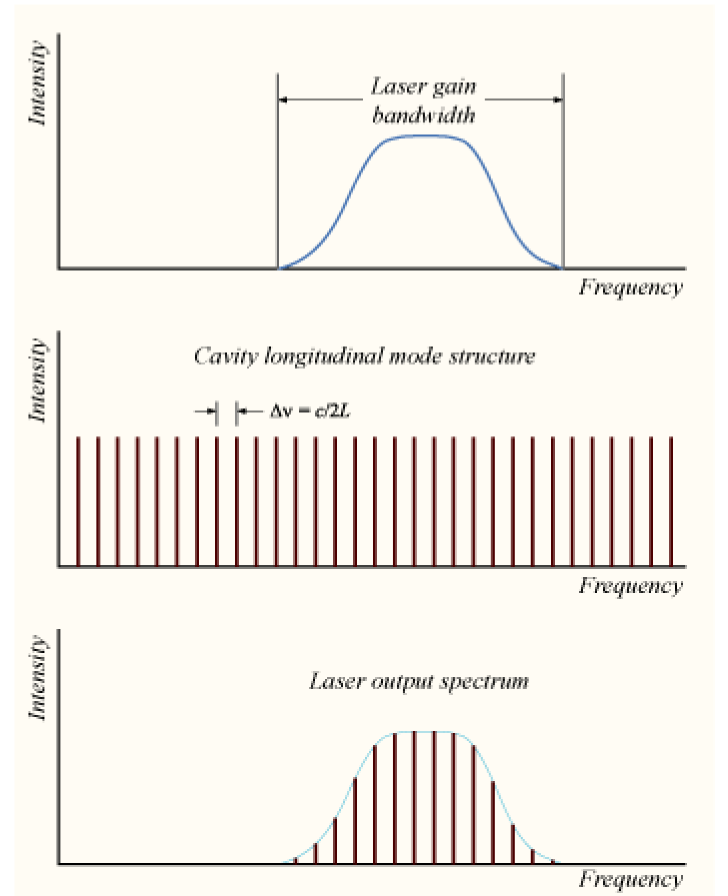


Laser running on multiple modes – a pulsed laser

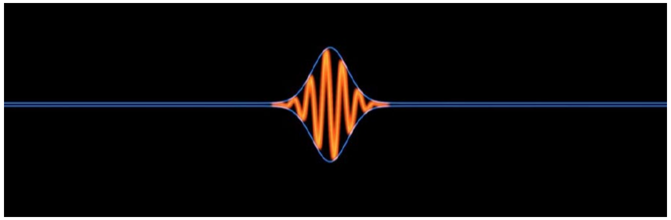
For lasers with 30 cm long caity:
HeNe, 1,5 GHz bandwidth – 3 modes
Ti:Sapphire, 128 THz bandwidth – 250 000 modes



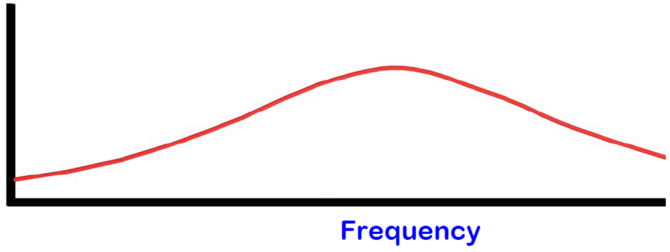




Fourier principle for short pulses:

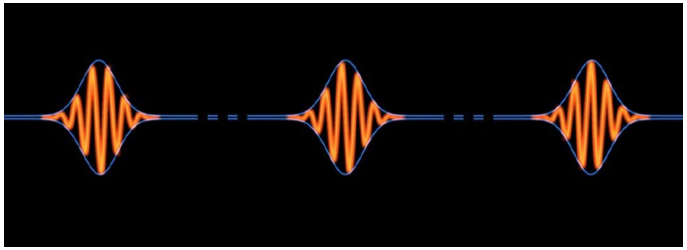


Time domain: short pulse

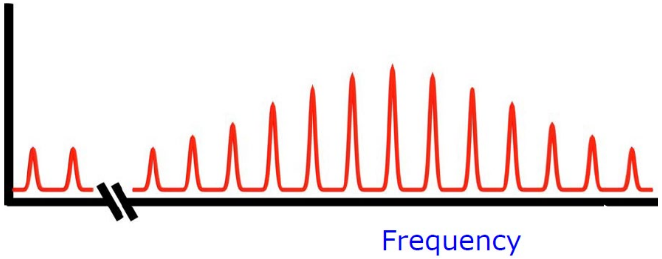


Spectral domain: wide spectrum

Frequency comb principle

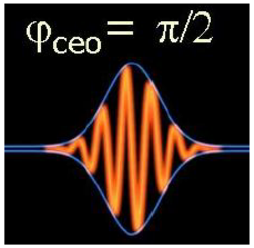


Time domain: pulse train



Spectral domain: comb-like spectrum, many narrow-band, well-defined frequencies

Some math: Propagation of a single pulse (described as a wave packet)



$$E(t,z) = \int_{-\infty}^{\infty} E(\omega) e^{ik(\omega)z} e^{-i\omega t} d\omega$$

Insert an inverse Fourier transform E(τ) for E(ω)

$$E(t,z) = \int_{-\infty}^{\infty} \frac{1}{2\pi} \int_{-\infty}^{\infty} E(\tau) e^{i\omega\tau} d\tau e^{ik(\omega)z} e^{-i\omega t} d\omega$$

$$E(t,z) = \int_{-\infty}^{\infty} E(\tau) G(t-\tau, z) d\tau$$

Propagator

$$G(t-\tau) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i(\omega(t-\tau)-k(\omega)z)} d\omega$$

Propagation of the field

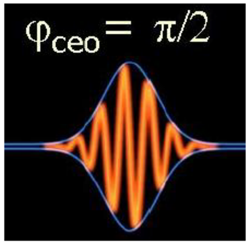
This can be used with $k(\omega) = k_0 + \left.\frac{dk}{d\omega}\right|_{\omega_l} (\omega - \omega_l) + O(k^2)$

$$E(t,z) = \exp[i\omega_l (\frac{1}{v_g} - \frac{1}{v_\phi}) z] E(t - \frac{z}{v_g})$$

Difference between group and phase velocity
causes an extra phase

When traveling through dispersive medium
The carrier/envelop phase continuously changes

Some math: Propagation of a multiple pulses in a train



$$E(t) = \sum_{n=0}^{N-1} E_{\mathrm{single}}(t - nT)$$

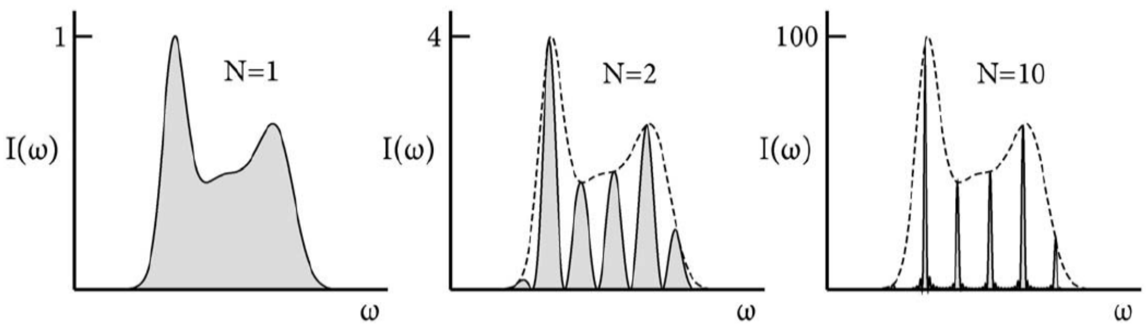
T is time delay between pulses

$$E_{\mathrm{train}}(\omega) = E_{\mathrm{single}}(\omega) \sum_{n=0}^{N-1} e^{-in\omega T} = E_{\mathrm{single}}(\omega) \frac{1 - e^{-iN\omega T}}{1 - e^{-i\omega T}}$$

$$I_{\mathrm{train}}(\omega) = I_{\mathrm{single}}(\omega) \frac{\sin^2(N\omega T/2)}{\sin^2(\omega T/2)}$$

In the limit

$$I_{\mathrm{train},\infty}(\omega) = I_{\mathrm{single}}(\omega) \sum_{n=0}^{\infty} \delta(\omega T - 2\pi n)$$

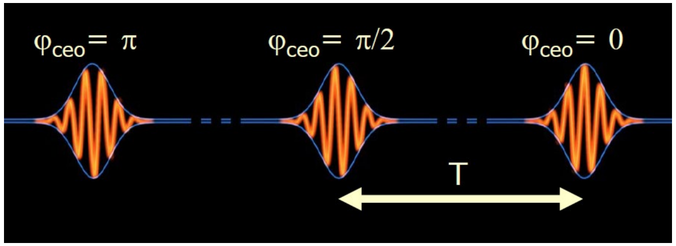


With dispersion

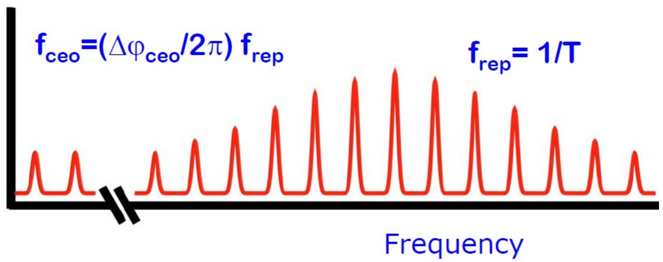
$$I_{\mathrm{train},\infty}(\omega) = I_{\mathrm{single}}(\omega) \sum_{n=0}^{\infty} \delta(\omega T - 2\pi n - \phi_{CE})$$

→ Phase shift

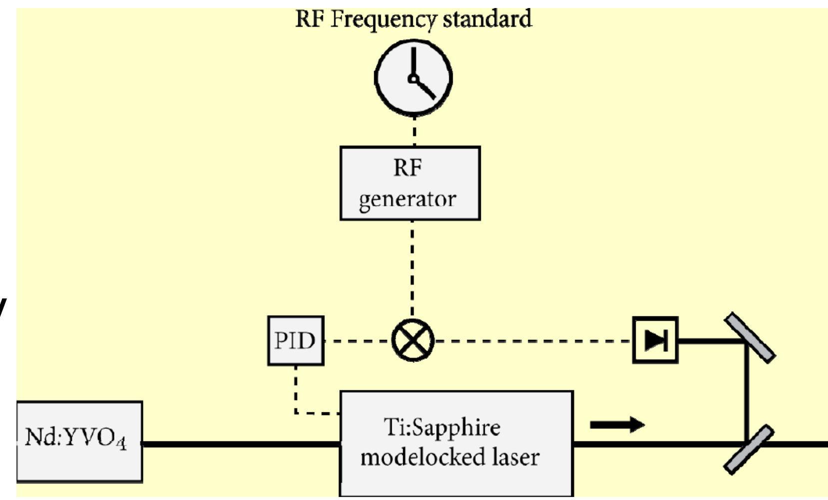
Frequency comb principle



Two rf frequencies determine the entire spectrum



$f = nf_{rep} + f_{CEO}$, tested to 10^{-19} level



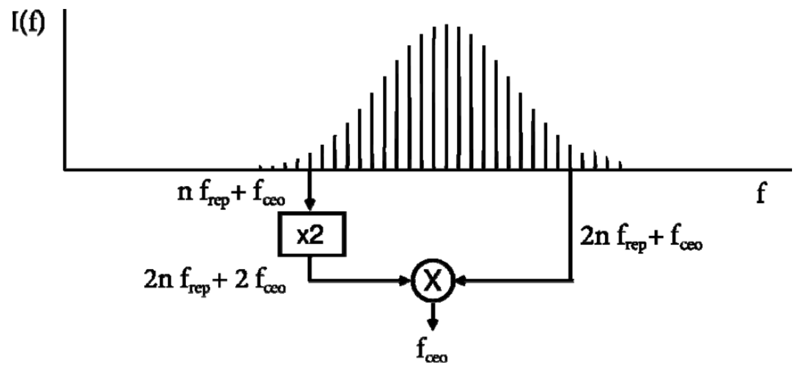
Stabilization of f_{rep}

Both f_{rep} and f_{CEO} are in the radio – frequency domain, can be detected using RF electronics

Measuring f_{rep} is starightforward - counting

Detection of f_{CEO}

Measuring f_{CEO} requires production of a beat signal between a high-frequency comb mode and the SHG of a low-frequency comb mode.



