Design and characterization of a Femtosecond Fluorescence spectrometer based on Optical Kerr Gating

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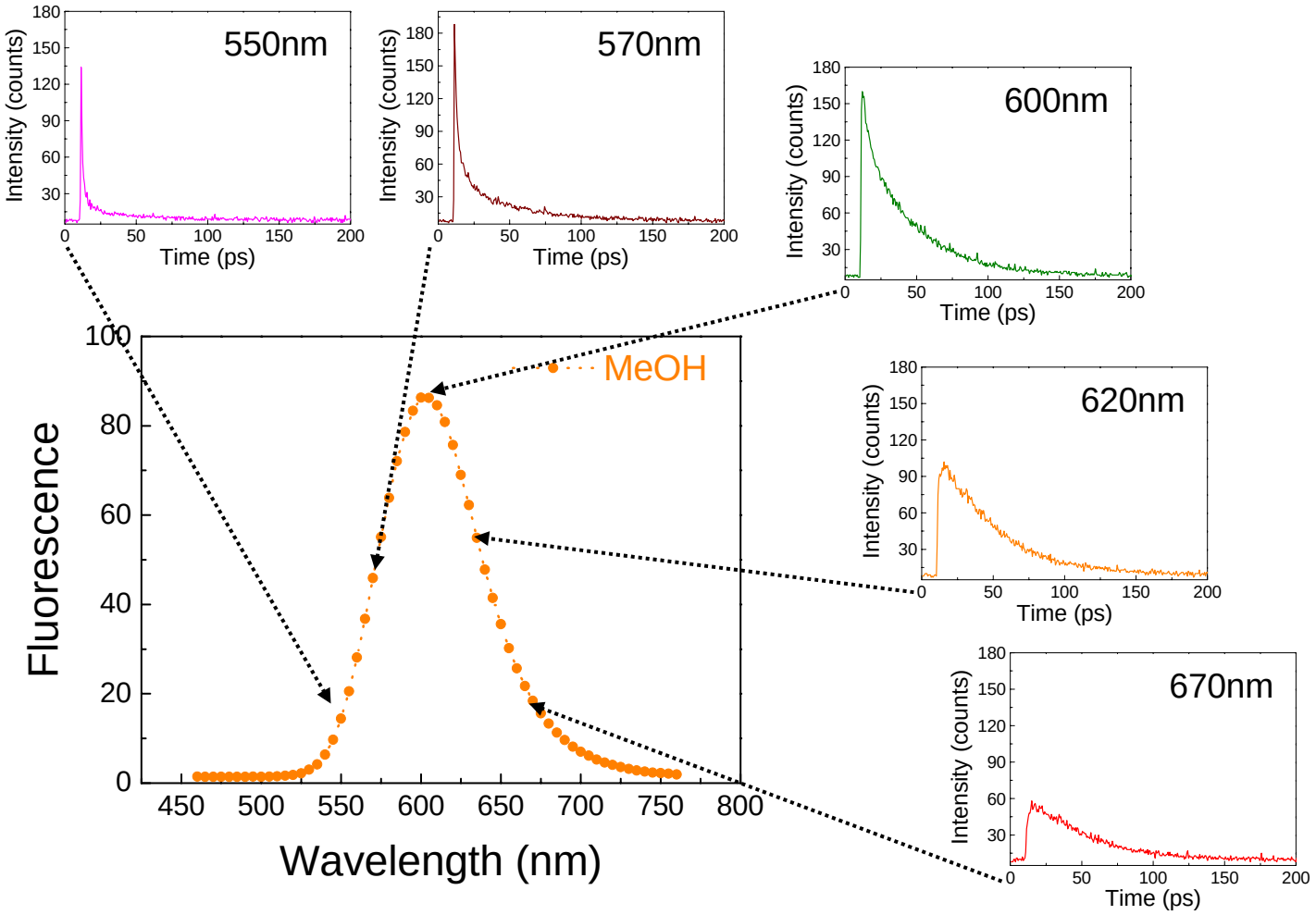
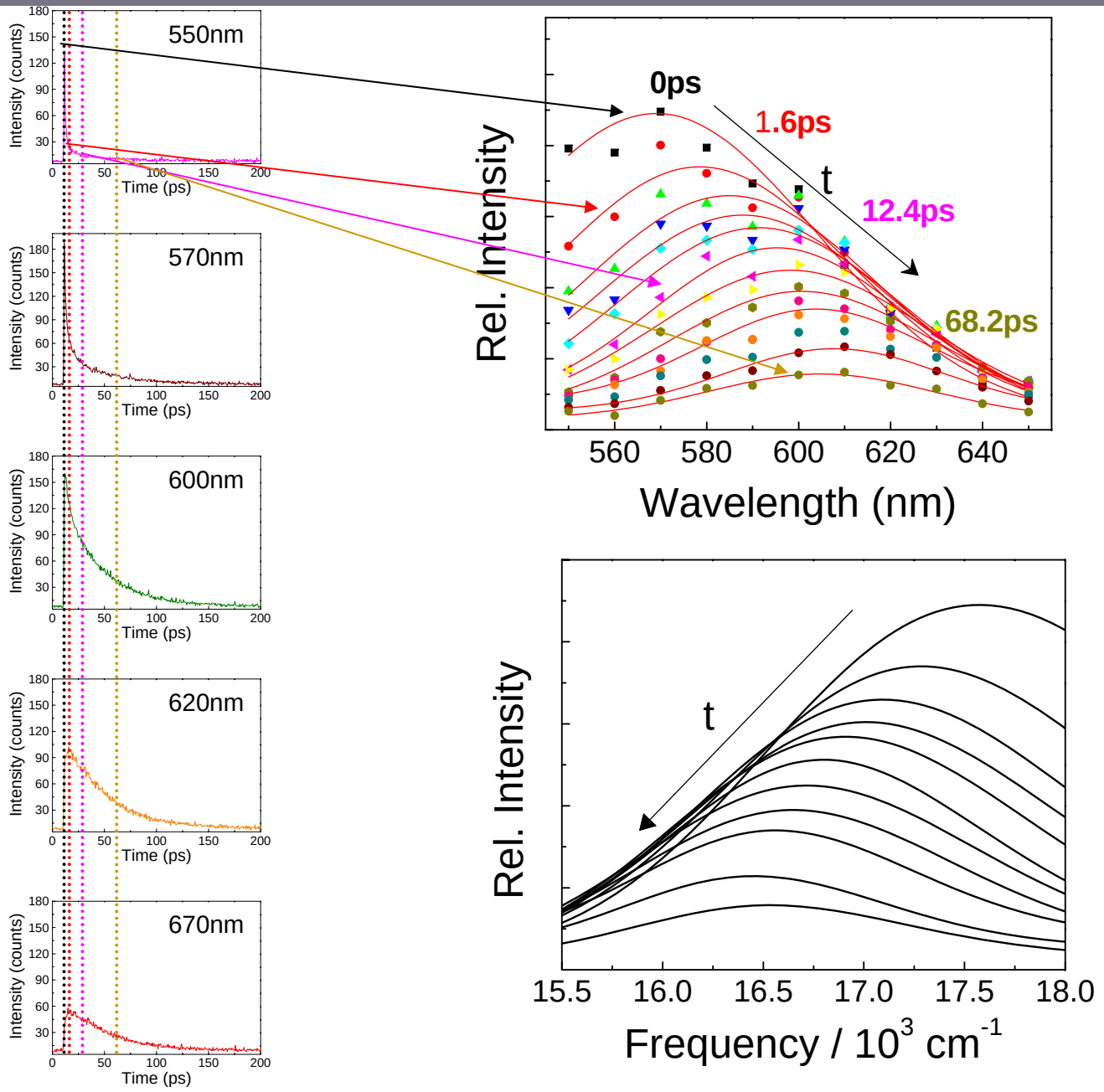
Introduction

