Cavity Ring Down Spectroscopy from gases to liquids and to shorter wavelengths

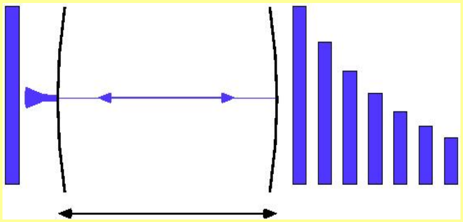
Wim Ubachs
Maarten Sneep, Dmitry Ityaksov, Hans Naus, Sandro Hannemann,
Harold Linnartz, Wim van der Zande,
Lineke van der Sneppen, Freek Ariese, Cees Gooijer

Laser Centre Vrije Universiteit, Amsterdam

Cavity Ring Down User Meeting 2006, Cork, Ireland
19 Sept. 2006

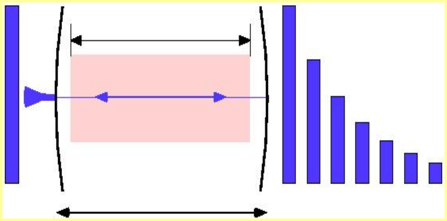
CRD; the paradigm

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)

- cf. LIF, REMPI, CARS, DFWM - CRD

- Gases,
  to Solids, Surfaces, Liquids

- Wavelength range
  (limited – mirror quality)

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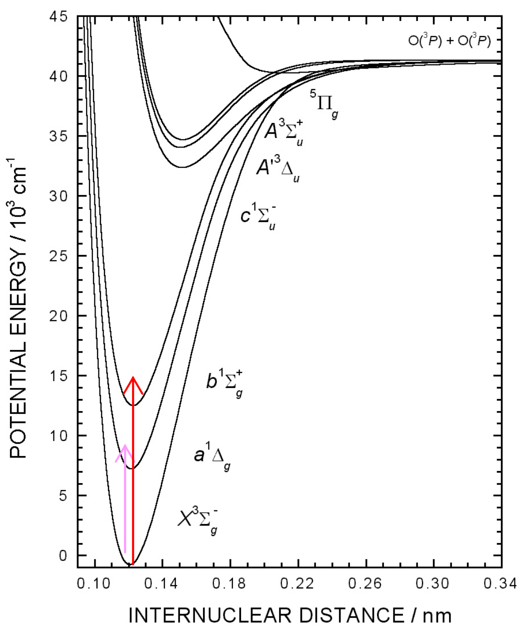
Weak transitions; in the benchmark CRD molecule: oxygen

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

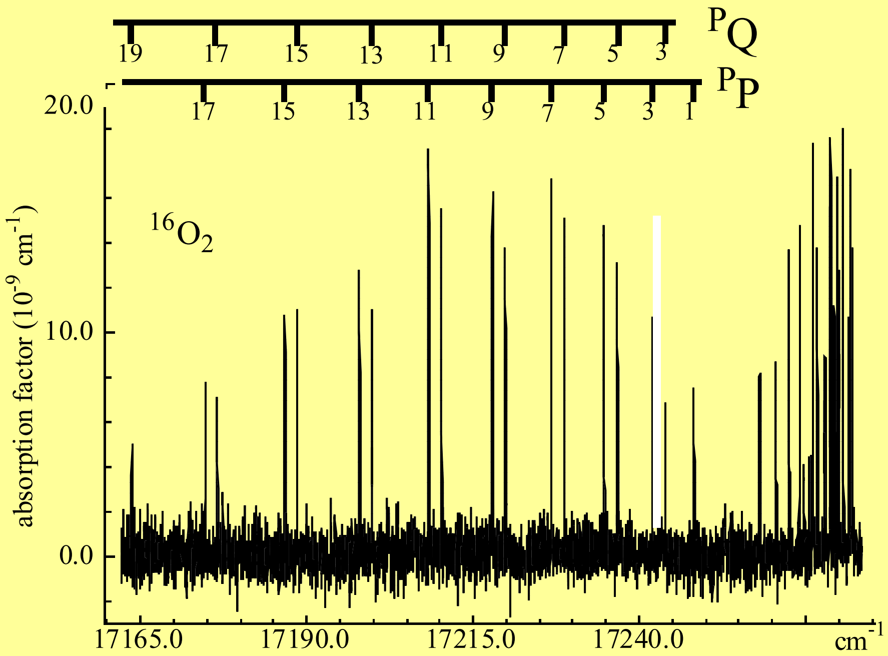


in electric dipole approximation:
all transitions “forbidden”

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

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

(10^4 times weaker than A-band)



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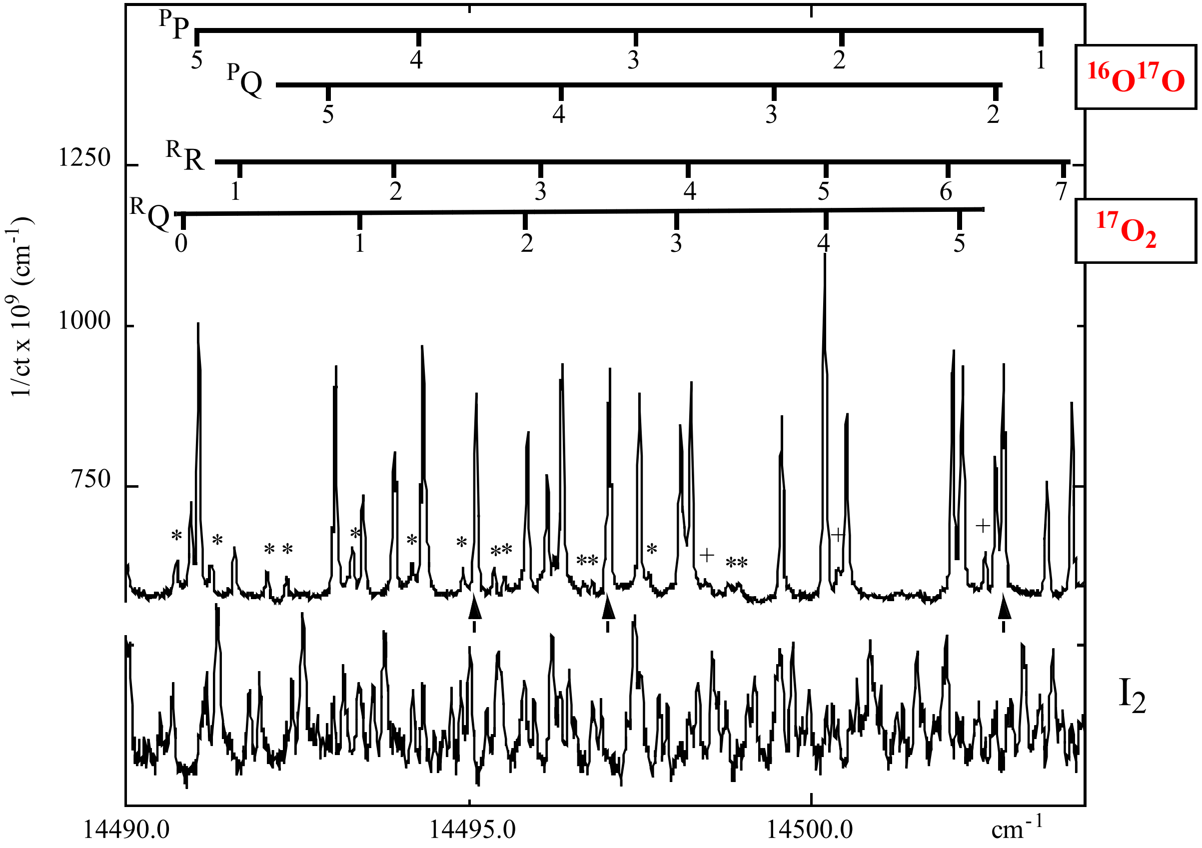
CRD: measurements on small samples

oxygen B-band, ^{17}O enriched



measurements on expensive isotopes

100 mbar x 25 cm^3
^{17}O (50%) enriched gas

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CRD for quantitative spectroscopy ?
The linewidth problem !

Jongma et al., Rev. Sci. Instr. (1995)
Zalicki & Zare, JCP (1995)
Hodges et al, (1996)

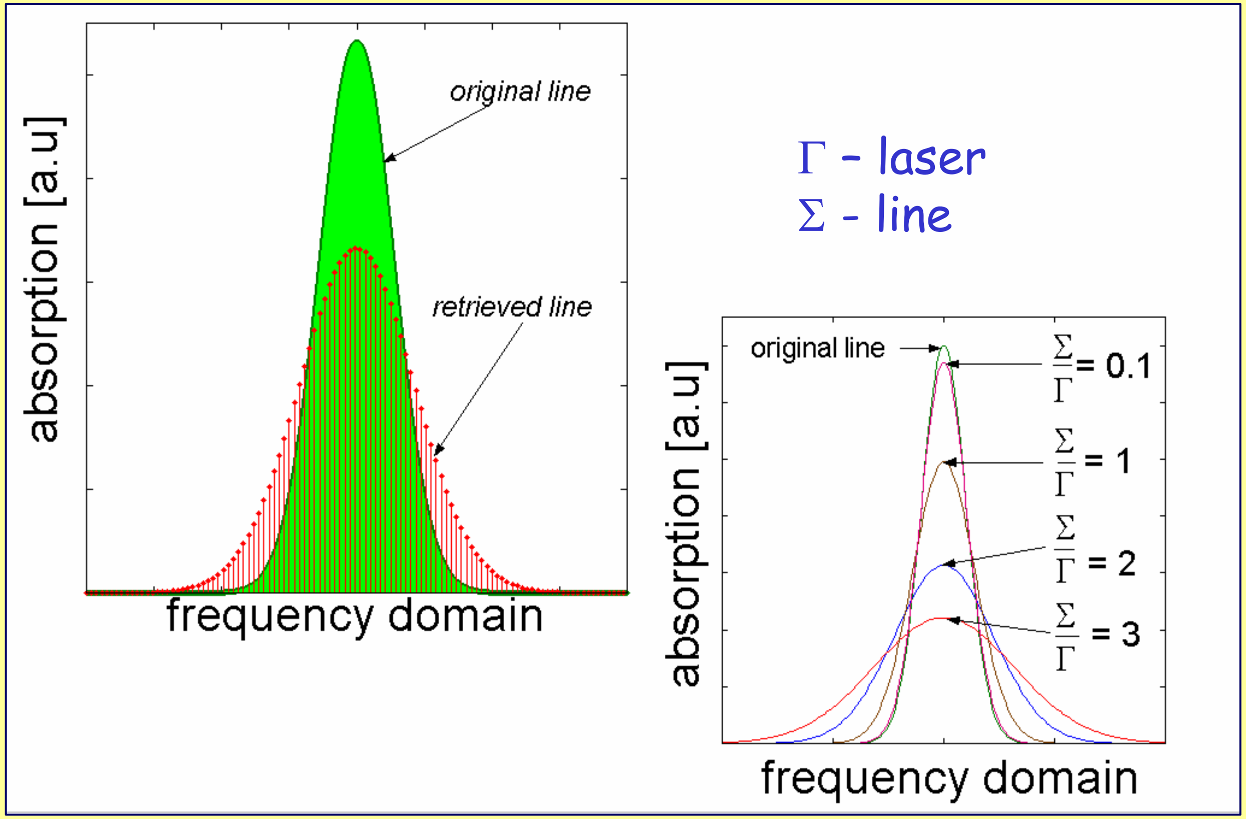
Single-Exponential:

$$I(t) = I_0 \exp(-\beta t) + I_{off}$$

$$\Sigma << \Gamma, \beta << 1$$

Multi-Exponential:

$$I(t) = I_0 \int_{\nu} S(\Sigma; \nu_s - \nu) \exp(-\beta(\Gamma; \nu_\alpha - \nu) t) d\nu + \hat{I}_{off}$$



Direct retrieval of a multi-exponential decay is mathematically impossible

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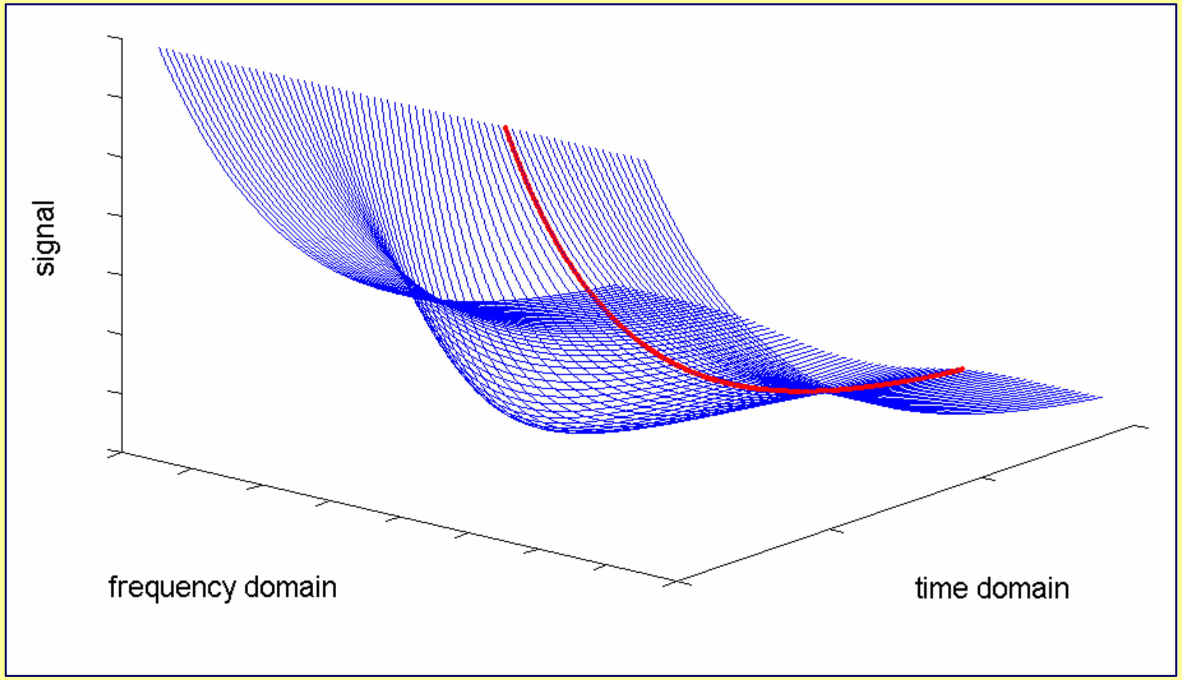
Multiple Transient Optimisation

$$\min_{\Gamma,S_\nu} \sum_i \sum_t \frac{1}{\varpi_t^2}\left[\tilde{I}_t^i - I_0^i \int_\nu S\left(\Sigma;\nu_s^i - \nu\right)\exp\left\{-\beta\left(\Gamma,\nu_\alpha - \nu,\bar{S}_\nu;R_i,n\right)t\right\}d\nu\right]^2$$

Mono transient, S.E., pre-fitting of I_0^i



Struggling by:

Hans Naus
Maarten Sneep
Michal Branicki
Rüdiger Lang
Joop Mes
Ivo van Stokkum
Ilse Aben
Wim Ubachs
Wim van der Zande

Store all decay transients in computer and perform off-line analysis on entire data set