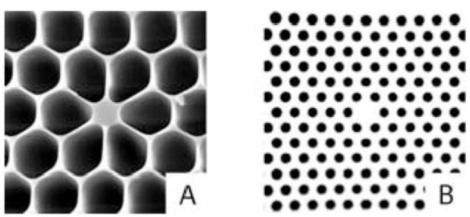
f:2f interferometer

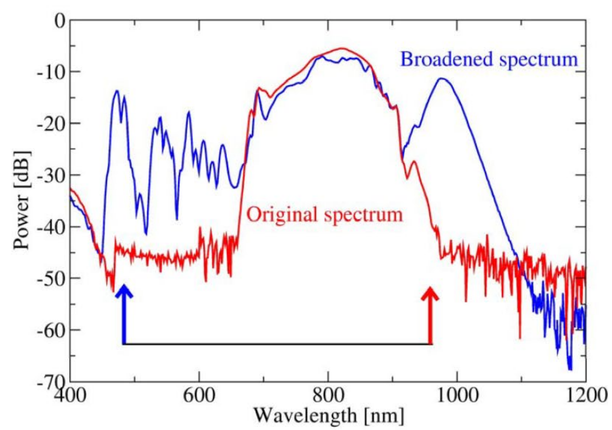
Supercontinuum generation

This f-to-2f detection scheme requires an octave-wide spectrum

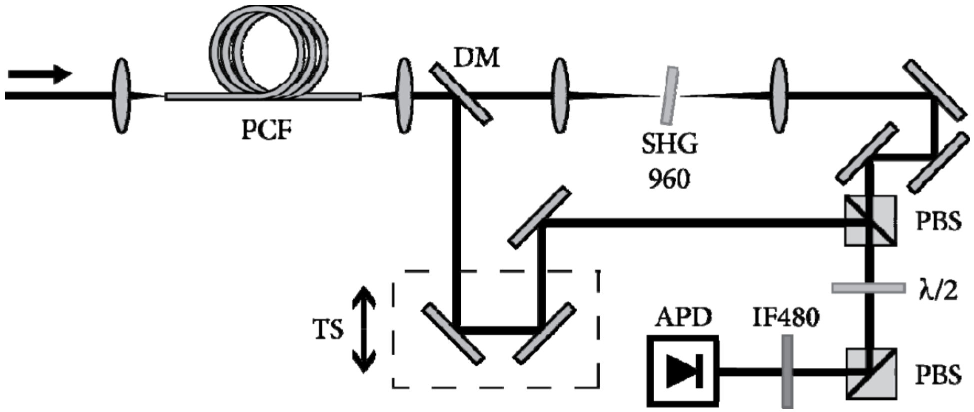
→ spectral broadening in nonlinear medium

Photonic crystal fiber:

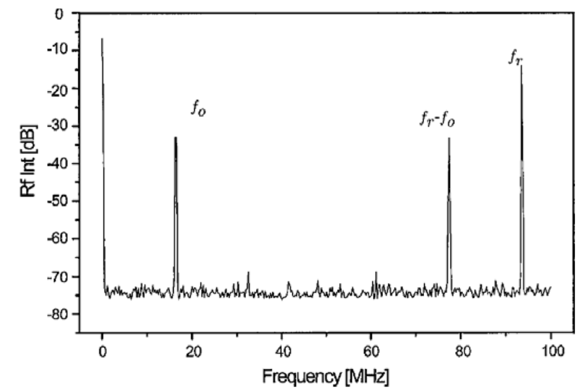




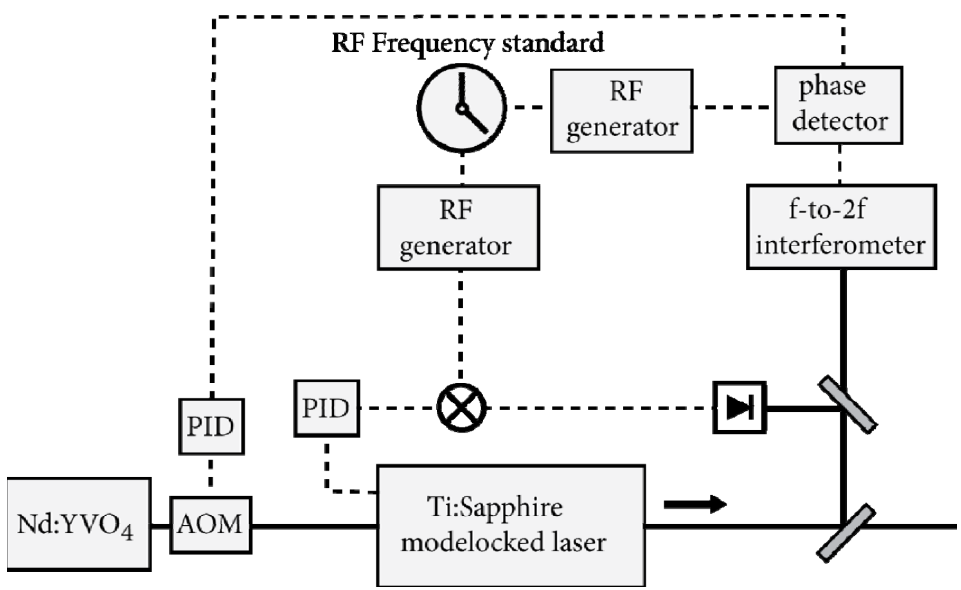
Detection of f_{CEO}



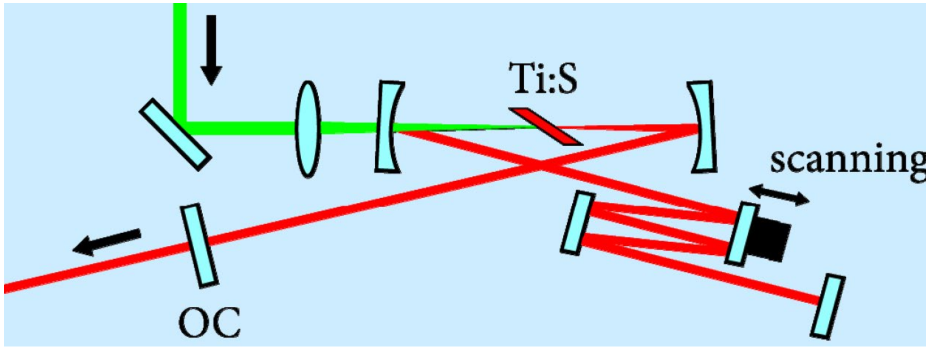
Beat note measurement



- The f-to-2f interferometer output is used in a feedback loop
- The AOM controls the pump power to stabilize f_{CEO}



Scanning of f_{rep}



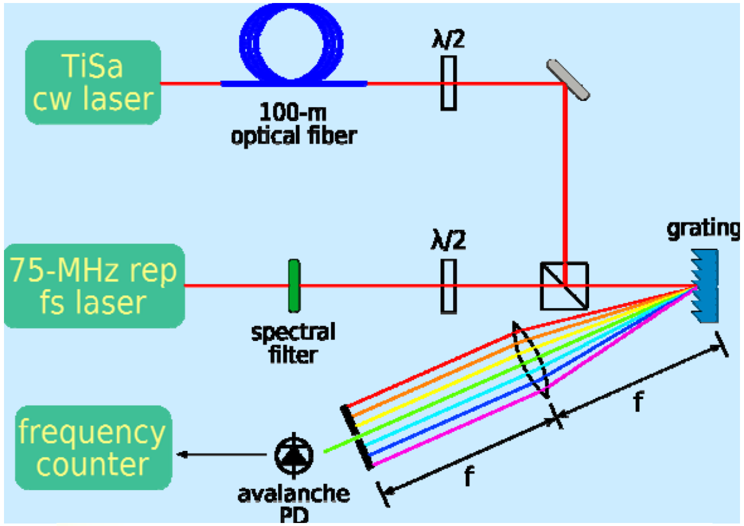
Linear cavity required for long-range scanning

Multiple reflections on a single mirror to increase scan range

Spectroscopy laser

Scan range determined by:

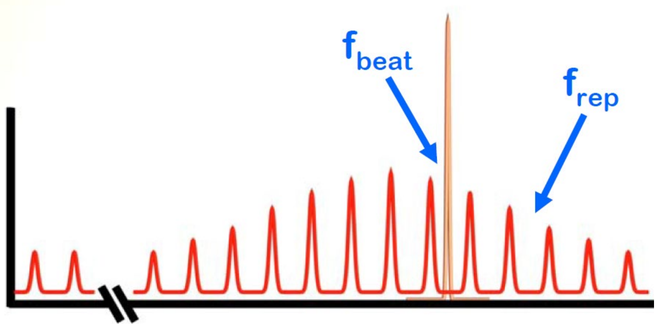
- Cavity stability range
- Alignment sensitivity



The frequency of a laser can be directly determined by beating it with the nearest frequency comb mode.

Frequency of the laser:

$f_{laser} = nf_{rep} + f_{CEO} \pm f_{beat}$



Spectroscopy laser frequency determination

Let's assume we want f_{laser}= 375,000,070 MHz

Frequency of the laser measured by the wavemeter (to within $f_{rep}/2$) :

$f_{laser/wavemeter} \approx nf_{rep} + f_{CEO} \pm f_{beat}$

$n = [\frac{f_{laser/wavemeter} - f_{CEO} \pm f_{beat}}{f_{rep}}]$

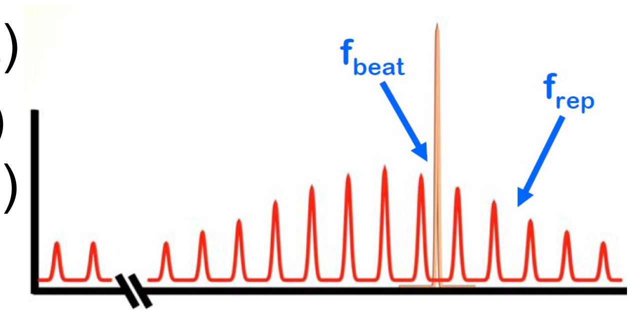
f_{CEO} = 40 MHz ; f_{rep} = 125 MHz ; f_{beat} = +30 MHz

eg. $f_{laser/wavemeter,1}$ = 375,000,130 MHz (+60 MHz)

$f_{laser/wavemeter,2}$ = 375,000,010 MHz (-60 MHz)

$f_{laser/wavemeter,3}$ = 375,000,140 MHz (+70 MHz)

$f_{laser/wavemeter,4}$ = 375,000,000 MHz (-70 MHz



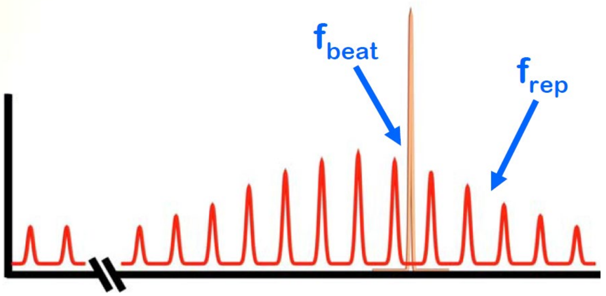
$n_1 = [\frac{375000130 - 40 - 30}{125}]$ = [3000000.48] = n_2 = [2999999.52] = 3000000