- Single-wavelength technique

  - TCSPC and Upconversion



Introduction



Introduction

❖ Time-resolved emission (kinetic information)

- used for characterizing the dynamics of chemical and biological systems.
- studying complex or low-barrier reactions,
- continuous relaxation process (such as solvation dynamics)

complete time- and wave- spectra are required

- TCSPC (Time-resolved single photon counting)
- Upconversion
- Streak camera
- Optical Kerr gating

Introduction

- TCSPC (Time-resolved single photon counting)
  - Coupled to stabe
  - High repetition rate lasers
  - High sensitivity
  - Large dynamics range
  - disadvantage TCSPC method : can't be pushed beyond the tens of picoseconds range

- Upconversion
  - High temporal resolution (< 200fs)
  - Exacting optical alignment
  - Low to moderate sensitivity
  - disadvantage upconversion method : low spectral resolution (< 20 wavelength are recorded)
  - Phase-matchig requirements

- Streak camera detection
  - Broad spectral coverage available
  - Simple optical alignment
  - streak camera of drawback : low dynamic range
  - Limitation on the time resolution (1~3 ps)

Introduction

- Kerr-gated fluorescence spectroscopy
  - high time resolution (200fs~400fs)
  - wide spectral range
  - Ease of alignment comparable to that of streak camera based systems
  - like fluorescence upconversion

    gate (upconversion : ultrafast laser pulse , Kerr gate : transient birefringence in Kerr medium)

