为什么需要超快时间分辨测量

- 很多原子分子中发生的过程在飞秒和皮秒量级
- 虽然荧光寿命在纳秒量级，非辐射驰豫过程可能要快得多

$$1/t_{ex} = 1/t_{fl} + 1/t_{nr}$$

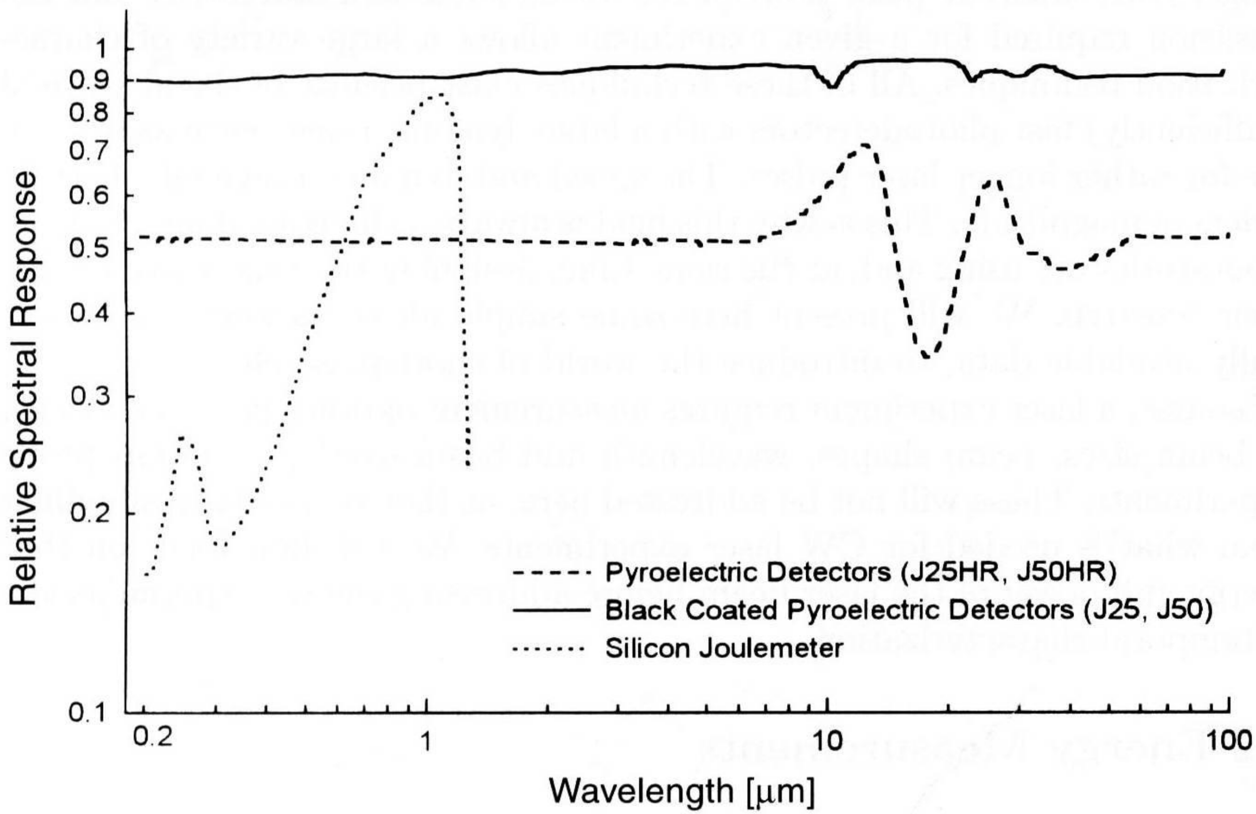
- 生物中很多重要的过程利用的是激发能，这些过程比荧光要快很多
- 室温下液体中的碰撞过程发生在几飞秒的量级，因此大多数液体中的过程都是超快的
- 半导体中很多我们感兴趣的过程是超快的

第十二章　飞秒激光光谱技术

12.1 激光脉冲的测量

12.2 飞秒分辨光谱技术

12.1.1 能量和功率的测量

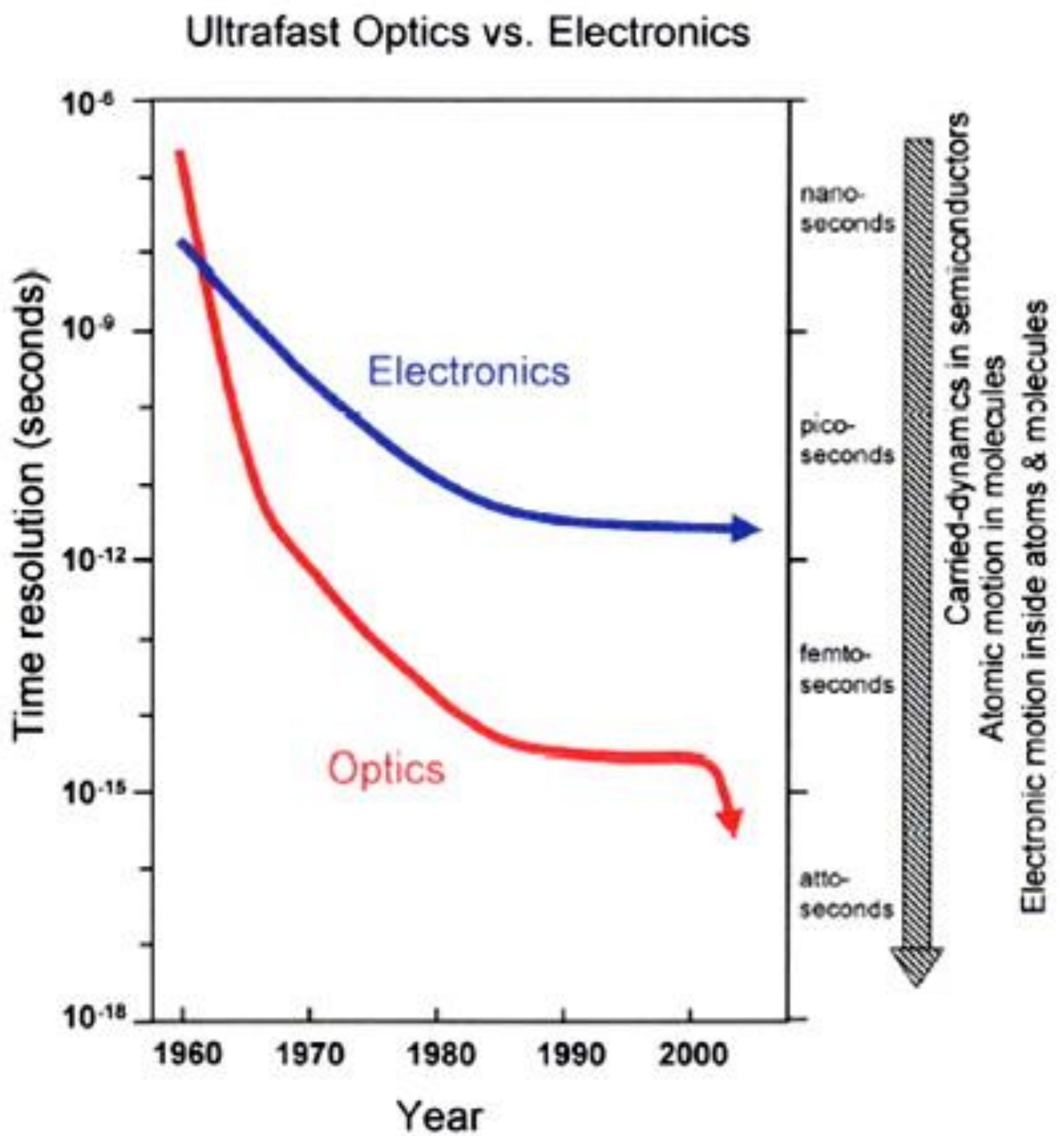


热电探测器和硅探测器的频谱响应

功率计的参数（Model 407A, Spectra-Physics）

Wavelength range	250 nm–11 μm
Power range	
Continuous	$<$ 5 mW to 20 W
Intermittent	up to 30 W
Maximum power density	20 kW/cm^2
Peak pulsed energy density (in 50 ns pulses)	300 mJ/cm^2
Sensitivity variation	±1 %, 400–1000 nm ±3 %, 250 nm–11 μm
Detector spatial sensitivity variation (2 mm beam)	±2.5 %
Meter time constant	$<$ 0.5 s, 1 W scale or higher $<$ 1 s, 30 mW scale

12.1.2 脉冲形状的测量

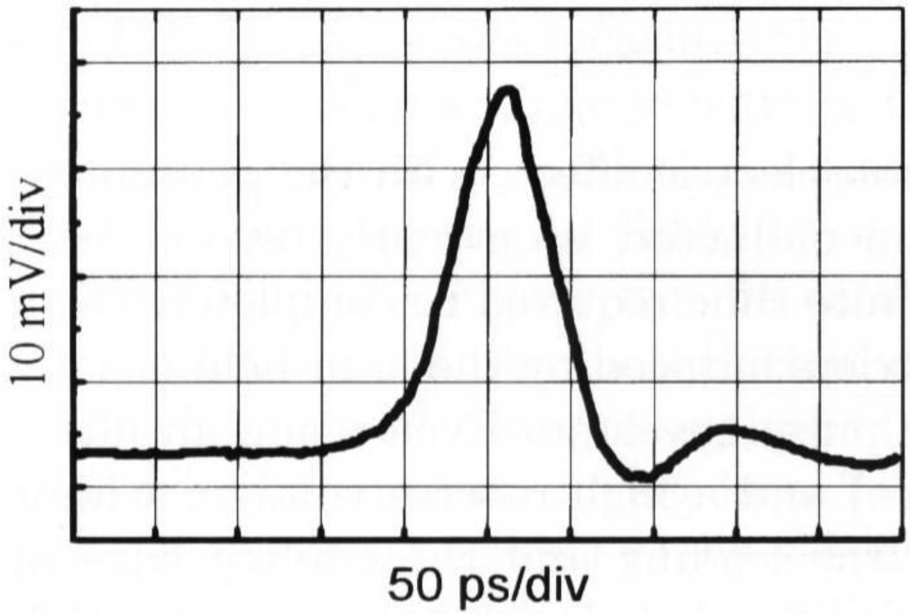


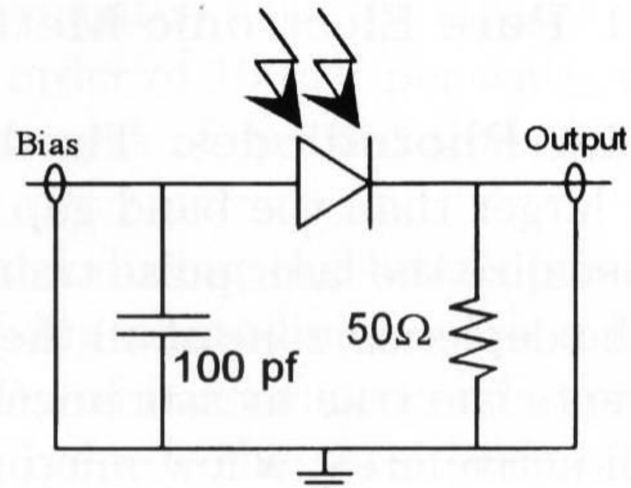
一. 纯电学方法

a. 光电二极管

Model (Si PIN)	Rise time [ps]	FWHM pulse response [ps]	−3dB Bandwith [GHz]	Responsivity [V/W]	Responsivity (in terms of density) [V/(W/mm^2)]
AR-S1	< 100	< 180	> 3.5	16	4
AR-S2	< 35	< 65	> 10	5	0.018
AR-S3	< 25	< 45	> 14	3.75	0.014