$f_{laser,1/2}$= (3000000*125+40 + 30) MHz = 375,000,070 MHz ≈ 799.4432 nm

but: n_3 = [3000000.56] = 3000001 ; n_4 = [2999999.44] =2999999

$f_{laser,3}$= 375,000,195 MHz ; $f_{laser,4}$= 375,999,945 MHz

Spectroscopy laser frequency determination without wavemeter



1. Change repetition rate by small amount (the same tooth)

$$f_l = N f_{r1} + f_0 + f_{b1}$$
$$f_l = N f_{r2} + f_0 + f_{b2}$$

$$N_{est} = \frac{f_{b2} - f_{b1}}{f_{r1} - f_{r2}}$$

$$\delta N = \sqrt{2}\,\delta f_b / \Delta f_{12}$$

For $\delta f_b \approx 1$ kHz, $\delta N \approx 30$

2. Change repetition rate by large amount (scan over m teeth)

$$f_l = N f_{r1} + f_0 + f_{b1},$$
$$f_l = (N + m) f_{r3} + f_0 + f_{b3},$$

$$m = \frac{N \Delta f_{13} + (f_{b1} - f_{b3})}{f_{r3}}$$

$$\delta m = \delta N \Delta f_{13} / f_{r3}$$

substitute N with N_{est}

Finally, the mode number N is calculated to be

$$N = \frac{m f_{r3} + (f_{b3} - f_{b1})}{\Delta f_{13}}$$

N spectroscopy lasers

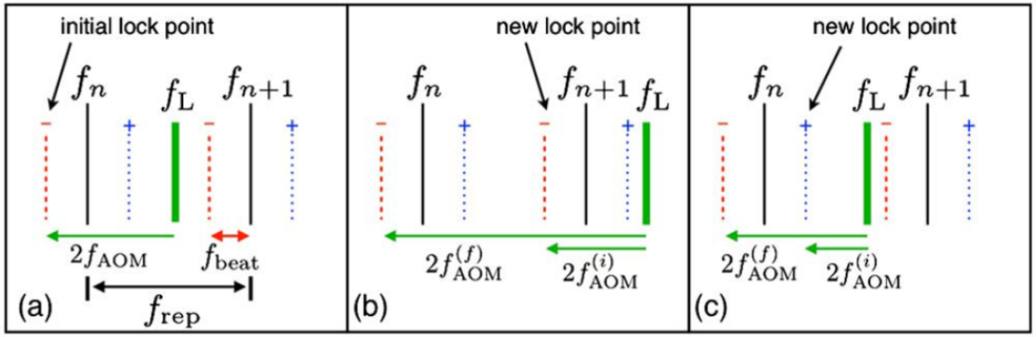
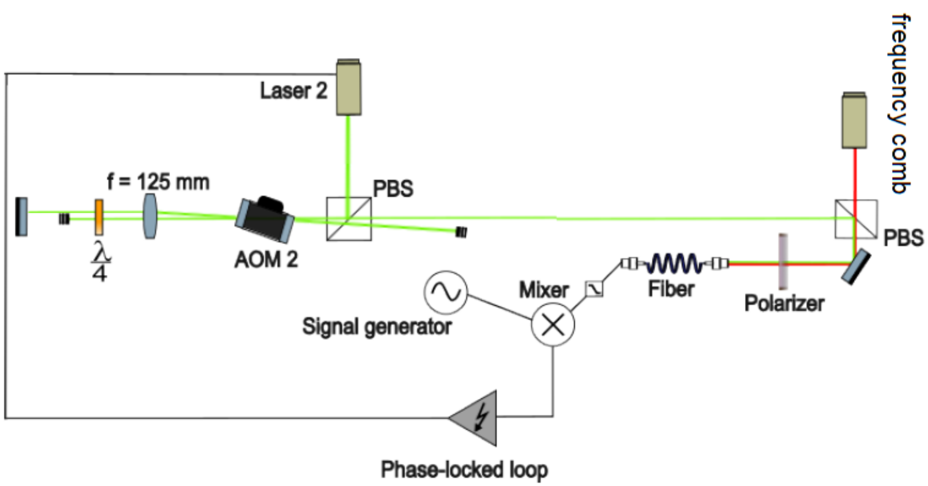
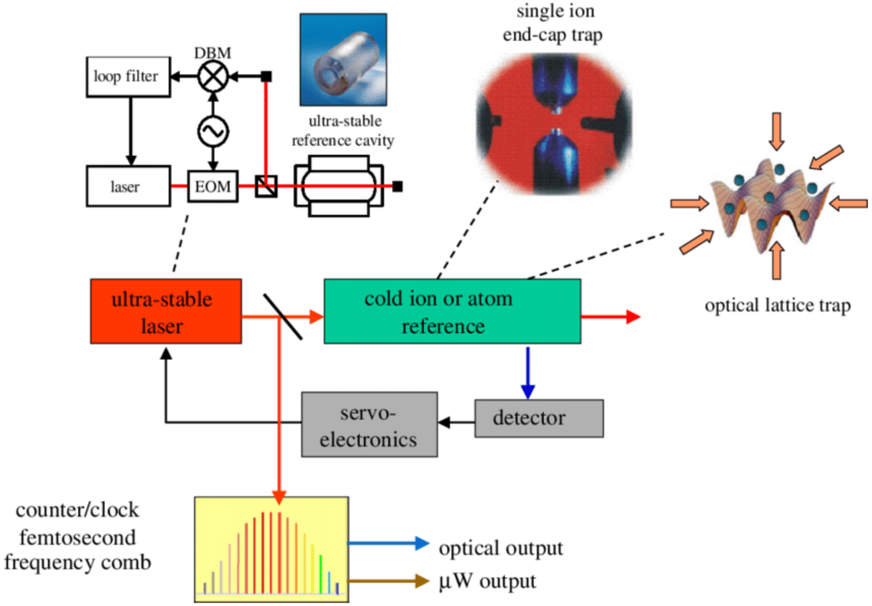
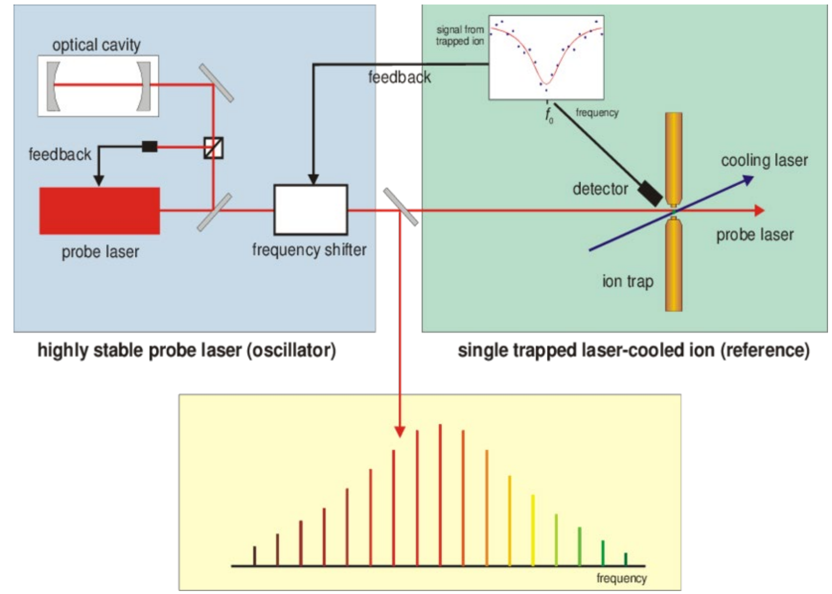


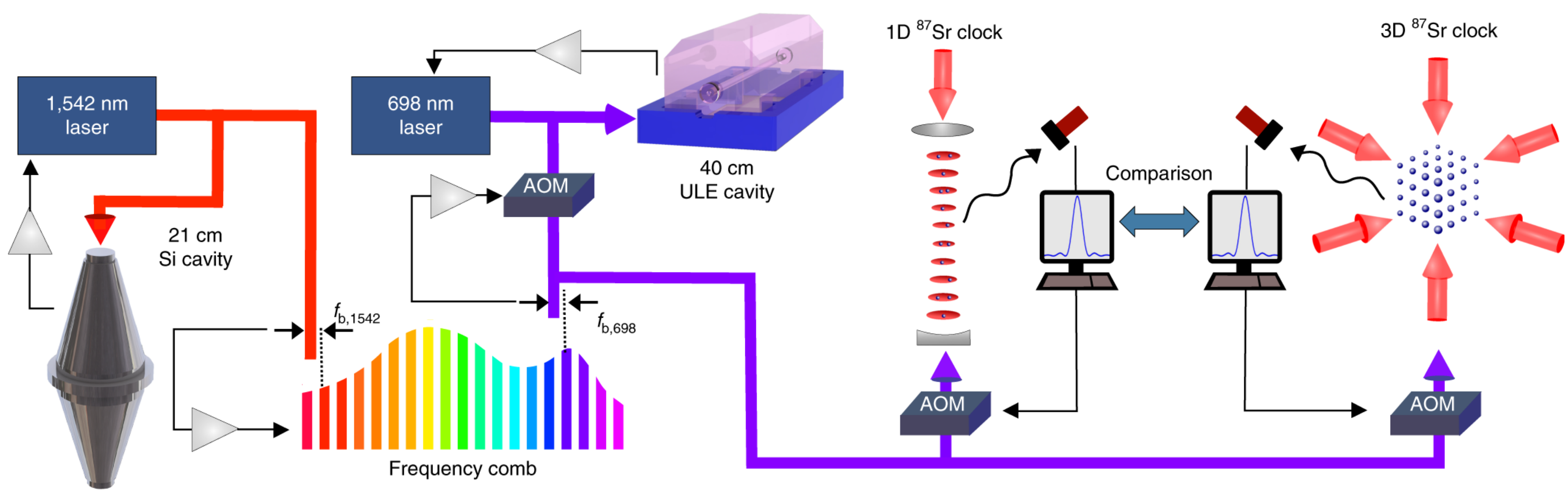
Figure 2.16: Illustration of the ratchet scanning method. In (a) the laser frequency f_L (vertical thick green line) is shifted down in frequency by $2f_{aom}$ before comparison with the comb element at f_n (vertical thin black line). In (b) the AOM tuning bandwidth spans f_{rep} and near the high end of the range the scan is stopped and f_{aom} is returned to it initial value and the laser re-establishes the lock to the line f_{n+1}. In (c) the AOM tuning bandwidth is only $f_{rep}/2$ and both the AOM frequency and the polarity of the error signal must be changed in order for the lock to be re-established. In this case, the lock alternates between being referenced to a comb tooth that is high in frequency, and one that is lower in frequency than the Ti:Sapphire. In our case, we employ the method in (c) as the scanning range of our double pass AOM is only $f_{rep}/2$. See text for details. Figure and caption (modified) from [78].



