Lectures on Spectroscopy and Metrology

1. How to do XUV precision spectroscopy
   - XUV-light and how to make it: Harmonic generation
   - Frequency chirping in lasers and harmonics
2. Frequency metrology with frequency comb lasers
   - Concepts of frequency combs
   - Use in calibration
   - Direct frequency comb excitation
3. Precision spectroscopy of hydrogen
   - Laboratory spectroscopy
   - Spectroscopic observations of quasars
   - Detecting a variation of the proton-electron mass ratio
4. Varying constants and a view on an evolutionary universe

Wim Ubachs

TULIP Summer School IV 2009
Noordwijk, April 15-18

XUV light

Lasers at very short wavelengths ?

competiton with spontaneous emission: A/B ~ ω^3

no media for tunability

Transparancy of the atmosphere

vacuum ultraviolet : λ < 200 nm

No window materials

LiF cutoff : λ ~ 105 nm; MgF at 118 nm; CaF at ~130 nm

No optics for beam manilupation - focusing

No nonlinear crystals

Harmonic conversion only in gases

Gases have inversion symmetry; so third order

Re-absorption still important in some cases – differentail pumping

Optical breakdown and plasma formation

Typical conversion effeiciens < 10^{-6}

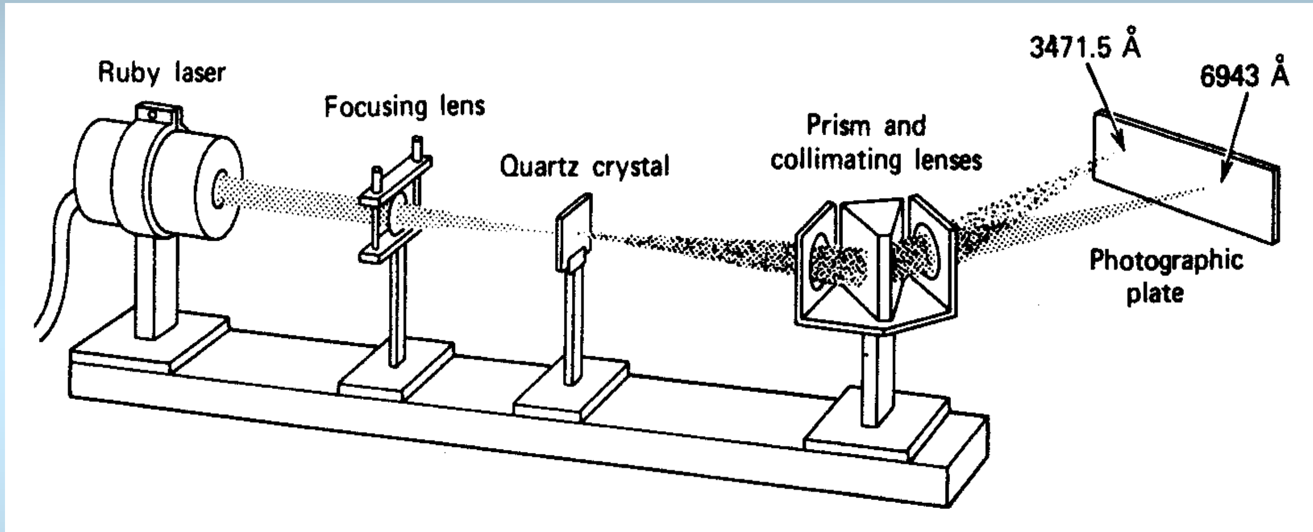
Other sources

Gas discharges (Hopfield continua)

Synchrotron radiation

Nonlinear Optics and the Production of XUV light

The first non-linear optical laser experiment



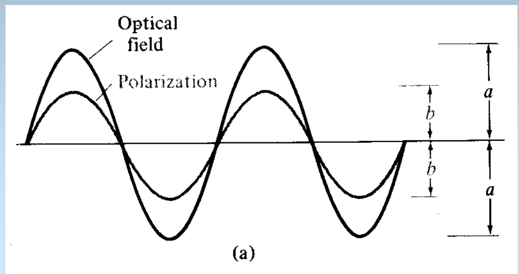
P.A. Franken, A.E. Hill, C.W. Peters and G. Weinreich, Phys. Rev. Lett. **7** (1961) 118

Nicolaas Bloembergen
Nobel prize 1981

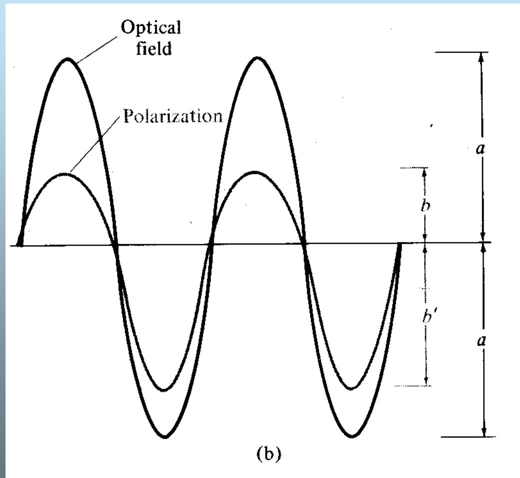
Further: Stimulated Raman, Stimulated Brillouin, CARS, Photon echoes, Four-wave mixing Surface sum-frequency-mixing

Graphical: Nonlinear response of a medium

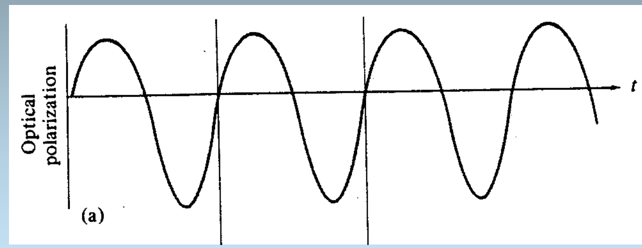
Linear response:
induced polarization follows
the applied field on the medium



Non-linear response:
induced polarization cannot follow
the applied field on the medium

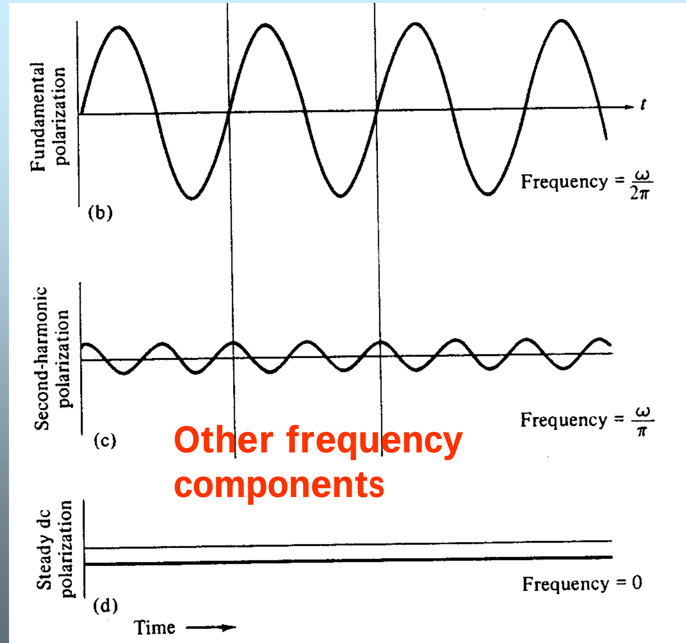


The medium becomes nonlinearly polarized



Polarization can be decomposed in
Fourier components

$$P = \sum a_n \sin\left(n\omega t + \phi_n\right)$$



Other frequency components

Nonlinear Optics and Maxwell's equations

Nonlinear polarization induced in a medium:

$$\vec{\mathbf{P}}_i = \chi^{(1)}_{ij}\vec{\mathbf{E}}_j + \chi^{(2)}_{ijk}\vec{\mathbf{E}}_j\vec{\mathbf{E}}_k + \chi^{(3)}_{ijkl}\vec{\mathbf{E}}_j\vec{\mathbf{E}}_k\vec{\mathbf{E}}_l + O(E^4)$$

In centrosymmetric media, such as gases, $\chi^{(2)}=0$:

$$\vec{\mathbf{P}}^{(3)}_i = \chi^{(3)}_{ijkl}\vec{\mathbf{E}}_j\vec{\mathbf{E}}_k\vec{\mathbf{E}}_l$$