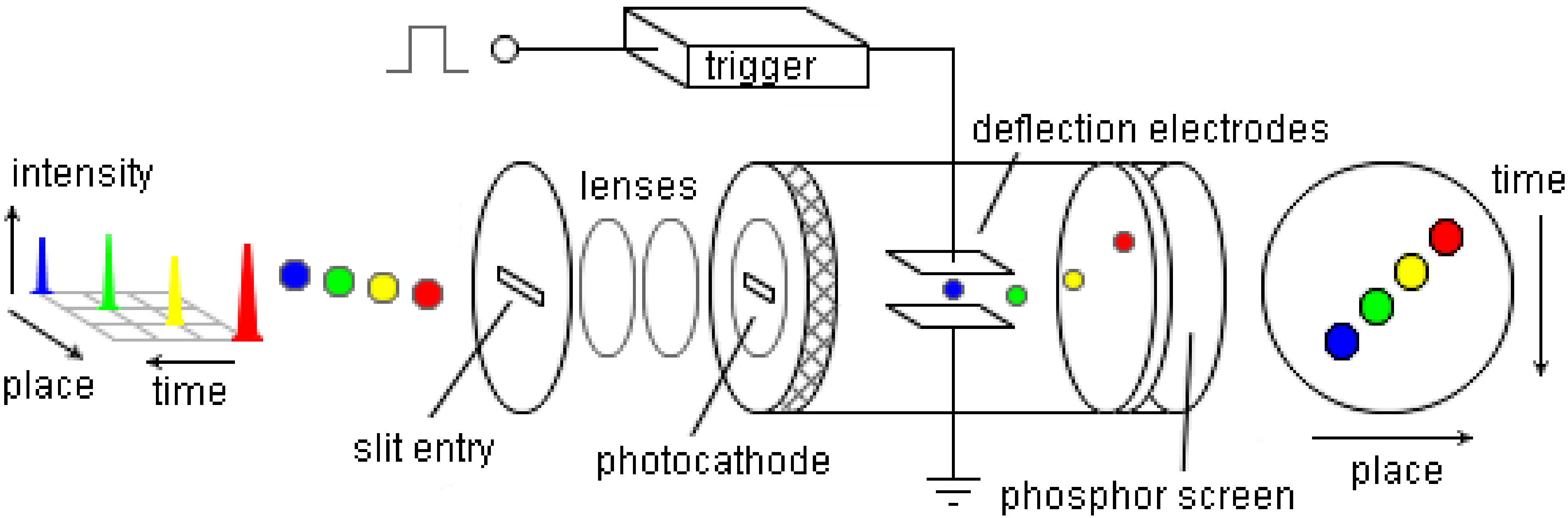
一些光电二极管的数据



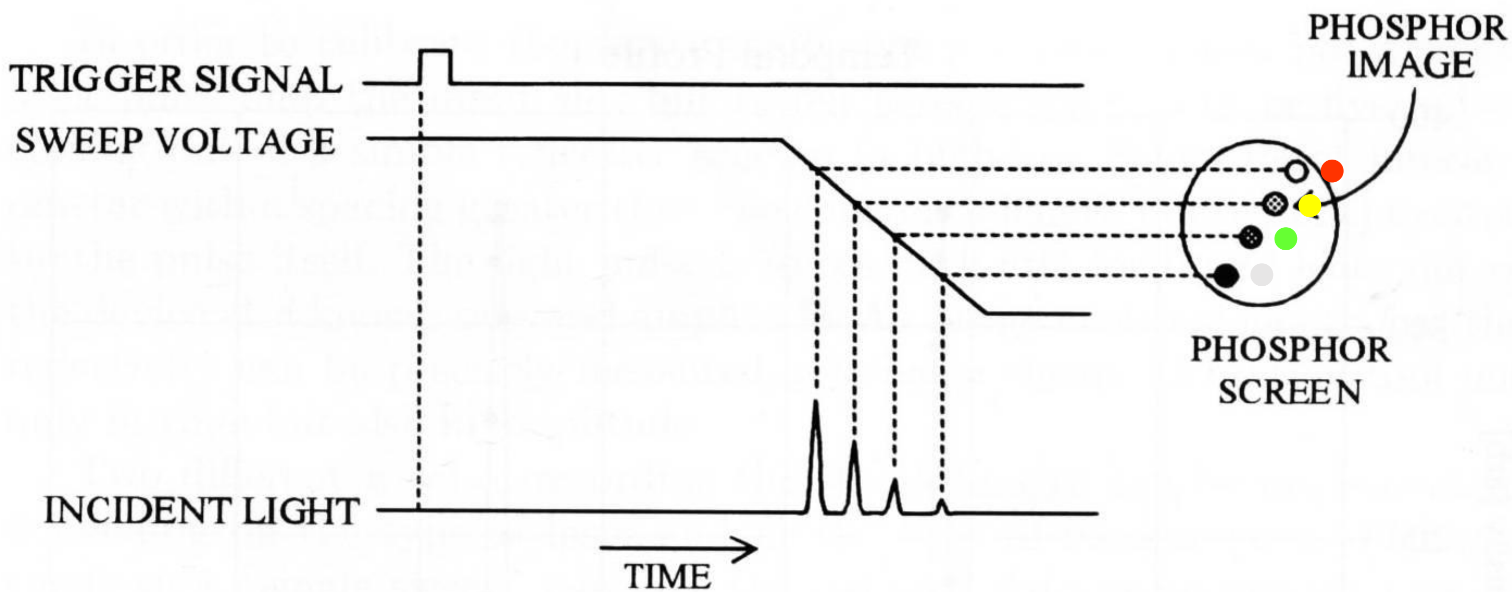


利用光电二极管测量飞秒脉冲得到的信号和电路

b. 条纹相机

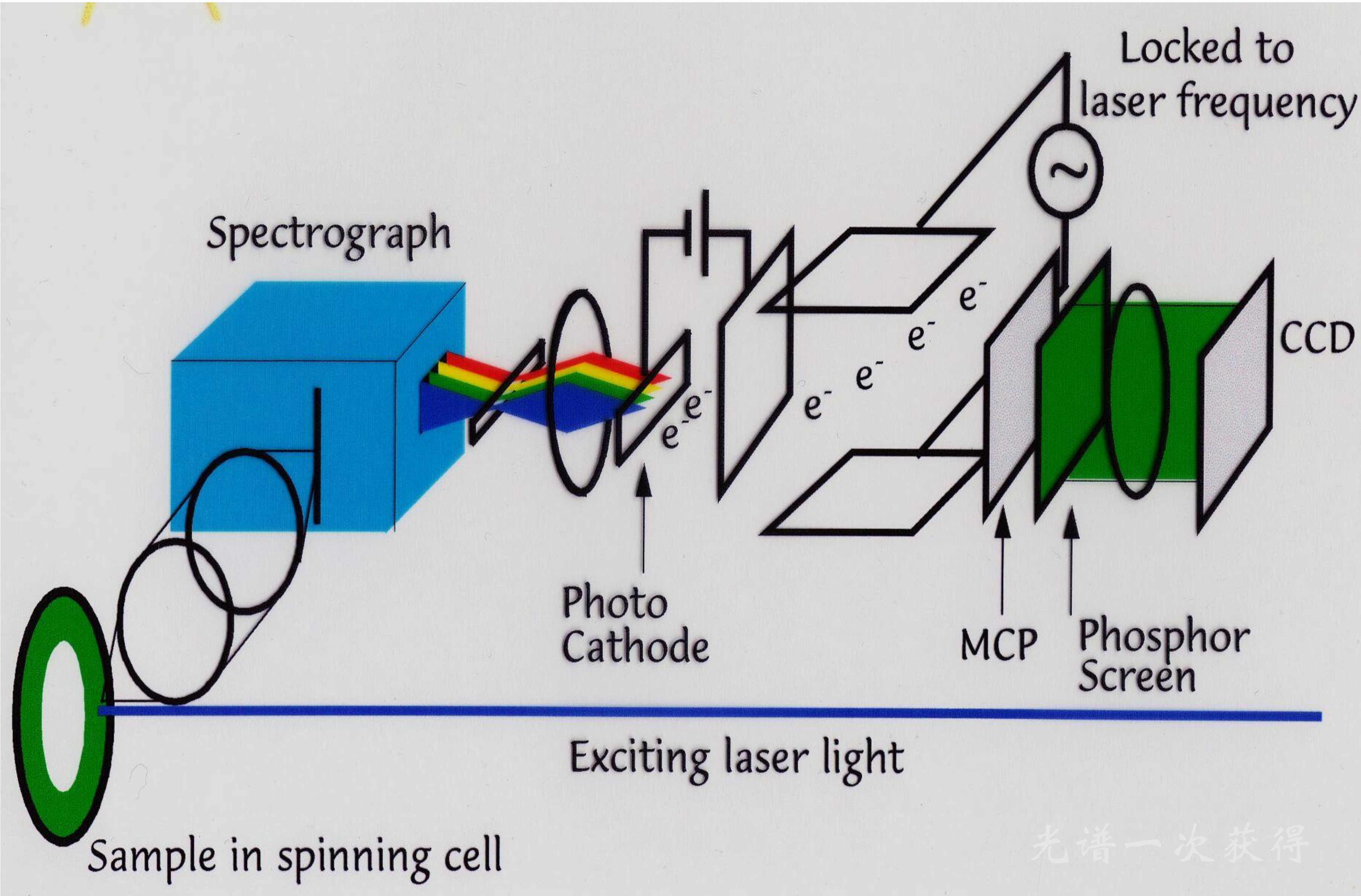


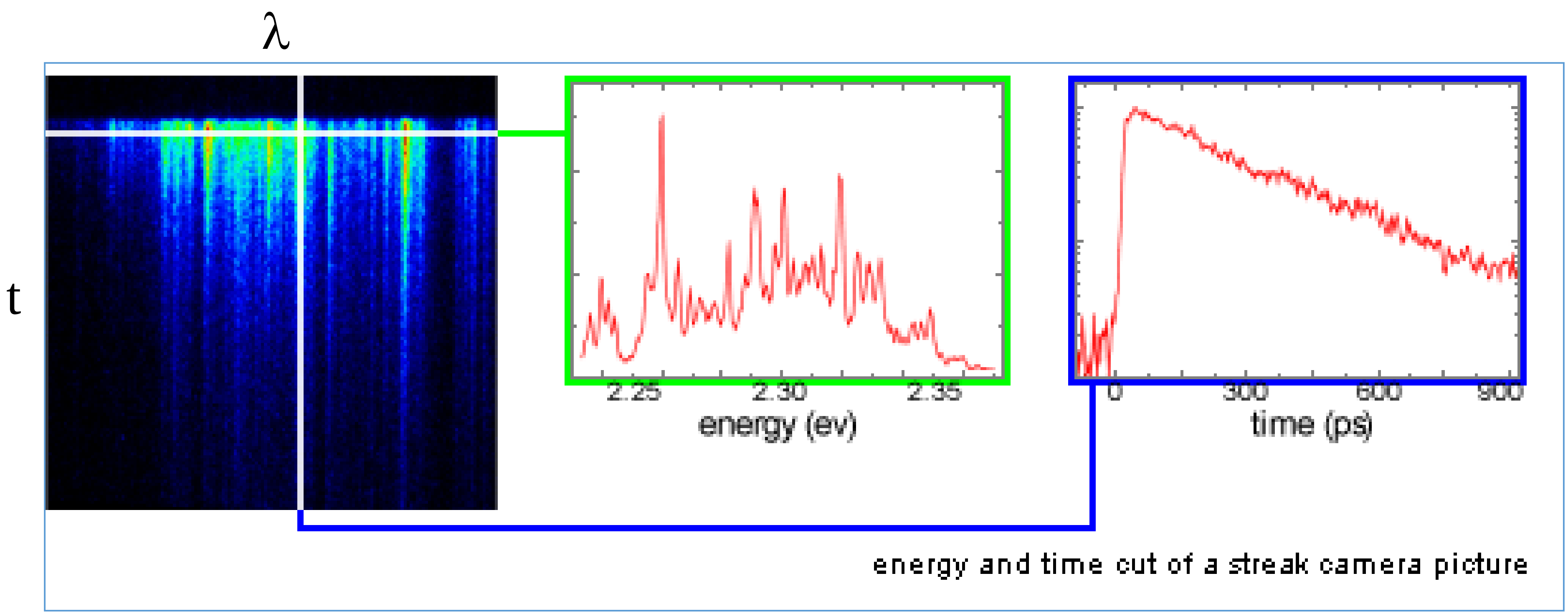
trigger
deflection electrodes
intensity
lenses
time
place
time
slit entry
photocathode
phosphor screen
place



PHOSPHOR IMAGE
TRIGGER SIGNAL
SWEEP VOLTAGE
PHOSPHOR SCREEN
INCIDENT LIGHT
TIME

利用条纹相机测量荧光光谱



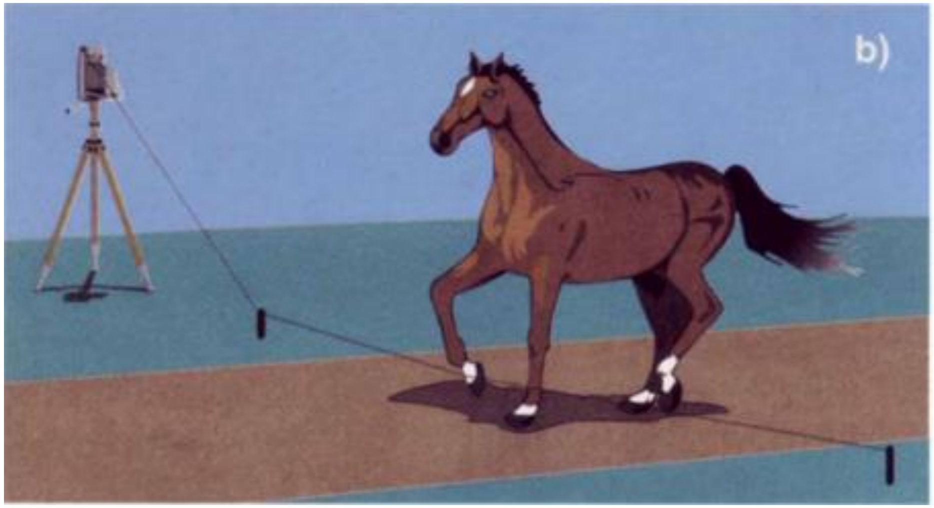


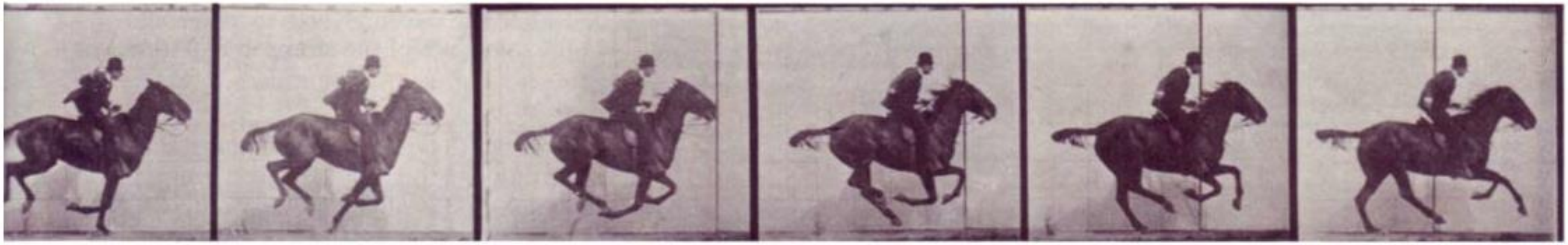
λ
t
2.25
2.30
2.35
energy (ev)
0
300
600
900
time (ps)
energy and time cut of a streak camera picture

条纹相机的输出

时间分辨测量的两种方式

1. 连续光源 + 时间分辨的记录系统





时间分辨率由记录系统决定

2. 脉冲光源 + 无时间分辨的记录系统

过程： 1. 触发： 声或扳机
2. 延时： 控制测量时刻
3. 测量： 曝光

时间分辨率：源的脉冲宽度 + 触发、延时系统精度

连续测量需要过程可重复

为了在时间上测量一个事件，
你需要一个更短的时间尺子

为了研究这样一个事件，
需要一个更短的闪光灯脉冲

Photograph taken by Harold Edgerton, MIT

但是，为了测量闪光灯的脉冲，需要一个响应时间更短的探测器

等等… …

于是，如何测量最短的事件？

二、全光学方法

两个关键：

- 相关函数，$G(\tau)=\int_{-\infty}^{+\infty}F'(t)F(t-\tau)dt$

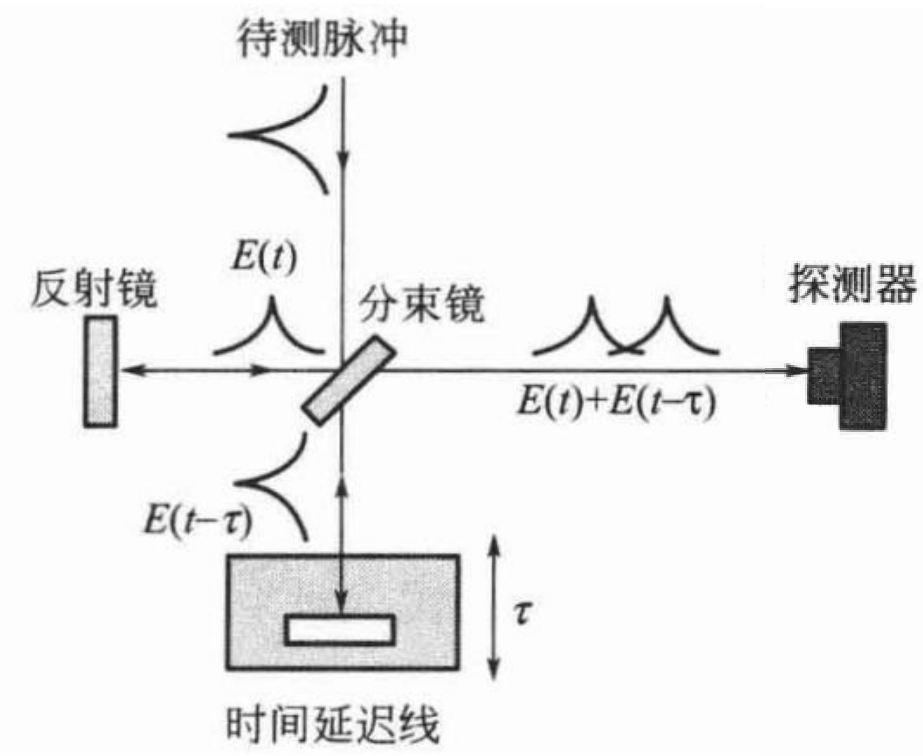
如果G(τ)和F′(t)已知，则可以求出F(t)

- 时间—空间转换，1ps $\leftrightarrow$ 300μm；

自相关：$\boxed{G_1(\tau)=\int_{-\infty}^{+\infty}F(t)F(t-\tau)dt}$

$G_2(\tau)=\int_{-\infty}^{+\infty}[F(t)F(t-\tau)]^2dt \quad G_3(\tau)=\int_{-\infty}^{+\infty}[F(t)F(t-\tau)]^3dt \quad \cdots\cdots$

未知脉冲本身作为测试函数，称为“自相关函数”(autocorrelation functions)。



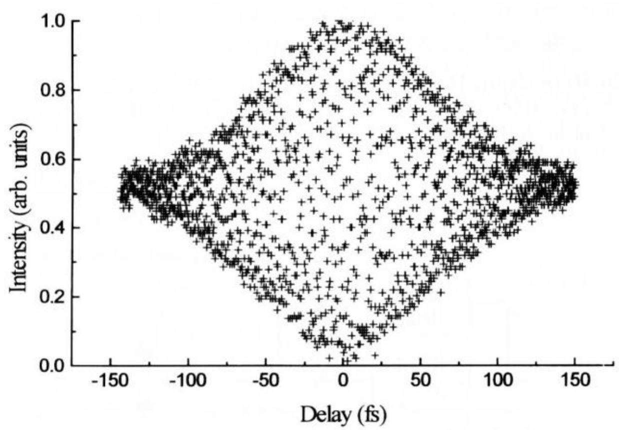
干涉仪自相关器的基本原理

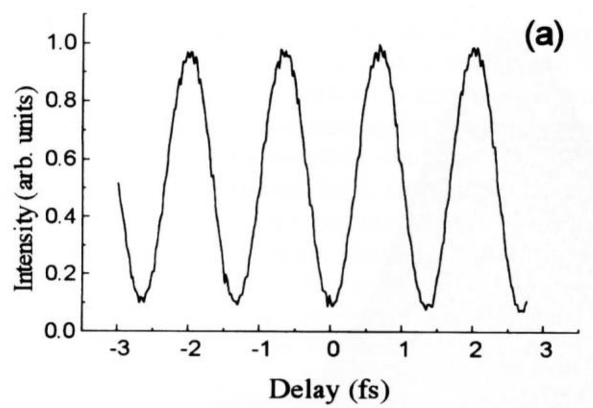
光电场：$E_1(t,\tau) = E(t) + E(t-\tau)$　　τ << 探测器的响应时间

$$I_1(\tau) = \int_{-\infty}^{\infty} [E^2(t) + E^2(t-\tau) + 2|E(t)E(t-\tau)|]dt$$

$$= 2\int I(t)dt + 2G(\tau)$$

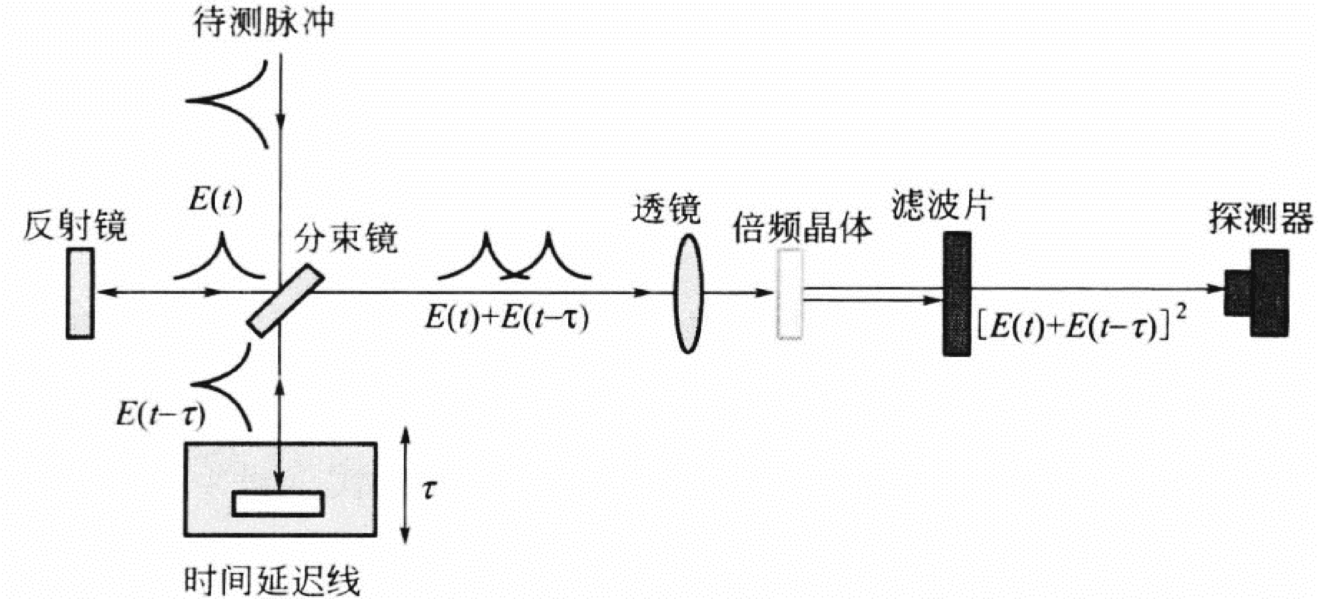
$$I_1(\tau = 0) = 4\int I(t)dt \qquad I_1(\tau \to \infty) = 2\int I(t)dt$$





一阶自相关给出的是相干长度的信息

800nm、100fs脉冲的一阶相关



二阶自相关器示意图

$$I_2(\tau) = \int_{-\infty}^{+\infty} \left| [\mathbf{E}(t) + \mathbf{E}(t-\tau)]^2 \right|^2 dt$$

二阶非线性过程

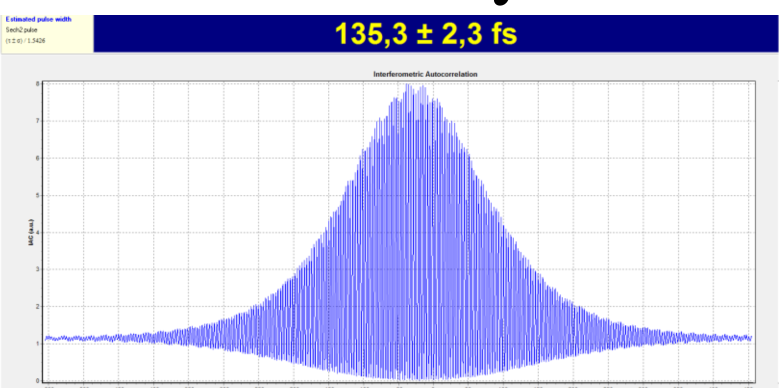
$$I_2(\tau)=\int_{-\infty}^{+\infty}\left|\{E(t)\exp i[\omega t+\Phi(t)]+E(t-\tau)\exp i[\omega(t-\tau)+\Phi(t-\tau)]\}^2\right|^2 dt$$

