Lecture Course

Advanced Experimental Methods

W. Ubachs; part B

Detection of molecular species (with lasers)

Techniques

Direct absorption techniques
- Cavity Ring Down
- Cavity Enhanced

Ionization detection (multi-photon)
Laser-induced fluorescence
Photo-acoustic technique
Nonlinear optical techniques
Optogalvanic technique

Issues

Resolution
Spectroscopy vs quantitative
Pressure
Color (excitation level)
Quantum state selectivity

Direct absorption

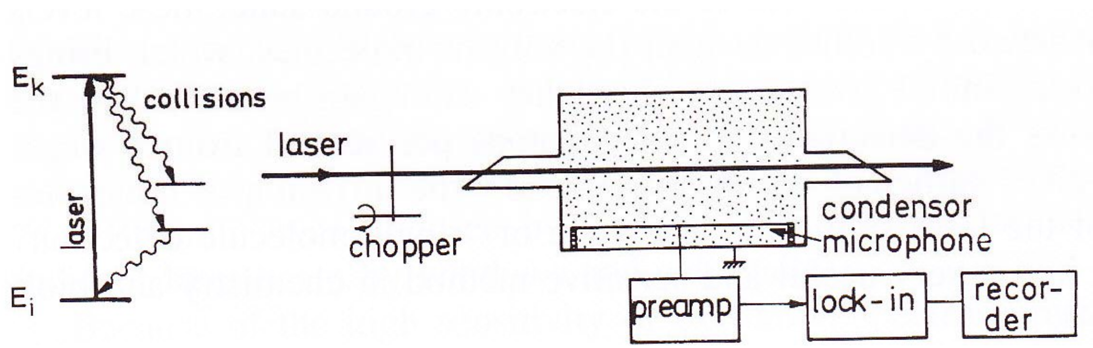
Beer's law, Beer-Lambert law

$$I_\nu = I_\nu^0 \exp\left[-\sigma_\nu n l\right]$$

Exponent	σ_ν	cross section in [cm^2]
	n	density in [cm^{-3}]
	l	absorption length in [cm]
	nl	column density in [cm^{-2}]

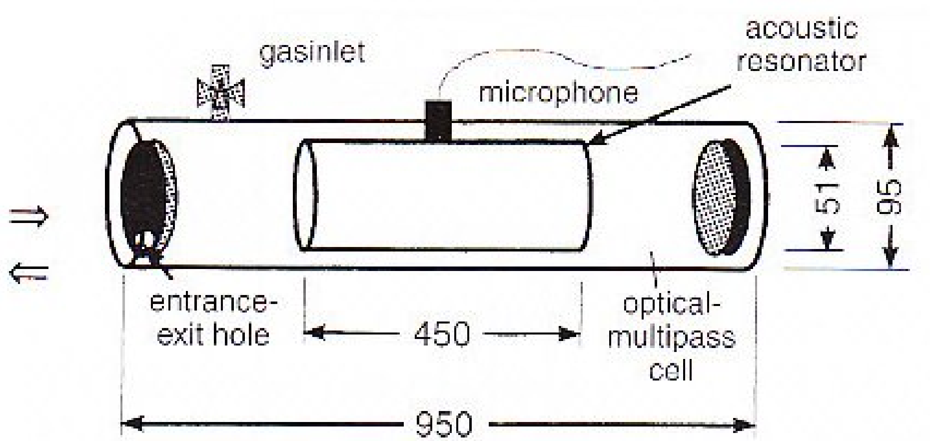
Problem:
- Measuring against a non-zero baseline