Method	Advantages	Disadvantages	Laser characteristics	Instrumental Resolution	Sensitivity
TCSPC	high sensitivity, mainly statistical nose	electronics-limited time resolution	pJ - nJ, ~ 4MHz	20 ~ 30ps	Single photon
Upconversion	excellent time resolution	difficult alignment, limited sensitivity	1nJ @ 80MHz, 1μJ @ 4kHz	100 ~ 200fs	Limited by SFG efficiency
Steak camera	ease of use, broad spectra	limited sensitivity and time resolution	1nJ @ 100MHz 10μJ @ 1kHz 1mJ @ 10Hz	2 ~ 10ps	Similar to current mode of PMT
Kerr gating	complete spectra with good time resolution	large background signals from long-lived samples	200mJ @ 1kHz 100nJ @ 200kHz	200 ~ 400fs	Similar to singe photon

Theoretical background

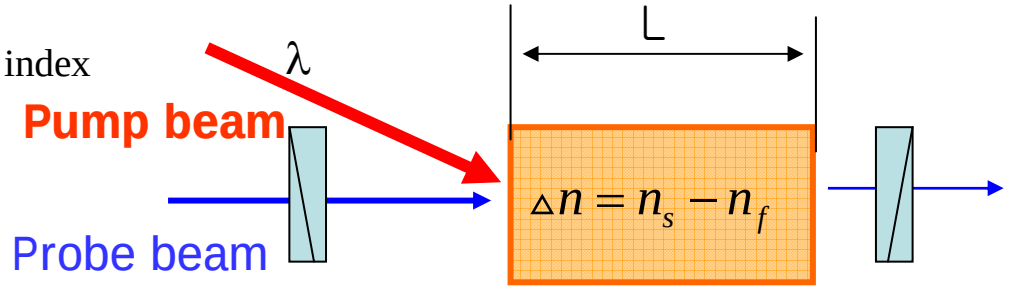
Optical Kerr effect refers to the light induced change in the anisotropy of the refractive index or birefringence

Birefringence (change of refractive index)

$$\triangle n = \gamma I$$

γ : nonlinear refractive index

I : light intensity



Phase shift

$$\phi = \phi_s - \phi_f = \frac{2\pi L \triangle n}{\lambda}$$

Transmission $T = \sin^2(\phi/2)$

ϕ : function of the wavelength, birefringence, and medium thickness, and by choosing a proper combination of L and $\triangle$n for a particular wavelength

The phase shift of an emission signal being gated is then

$$\phi_{em}(t) = \frac{2\pi L \gamma I_g(t)}{\lambda_{em}}$$

Transmittance of the signal

$$T = \sin^2\left[\frac{(\phi_{em}(t))}{2}\right] = \sin^2\left[\frac{\pi L \gamma}{\lambda_{em}} I_g(t)\right]$$