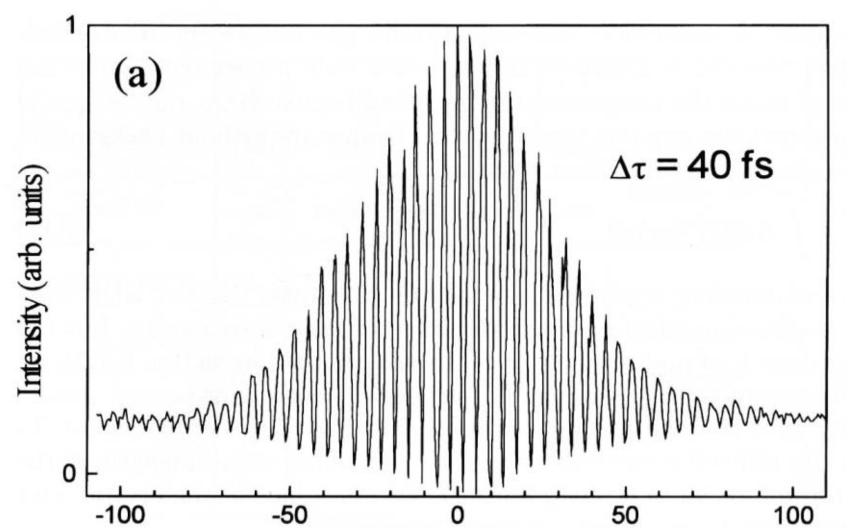
展开并对e$^{i\omega t}$求模：

$$I_2(\tau)=\int_{-\infty}^{+\infty}|\,2E^4+4E^2(t)E^2(t-\tau)+4E(t)E(t-\tau)[E^2(t)+E^2(t-\tau)]\cdot$$
$$\cos[\omega\tau+\Phi(t)-\Phi(t-\tau)]+2E^2(t)E^2(t-\tau)\cos\{2[\omega\tau+\Phi(t)-\Phi(t-\tau)]\}\,|\,dt$$

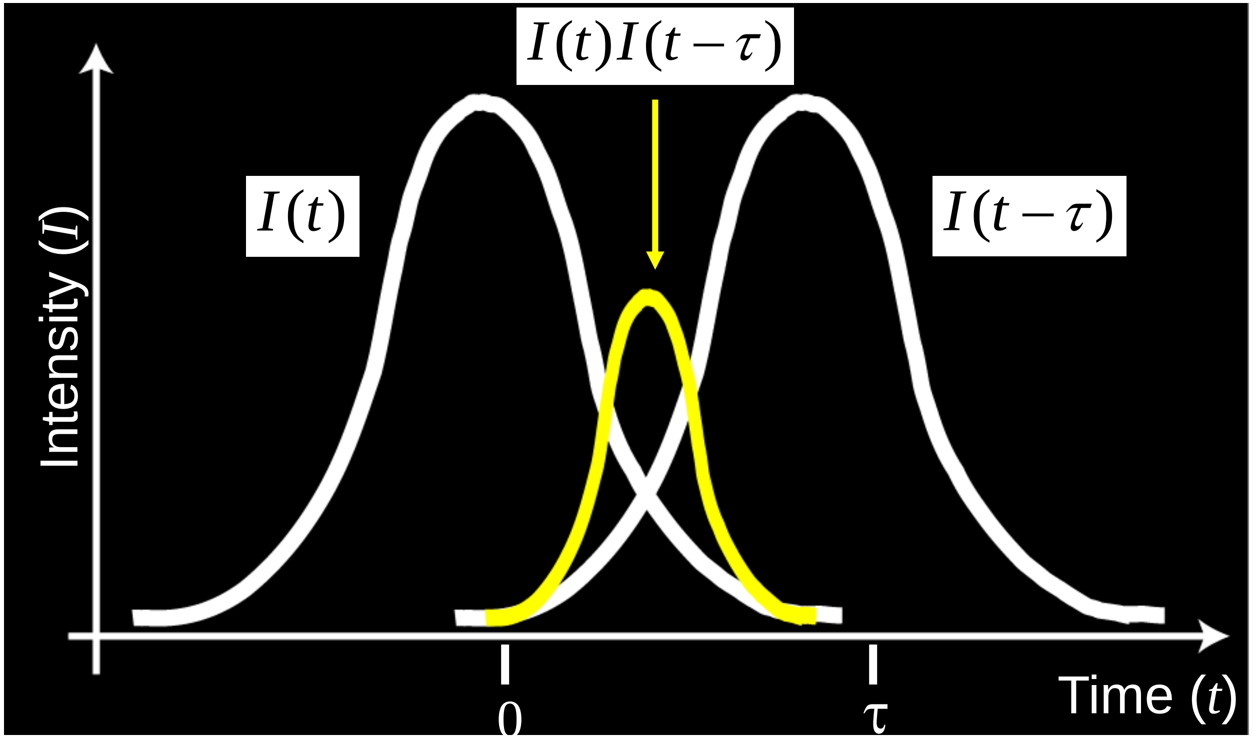
$$I_2(\tau=0)=2^4\int E^4(t)dt$$

$$I_2(\tau\to\infty)=2\int E^4(t)dt$$





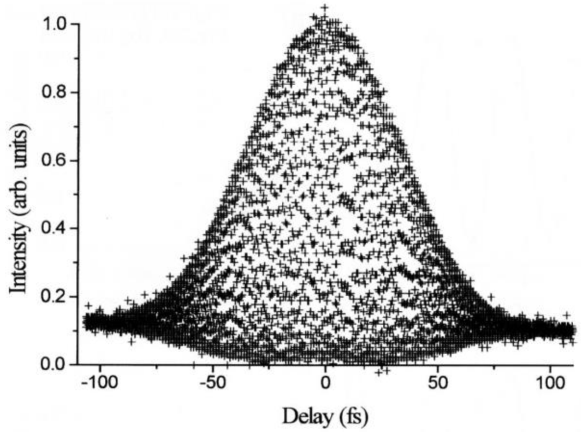
二阶自相关： $G_2(\tau)=\frac{\int I(t)I(t-\tau)dt}{\left|\int I^2 dt\right|}$

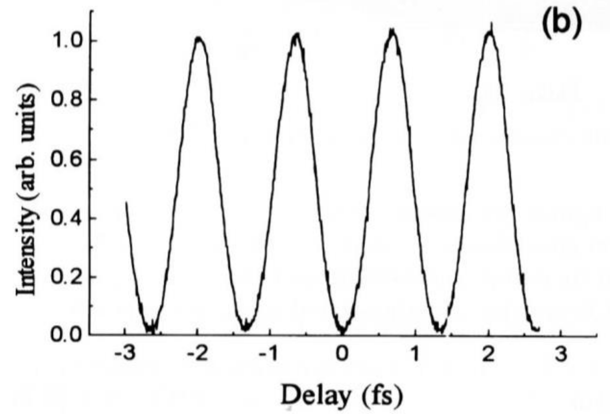


改变两个脉冲间的延时，在两个脉冲重叠处二阶相关不为零

二阶自相关：能给出脉冲重叠的信息，无论两个脉冲是否相干

$$I_2(\tau)=\int_{-\infty}^{+\infty}|\,2E^4+4E^2(t)E^2(t-\tau)+4E(t)E(t-\tau)[E^2(t)+E^2(t-\tau)]\cdot$$
$$\cos[\omega\tau+\Phi(t)-\Phi(t-\tau)]+2E^2(t)E^2(t-\tau)\cos\{2[\omega\tau+\Phi(t)-\Phi(t-\tau)]\}\,|\,dt$$

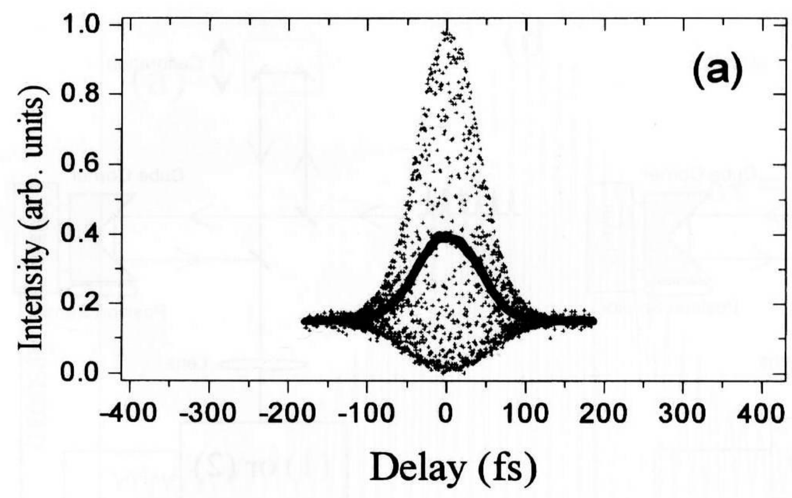


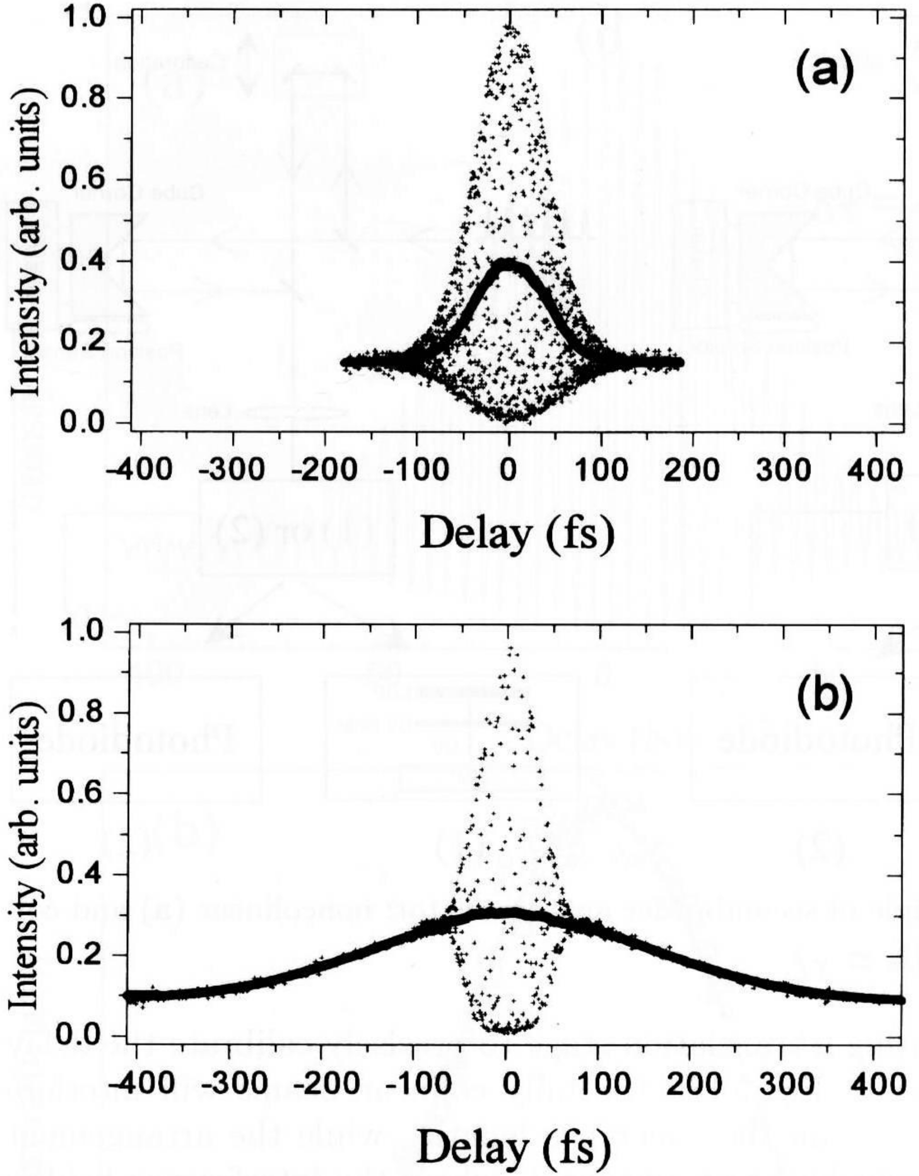


强度相关：

$$S_1=2\int I^2dt+4\int I(t)I(t-\tau)dt$$

对比度为3:1



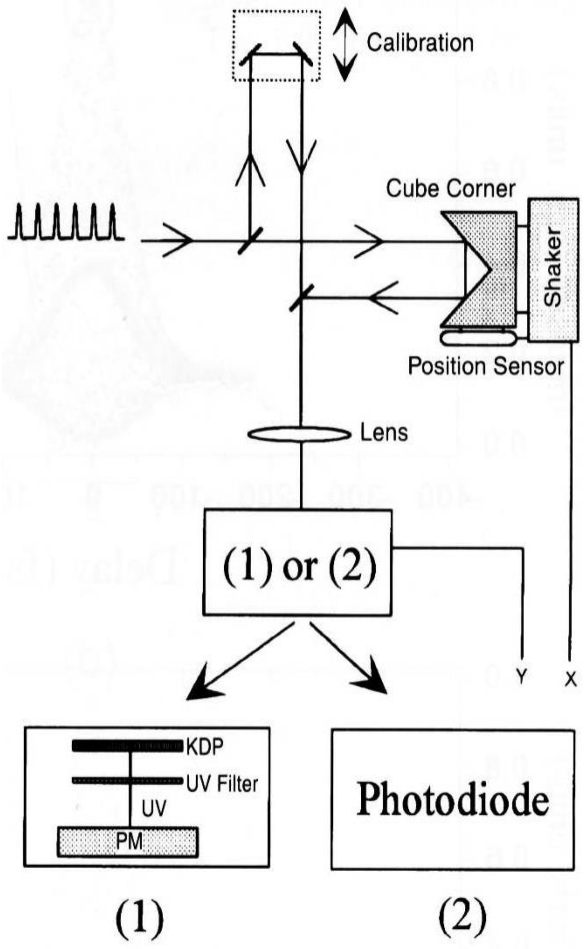


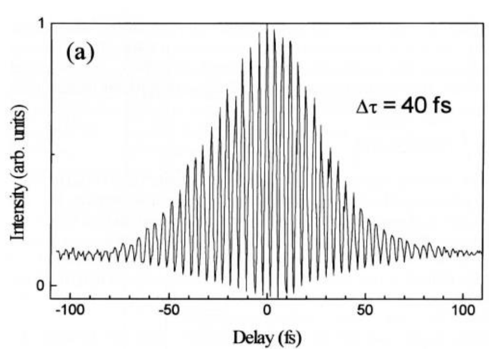
原始脉冲

经过5cm厚玻璃板
展宽后的脉冲

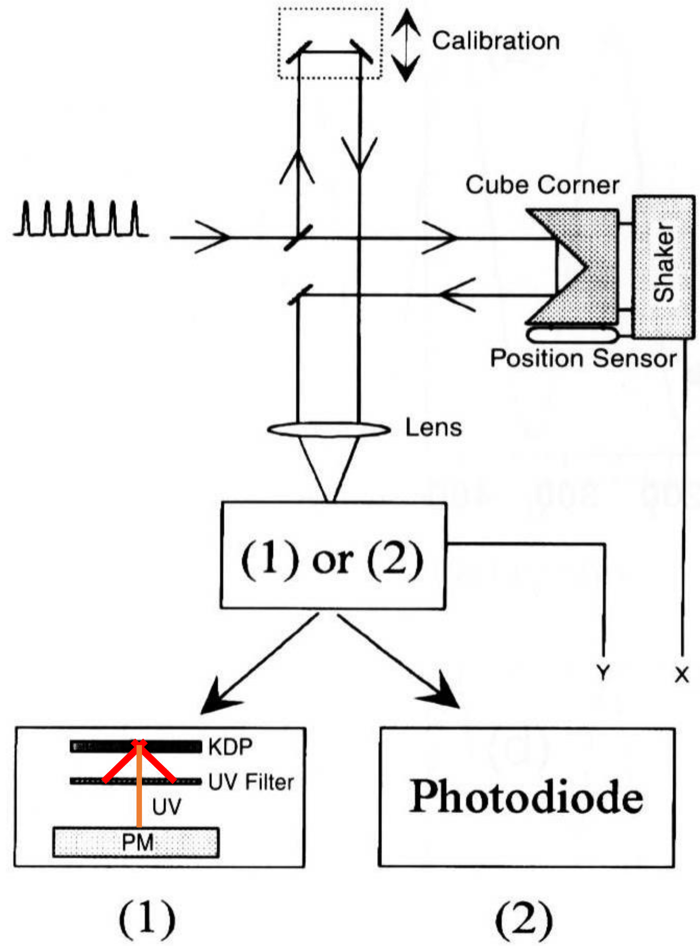
强度（实线）和干涉（点）相关轨迹

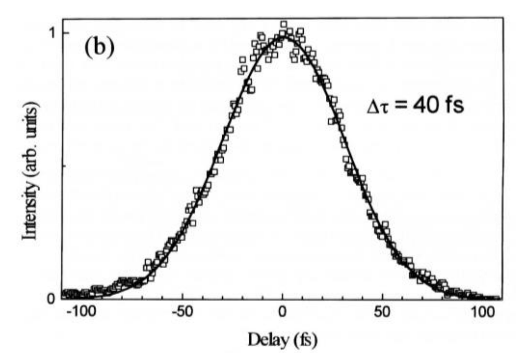
共线


Calibration
Cube Corner
Shaker
Position Sensor
Lens
(1) or (2)
Y
X
KDP
UV Filter
UV
PM
Photodiode
(1)
(2)


(a)
Δτ = 40 fs
Intensity (arb. units)
Delay (fs)
1
0
-100
-50
0
50
100

非共线

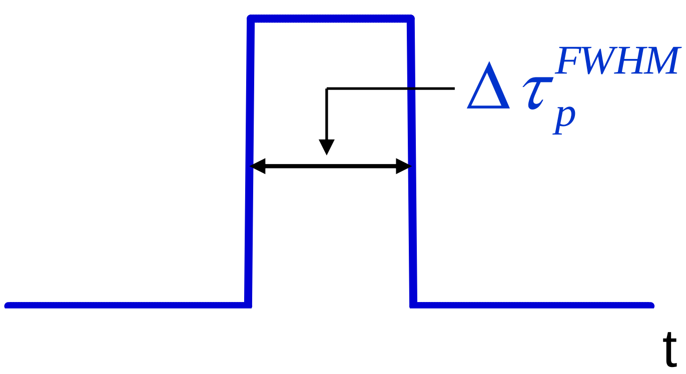

Calibration
Cube Corner
Shaker
Position Sensor
Lens
(1) or (2)
Y
X
KDP
UV Filter
UV
PM
Photodiode
(1)
(2)