A source term for Maxwell's equation:

$$\nabla^2\vec{E} - \mu\sigma\frac{\partial\vec{E}}{\partial t} - \mu\varepsilon\frac{\partial^2\vec{E}}{\partial t^2} = \mu\frac{\partial^2}{\partial t^2}\vec{P}^{NL}$$

Input fields:

$$E_1(z,t) = E_1(z)\exp(i\omega_1 t - ik_1 z)$$
$$E_2(z,t) = E_2(z)\exp(i\omega_2 t - ik_2 z)$$
$$E_3(z,t) = E_3(z)\exp(i\omega_3 t - ik_3 z)$$

A new field $E_4(z,t)$ is created at frequencies: $\omega_4 = \pm\omega_1 \pm\omega_2 \pm\omega_3$

At polarization: $P_{NL}(z,t) = dE_1(z)E_2(z)E_3(z)\exp[i(\omega_1+\omega_2+\omega_3)t - i(k_1+k_2+k_3)z]$

Nonperturbative

$$\chi^{(2n+3)}|\mathbf{E}|^2 \approx \chi^{(2n+1)}$$

Theory: Corkums 3-step model (classical)
Lewenstein: Quantum-Mech. model

Coupled wave equations

Maxwell's equation with nonlinear source term:

$$\nabla^2 \vec{E}_4 - \mu\sigma \frac{\partial \vec{E}_4}{\partial t} - \mu\varepsilon \frac{\partial^2 \vec{E}_4}{\partial t^2} = \mu \frac{\partial^2}{\partial t^2} \vec{P}^{NL}$$

Substitute left side:

use: $E_4(z,t) = E_4(z)\exp(i\omega_4 t - ik_4 z)$

$$\frac{d^2}{dz^2}E_4(z,t) - \mu\sigma\frac{d}{dt}E_4(z,t) - \mu\varepsilon\frac{d^2}{dt^2}E_4(z,t) =$$

$$\frac{d^2}{dz^2}E_4(z,t) + 2ik_4\frac{d}{dz}E_4(z,t) - k_4^2 E_4(z,t)$$

$$+ i\omega_4\mu\sigma E_4(z,t) + \mu\varepsilon\omega_4^2 E_4(z,t)$$

Slowly varying amplitude approximation

$$\left|\frac{d^2}{dz^2}E_4(z,t)\right| << \left|2ik_4\frac{d}{dz}E_4(z,t)\right|$$

Variation of the amplitude of the distance of a wavelength is small

$$\cancel{\frac{d^2}{dz^2}E_4(z,t)} + 2ik_4\frac{d}{dz}E_4(z,t) \cancel{- k_4^2 E_3(z,t)}$$

$$+ i\omega_4\mu\sigma E_4(z,t) \cancel{+ \mu\varepsilon\omega_4^2 E_4(z,t)}$$

For plane waves in a medium;

$$\mu\varepsilon\omega_4^2 - k_4^2 = \frac{\omega_4^2}{c^2} - k_4^2 = 0$$

So left side of wave equation;

$$2ik_4\frac{d}{dz}E_4(z,t) + i\omega_4\mu\sigma E_4(z,t)$$

Coupled wave equations

$$\nabla^2 \vec{E}_4 - \mu\sigma \frac{\partial \vec{E}_4}{\partial t} - \mu\varepsilon \frac{\partial^2 \vec{E}_4}{\partial t^2} = \mu \frac{\partial^2}{\partial t^2} \vec{P}^{NL}$$

left side of wave equation;

$$2ik_4 \frac{d}{dz} E_4(z,t) + i\omega_4 \mu\sigma E_4(z,t)$$

reabsorption

right side of wave equation;

$$\mu \frac{\partial^2}{\partial t^2} \vec{P}^{NL} = \mu \frac{d^2}{dt^2} \chi E_1(z) E_2(z) E_3(z) \exp[i(\omega_1 + \omega_2 + \omega_3)t - i(k_1 + k_2 + k_3)z] =$$

$$-\mu(\omega_1 + \omega_2 + \omega_2)^2 \chi E_1(z) E_2(z) E_3(z) \exp[i(\omega_1 + \omega_2 + \omega_3)t - i(k_1 + k_2 + k_3)z]$$

Conservation of energy; $\omega_4 = \omega_1 + \omega_2 + \omega_3$

This does not hold for the wave vectors, because; $\omega_i = \frac{k_i}{\sqrt{\mu\varepsilon(\omega_i)}} = \frac{ck_i}{n(\omega_i)}$

Hence; $\Delta\vec{k} = \vec{k}_4 - \vec{k}_1 - \vec{k}_2 - \vec{k}_3$

Coupled equation; $$\frac{d}{dz} E_4(z) \propto \chi^{(3)} E_1(z) E_2(z) E_3(z) \exp[-i\Delta kz]$$

Result $$I(\omega_4) = |\chi^{(3)}|^2 I(\omega_1) I(\omega_2) I(\omega_3) \Phi_{\rm pm}(\overrightarrow{\mathbf{k}}_1, \overrightarrow{\mathbf{k}}_2, \overrightarrow{\mathbf{k}}_3, \overrightarrow{\mathbf{k}}_4)$$

Perturbative analysis of THG

Result

$$I(\omega_4) = |\chi^{(3)}|^2 I(\omega_1) I(\omega_2) I(\omega_3) \Phi_{\mathrm{pm}}(\overrightarrow{\mathbf{k}}_1, \overrightarrow{\mathbf{k}}_2, \overrightarrow{\mathbf{k}}_3, \overrightarrow{\mathbf{k}}_4)$$

Susceptibility
of the medium:
material property
(quantum resonances)

Input field intensities
High power;
Focused laser beams

Phases of input fields;
Geometry of setup
(confocal parameter,
Gouy phase, phase matching)

Susceptibility, quantum level structure, reabsorption and resonance enhancement

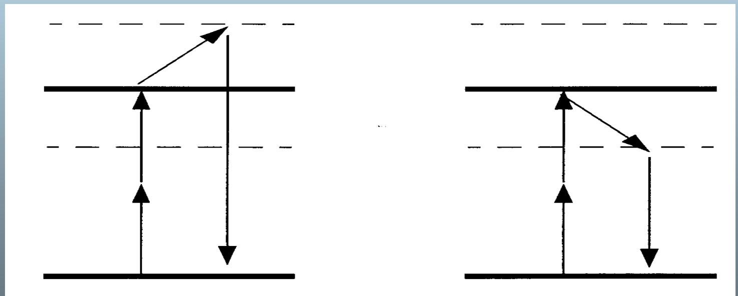
Non-linear susceptibility:

$$\chi^{(3)} \propto \sum_{gijk} \sum_{terms} \frac{\langle g|\mathbf{r}|i\rangle\langle i|\mathbf{r}|j\rangle\langle j|\mathbf{r}|k\rangle\langle k|\mathbf{r}|g\rangle}{(\omega_{gi} \pm \omega)(\omega_{gj} \pm 2\omega)(\omega_{gk} \pm 3\omega)}$$

Resonances possible at the
- One photon
- Two-photon
- Three photon levels (reabsorption)

Advantage at two-photon-level

$$\chi^{(3)} \propto \sum_{ik} \sum_{terms} \frac{\langle g|\mathbf{r}|i\rangle\langle i|\mathbf{r}|J'\rangle\langle J'|\mathbf{r}|k\rangle\langle k|\mathbf{r}|g\rangle}{(\omega_{gi} \pm \omega)(\omega_{gj} - 2\omega - i\Gamma)(\omega_{gk} \pm 3\omega)}$$



Process I　　　Process II

Again level structure of the noble gases is favorable:

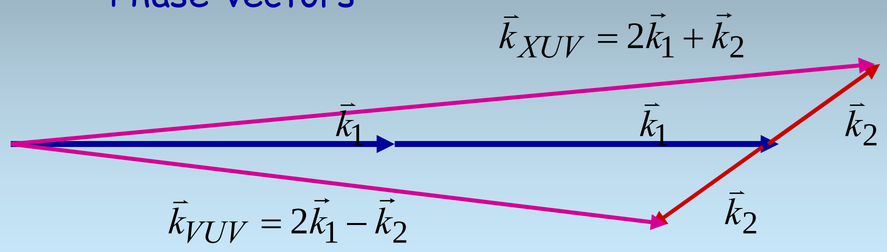
	Two-photon resonance	excitation energy (cm^{-1})	resonance wavelength (nm)	relative efficiency[a]
	5p - 6p' $[3/2]_2$	89162.9	224.3	40
	$[1/2]_0$	89860.5	222.6	187
	7p $[5/2]_2$	88352.2	226.4	4
Xe	$[3/2]_2$	88687.0	225.5	9
	$[1/2]_0$	88842.8	225.1	26
	8p $[5/2]_2$	92221.9	216.9	9
	$[3/2]_2$	92371.4	216.5	5
	$[1/2]_0$	92555.7	216.1	119
	4p - 5p $[5/2]_2$	92308.2	216.7	167
Kr	$[3/2]_2$	93124.1	214.8	56
	$[1/2]_0$	94093.7	212.6	1000

[a] Fundamental power is 20 kW.

