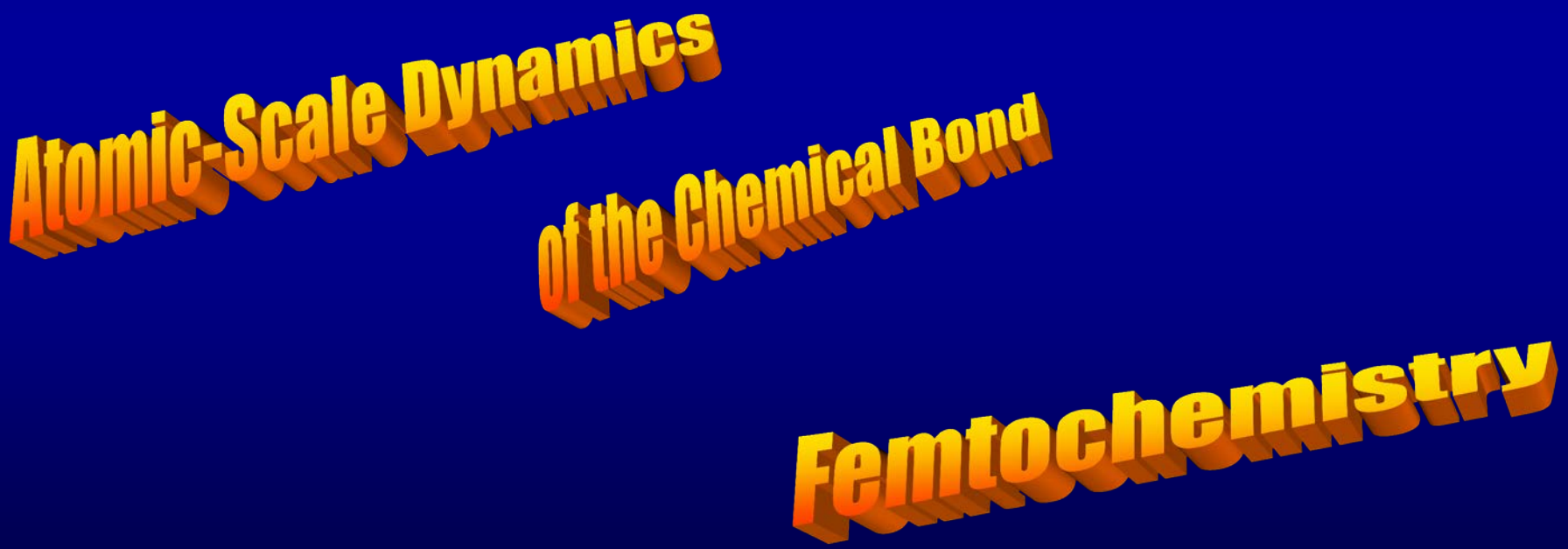
PC5 Reaktionsdynamik

Kapitel VII
Experimentelle Methoden



Das ideale Experiment….

Das Idealexperiment müsste den Streuquerschnitt und die Winkelverteilung der Produkte für einen vollständig spezifizierten Stossvorgang bestimmen. In der Praxis versuchen wir dem möglichst nahezukommen, nicht zuletzt, um mit der Theorie vergleichen zu können. Das bedeutet in der Reihenfolge immer größeren Details die Messung folgender Größen: Integraler Reaktionsquerschnitt bei vorgegebener Stossenergie, Winkelverteilungen der Produkte, möglichst zusätzlich die Geschwindigkeitsverteilung bei jedem Winkel, aus der man wegen der Energieerhaltung ihre innere Energie rekonstruieren kann, Zustandsanalyse der Produkte, Zustandsvorgabe der Reaktanden, Vorgabe der Orientierung der Reaktanden, Analyse der Orientierung der Produkte. Experimente mit orientierten Molekülen würden wir auch noch die Spezifikation der Quantenzahlen m_j und m'_j verlangen, die die Orientierung der Reaktanden bzw. Produkte bezüglich einer gegebenen Richtung beschreiben Im übrigen sind alle oben genannten Eigenschaften nicht unabhängig voneinander, so dass wir uns auch noch für die Korrelationen interessieren müssen!

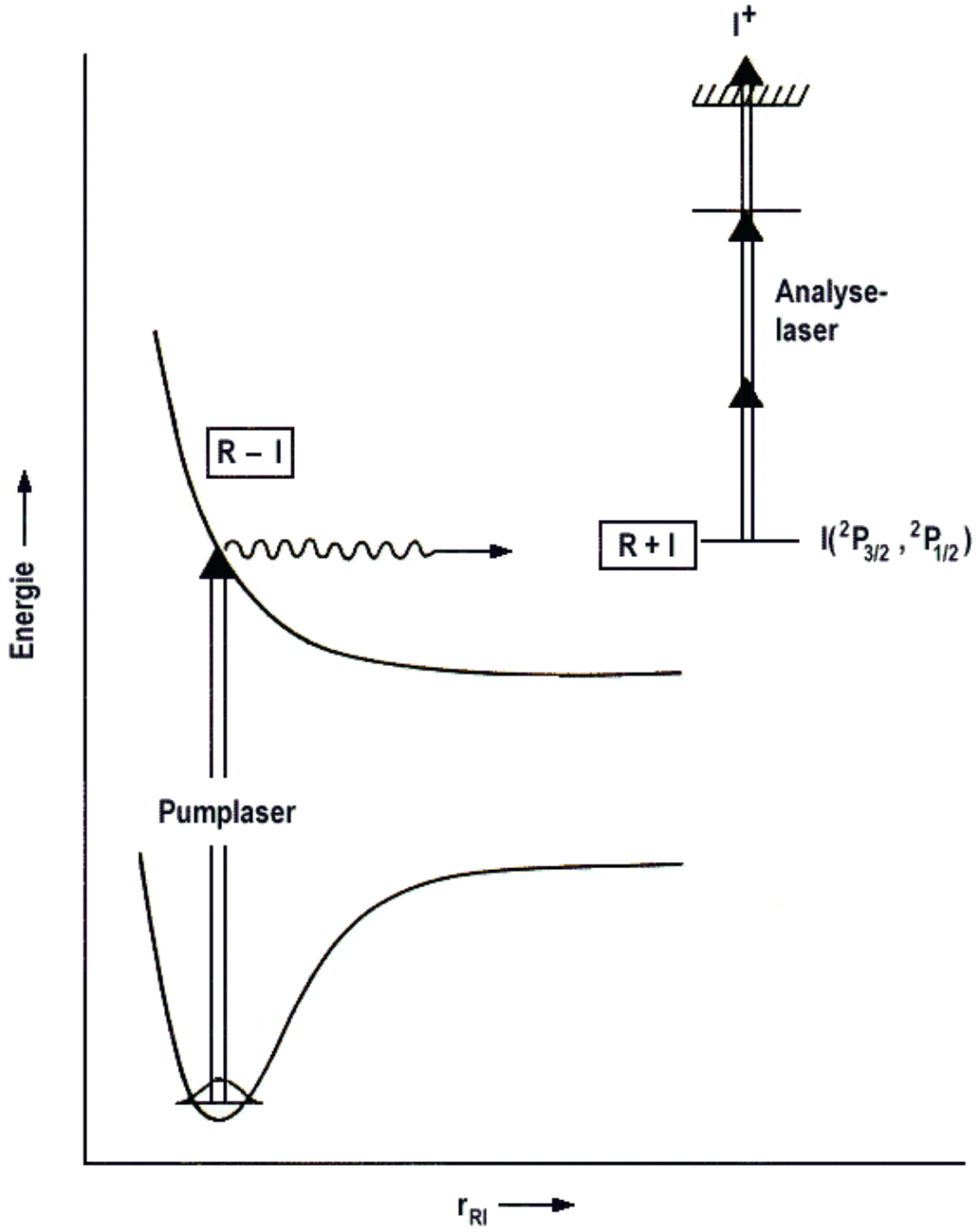
…gibt es nicht

z.B. H + ICl

Eine vollständige Festlegung des Stoßvorgangs verlangt nicht nur die (chemische) Identifizierung des Produkts (HCl oder HI), sondern auch die Feststellung des inneren Zustands von Edukten und Produkten, sowie deren Geschwindigkeiten (Vektoren!) d.h. (beispielhaft für Cl-Spinzustände):

$$H(^2S) + ICl(v,j,m_j) \rightarrow HI(v',j',m_j') + Cl(^2P_{1/2})$$
$$\rightarrow HI(v',j',m_j') + Cl(^2P_{3/2})$$

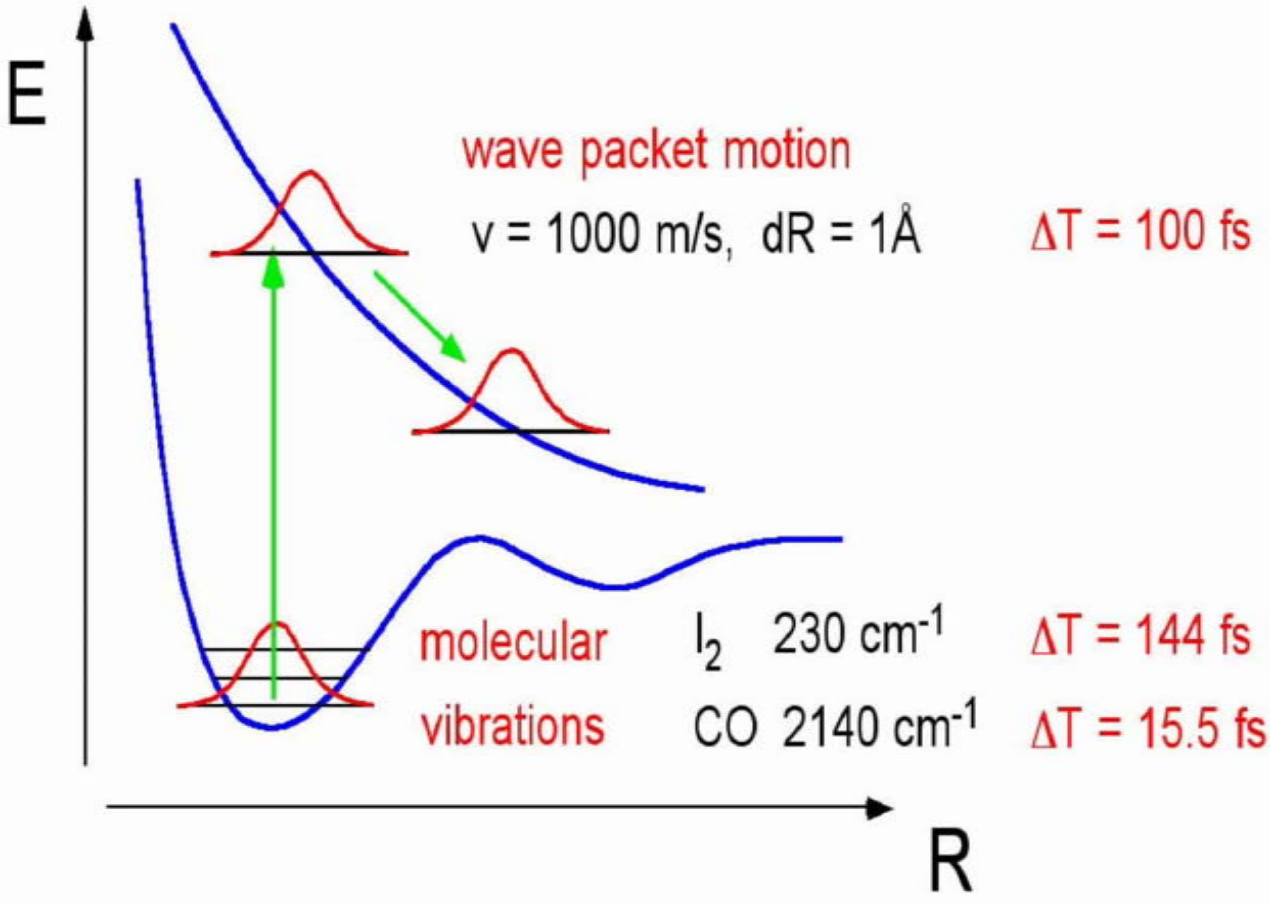
Pump and probe experiments

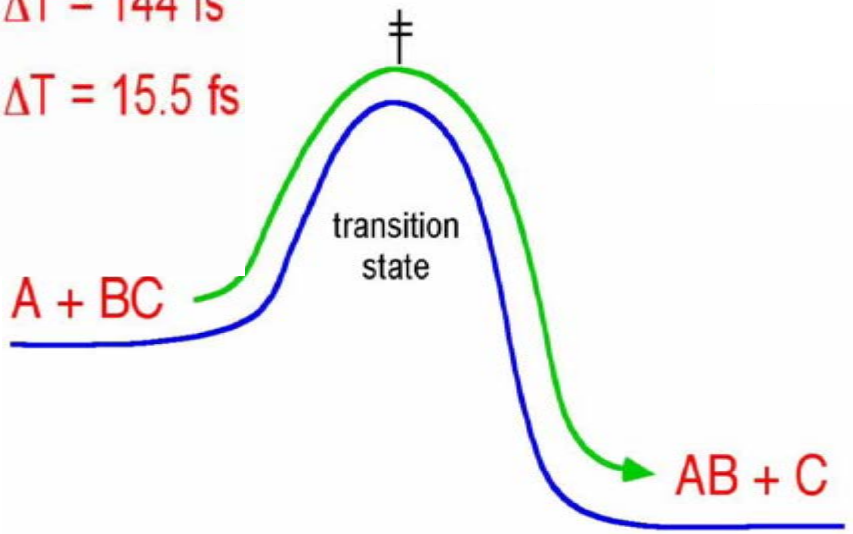


Wesentliche Fortschritte auf dem Gebiet der Reaktionsdynamik wurden durch den Einsatz von Lasern erzielt. Typisch sind hier „pump and probe“-Experimente, bei denen ein Laser(puls) die Edukte präpariert und ein zweiter die Produkte probt (analysiert).

1. Time resolution

*Need femtosecond laser pulses for direct observation in **time domain** (low energy resolution), …*



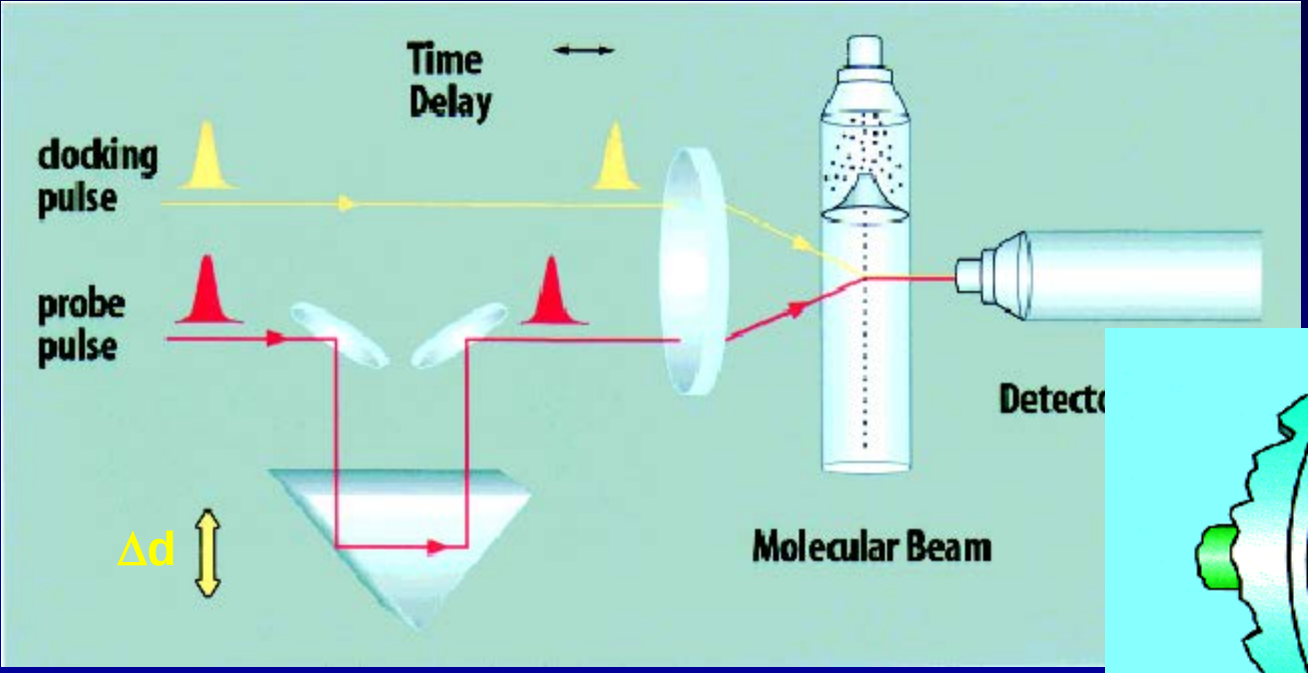


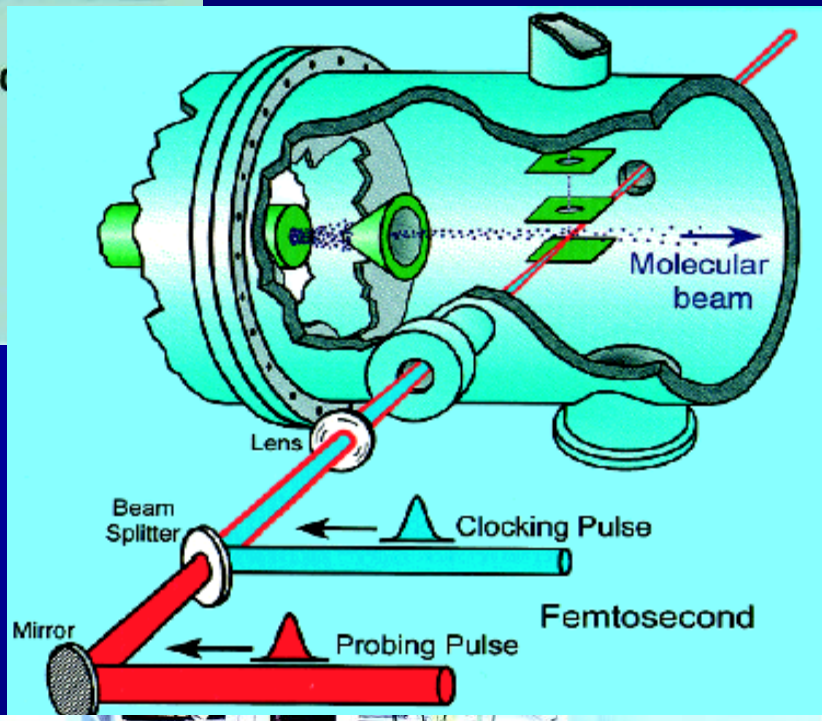
2. High resolution

… but nanosecond laser pulses for sufficient energy resolution (v,J,s quantum states)

time resolution

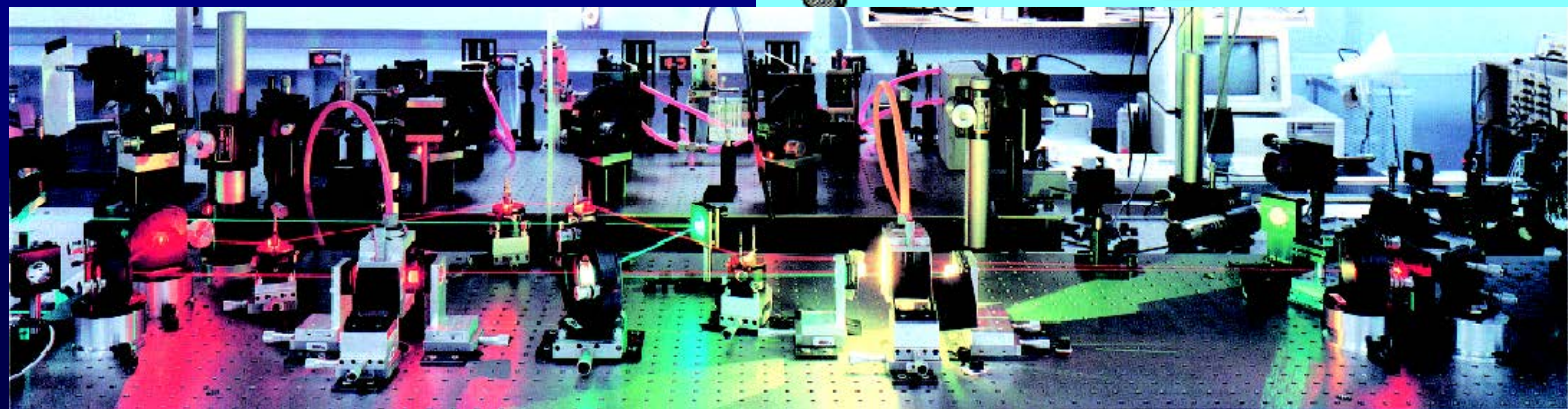
In principle…





$\Delta t = 2\,\Delta d / c$ 1 µm = 6.7 fs

....and
in reality



Dynam
Fem

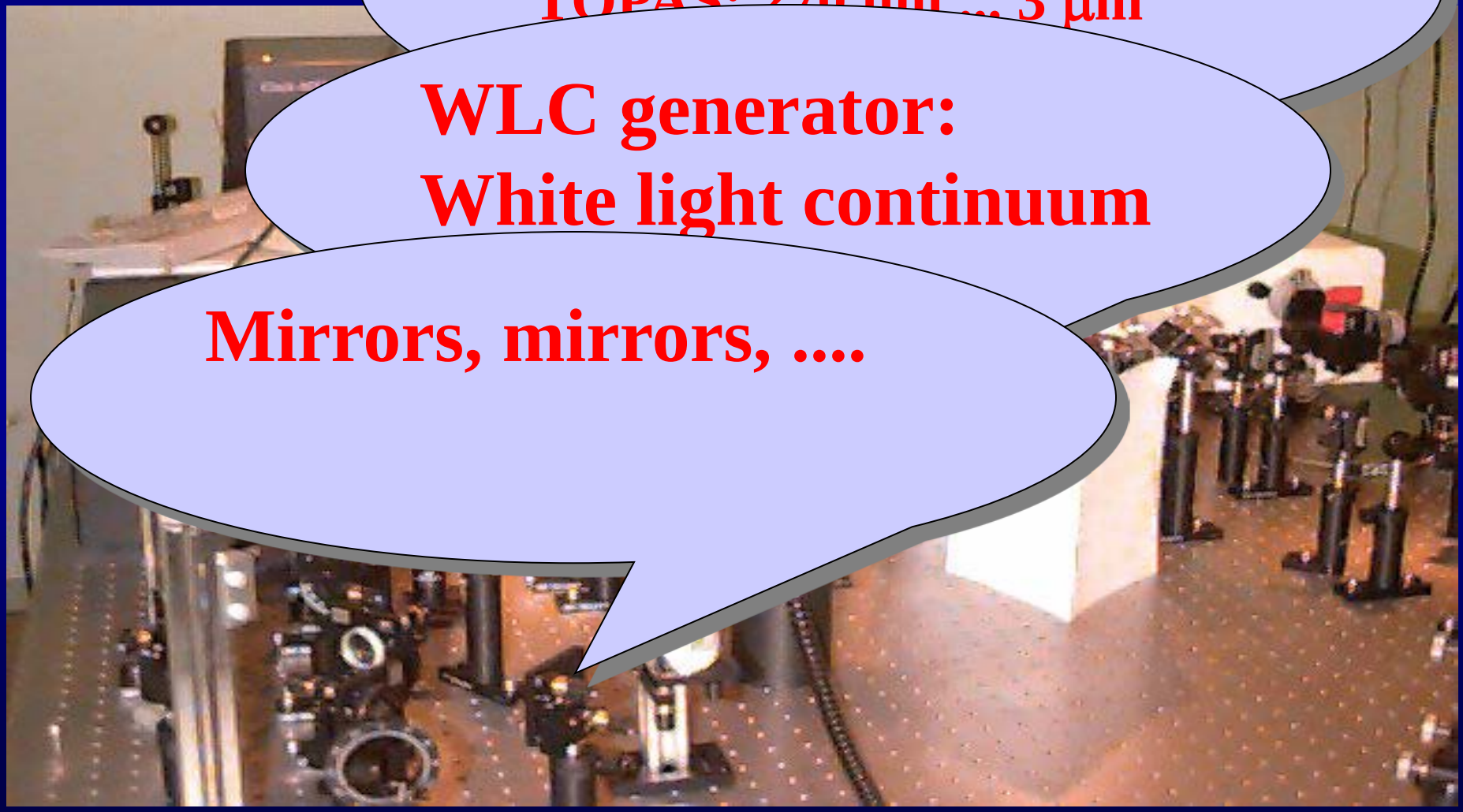
Femtosecond laser:

Non-linear setups

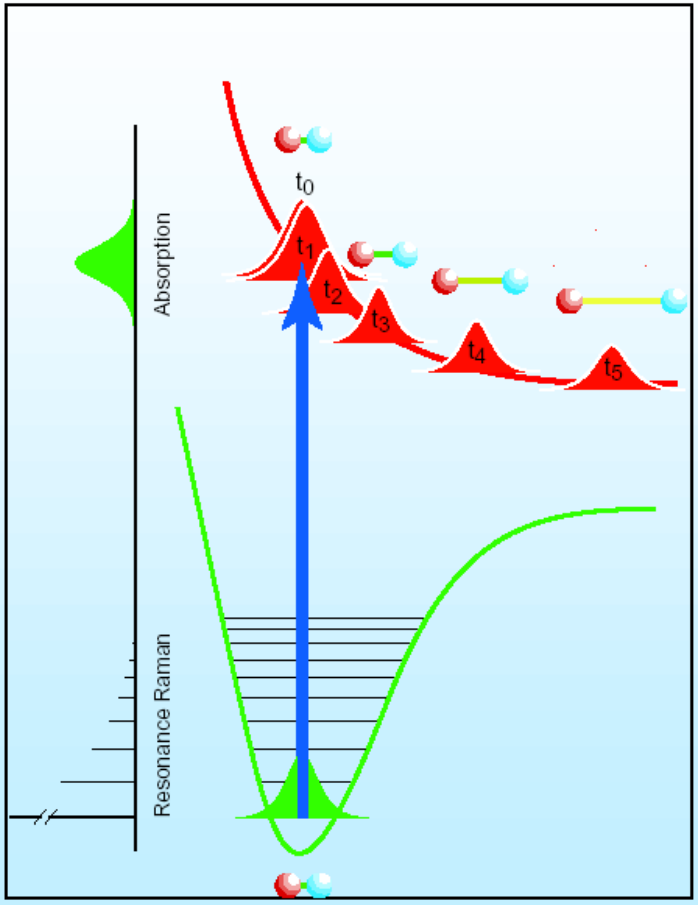
TOPAS: 270 nm ... 3 μm

WLC generator:
White light continuum

Mirrors, mirrors, ...



Wavepacket evolution in time and space



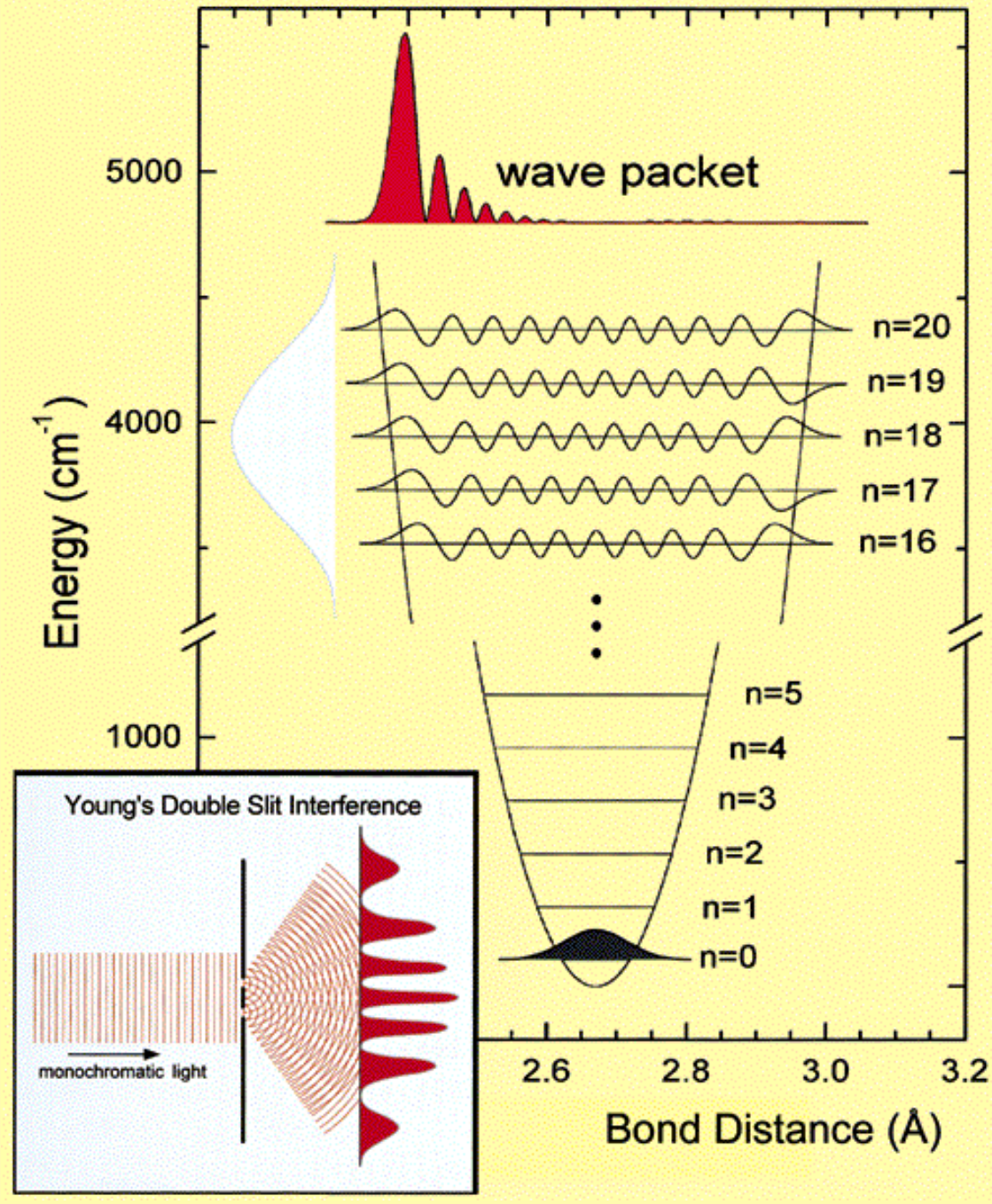
Photodissociation of an isolated diatomic molecule is the simplest of chemical reactions.

t=0 is easily defined

The initial wave-function is well defined

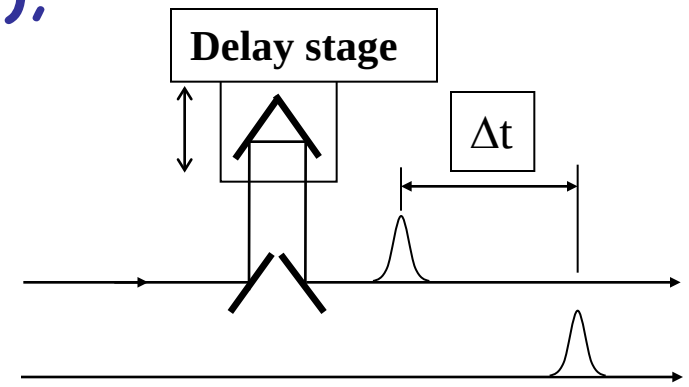
The wave-function remains localized throughout the reaction

investigate these reactions



Coherent, localized wave packet (de Broglie length ~0.04 Å) calculated for a diatomic molecule (iodine) for a 20 fs pulse. The contrast with the diffuse wave function limit (quantum number n) is clear. The inset shows Thomas Young's experiment (1801) with the interference which is useful for analogy with light.