(b)
Δτ = 40 fs
Intensity (arb. units)
Delay (fs)
1
0
-100
-50
0
50
100

方形脉冲和它的自相关

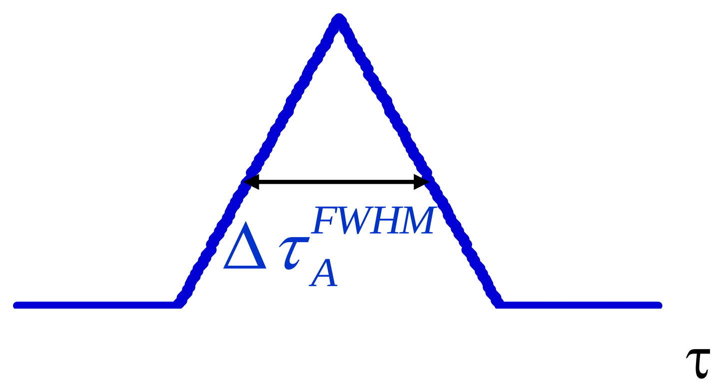
Pulse

$$I(t) = \begin{cases} 1; & |t| \le \Delta\tau_p^{FWHM}/2 \\ 0; & |t| > \Delta\tau_p^{FWHM}/2 \end{cases}$$



Autocorrelation

$$G^{(2)}(\tau) = \begin{cases} 1 - \left|\dfrac{\tau}{\Delta\tau_A^{FWHM}}\right|; & |\tau| \le \Delta\tau_A^{FWHM} \\ 0; & |\tau| > \Delta\tau_A^{FWHM} \end{cases}$$



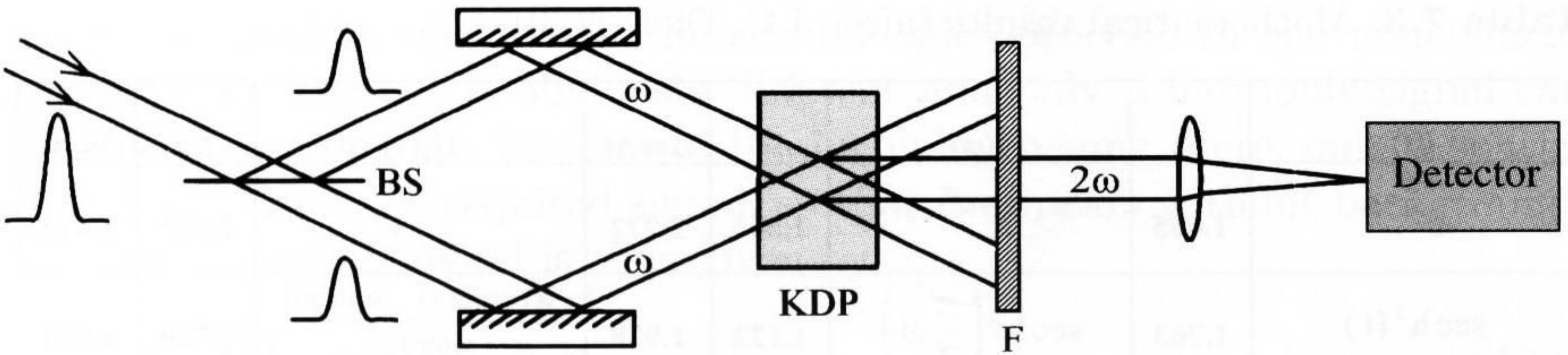
$$\Delta\tau_p^{FWHM} = \Delta\tau_A^{FWHM}$$

脉冲半宽 → Δt　　强度相关半宽 → $\Delta\tau$

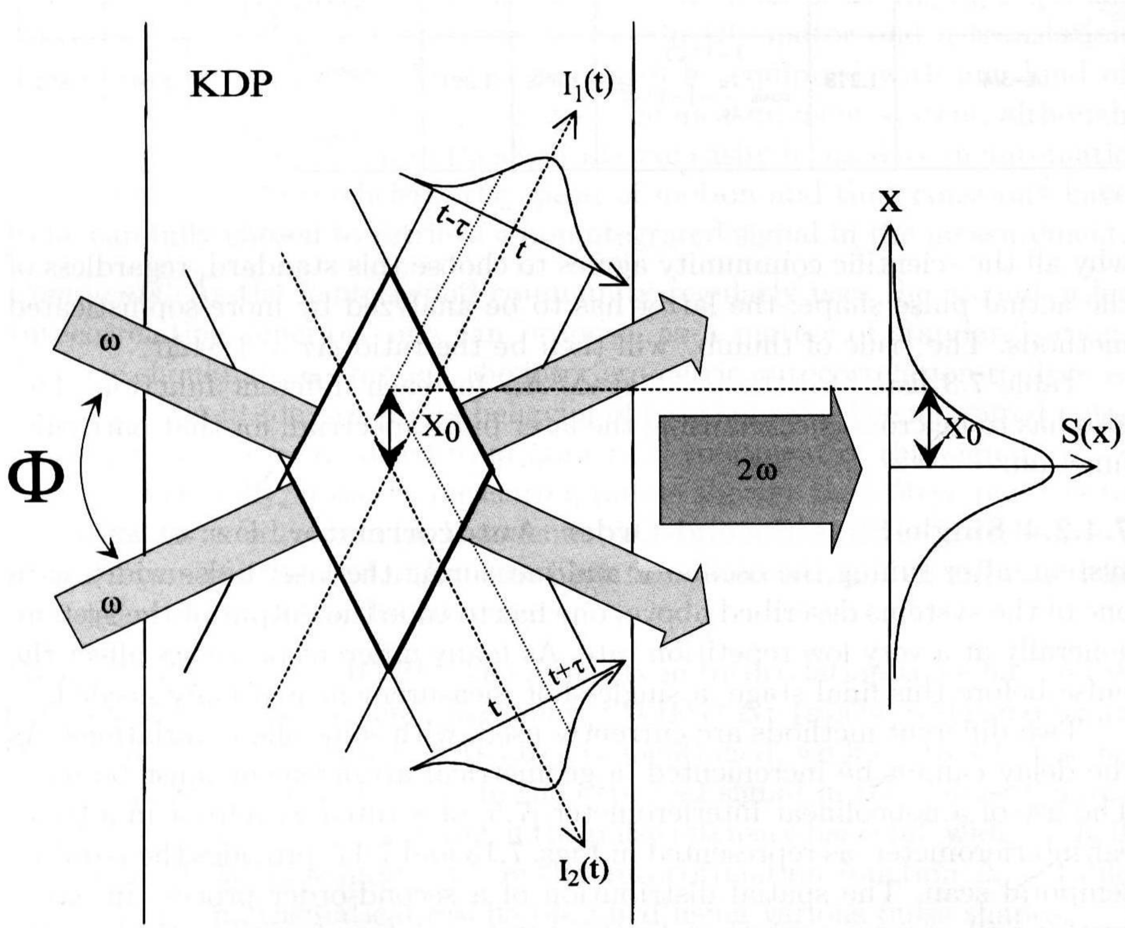
$I(t)$	Δt	$I(\omega)$	$\Delta\omega$	$\Delta\omega\cdot\Delta t$	$G_2(\tau)$	$\Delta\tau$	$\Delta\tau/\Delta t$
e^{-t^2}	1.665	$e^{-\omega^2}$	1.665	2.772	$e^{-\frac{\tau^2}{2}}$	2.355	1.414
$\operatorname{sech}^2(t)$	1.763	$\operatorname{sech}^2\left(\frac{\pi}{2}\omega\right)$	1.122	1.978	$\frac{3[\tau\cosh(\tau)-\sinh(\tau)]}{\sinh^3(\tau)}$	2.720	1.543
$\frac{1}{e^{t/(t-A)}+e^{-t/(t-A)}}$ A=1/4						2.648	1.544
A=1/2	1.565	$\operatorname{sech}\left(\frac{3\pi}{4}\omega\right)$	1.118	1.749	$\frac{3\sinh(\frac{8}{3}\tau)-8\tau}{4\sinh^3\left(\frac{4}{3}\tau\right)}$	2.424	1.549
A=3/4	1.278	$\frac{1-1/\sqrt{2}}{\cosh\left(\frac{7\pi}{16}\omega\right)-1/\sqrt{2}}$	1.088	1.391	$\frac{2\cosh(\frac{16}{7}\tau)+3}{5\cosh^3\left(\frac{8}{7}\tau\right)}$	2.007	1.570

$$\Delta\tau = 1.54\Delta t$$

单脉冲二阶自相关



单脉冲非共线干涉自相关仪的原理



几何结构

偏离中心x_0处的光脉冲时间波形为$I_1(t-\tau)$和$I_2(t+\tau)$
倍频光正比于$I_1(t-\tau)I_2(t+\tau)$

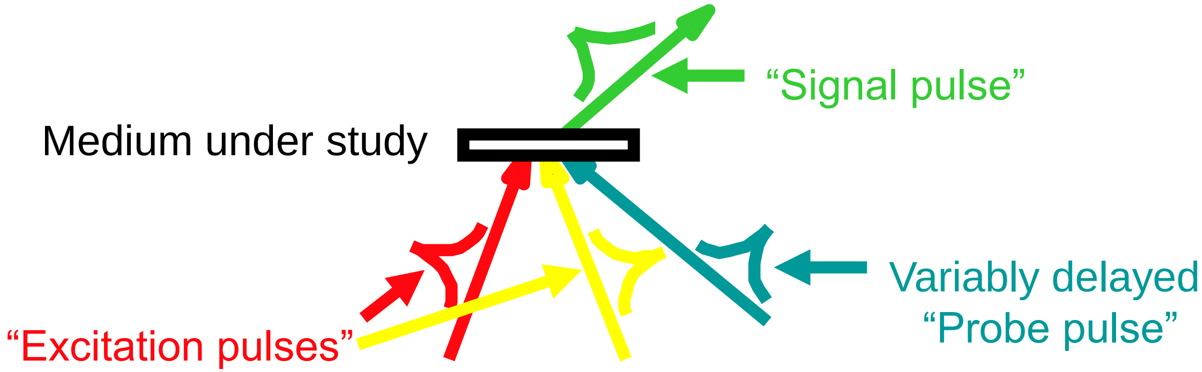
延时： $\tau = \dfrac{n x_0 \sin(\Phi / 2)}{c}$

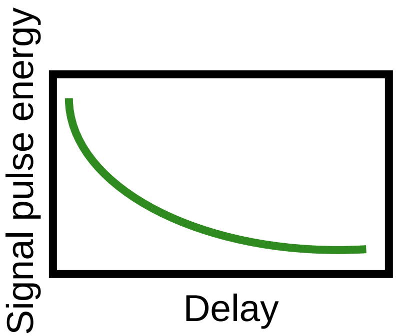
12.2 飞秒分辨光谱技术

12.2.1 泵浦—探测方法

12.2.2 时间分辨发射谱：光学方法

12.2.3 瞬态光栅技术

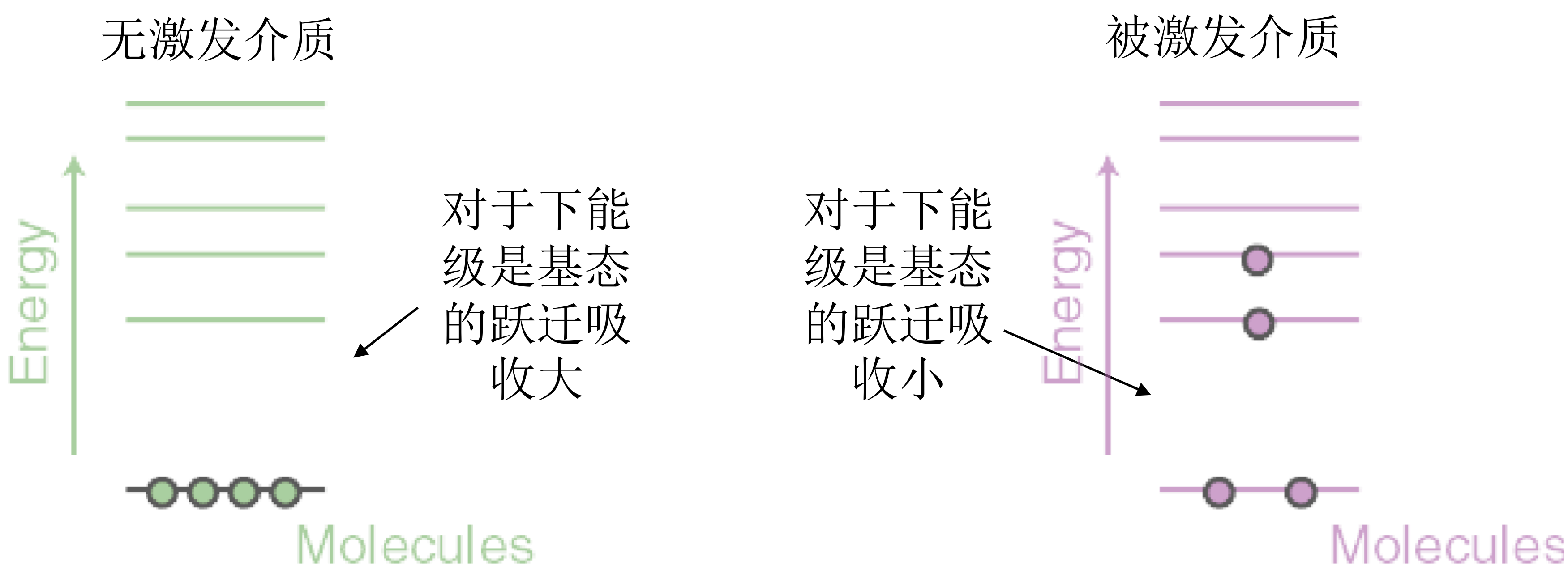




给出光信号随延时的变化关系，时间分辨率为脉冲宽度

时间分辨光谱

激发脉冲将分子激发到激发态，改变吸收、折射率和布居数。



经一段时间，系统恢复原状(设弛豫为单指数)

吸收：$\alpha(t) = \alpha_0\,[1\text{-}\exp(-t/\tau)]$ for $t > 0$ （时间分辨率：脉冲宽度）

荧光：$I(t) = I_0 \exp(-t/\tau)$ for $t > 0$

12.2.1 泵浦－探测方法

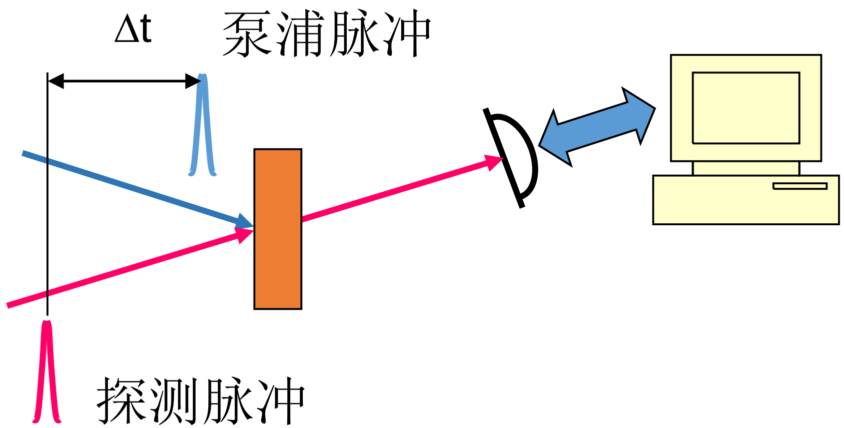
两种方法分析泵浦光对样品的作用引起的改变：

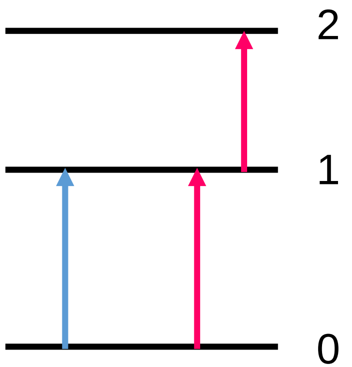
(1)比较泵浦光作用前后探测光的改变（密度、相位和波矢），叫做时间分辨吸收技术；

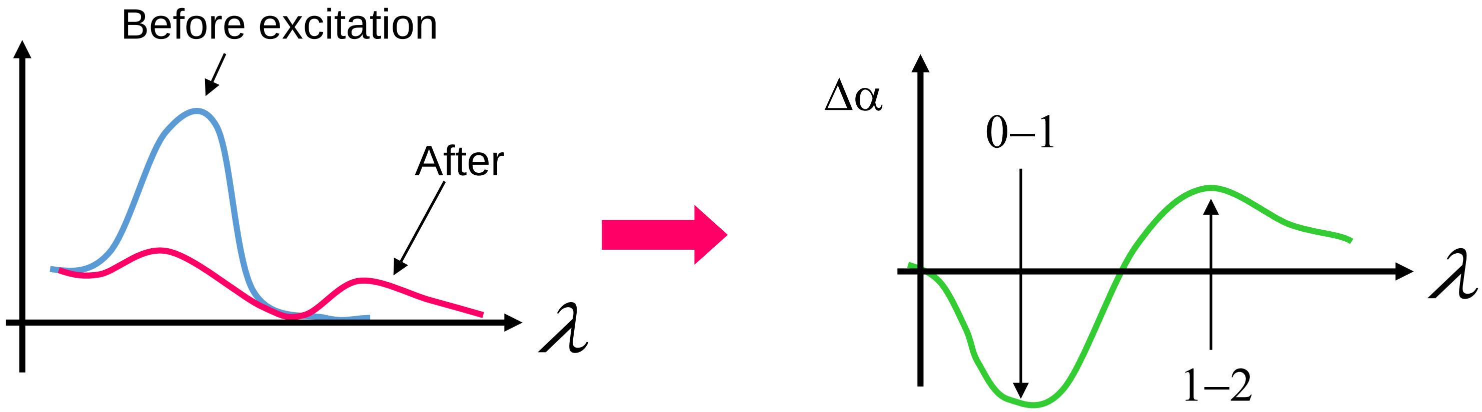
(2)观察泵浦光作用前后探测光本身引起的新的效应，如喇曼散射光谱、光荧光谱和相干反斯托克斯喇曼谱等。