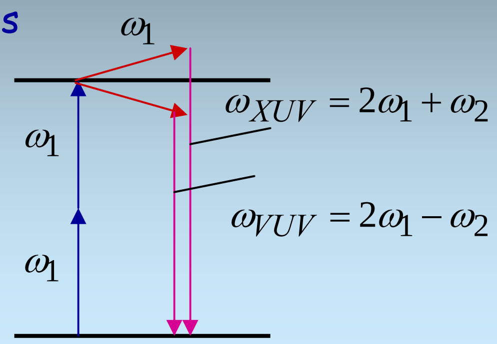
λ = 212.5 nm resonance in Kr
"strongest two-photon resonance in nature"

Non-colinear Phase-matching for sum-frequency generation

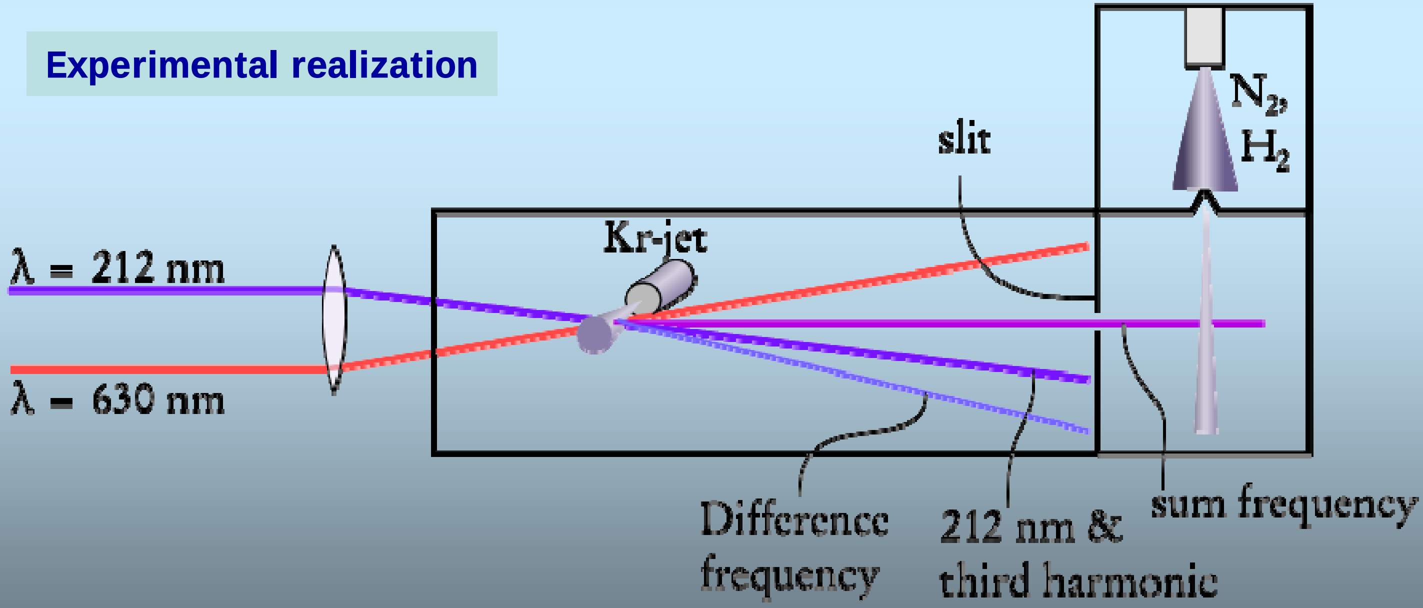
Phase-vectors



Energy levels



Experimental realization

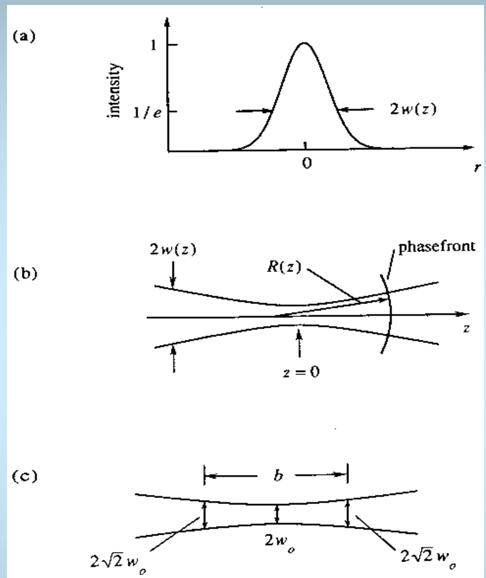


Volume considerations

Opt. Lett. 20 (2005) 1494

Problems and solutions in colinear phase-matching in THG

Beams must be **focused**: this has an effect on the wave front



w_0 beam waist radius

n index of refraction

θ far-field diffraction angle

$$\xi = \frac{2(z-f)}{b}$$ normalized coordinate along z

Confocal parameter b

$$b = \frac{2\pi w_0^2}{\lambda} = \frac{2\pi w_0^2 n}{\lambda_0} = \frac{2\lambda_0}{n\theta^2} = k w_0^2$$

Electromagnetic fields (for TEM_{00}):

$$\mathbf{E}_n(\mathbf{r}) = \mathbf{E}_{n0}(\mathbf{r}) \frac{\exp(ik_n z)}{1+i\xi} \exp\left[\frac{-k_n(x^2+y^2)}{b(1+i\xi)}\right]$$

Lowest order Gaussian beam undergoes phase shift $\arctan\xi$ when propagating through the focus (**Gouy phase**), adding up to π for $(-\infty,\infty)$

Conditions for the phase-matching integral in THG

Solutions, process THG

$$E_4(\mathbf{r}) = i\frac{3N}{2k_4}\pi k_0^2 b\chi^{(3)}(-\omega_4;\omega_1,\omega_2,\omega_3)E_{10}E_{20}E_{30}\frac{\exp(ik'z)}{(1+i\xi)}$$
$$\times\exp\left[\frac{-k'(x^2+y^2)}{b(1+i\xi)}\right]\int_{-\zeta}^{\xi}\frac{\exp[-(ib/2)\Delta k(\xi'-\xi)]}{(1+i\xi')^2}d\xi'$$

Phases get into the integral: wave front + dispersion

Field $E_4(\mathbf{r})$ to be calculated, integration over x and y, and z to z=L.

$$\int_0^\infty 2\pi R|E_4(R)|^2 dR \qquad R=\sqrt{x^2+y^2}$$

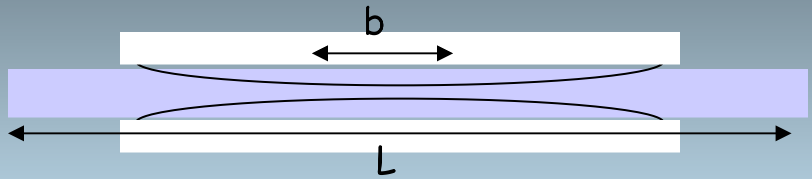
Then generated Power at P_4 is

$$P_4 = \eta\frac{k_0^4 k_1 k_2 k_3}{k_4^2 k'}N^2\chi^2 P_1 P_2 P_3 F_j\left(b\Delta k, \frac{b}{L}, \frac{f}{L}, \frac{k''}{k'}\right)$$

With the phase-matching integral

$$F_I\left(b\Delta k, \frac{b}{L}, \frac{f}{L}, \frac{k''}{k'}\right) = \left|\int_{-\zeta}^{\xi}\frac{\exp[-(ib/2)\Delta k\xi']}{(1+i\xi')^2}d\xi'\right|$$

Influence of the geometry in THG



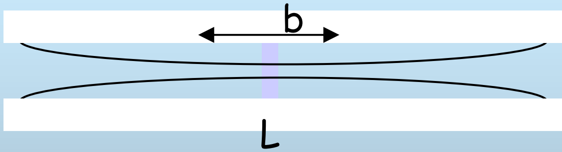
Tight-focus

Process THG – evaluation of integral for b<<L:

$$F_I(b\Delta k, 0, 0.5, 1) = \begin{cases} \pi^2 (b\Delta k)^2 e^{(b\Delta k/2)} & \Delta k < 0 \\ 0 & \Delta k \geq 0 \end{cases}$$

THG only possible,
in the tight-focusing limit if $\Delta k < 0$

So: only if the medium has
NEGATIVE DISPERSION !!