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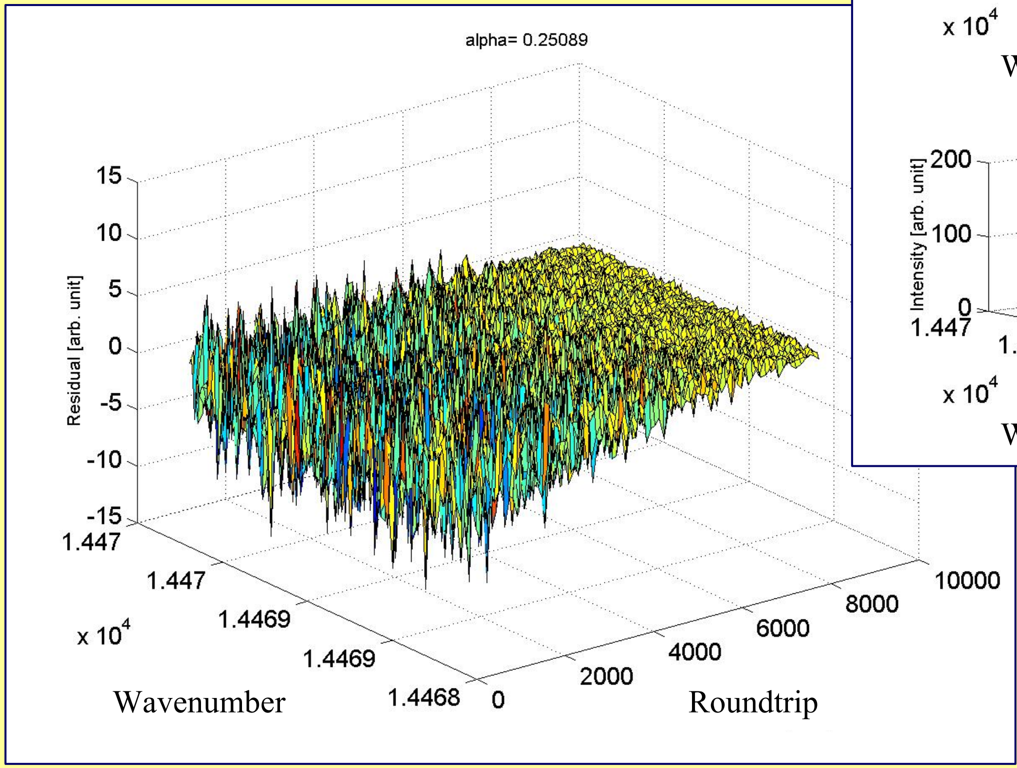
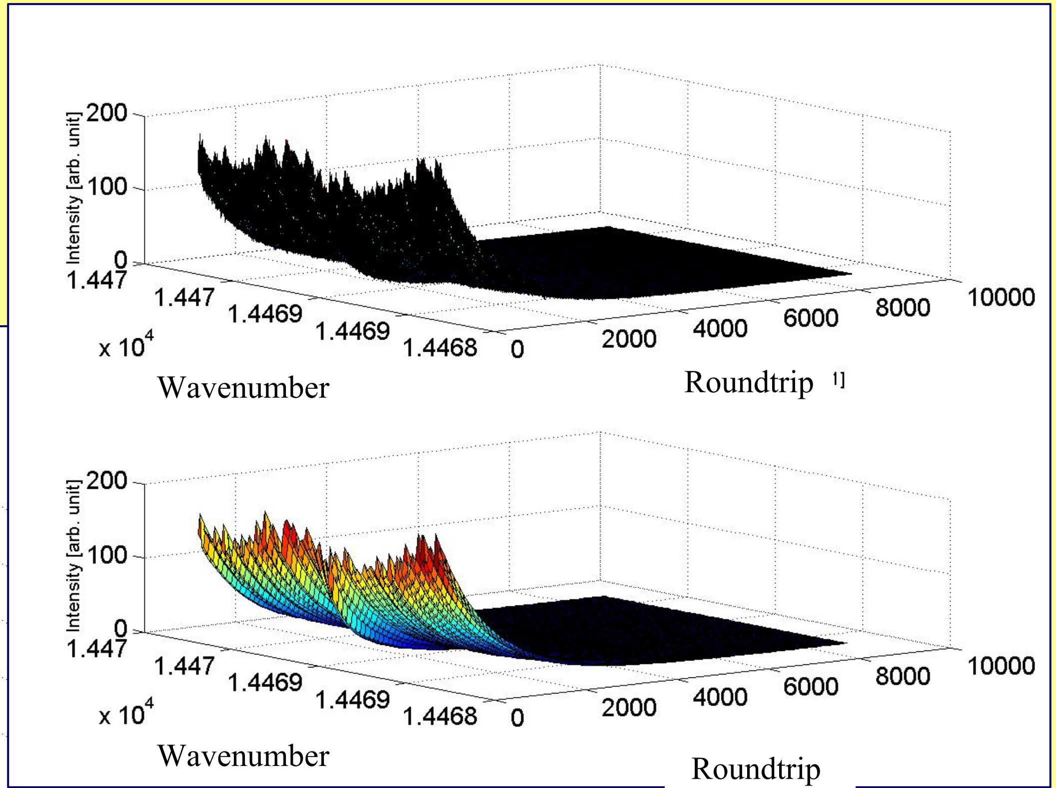
Self-Consistency check of Model using realistic input from B-band (O_2): PP15

Fit to Measurement:

Σ=0.03





Result:

LINESTRENGTH:

Input: 3.139e-025

Fit: 3.3298e-025

Rel diff. [%]: -7.9

Further pursuit: Hans Naus & Wim van der Zande → P10

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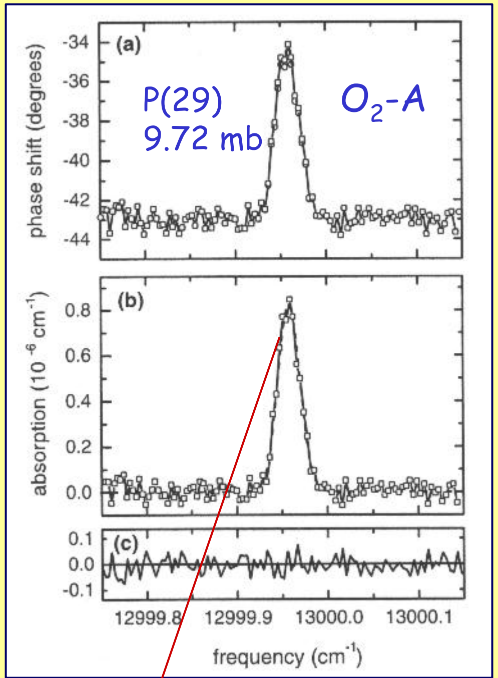
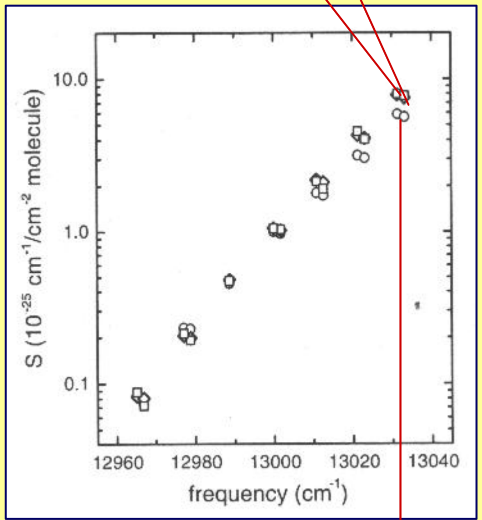
Problems with spontaneous emission





correction
HITRAN

correction for ASE

direct
measurement

CW diode laser –
narrow bandwidth
(phase-shift CRD)

Accuracy:
"agreement with HITRAN
< 4% on average"

Cf. also work by
Hodges, van Zee, Looney
Quantitative !

v. Helden, Schram, Engeln, CPL 400 (2004) 320

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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

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

ρ_n, ρ_p molecular depolarization,

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

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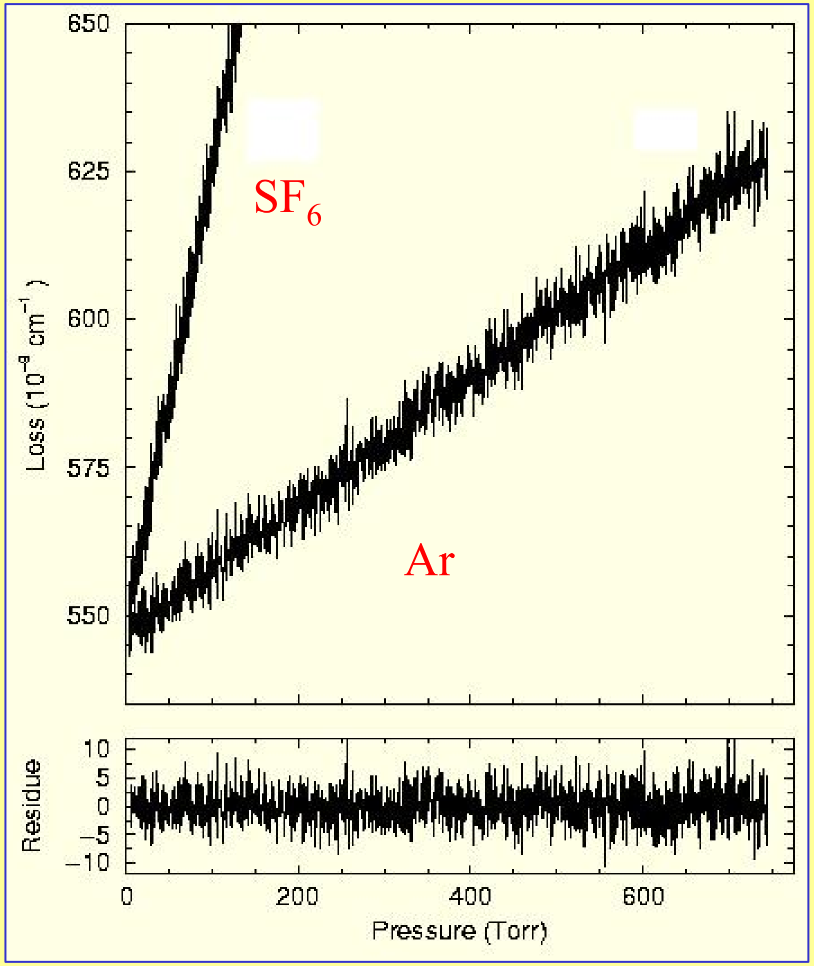
Rayleigh scattering: pressure ramp method



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

σ(N_2, 500 nm): 6.2 x 10^{-27} cm^2/molecule (10% off)

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

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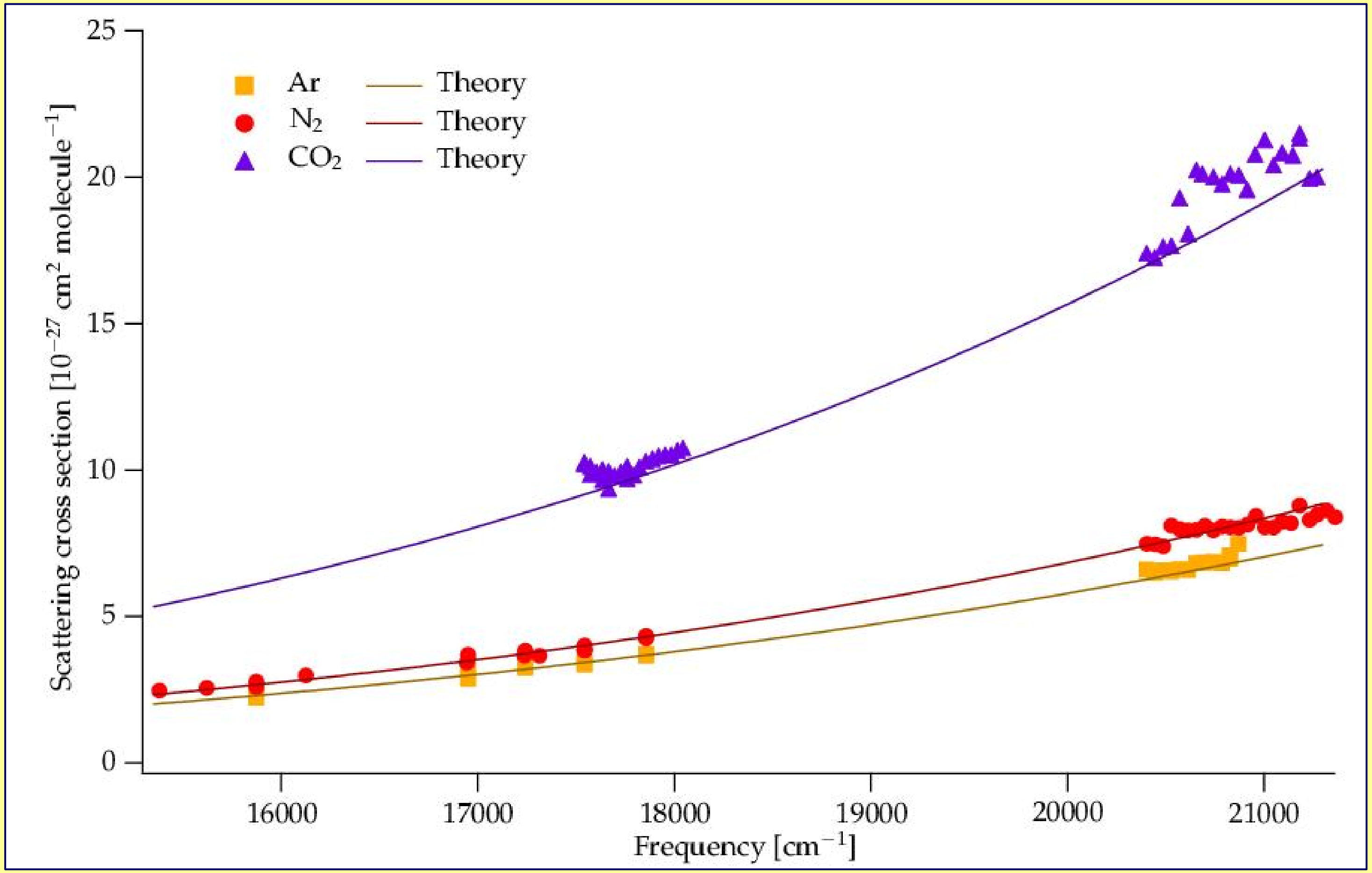
Extended measurements on Rayleigh cross sections



Ar
Within 1%
→ confidence

CO_2:
overestimated
King factor ?