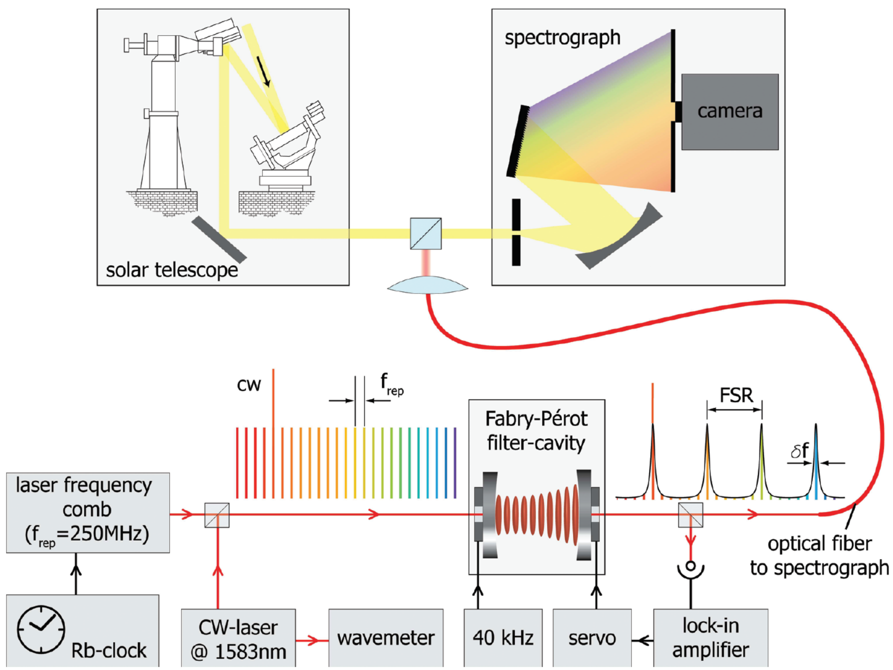
Spectroscopy for time standards



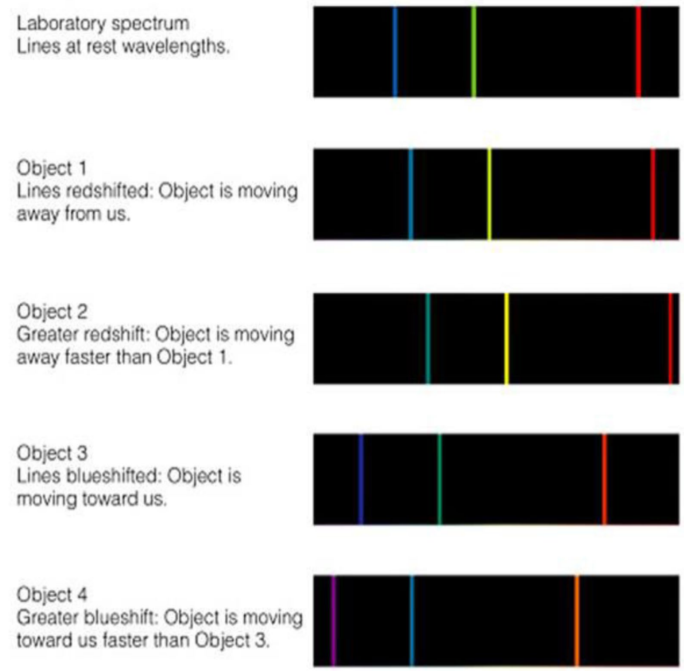




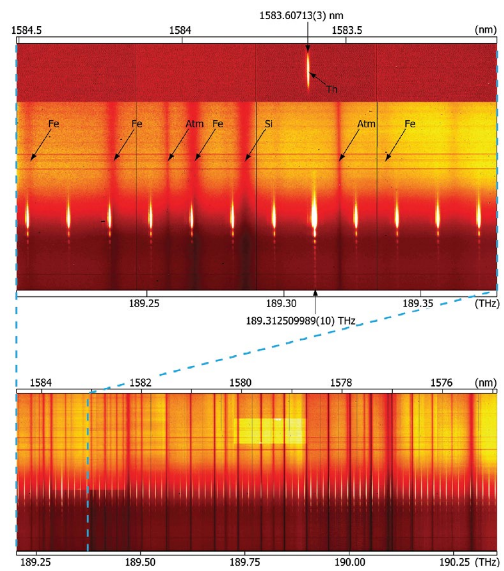
Astrocombs



spectrograph
camera
solar telescope
cw
f_{rep}
Fabry-Pérot filter-cavity
FSR
δf
laser frequency comb (f_{rep}=250MHz)
optical fiber to spectrograph
Rb-clock
CW-laser @ 1583nm
wavemeter
40 kHz
servo
lock-in amplifier

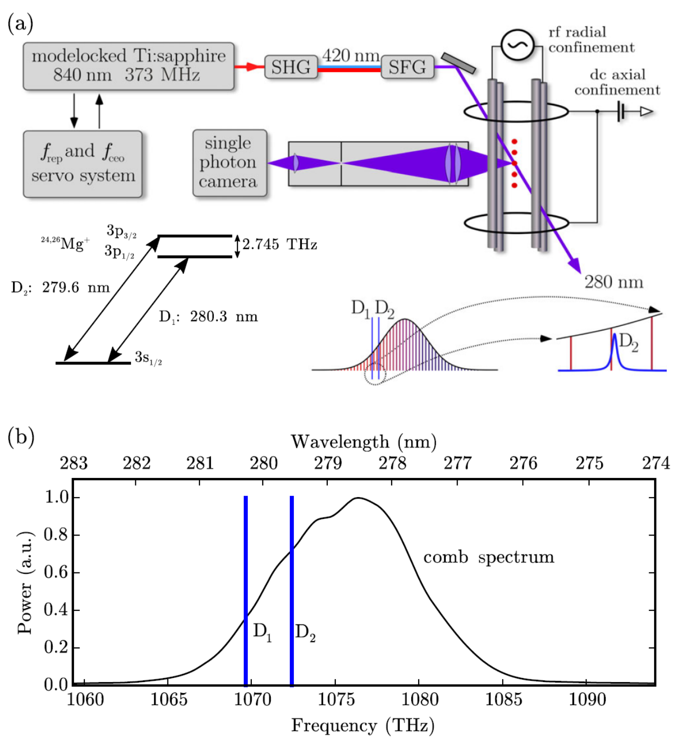


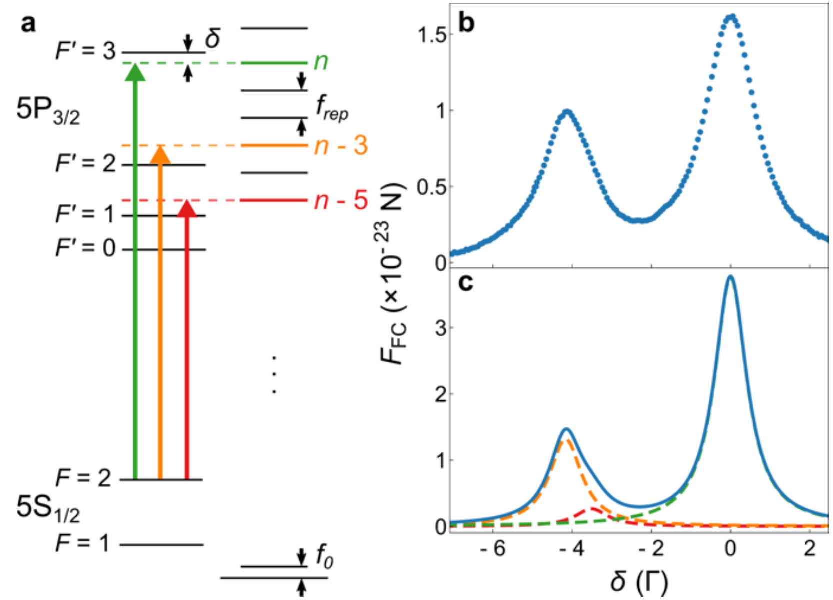
Laboratory spectrum
Lines at rest wavelengths.
Object 1
Lines redshifted: Object is moving away from us.
Object 2
Greater redshift: Object is moving away faster than Object 1.
Object 3
Lines blueshifted: Object is moving toward us.
Object 4
Greater blueshift: Object is moving toward us faster than Object 3.



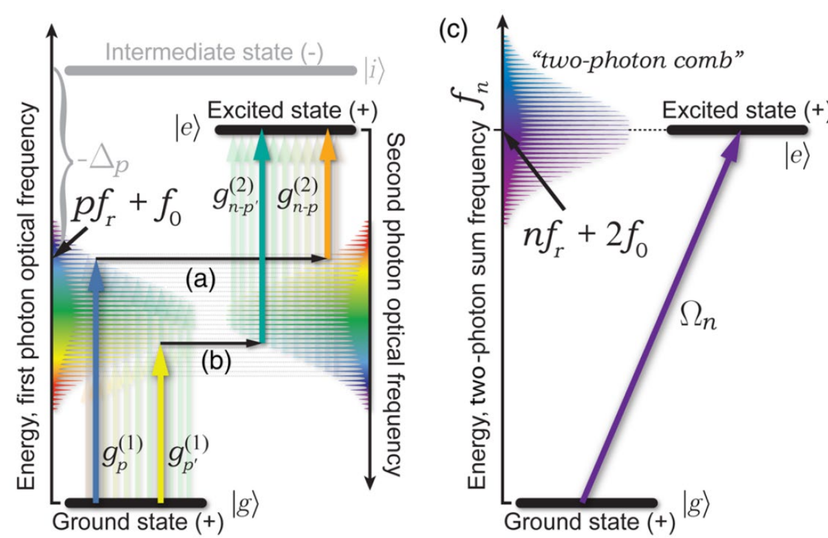
1583.60713(3) nm
1584.5
1584
1583.5
(nm)
Th
Fe
Fe
Atm
Fe
Si
Atm
Fe
189.25
189.30
189.35
(THz)
189.312509989(10) THz
1584
1582
1580
1578
1576
(nm)
189.25
189.50
189.75
190.00
190.25 (THz)

Laser cooling with frequency combs



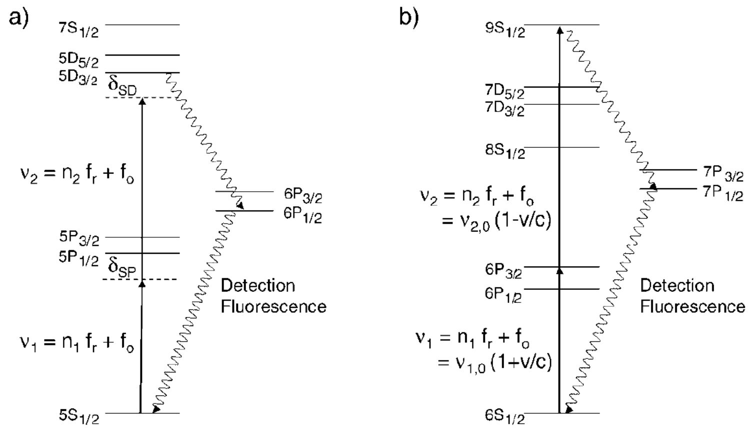


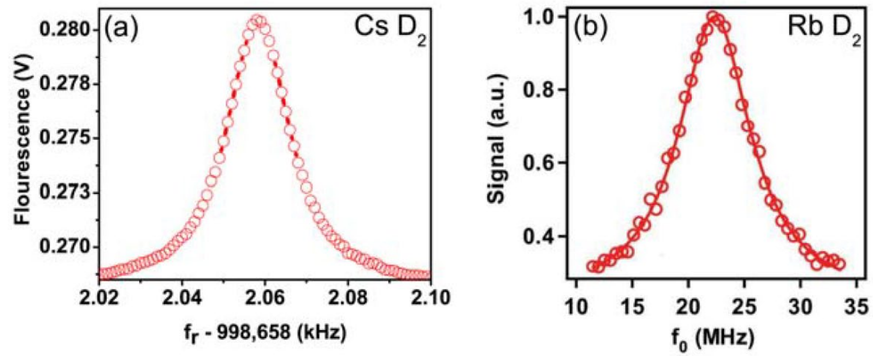
„single - photon”