Plane wave limit

Process THG – evaluation of integral for b>>L:

$$\lim_{b/L \to \infty} F_I\left(b\Delta k, \frac{b}{L}, 0.5, \frac{k''}{k'}\right) = \frac{4L^2}{b^2} \operatorname{sinc}^2\left(\frac{\Delta kL}{2}\right)$$

The known sinc-function
Also found in frequency-doubling
(for plane waves)

Less efficient than tight-focusing

Real example: Negative and positive dispersion in the Kr and Xe

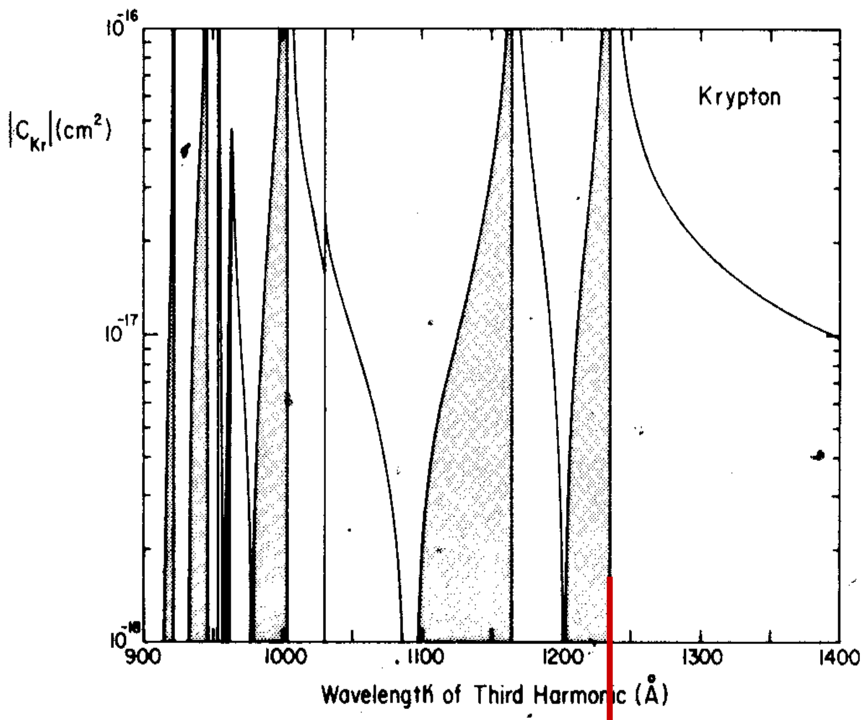
Wave vector mismatch
Related to dispersion

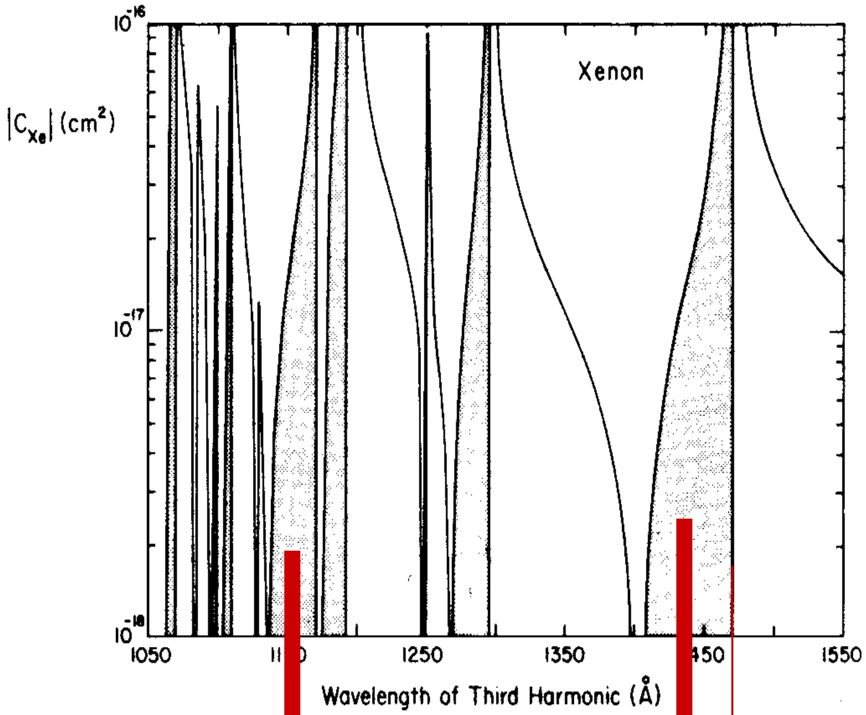
$$\Delta k = CN = \frac{2\pi(n_1 - n_3)}{\lambda}$$

with

$$(n-1)_{lines} = \frac{Nr_e}{2\pi}\sum_i \frac{f_i}{\lambda_i^{-2} - \lambda}$$

Shaded areas – "anomalous dispersion in the medium"

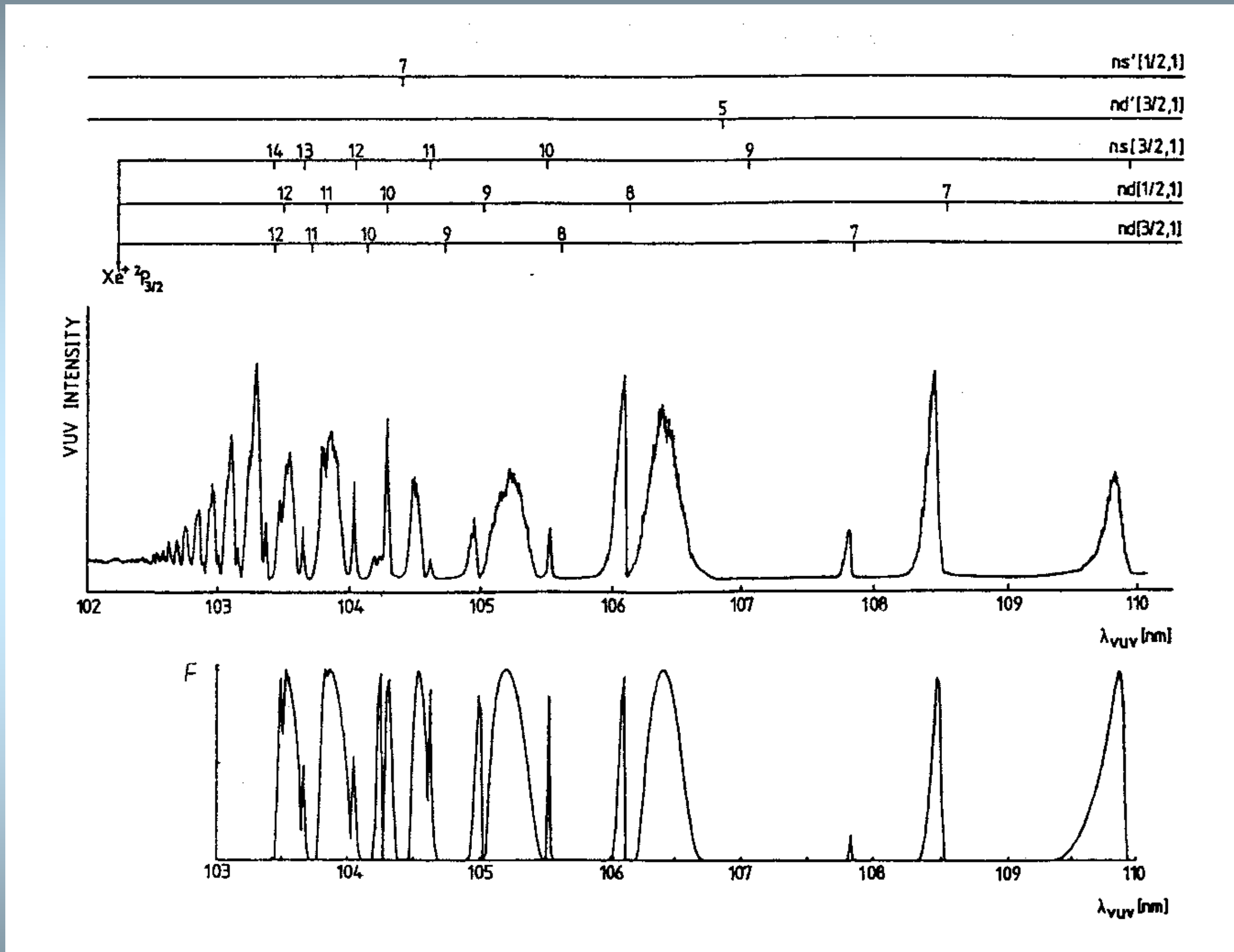




first resonance line

Regions of efficient THG

THG in Xe; experiment



Experiment THG production

Calculation of
Phase-matchingintegral

Conclusion: 1) theory of phase-matching works
2) THG effective at blue side of ns and nd resonances