Sneep, Ubachs, JQSRT 92 (2005) 293

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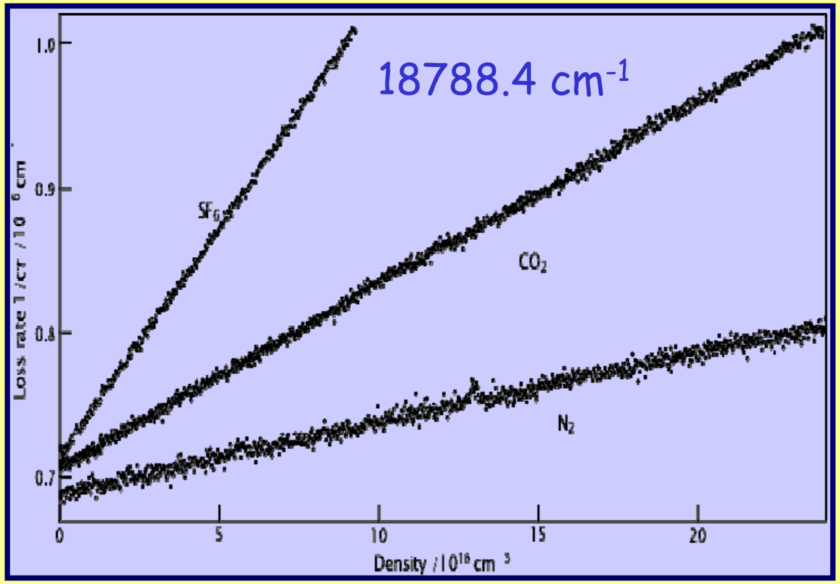
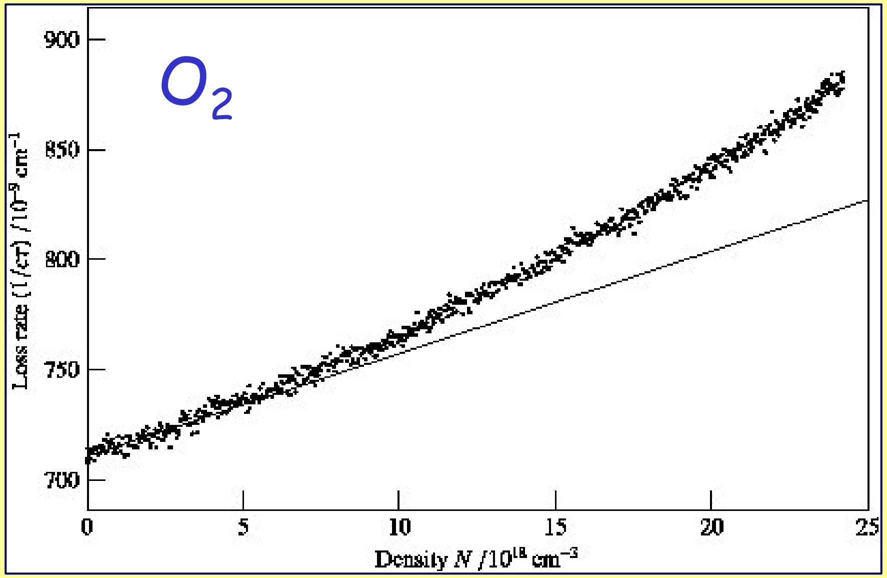
Rayleigh scattering at 532 nm : LIDAR wavelength





Rayleigh cross sections:
Ar, N_2 agreement < 1 %
CO_2 < 4 %
NO_2 largest offset; $F_k = 1.225$?

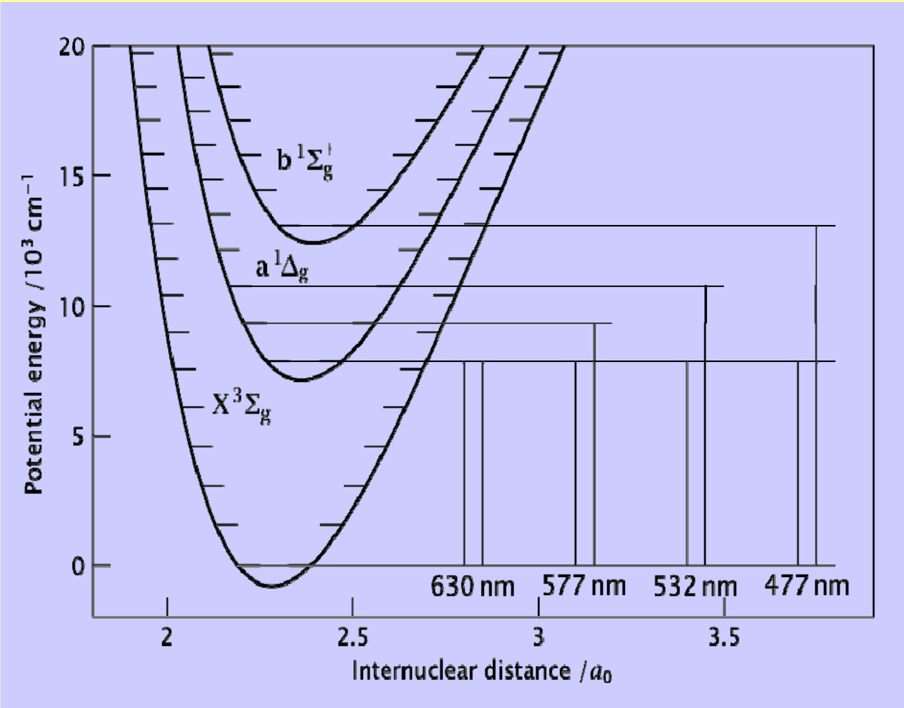
Quadratic pressure dependence in O_2

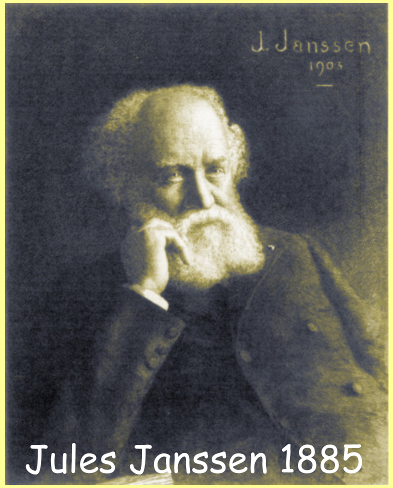
Sneep, Ubachs, JQSRT 92 (2005) 293

Collision-induced absorption phenomena in O_2

"two molecules absorb one photon"

$$[X^3\Sigma_g^-, v=0]_2 + h\nu \rightarrow a^1\Delta_g(v_1) + b^1\Sigma_g^+(v_2)$$





many measurements thereafter

Ellis-Kneser, Z. Phys. 1933
liquid oxygen

Greenblatt et al 1990
high pressure gaseous oxygen

Pfeilsticker et al 2001
balloon in atmosphere

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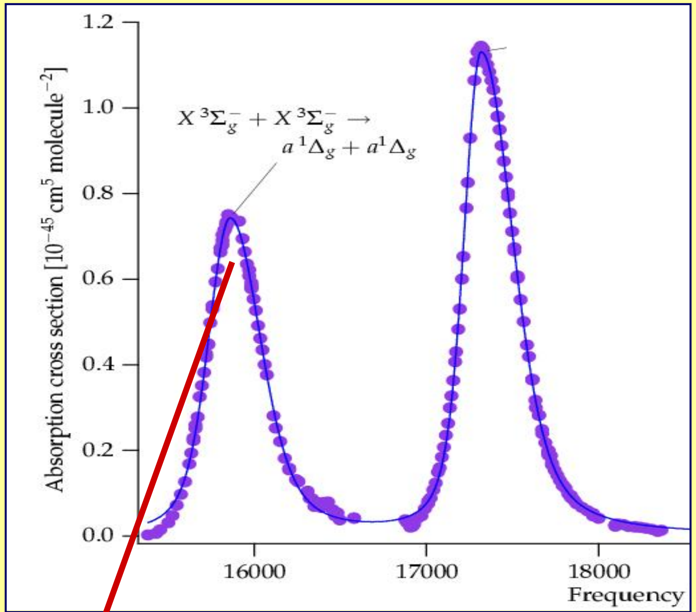
CIA and complexes

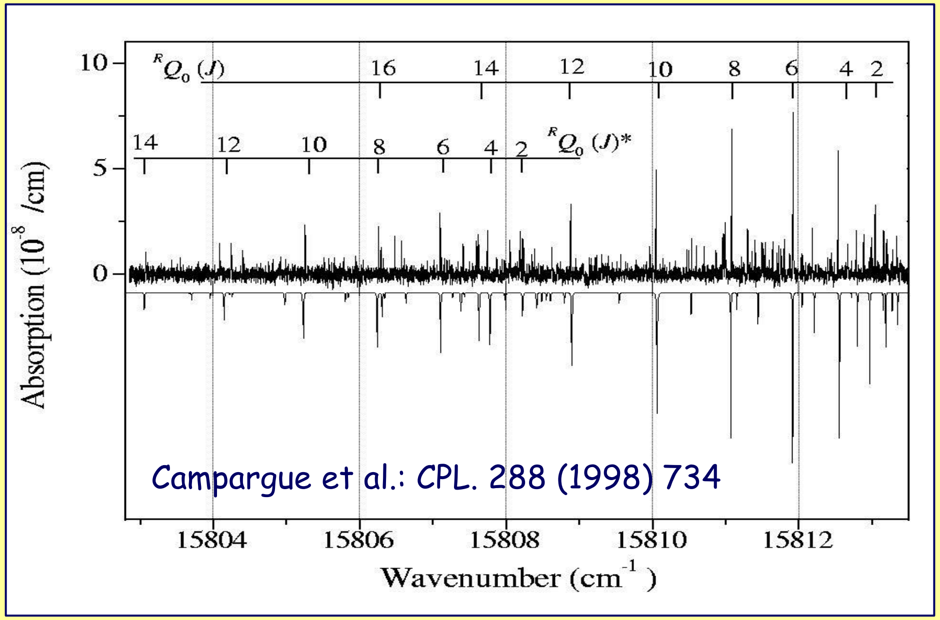
room temperature



Naus & Ubachs: Appl. Opt. 38 (1999) 3423
Sneep & Ubachs: JQSRT 78 (2003) 171

quadratic component

low temperature in jet



Campargue et al.: CPL. 288 (1998) 734

→Andrei Vigasin: thermodynamics and CIA

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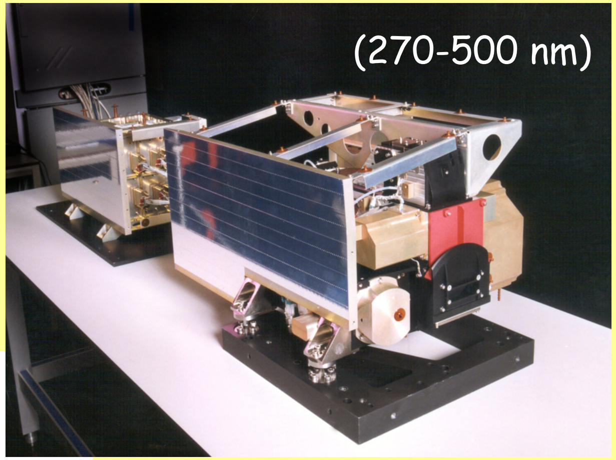
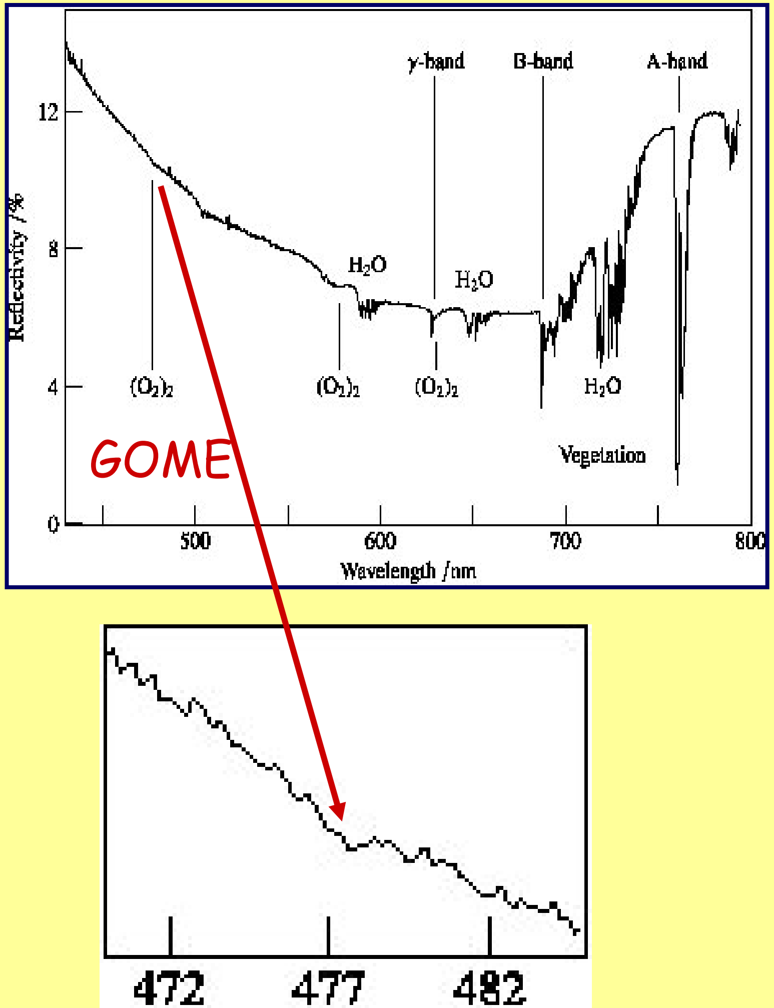
Rationale for study of 477 nm CIA-feature





1. Goal: determine global O_3 trends
2. Ozone column from DOAS 331-336 nm
3. Correction for air-mass factor; dependent on cloud and top heights
4. Top heights from O_4-DOAS at 460-490 nm
5. Accuracy depends on $\sigma(T)$ of O_4 feature

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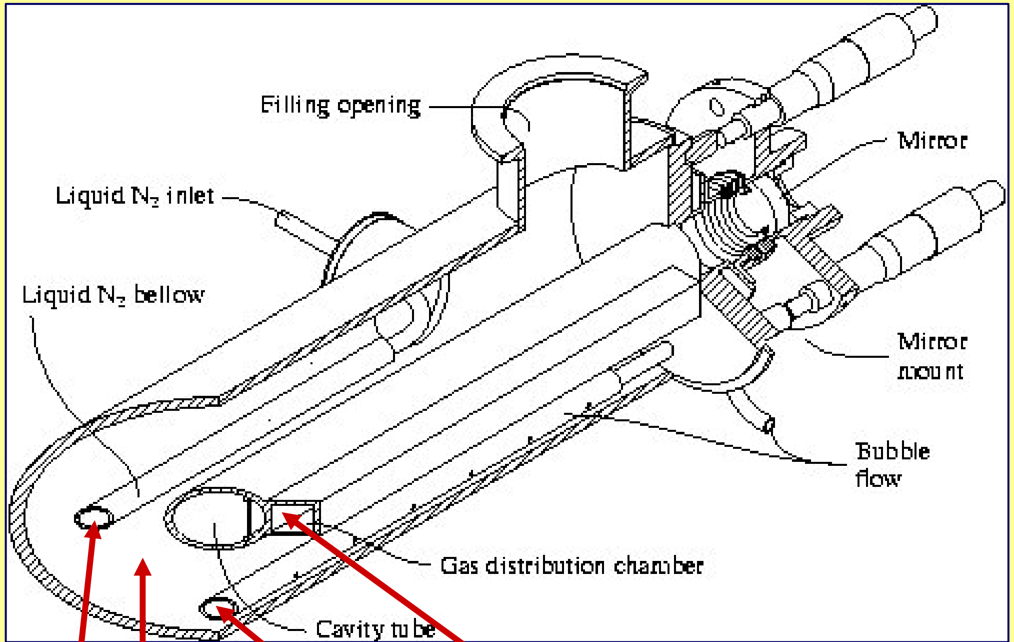
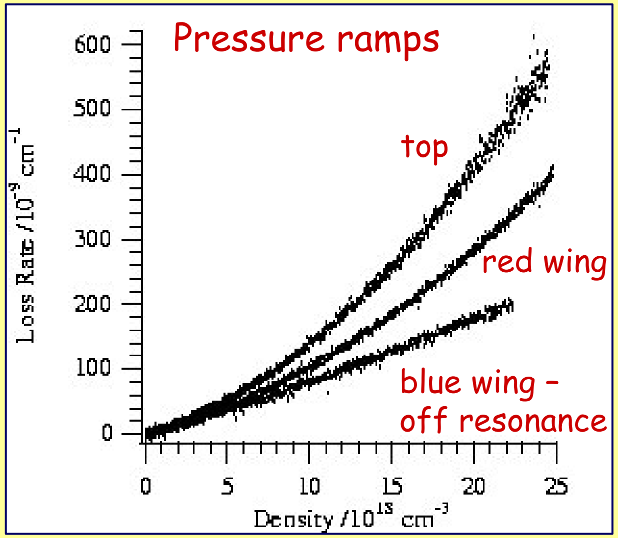
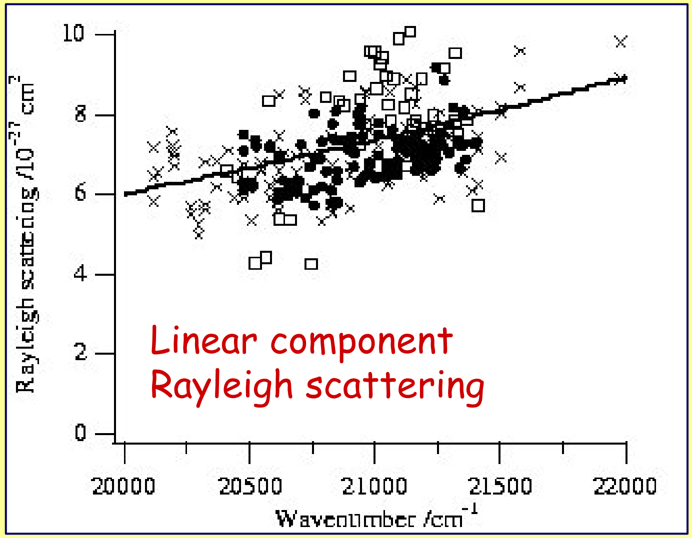
Low-temperature cell for pressure ramp method