Photo-acoustic detection



RT-VT relaxation

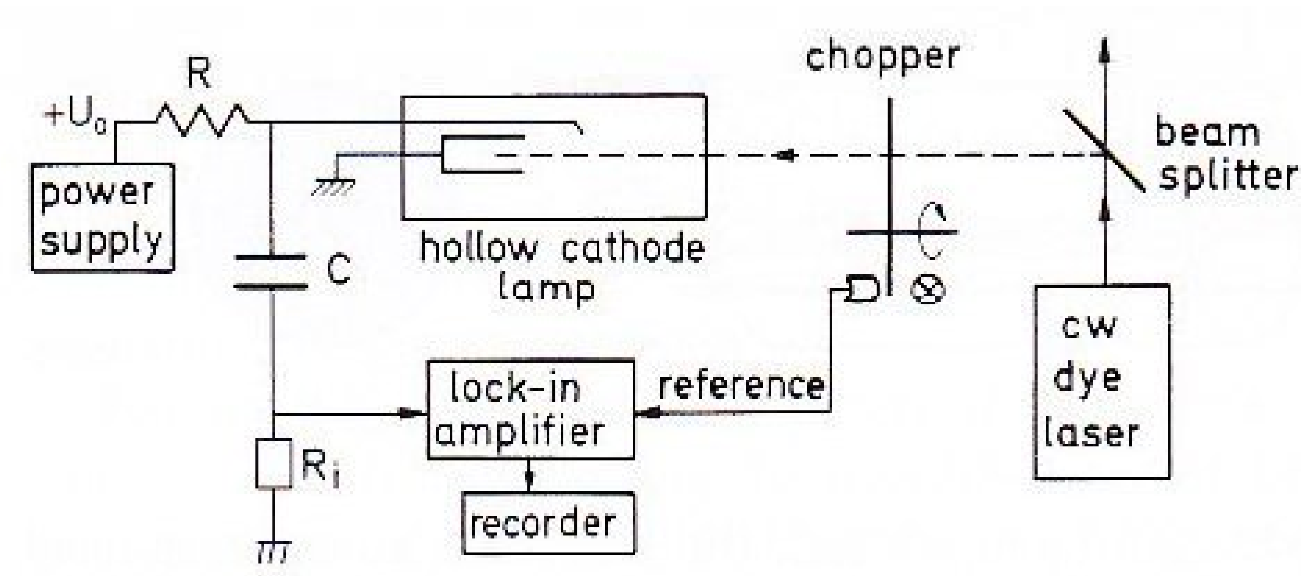
Kinetic energy
= acoustics



Use of acoustic resonator

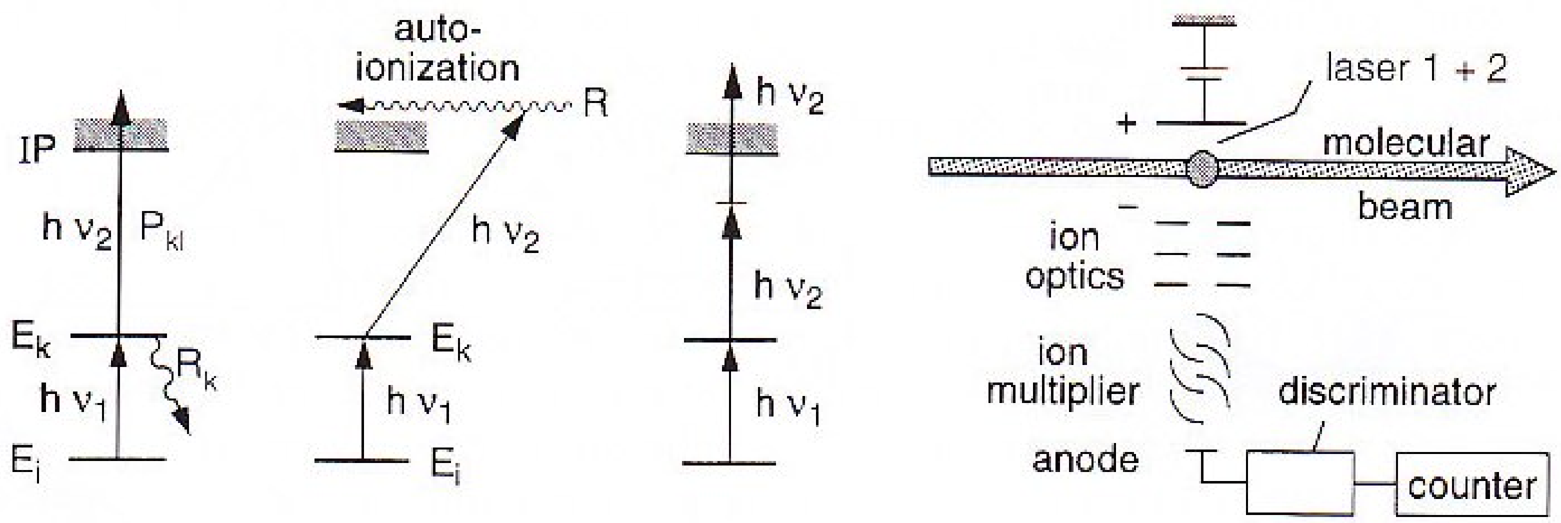
Phase sensitive detection
Acoustic modulation

Optogalvanic detection



Principle: change the resistance over a plasma discharge
by resonantly exciting atoms/molecules

Ionization detection



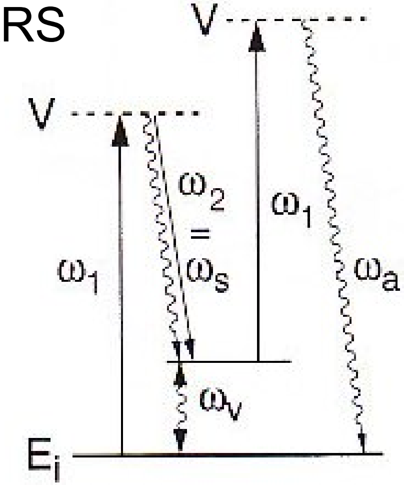
Various production schemes for ions

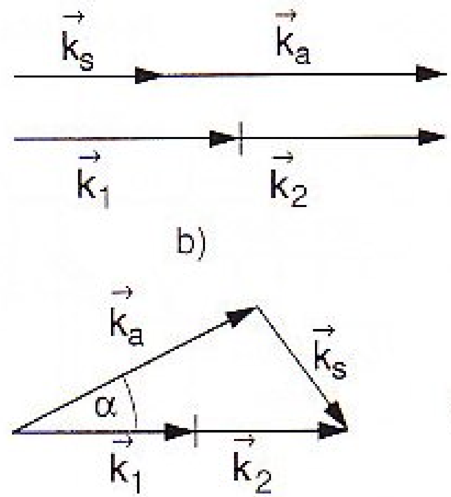
Ions/charged particles sensitive detection