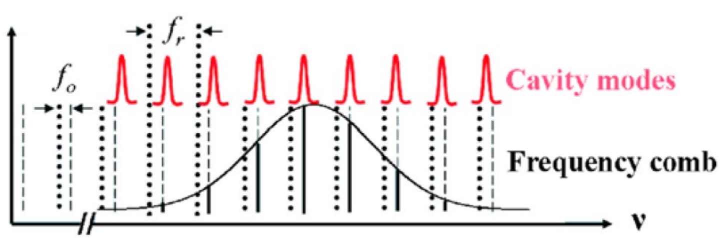
„two - photon”

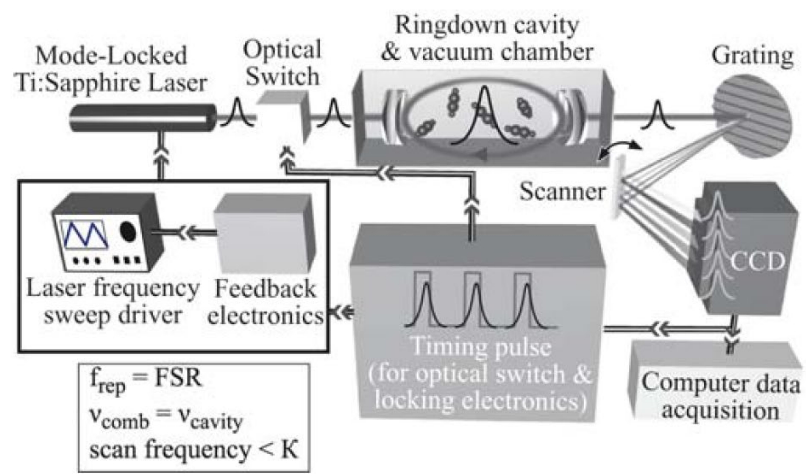
Direct spectroscopy





CRDS with frequency combs





Direct spectroscopy

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RESEARCH ARTICLE

Two-photon frequency comb spectroscopy of atomic hydrogen

Alexey Grinin[1,*], Arthur Matveev[1], Dylan C. Yost[1,†], Lothar Maisenbacher[1], Vitaly Wirthl[1], Randolf Pohl[1,‡], ...
+ See all authors and affiliations

Science 27 Nov 2020:
Vol. 370, Issue 6520, pp. 1061-1066
DOI: 10.1126/science.abc7776

Article | Figures & Data | Info & Metrics | eLetters | PDF

Testing physics using the hydrogen atom

Discrepancy between the proton radius determined from hydrogen and muonic hydrogen spectroscopy data, the so-called "proton radius puzzle," has been a focus of the physics community for more than a decade now. Using two-photon ultraviolet frequency comb spectroscopy below 1 kilohertz, Grinin *et al.* report a high-precision measurement of the 1S-3S transition frequency in atomic hydrogen (see the Perspective by Ubachs). Combining this measurement with the data for the 1S-2S transition, the authors obtained the Rydberg constant with improved accuracy and an independent value for the proton charge radius that favors the data from muonic hydrogen. However, the present frequency value differs from the one obtained previously using a different spectroscopic technique, leaving the puzzle still unresolved.

Science, this issue p. 1061; see also p. 1033

Abstract

We have performed two-photon ultraviolet direct frequency comb spectroscopy on the 1S-3S transition in atomic hydrogen to illuminate the so-called proton radius puzzle and to demonstrate the potential of this method. The proton radius puzzle is a significant discrepancy between data obtained with muonic hydrogen and regular atomic hydrogen that could not be explained within the framework of quantum electrodynamics. By combining our result [f_{1S-3S} = 2,922,743,278,665.79(72) kilohertz] with a previous measurement of the 1S-2S transition frequency, we obtained new values for the Rydberg constant [R_∞ = 10,973,731.568226(38) per meter] and the proton charge radius [r_p = 0.8482(38) femtometers]. This result favors the muonic value over the world-average data as presented by the most recent published CODATA 2014 adjustment.

Science
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27 November 2020

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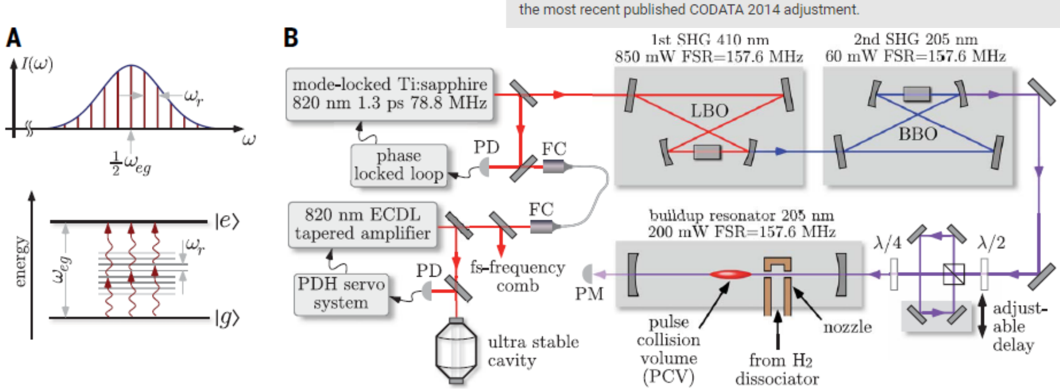


Fig. 2. Principle and experimental setup for two-photon direct frequency comb spectroscopy. (**A**) Spectral envelope of the frequency comb with repetition rate ω_r (not to scale) tuned to excite a two-photon transition between $|g\rangle$ and $|e\rangle$ at the frequency ω_{eg}. On resonance, pairwise addition of properly phased modes provides an efficient excitation of the atoms. (**B**) A mode-locked titanium sapphire laser (78.8 MHz, 1.3 ps, 2.8 W) is referenced to a transfer laser that is itself locked to an ultrastable cavity and referenced to a femtosecond-frequency comb. This frequency comb is then frequency quadrupled in two successive intracavity doubling stages to generate a deep ultraviolet frequency comb at 205 nm. The optical cavities used for frequency doubling are built with half the length of the fundamental laser cavity, which effectively doubles the repetition rate of the quadrupled frequency comb to 157.6 MHz. The pulse train is then sent to a beam splitter and delay line used to generate counterpropagating pulses within a final enhancement cavity where the hydrogen spectroscopy takes place. PM, power meter; FC, fiber coupler; FSR, free spectral range; PDH, Pound-Drever-Hall stabilization (*33*); ECDL, extended cavity diode laser; SHG, second-harmonic generation; LBO/BBO, lithium triborate and β–barium borate crystals; PD, photodetector.

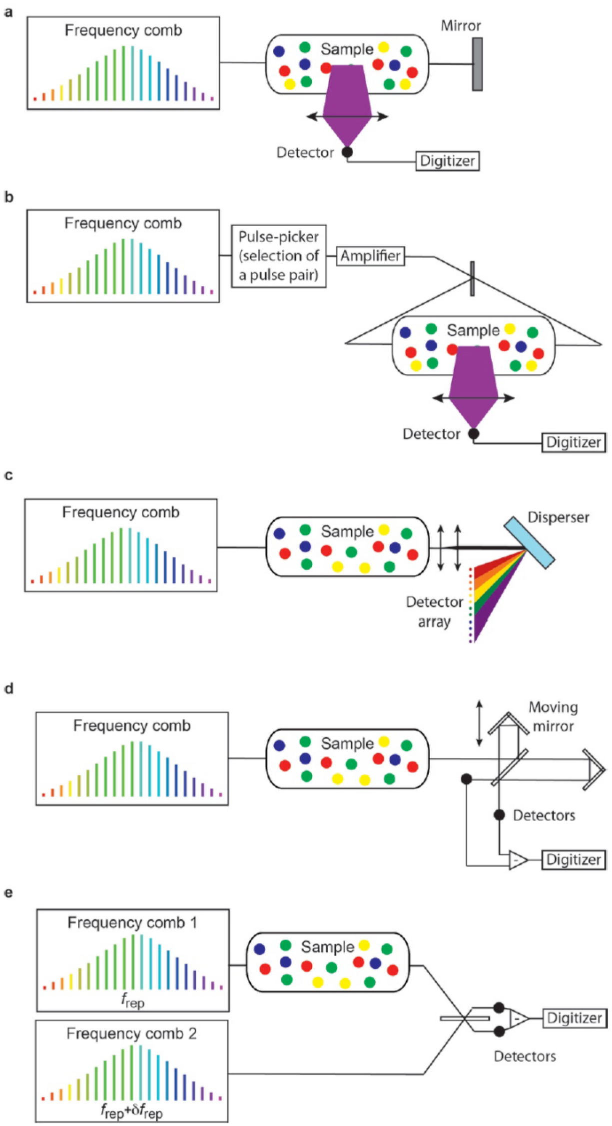


Figure 3. Spectrometric techniques for frequency comb spectroscopy.

a. Direct frequency comb spectroscopy with the example of two-photon Doppler-free excitation in a standing wave and detection of fluorescence of the sample.

b. Ramsey-comb spectroscopy also with the example of two-photon Doppler-free excitation in a standing wave and detection of fluorescence of the sample.

c. Frequency-comb spectrometry with a disperser for absorption measurements. Here a simple grating and a detector array are represented.

d. Frequency-comb Fourier transform spectroscopy with a scanning Michelson interferometer and an absorbing sample.

e. Dual-comb spectroscopy with one comb interrogating the sample and the other acting as a local oscillator. The absorption and the dispersion of the sample are measured.

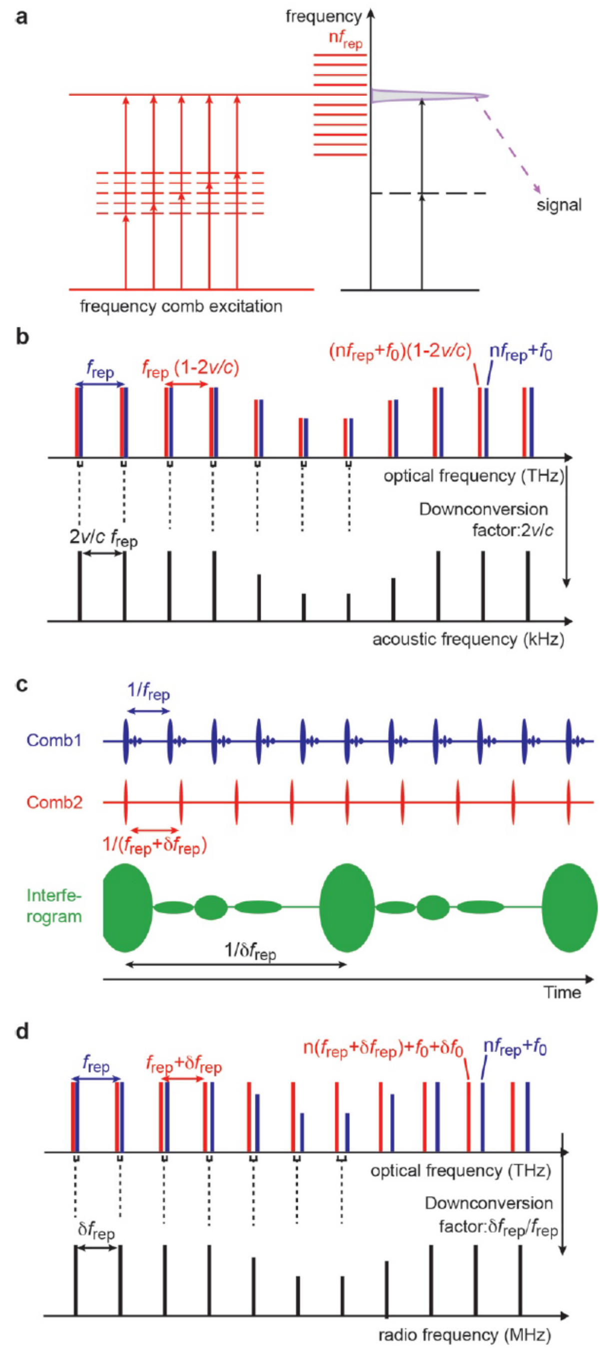


Figure 4. Physical principle of some of the described spectrometric techniques

a. In direct frequency comb spectroscopy with two-photon excitation, many pairs of comb lines may contribute to the excitation of the transition. However the spectrum is only measured modulo the comb repetition frequency. Fluorescence during decays towards lower energy levels may be detected.

b. In the moving arm of a scanning Michelson interferometer, the frequency of all the comb lines is Doppler-shifted. The beat notes between pairs of shifted and unshifted comb lines at the detector produce an acoustic comb.

c. Interferometric sampling in the time-domain stretches free-induction decay. With a dual-comb system, the interferogram recurs automatically at a period $1/\delta f_{rep}$ which is the inverse of the difference in repetititon frequencies of the two combs.

d. Frequency-domain picture of c for dual-comb interferometry. The beat notes between pairs of comb lines, one from each comb, generates a radio-frequency comb. The physical principle is the same as that of b., except that the down-conversion factor no longer depends on the speed of a moving part. Furthermore, dual-comb systems render the implementation of a dispersive interferometer easier.