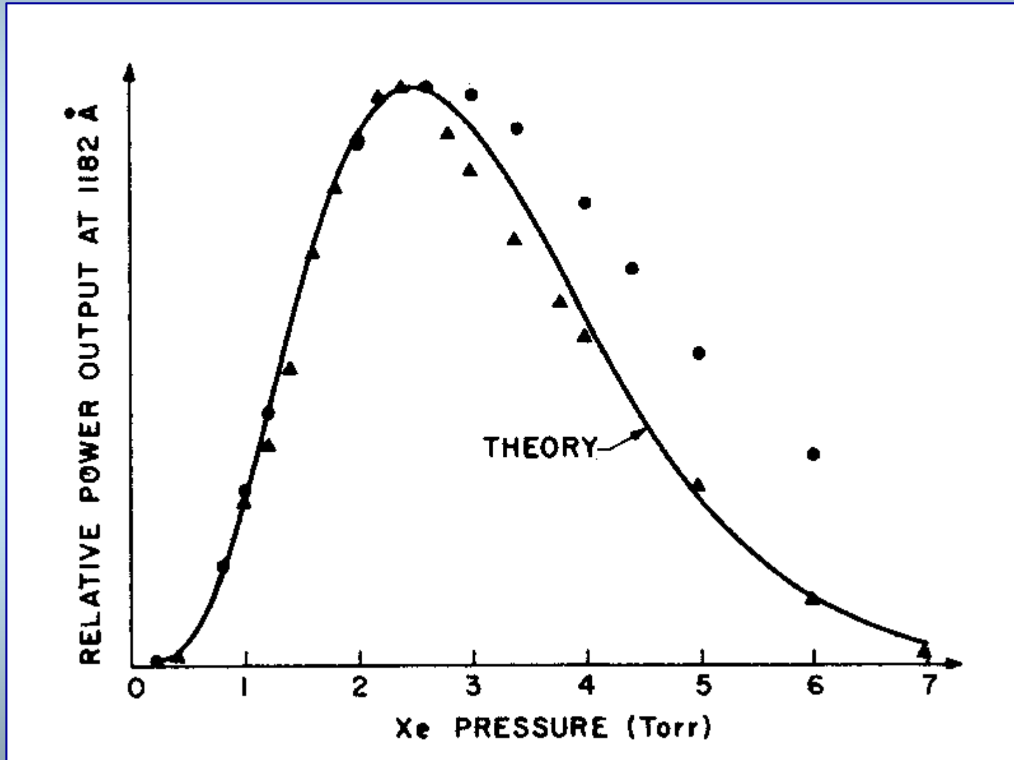
Note : absolute intensities at the 10^{-6} - 10^{-7} scale

Density effect on THG in Xe

Wave vector mismatch
Related to dispersion

$$\Delta k = CN = \frac{2\pi(n_1 - n_3)}{\lambda}$$

Phase mismatch is macroscopic (like the refractive index): dependent on gas density



NB: use mixing of gases with opposite dispersion

Polarization (orientation of the E-vector)

Nonlinear susceptibility:

$$\chi^{(3)} \propto \sum_{gijk} \sum_{terms} \frac{\langle g|\mathbf{r}|i\rangle\langle i|\mathbf{r}|j\rangle\langle j|\mathbf{r}|k\rangle\langle k|\mathbf{r}|g\rangle}{(\omega_{gi}-\omega)(\omega_{gj}-2\omega)(\omega_{gk}-3\omega)}$$

Note: parametric four-wave mixing: no energy/angular momentum exchange with the medium

Involves a sequence of four coherent photon interactions (no relaxation)

$$\langle g|\mathbf{r}|i\rangle = \langle J_g M_g|\mathbf{r}_q^{(1)}|J_i M_i\rangle = (-)^{J_i - M_i}\begin{pmatrix} J_i & 1 & J_g \\ -M_i & q & M_g \end{pmatrix}\langle J_g\|\mathbf{r}^{(1)}\|J_i\rangle$$

(Wigner-Eckhart)

Hence in four-wave mixing:

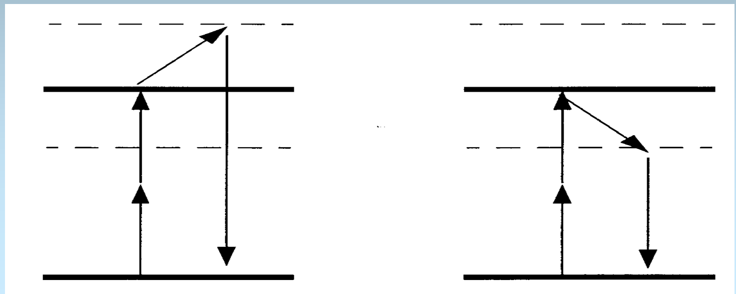
$$\chi^{(3)} \propto \begin{pmatrix} J_i & 1 & J_g \\ -M_i & q_1 & M_g \end{pmatrix}\begin{pmatrix} J_j & 1 & J_i \\ -M_j & q_2 & M_i \end{pmatrix}\begin{pmatrix} J_k & 1 & J_j \\ -M_k & q_3 & M_j \end{pmatrix}\begin{pmatrix} J_g & 1 & J_k \\ -M_g & q_4 & M_k \end{pmatrix}$$

The coherent sum requires $\Delta M=0$ over four-photon cycle;
q=0, q=-1, q=1 projections of dipole moment on angular basis (polarizations)
Evaluate the four-product of Wigner-3j symbols

Results: 1) all polarizations linear is possible $q_1 = q_2 = q_3 = q_4 = 0$

2) THG with circular light is NOT possible: $q_1 = q_2 = q_3 = 1$

Production of Polarized XUV



Well defined quantum level;