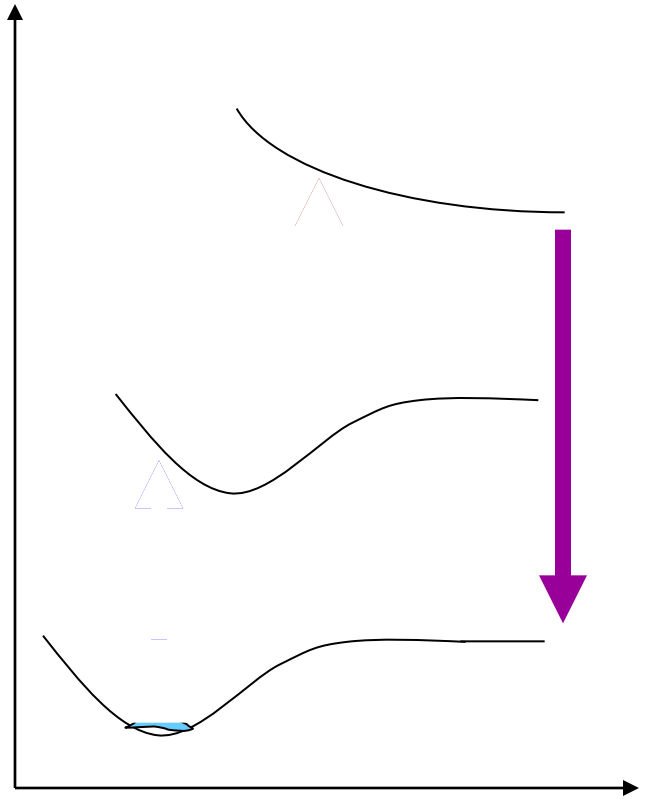
Molecular quantum dynamics (MQD), Wavepacket (WP) and fs laser spectroscopy



1. **MQD – nuclear vibration, rotation & change of electronic configuration.**

2. **WP – nonstationary superposition of a set of wavefunctions with fixed phase relationship.**

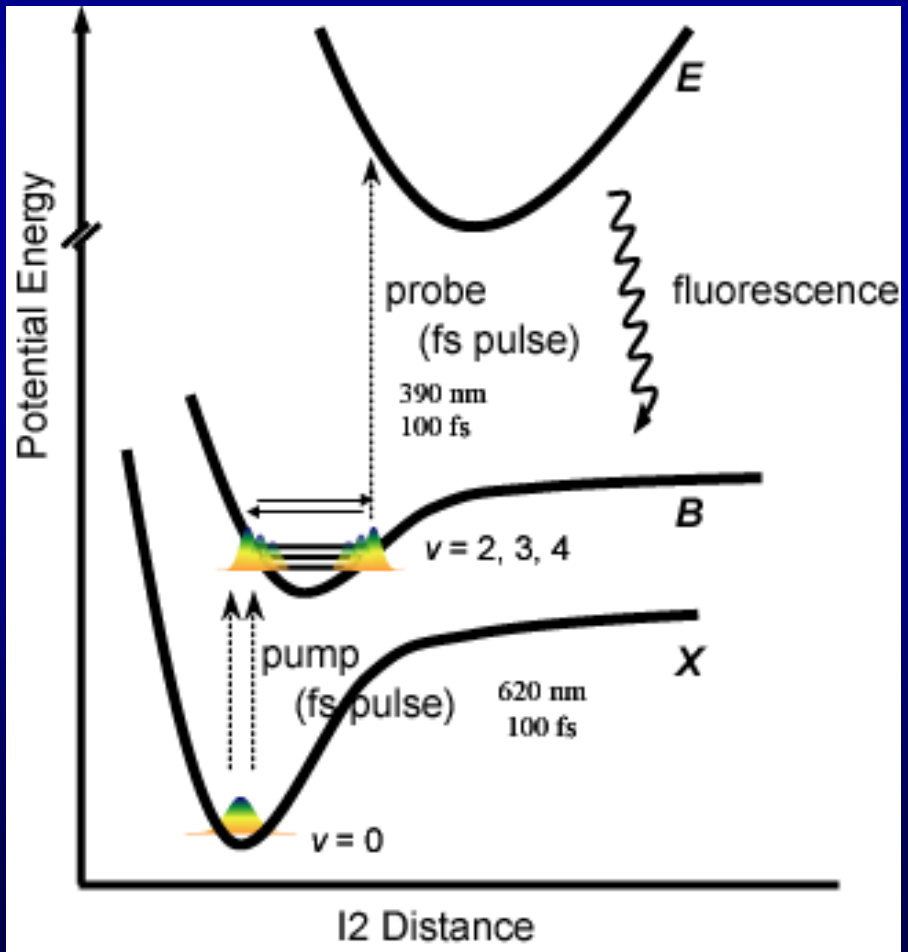
3. **Pump-probe technique – pump process, probe process, delay time and time zero.**

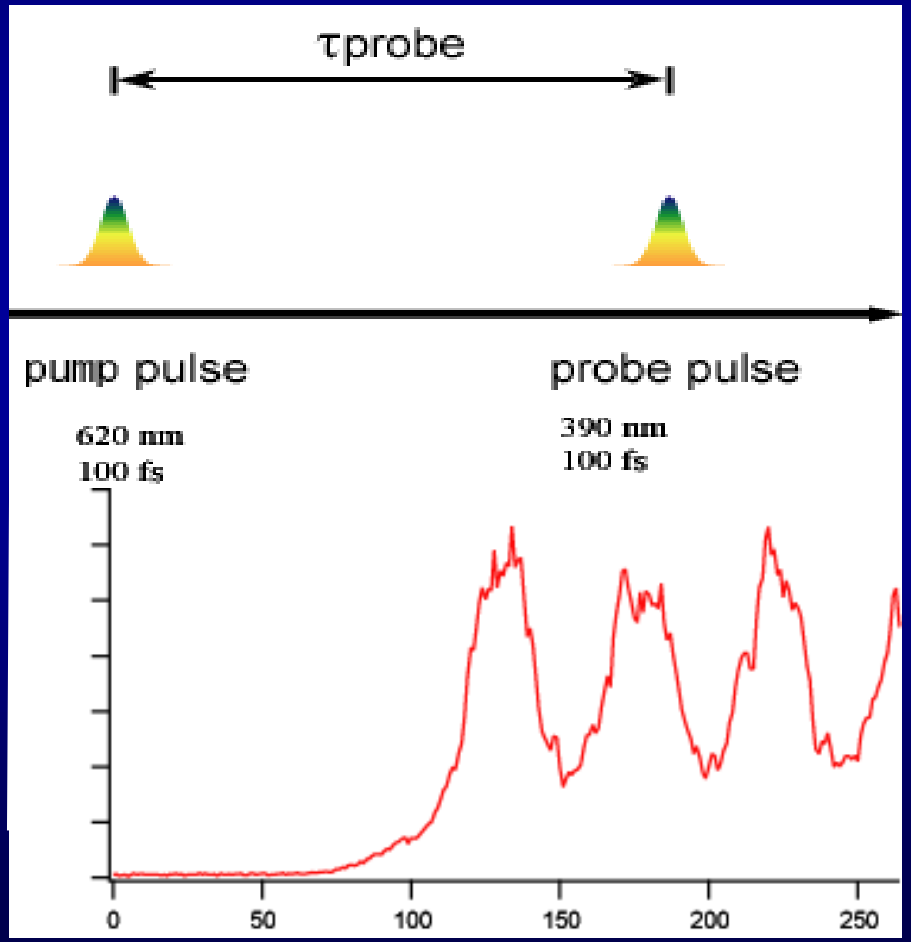


Zewail's Femtochemistry

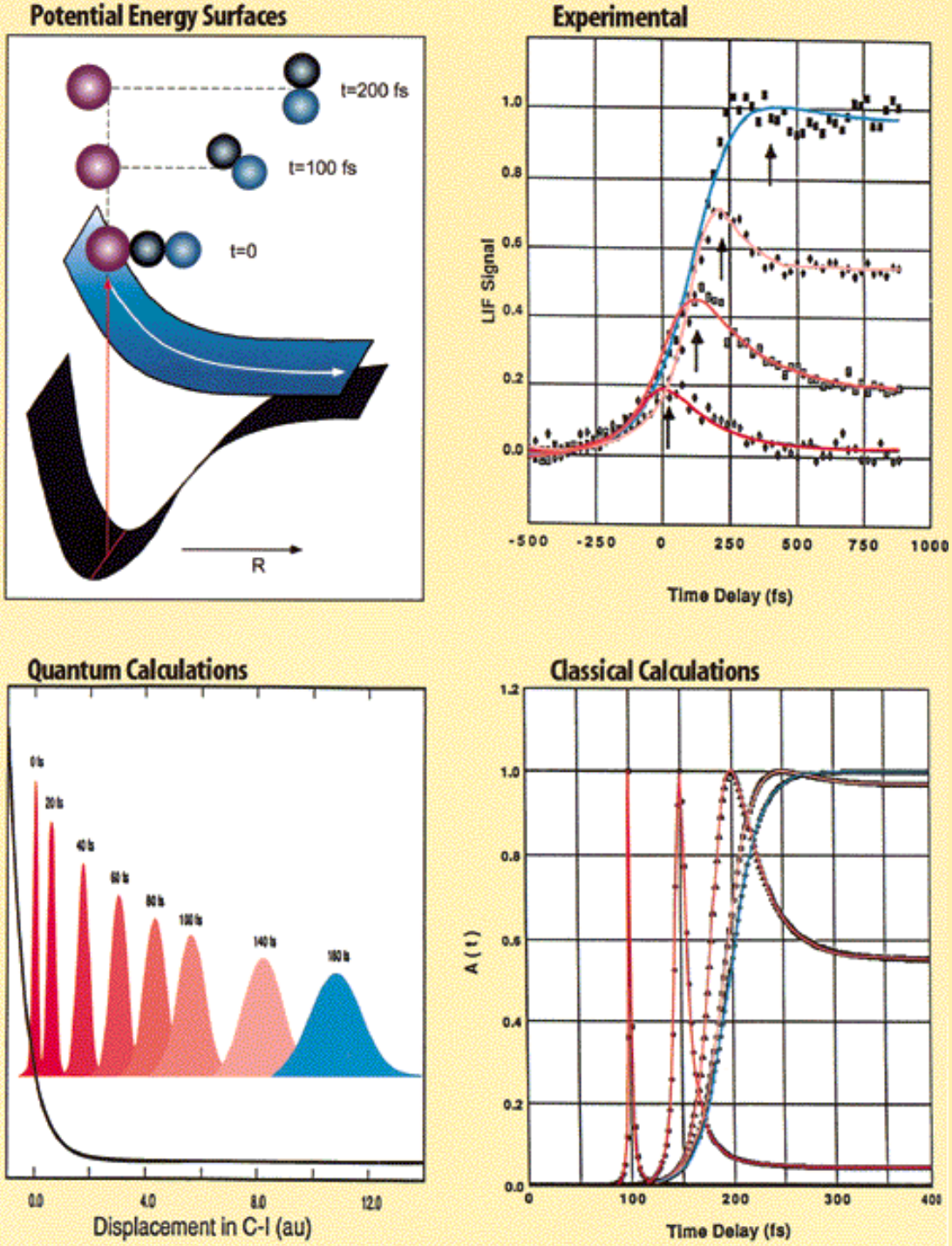
Femtosecond time-resolved pump-probe experiments made a nuclear motion of a molecular system visible.

"Conventional" time-resolved pump-probe measurement for vibrational motion in I_2 molecules



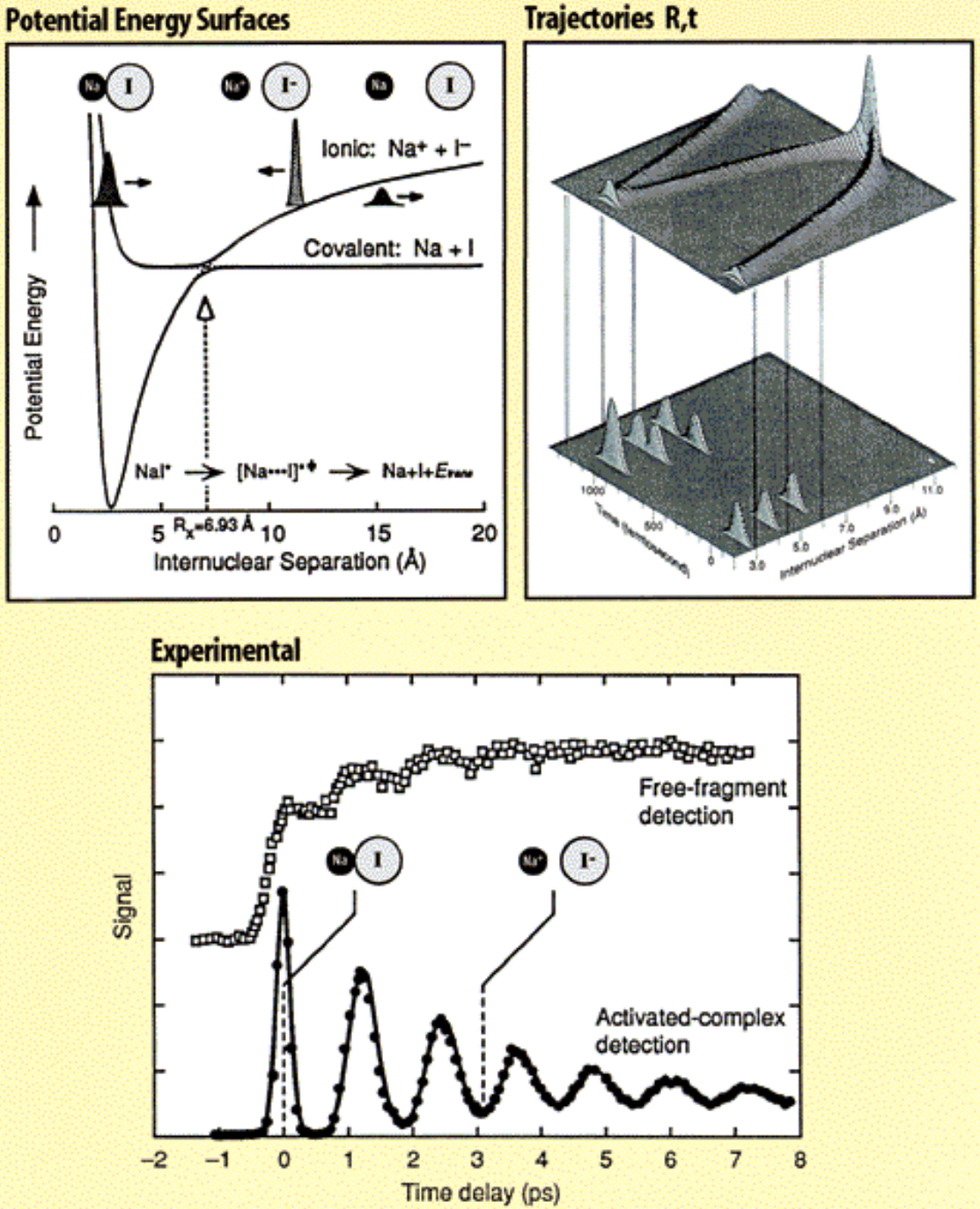


Revisit to Zewail's Novel prize experiment.



Figure

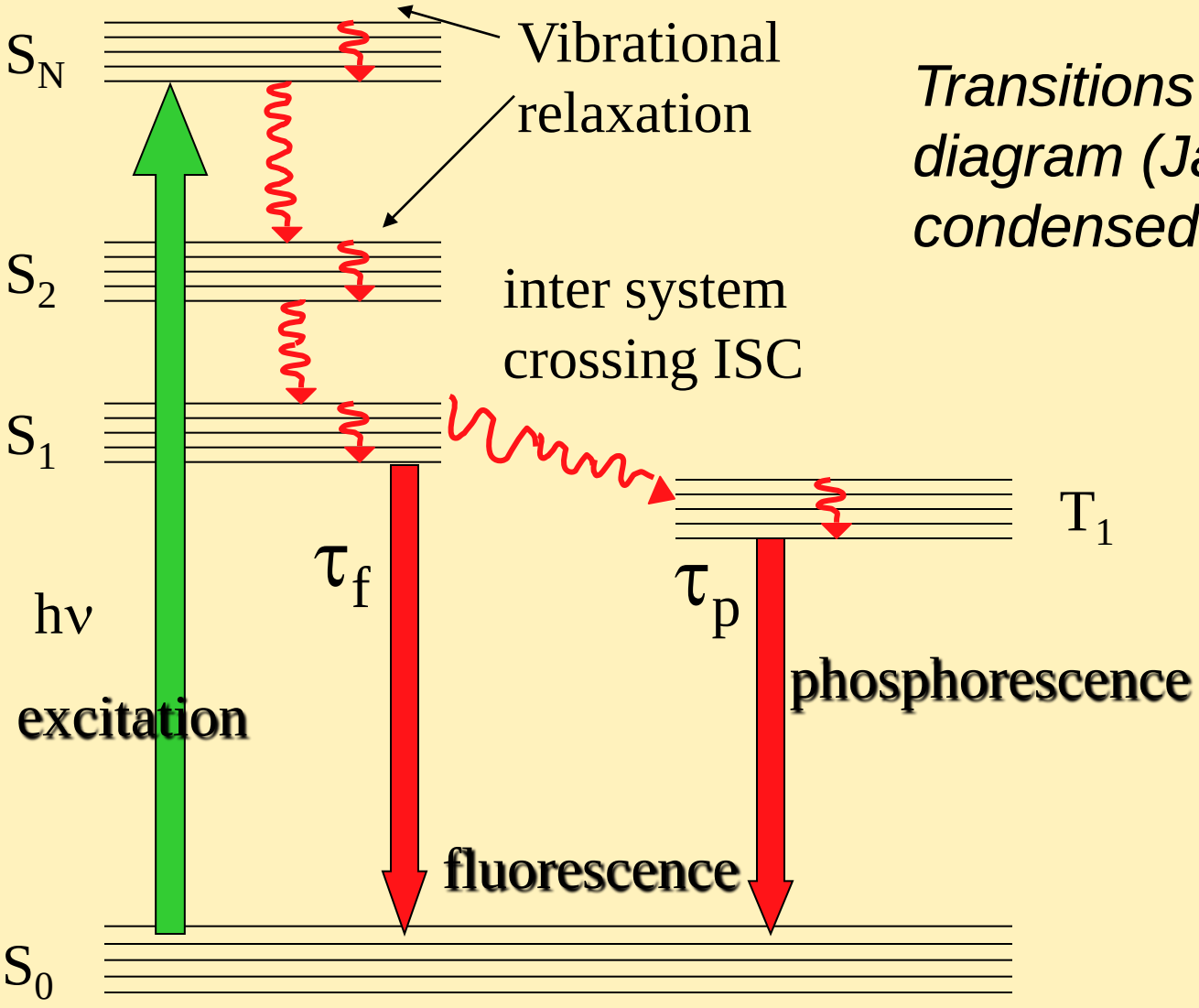
Femtochemistry of the ICN reaction, the first to be studied. The experimental results show the probing of the reaction in the transition-state region (rise and decay) and the final CN fragment (rise and leveling) with precise clocking of the process; the total time is 200 fs. The I fragment was also detected to elucidate the translational energy change with time. Classical and quantum calculations are shown.



Figure

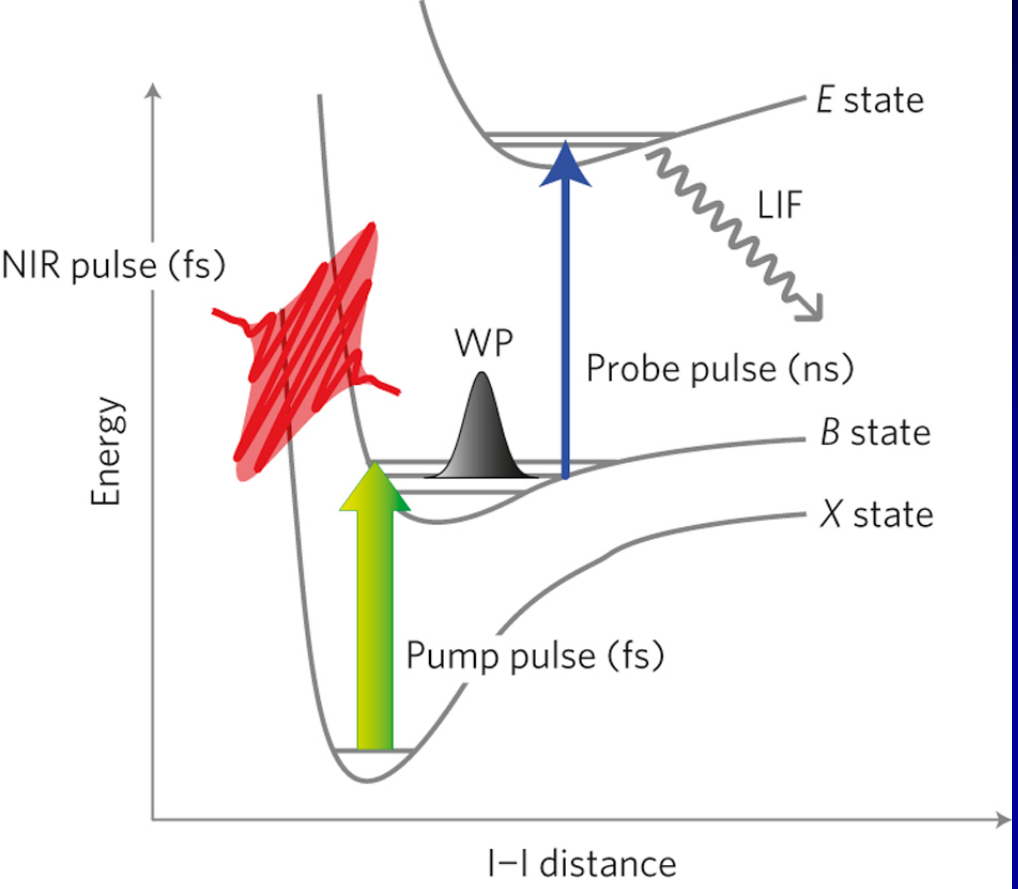
Femtochemistry of the NaI reaction, the paradigm case. The experimental results show the resonance motion between the covalent and ionic structures of the bond, and the time scales for the reaction and for the spreading of the wave packet. Two transients are shown for the activated complexes in transition states and for final fragments. Note the "quantized" behavior of the signal, not simply an exponential rise or decay of the ensemble. The classical motion is simulated as trajectories in space and time.

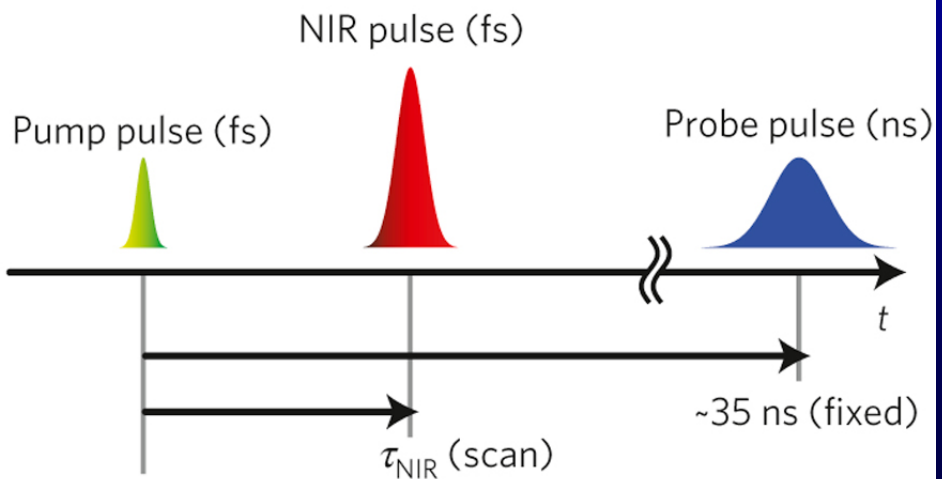
Basic photophysics



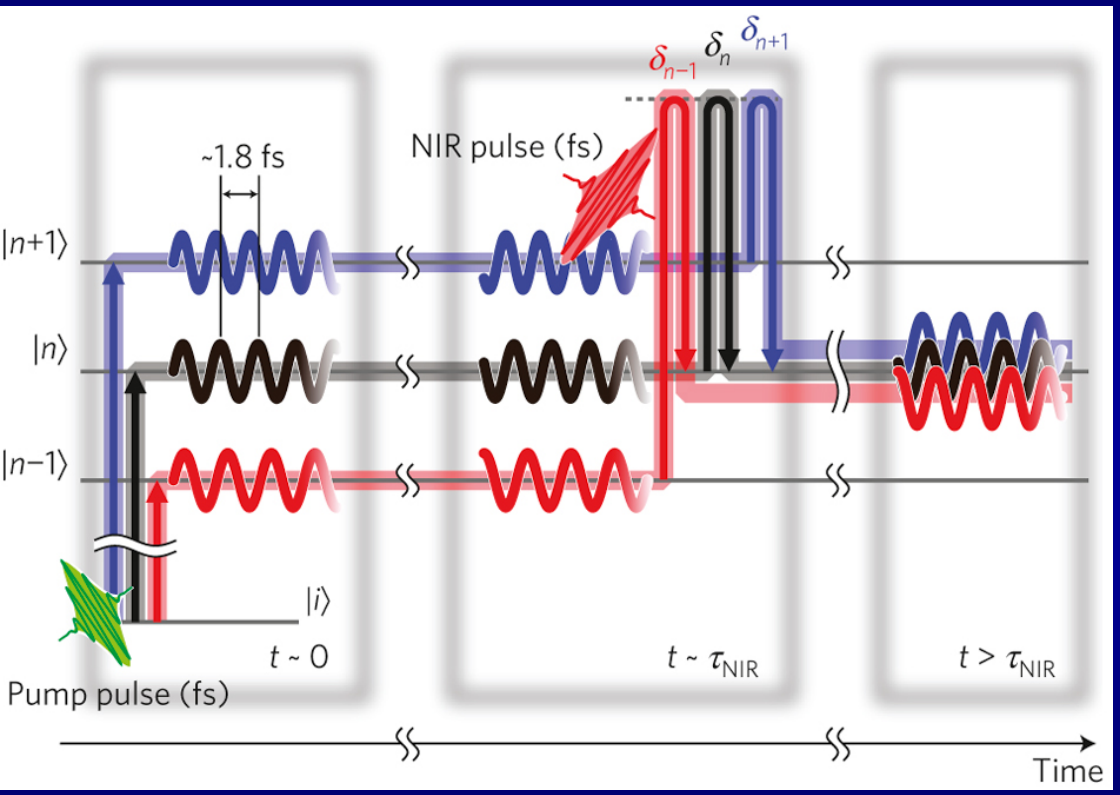
Transitions in an energy diagram (Jablonski) of the condensed phase

Wellenpakete und Interferenz

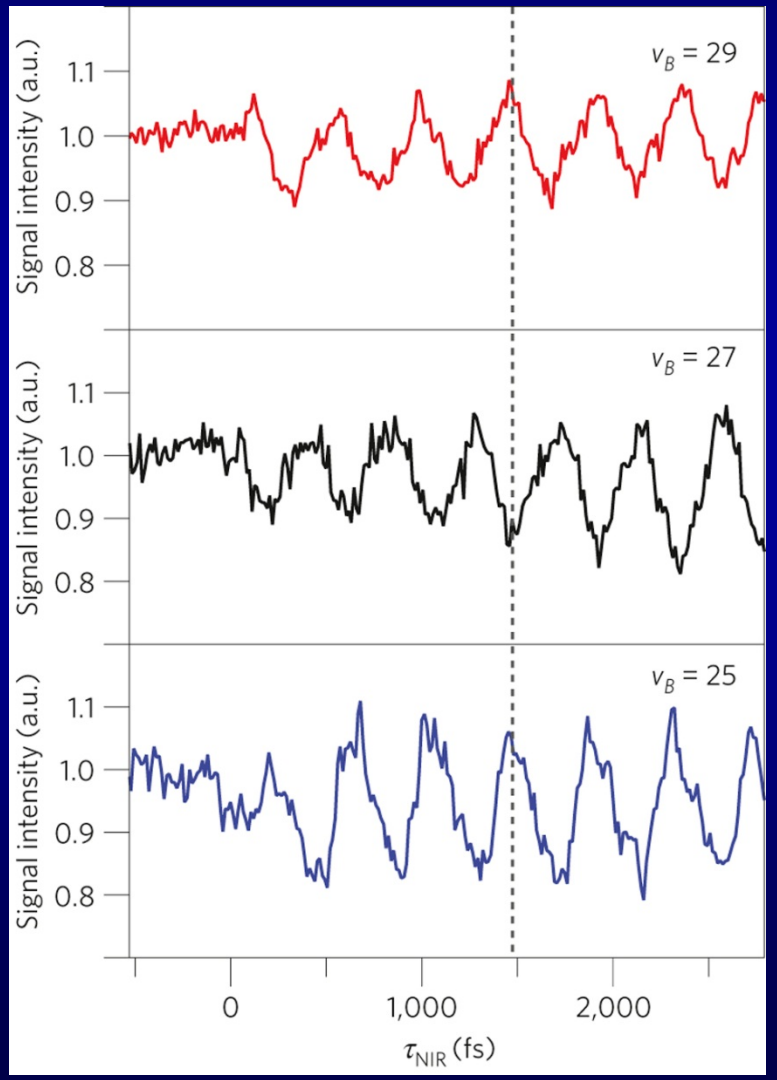




Strong-laser-induced quantum interference
Haruka Goto, Hiroyuki Katsuki, Heide Ibrahim, Hisashi Chiba **&** Kenji Ohmori
Nature Physics,7 (2011) 383–385
doi:10.1038/nphys1960

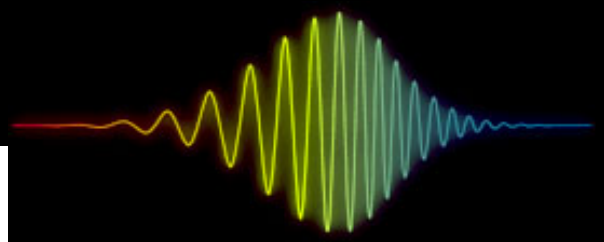


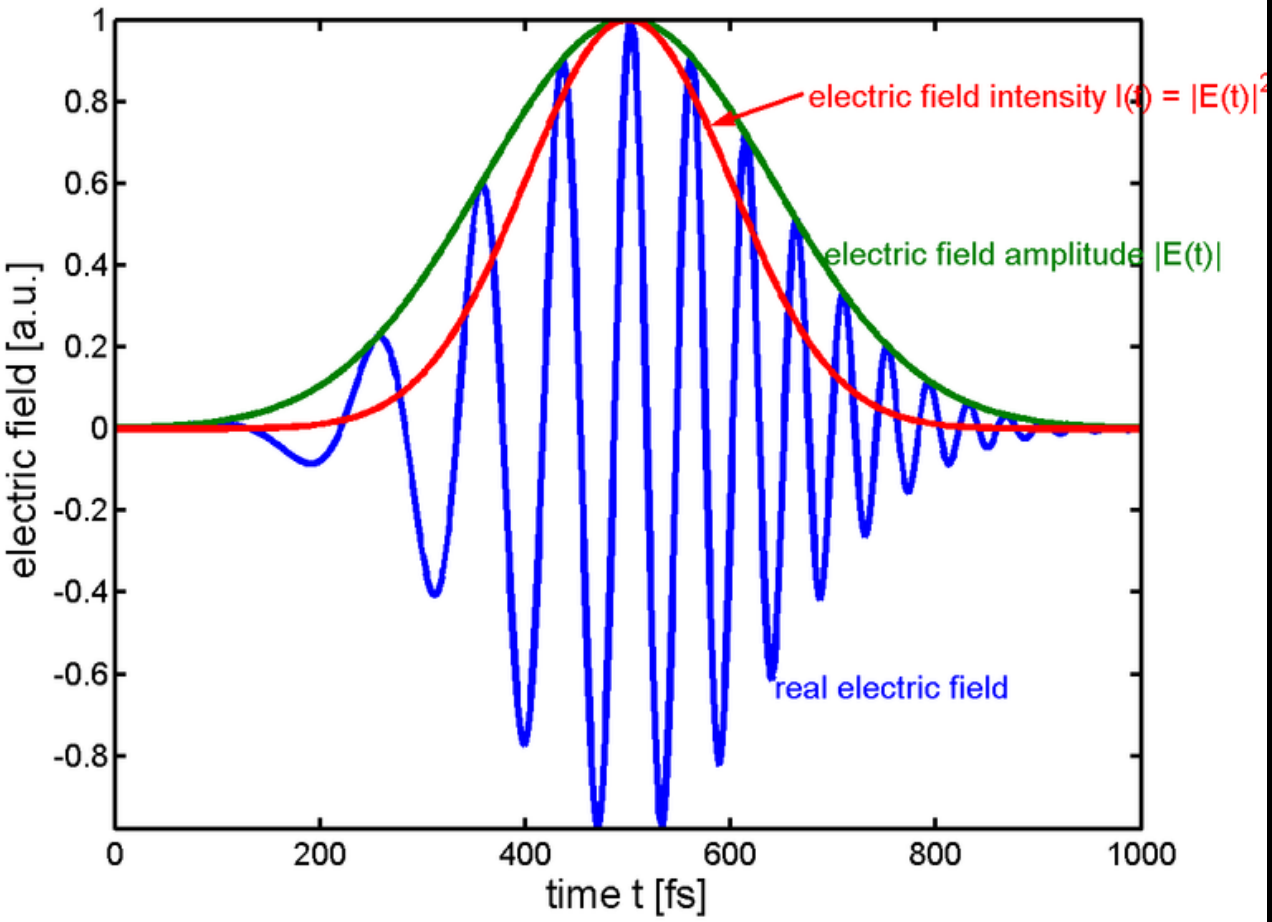
Die möglichen Wege über |n-1>, |n> und |n+1> interferieren miteinander.