Nonlinear absorption spectroscopy

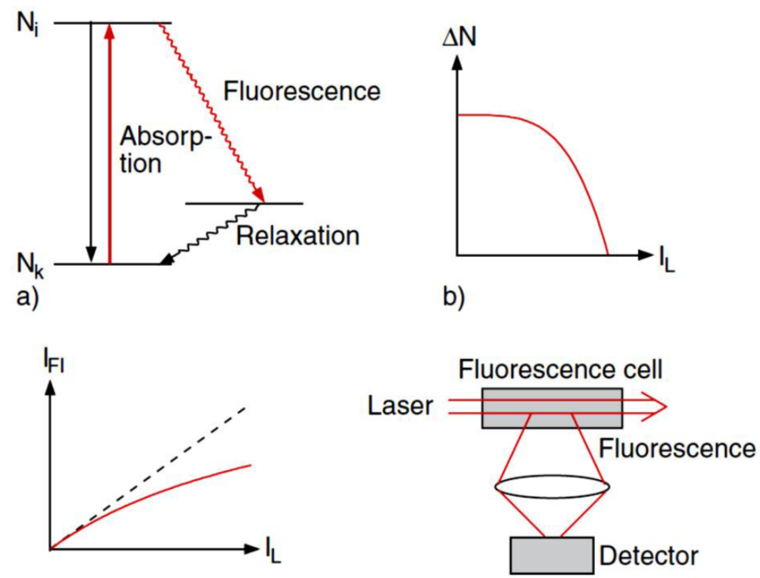
Attenuation *dI* of a plane e-m wave $\mathrm{d}I = -\alpha I \,\mathrm{d}x$
where absorption coeff.

$$\alpha(\omega) = [N_k - (g_k/g_i)N_i]\sigma(\omega) = \Delta N \cdot \sigma(\omega)$$

ΔN – population difference, σ – absorption cross section

$$\mathrm{d}I = -\Delta N \cdot \sigma(\omega) \cdot I \cdot \mathrm{d}x$$

For small *I* population densities N_k, N_i do not depend on *I*



Figs. ref. [1]

Then α independent of *I* ⟶ Lambert-Beer law $I = I_0 \mathrm{e}^{-\alpha x} = I_0 \mathrm{e}^{-\Delta N \sigma x}$

For high *I* : $\mathrm{d}I = -\Delta N(I) \cdot I \cdot \sigma \cdot \mathrm{d}x$ (finite relaxation rate)
Intensity dependent population density (power series expansion)

$$N_k = N_{k0} + \frac{\mathrm{d}N_k}{\mathrm{d}I} I + \frac{1}{2}\frac{\mathrm{d}^2 N_k}{\mathrm{d}I^2} I^2 + \ldots$$

for lower and upper level:

$$\mathrm{d}N_k/\mathrm{d}I < 0 \text{ and } \mathrm{d}N_i/\mathrm{d}I > 0$$

Population difference

$$\Delta N(I) = \Delta N_0 + \frac{\mathrm{d}(\Delta N)}{\mathrm{d}I} I + \frac{1}{2}\frac{\mathrm{d}^2(\Delta N)}{\mathrm{d}I^2} I^2 + \ldots$$

Attenuation

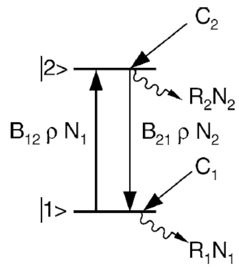
$$\mathrm{d}I = -[\Delta N_0 \sigma I + \frac{\mathrm{d}}{\mathrm{d}I}(\Delta N) I^2 \sigma + \ldots]\,\mathrm{d}x$$

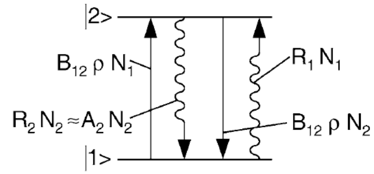
linear **nonlinear**

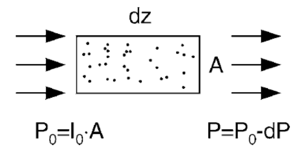
$\mathrm{d}(\Delta N)/\mathrm{d}I < 0$ - decrease of absorption

Nonlinear absorption can be observed on fluorescence (LIF) signal

Nonlinear absorption spectroscopy



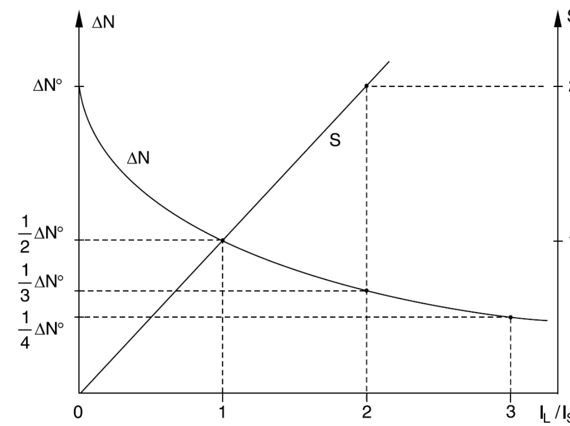




$$\frac{\mathrm{d}N_1}{\mathrm{d}t} = B_{12}\rho_\nu(N_2 - N_1) - R_1N_1 + C_1,$$
$$\frac{\mathrm{d}N_2}{\mathrm{d}t} = B_{12}\rho_\nu(N_1 - N_2) - R_2N_2 + C_2,$$

$$C_i = \sum_k R_{ki}N_k + D_i$$

Fig. 2.3 Population difference ΔN and saturation parameter S as a function of incident laser intensity I_L



Steady state solution

$$\Delta N = \frac{\Delta N^0}{1 + B_{12}\rho_\nu(1/R_1 + 1/R_2)} = \frac{\Delta N^0}{1+S}$$

$$S = \frac{B_{12}\rho_\nu}{R^*} = \frac{B_{12}I_\nu/c}{R^*} = \frac{B_{12}I}{c \cdot R_1R_2} \qquad R^* = \frac{R_1R_2}{R_1 + R_2}$$

Closed system

$$N_1 = \frac{B_{12}I/c + R_2}{2B_{12}I_\nu/c + R_1 + R_2}N, \quad \text{with } N = N_1 + N_2 \qquad N_1 \geq \lim_{I\to\infty} N_1 = N/2 \to N_1 \geq N_2$$

Open system

$$N_1 = \frac{(C_1 + C_2)B_{12}I_\nu/c + R_2C_1}{(R_1 + R_2)B_{12}I_\nu/c + R_1R_2}N \qquad N_1(S \to \infty) = \frac{C_1 + C_2}{R_1 + R_2}N$$

Saturation (Doppler free) spectroscopy

- Doppler broadened absorption line centered at ω_0
- laser beam at ω

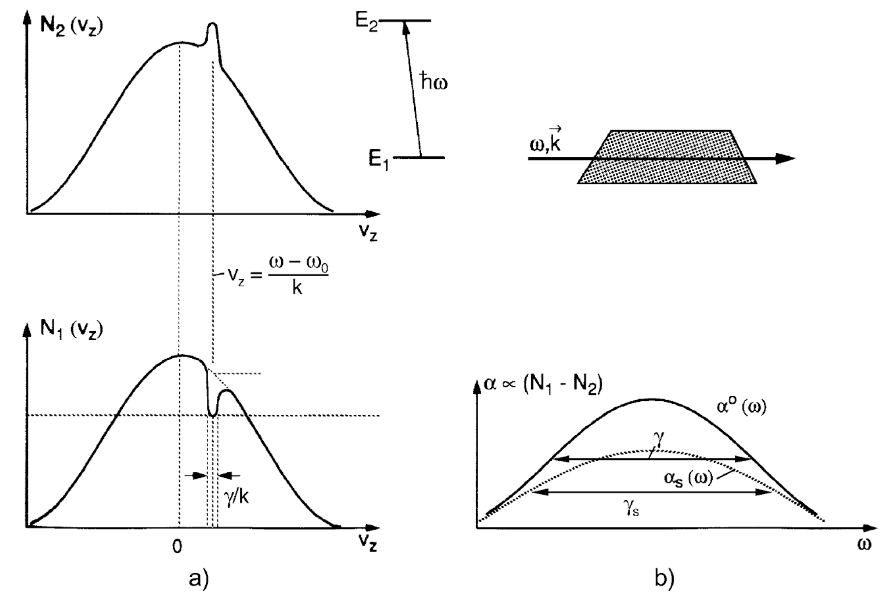
Doppler shift: $\Delta\omega = kv_x$

only molecules with given velocity may absorb radiation

$$\omega = \omega_0(1 + kv_x)$$

Nonlinear absorption – decrease of $N_k(v_x)$, increase of $N_i(v_x)$

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



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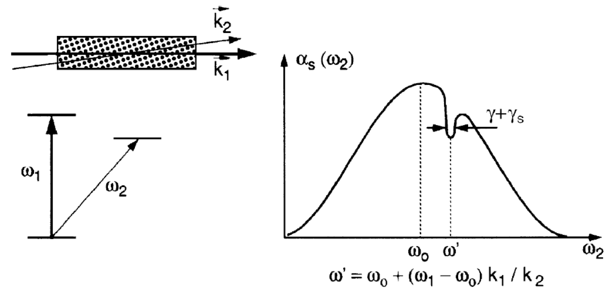


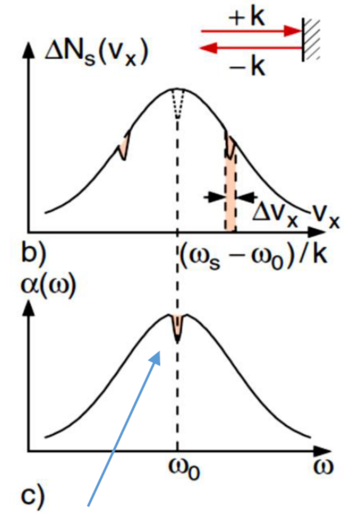
Nonlinear absorption – decrease of $N_k(v_x)$, increase of $N_i(v_x)$