gas inlet through pores for homogeneous distribution

Liquid-solid mixture determining T

bubbling gas through slurry for homogeneous T

cooling of slurry by LN$_2$ flow

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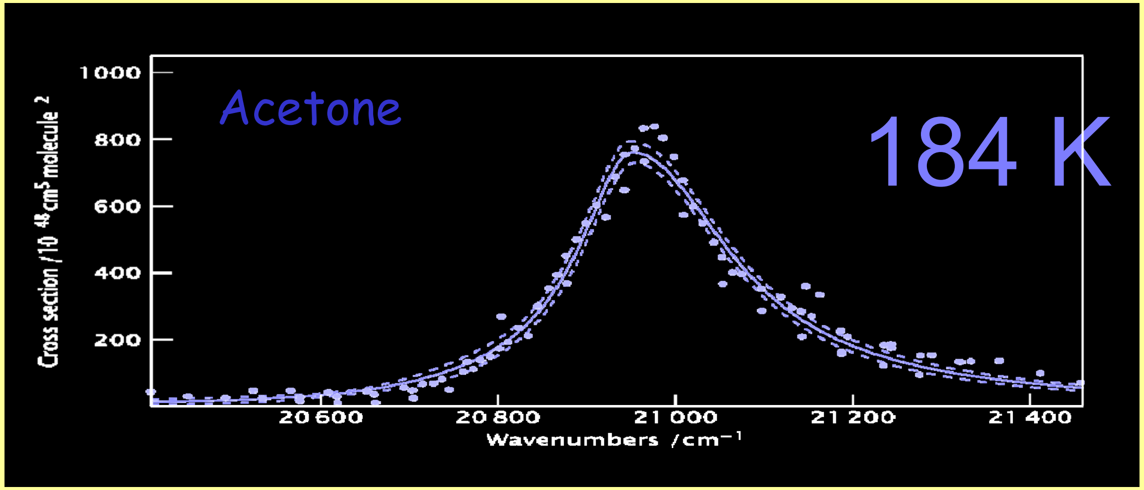
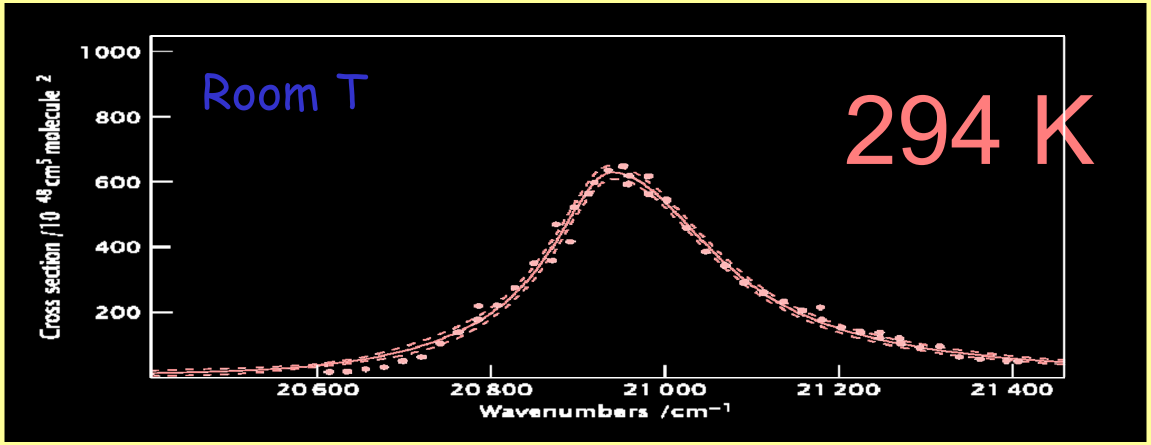


Anti-freeze

230 K



Fitting to model functions

$$F(\nu) = (1-b)\frac{a}{1+\left[4(\Delta\nu)^2/\Gamma^2\xi^2\right]} + ba\exp\left[-4\ln 2\left(\frac{\Delta\nu}{\Gamma\xi}\right)^2\right]$$

with ξ skewing function

↓

Derive numerical representation of the data:

Integral
Peak
Width

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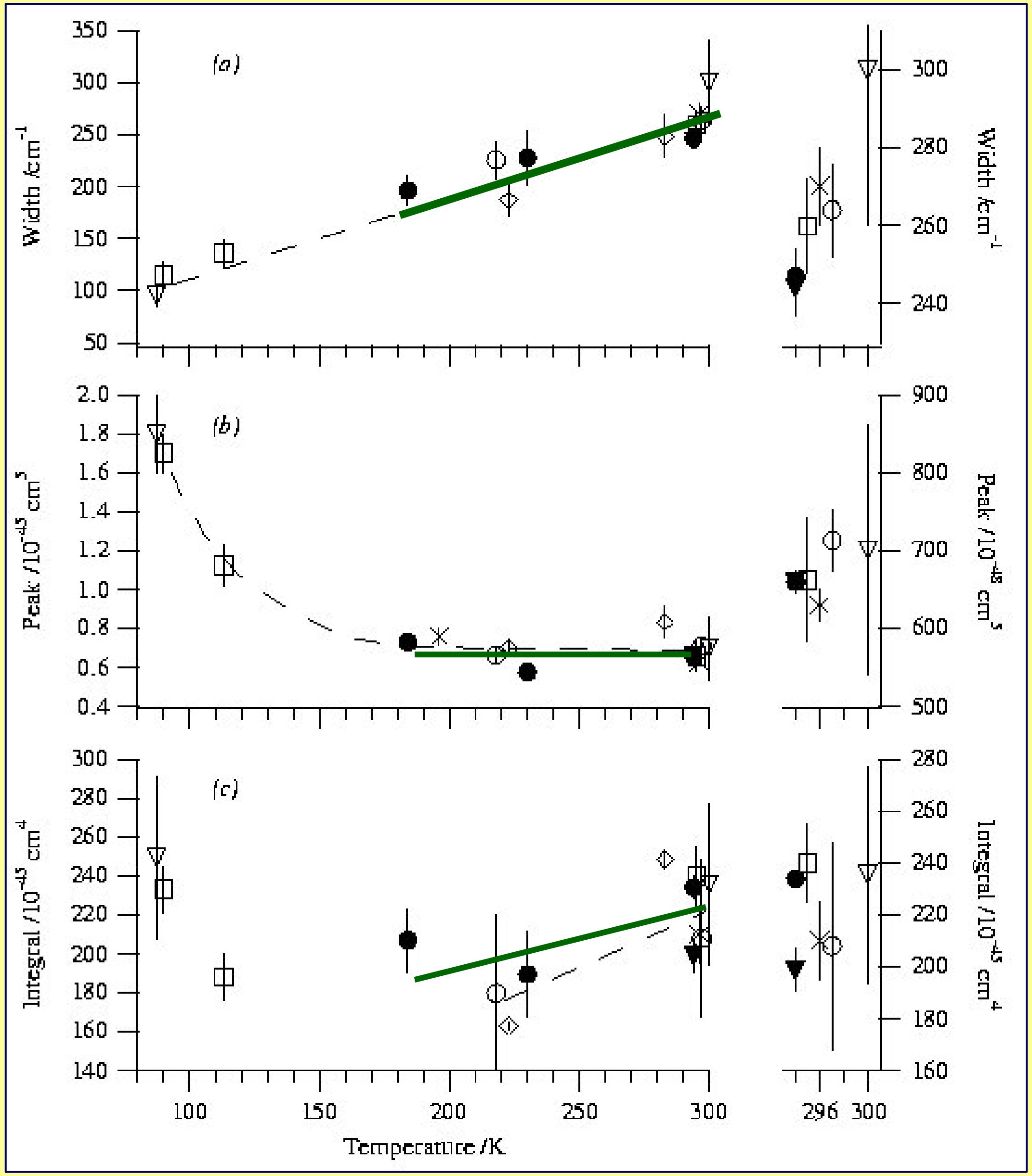
Compilation and critical analysis of data: "477 feature"



- ● Our data (low p)
- ▼ Hermans et al. (low p)
- ■ Tiedje et al.
- ▽ Ewing et al. (high p)
- □ McKellar
- ○ Tabisz
- ✕ Greenblatt et al.
- △ Morville et al.
- ◇ Newnham and Ballard

Trend of broadening firmly established +
Some increase of integral
in atmospheric range

Sneep, Ityaksov, Aben
Linnartz, Ubachs
JQSRT 98 (2006) 405

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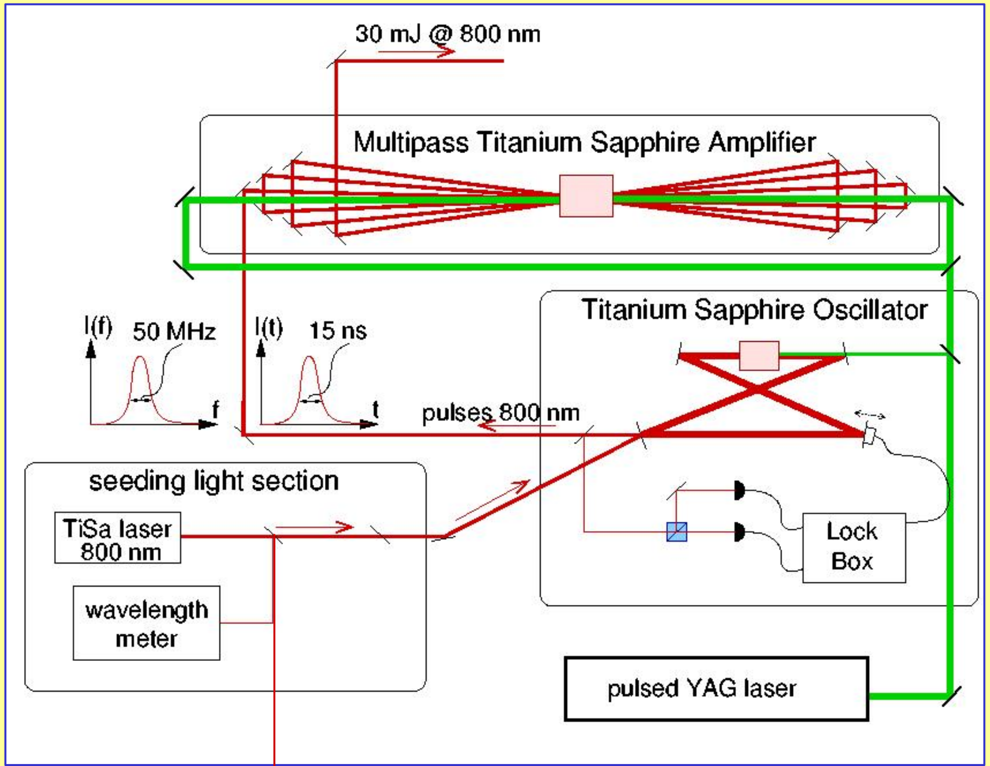
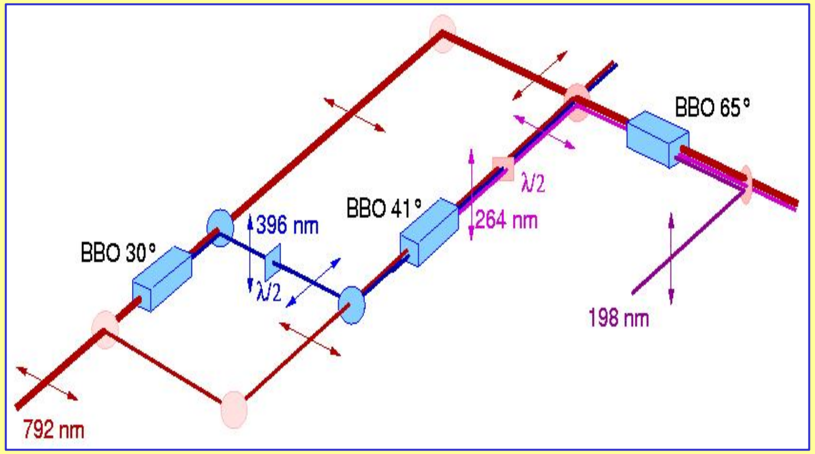
Towards the Deep-UV