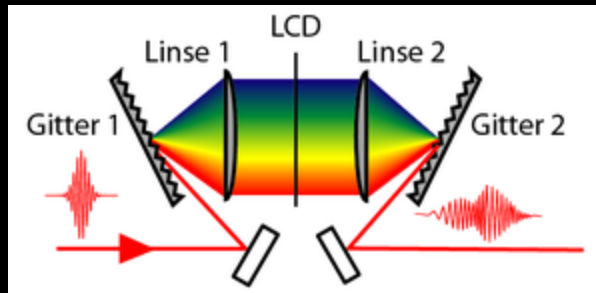
The road ahead

A chirp…

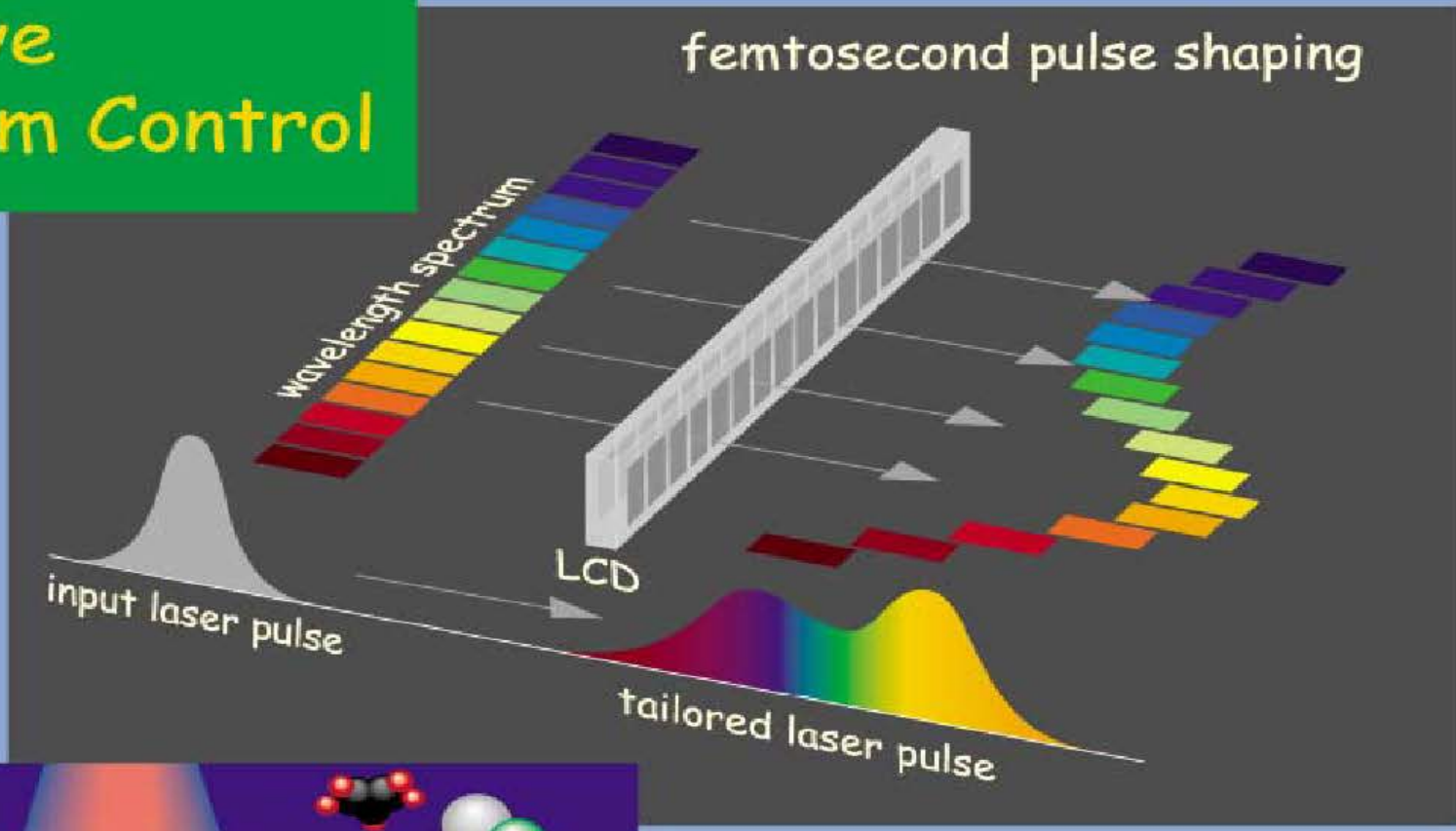


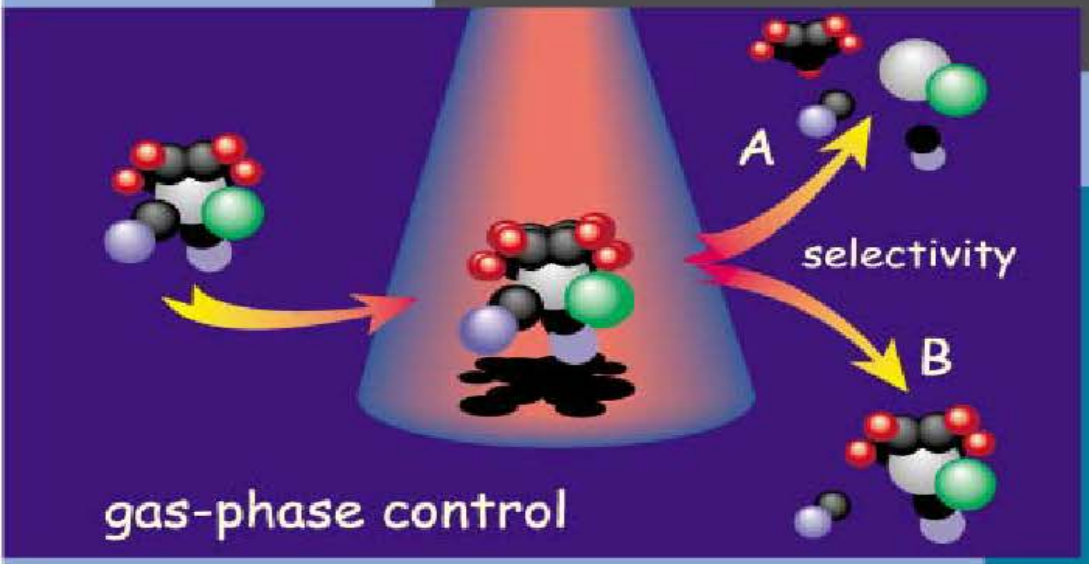


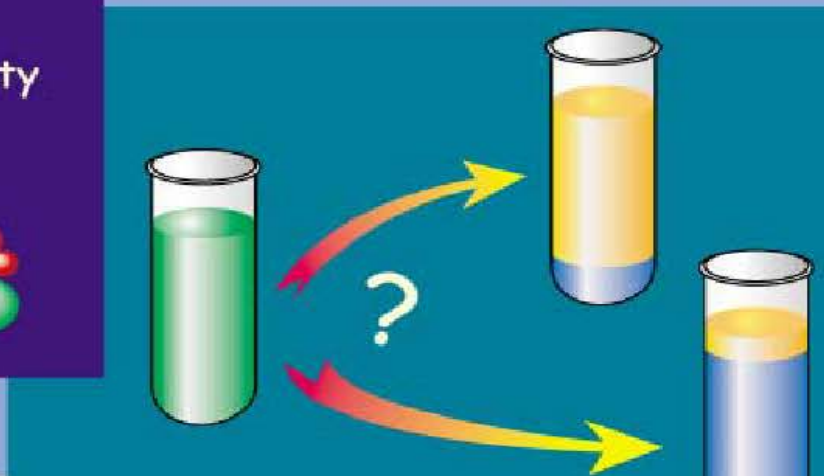
and it‘s creation…



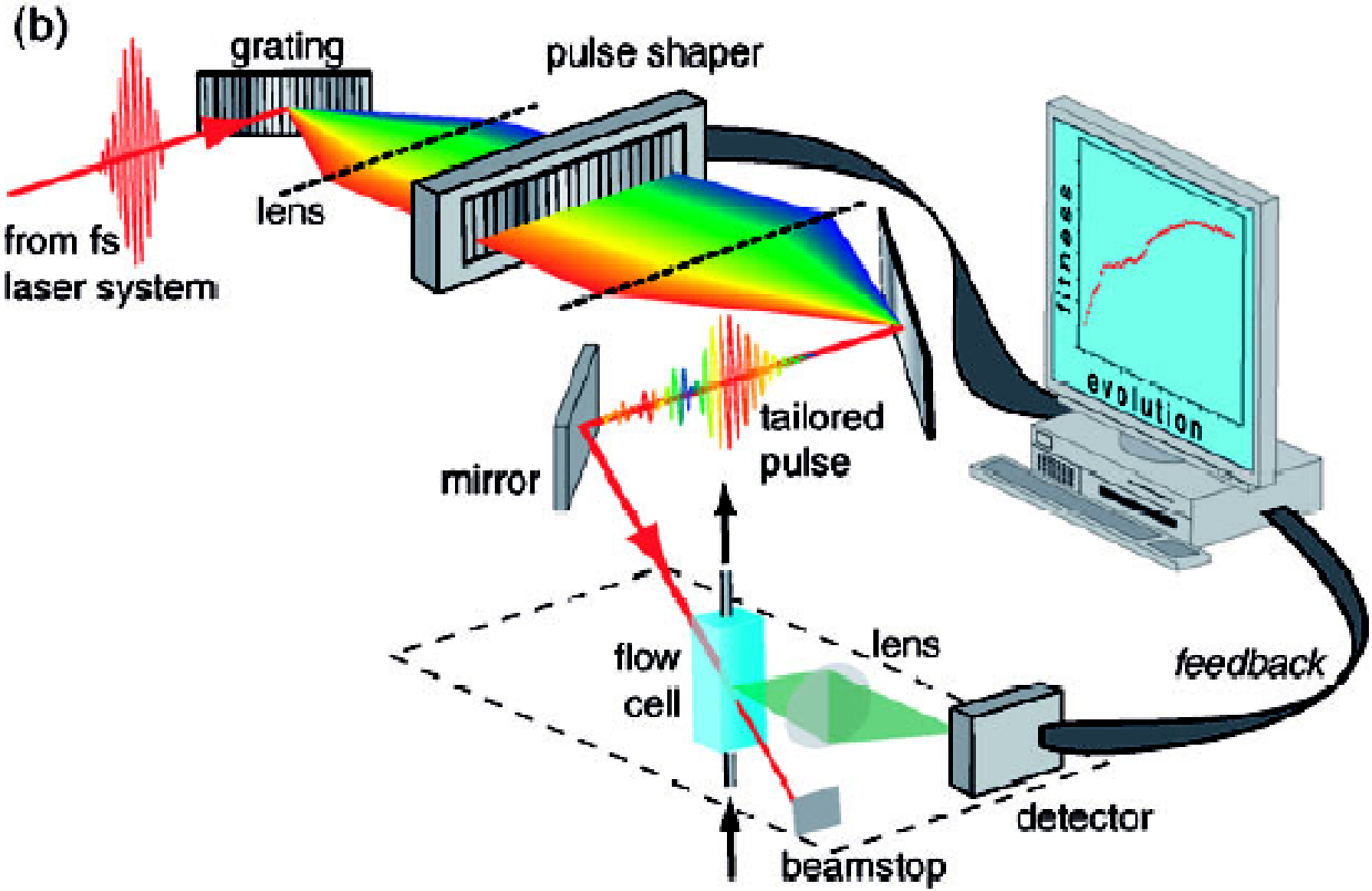
Adaptive Quantum Control



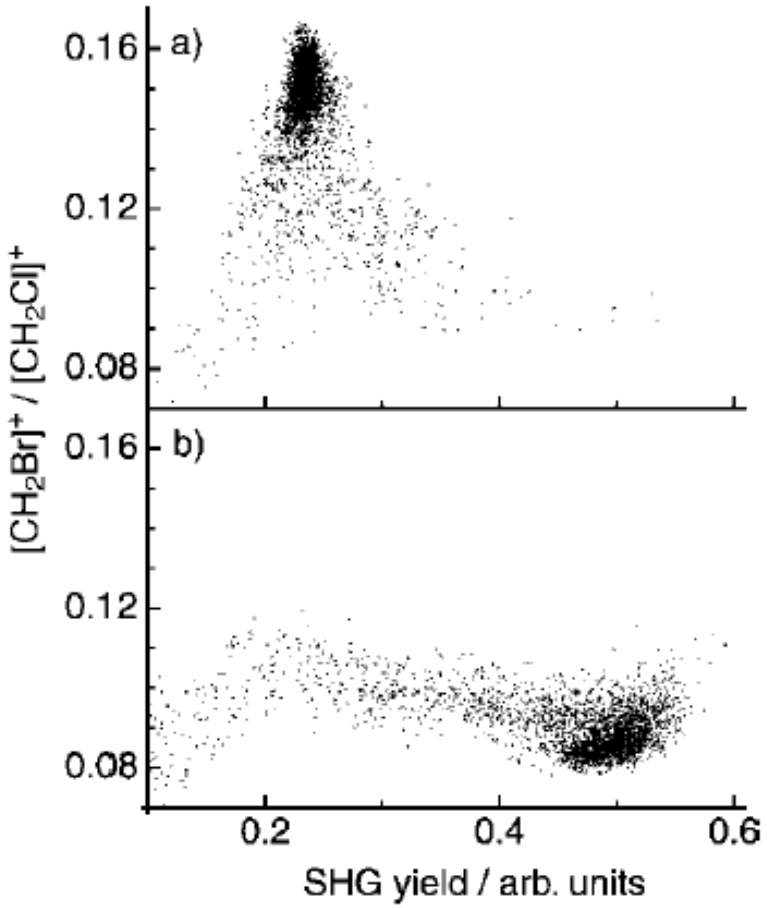




Adaptive Quantum Control



Quantum control



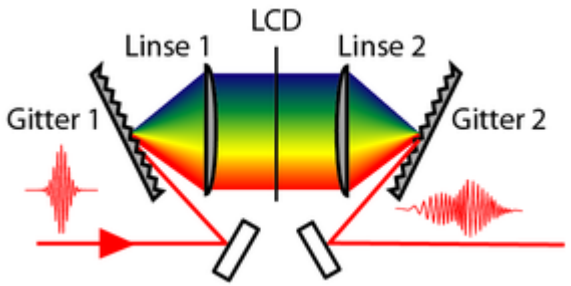


Figure 12. *Correlation diagrams for selective bond breakage in CH_2BrCl. The value of the $[CH_2Br]^+/[CH_2Cl]^+$ branching ratio is plotted versus SHG yield for all laser pulses explored in the two optimizations of a) $[CH_2Br]^+/[CH_2Cl]^+$ maximization and b) SHG maximization.*

T. Brixner, G. Gerber

CHEMPHYSCHEM 2003, 4, 418 - 438

Quantum control

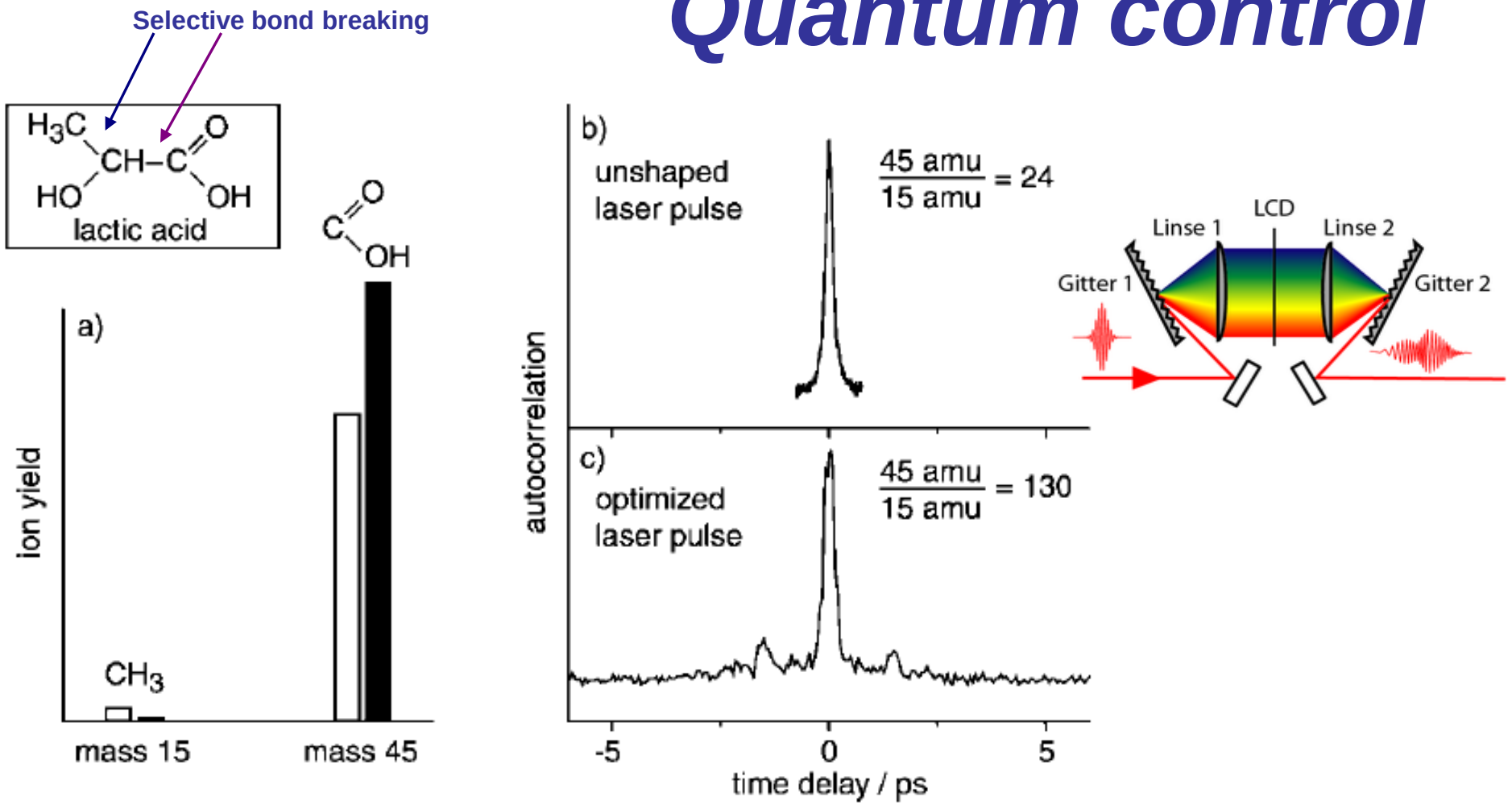
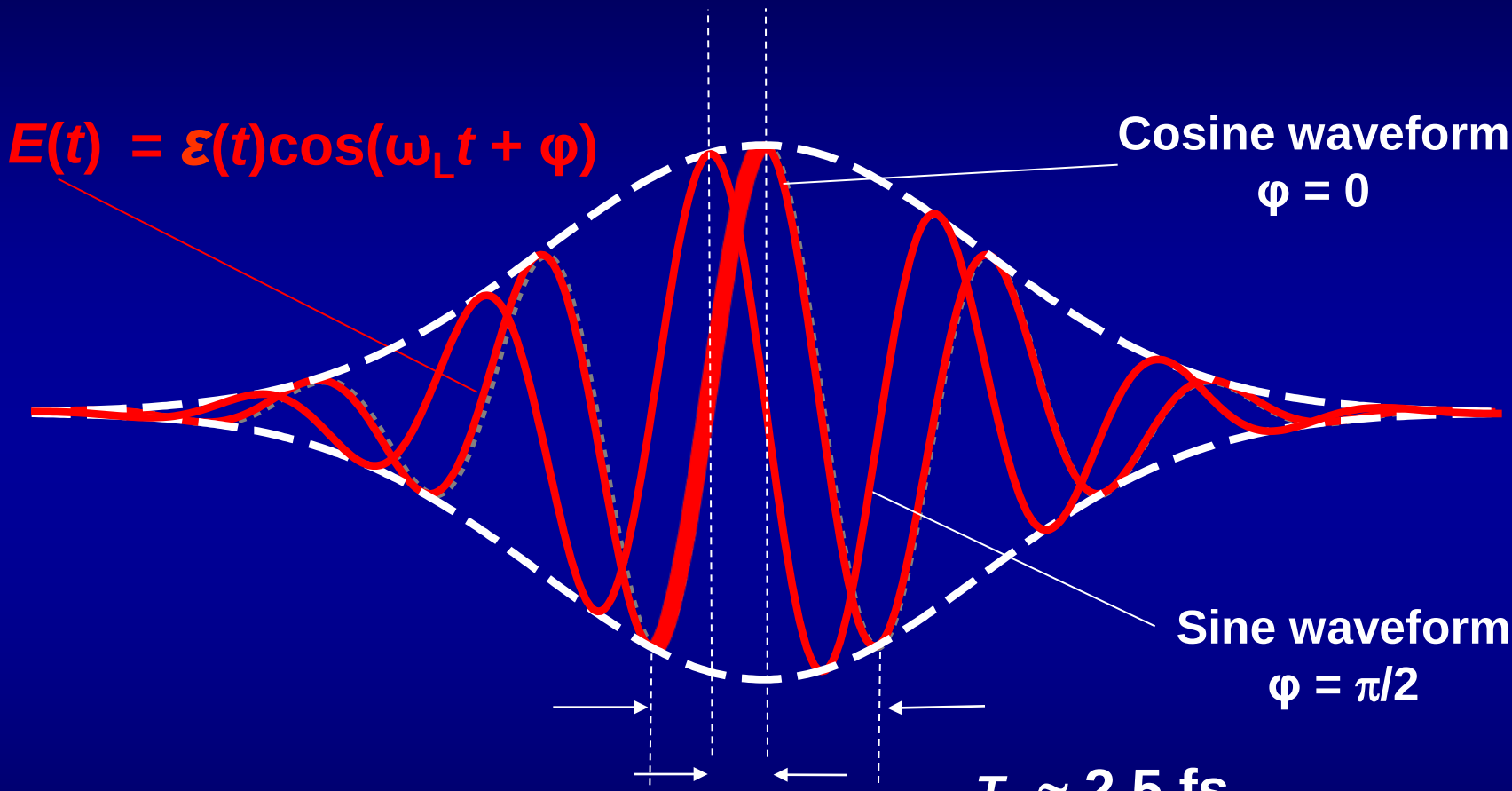


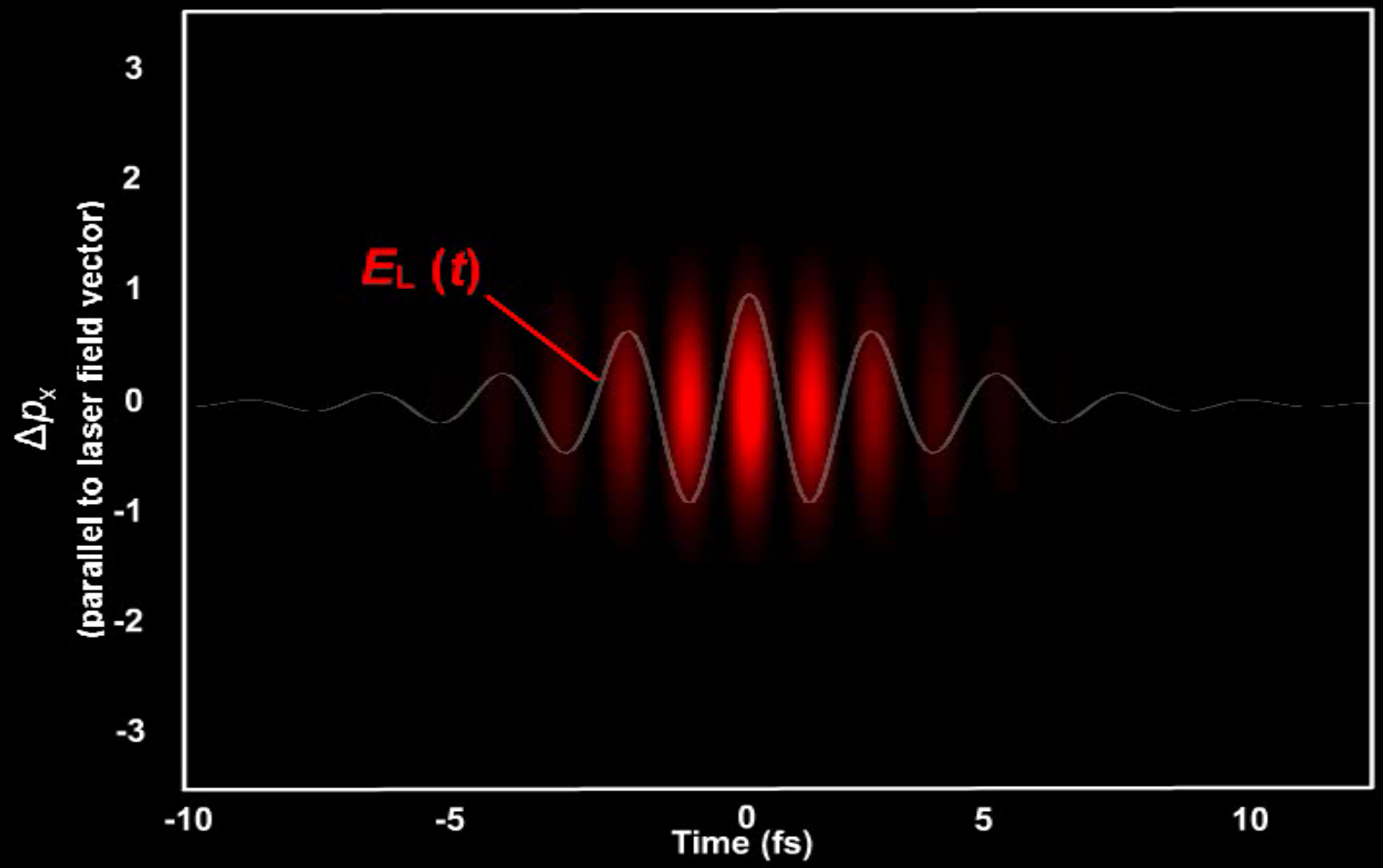
Figure 13. *Selective bond breaking in lactic acid. The desired fragment is [COOH], the undesired fragment is [CH_3]. a) Absolute ion yields of these two fragments are plotted for unmodulated laser pulses (b) and for laser pulses where the $COOH^+/CH_3^+$ ratio was maximized (c). The branching ratio is increased by over a factor of 5 from 24 to 130. Intensity autocorrelations are shown after many-parameter $[COOH]^+/[CH3]^+$ maximization.*

Attosecond metrology: requires *controlled* variation of a physical quantity within 1 femtosecond

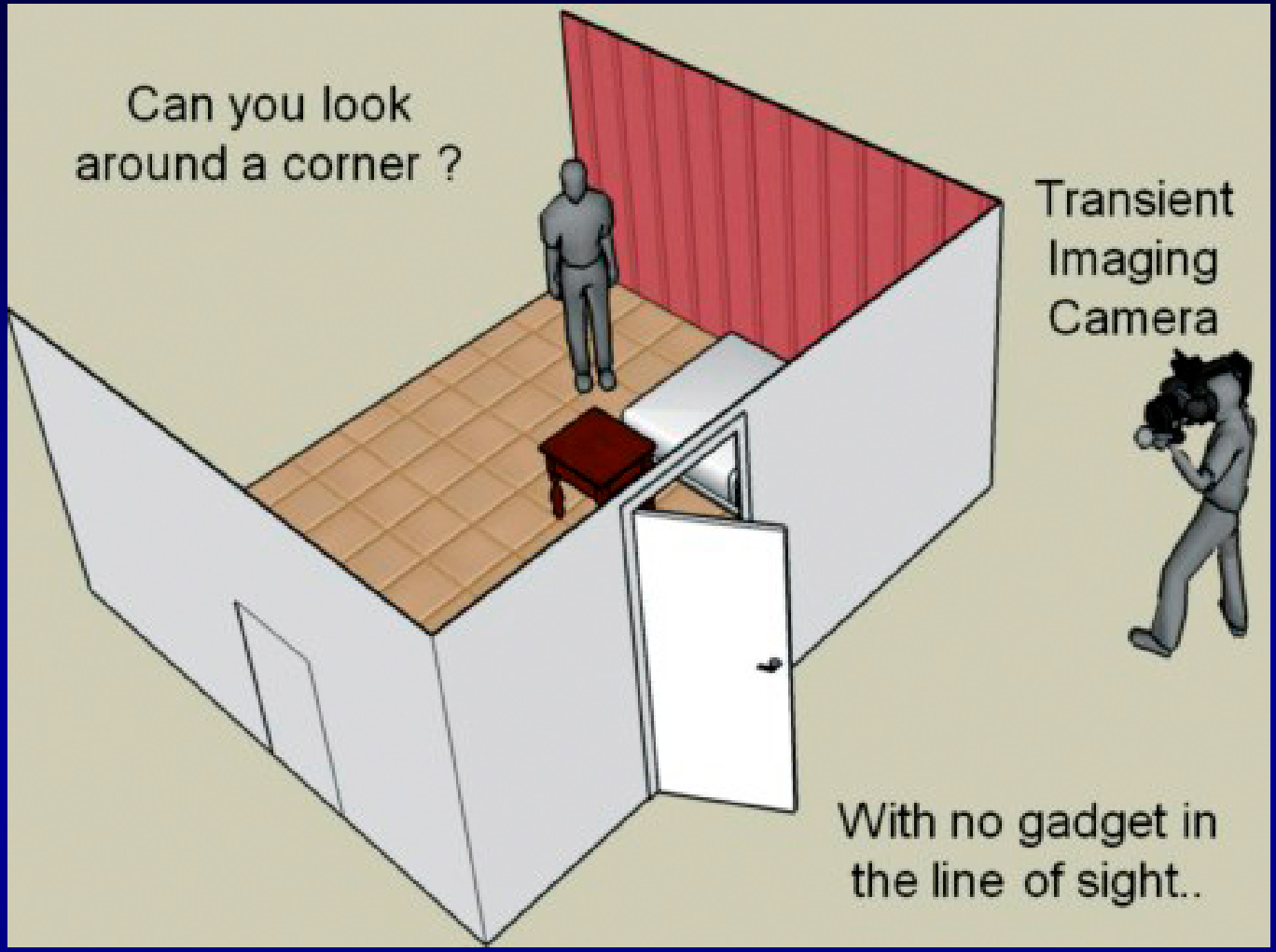


Requires measurement & control of φ

Momentum transfer depends on instant of electron release within the wave cycle



$$\Delta p(t) = e\int_{t}^{\infty} E_L(t')dt' = eA_L(t)$$



Über ihren Blitz schickt eine Kamera extrem kurze, genau gerichtete Lichtpulse aus, die von der Tür abprallen und von dort aus in alle Richtungen verstreut werden. Teils gelangen die Photonen direkt zur Kamera zurück, teils dringen sie auch in den Raum ein und erfassen unter anderem die Person. Ein Bruchteil dieser Teilchen erreicht wieder die Tür, die der Kamera ja bereits bekannt ist, wiederum nur ein Teil davon gelangt zurück in die Linse und wird von einem Computer analysiert.