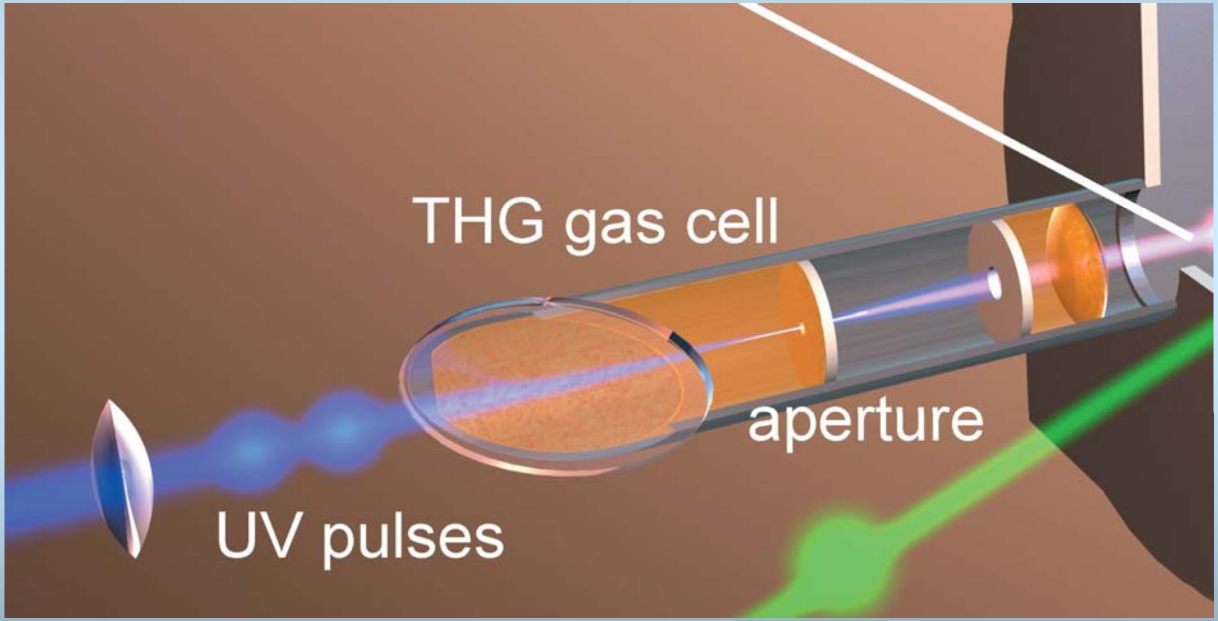
Real intermediate level

J_2 = 0 or 2

ω_R	ω_{tun}	ω_{XUV}	J_2=0	J_2=2
→	→	→	0.333	0.298
→	↑	↑	0.333	-0.149
→	↻	→	0.236	0.211
→	↻	↑	-0.236i	0.105i
↻	↺	↻	0	-0.447
↻	→	↻	0	0.316

Defeating the negative dispersion problem

All calculations performed for integral from –L to +L.
Cut-off the medium at f; stop the destructive interference.
Can be done in “forbidden region”.
Efficiency remains low; but not zero.

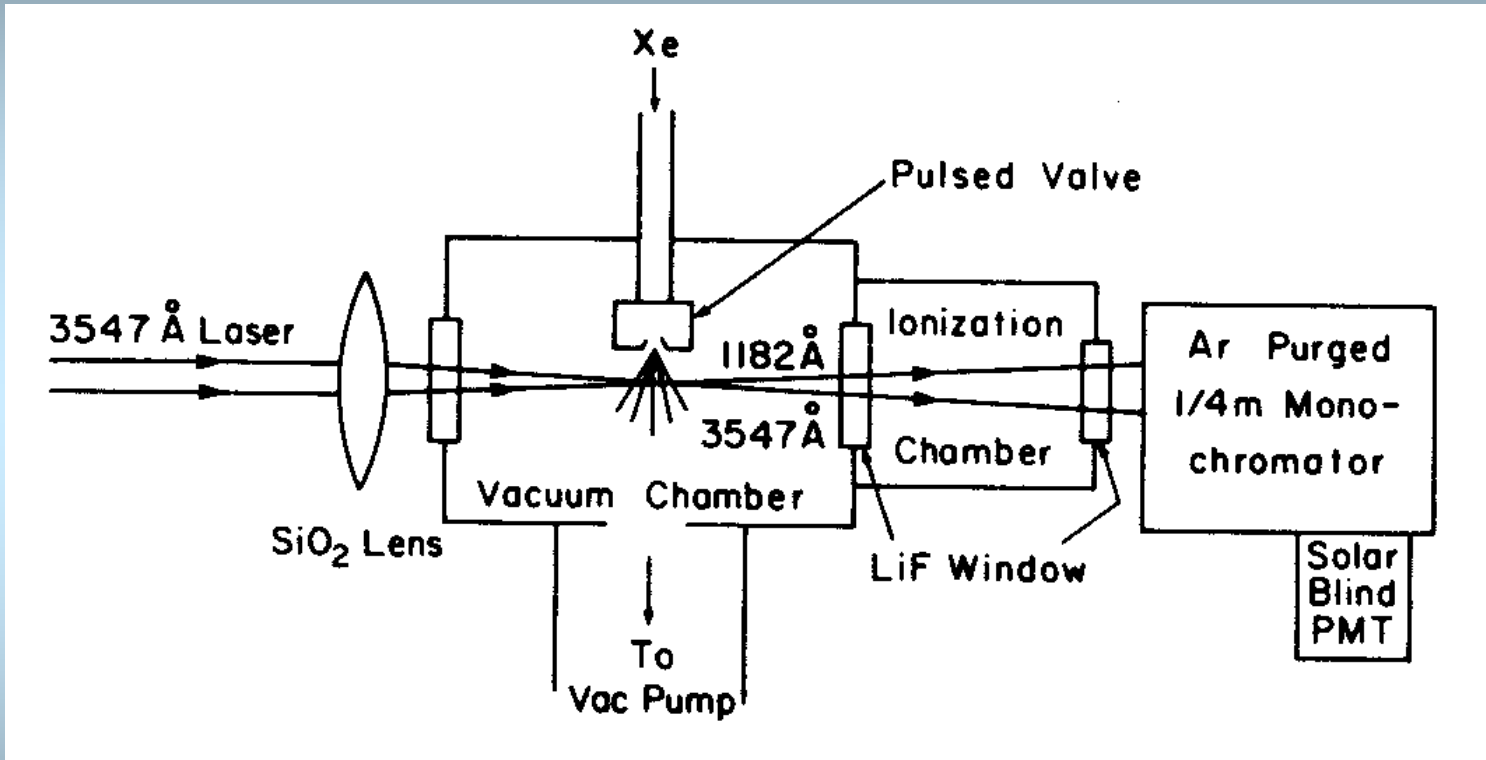


cutoff

Cutoff of the phase-matching integral $F_I\left(b\Delta k, \frac{b}{L}, \frac{f}{L}, \frac{k''}{k'}\right) = \left| \int_{-\zeta}^{0} \frac{\exp[-(ib/2)\Delta k \xi']}{(1+i\xi')^2} d\xi' \right|$

Qualitatively: stop the process when negative dispersion sets in

Pulsed jets and differential pumping – the road to the windowless regime

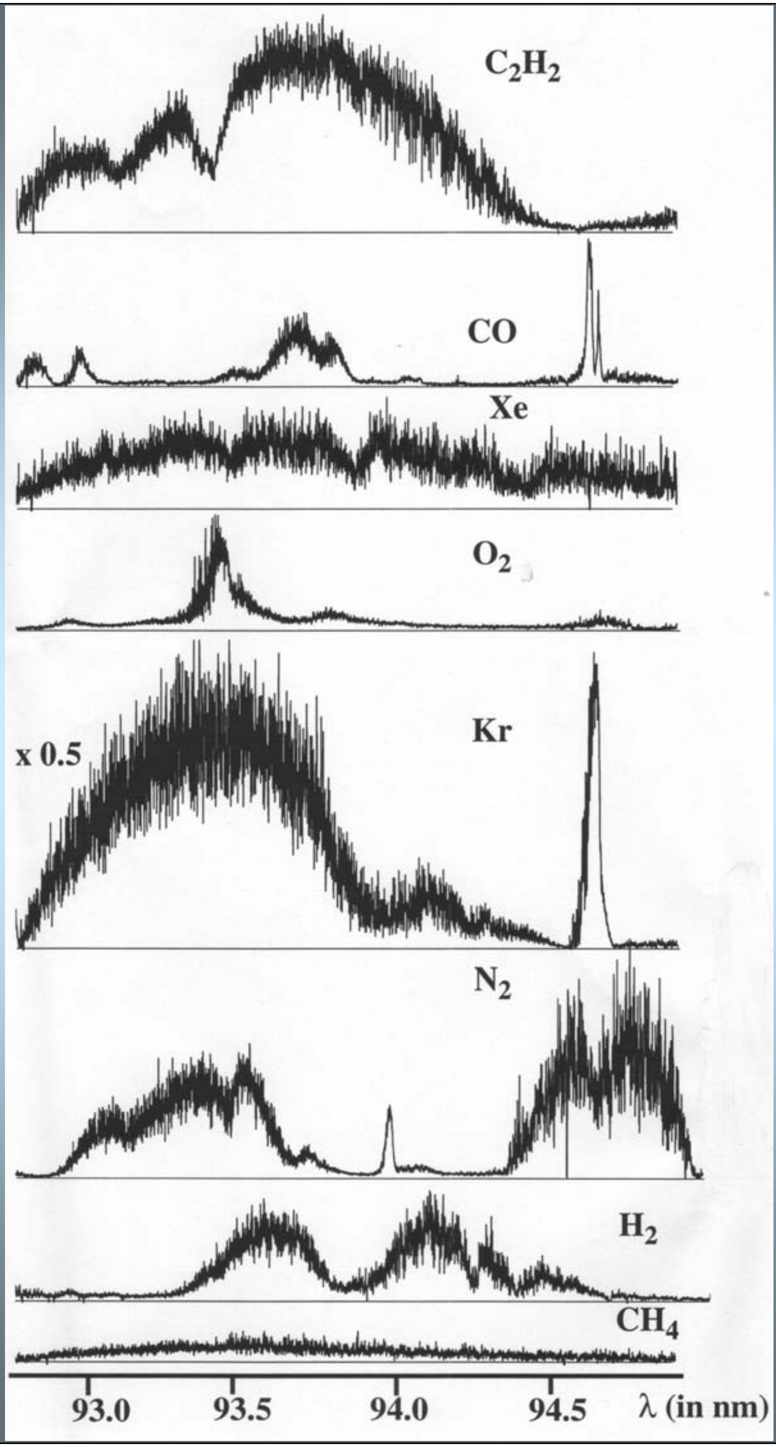


A.H. Kung, Opt. Lett. **8**, 24 (1983).