frequency comb
+ chirp detection

$\Delta\nu_{DUV} < 80$ MHz
$\Delta\tau = 10\text{-}20$ ns
at 200 nm

+ on-line chirp analysis
+ frequency comb calibration
accuracy few MHz at 200 nm

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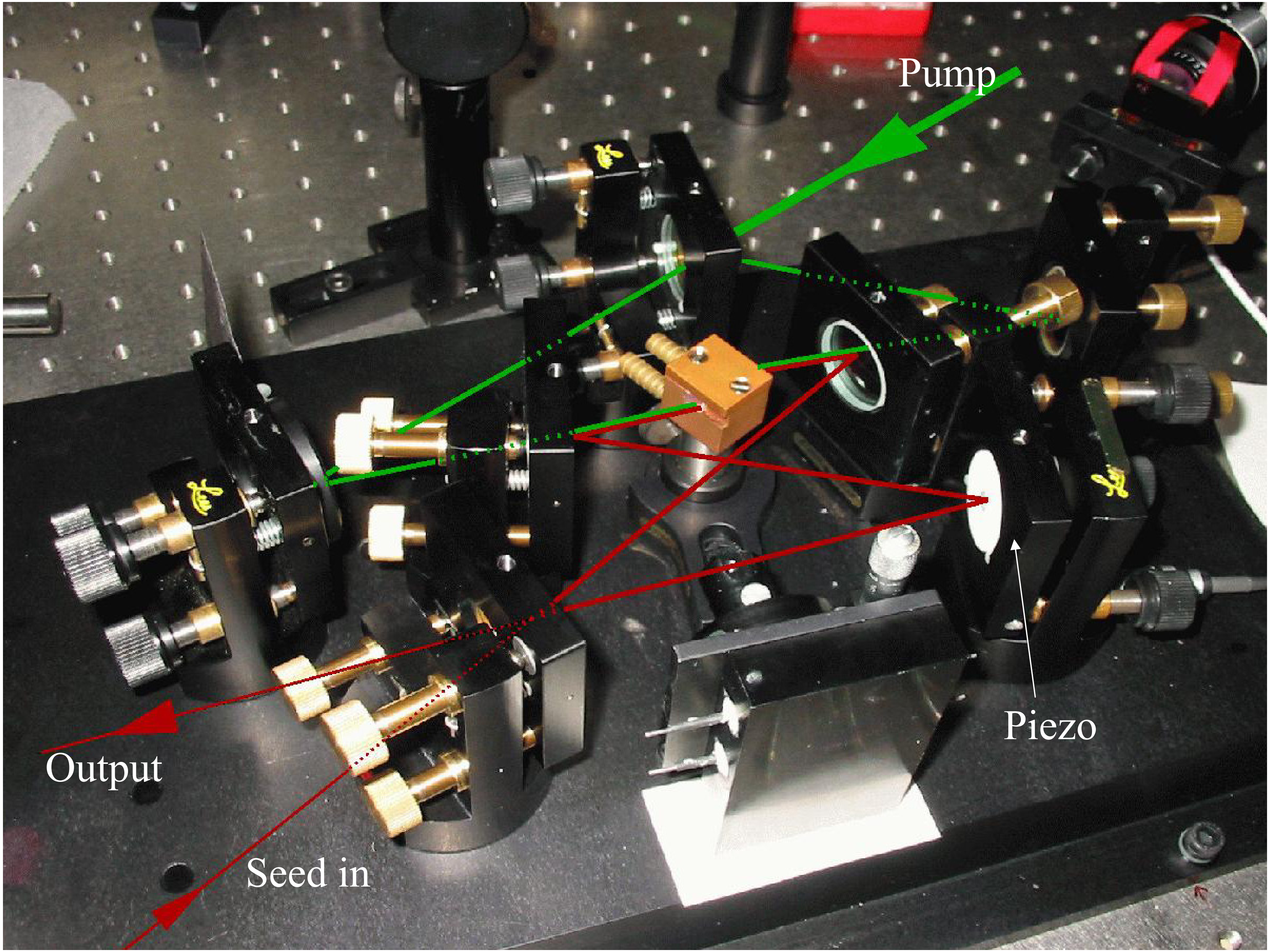
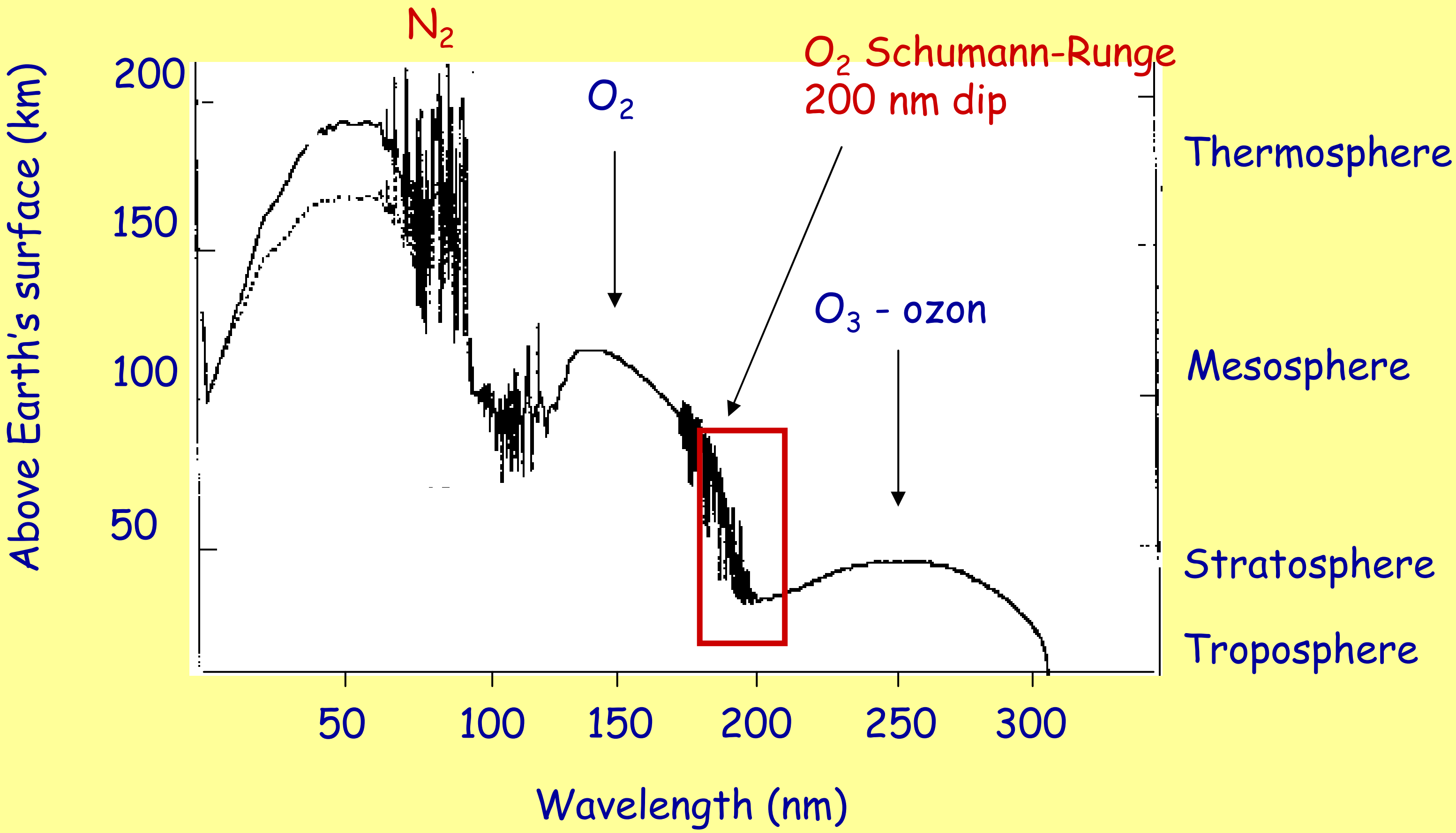

Pump
Piezo
Output
Seed in

Sunlight penetrating in the Earth's atmosphere



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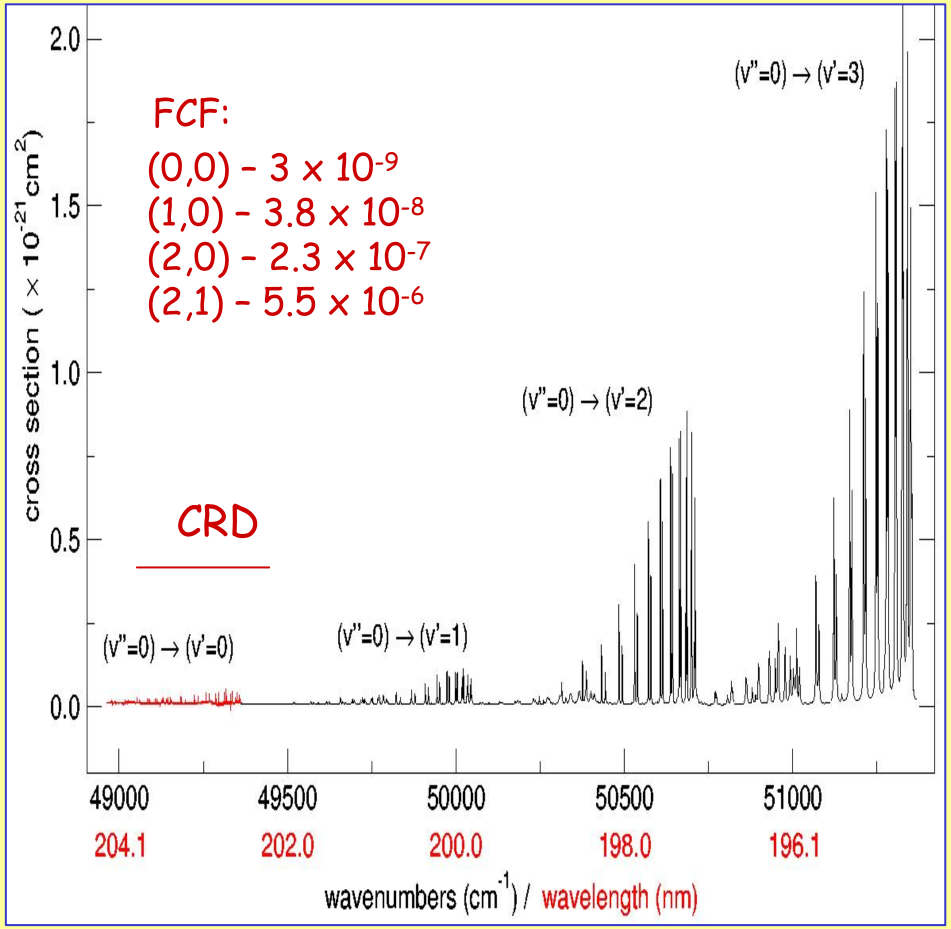
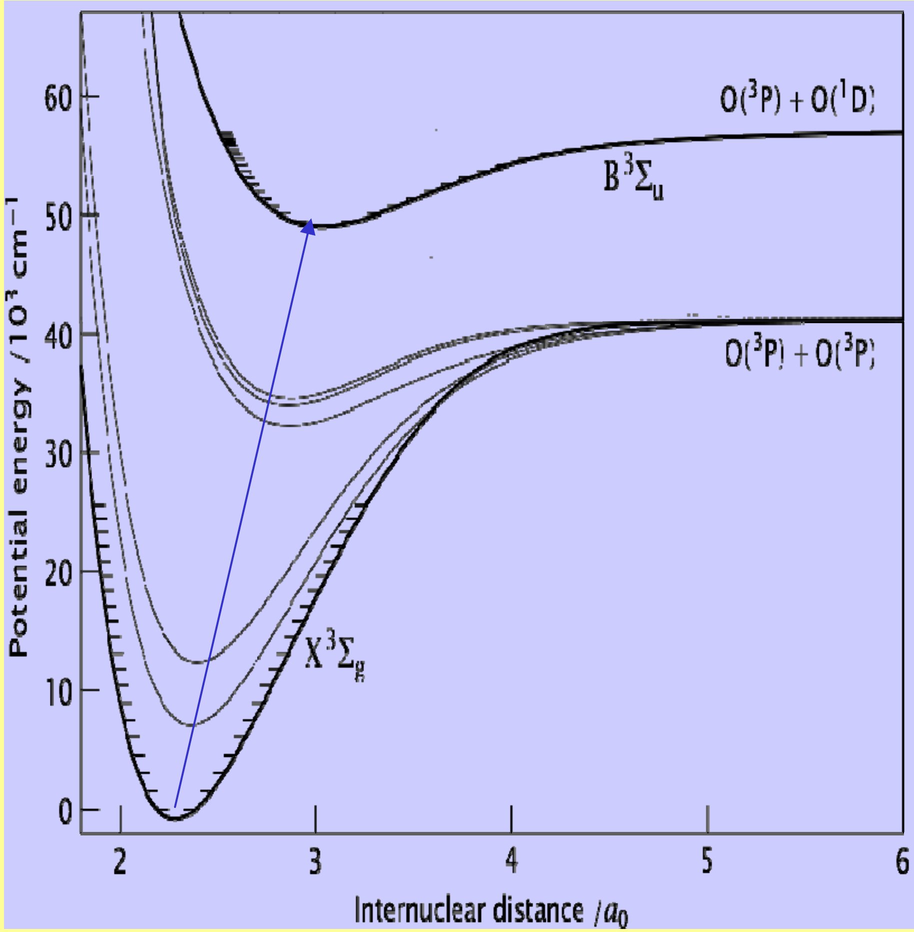
O_2-Schumann-Runge (Cheung, Yoshino *et al.*)





Goal: study spectroscopy, predissociation dynamics and collisional effects of low v

R = 97% at λ = 197-203 nm
Rocky Mountain Optics
CRD decay 100 ns

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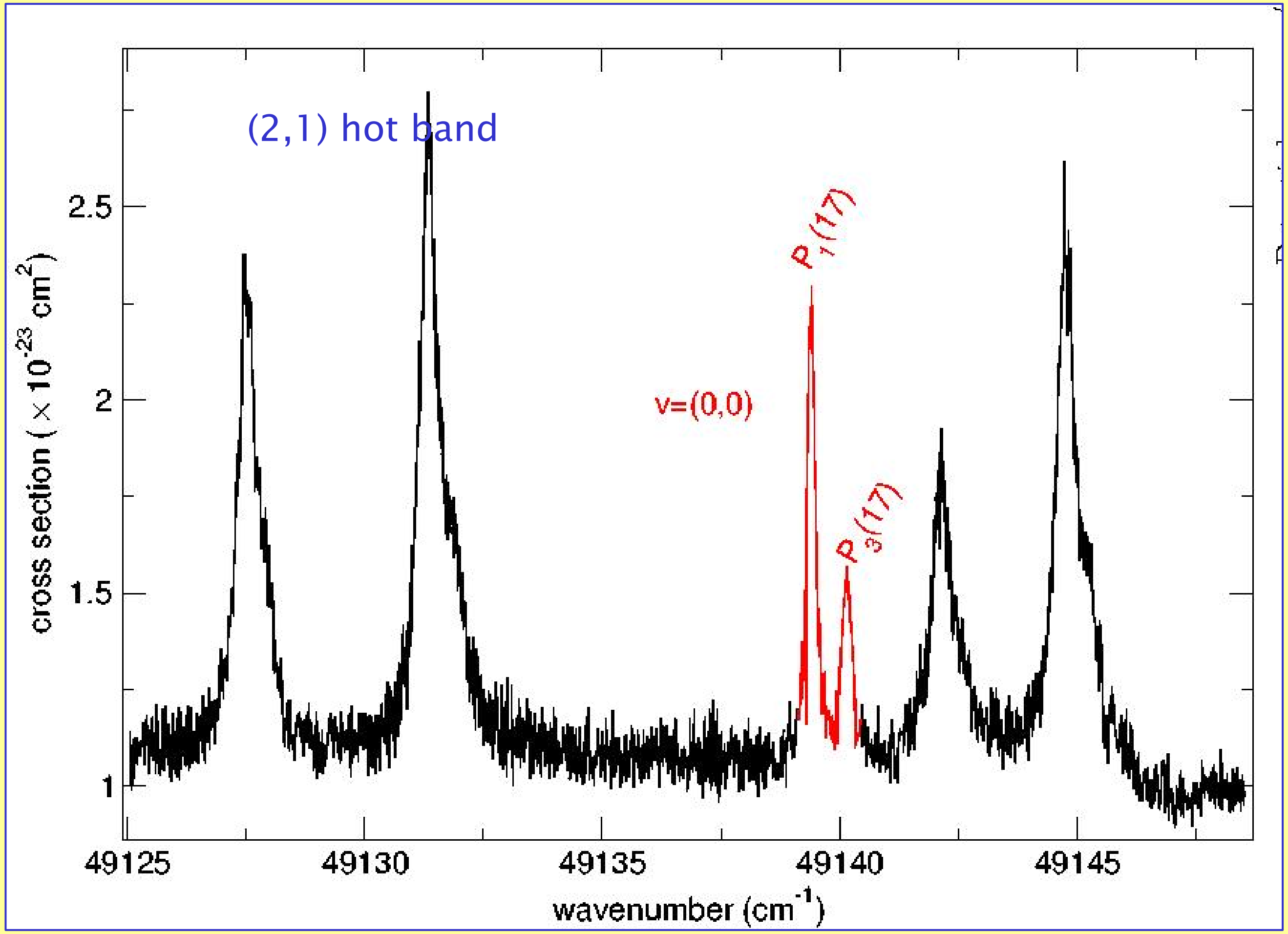
Vibrational excitation in room temperature deep-UV CRD