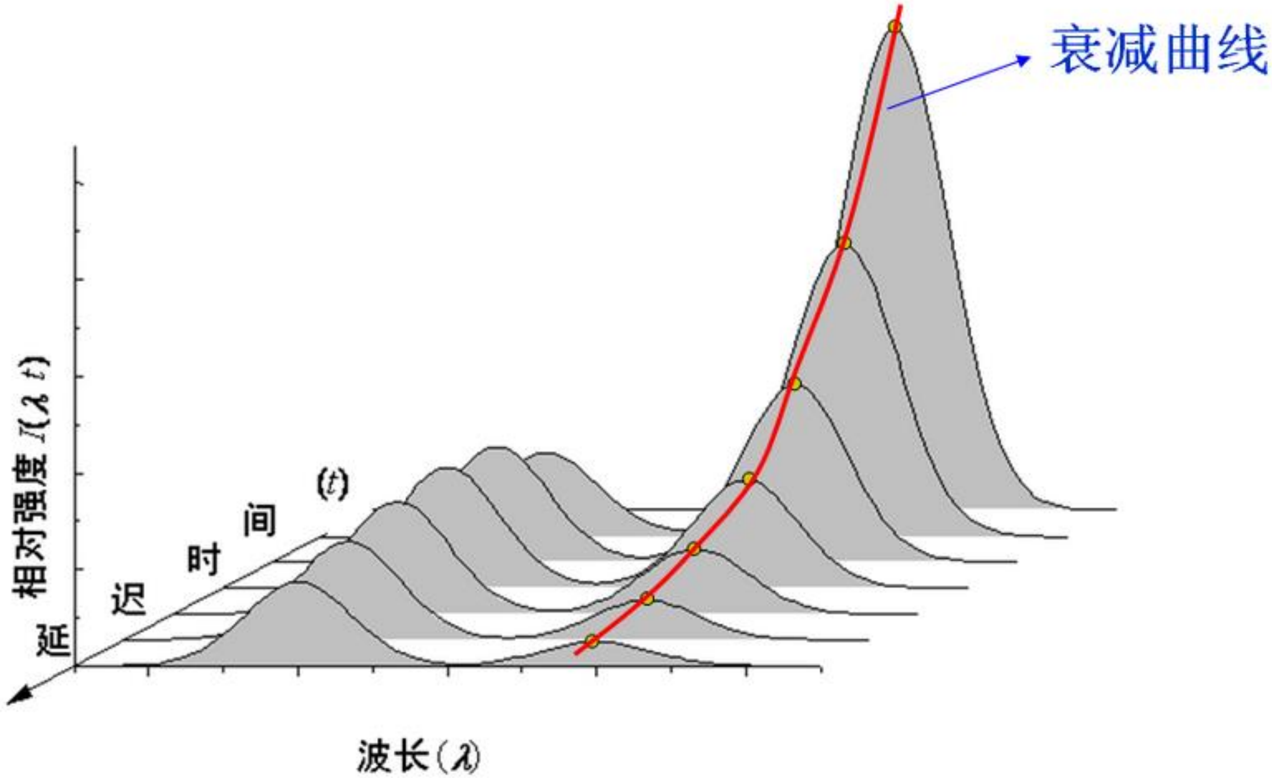
<u>泵浦－探测技术</u>：通过测量泵浦光照射前和照射后探测光的变化，给出吸收随时间的变化，以此来构造布居动力学。

泵浦—探测实验

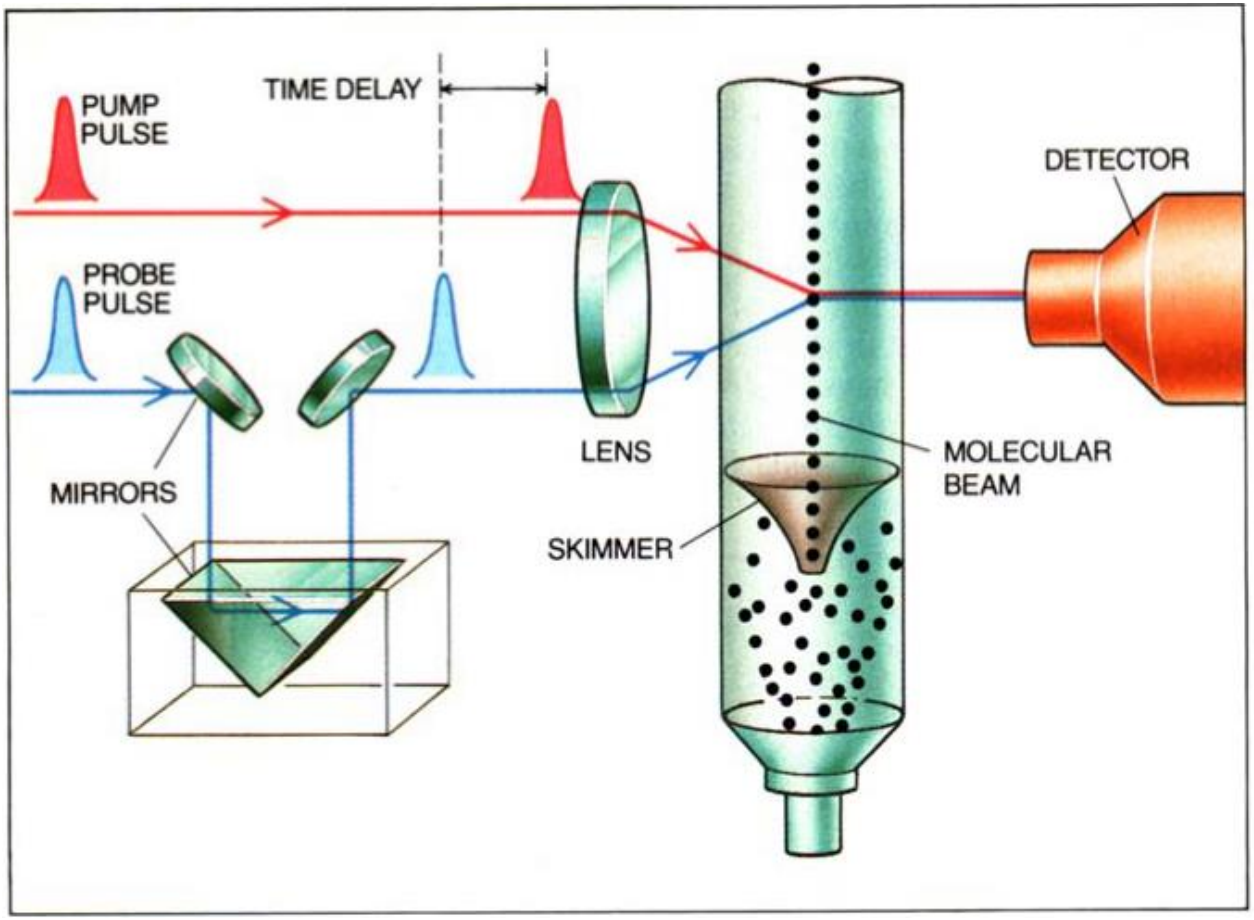






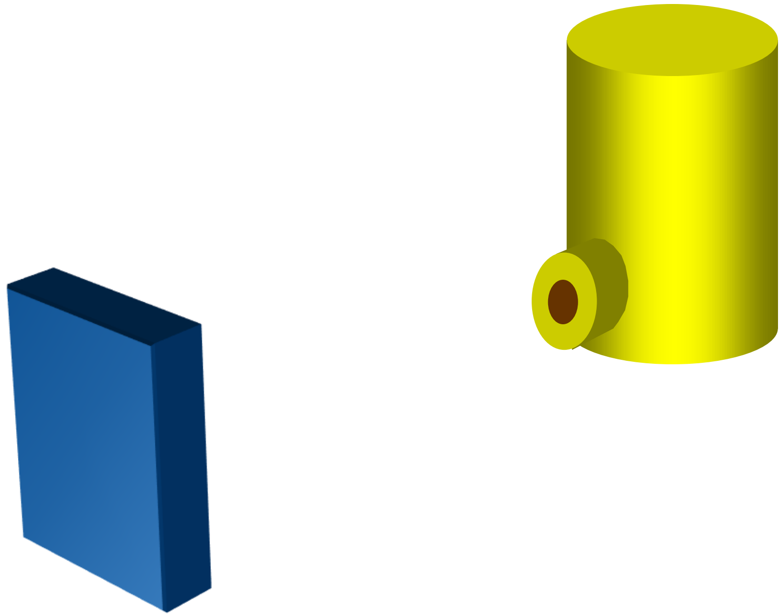


衰减曲线
相对强度 I(λ t)
延迟时间 (t)
波长(λ)