Time-of-flight mass spectrometry

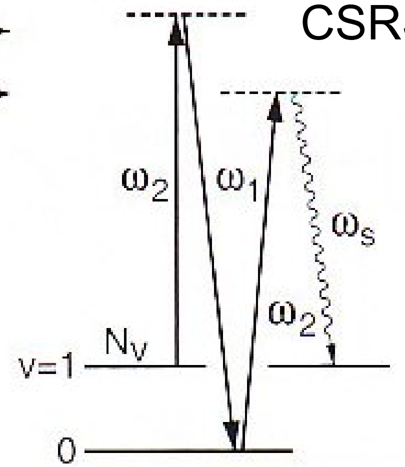
CARS = Coherent Anti-Stokes Raman

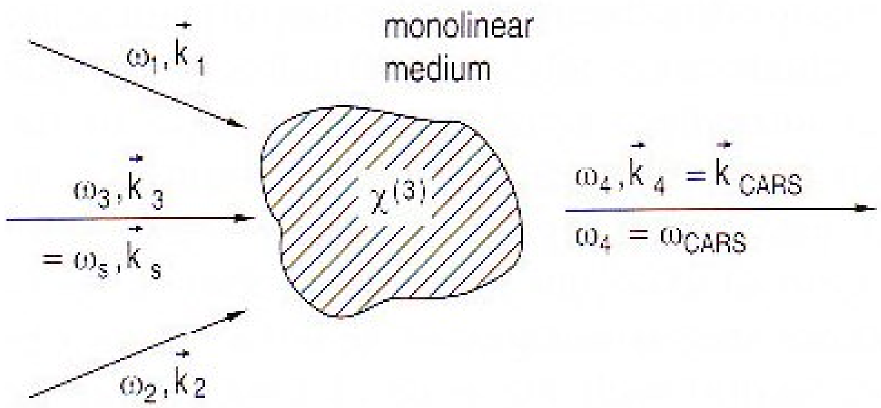
CARS





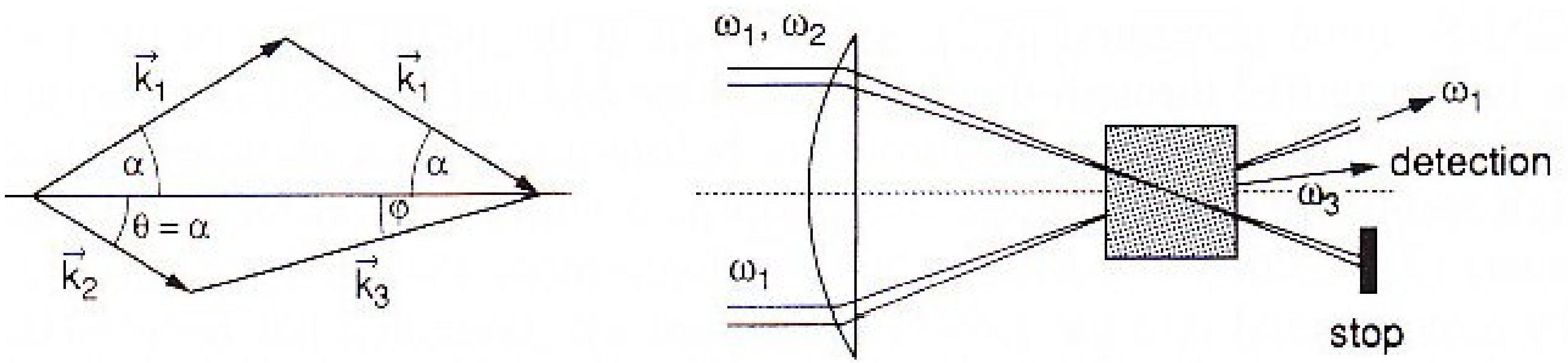
CSRS





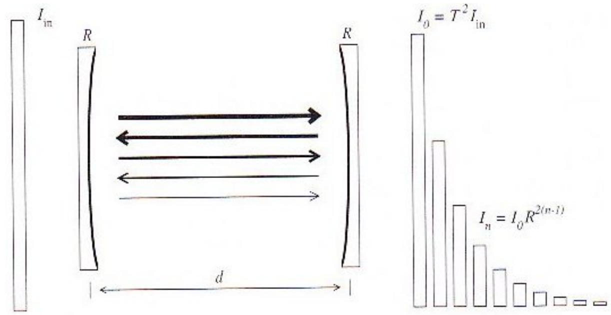
Production of a coherent beam of light

BOXCARS



Coherent beams in 3 dimensions

Cavity Ring-Down spectroscopy



CRD-analysis (assumption: no interference)

First pulse of light leaking out of the cavity: $$I_0 = T^2 I_{in}$$

The n^th pulse with intensity: $$I_n = I_0 R^{2(n-1)} = I_0 e^{2(n-1)\ln R}$$

Will leak out of the cavity later: $$t_n = 2d(n-1)/c$$

Smoothing over individual pulses: $$I(t) = I_0 e^{-\left(\frac{c}{d}\right)|\ln R| t}$$

Hence for empty cavity: decay time: $\tau_0 = 1/\beta_0$ with: $$\beta_0 = \frac{c|\ln R|}{d}$$

Cavity with absorbing species

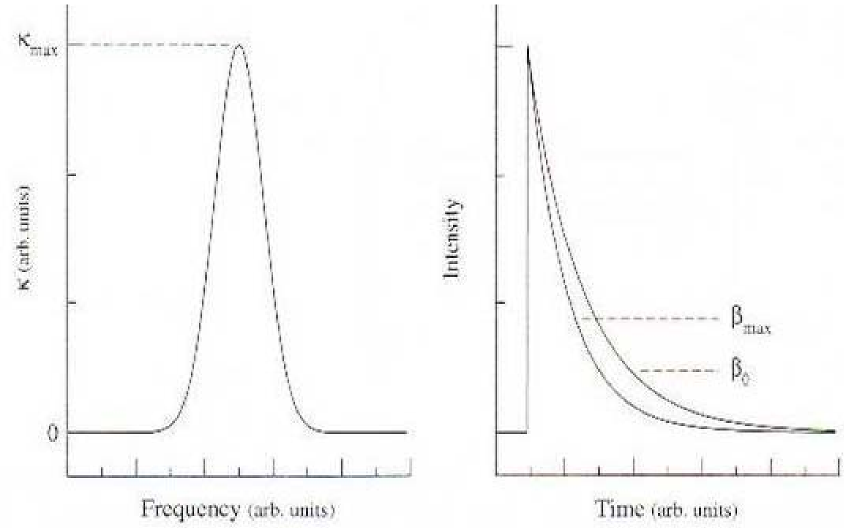
Absorption coefficient : κ_ν

Cavity loss with absorption for n^th pulse: $I_n = I_0 R^{2(n-1)} e^{-2(n-1)\kappa_\nu} = I_0 e^{2(n-1)\ln R - 2(n-1)\kappa_\nu}$

Hence: $I(t) = I_0 e^{-\frac{c}{d}(|\ln R| + \kappa_\nu l)t}$

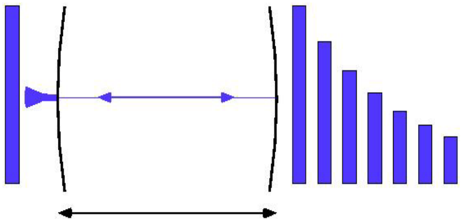
Decay rate for cavity:

$$\beta_\nu = \frac{c}{d}\left(|\ln R| + \kappa_\nu l\right)$$



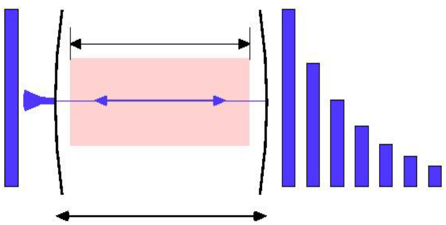
CRD; the paradigm

empty cavity



$$\tau_0 = \frac{L}{c(1-R)}$$

cavity filled with absorbing gas



$$\tau_0 = \frac{L}{c(1-R+kL)}$$

absorption coefficient; cross section

$$k = n\sigma = \frac{1}{c}\left(\frac{1}{\tau_0} - \frac{1}{\tau}\right)$$

What is it good for ?