FCF

(0,0) - 3 x 10^{-9}
(2,1) – 6 x 10^{-6}

Thermal population
v=1 : 4.9 x 10^{-3}

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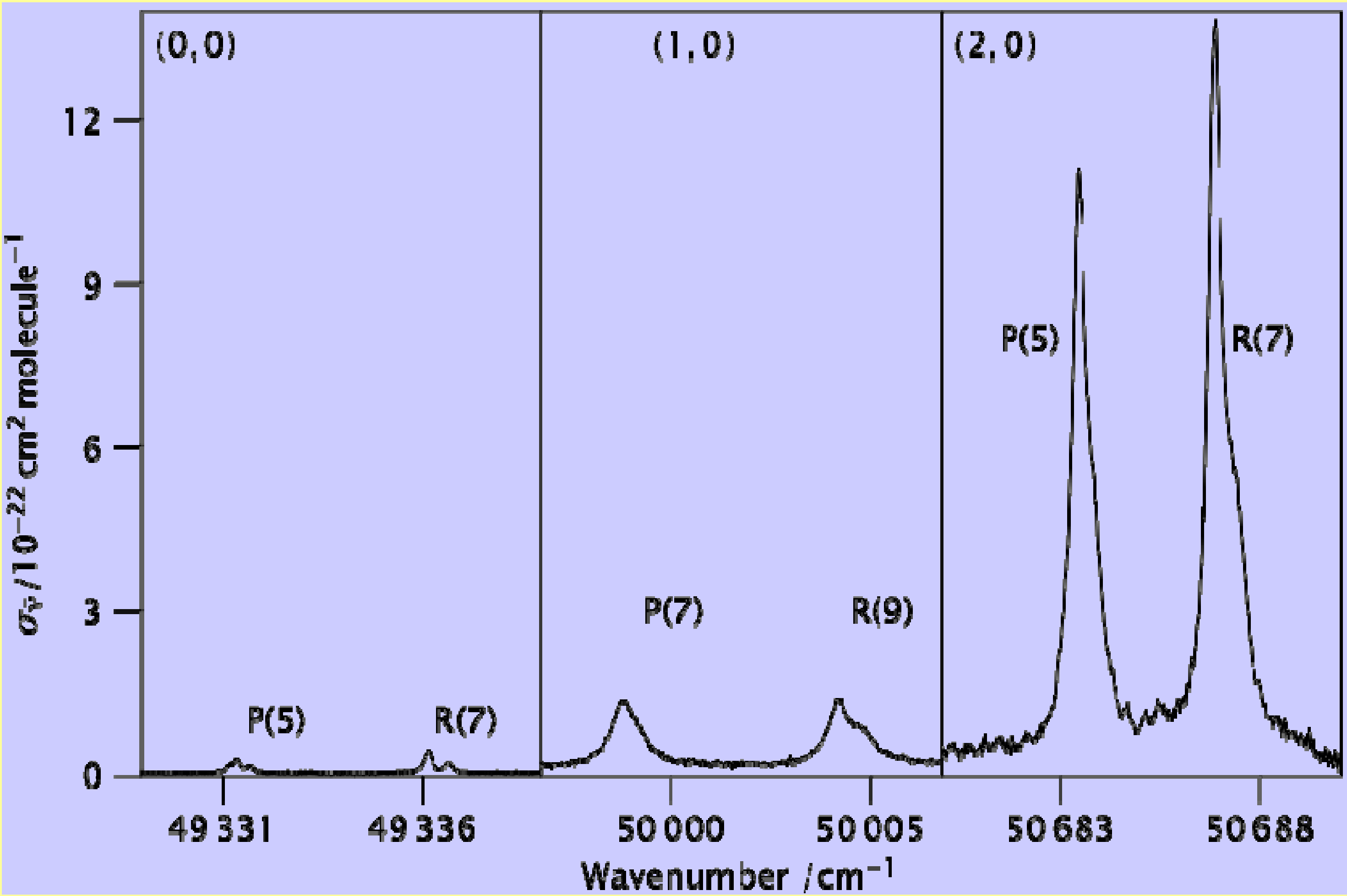
(v, J, F_j) dependent predissociation



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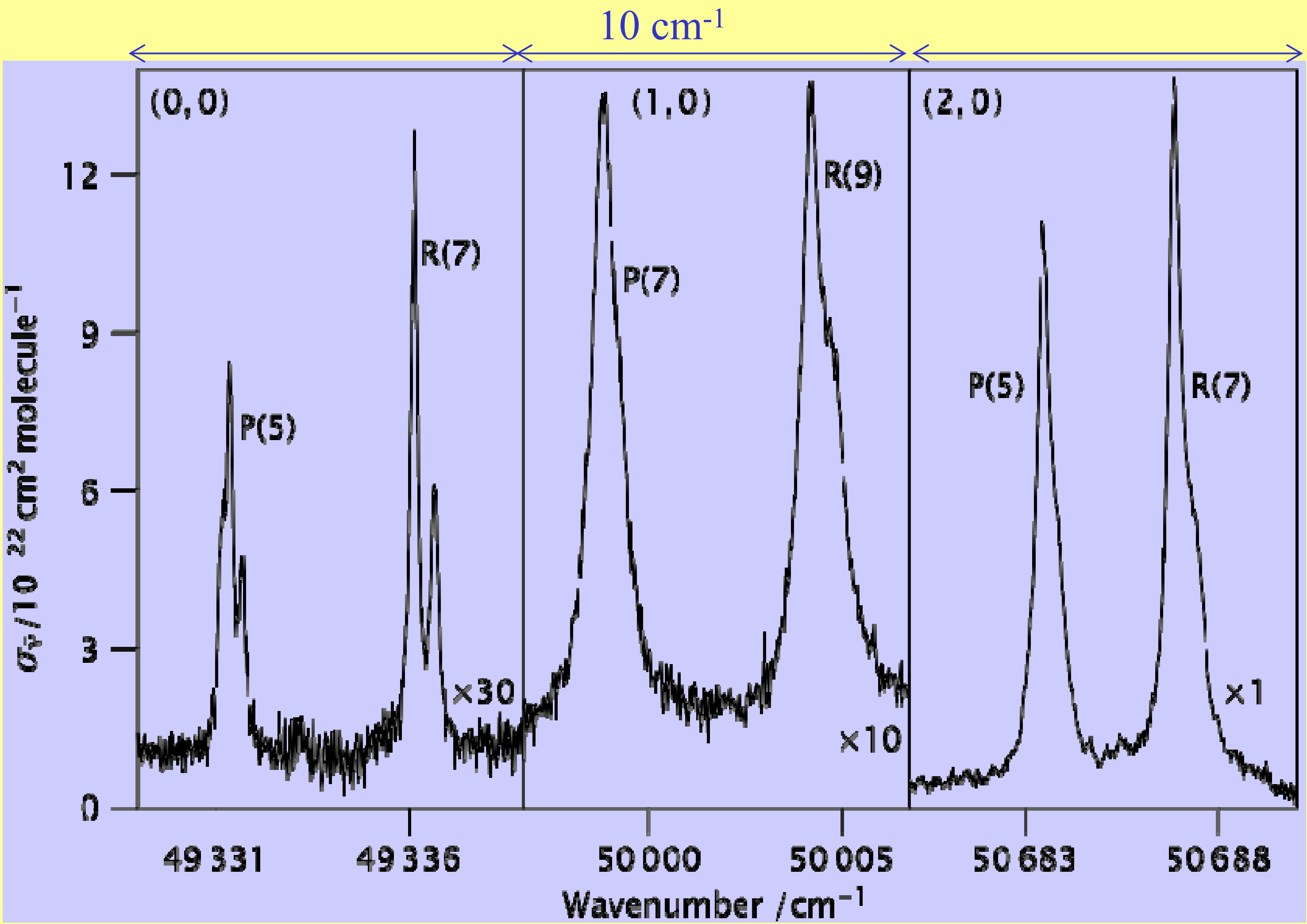
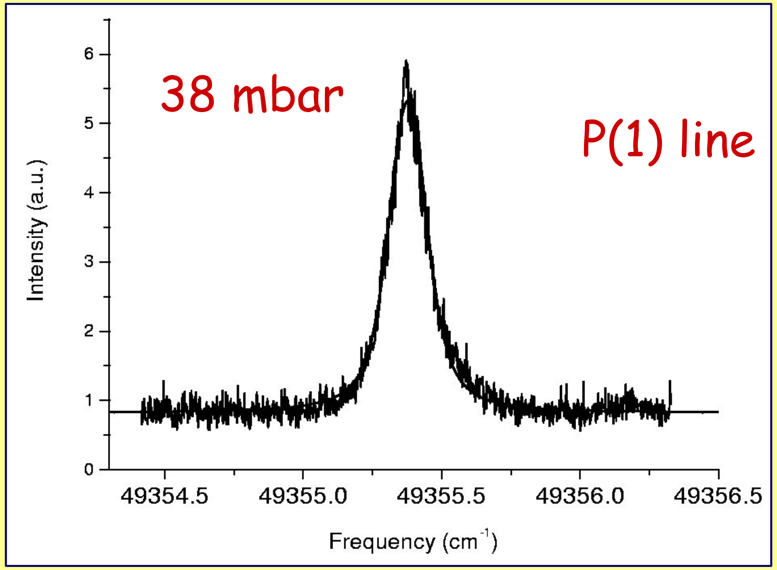
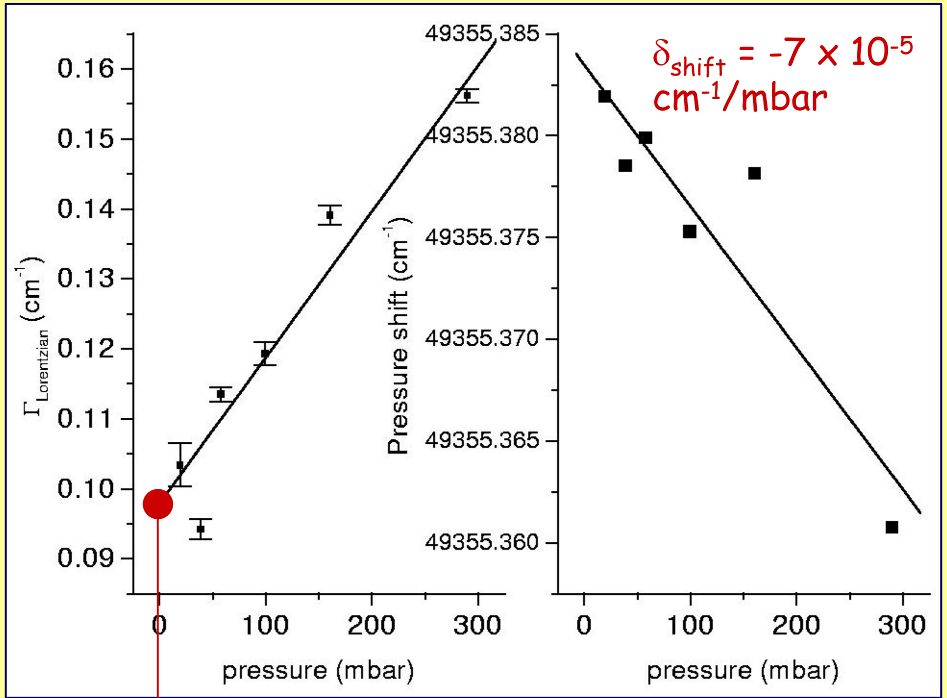

10 cm-1
(0,0)
(1,0)
(2,0)
12
9
6
3
0
R(7)
P(5)
×30
P(7)
R(9)
×10
P(5)
R(7)
×1
σ_ν̃ /10 22 cm2 molecule-1
49 331
49 336
50 000
50 005
50 683
50 688
Wavenumber /cm-1

Predissociation, pressure broadening and pressure shift





Δ_D = 0.107 cm^{-1}
$F_{profile} = F_D \otimes F_L$
F_L – Lorentzian Γ
Fit with $F_{profile}$

$\Gamma_L = \Gamma_{pred} + \Gamma_{col}p$

Γ_{pred} = 0.097 (2) cm^{-1}
Γ_{col} = 2.2 (0.3) x 10^{-4} cm^{-1}/mbar

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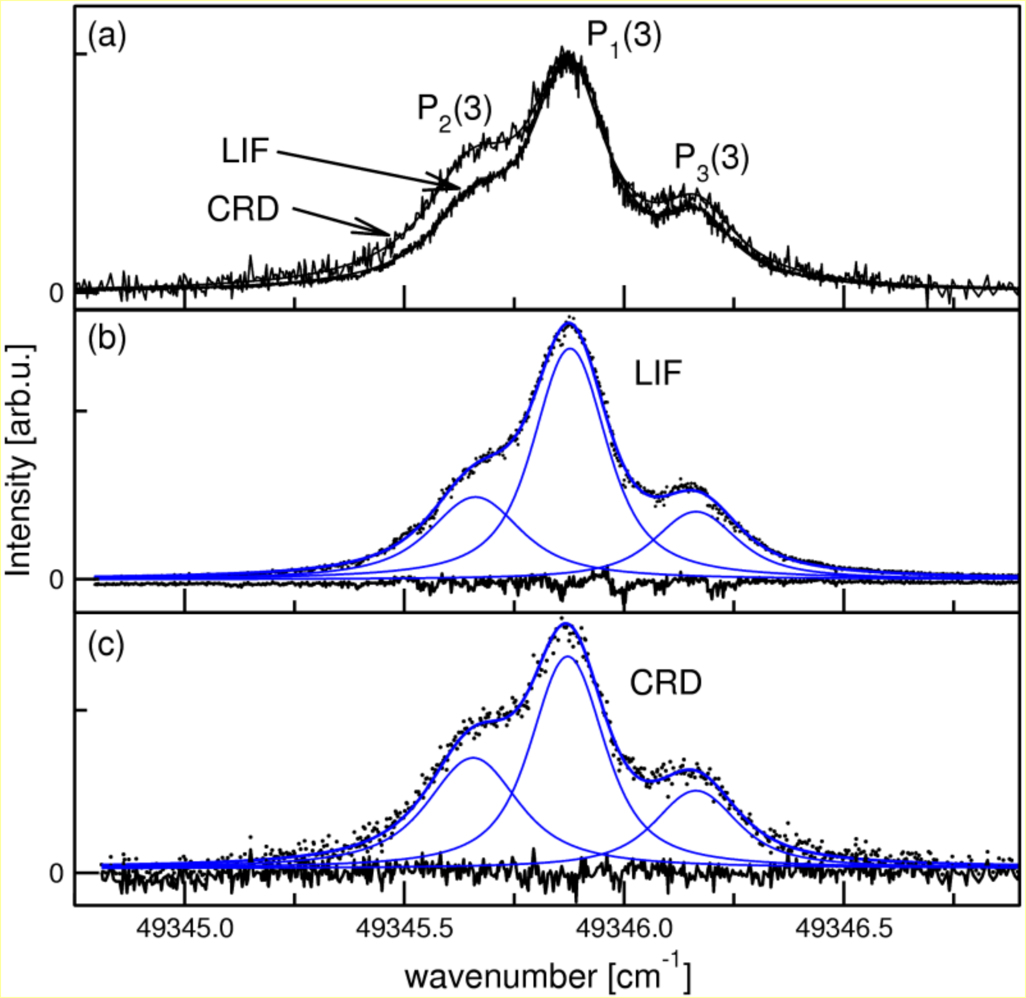
Fine-structure dependent predissociation: CRD and LIF compared