Double pass configuration

decreased absorption at $\omega = \omega_0(1 \pm kv_x)$

at line center doubly decreased absorption – **Lamb dip**

reflected laser beam

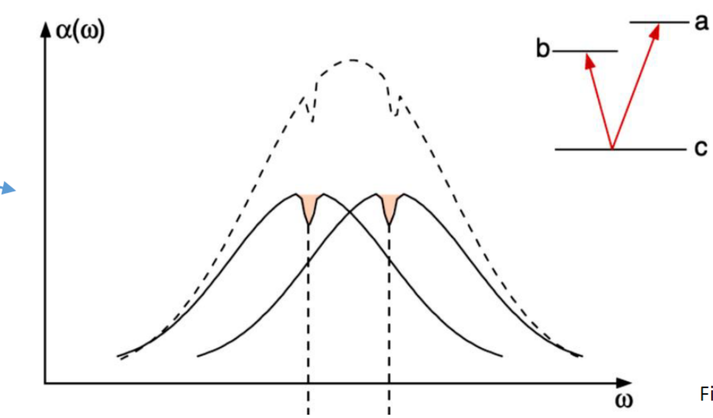


both beams interact with the same group of molecules

Width of Lamb dip depends on homogeneous line width

- natural width
- collisional broadening

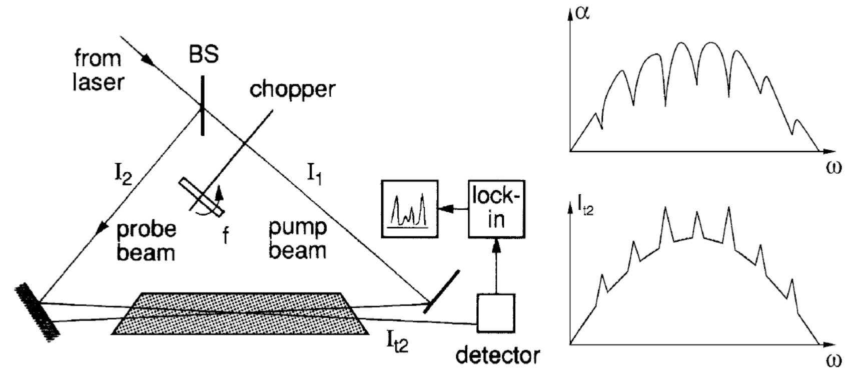
Overlapped Doppler-broadened lines can be resolved

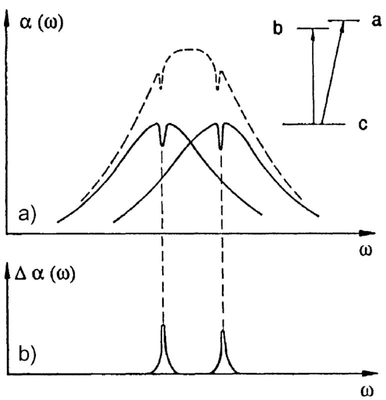


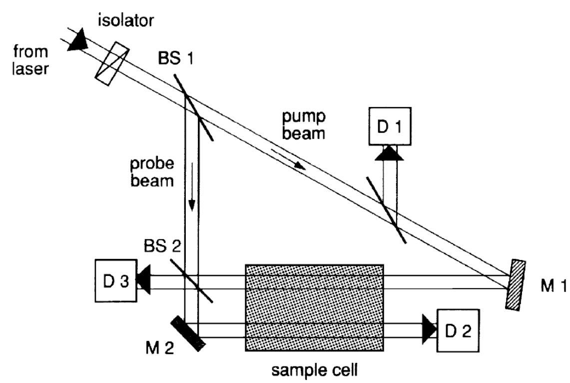
Figs. ref. [1]

Saturation (Doppler free) spectroscopy

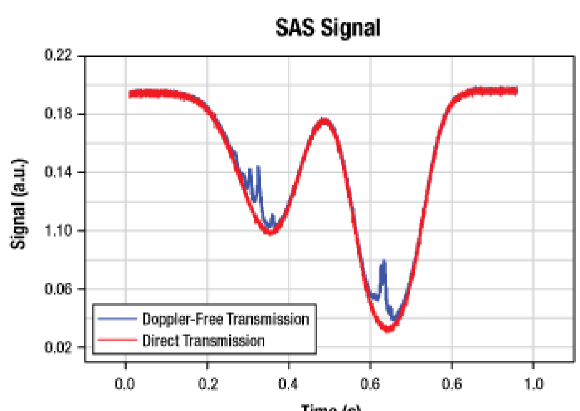
Pump and Probe beam configuration:
Doppler-broadened shape can be eliminated

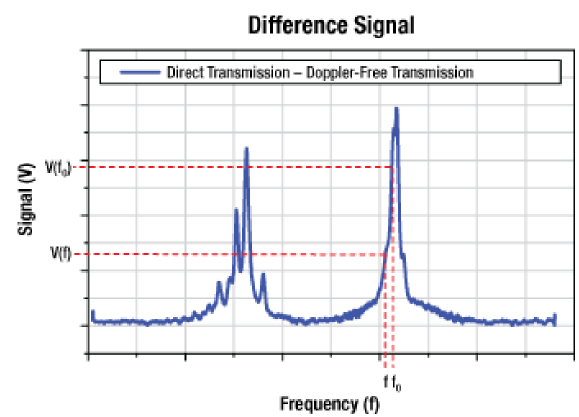






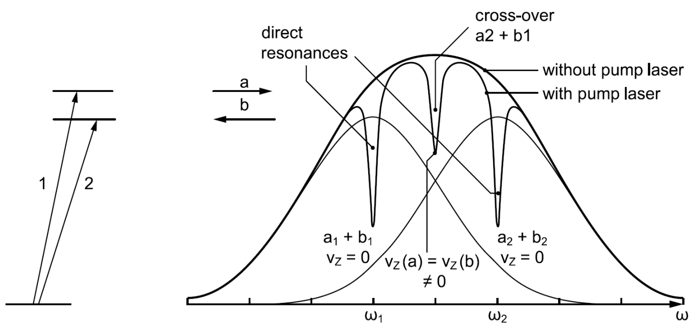
$\Delta\omega = \omega_{ca} - \omega_{cb} > 2\gamma_s$





Saturation (Doppler free) spectroscopy

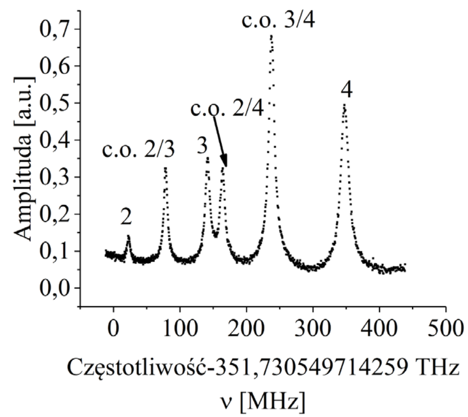
Cross-Over Signals



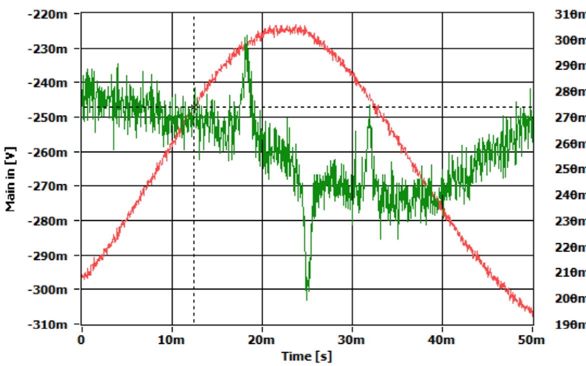
$$\omega = (\omega_1 + \omega_2)/2$$

$$\Delta\omega = \omega - \omega_1 = (\omega_2 - \omega_1)/2$$

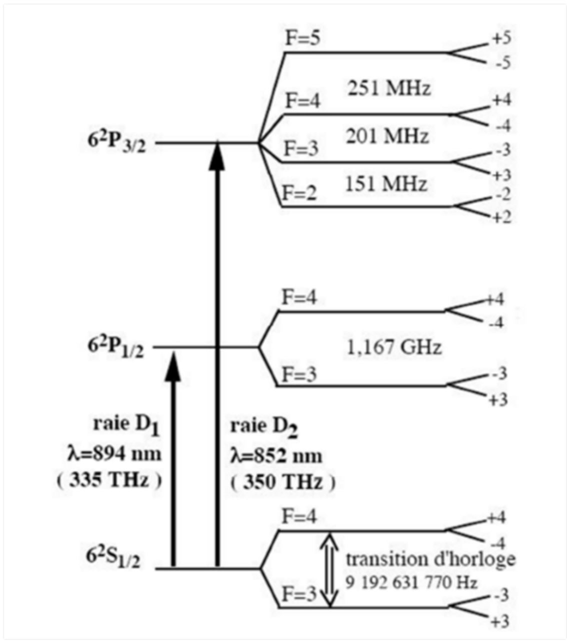
$$(v_z \pm \mathrm{d}v_z) = (\omega_2 - \omega_1)/2k \pm \gamma k$$

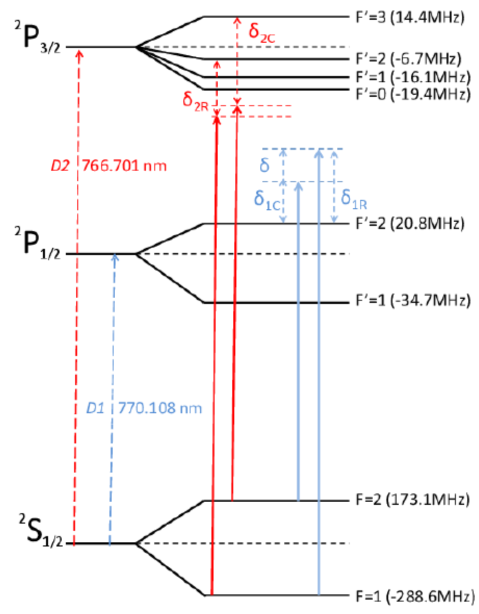


The same ground state

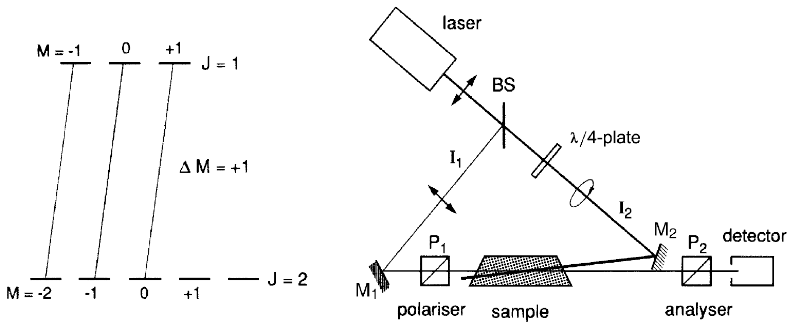


The same excited state





Polarization Spectroscopy

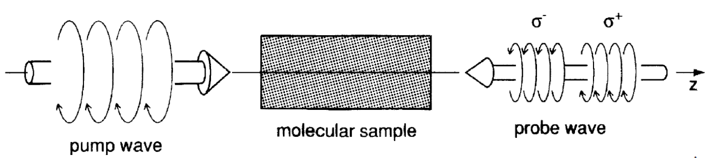


a) b)

$$\boldsymbol{E} = \boldsymbol{E}^+ + \boldsymbol{E}^-$$

$$E^+ = E_0^+ \mathrm{e}^{\mathrm{i}(\omega t - k^+ z)}, \qquad E_0^+ = \frac{1}{2} E_0 (\hat{\boldsymbol{x}} + \mathrm{i}\hat{\boldsymbol{y}}),$$