High resolution experiments

$$A(q_A)+B(q_B,\vec{v})\rightarrow C(q_C,\vec{v})+D(q_D,\vec{v})$$

- Präparation der Edukte
  Einfluss der Translation und der inneren Energie, wie Vibration, Rotation, Feinstrukturzustände
- Beobachtung der Produkte
  in den einzelnen Quantenzuständen, Geschwindigkeitsvektoren (räumliche Verteilung)

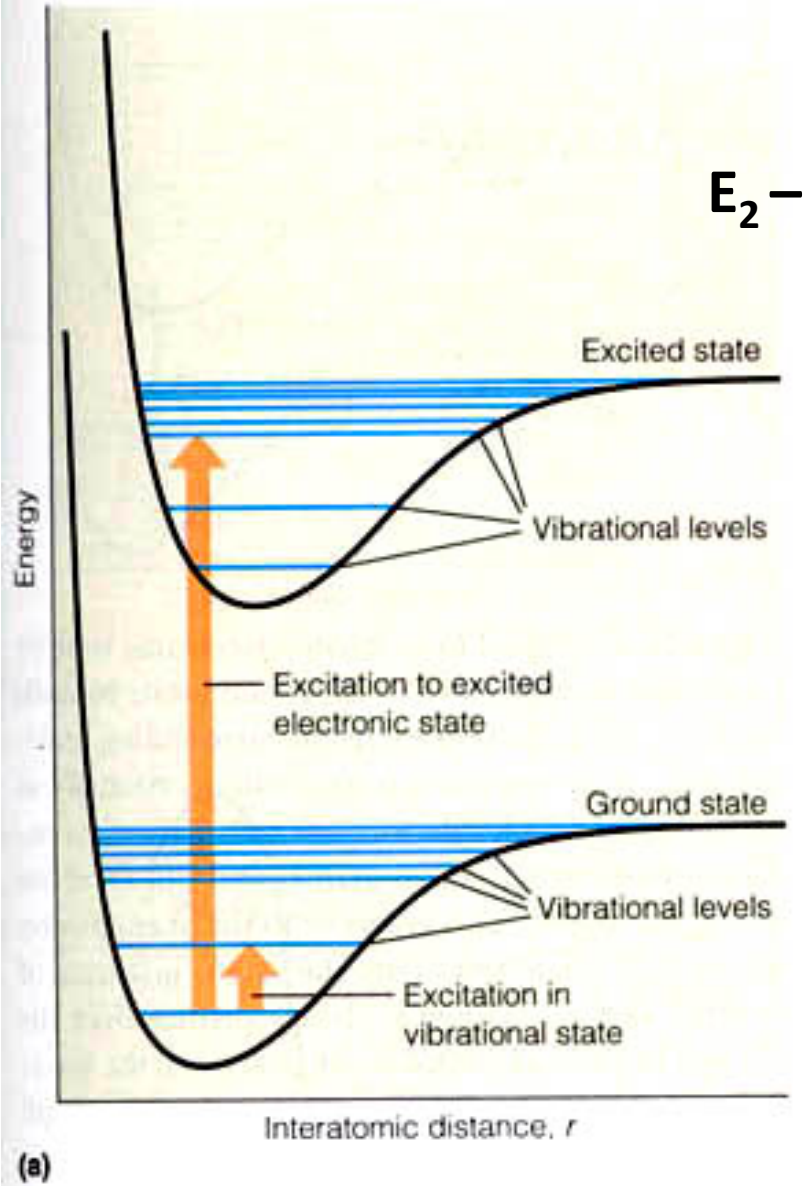
Detection Techniques - Requirements

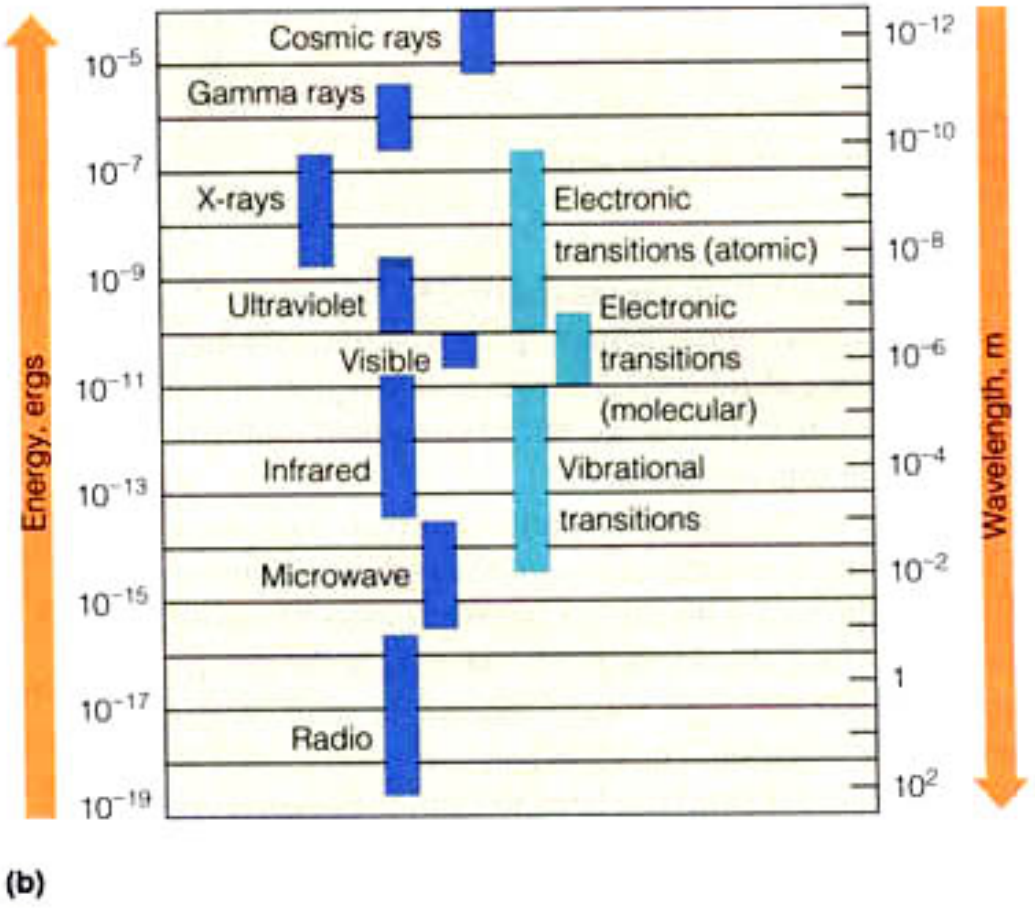
- Selectivity
- Sensitivity
- Dynamic Range
- No Interference (with surounding)
- Universal
- Time Resolution (to observe nascent products)

Laser & Spectroscopy

Spektroskopie

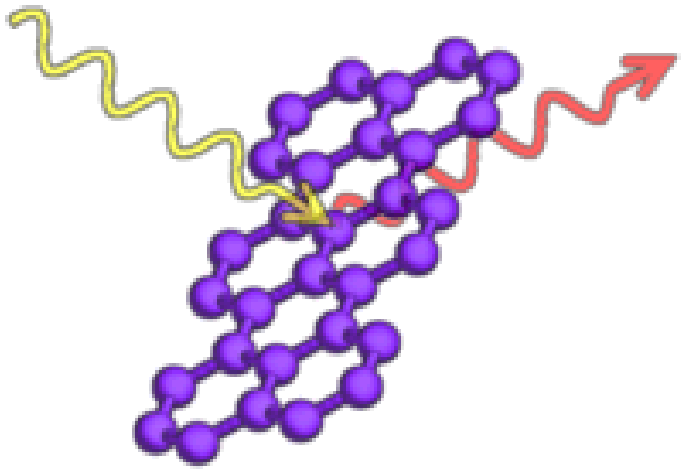
$$E_2 - E_1 = h\nu, \quad \lambda = {}^{c}/_{\nu}$$





Was ist hier falsch?

Solch schöne Bilder findet man für gewöhnlich in Lehrbüchern über die Absorption oder Fluoreszenz eines Moleküls:



Properties of Laser Radiation

1. The laser light can be very monochromatic and can be effectively used for **high resolution spectroscopy**: $\Delta\lambda/\lambda \approx 10^{-15}$.

2. The laser beam can be of very low divergent (spatial coherence), i.e. its diameter is increased only slowly in space. With laser beams the diffraction limit is reached:

$$\theta \approx 2\lambda / \pi D$$

It is possible to focus a laser beam of diameter D on a spot of the diameter d:

$$d \approx 2\lambda f / \pi D \approx \lambda / 2$$

where, f denotes the focal distance of the lens.

3. Extremely short laser pulses can be produced. Pulse durations in the **nanosecond** (10^{-9}), **picosecond** 10^{-12}, and **femtosecond** 10^{-15} range are now commercially available. Particularly, **femtosecond** laser pulses are of great importance, because they allow to investigate chemical processes **in the real-time domain**.

4. High power output. The continuous CO_2 lasers can produce a high power output of up to 100 kW. These technological lasers are now widely used in industry and military. The pulsed lasers, especially those operating in the pico- and femtosecond time-domain can have peak powers from **10^9 to 10^{12} Watt.** High power pulsed lasers are widely used for investigation of **nonlinear** and **multiple photon processes**.

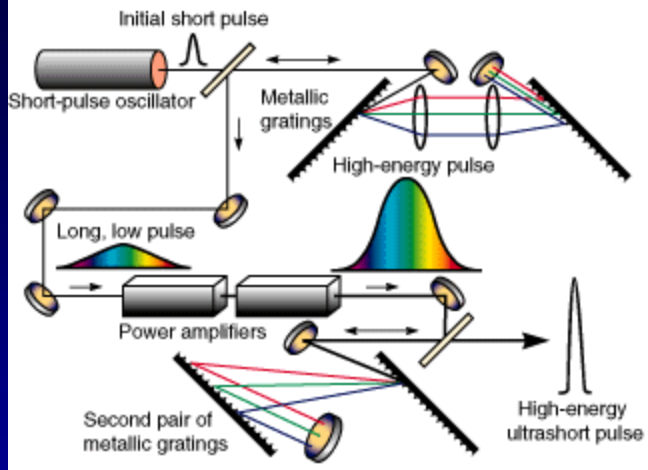
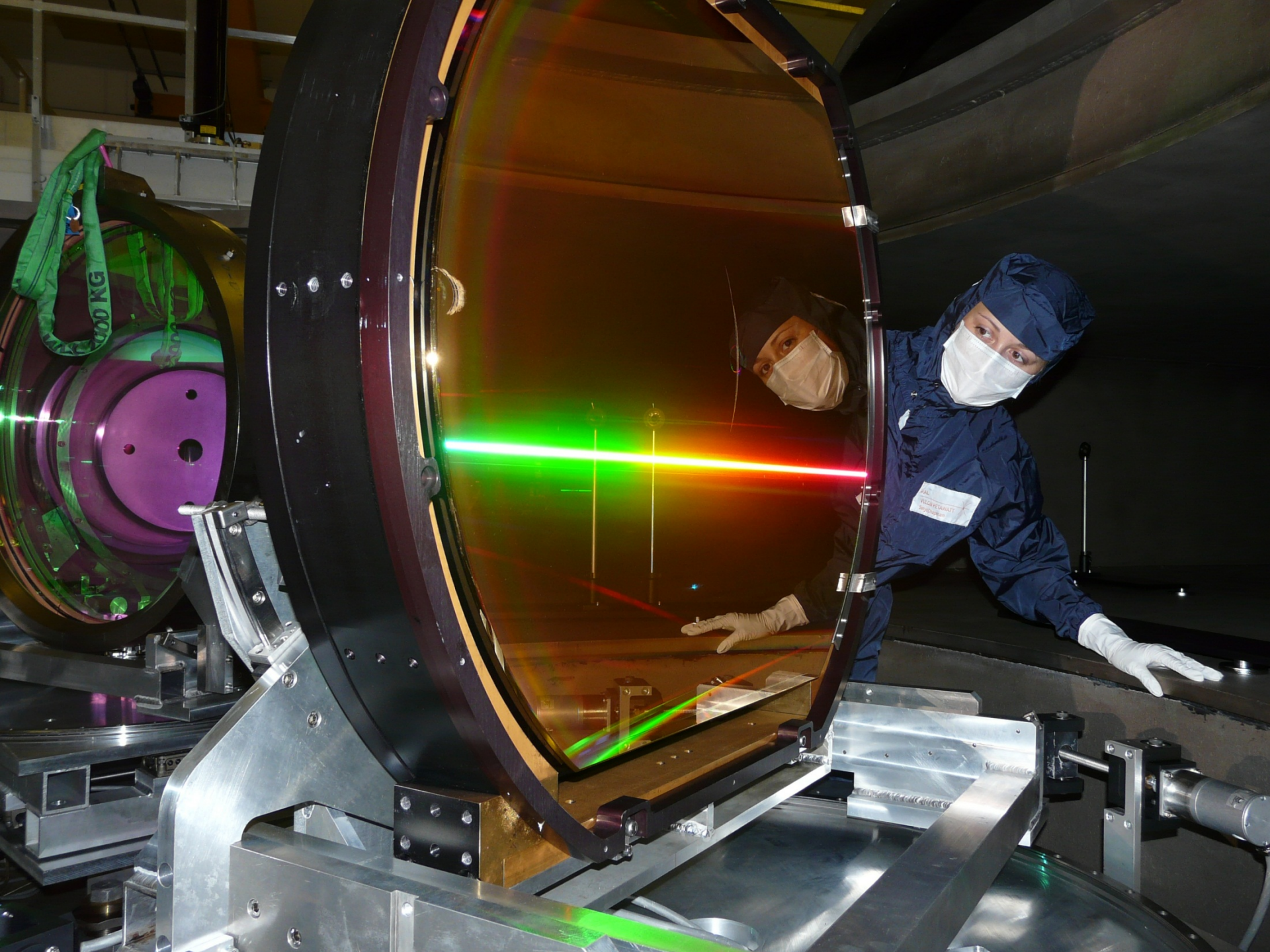
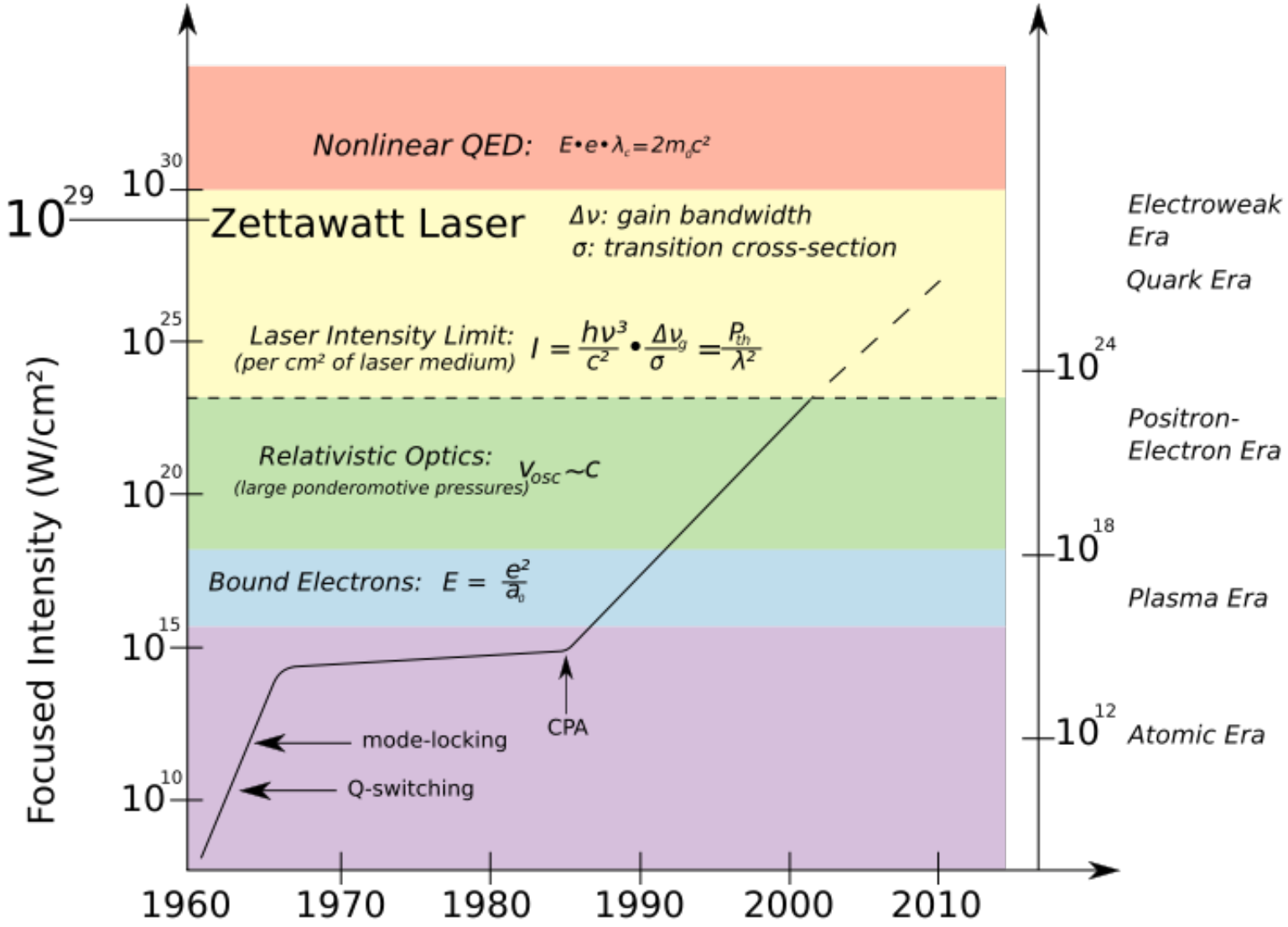


Figure 3. The concept of how chirped-pulse amplification and other new technologies enable the production of the petawatt (quadrillion-watt) pulses.


000 KG

Laser (pulse) power



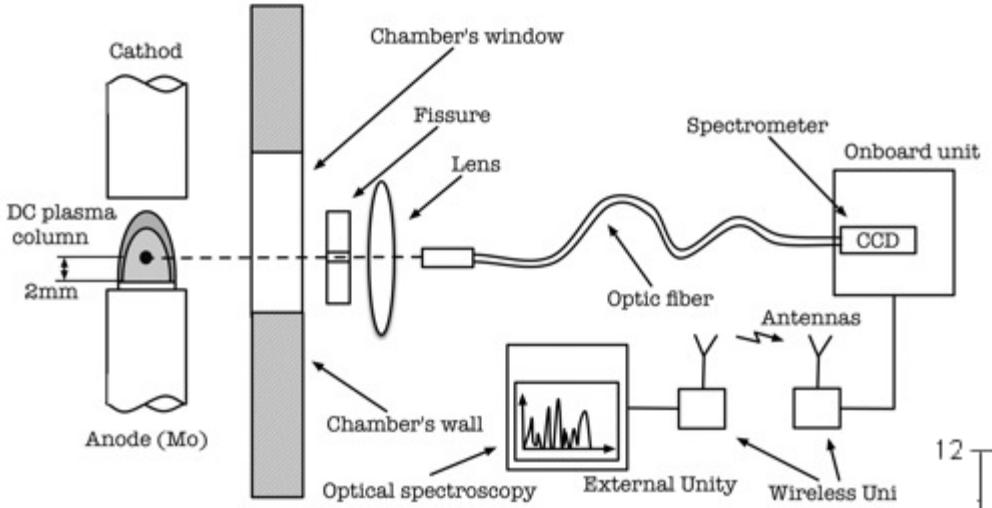
SI-Präfixe

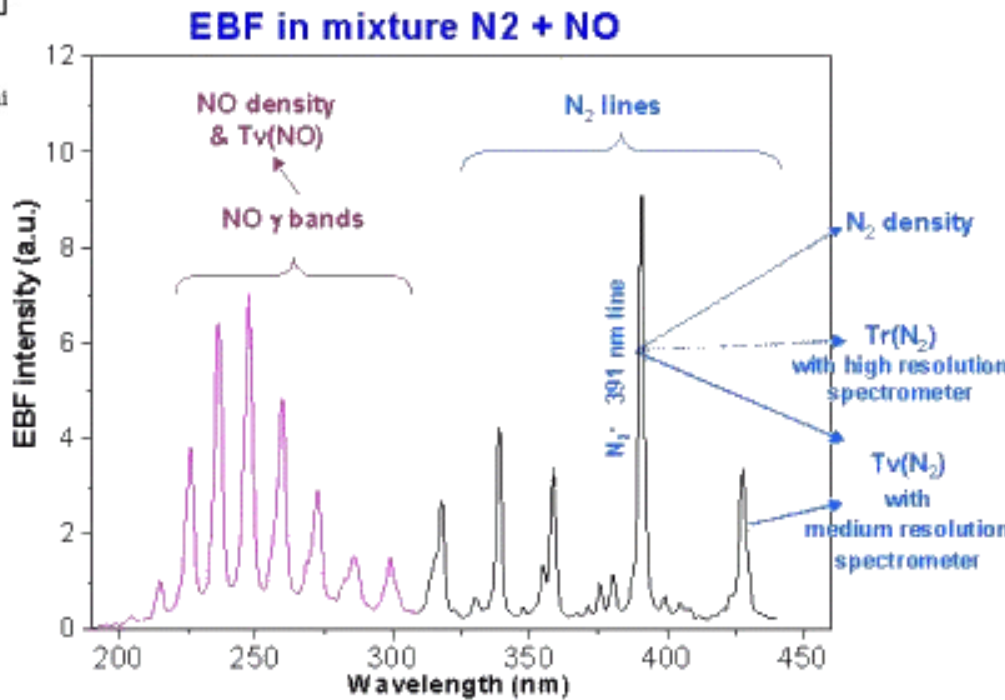
Factor	Name	Symbol	Factor	Name	Symbol
10^{1}	deca	da	10^{-1}	deci	d
10^{2}	hecto	h	10^{-2}	centi	c
10^{3}	kilo	k	10^{-3}	milli	m
10^{6}	mega	M	10^{-6}	micro	µ
10^{9}	giga	G	10^{-9}	nano	n
10^{12}	tera	T	10^{-12}	pico	p
10^{15}	peta	P	10^{-15}	femto	f
10^{18}	exa	E	10^{-18}	atto	a
10^{21}	zetta	Z	10^{-21}	zepto	z
10^{24}	yotta	Y	10^{-24}	yocto	y

Detection Techniques

- Optical Emission Spectroscopy (OES)
- Absorption techniques
- Photoacoustic Spectroscopy
- Laser induced fluorescence (LIF)
- Resonant Enhanced Multi Photon Ionisation (REMPI)

OES:
Optical Emission Spectroscopy

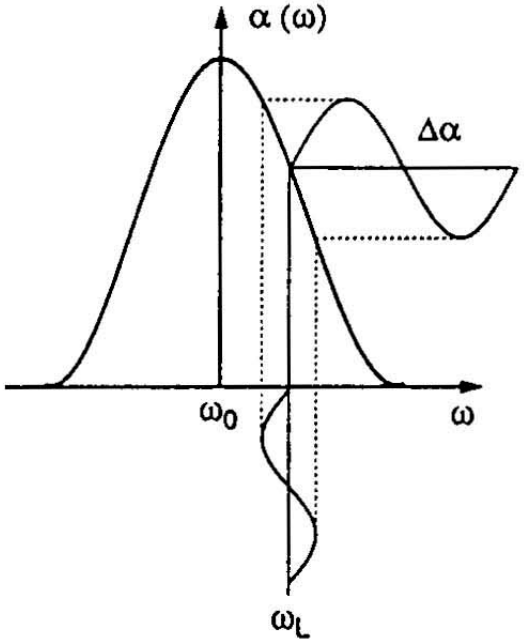


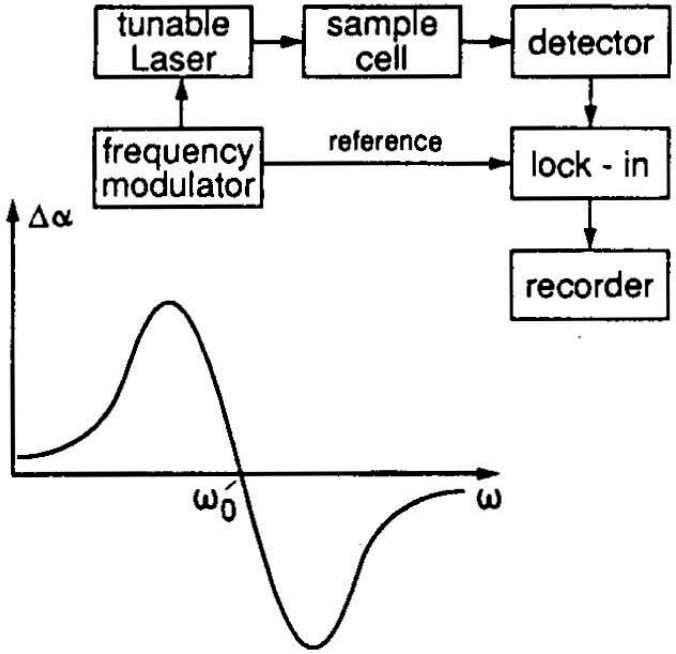


Absorption Spectroscopy with a Frequency Modulated Laser

$(I-I_o)/I_o = \sigma N \ell =$ *Absorbance* Detection limit $A=10^{-3}$

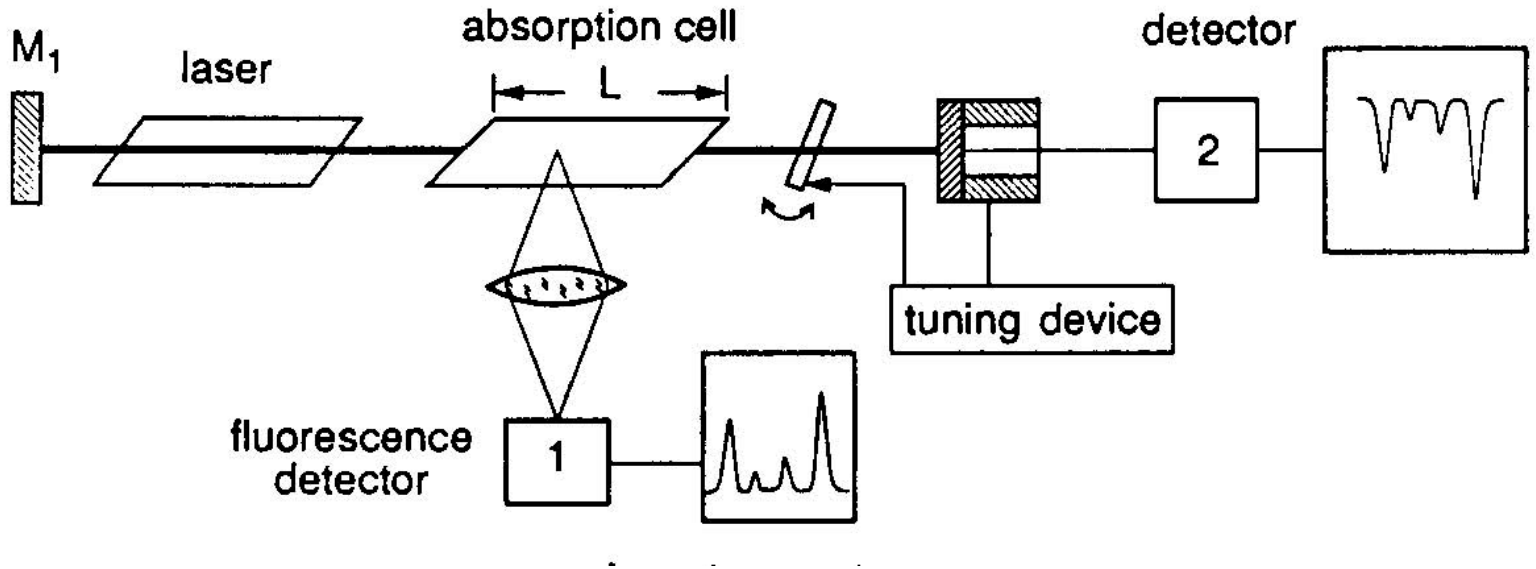
$\sigma = 10^{-18} cm^2$ $\ell = 10$ cm $\Rightarrow$ $N = 10^{-3} / (10^{-18} \cdot 10) = 10^{14}$ molecules/cm^3





Detection limit $A=10^{-6}$

Intracavity Absorption Technique

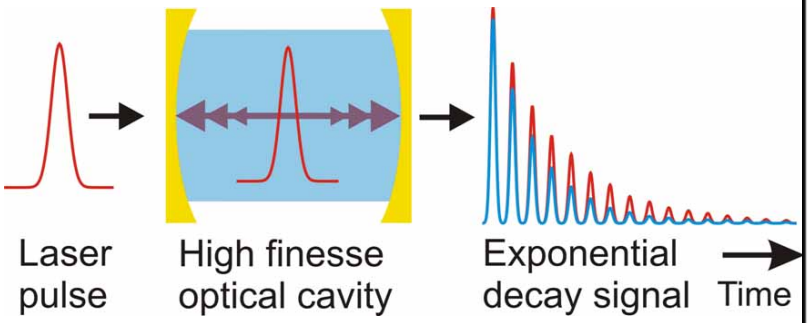


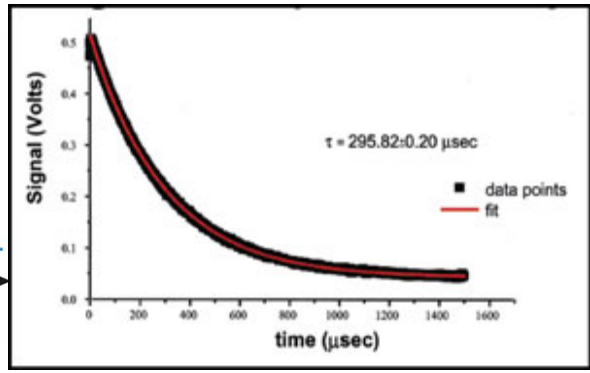
Operation close to laser threshold

+ high sensitivity ($A=10^{-8}$)
- non linear response
- interference with other absorber within resonator

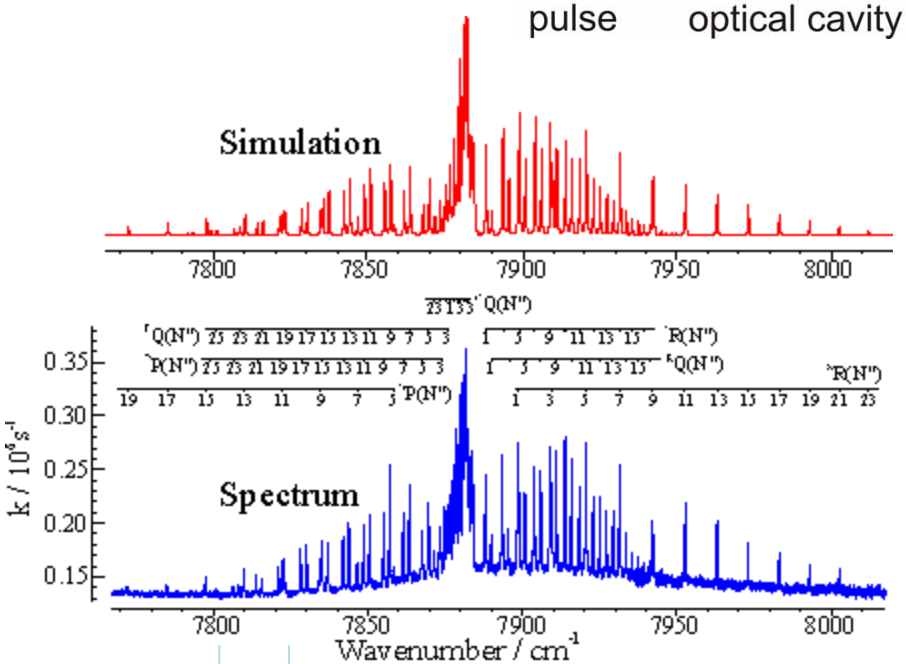
CRD: Cavity Ring Down Spectroscopy

CRD spectroscopy is a highly sensitive direct absorption technique.