- Spectroscopy (not extreme precision)
- Sensitive detection (within limits)
- Intensity – quantitative
  (within severe limits/difficulty)

- Gases,
  to Solids, Surfaces, Liquids

- Wavelength range
  (limited – mirror quality)

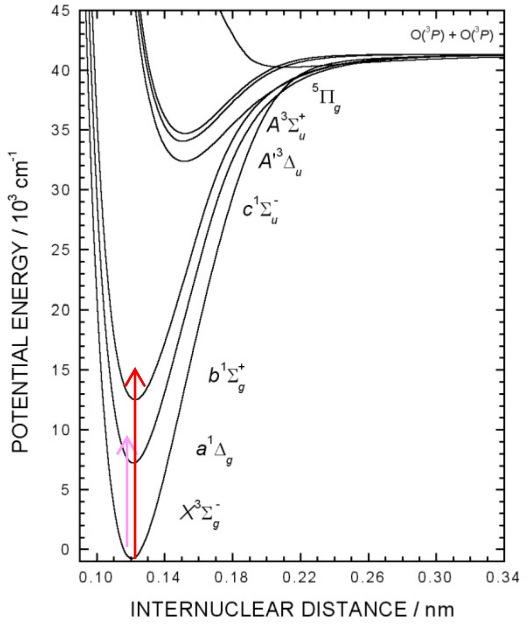
Advantages:
-No dependence on laser fluctuations
-Extremely long effective path lengths
-Easy to make “absolute”

L=1 m
R=99.99%

τ = 30μs
Path=10 km

Weak transitions; in the benchmark CRD molecule: oxygen

lowest electronic states: O(^{3}P) +O(^{3}P)

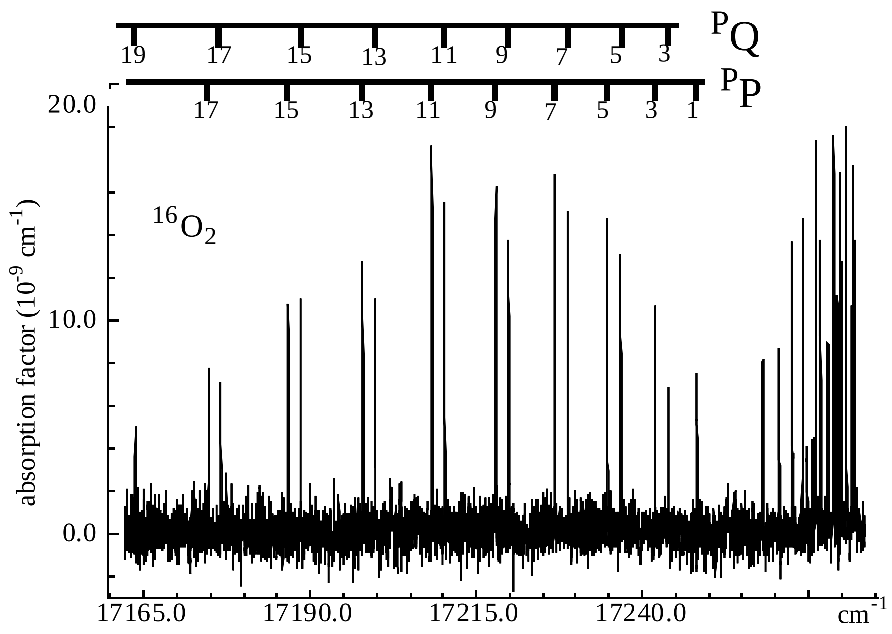


in electric dipole approximation:
all transitions "forbidden"

$b^1\Sigma_g^+ - X^3\Sigma_g^+$ (3,0) or δ-band

$f = 1.3 \times 10^{-14}$

(10^4 times weaker than A-band)



CRD in quantitative spectroscopy: Rayleigh Scattering

J.W. Strutt,
3rd Baron of Rayleigh

1899: full theory based on Electromagnetism

1918: Depolarization effects R.J. Strutt

1923: Depolarization and Cross section: King

1969: Full QM theory - Penney

No distinction of fine structure:
Raman, Brillouin, Rayleigh wing, Cabannes

single molecule cross section

$$\sigma(\nu) = \frac{24\pi^3\nu^4}{N^2}\frac{\left(n_\nu^2-1\right)^2}{\left(n_\nu^2+2\right)^2} F_{k(\nu)}$$

King factor: polarization effect

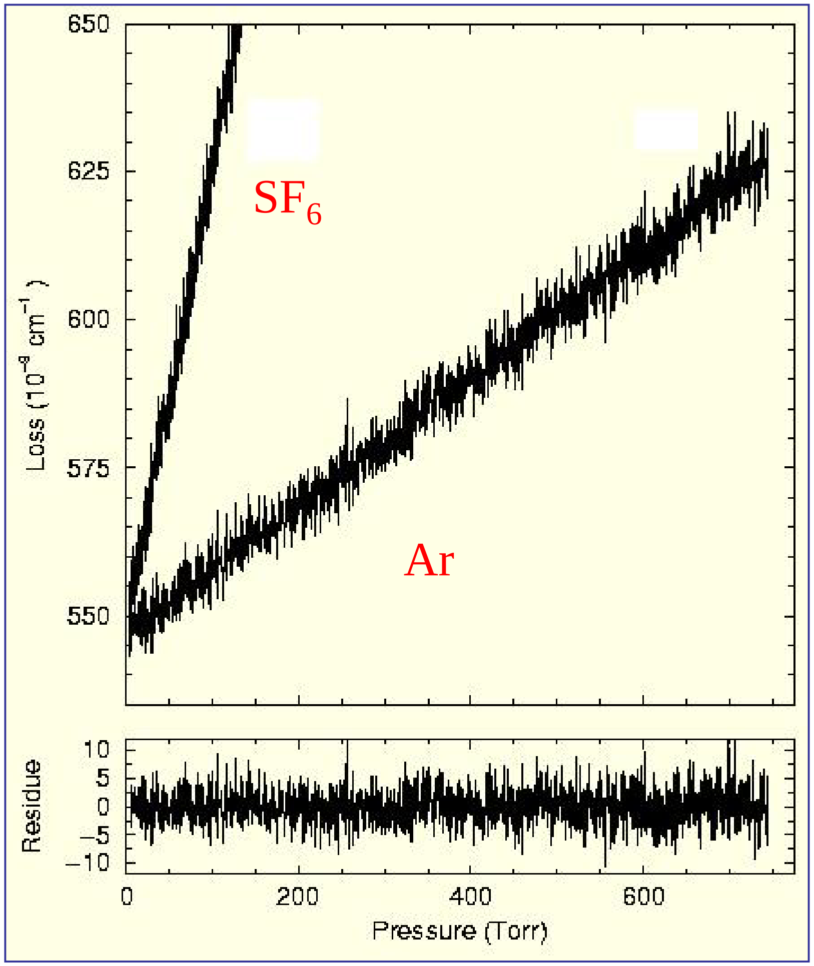
$$F_{k(\nu)} = \frac{6+3\rho_n(\nu)}{6-7\rho_n(\nu)} = \frac{3+6\rho_p(\nu)}{3-4\rho_p(\nu)} = 1+2\left(\frac{\gamma_\nu}{3\overline{\alpha}_\nu}\right)^2 > 1$$