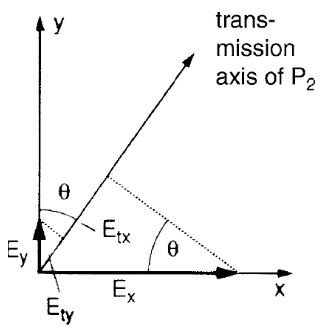
$$E^- = E_0^- \mathrm{e}^{\mathrm{i}(\omega t - k^- z)}, \qquad E_0^- = \frac{1}{2} E_0 (\hat{\boldsymbol{x}} - \mathrm{i}\hat{\boldsymbol{y}}),$$



$$E^+ = E_0^+ \mathrm{e}^{\mathrm{i}[\omega t - k^+ L + \mathrm{i}(\alpha^+/2)L]}, \qquad \Delta n = n^+ - n^-$$

$$E^- = E_0^- \mathrm{e}^{\mathrm{i}[\omega t - k^- L + \mathrm{i}(\alpha^-/2)L]}. \qquad \Delta\alpha = \alpha^+ - \alpha^-$$

$$\Delta\phi = \left(k^+ - k^-\right)L = (\omega L/c)\Delta n \qquad \Delta E = \frac{E_0}{2}\left[\mathrm{e}^{-(\alpha^+/2)L} - \mathrm{e}^{-(\alpha^-/2)L}\right]$$

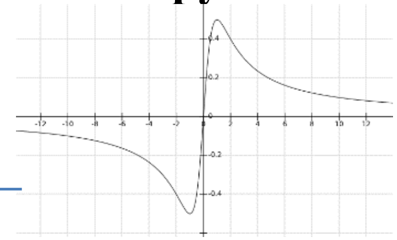


$$E_\mathrm{t} = E_x \sin\theta + E_y \cos\theta$$

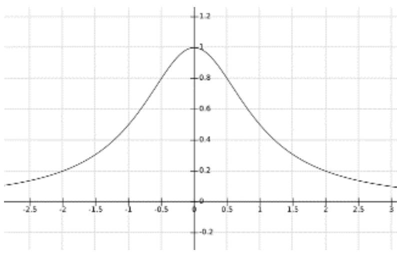
$$S(\omega) \propto I_\mathrm{T}(\omega) = c\epsilon_0 E_\mathrm{t} E_\mathrm{t}^*$$ Detector signal

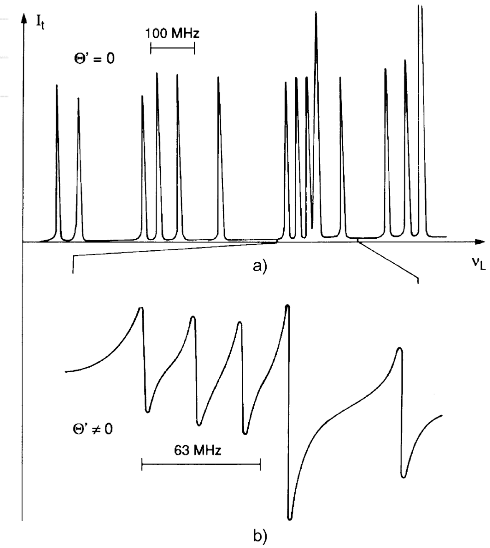
$$S^{\mathrm{cp}} = I_\mathrm{t}(\omega) = I_0 \mathrm{e}^{-\alpha L - a_\mathrm{w}} \left\{ \xi + \theta'^2 + \frac{1}{4}\Delta a_\mathrm{w}^2 + \frac{1}{2}\theta' \Delta\alpha_0 L \frac{x}{1+x^2} + \left[\frac{1}{4}\Delta\alpha_0 \Delta a_\mathrm{w} L + \left(\frac{\Delta\alpha_0 L}{4}\right)^2\right] \frac{1}{1+x^2} + \frac{3}{4}\left(\frac{\Delta\alpha_0 x}{(1+x^2)}\right)^2 \right\}.$$

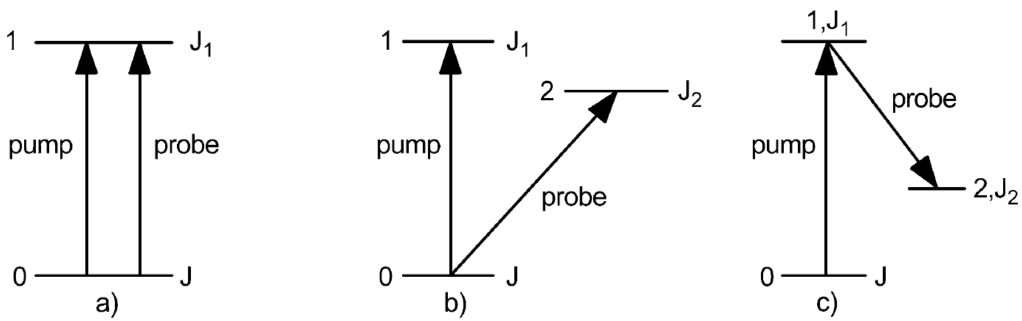
Polarization Spectroscopy



$$S^{\mathrm{cp}} = I_{\mathrm{t}}(\omega) = I_0 \mathrm{e}^{-\alpha L - a_{\mathrm{w}}} \left\{ \xi + \theta'^2 + \frac{1}{4}\Delta a_{\mathrm{w}}^2 + \frac{1}{2}\theta' \Delta\alpha_0 L \frac{x}{1+x^2} + \left[\frac{1}{4}\Delta\alpha_0 \Delta a_{\mathrm{w}} L + \left(\frac{\Delta\alpha_0 L}{4}\right)^2\right] \frac{1}{1+x^2} + \frac{3}{4}\left(\frac{\Delta\alpha_0 x}{(1+x^2)}\right)^2 \right\}$$







Doppler-free two-photon spectroscopy

Two photons simultaneously absorbed – induce optical transition with $\Delta L = 0$ or $\Delta L = \pm 2$ depending on two-photon spins

- much weaker than one-photon transitions
- probability enhanced if intermediate level E_m is present

From energy conservation $E_f - E_k = \hbar(\omega_1 + \omega_2)$

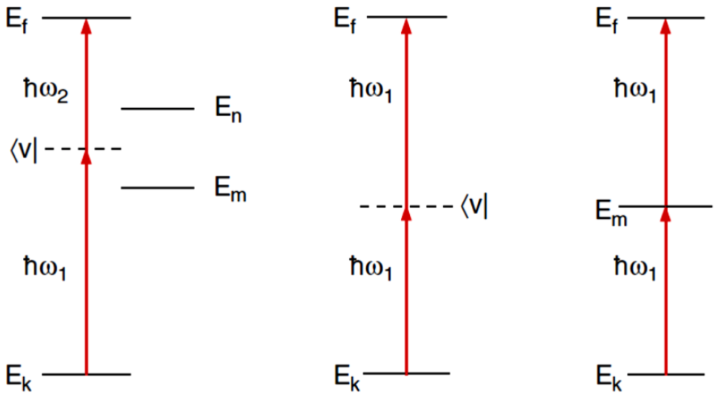
For moving molecule - Doppler shift $\omega' = \omega - \boldsymbol{k} \cdot \boldsymbol{v}$

$$E_f - E_k = \hbar(\omega_1 + \omega_2) - \hbar \boldsymbol{v}(\boldsymbol{k}_1 + \boldsymbol{k}_2)$$

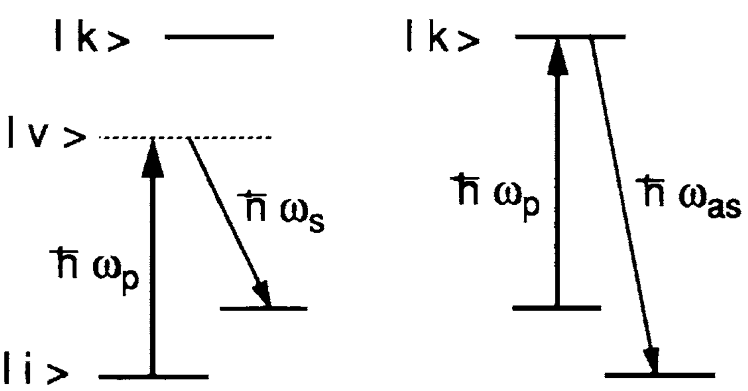
For two beams from the same laser with opposite direction

$$\omega_1 = \omega_2 \text{ and } \boldsymbol{k}_1 = -\boldsymbol{k}_2$$

Molecules with all speeds contribute to the Doppler-free two-photon absorption

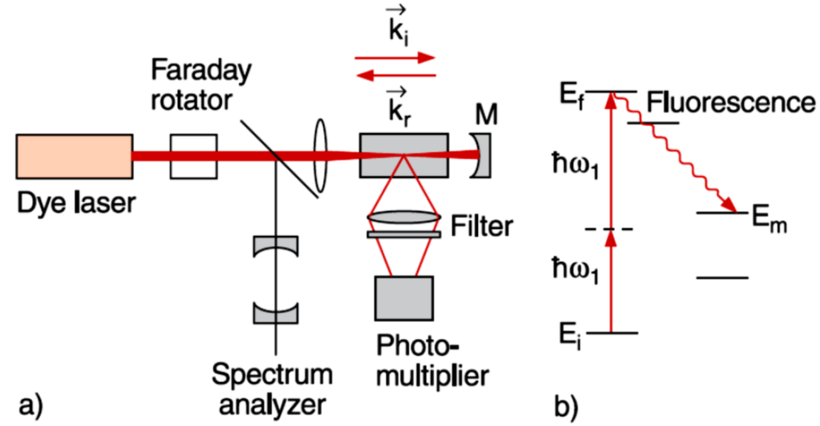


Figs. ref. [1]



Doppler-free two-photon spectroscopy

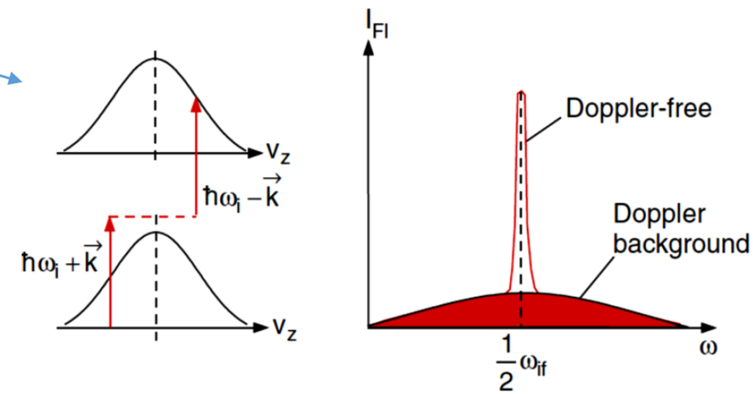
Experimental setup for two-photon spectroscopy – fluorescence detection

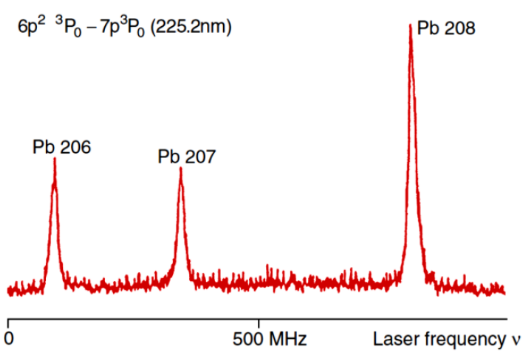


Two photons travelling the same direction (equal ***k***) – Doppler broadened spectrum

Two photons travelling opposite direction (opposite ***k***) – Doppler-free spectrum (two times more probable)

Doppler-free peak is $2 \times \Delta\omega_D / \Delta\omega_n$ times higher than Doppler-broadened background





Isotope shifts of lead – two-photon spectroscopy

Figs. ref. [1]