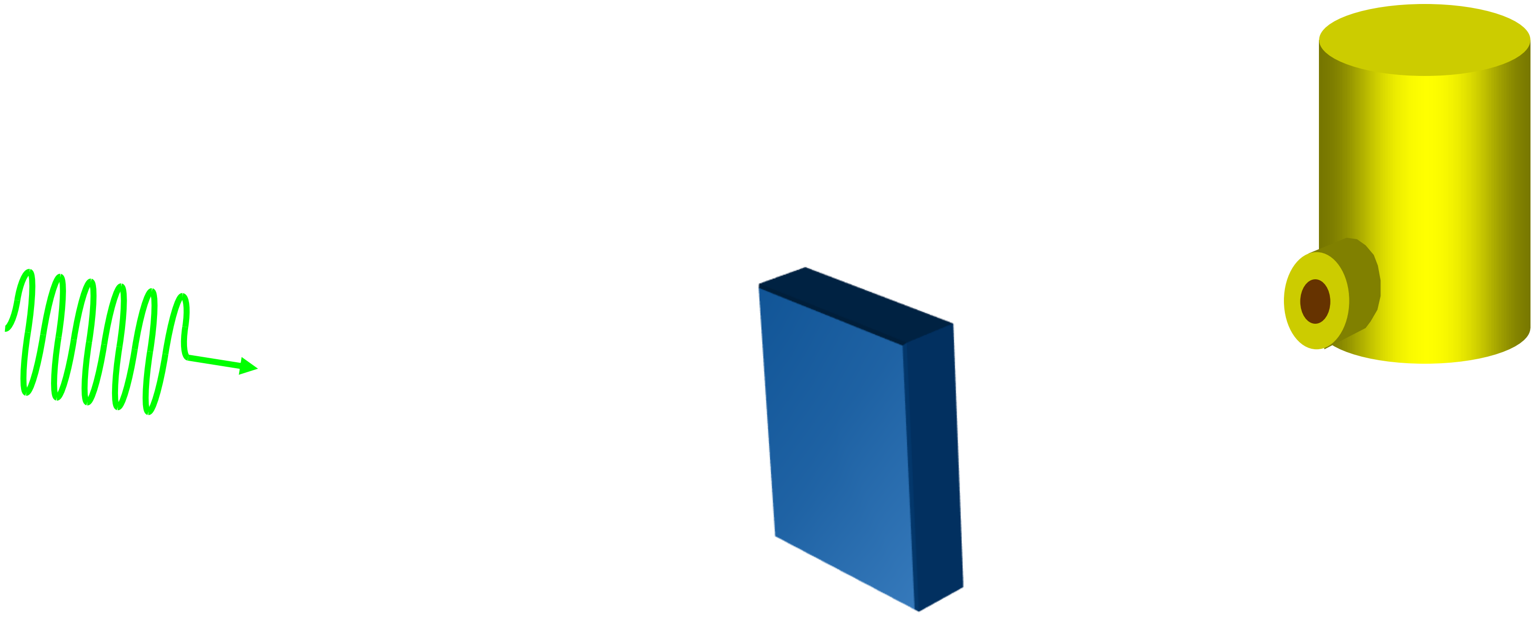

TIME DELAY
PUMP PULSE
PROBE PULSE
DETECTOR
LENS
MIRRORS
MOLECULAR BEAM
SKIMMER

泵浦一探测实验示意图

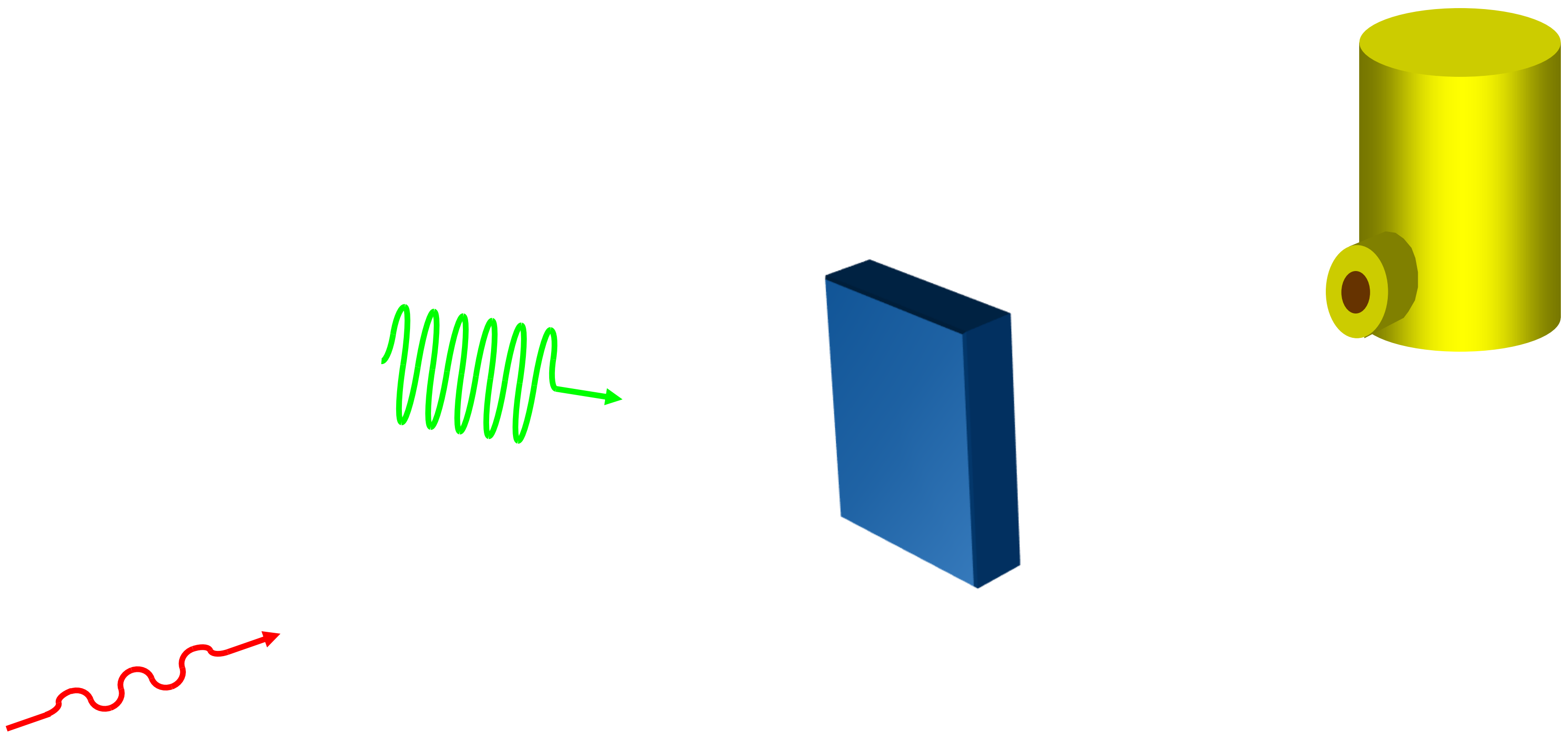
Pump-probe Spectroscopy



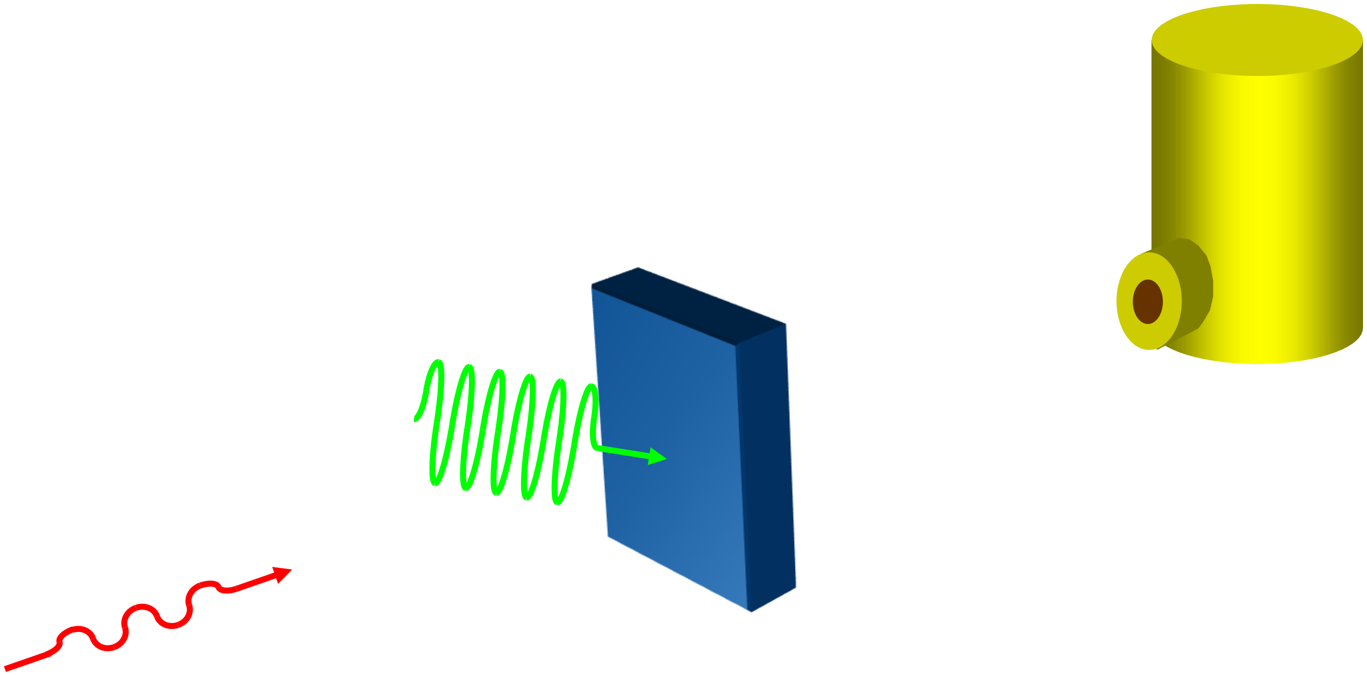
Pump-probe Spectroscopy



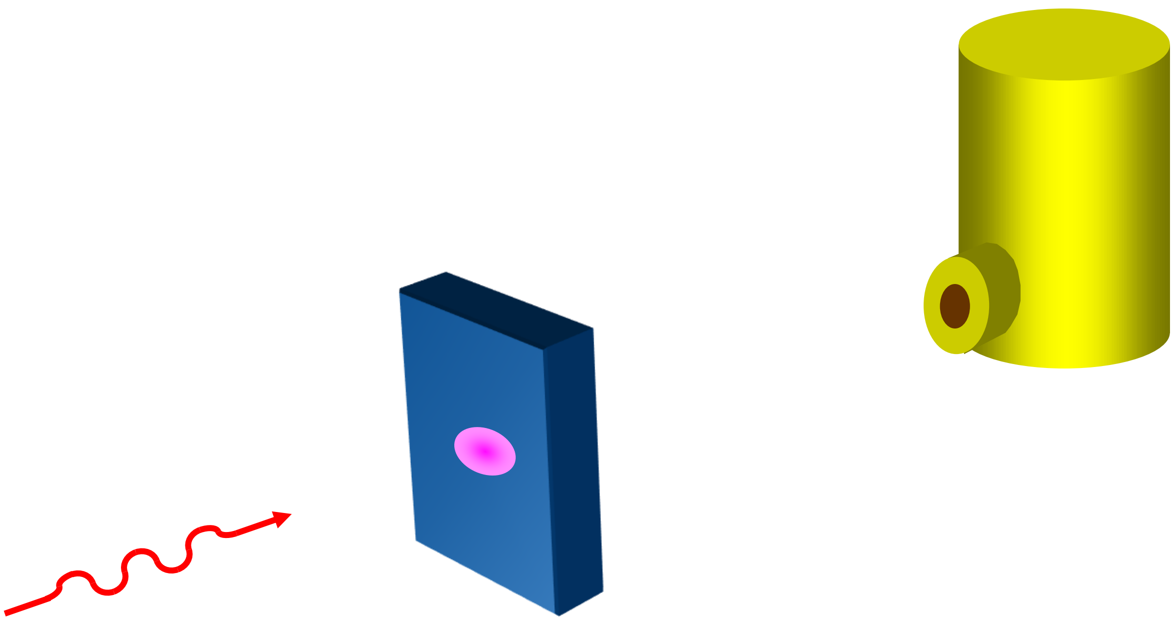
Pump-probe Spectroscopy



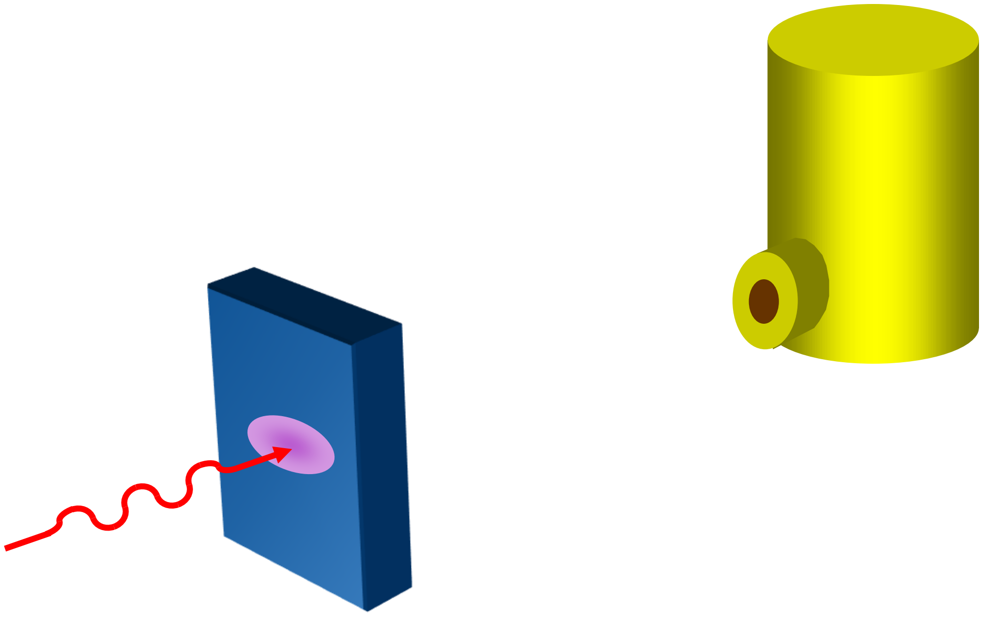
Pump-probe Spectroscopy



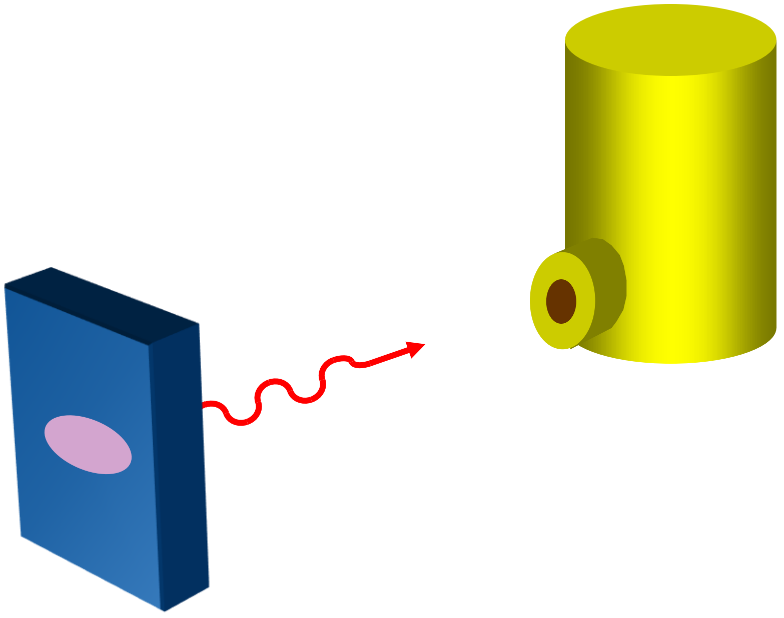
Pump-probe Spectroscopy



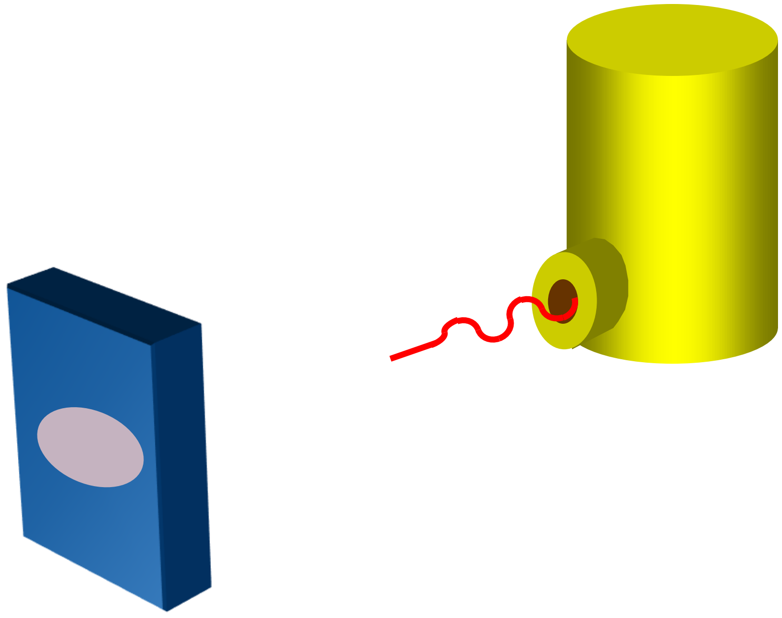
Pump-probe Spectroscopy



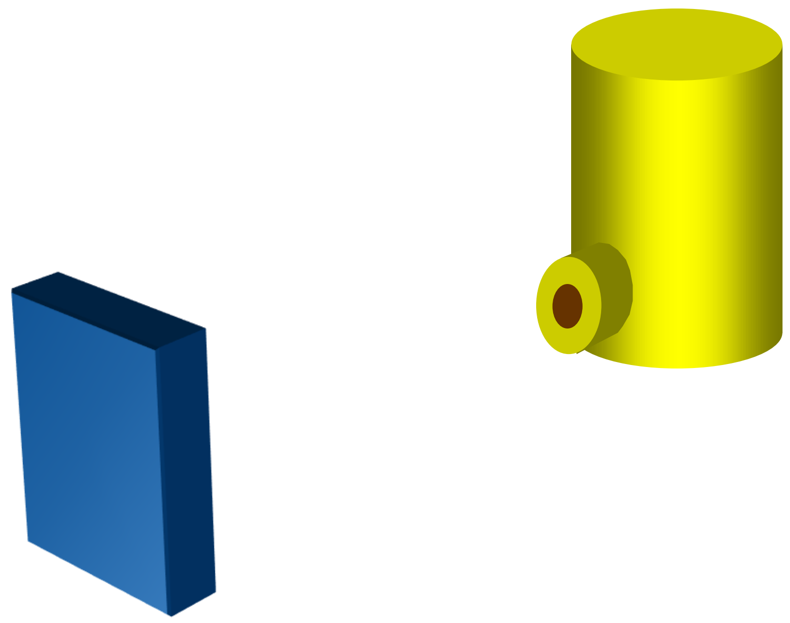
Pump-probe Spectroscopy

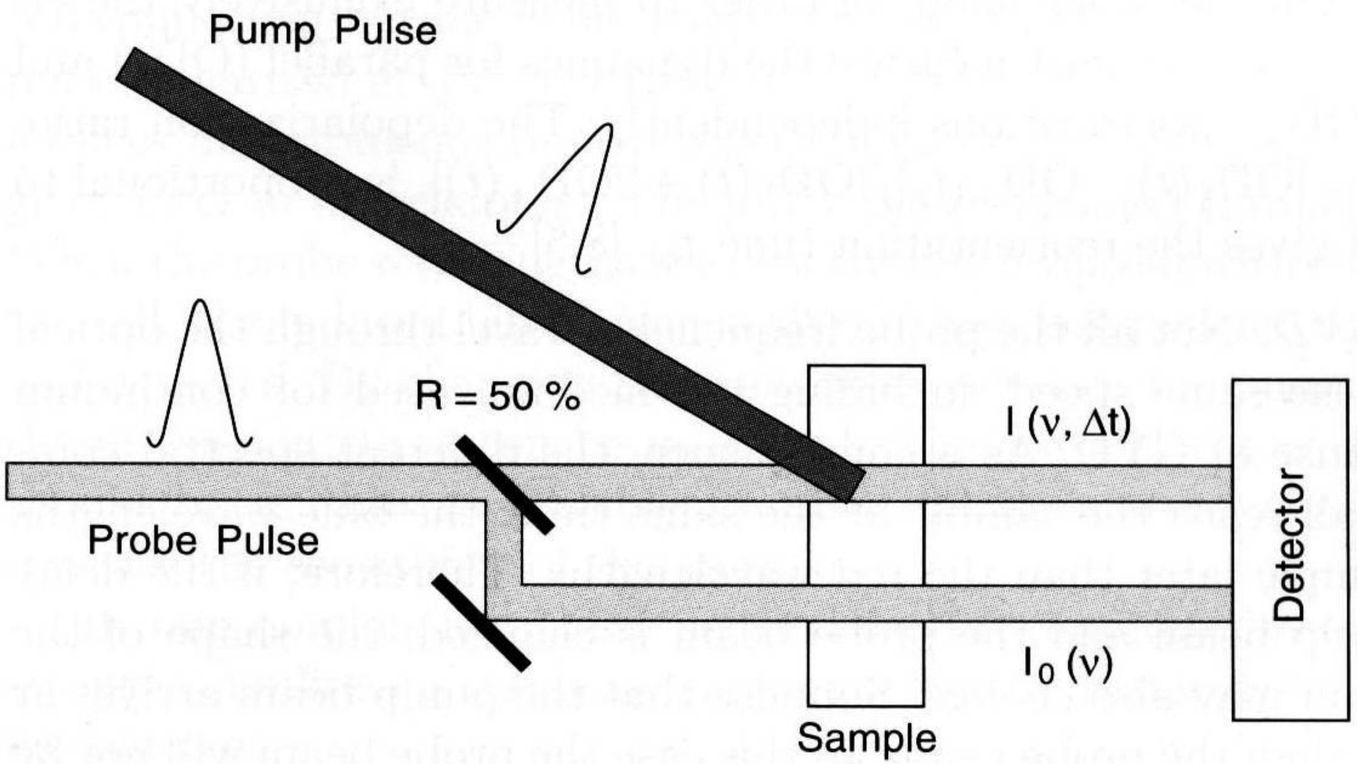


Pump-probe Spectroscopy