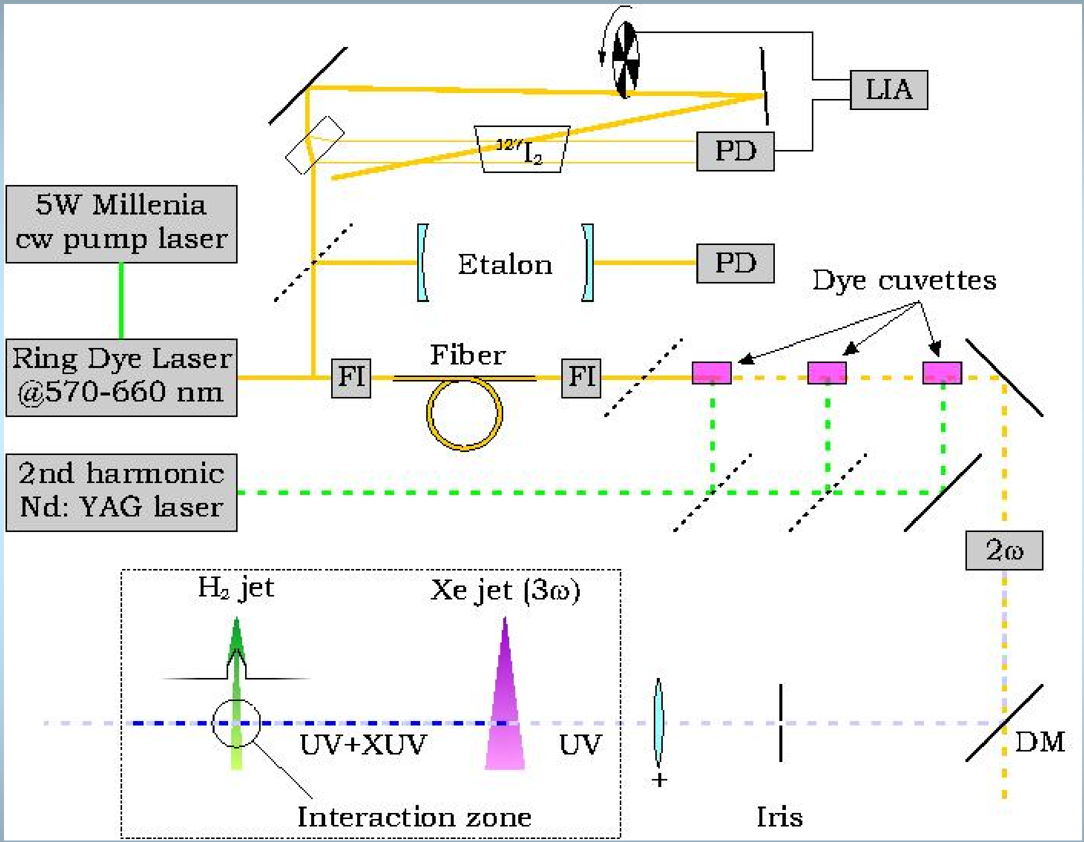
Real life THG conversion at high laser powers

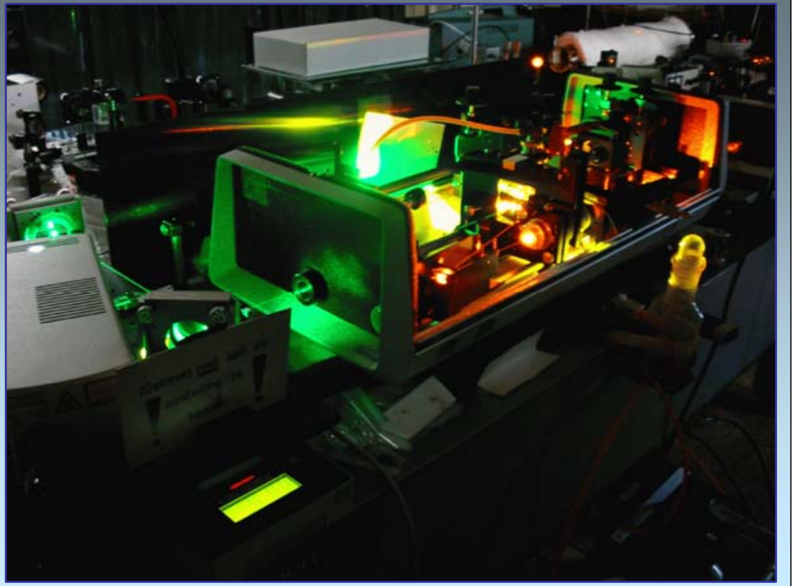
Features of the quantum mechnical level structure visible, via resonance enhancement

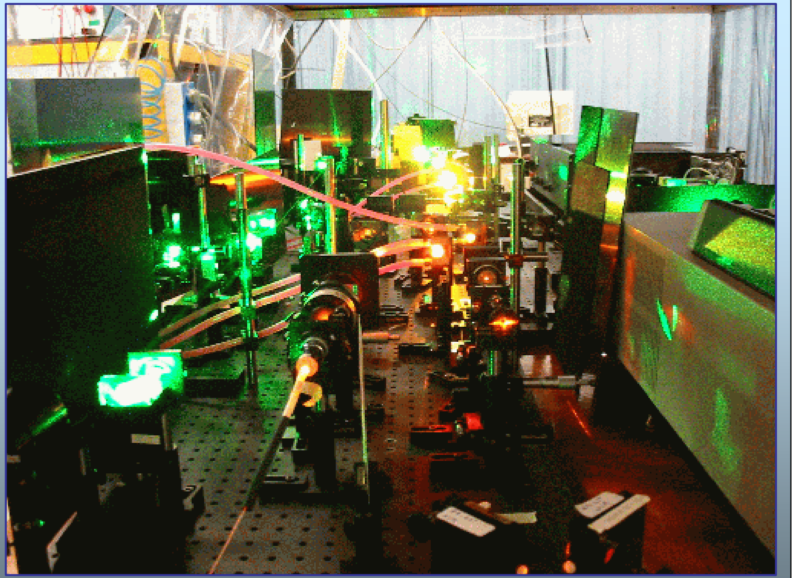
Practical:
XUV production possible at all wavelengths



XUV-laser setup with
Pulsed Dye Amplification;
bandwidth ~250 MHz







$\lambda = 90 - 110$ nm

For metrology: is $f_{seed} = f_{pulsed}$?