$\rho_{n,}\ \rho_p$ molecular depolarization,

$$\sigma(\nu) = \bar{\sigma}\nu^{4+\varepsilon}$$

→Rayleigh scattering from the Index of refraction !

Rayleigh scattering: direct measurement



Cavity Loss:

$$\beta_\nu/c = |\ln R|/L + \sigma_\nu N$$

$$\sigma_\nu = \underline{\sigma}\nu^{4+\varepsilon}$$

for N_2: $\underline{\sigma}_{th}$ = 23.00 (0.23) 10^{-45}
$\underline{\sigma}_{exp}$ = 22.94 (0.12) 10^{-45}

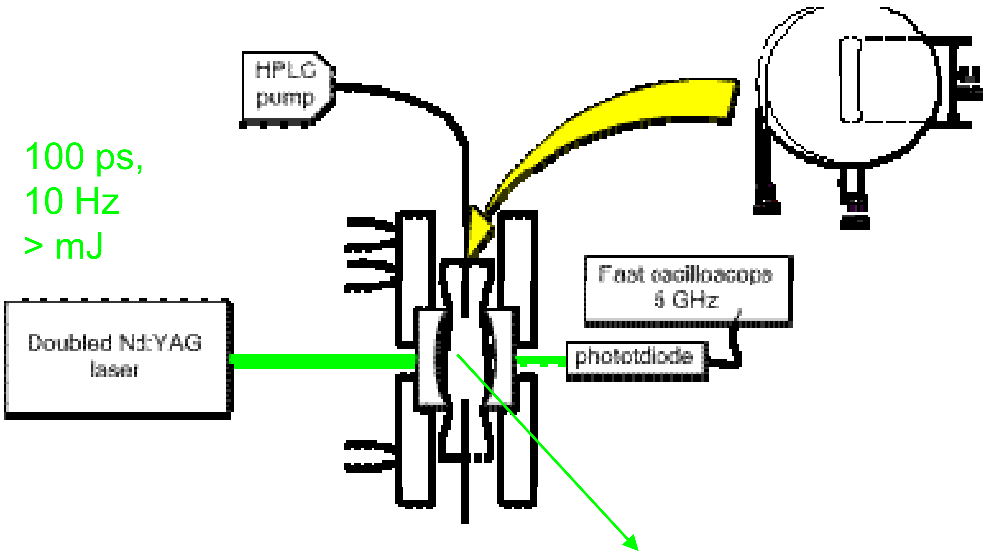
for Ar: $\underline{\sigma}_{th}$ = 20.04 (0.05) 10^{-45}
$\underline{\sigma}_{exp}$ = 19.89 (0.14) 10^{-45}

for SF_6: $\underline{\sigma}_{th}$ = 183 (6) 10^{-45}
$\underline{\sigma}_{exp}$ = 180 (6) 10^{-45}

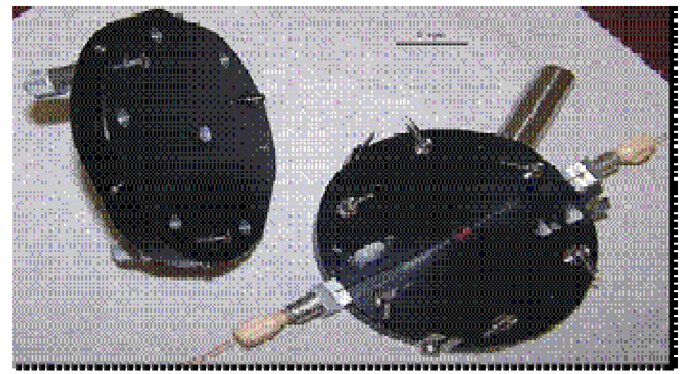
Theory – QM - ab initio: Oddershede/Svendsen
$\sigma(N_2$, 500 nm): 6.2 x 10^{-27} cm^2/molecule (10% off)