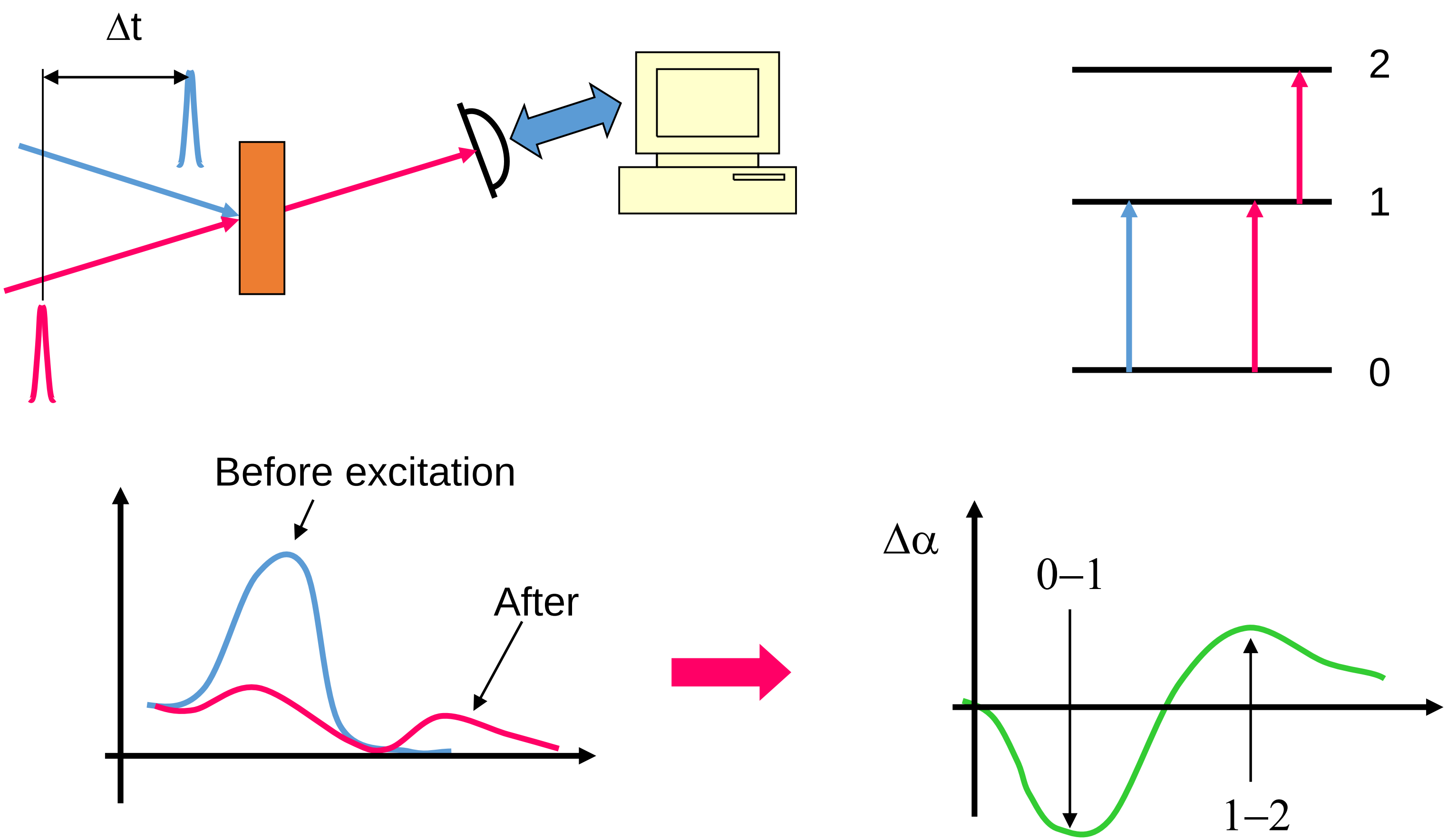
Pump-probe Spectroscopy





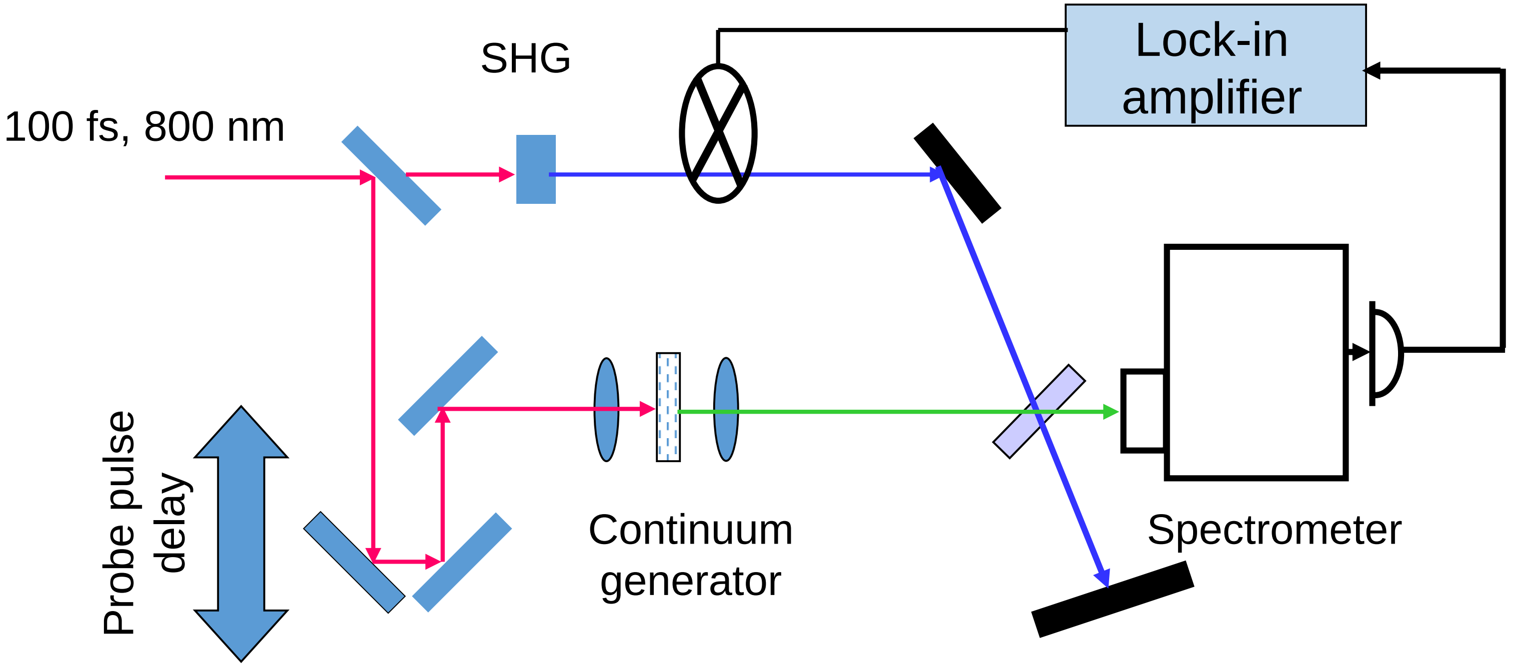
双束泵浦一探测实验

泵浦—探测实验

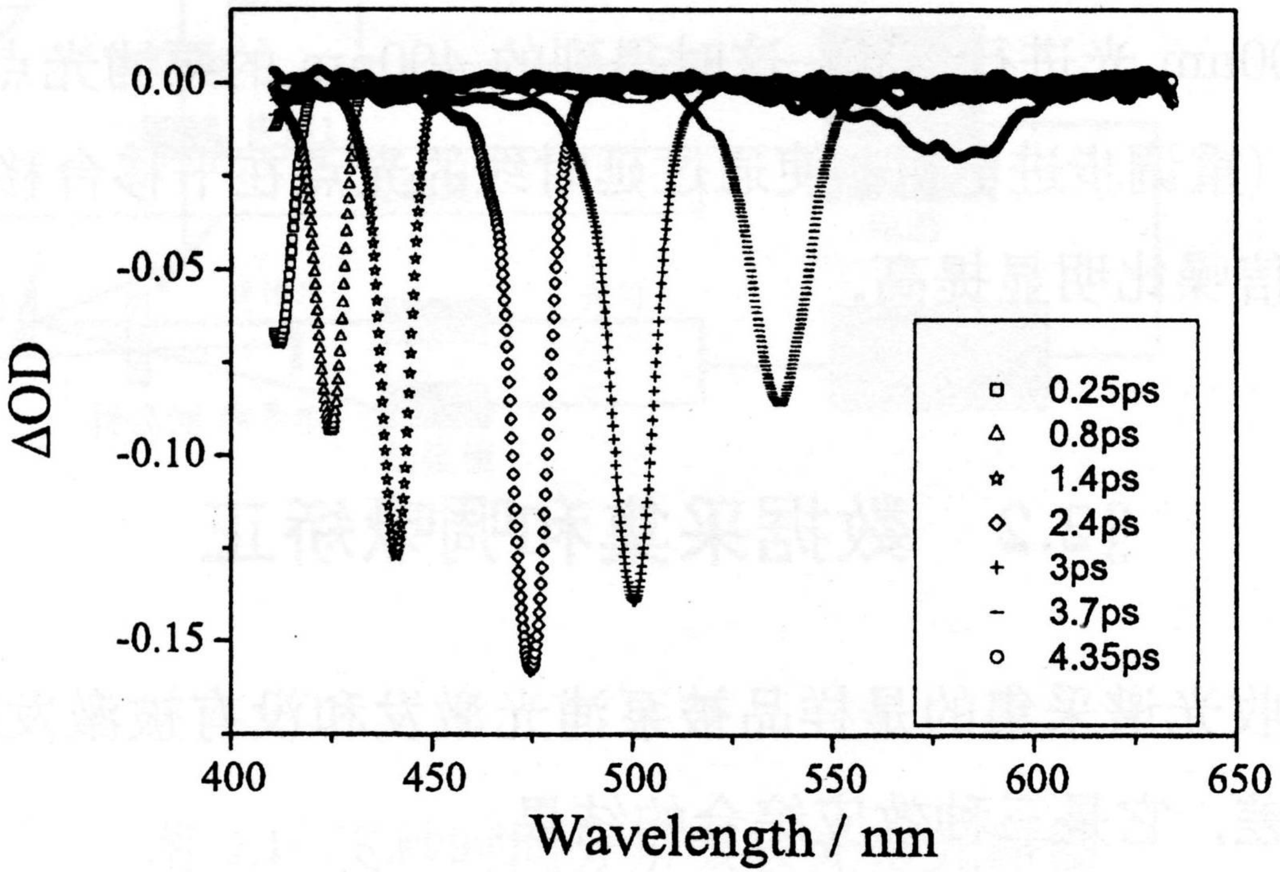


扫描一次延时线只能测量一个探测波长

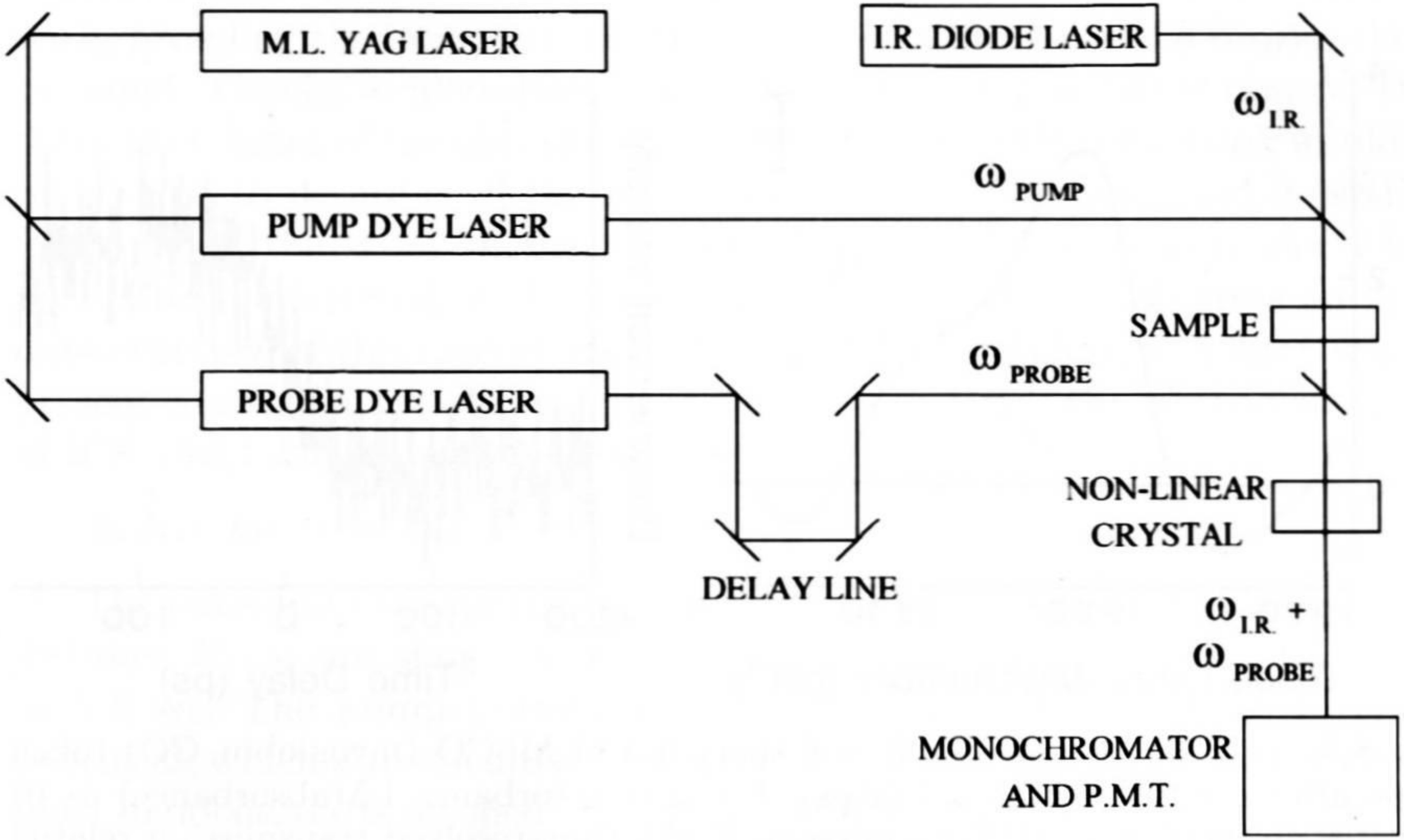
利用超连续光的泵浦－探测技术



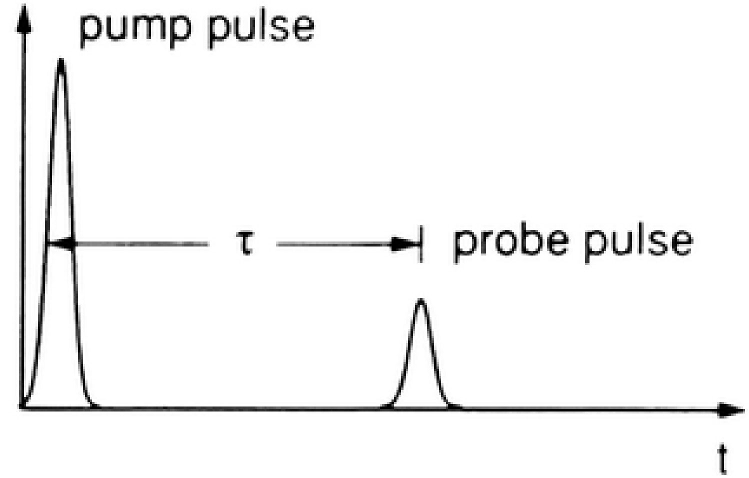
利用超连续光的产生可以覆盖整个可见光和近红外波段

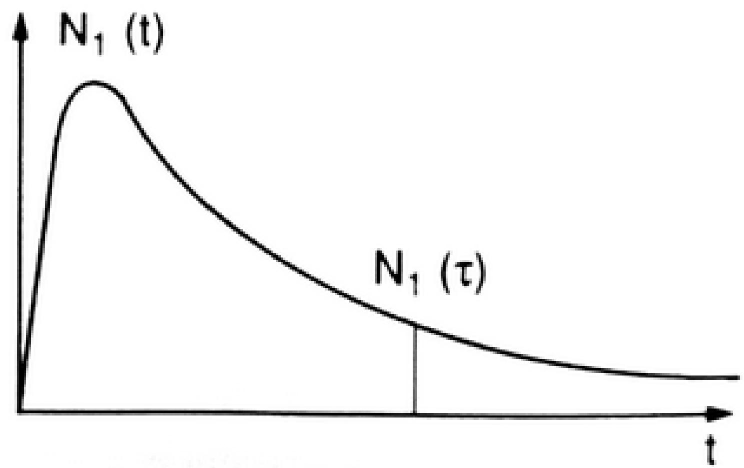


不同时间延时克尔门所采到的一系列光谱



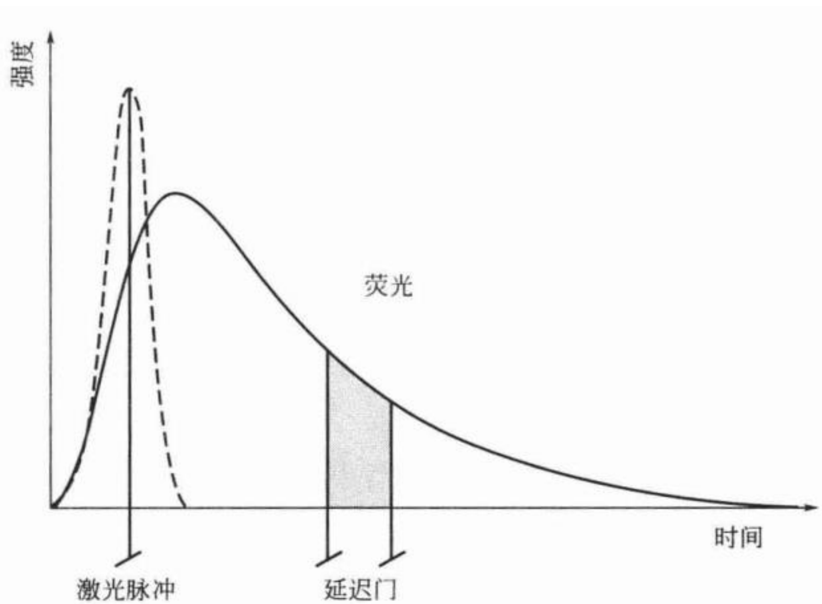
时间分辨红外谱的实验装置


pump pulse
τ
probe pulse
t

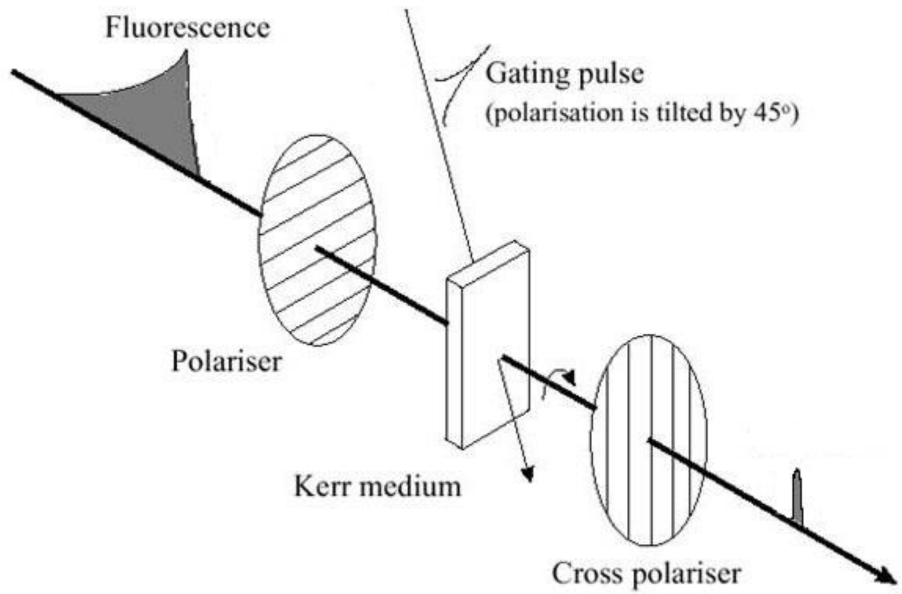

N1 (t)
N1 (τ)
t

2. 时间分辨发射谱

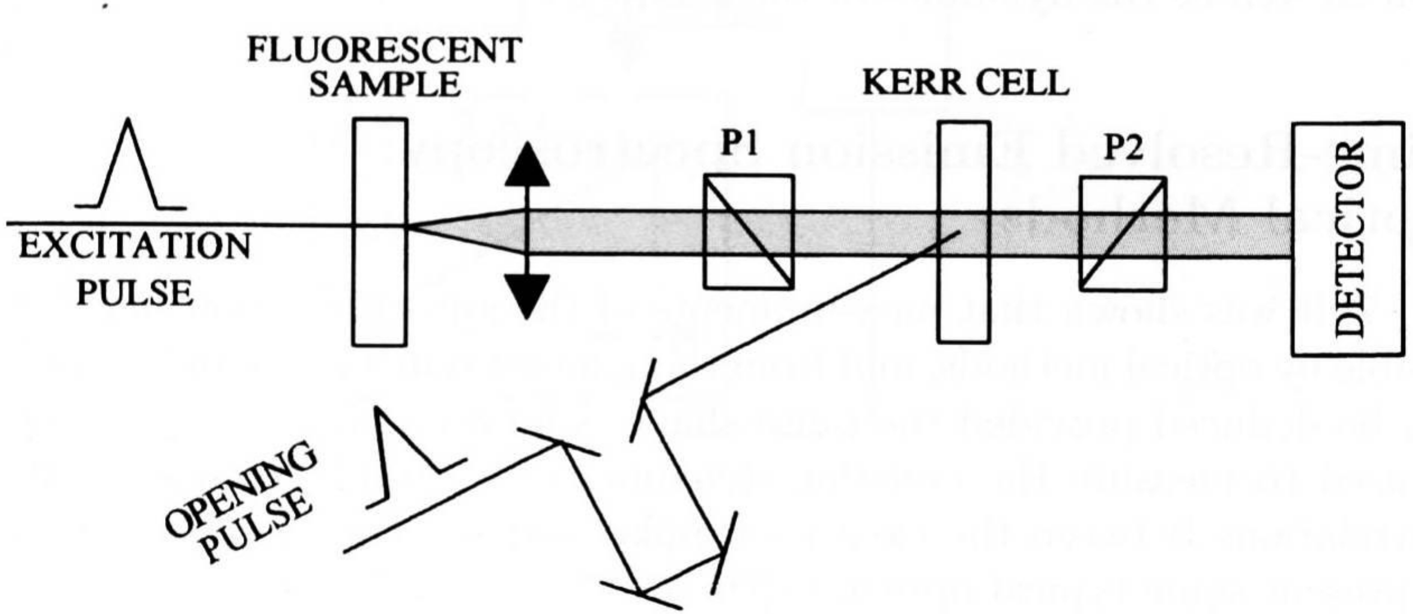
(1)克尔开关



超快荧光测量示意图



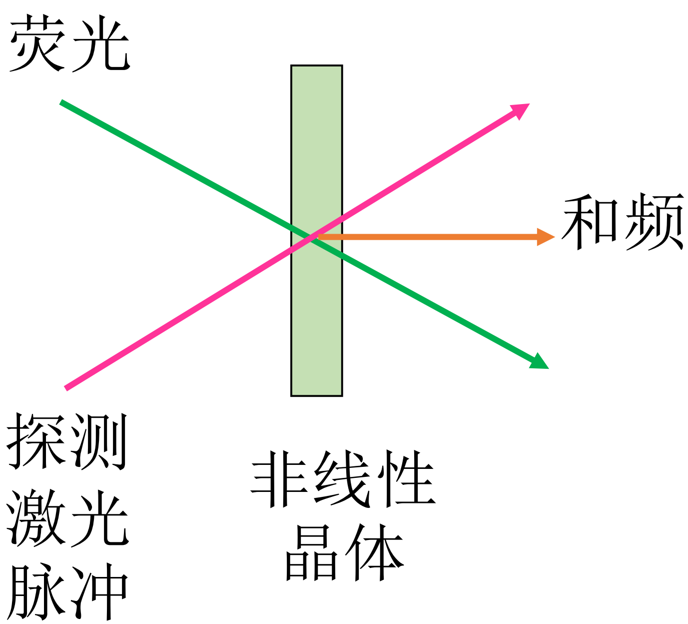
克尔开关示意图

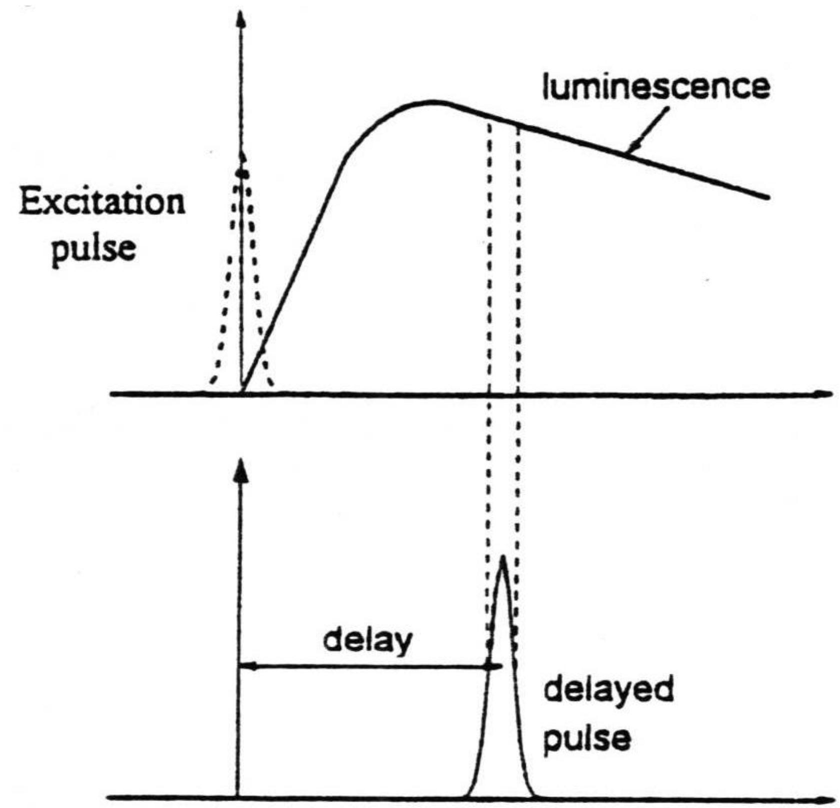