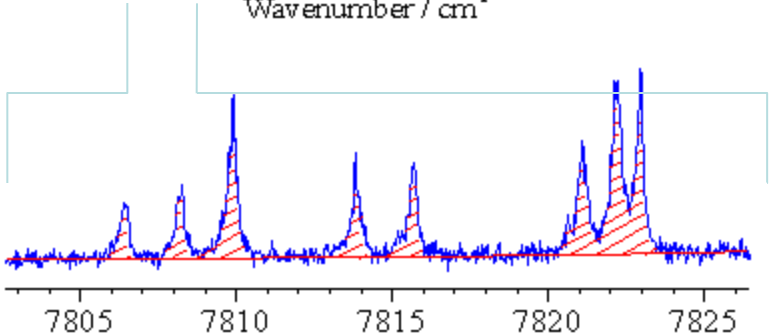




$I = I_o e^{-t/\tau}$ → absorption cross section

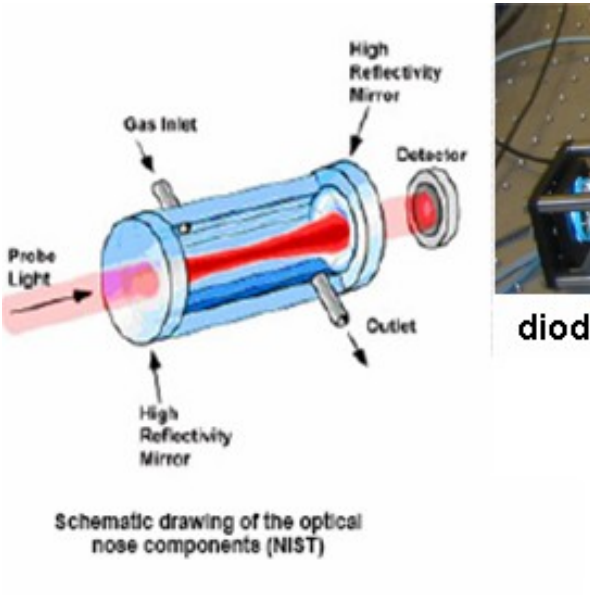


CRD of O_2: $a^1\Delta_g - X^3\Sigma_g^-$ (0,0)

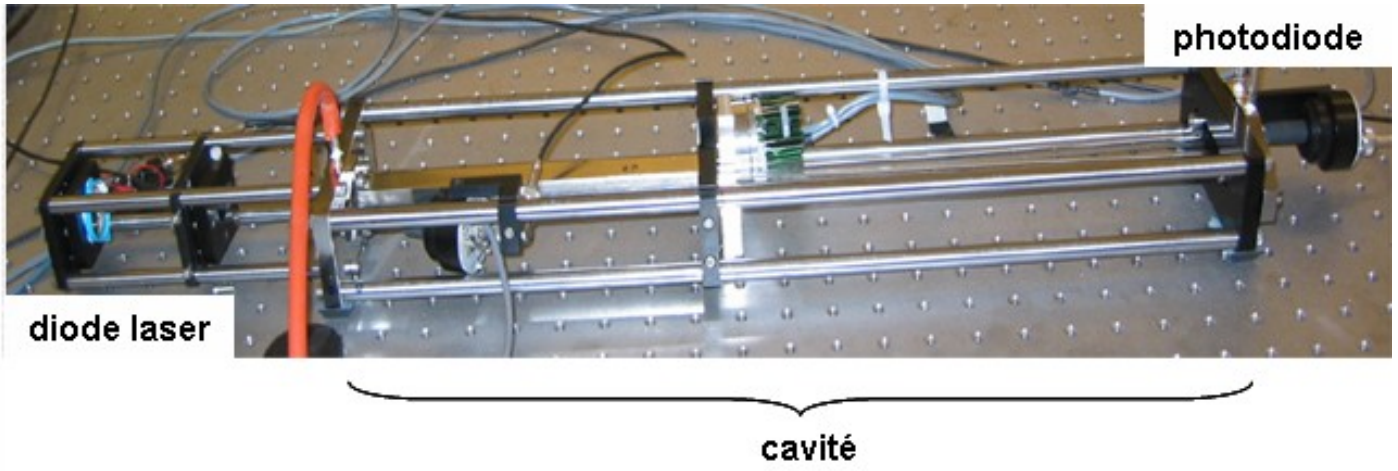


Integrated absorption ⟶ B ⟶ A ⟶ lifetime 0.2 ms

CRD: Cavity Ring Down



Schematic drawing of the optical nose components (NIST)



Species	1Hz detection limit [ppb]	λ[nm]
CO_2	300	1600
CO	300	1566
H_2S	100	1600
C_2H_4	50	1620
CH_4	0.5	1653
NH_3	2	1530
H_2O	1	1390
HCl	1	1742
HF	0.1	1297

Improvement: $^{1}/_{(1\text{-Reflectivity of mirrors})}$ R=99.999%

Photoacoustic Spectroscopy

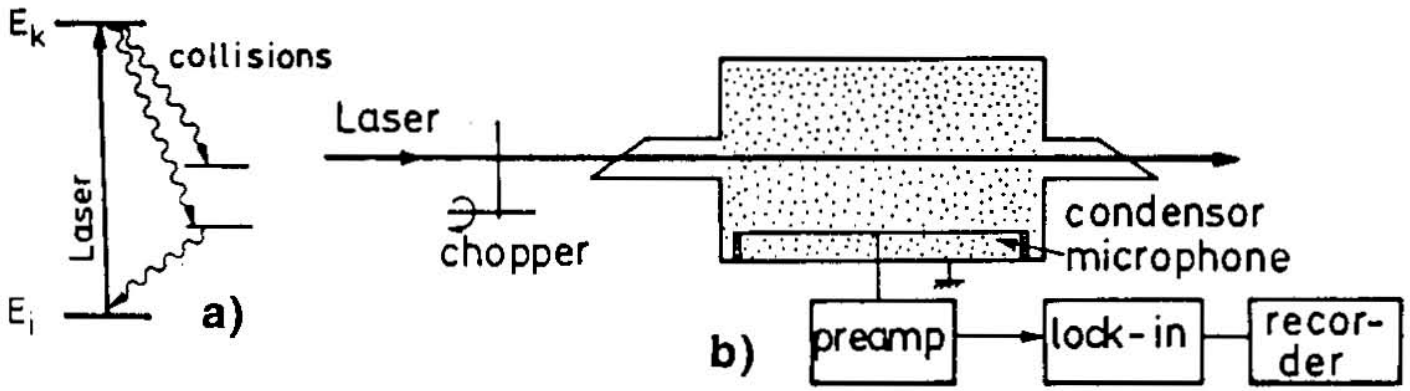


Fig.6.13. Photoacoustic spectroscopy **(a)** level scheme **(b)** schematic experimental arrangement

Photoacoustic Spectroscopy: C_2H_2

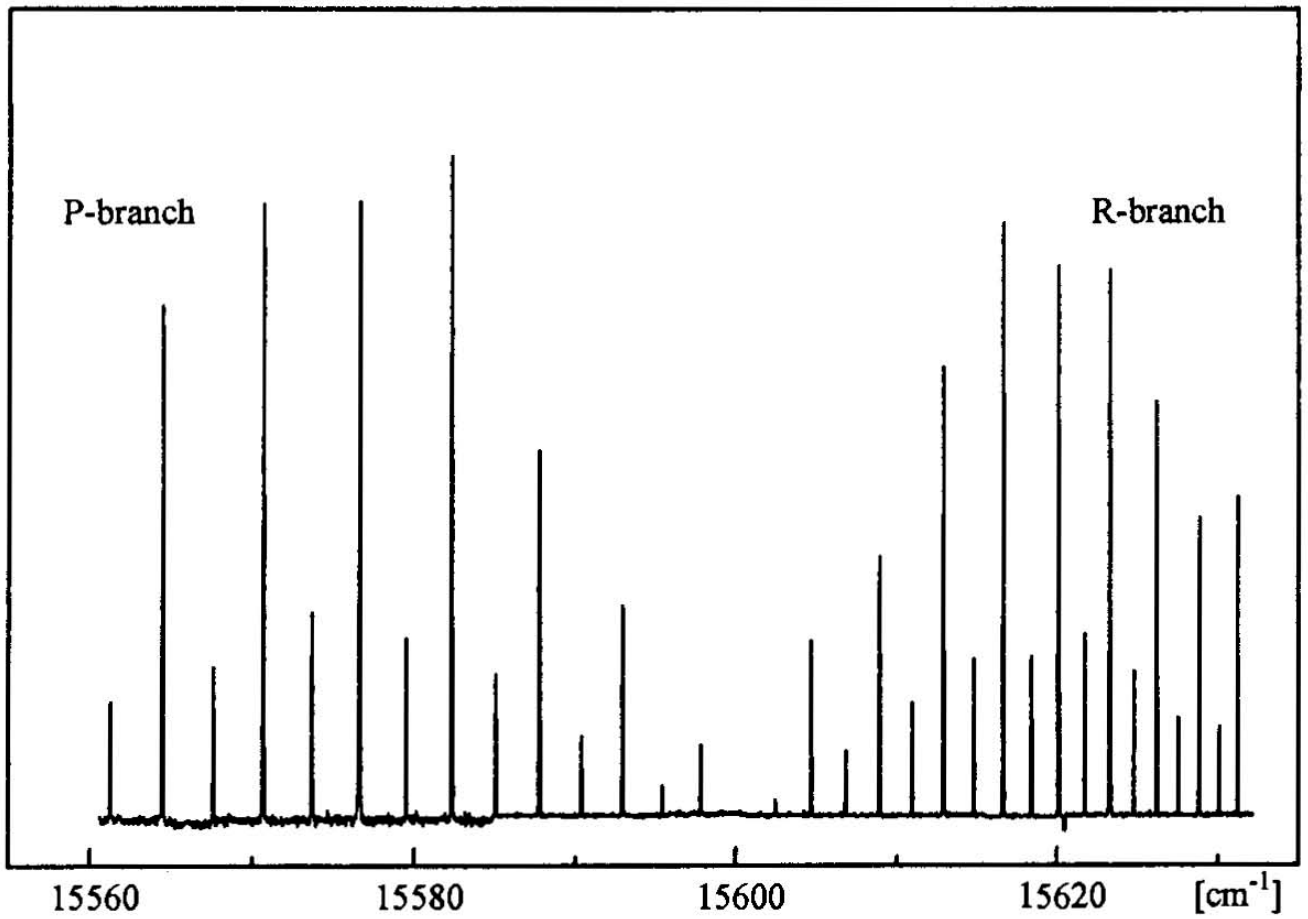
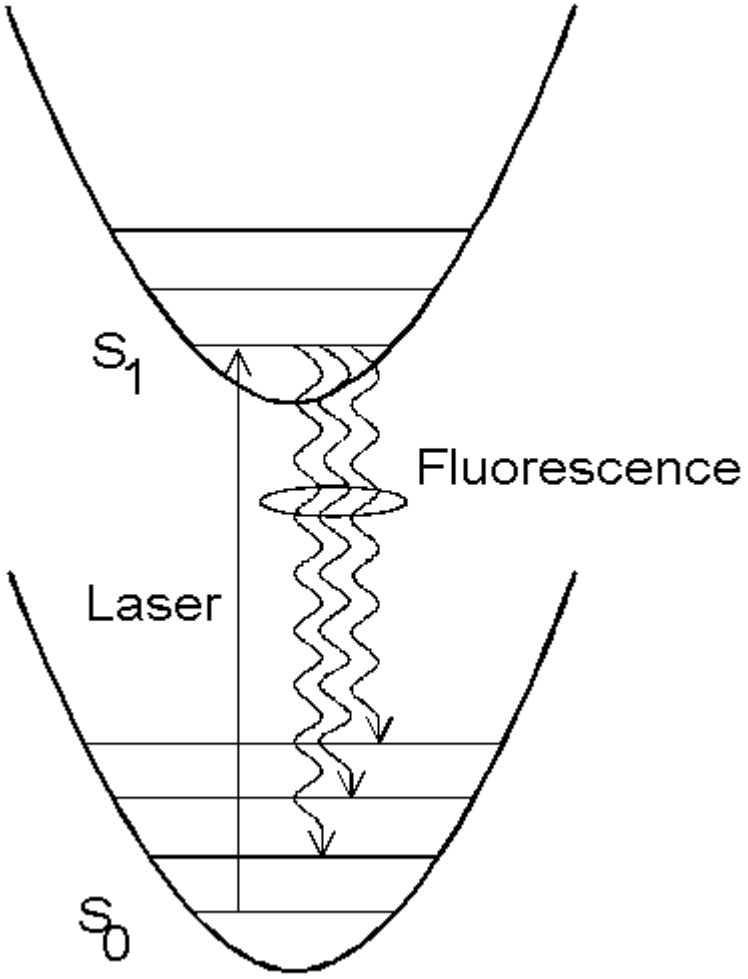
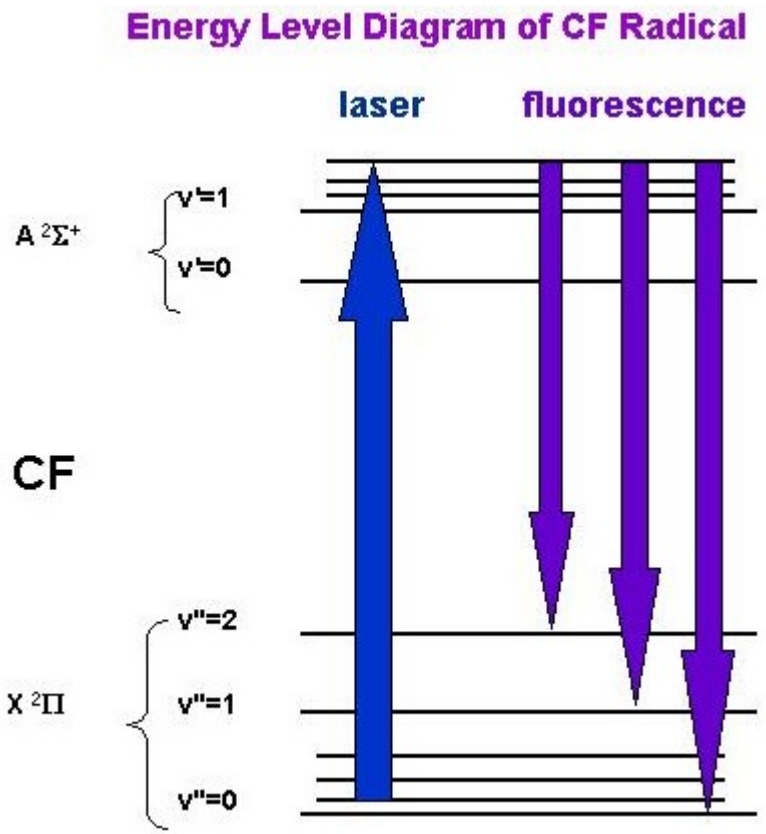


Fig.6.15. Optoacoustic overtone absorption spectrum of acethylene around $\bar{\nu}$ = 15600 cm^{-1} corresponding to the excitation of a local mode by 5 quanta vibrations [6.45]

Laser induced fluorescence (LIF)

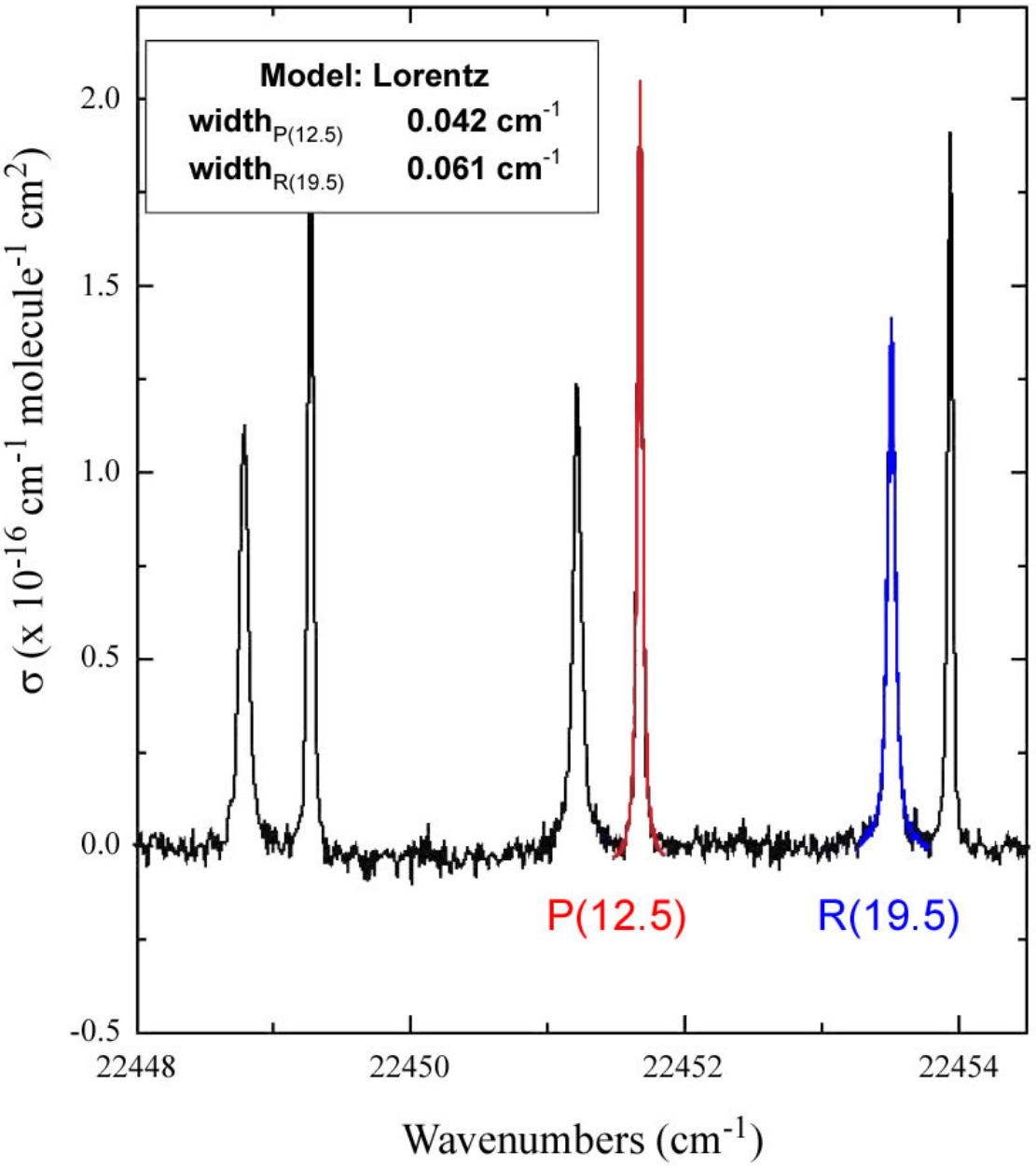




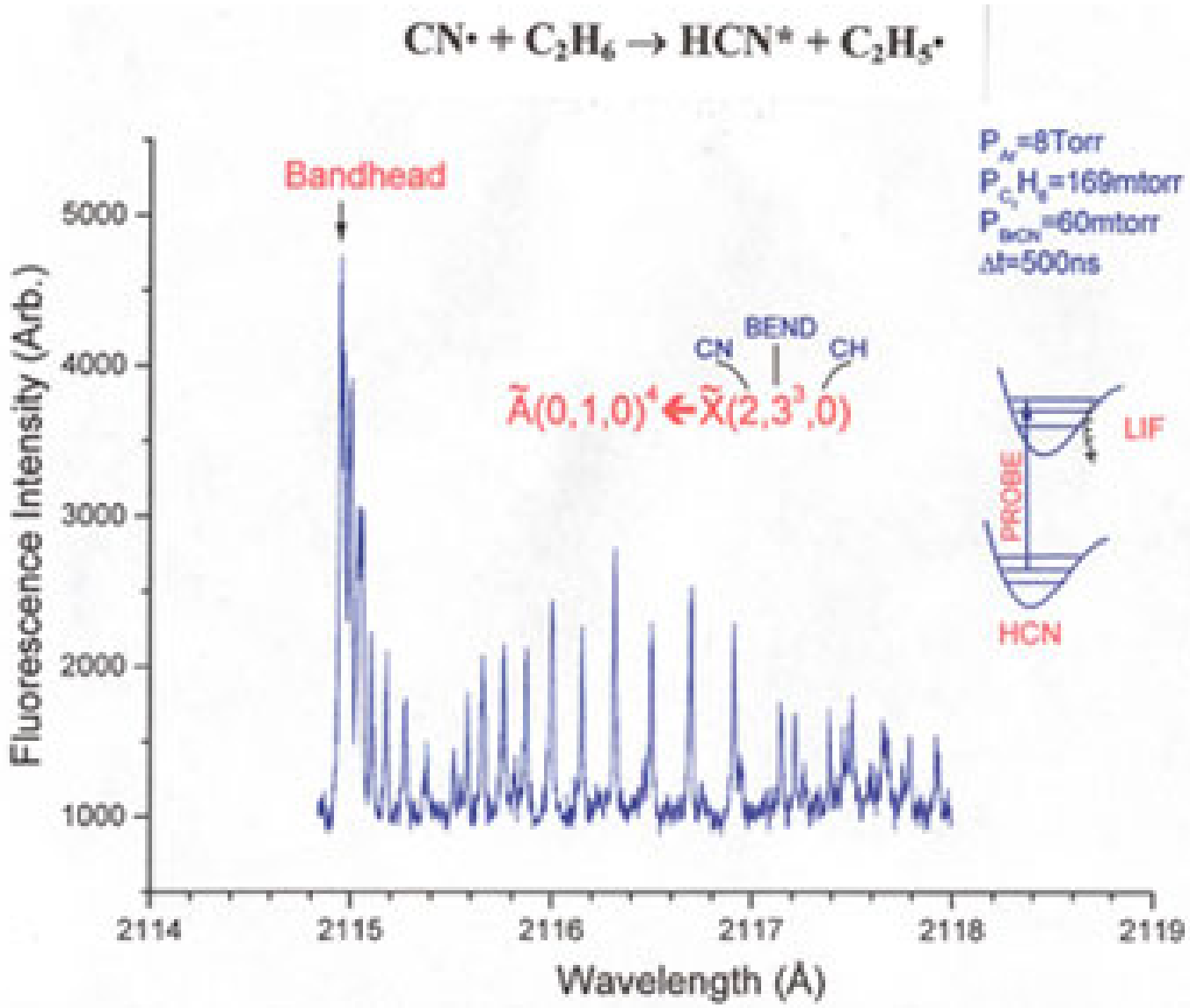
LIF

IO(v‘=2-v‘‘=0) around 445 nm

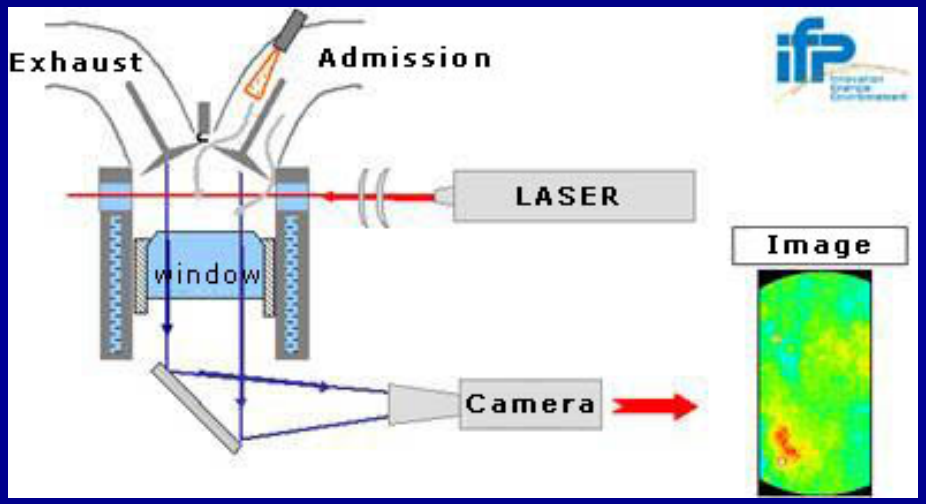
+ extremely sensitive
+ selective
- calibration
- handling
- costs



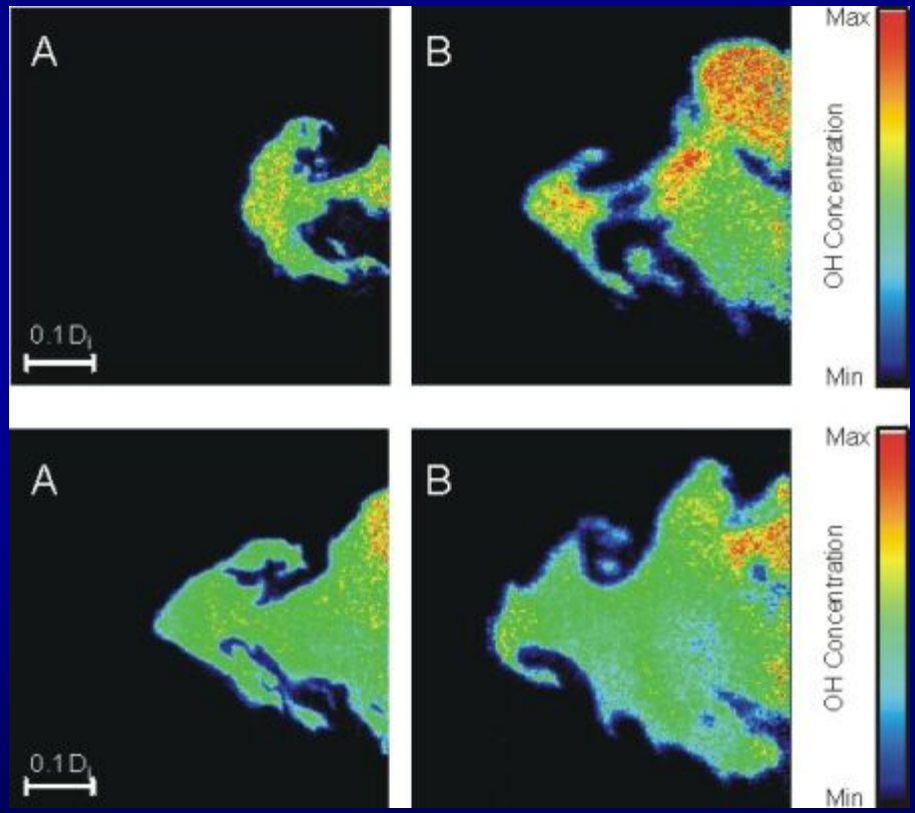
Laser induced fluorescence (LIF)



Laser induced fluorescence (LIF)



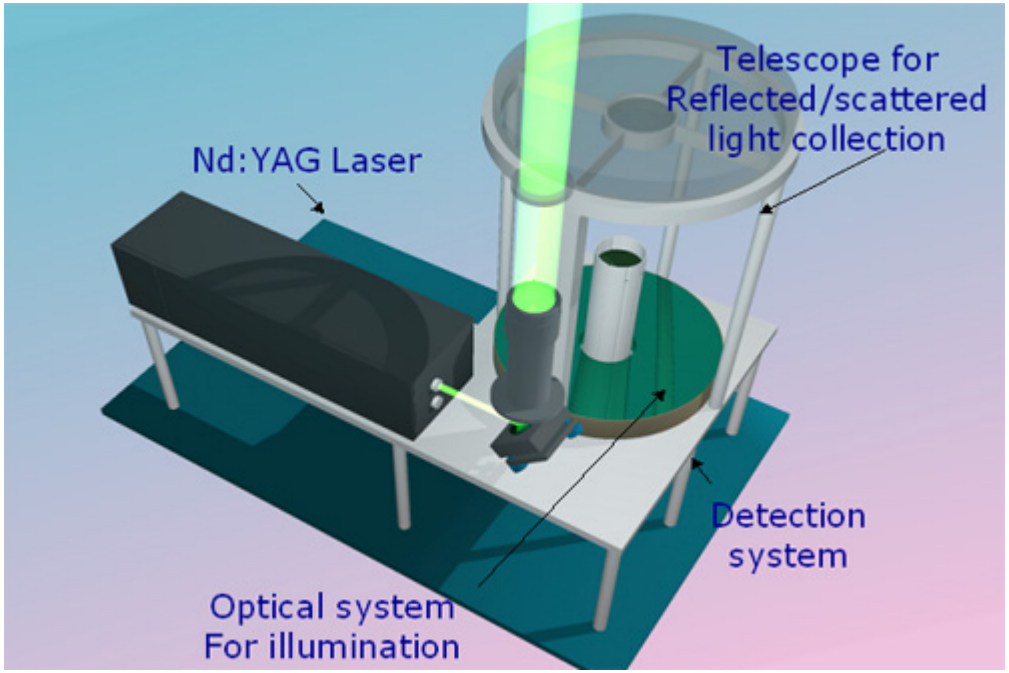
LIF in a running engine of a car

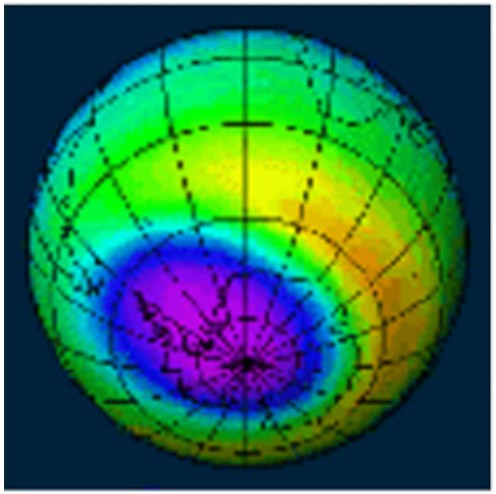


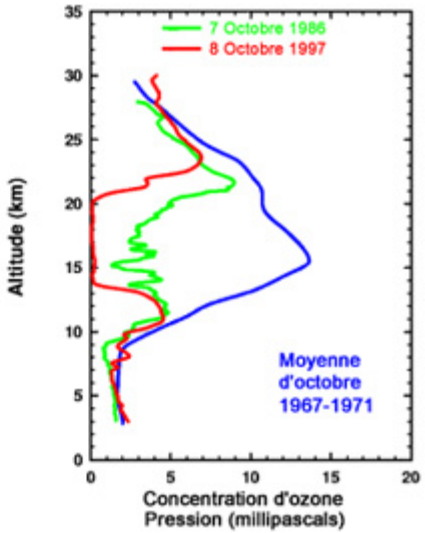
LIDAR: Light Detection And Ranging

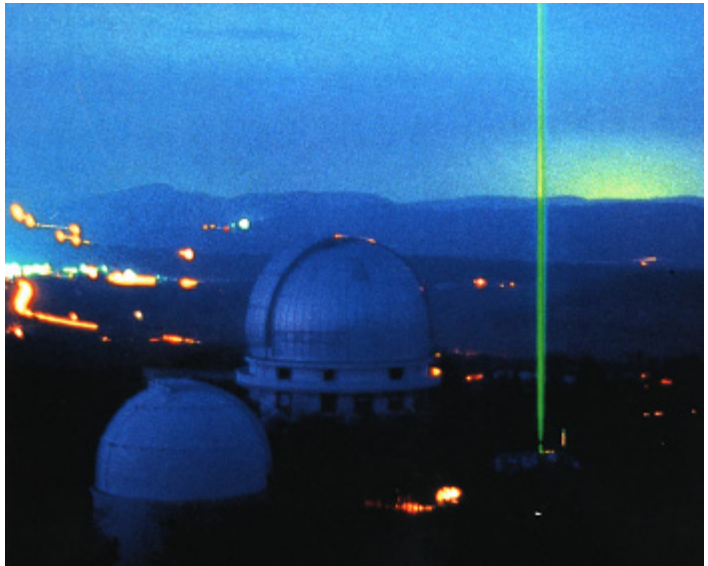
LIDAR: A remote-sensing technique that uses a laser light source to probe the characteristics of a target:

- Atmosphere control
  - Density
  - Temperature
  - Wind
  - Pollution
- Distance, speed measurement
- Rayleigh, Mie scattering
- Raman scattering
- Fluorescence
- Doppler shift









Laser Induced Fluorescence: Na_2

$B^1\Pi_u$

$X^1\Sigma_g$

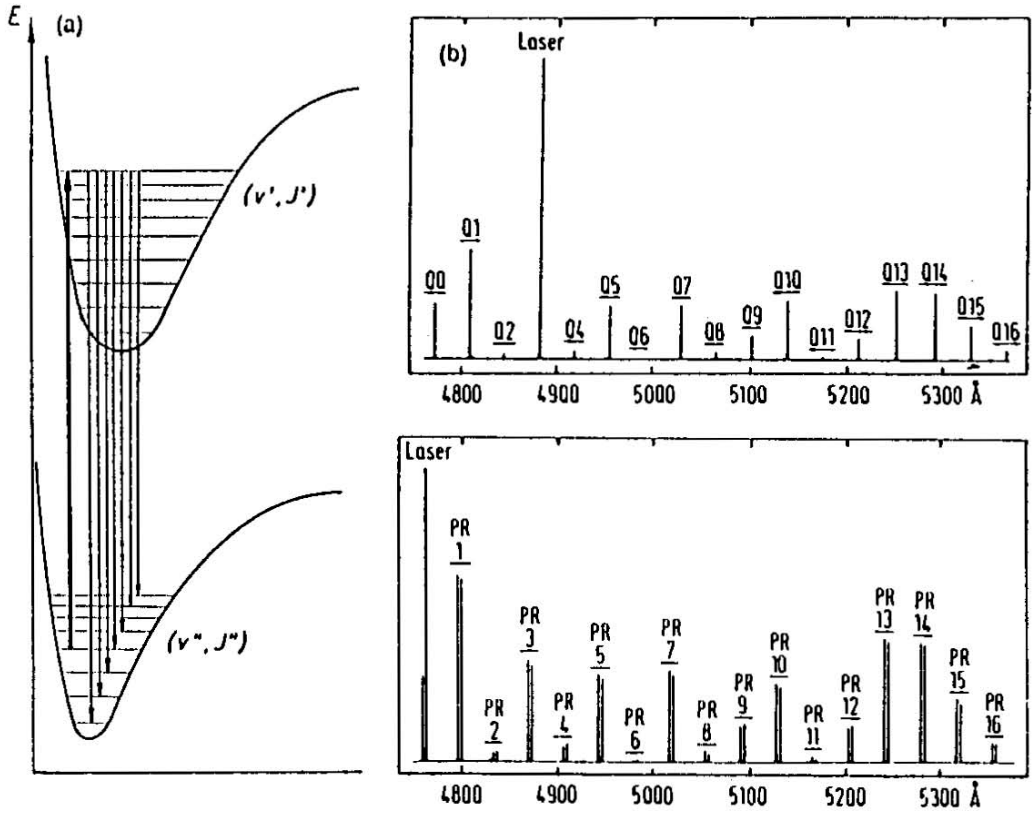
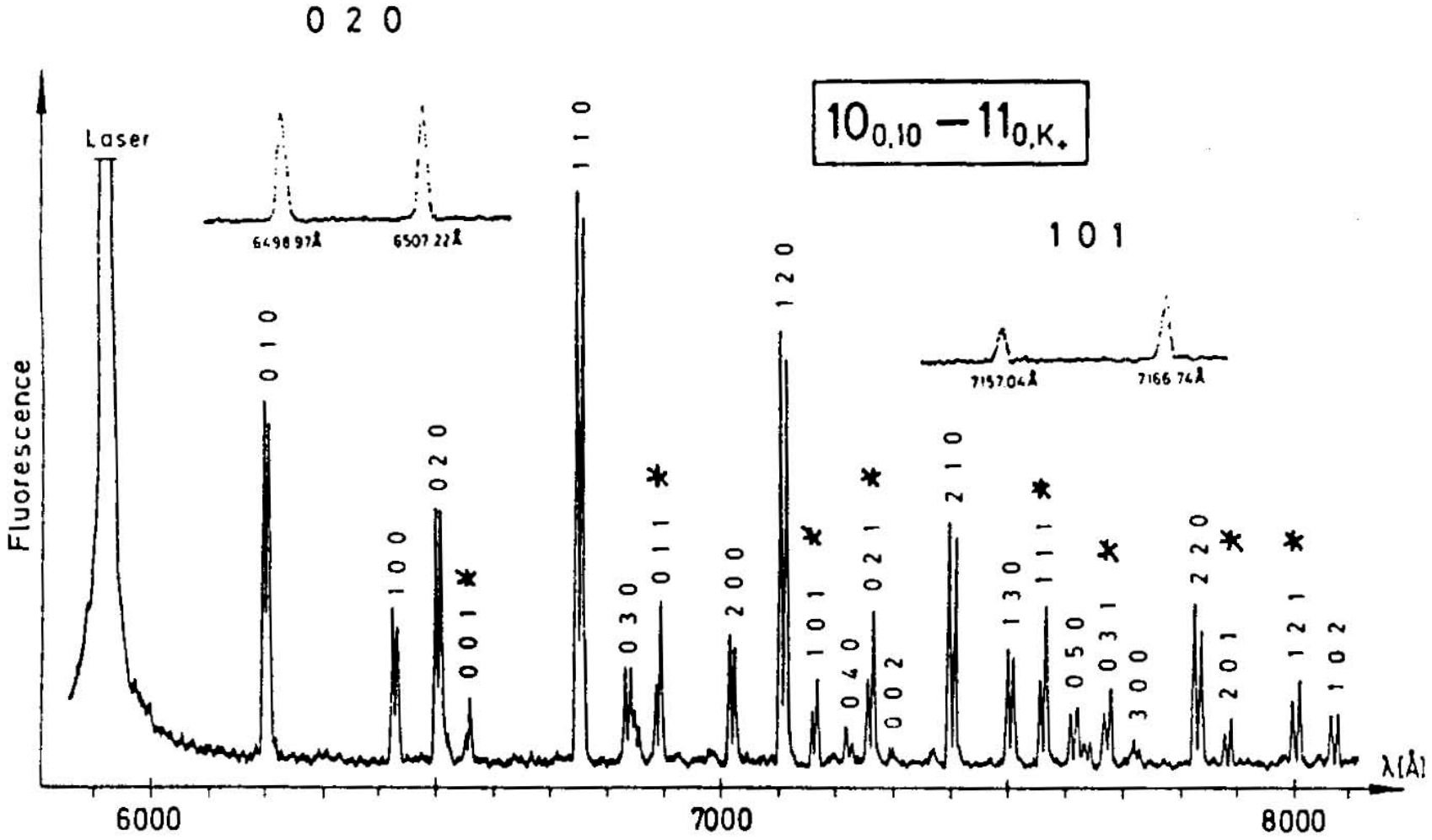


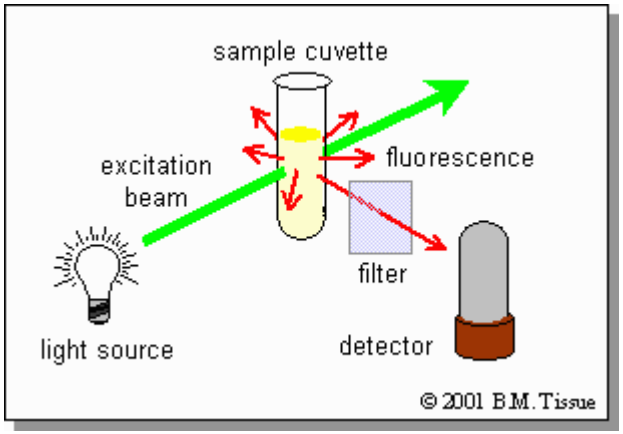
Fig.6.34. Laser-induced fluorescence of the Na_2 molecule excited by argon laser lines (a) term diagram (b) fluorescence lines with $\Delta J = 0$ (Q-lines) emitted from the upper level ($v'=3$, $J'=43$) of the $B^1\Pi_u$ state, excited at $\lambda = 488$ nm. (c) P and R doublets, emitted from the upper level ($v'=6$, $J'=27$)

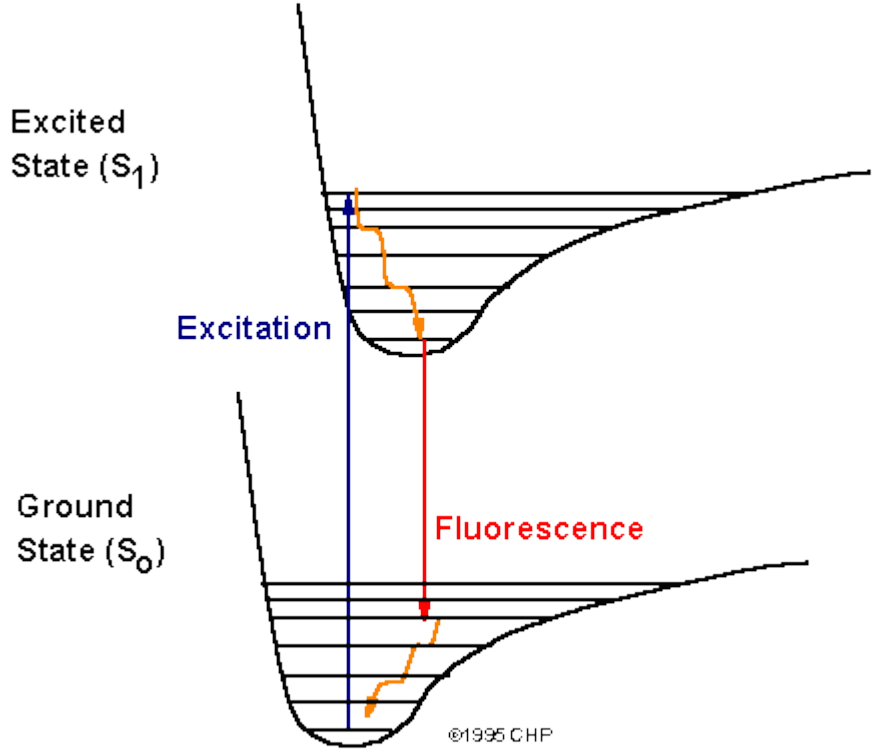
Advantage: very high selectivity. 488 nm line excites a positive Λ component of the v' = 6, J' = 43 which emits only Q lines. 476,5 nm line excites a negative Λ component of the v' = 6, J' = 27 level which emits P and R lines.

Laser Induced Fluorescence: NO_2



Molecular Fluorescence Spectroscopy





Jablonski Diagram

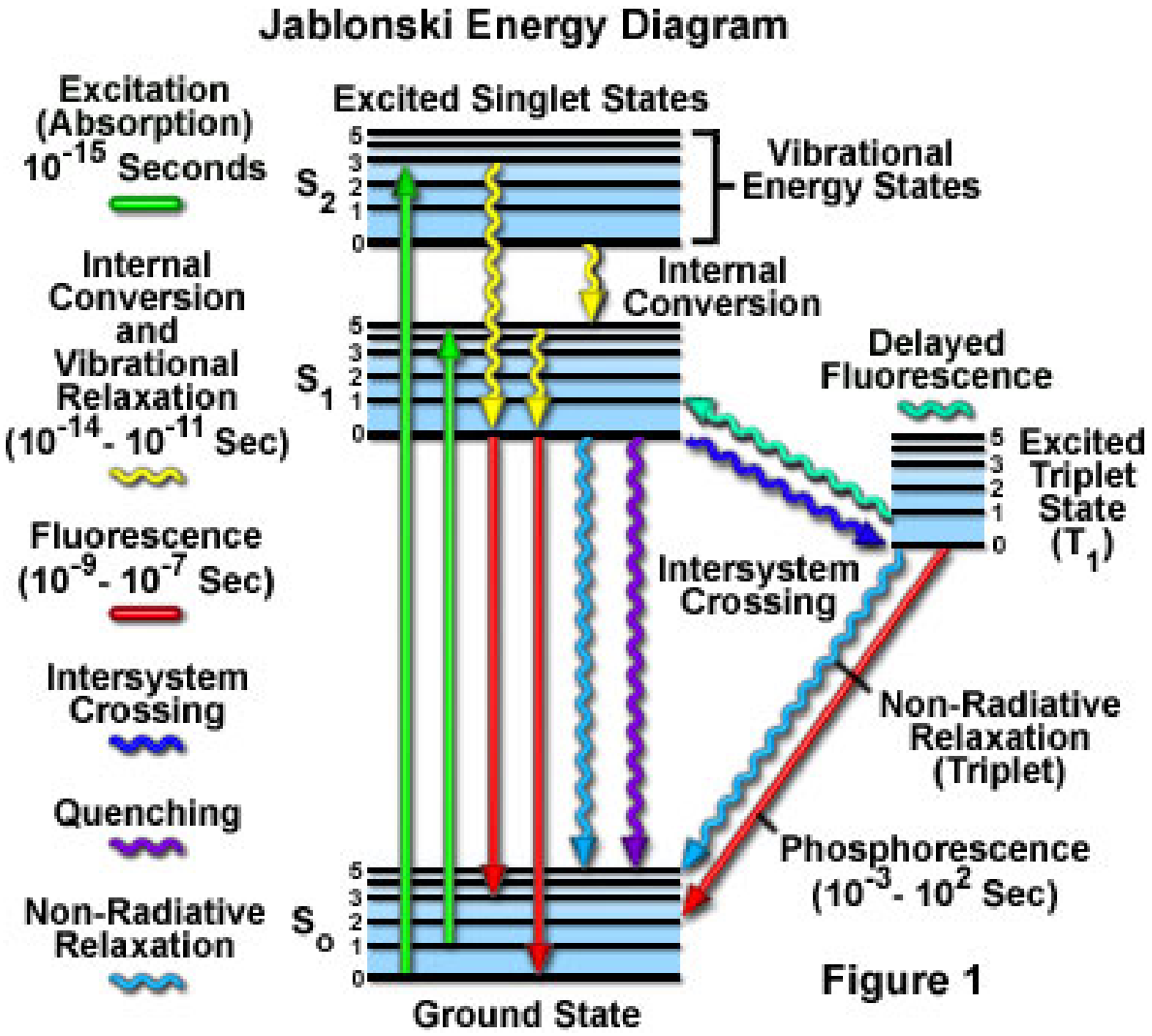
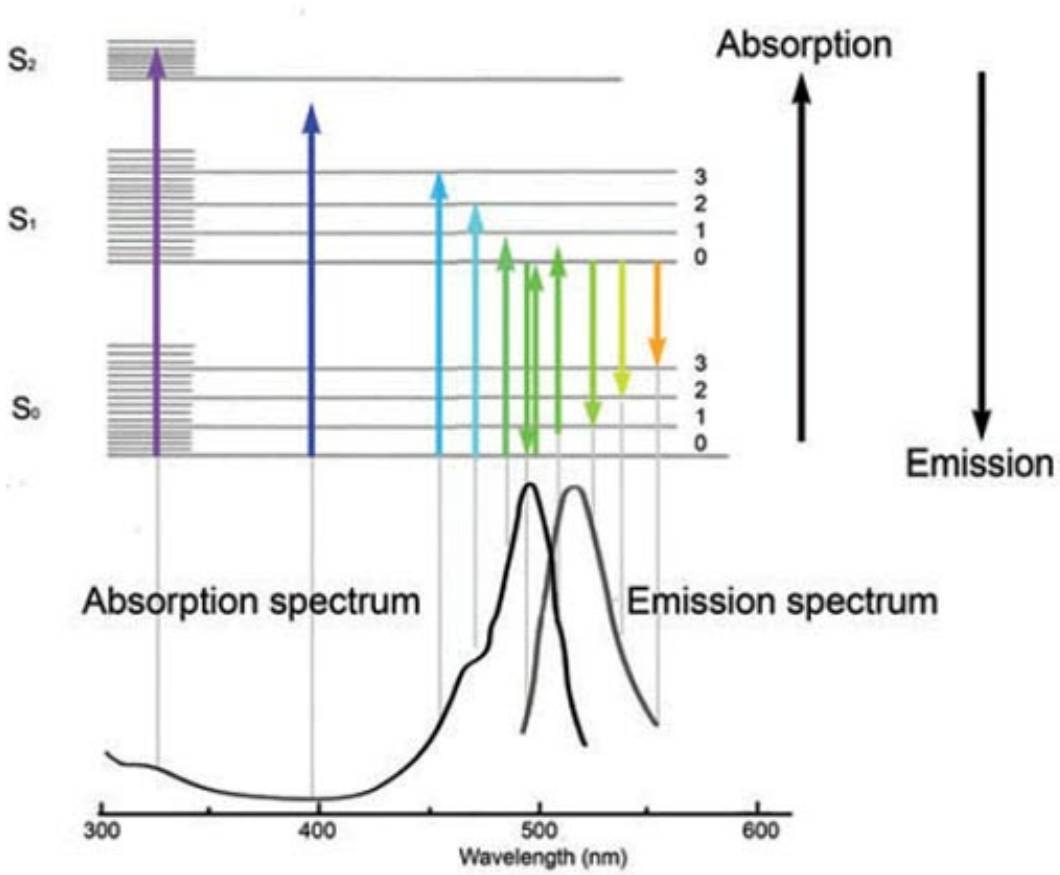
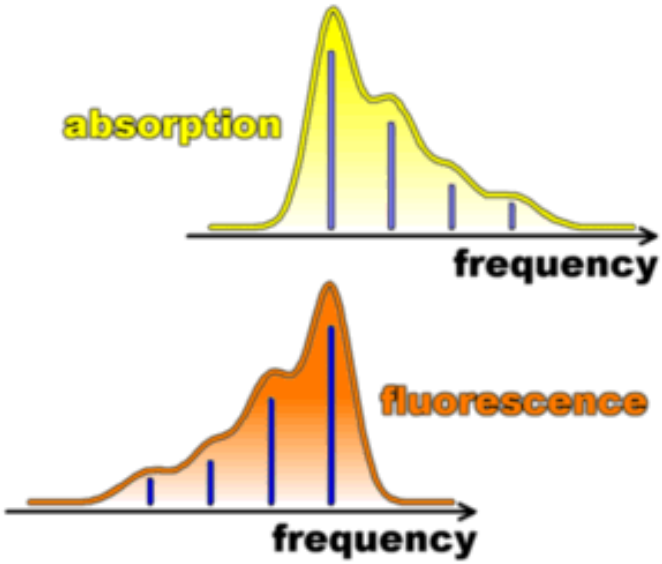
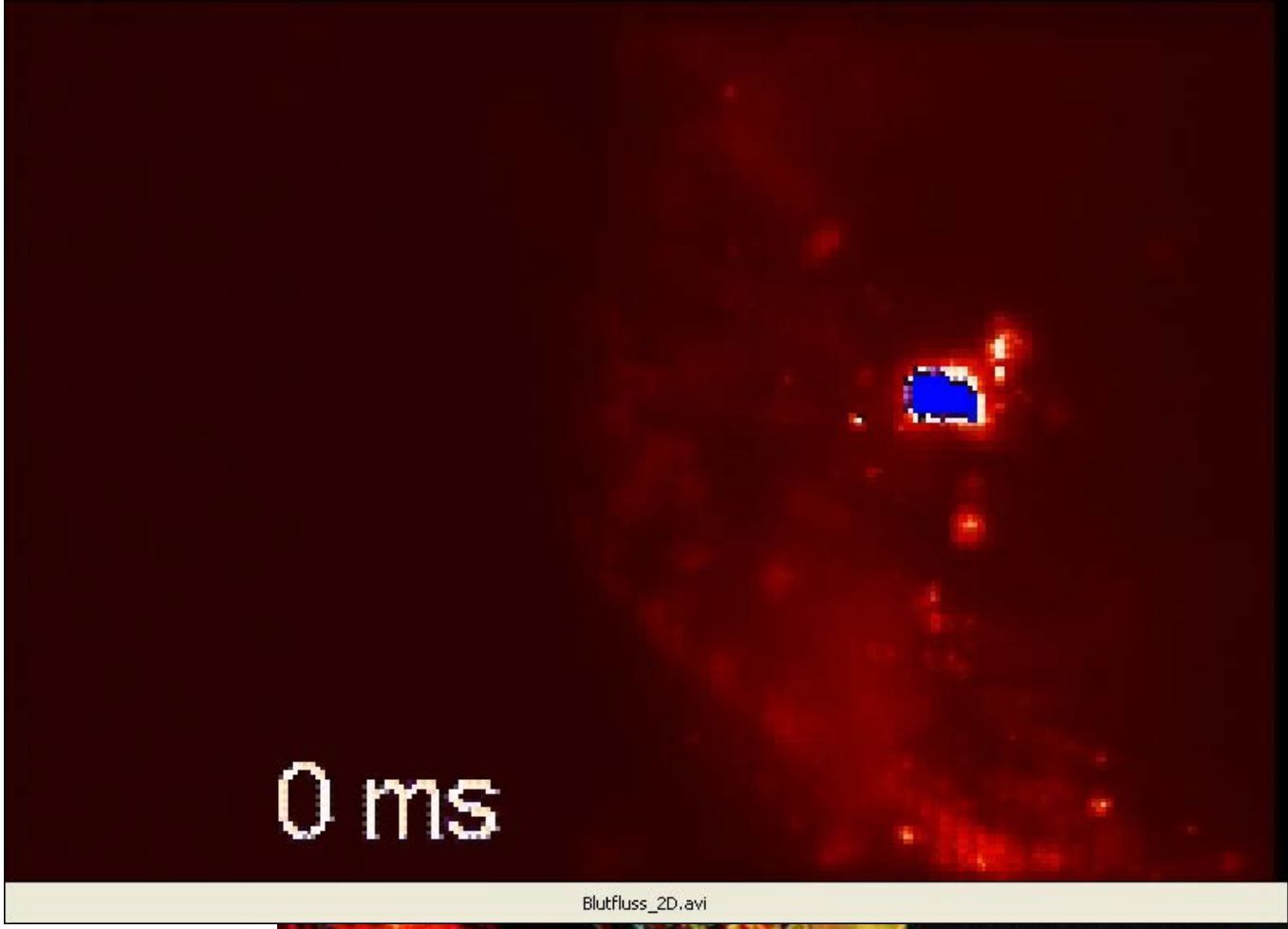


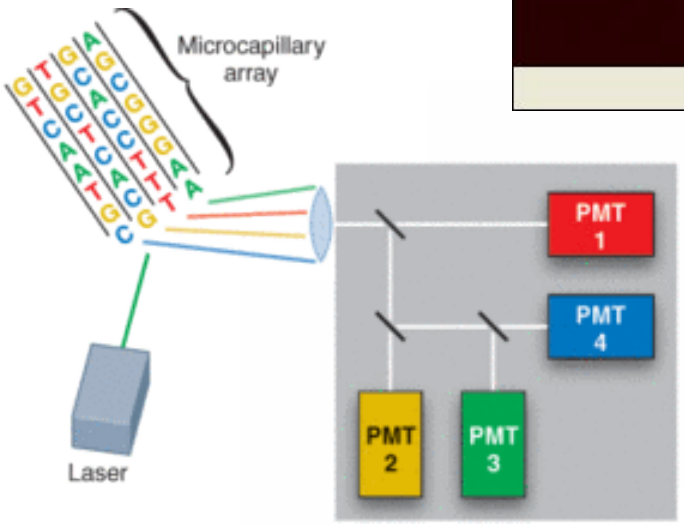
Figure 1

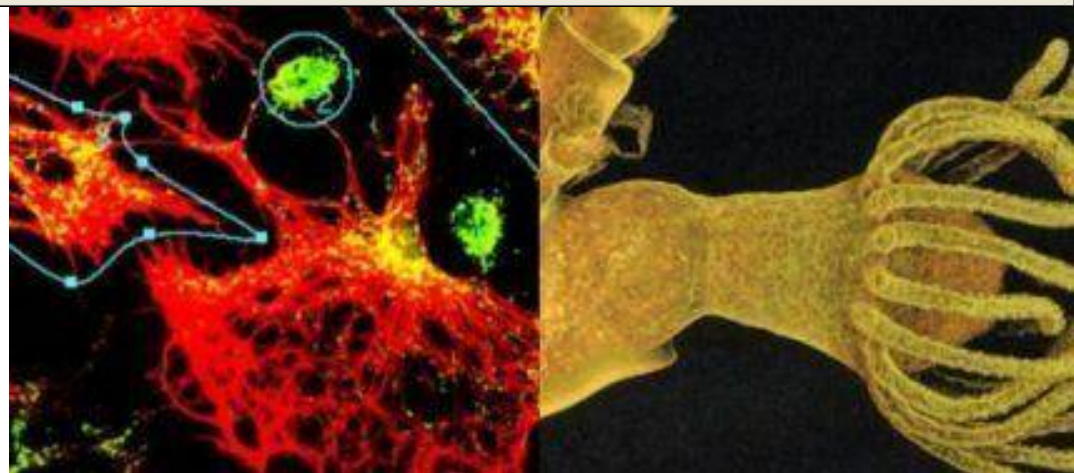

S2
S1
S0
3
2
1
0
3
2
1
0
Absorption
Emission
Absorption spectrum
Emission spectrum
300
400
500
600
Wavelength (nm)