method: Naus and Ubachs, Opt. Lett. 25 (2000) 347

To the liquid phase: The combination CRD – HPLC in our approach



effective volume
12 μL

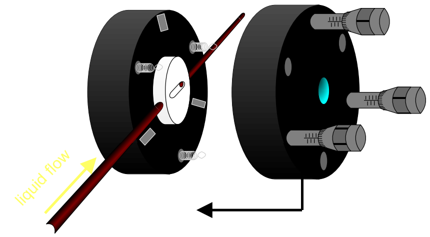


Philosophy: Liquid-Only cell

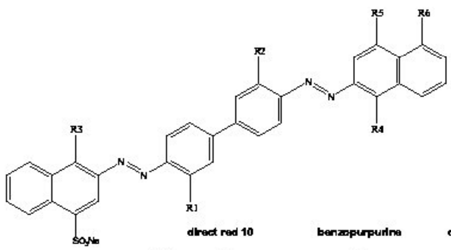
First steps
and goals

Detection, not spectroscopy
Small volumes
Universal wavelengths

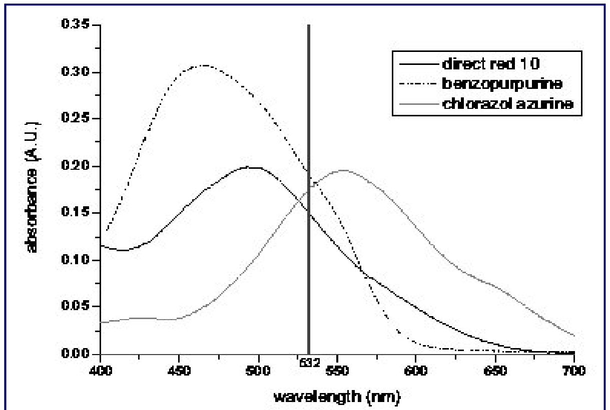
Demonstration of online HPLC detection in Liquid-Only cell

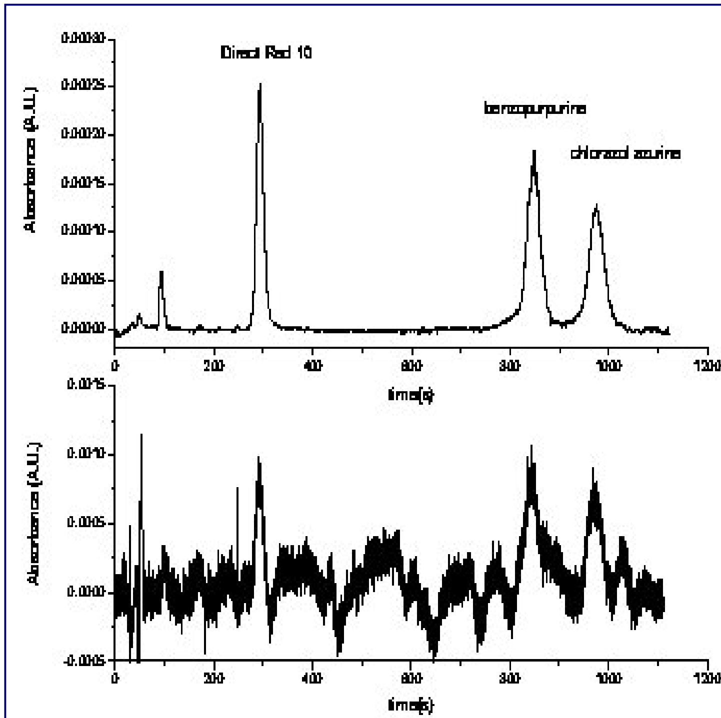


liquid-only cavity
(14 μl)
R = 99.996 %
532 nm, 100 ps,
10 Hz, τ =70 ns



	direct red 10	benzopurpurine	chlorazol azurine
R1 =	H	CH_3	OCH_3
R2 =	H	CH_3	OCH_3
R3 =	NH_2	NH_2	OH
R4 =	OH	NH_2	OH
R5 =	SO_3Na	SO_3Na	H
R6 =	H	H	SO_3Na





CRD chromatogram

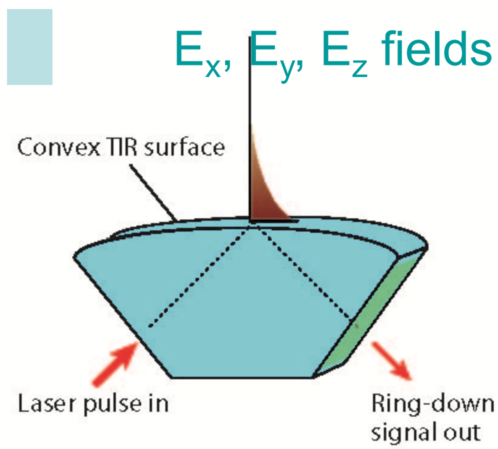
Conventional chromatogram

Detection limit: 15 nM for $\varepsilon = 1 \times 10^4\ M^{-1}cm^{-1}$
Baseline: 2.7×10^{-6} A.U. (1s)

vd Sneppen et al, Anal. Chim. Acta 2006

Evanescent wave CRDS

EW-CRDS principle



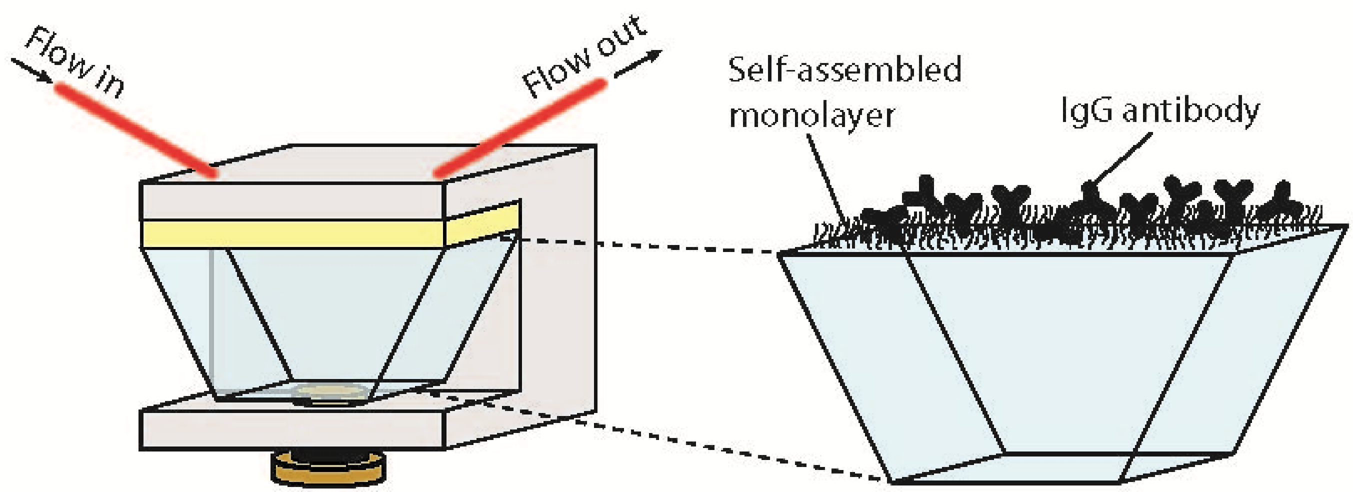
Penetration depth, vs.
Effective depth

$$d_e = \frac{n_{21}\lambda(2\sin^2\theta - n_{21}^2)\cos\theta}{n_1\pi(1-n_{21}^2)[(1+n_{21}^2)\sin^2\theta - n_{21}^2]\sqrt{\sin^2\theta - n_{21}^2}}$$