Phenomena of frequency chirp and precision metrology

In harmonic conversion exact harmonics produced $$\omega_n = n \times \omega_f$$

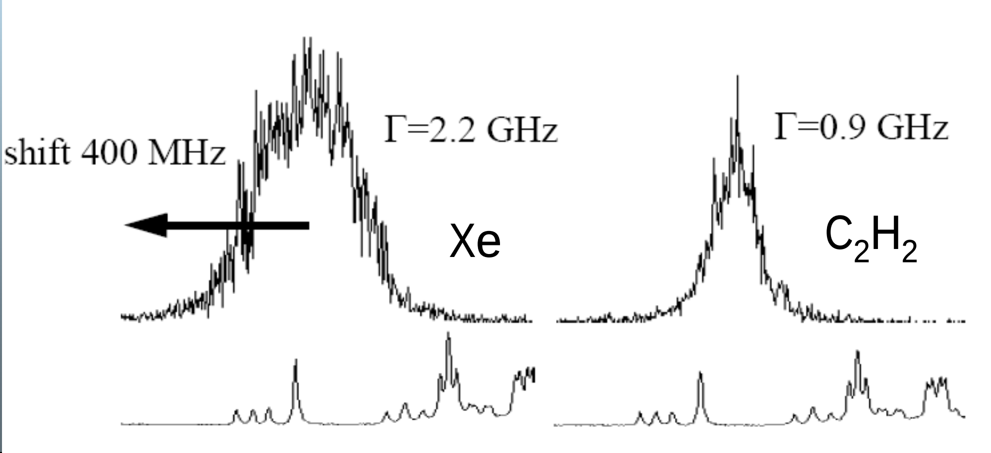
Bandwidths: $\sqrt{n} \times \Delta\omega_f$ for Gaussian beam profile

$n \times \Delta\omega_f$ for Lorentzian beam profile

For non-FT-limited pulses, with possible chirp: $$f(t) = \frac{1}{2\pi} \frac{\partial \phi(z,t)}{\partial t}$$

Phase variations possibly due to index modulation $$\phi(z,t) = -\frac{\partial n}{\partial t}$$

Example: 5th harmonics (atom as a ruler)

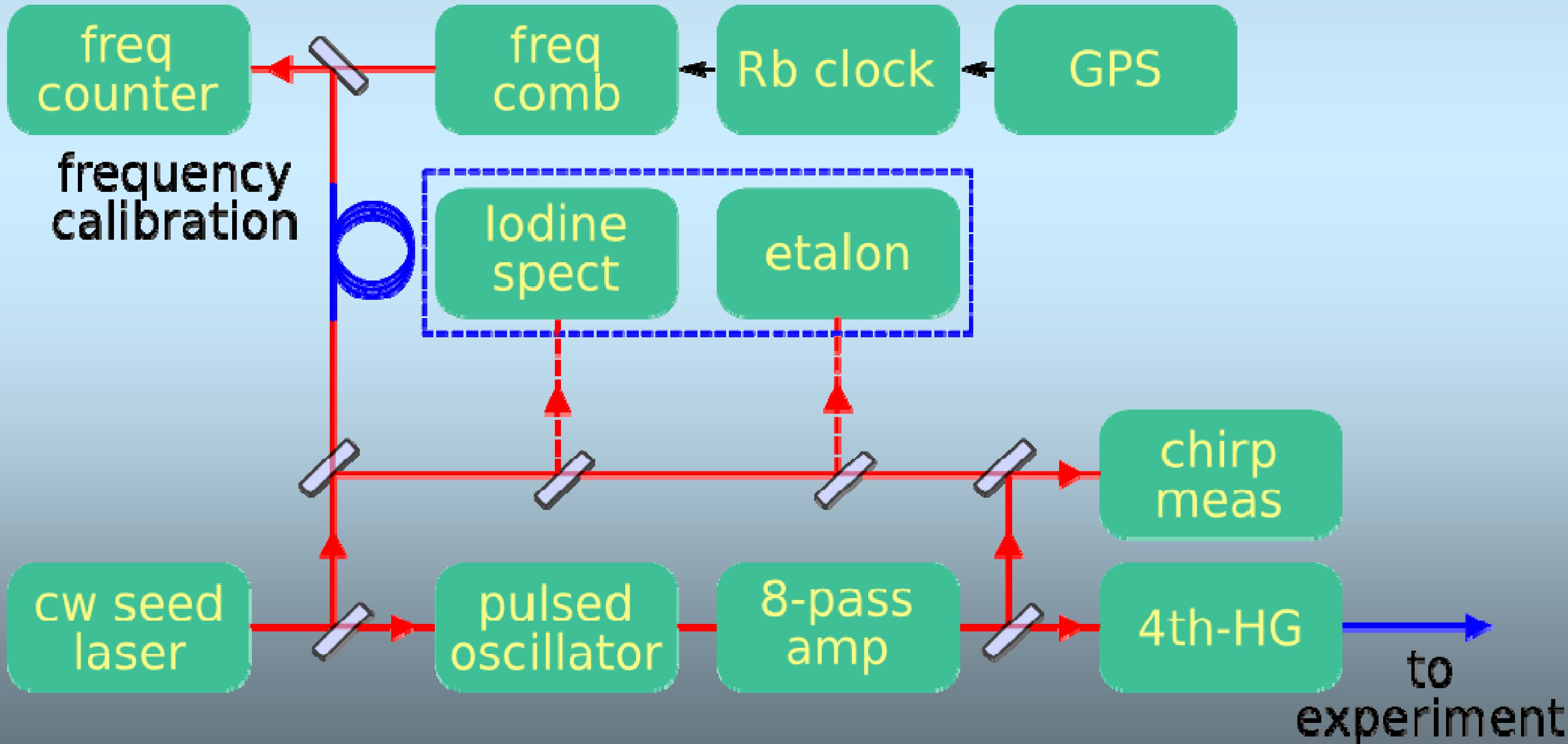


Ionization in the focus modulates the index:

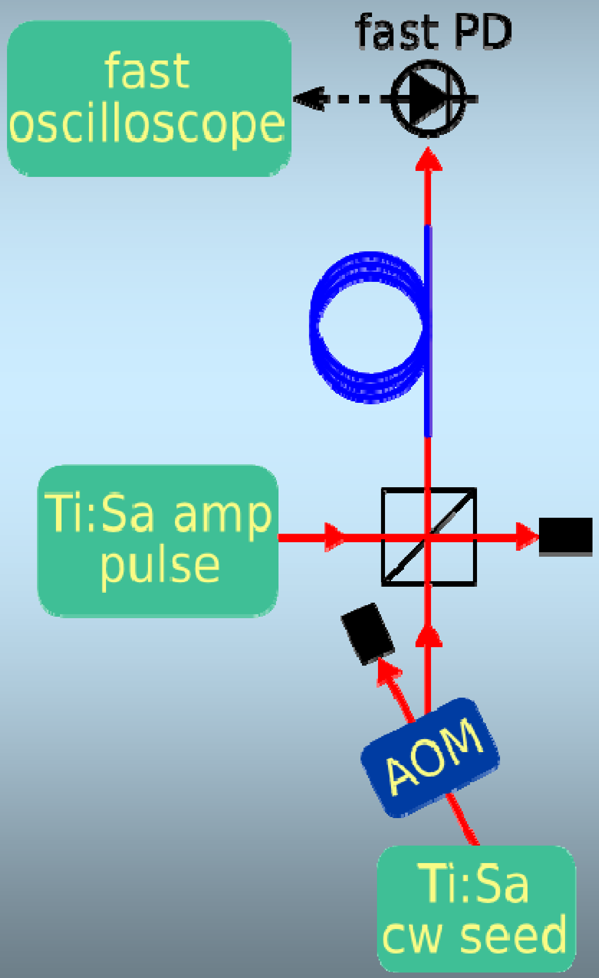
$$n_e(t) = 1 - \frac{e^2 N_e(t)}{8\pi^2 m_e \epsilon_0 \nu^2}$$

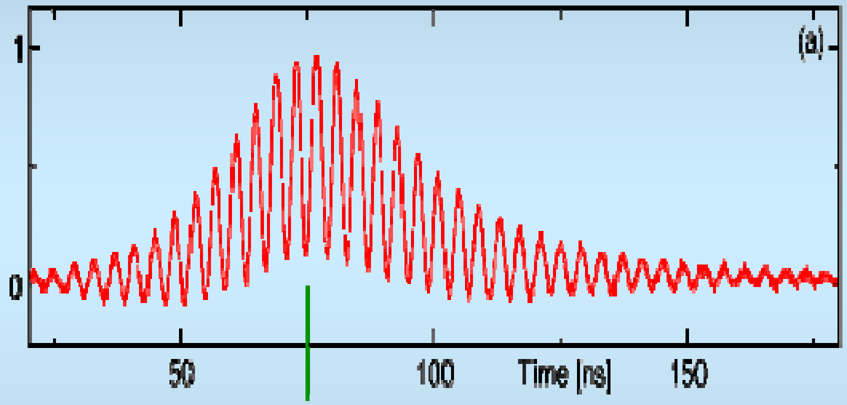
Frequency chirp in precision metrology of pulsed lasers

Spectroscopy performed with an injection seeded laser (+upconversion)
Calibration of the CW seed laser
Verification of chirp effect in pulsed systems



Chirp detection scheme





Chirp detection and chirp analysis

CW-pulse
beat detection

FT

Reverse FT's