absorption
frequency
fluorescence
frequency

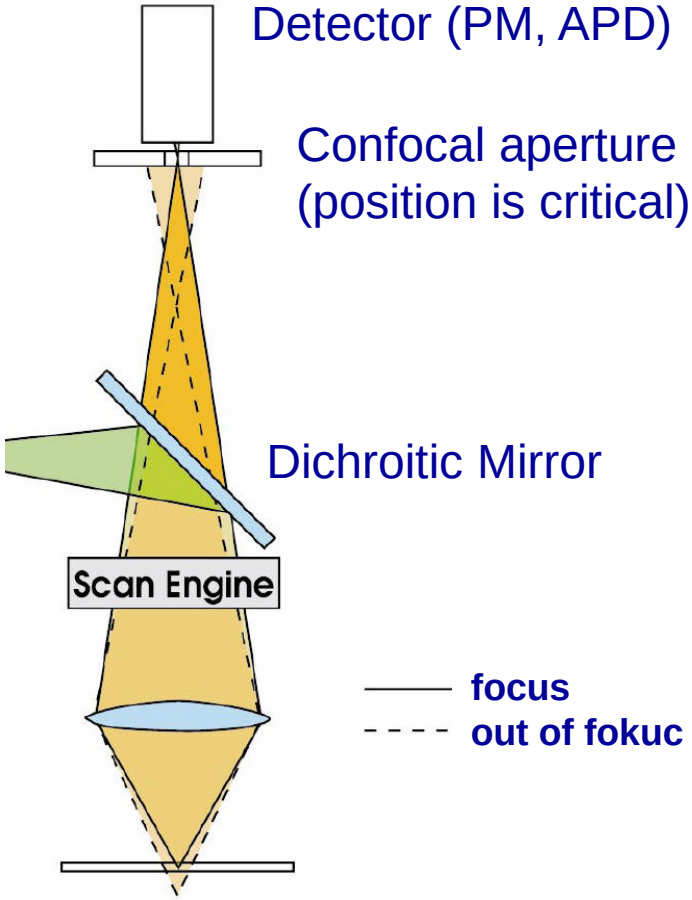
Modern Microscopy is LIF



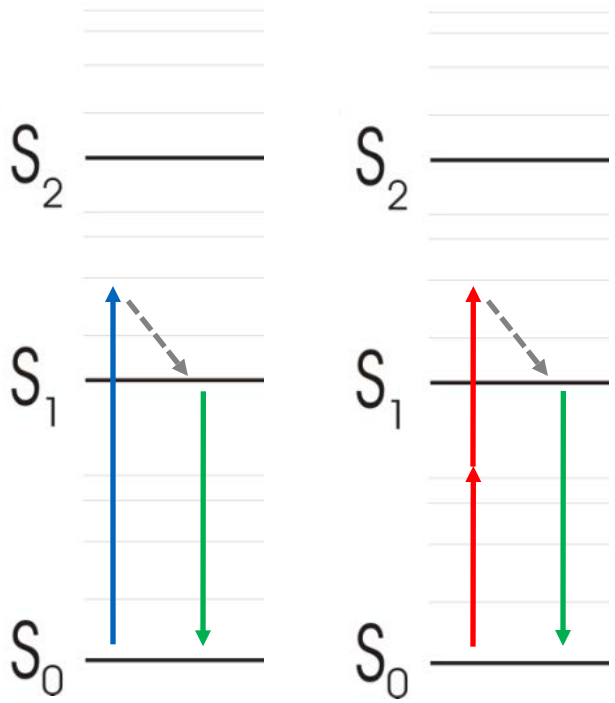




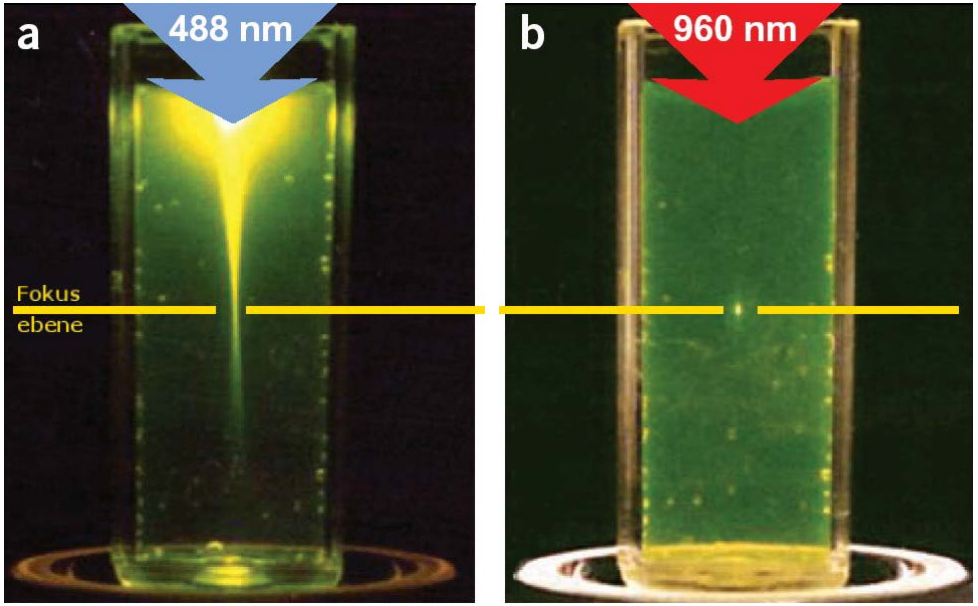
Confocal Microscope



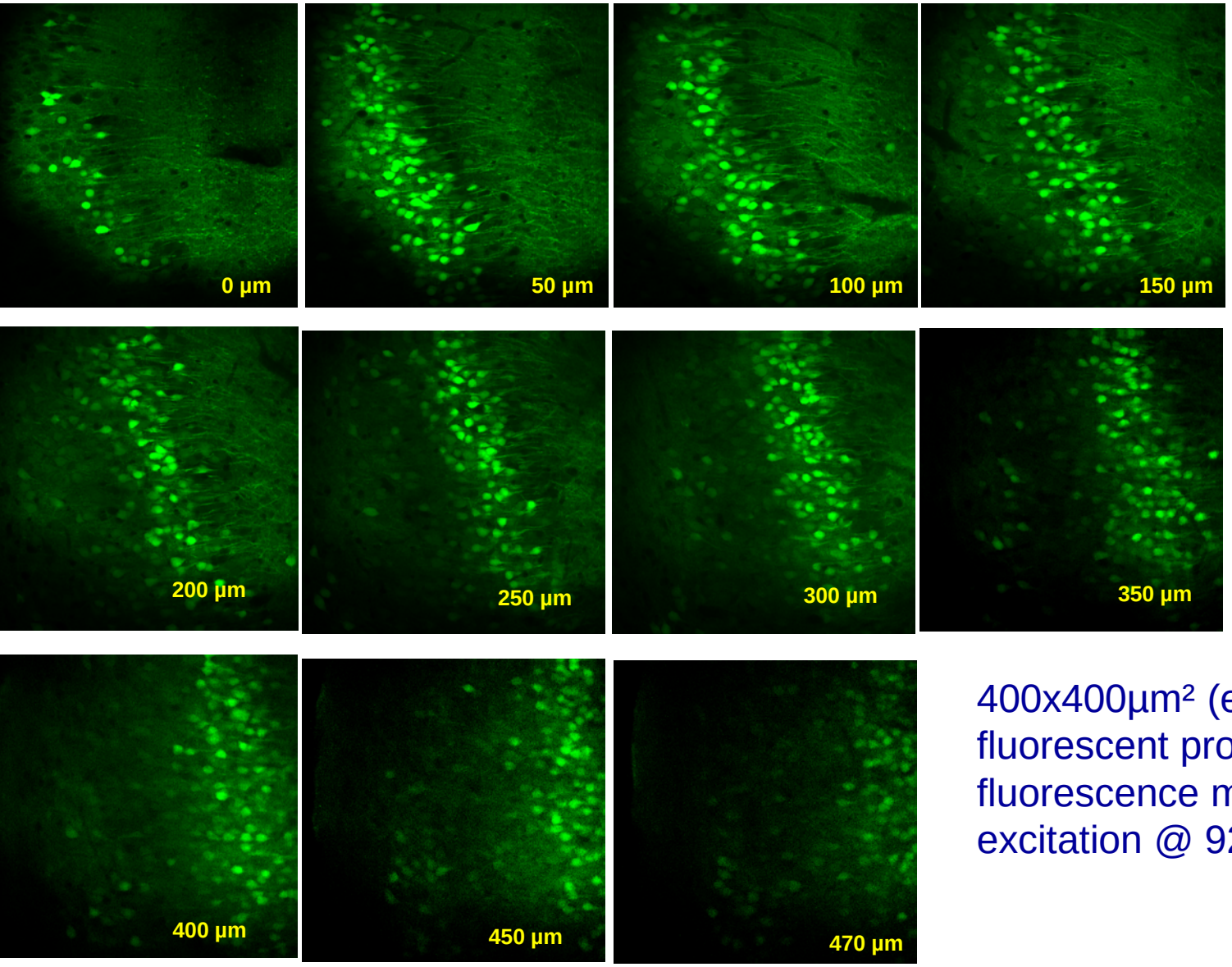
one-photon vs. two-photon excitation



one-photon two-photon

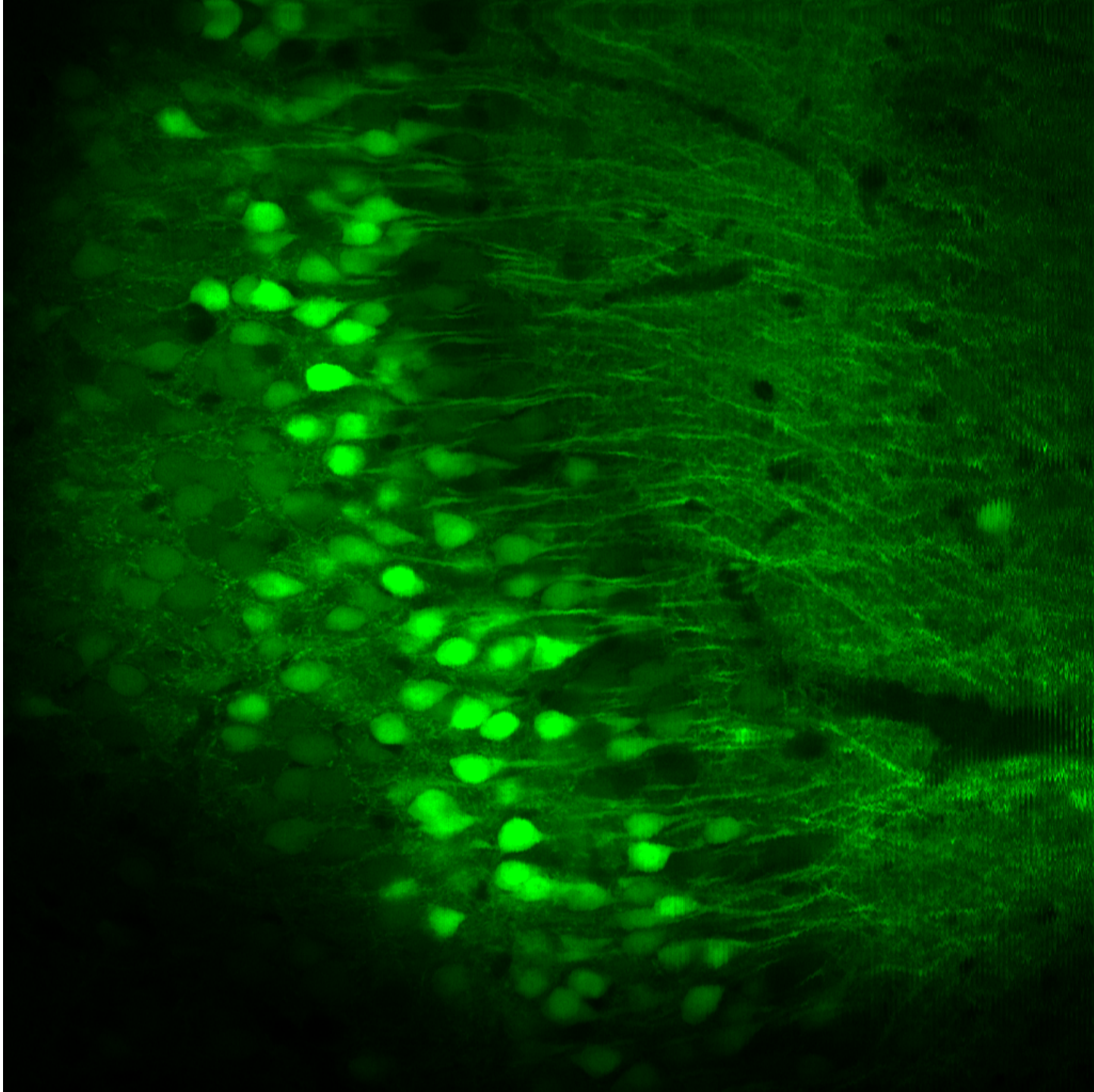


Inside the brain of a mouse…



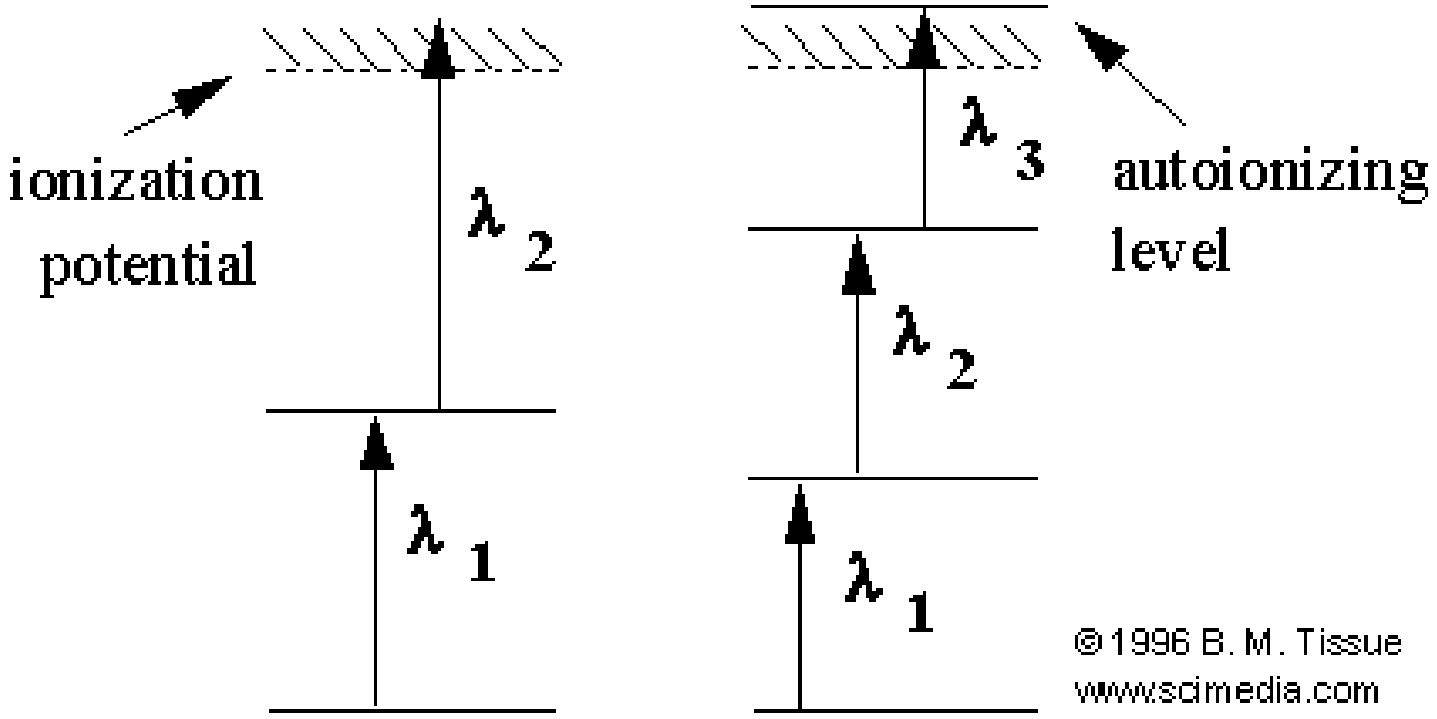
400x400µm² (enhanced yellow fluorescent protein EYFP): fluorescence max. @ 535nm; excitation @ 920nm

In 3D…



Ionization Spectroscopy

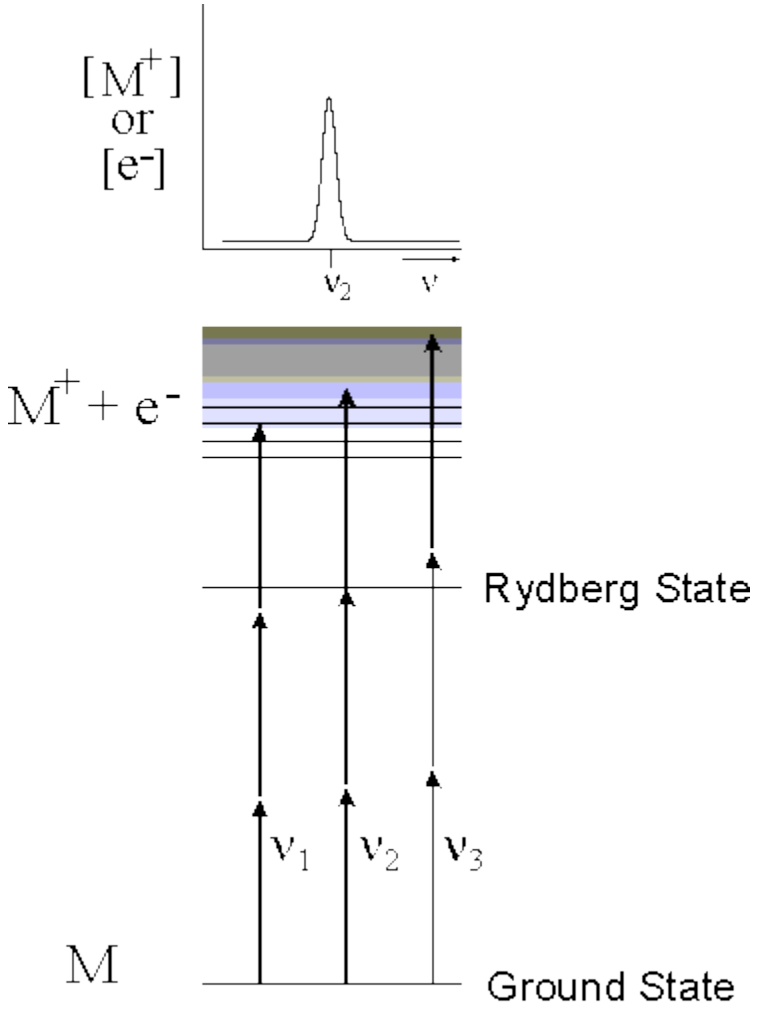
Absorption of photons on the molecular transition $E_i \rightarrow E_k$ is monitored by detection of the ions or electrons, produced by some means from the molecular excited state E_k. The ionization of the excited molecule may be performed by photons, by collisions, or by an external electric, or magnetic field.



The ionization methods used in molecular spectroscopy and particularly, for determination of the internal-state distribution in reaction products of chemical reactions are in general called resonance-enhanced multiphoton ionization (**REMPI**).

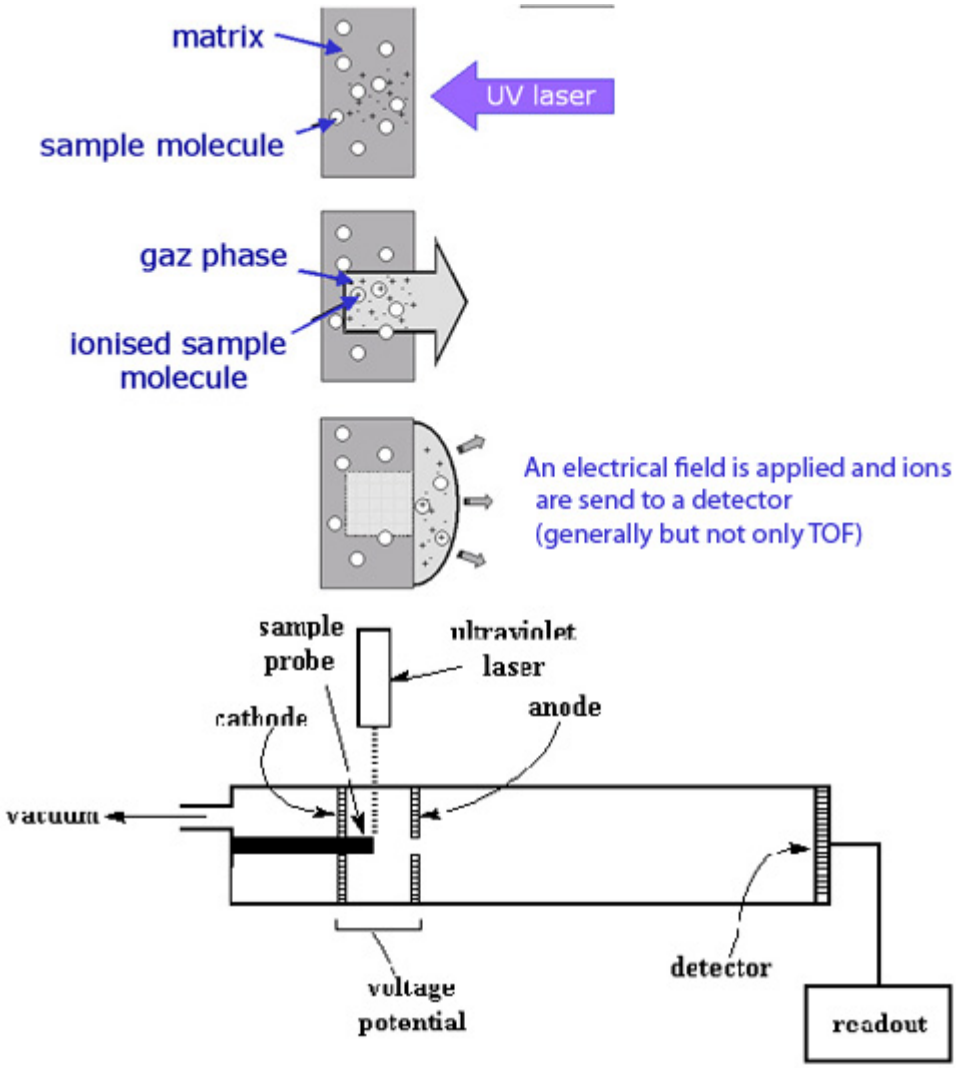
REMPI:
Resonant Enhanced Multi-Photon Ionisation

REMPI involves a resonant single or multiple photon absorption to an electronically excited intermediate state followed by another photon which ionizes the atom or molecule.



MALDI: Matrix Assisted Laser Desorption/Ionisation

A time of flight spectrometry technique, allowing the analysis of biomolecules and large organic molecules

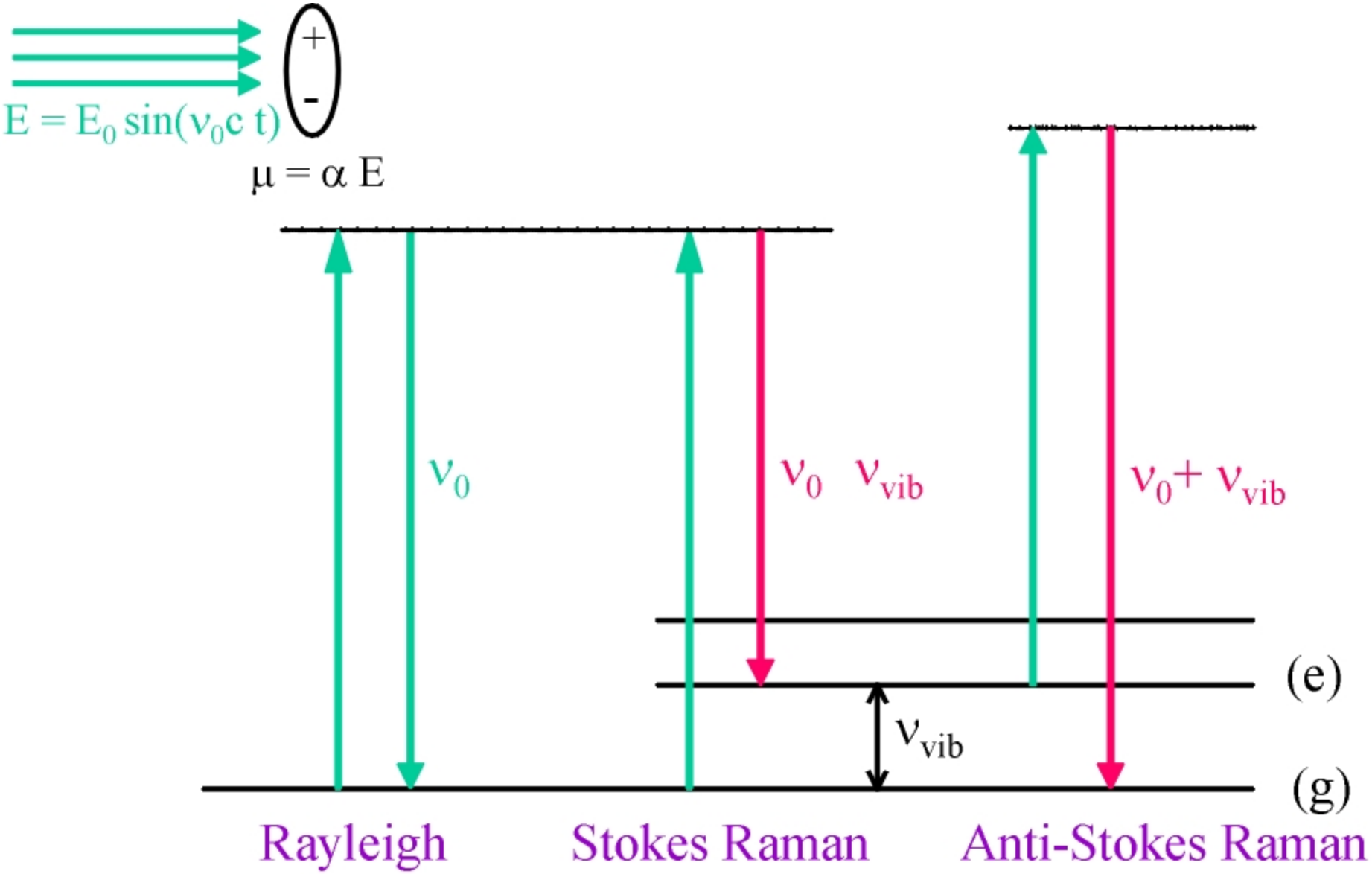


A simplified diagram of a MADLI apparatus
(After Creel, H., *Trends in Polym. Sci.*, 1993, *1(11)*, 336-342.)

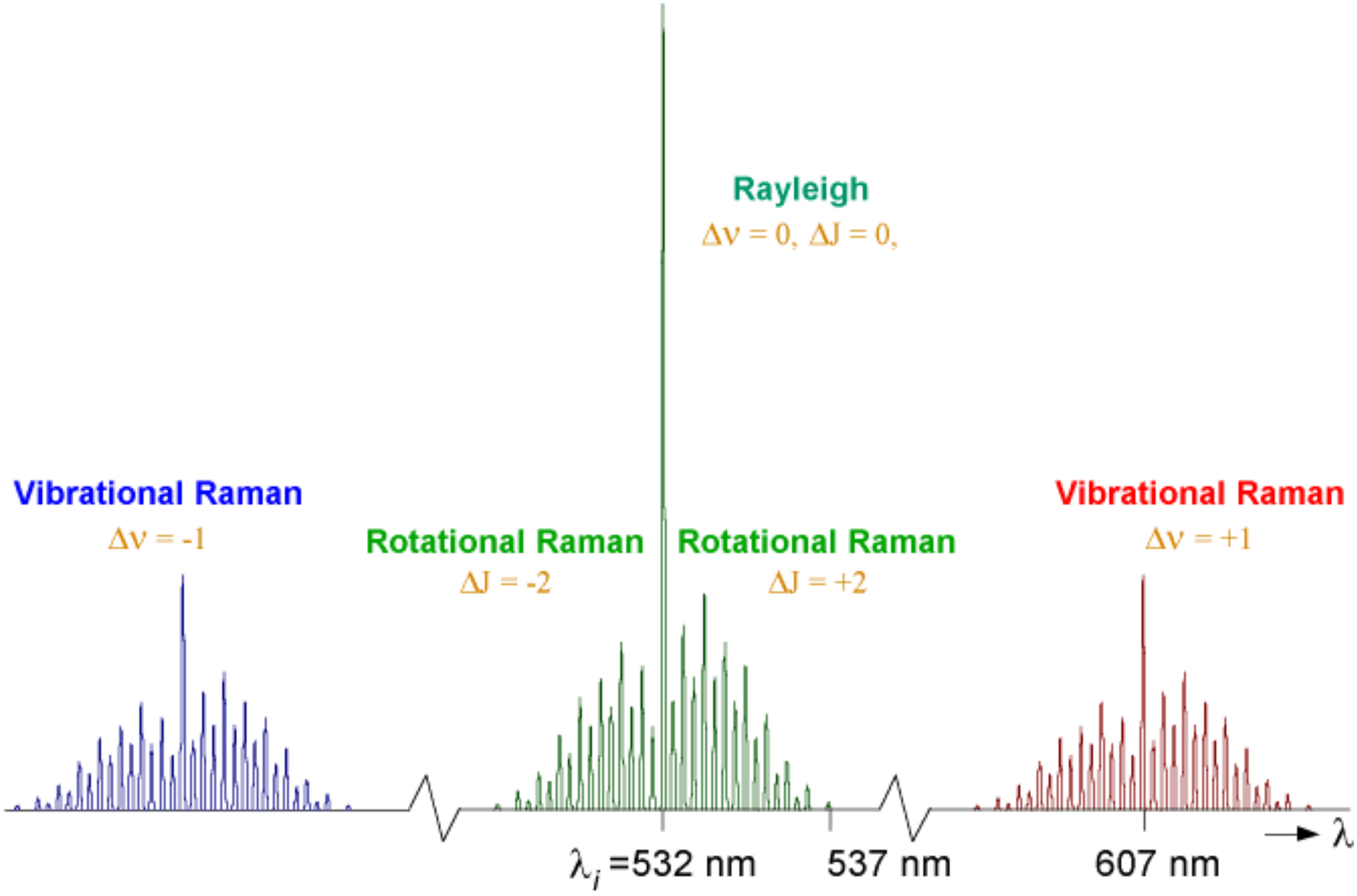
AND MUCH MORE TECHNIQUES…..

RAMAN
SERS
CARS
FLUORESCENCE LIFETIME
FLUORESCENCE POLARISATION
HETERODYNE

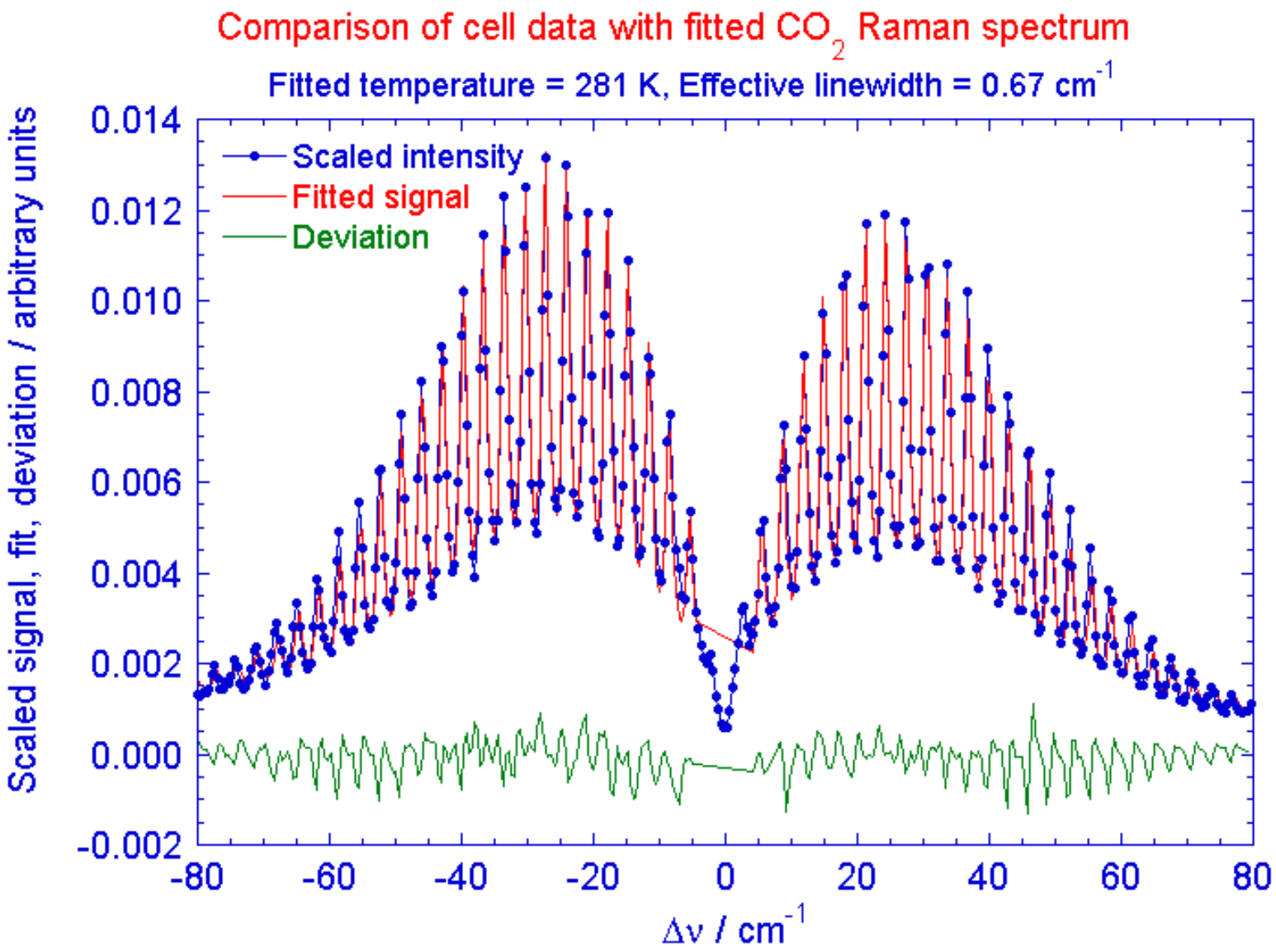
Raman


+
-
$E = E_0 \sin(\nu_0 c\, t)$
$\mu = \alpha E$
ν_0
ν_0 ν_{vib}
$\nu_0 + \nu_{vib}$
(e)
ν_{vib}
(g)
Rayleigh
Stokes Raman
Anti-Stokes Raman

Raman spectrum of N_2



Raman spectrum



Rotational Raman Spectroscopy: C_2N_2

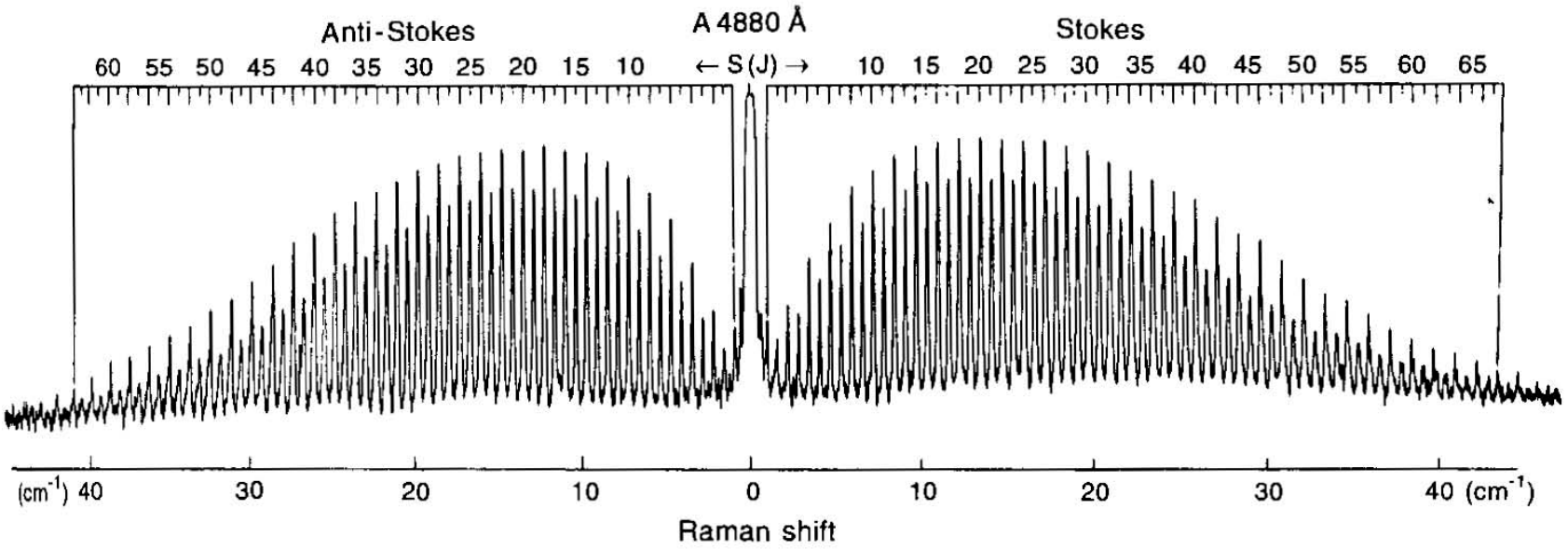
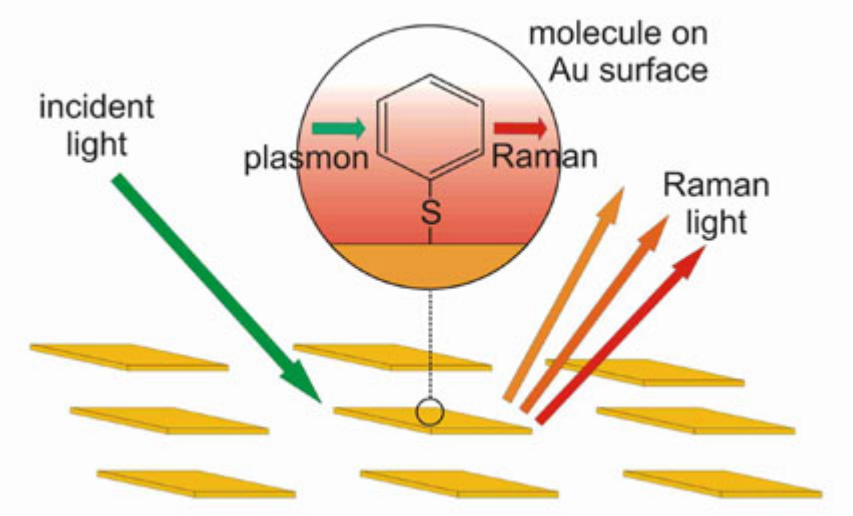


Fig.8.3. Rotational Raman spectrum of C_2N_2 excited with the 488 nm line of the argon laser in the experimental setup of Fig.8.2 and recorded on a photographic plate with 10 min exposure time [8.20]

The general disadvantage of the Raman spectroscopy is very small scattering cross section which is about $\sigma_{sc} \sim 10^{-30}cm^2$. Therefore, the sensitivity of the method is not very high and the typical experimental problem is detection of a weak signal in the presence of an intense background radiation.