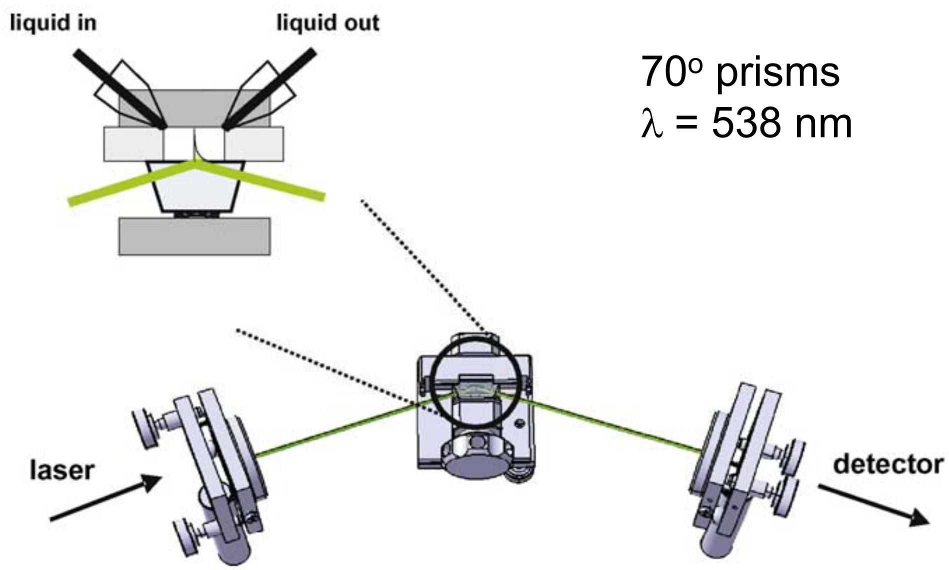
η=~8 (high sensitivity for top layer)

Target

Biosensor

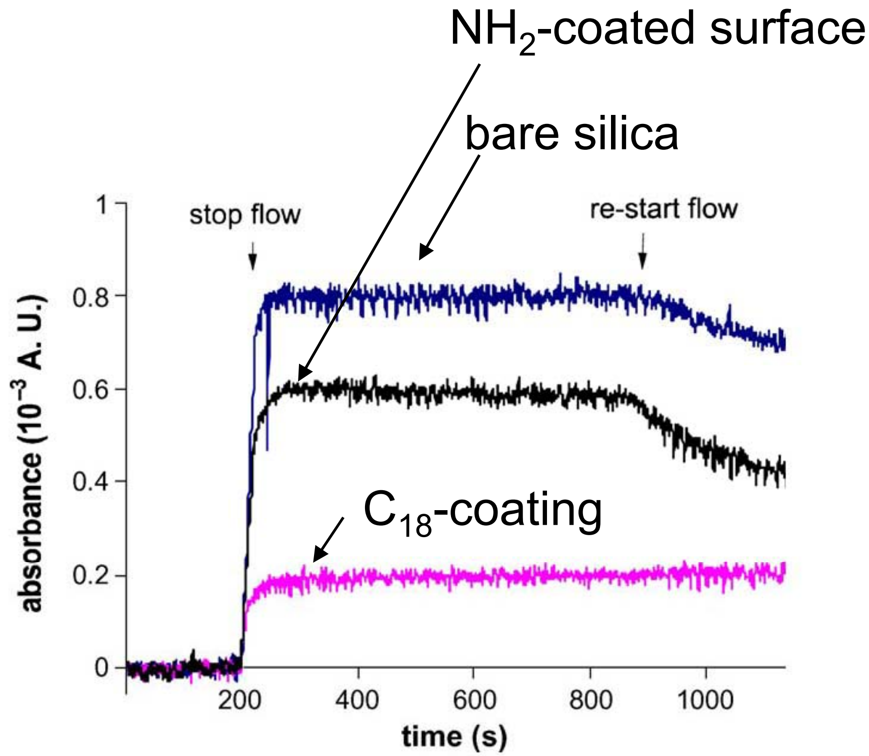


Toward a biosensor (cytochrome *c* as test molecule)



70° prisms
λ = 538 nm

Absorption signal of cyt c
on various surfaces

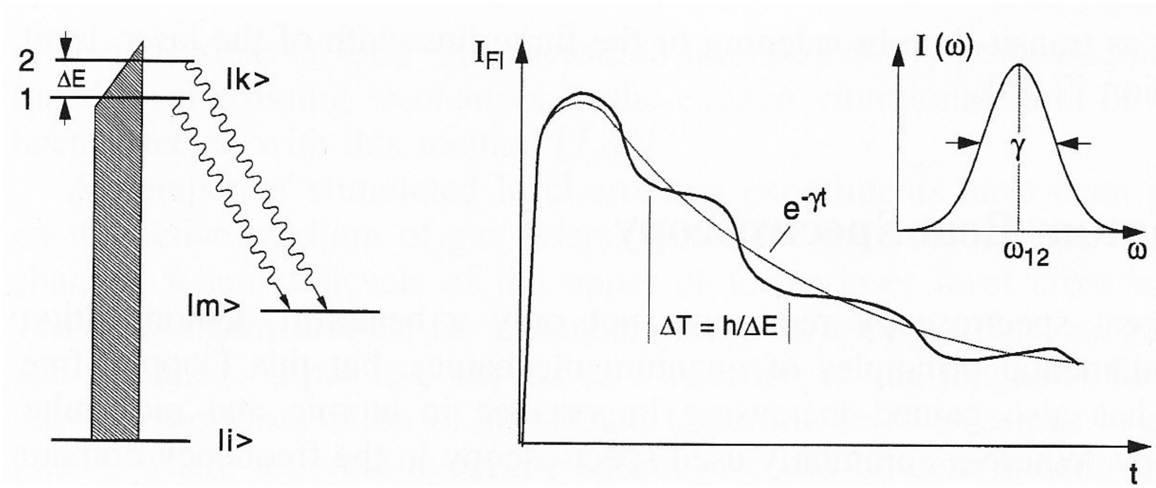


Result:
C18 surface yields irreversable binding
NH2 surface (+ charged) releaves cyt c