- In CRD: Intensities set to Hönl-London x Population

$$2\pi\Gamma_L = k_{col} + k_{pred} + k_{rad} = k_{tot}$$

- fluorescence intensities F_i

- Comprehensive fit, constraint:

$$\left(\frac{F_i}{F_j}\right)_{LIF} = \left(\frac{F_i}{F_j}\right)_{ABS} \frac{k_j^{tot}}{k_i^{tot}}$$

→ Spin-dependent predissociation rates

Hannemann, Wu, v Duijn, Ubachs, Cosby, JCP 123 (2005) 174318

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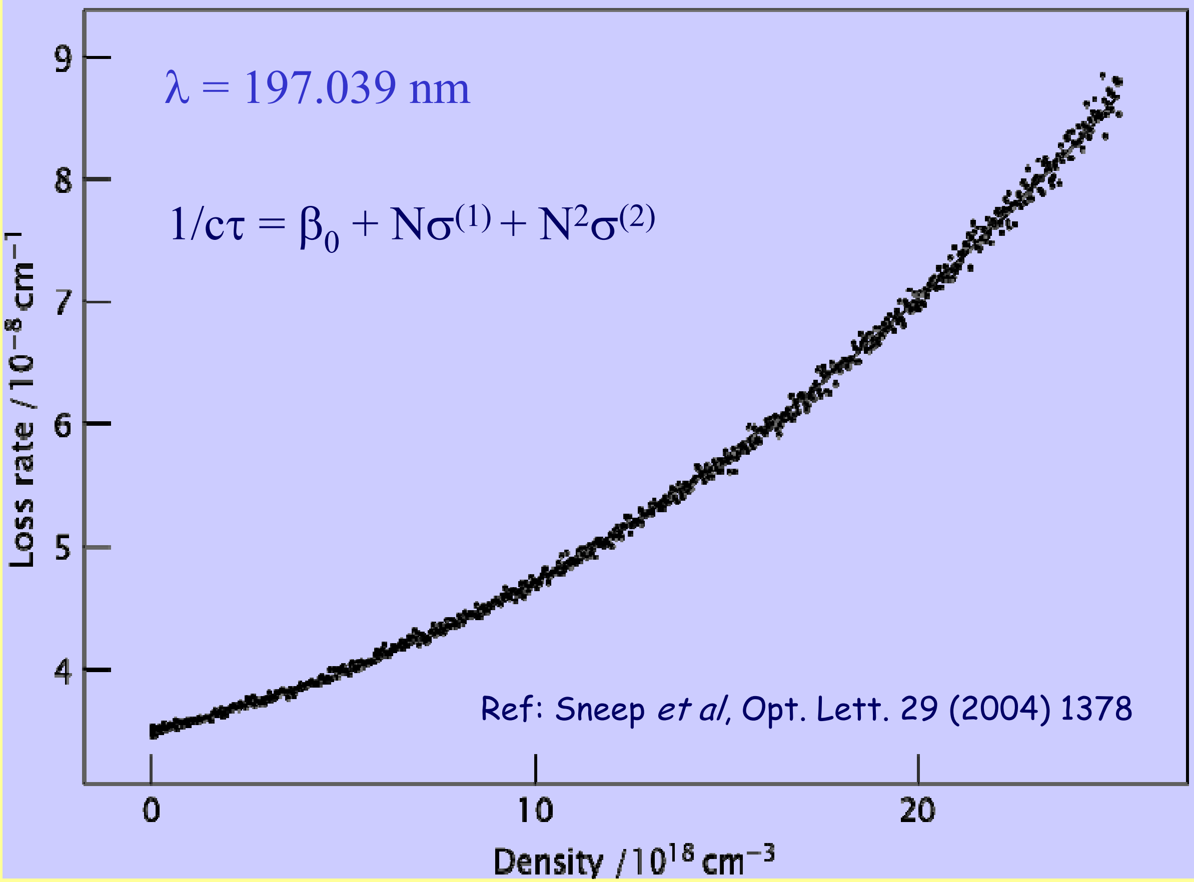
Extinction in the Herzberg continuum



CRD Experiment

$\sigma^{(1)}$ = 6.6(8) x 10^{-24} cm^{2}mol^{-1}

$\sigma^{(2)}$ = 549(15) x 10^{-45} cm^{5}mol^{-2}

Cf. Couquart et al. Planet Space Sciences 1990

$\sigma^{(1)}$ = 8.10(14) x 10^{-24} cm^{2}mol^{-1}

$\sigma^{(2)}$ = 521(6) x 10^{-45} cm^{5}mol^{-2}

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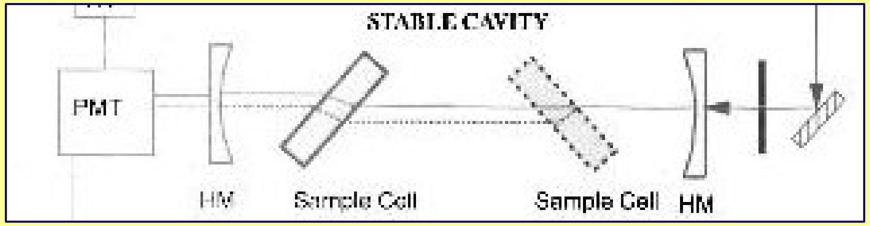
CRD in the liquid phase: bulk liquids

REVIEW OF SCIENTIFIC INSTRUMENTS VOLUME 73, NUMBER 2 FEBRUARY 2002

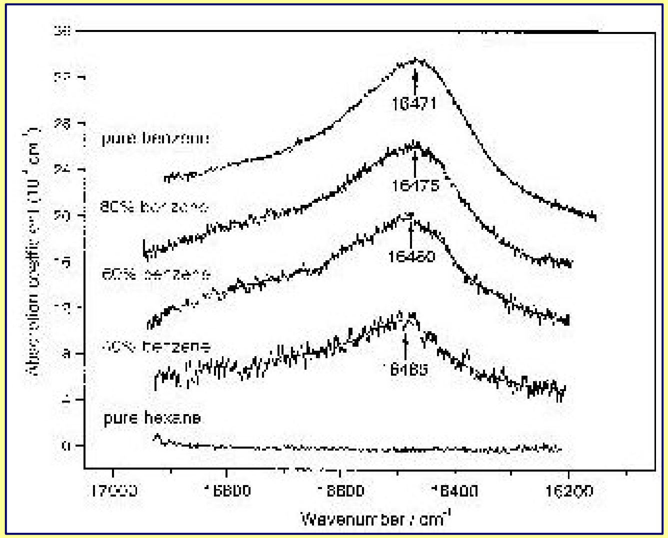
Cavity ring-down spectroscopy in the liquid phase

Shucheng Xu,[a] Guohe Sha, and Jinchun Xie
State Key Laboratory of Molecular Reaction Dynamics, Dalian Institute of Chemical Physics, Dalian 116023, People's Republic of China

(Received 3 January 2001; accepted for publication 30 October 2001)

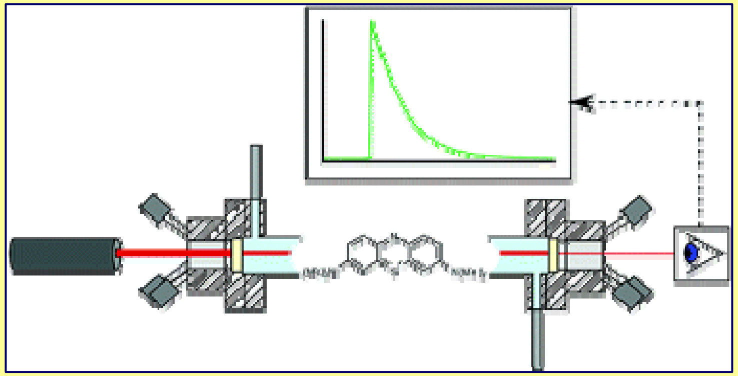


Static Brewster cell inserted in cavity



5^{th} overtone of Benzene dissolved in hexane

Hallock, Berman, Zare
Anal Chem (2002); JACS (2003)
Bulk studies and kinetics



Direct contact with mirrors

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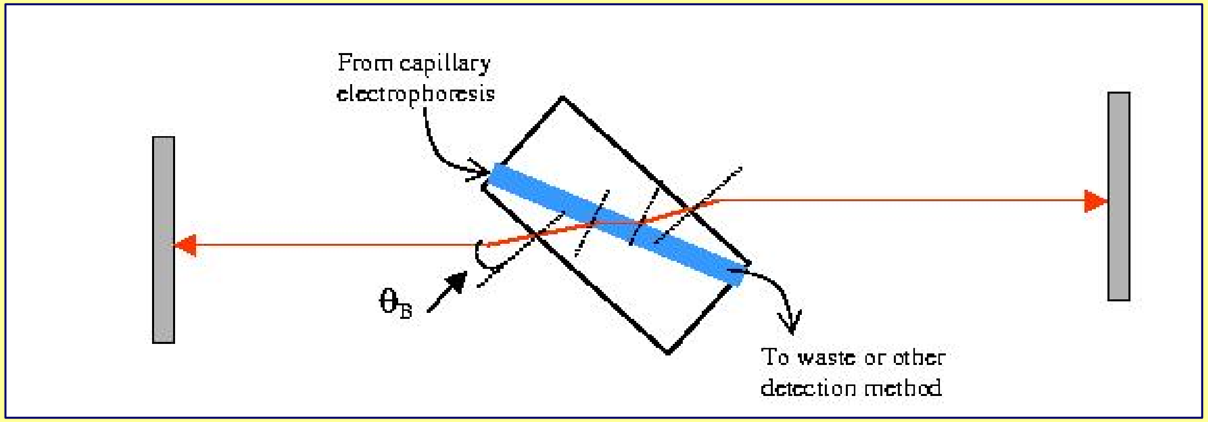
CRD in the liquid phase: sensitive detection after separation

Flow injection: Leach, Wheeler, Zare, Anal. Chem. (2003)
HPLC: Snyder, Zare, Anal. Chem. (2003)
HPLC + cw CRD: Bechtel, Zare et al. Anal. Chem. (2005)



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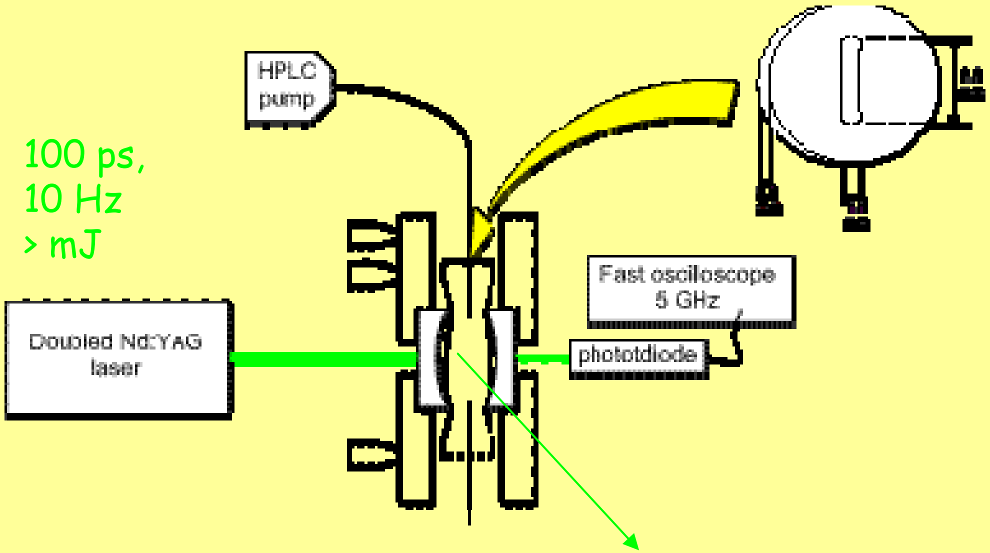
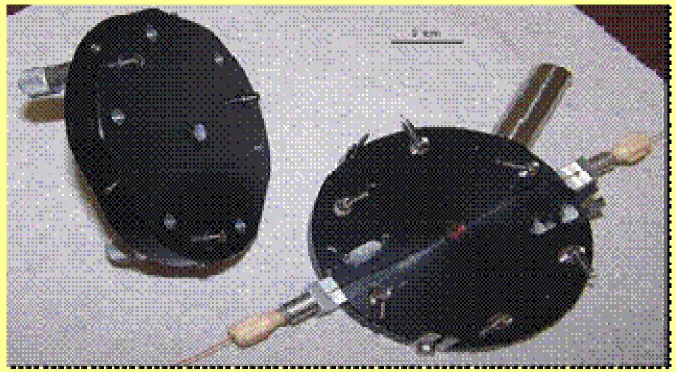
To the liquid phase: The combination CRD – HPLC in our approach

100 ps,
10 Hz
> mJ



effective volume
12 μL



Philosophy: Liquid-Only cell

First steps
and goals

Detection, not spectroscopy
Small volumes
Universal wavelengths

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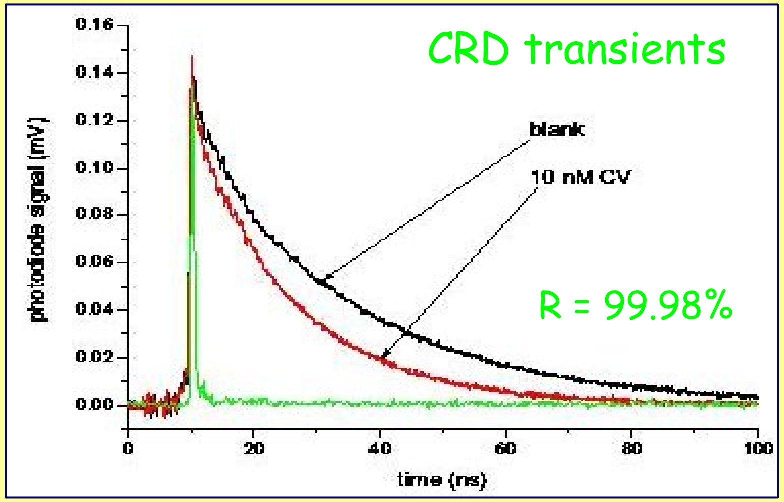
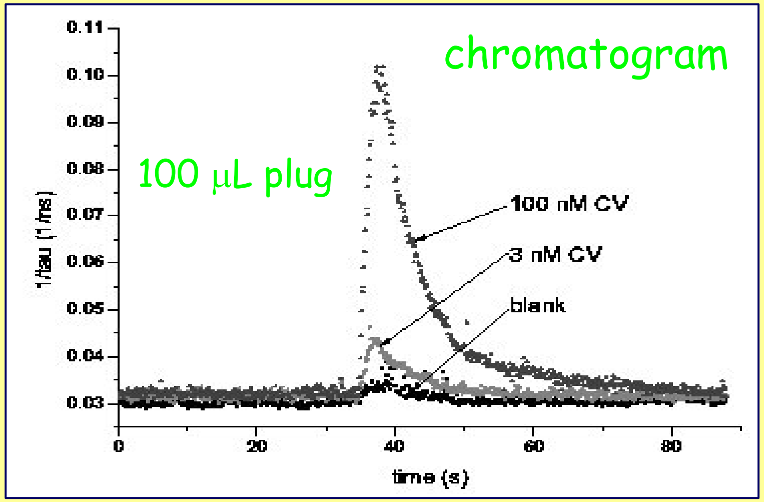
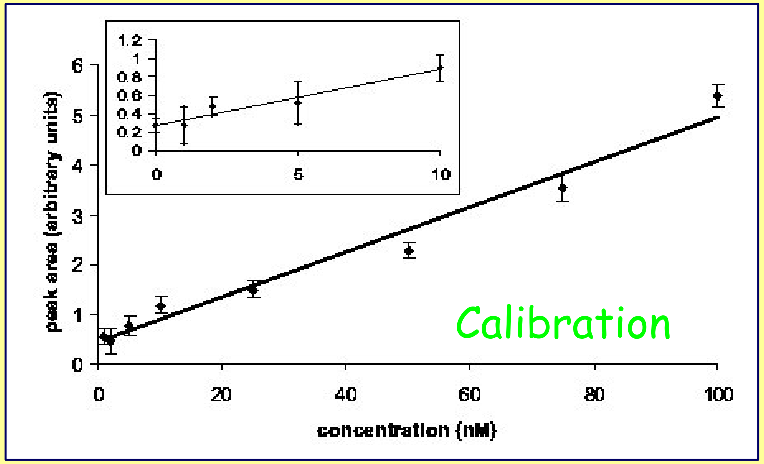
To the liquid phase: The combination CRD – HPLC in our approach