Surface Enhanced Raman Scattering (SERS)

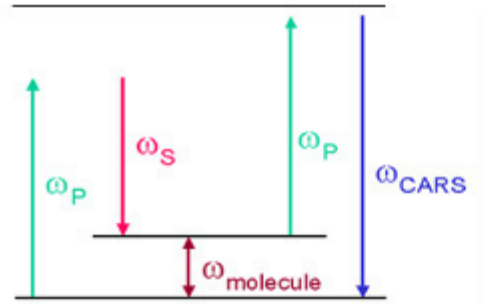
SERS is a surface sensitive technique that results in the enhancement of Raman scattering by molecules adsorbed on rough metal surfaces. Improvement of the detection limits by a factor of 10^{12} - 10^{14}.



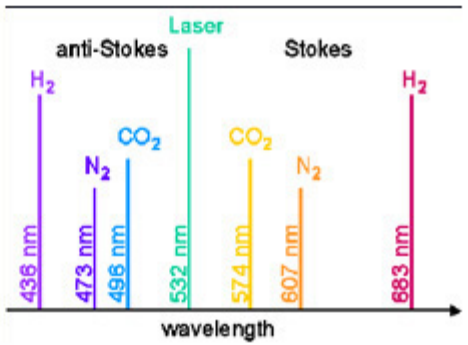
The excitation laser is selected to be in resonance with the surface absorption band, or surface plasmon associated with the metal surface. The analyte that adsorbs in the interaction region is perturbed, leading to enhanced spectral features. Since SERS is a direct measure of the analyte's bonding structure, unique spectral signatures are collected and false positives are minimized. SERS techniques have permitted trace level detection and identification of pollutants such as cyanide and pesticides in water supplies.

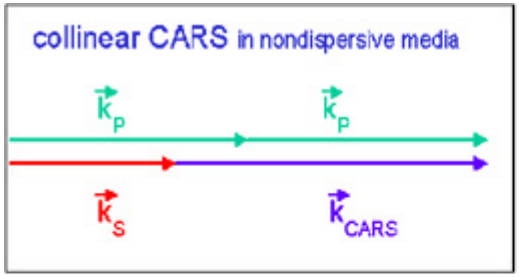
CARS:
Coherent Antistoke Raman Scattering

A (coherent non linear 4 wave mixing) diagnostic technique used to determine temperature and concentration in combustion processes.

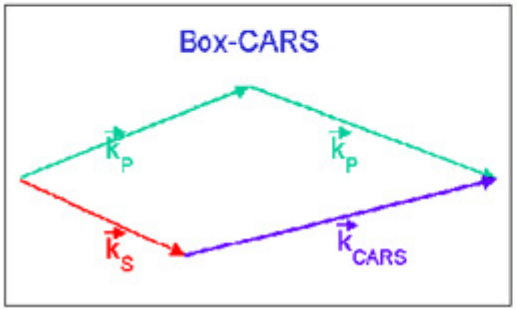


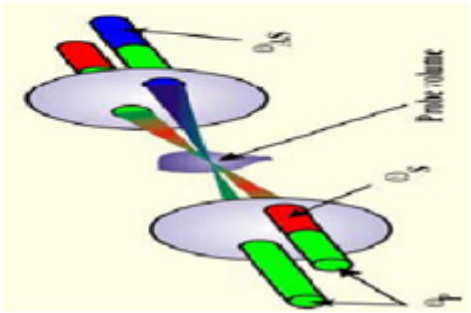
ω_p: **pump laser frequency**
ω_s: **stokes**
ω_{CARS}: **raman frequency of a molecular transition**



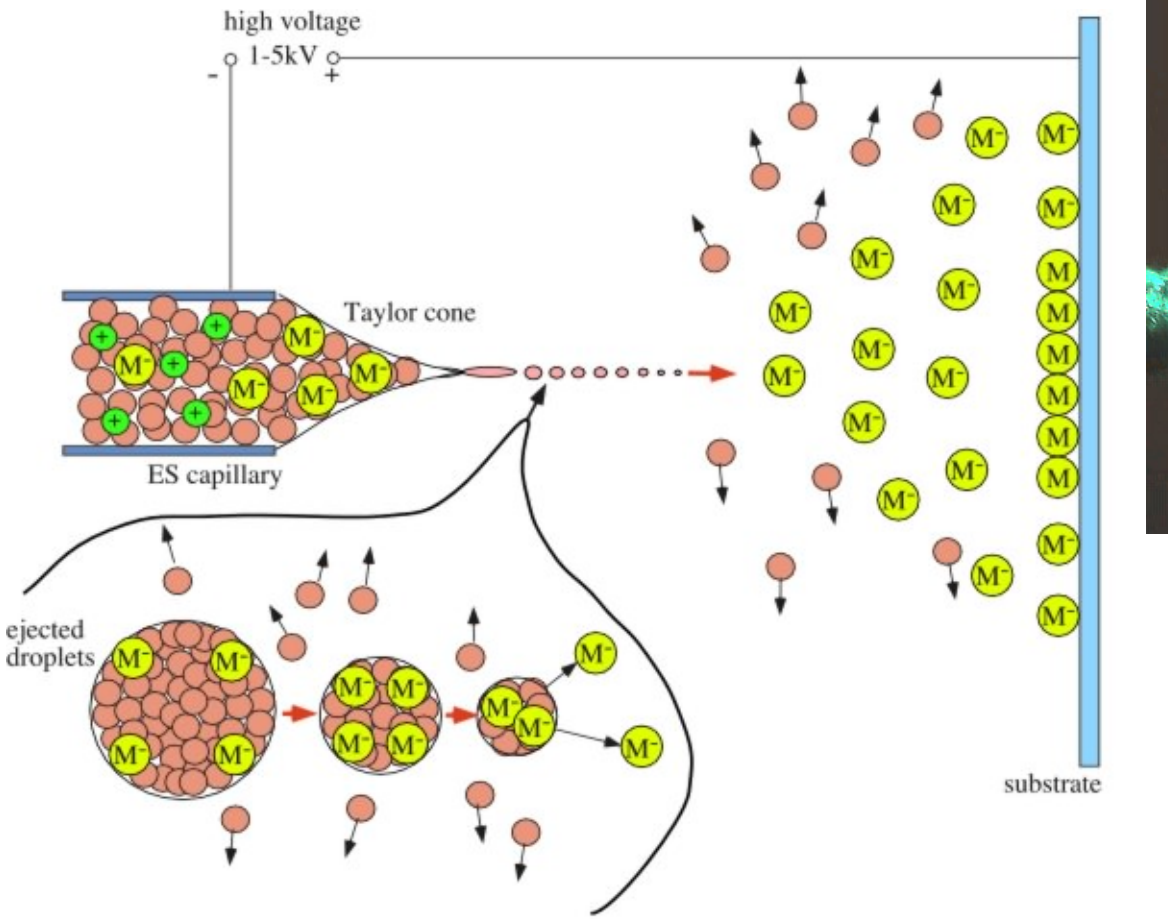


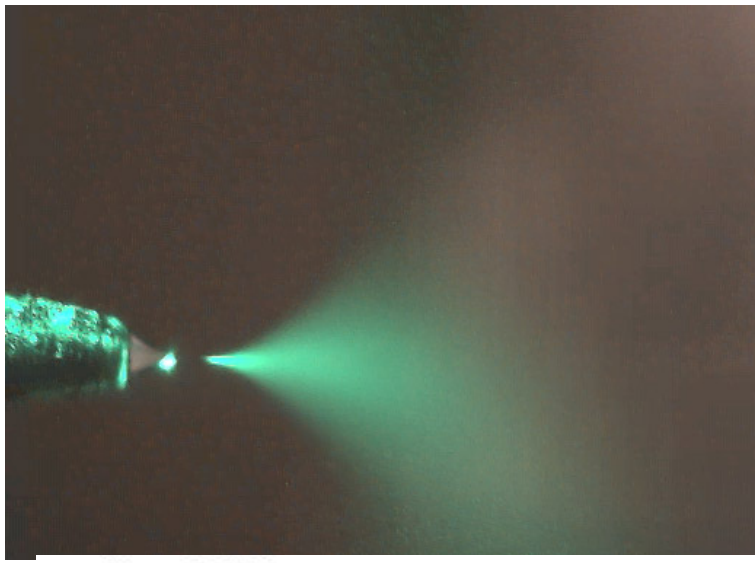
$\vec{k}_P + \vec{k}_P = \vec{k}_S + \vec{k}_{CARS}$

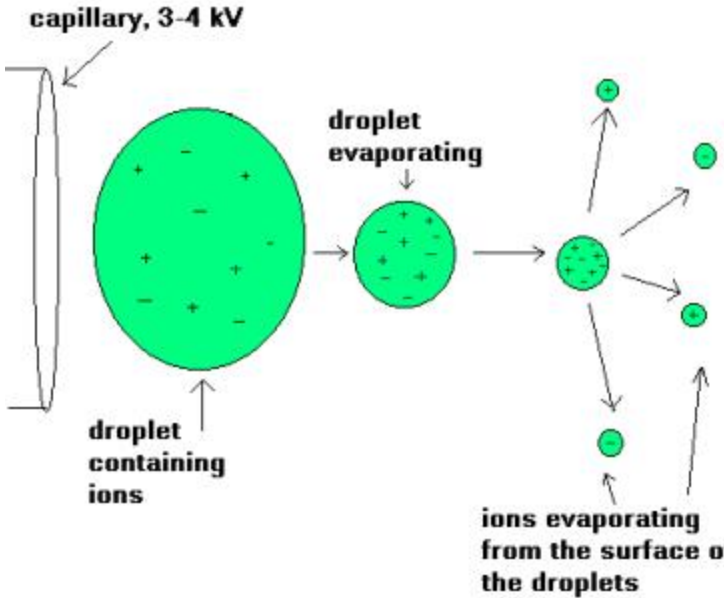




Electrospray







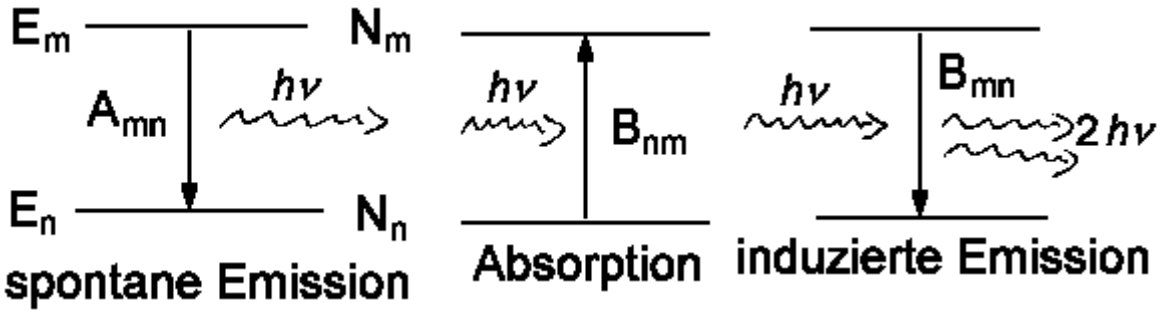
Heterodyne detection

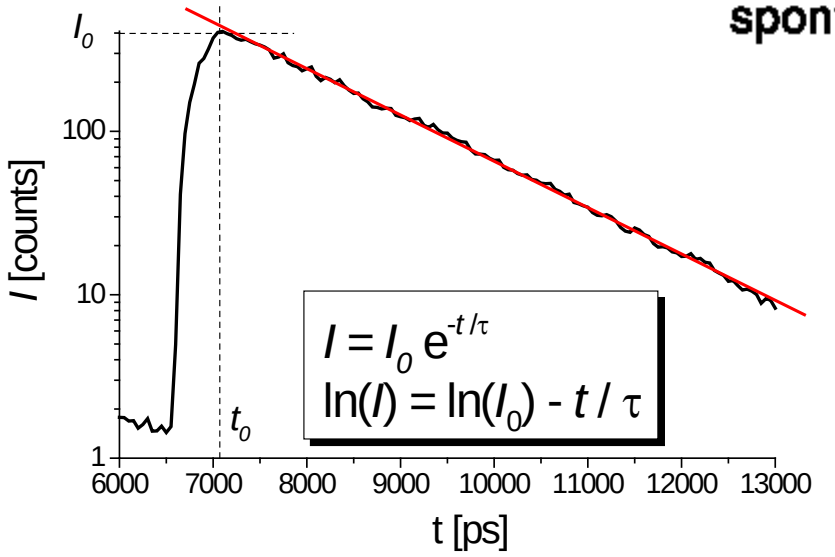
Heterodyne detection is a method of detecting radiation by non-linear mixing with radiation of a reference frequency. It is commonly used in telecommunications and astronomy for detecting and analysing signals.

So weit mit zustandsaufgelösten Messungen.

Jetzt:
Die Geschwindigkeit

Zusammenhang zwischen R_{mn}, Emission A_{mn}, Lebensdauer τ und induzierter Absorption B_{mn}





$$A_{mn}/B_{mn} = 8\pi h\nu^3/c^3$$

$$1/\tau = A_{mn} = 8\pi^2 e^2/(3\,\hbar\varepsilon_o c^3 \cdot \nu_{mn}^3\,|R_{mn}|^2)$$

Zusammenhang zwischen R_{mn}, integriertem Absorptionsquerschnitt σ_0, induzierter Absorption B_{mn} und Oszillatorstärke f_{mn}

$$|R_{mn}|^2 = \frac{3\epsilon_0 \hbar c}{\pi e^2 \nu} \cdot \sigma_o = \frac{6\epsilon_0 \hbar^2}{e^2} \cdot B_{mn} = \frac{3\hbar}{4\pi \nu m_e} \cdot f_{mn}$$

$$I_{trans} = I_0 \cdot e^{-\sigma N l}$$

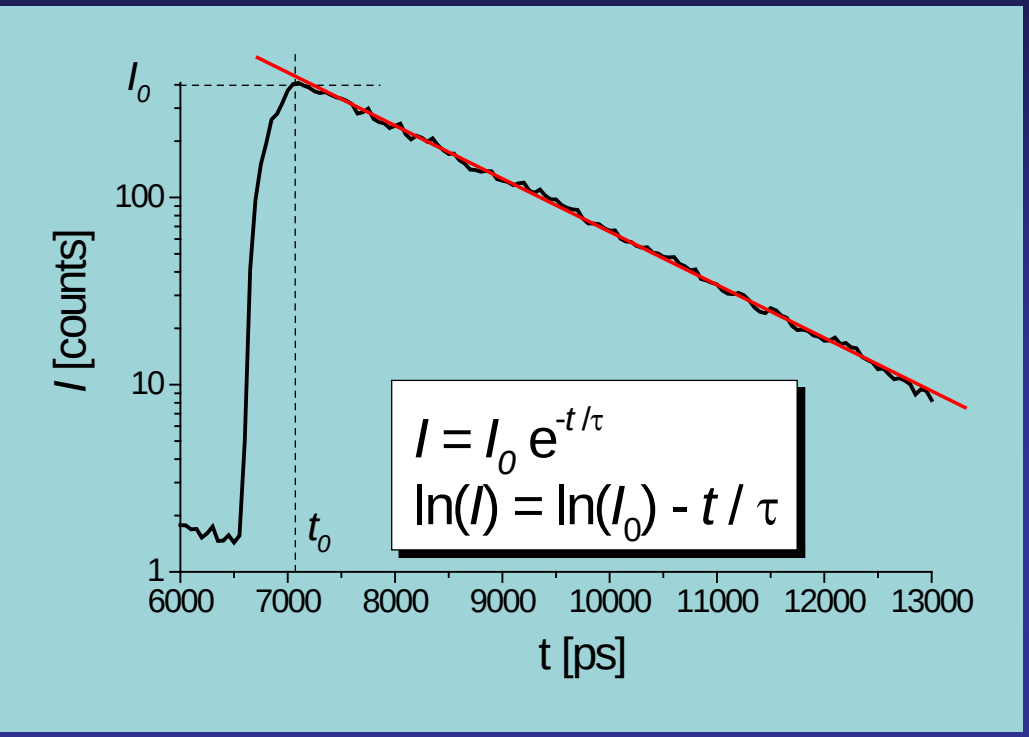
$$\sigma_o = B_{mn} \cdot \frac{h\nu}{c} = \frac{\pi e^2 \nu}{3\epsilon_0 \hbar c} \cdot |R_{mn}|^2 = \frac{e^2}{4\epsilon_0 c m_e} \cdot f_{mn}$$

$$\sigma_o = \int \sigma \, d\nu$$

$$B_{mn} = \frac{c}{h\nu} \cdot \sigma_o = \frac{e^2}{6\epsilon_0 \hbar^2} \cdot |R_{mn}|^2 = \frac{e^2}{4\epsilon_0 h \nu m_e} \cdot f_{mn}$$

$$f_{mn} = \frac{4\epsilon_0 c m_e}{e^2} \cdot \sigma_o = \frac{4\epsilon_0 h \nu m_e}{e^2} \cdot B_{mn} = \frac{4\pi \nu m_e}{3\hbar} \cdot |R_{mn}|^2$$

Fouriertransformation Zeit - Frequenz



Die Fouriertransformierte eines exponentiellen Zerfalls ist eine Lorentzkurve (s. nachfolgende Seite):

$$F(e^{-t/\tau}) \sim {}^{1}/_{(\nu-\nu_0)^2+ (\Delta\nu/2)^2}$$

Die natürliche Linienbreite ist daher mit der Lebensdauer verknüpft:

$$\Delta\nu = {}^{1}/_{2\pi\tau}$$

Die Linienform wird durch eine Lorentzkurve bestimmt.

Ein exponentieller Zerfall führt zur Lorentzkurve

Man beobachtet entsprechend eine exponentielle Abnahme der Strahlungsintensität:

$$I = I_o e^{-t/\tau}$$

Da die Strahlungsintensität proportional zum Quadrat der Amplitude des elektrischen Feldes ist, gilt:

$$A(t) = A_o \, e^{-t/2\tau} \, e^{i\omega_o t}$$

Dabei ist ω_o die Kreisfrequenz der ungedämpften Schwingung. Vor dem Zeitpunkt t=0 sei kein Feld vorhanden. Man erhält nach einer Fourier-Transformation :

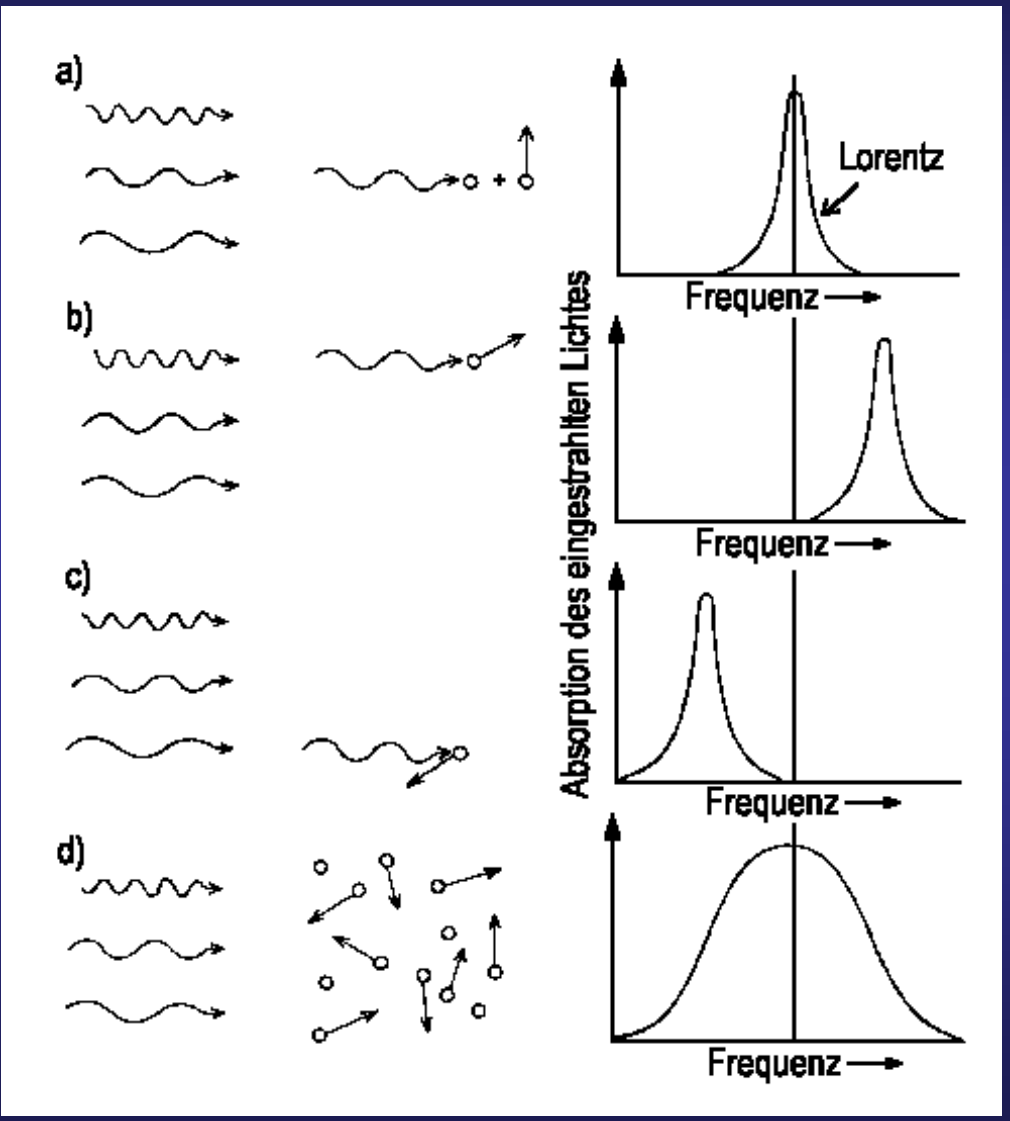
$$\mathcal{A}(\omega) = \int_0^\infty A_o e^{-t/2\tau} e^{i\omega_o t} e^{-i\omega t} dt = A_o / \left(1/2\tau + i(\omega - \omega_o)\right)$$

$$|\mathcal{A}(\omega)|^2 = A_o^2 / \left((\omega - \omega_o)^2 + (1/2\tau)^2\right)$$

Da die Spektralverteilung der Intensität proportional zu $|\mathcal{A}(\omega)|^2$ ist, hat die Linie die Form einer Lorentz-Kurve. Unter der Halbwertsbreite einer Spektrallinie versteht man ihre Breite auf der halben Höhe ihres Spitzenwertes. Für ein Lorentz-Profil ist diese:

$$\Delta\omega = 2\pi\Delta\upsilon = 1/\tau$$

Lorentz- und Dopplerprofil



Lorentzprofil

$$L(\nu,\nu_o) = {}^{1}/_{2\pi}\,{}^{\Delta\nu_L}/_{(\nu-\nu_o)^2+(\Delta\nu_L/2)^2}$$

Aufgrund der Geschwindigkeit v der Moleküle wird ν_o „verschoben“ (Dopplereffekt):

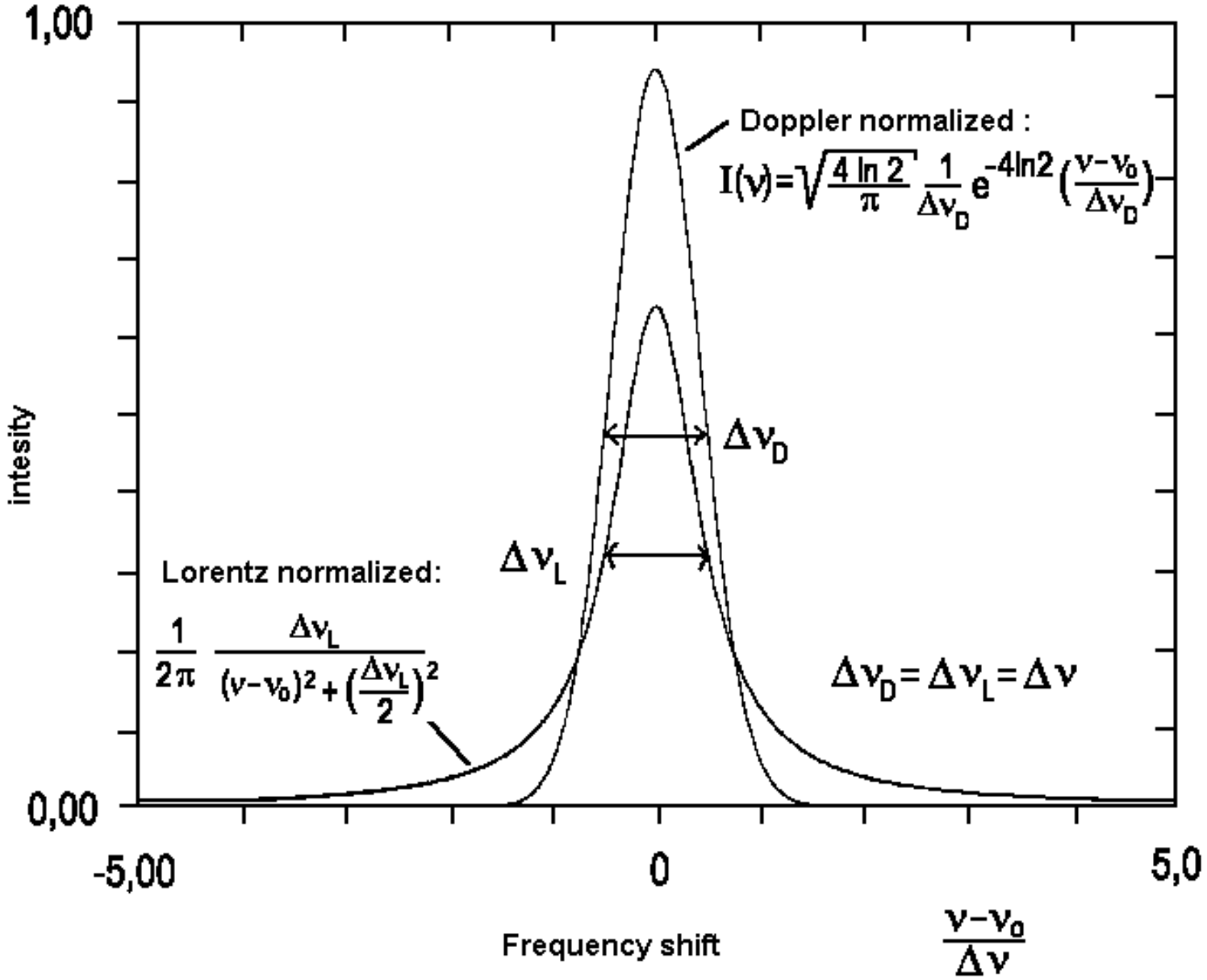
$$\nu = \nu_o(1 - {}^{v}/_{c})$$

Dopplerprofil:

$$I = I_o({}^{4\ln 2}/_{\pi})^{1/2}\cdot {}^{1}/_{\Delta\nu_D}\, e^{-4\ln 2((\nu_o-\nu)/\Delta\nu_D)^2}$$

$$\Delta\nu_D = 2\,{}^{\nu_o}/_{c}(2\ln 2\,{}^{kT}/_{m})^{1/2}$$

Lorentz and Doppler Line Shapes



Aufgabe: Anregung von OH im UV (308nm)

1. Wie groß ist die natürliche Linienbreite (τ = 700ns)?
2. Wie groß ist die Dopplerbreite bei Raumtemperatur?
3. Wie groß ist die Dopplerverschiebung, wenn OH in einer Reaktion mit einer (festen) Geschwindigkeit von 1000 m/s gebildet wird?
4. Zeichnen Sie ein Lorentz- und ein Dopplerprofil unter der Annahme gleicher Breite und gleicher Höhe.