Quantum beat spectroscopy

Excitation of a coherent superposition of quantum states

$$\psi(t=0)=\sum_k c_k\psi_k(0)=c_1\psi_1(0)+c_2\psi_2(0)$$



Limitation
→Natural lifetime
(not laser pulse !!)

Temporal evolution of the superposition

$$\psi(t)=\sum_k c_k\psi_k(0)e^{-(i\omega_k+\gamma_k/2)t}$$

Total fluorescence emitted

$$I(t)\propto\left|\langle\psi(t)|\varepsilon\cdot\mu|\psi_m\rangle\right|^2$$

So $I(t)\propto e^{-\gamma t}\left(A+B\cos\omega_{21}t\right)$

with $A=c_1^2\left|\langle\psi_1|\varepsilon\cdot\mu|\psi_m\rangle\right|^2+c_2^2\left|\langle\psi_2|\varepsilon\cdot\mu|\psi_m\rangle\right|^2$

$B=2c_1c_2\left|\langle\psi_1|\varepsilon\cdot\mu|\psi_m\rangle\right|\cdot\left|\langle\psi_2|\varepsilon\cdot\mu|\psi_m\rangle\right|$

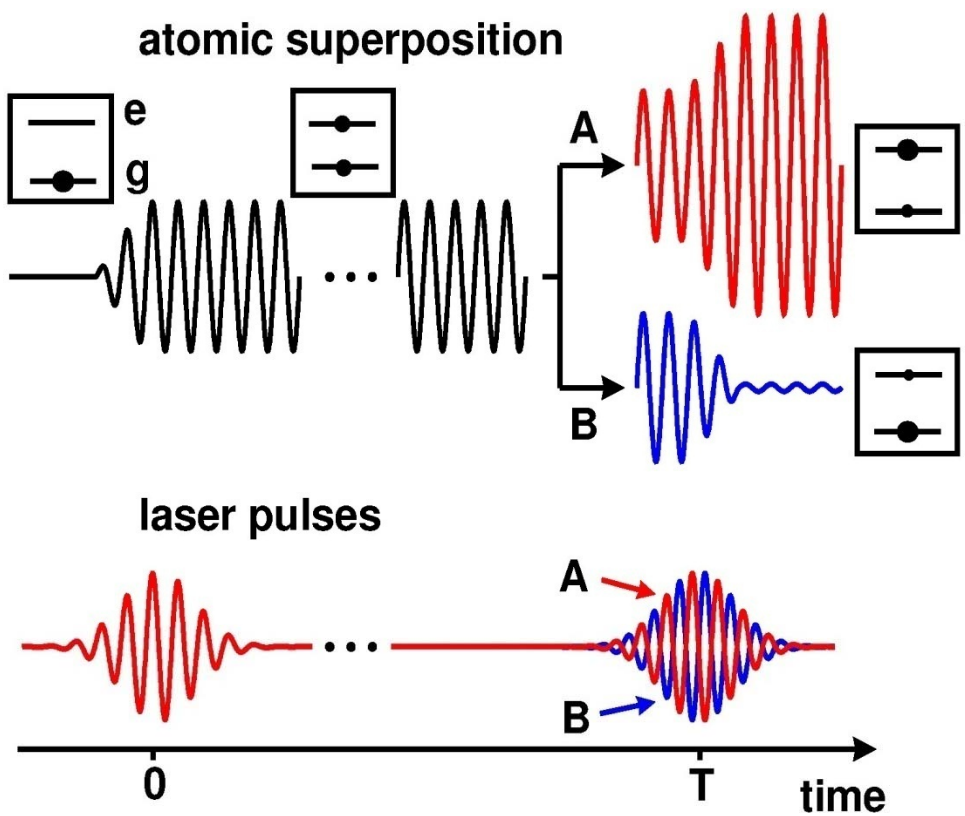
Direct frequency comb spectroscopy

- Excitation with phase controlled ultra-short pulses.

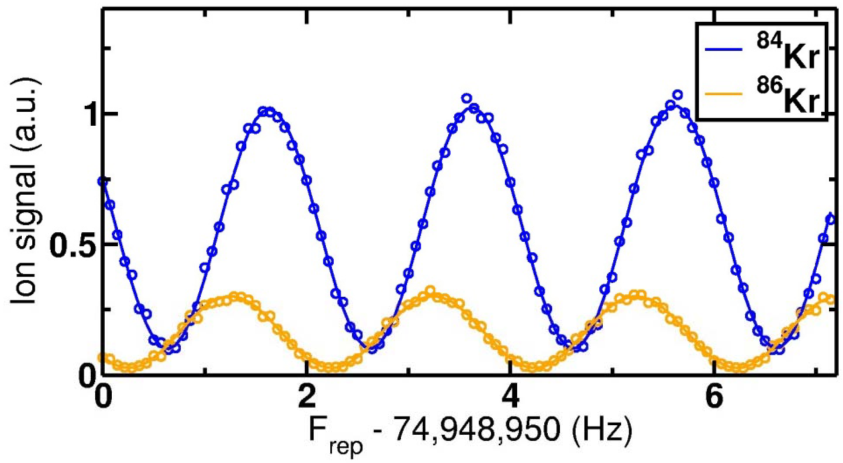
- Evolution atomic phase:

$$\exp\left[-i\frac{(E_e - E_g)}{\hbar}\quad t\right]$$

- Interference between pulse contributions; Ramsey fringes in time



Direct frequency comb spectroscopy



Probe the oscillation of the wave function

Find the right “mode”