1st step measuring a "plug"

CV: Crystal Violet/ethanol
ε =54500 $M^{-1}cm^{-1}$







Detection limit: 2.5 nM
Problem of blank

Bahnev, vd Sneppen et al, Anal. Chem. (2005)

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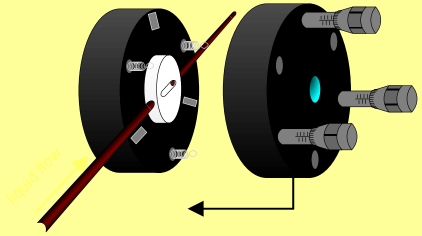
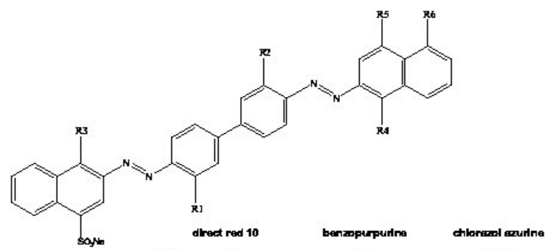
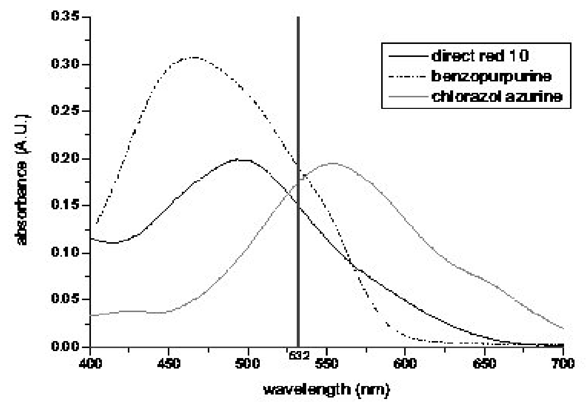
Demonstation of online HPLC detection in Liquid-Only cell

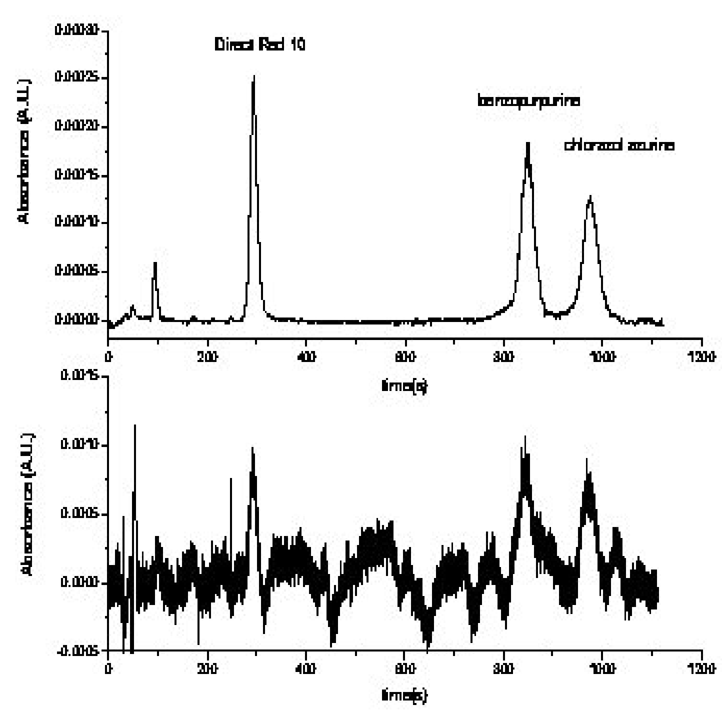


liquid-only cavity
(14 μl)
R = 99.996 %
532 nm, 100 ps,
10 Hz, τ =70 ns



	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

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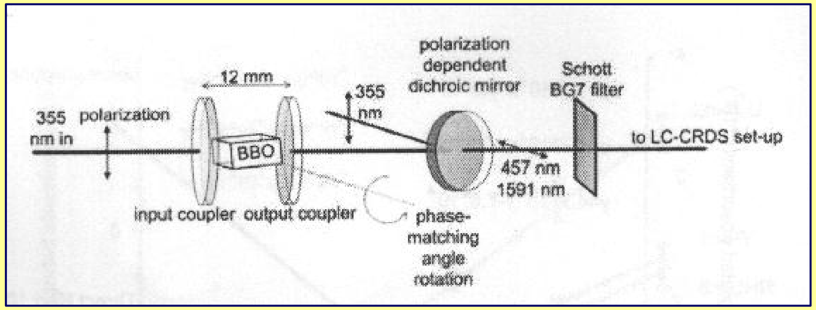
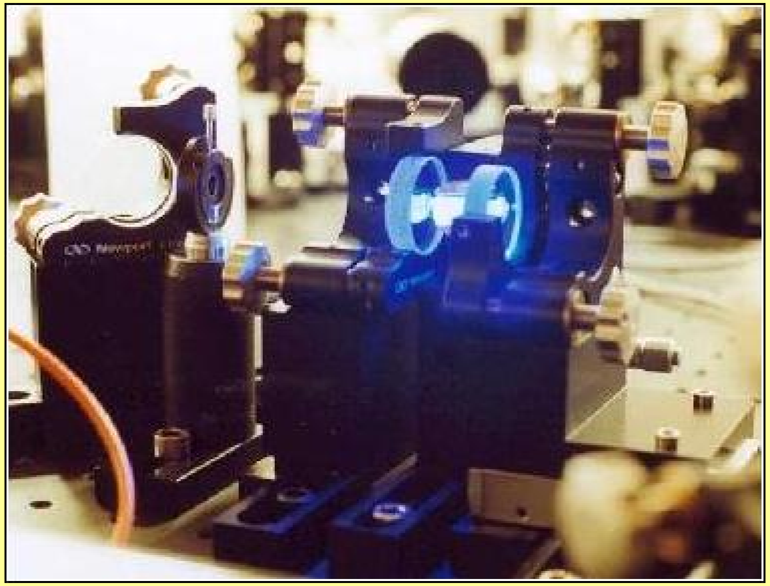
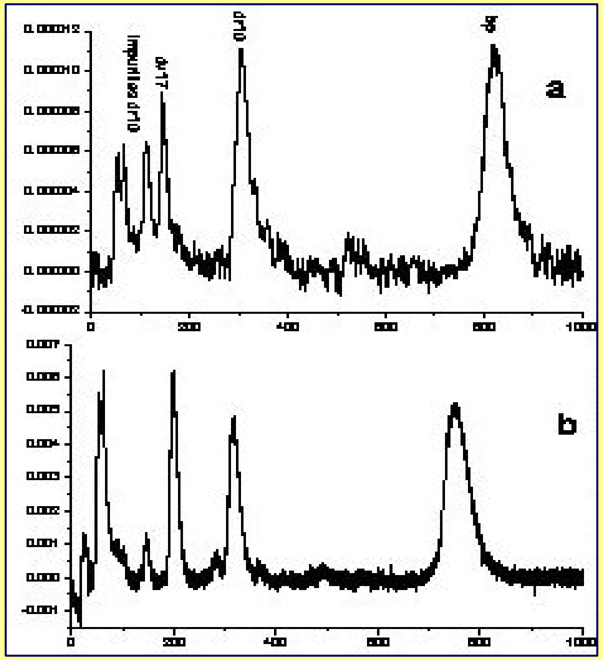
Steps toward blue and higher rep. rates

457 nm; OPO – 100 Hz; R=99.993%



Tunability: 420-480 nm; $\Delta\nu$ = 10 cm^{-1}





CRDS
100 ppb
injected
before column

Conventional
10 ppm
injected

Mixture of AZO-dyes
- Direct Violet 17
- Direct Red 10
- benzopurporine

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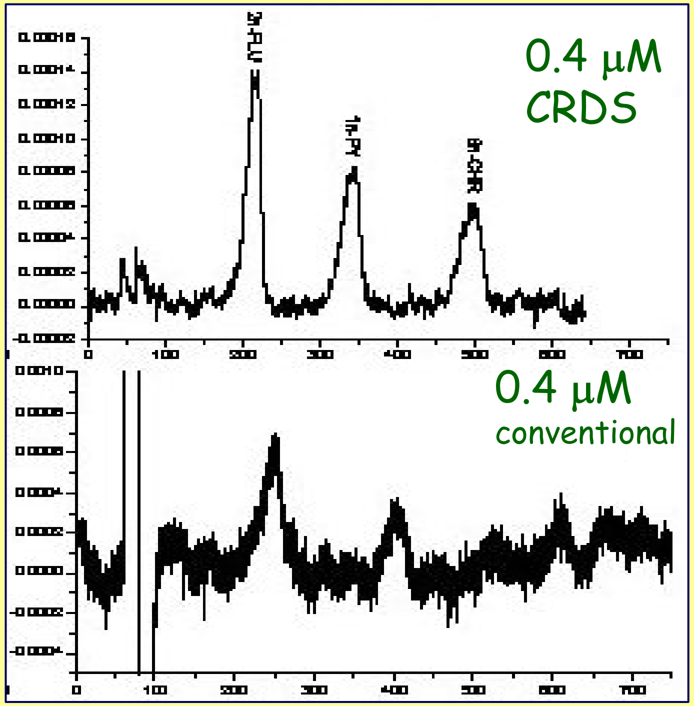
Steps toward UV – 355 nm

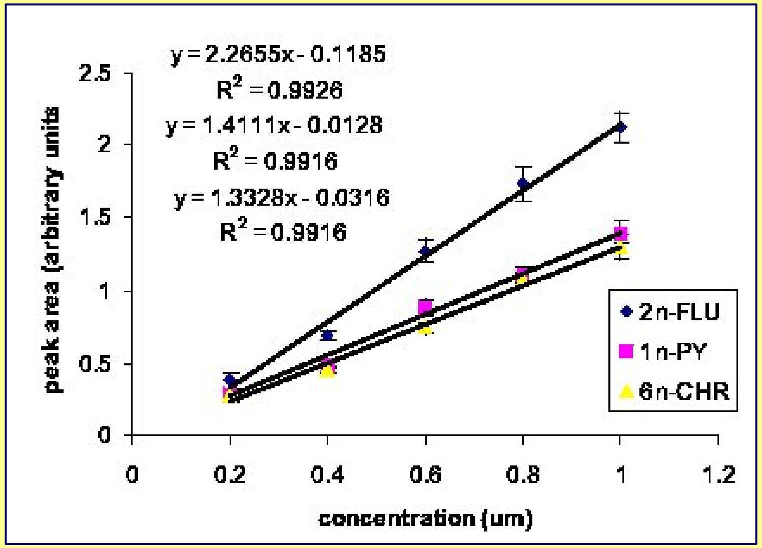
Pico Nd:YAG 3rd HG; R=99.95% - Layertec
ROC = 5 cm
CRD transients 15-20 ns



Mixture of carcinogenic nitro-substituted PAHs

2-nitrofluorene
1-nitropyrene
6-nitrochrysene

Linearity in detection > 200 ppb



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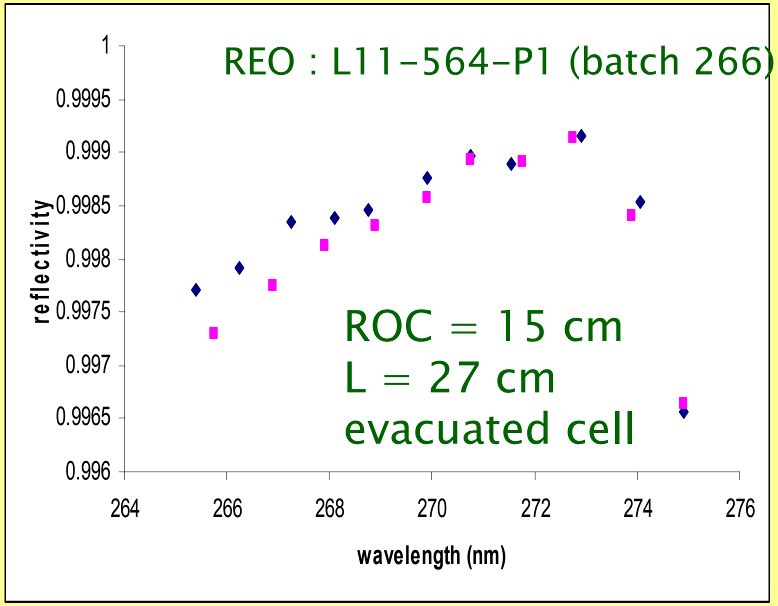
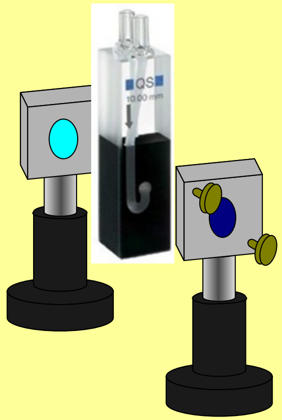
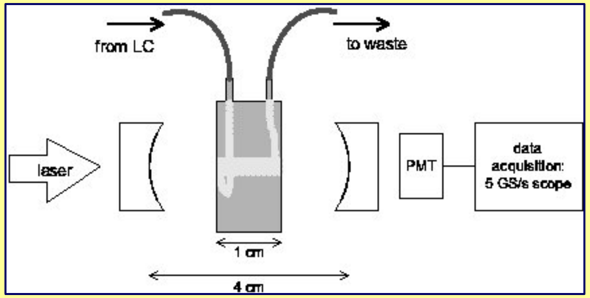
Further to the deep UV ? 266 nm ?



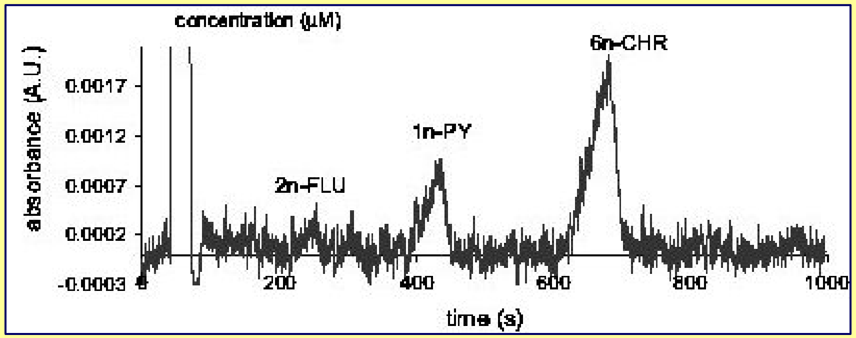


flow cuvette (80 µl)



Decays ~ 120 ns (empty cavit
Decays ~ 15 ns in operation

→Measurements at λ = 273 nm
R = 99.91%
Pulsed dye laser system Δt = 4 ns



Limitation
1) Mirror R at 266 nm
2) Surface roughness

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