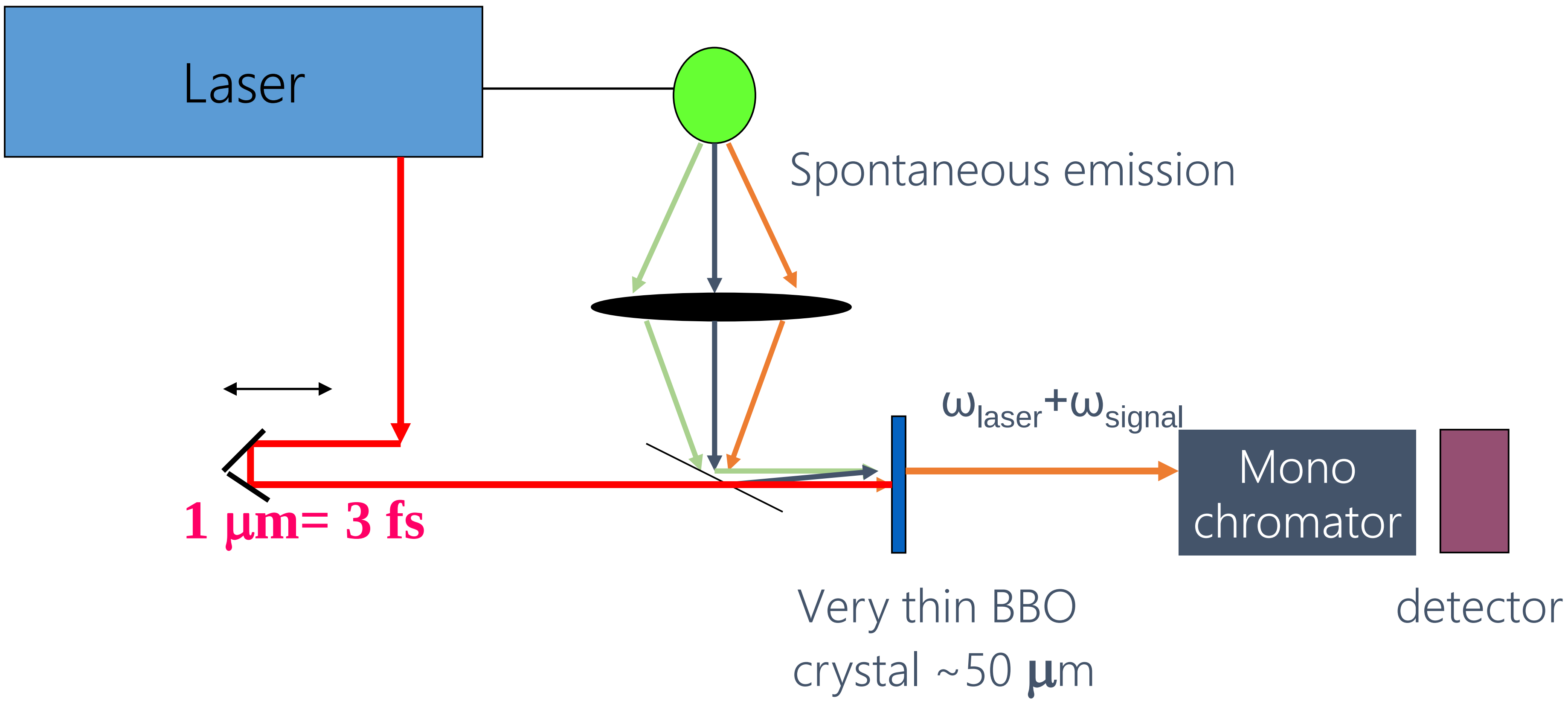
(b)

利用光克尔门的时间分辨发射技术

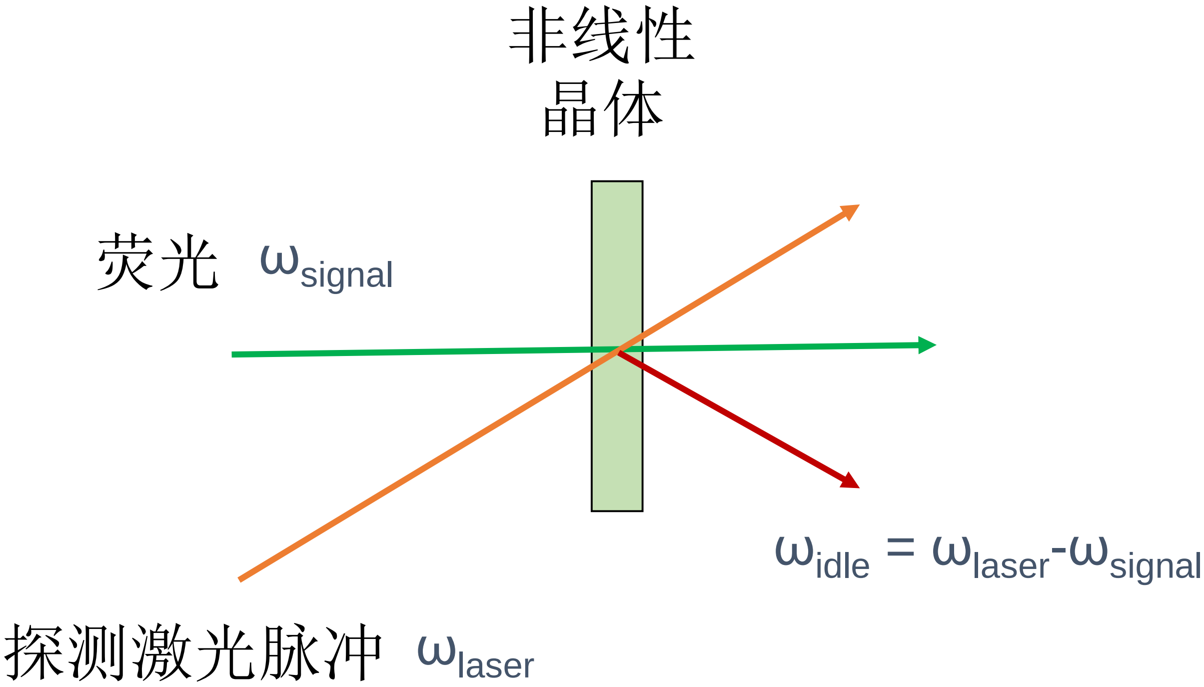
(2)荧光上转换

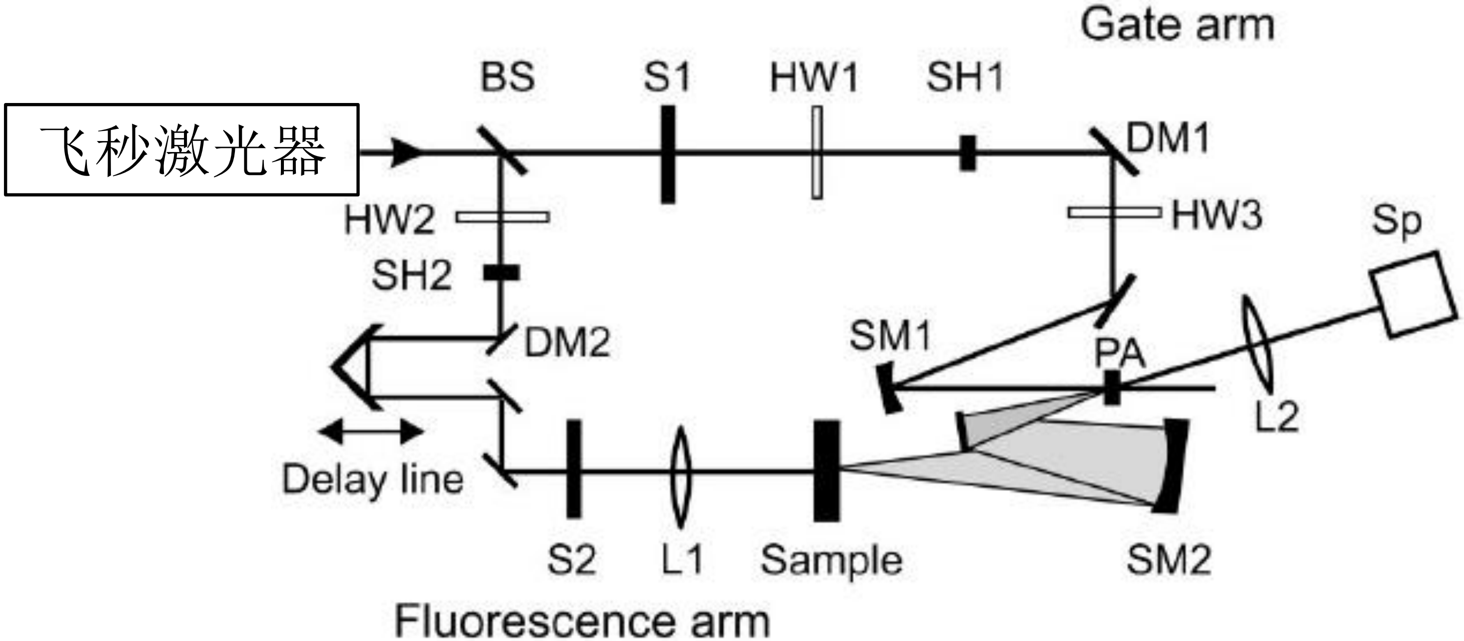

荧光
和频
探测激光脉冲
非线性晶体


luminescence
Excitation pulse
delay
delayed pulse


Laser
Spontaneous emission
ωlaser+ωsignal
Mono chromator
1 μm= 3 fs
Very thin BBO crystal ~50 μm
detector

三. 时间分辨荧光参量放大技术





SH1, SH2, PA: 0.5 mm厚BBO晶体

注意事项：1. 波长选择，2. 匹配光谱范围

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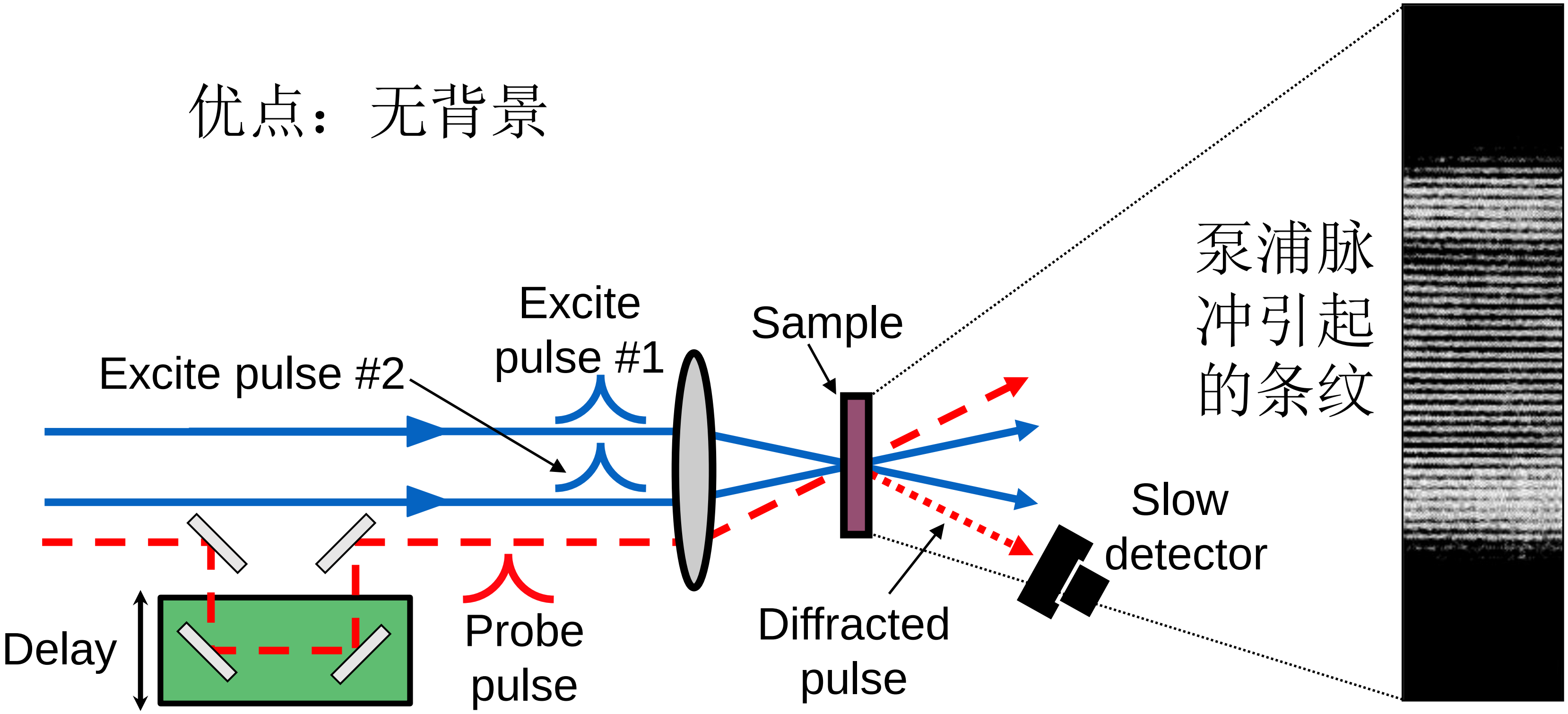
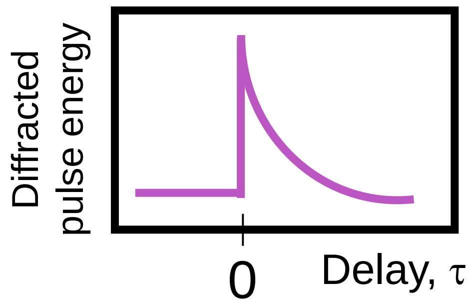
12.2.3 瞬态光栅技术

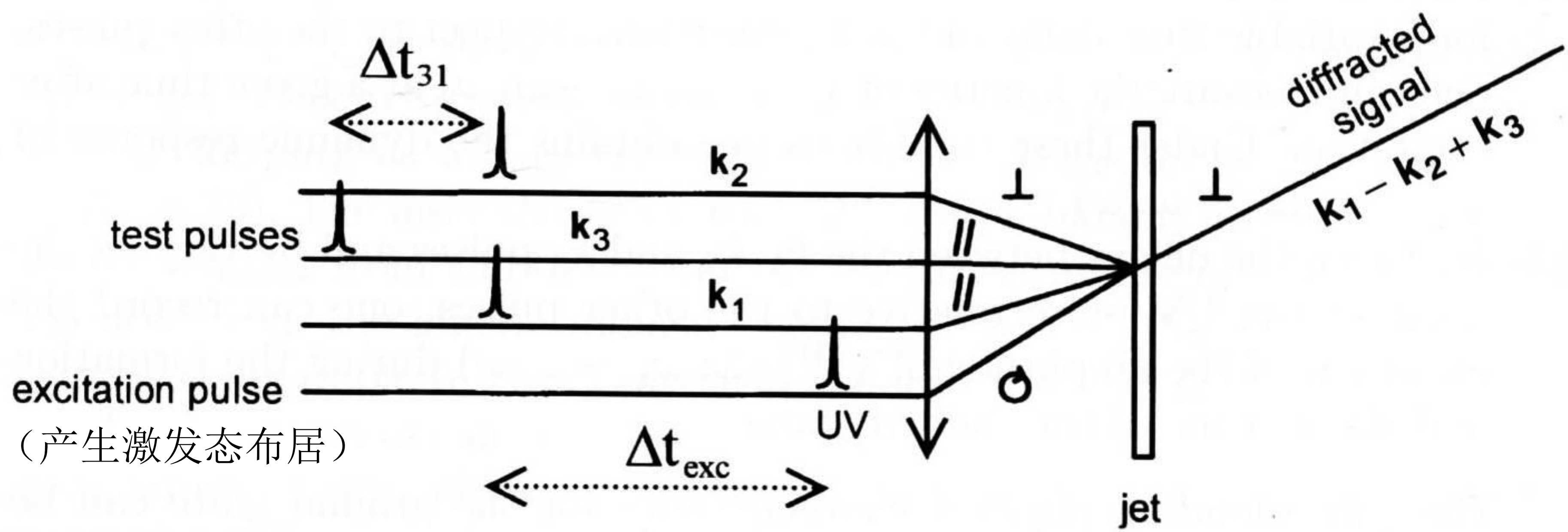
优点：无背景



泵浦脉冲强度在样品内为正
弦分布，引起折射率栅。



研究激发态动力学的瞬态栅技术



简并四波混频实验示意图