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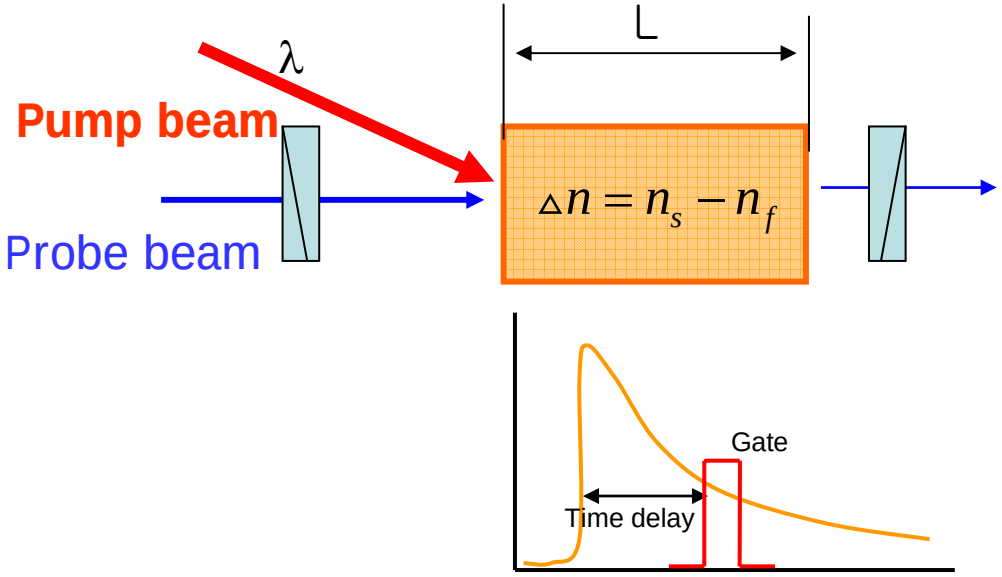
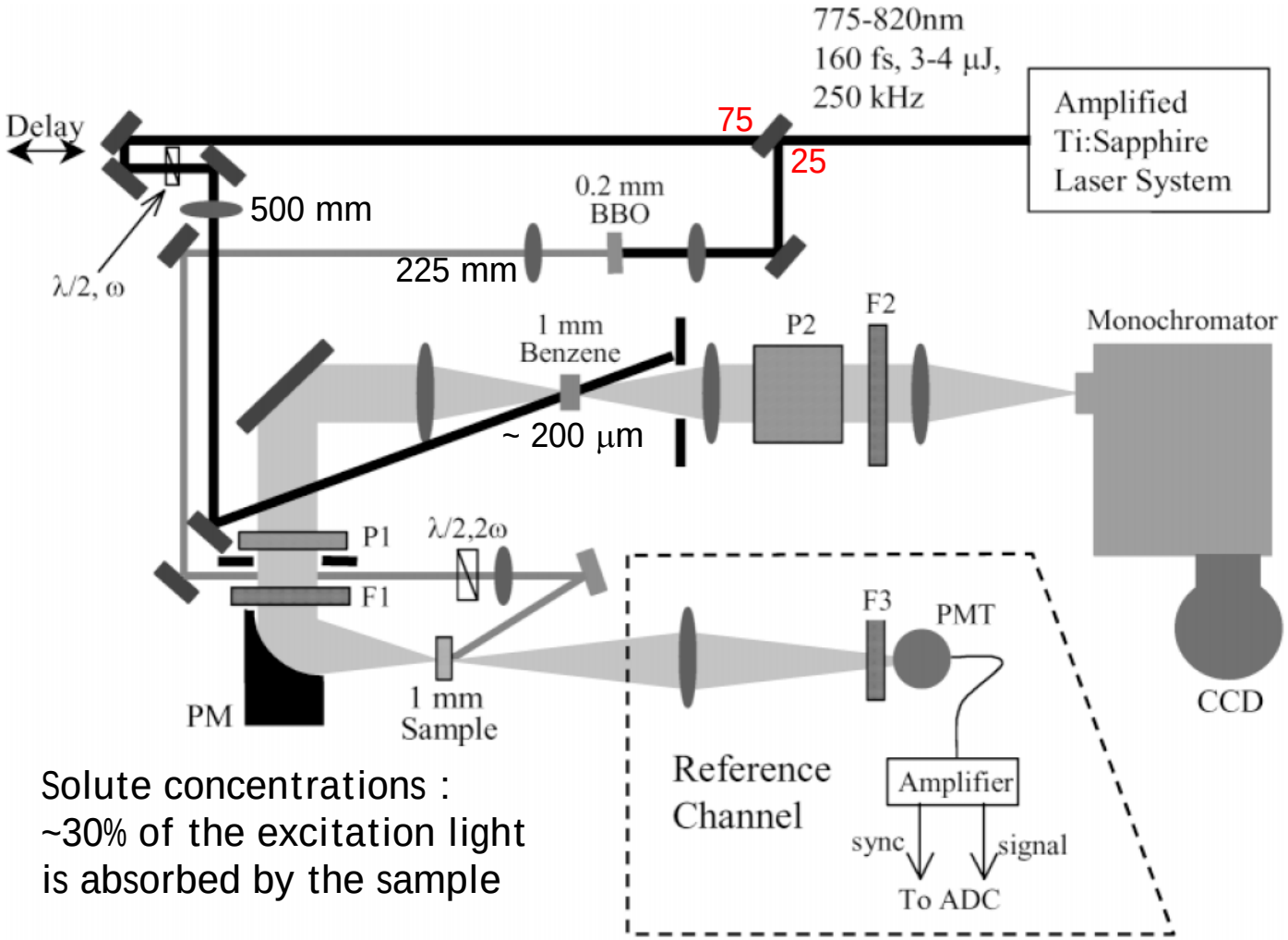
Time-resolved signal detected using the optical Kerr shutter



$$I_{gate}(t) = \int_{-\infty}^{t} T(t-t')I_{em}(t')dt'$$

t : delay between the excitation and gate pulse.

Experimental



Solute concentrations :
~30% of the excitation light
is absorbed by the sample

Experimental

Selection of the kerr medium and gate efficiency

TABLE II. Some characteristics of potential Kerr media.[a]

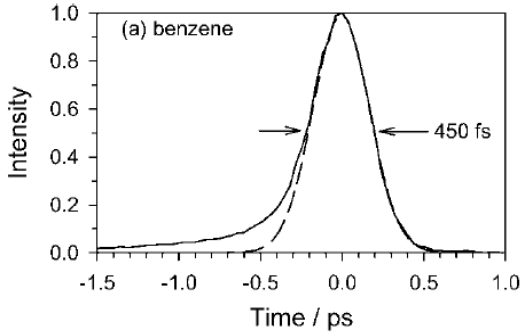
Medium	$\gamma/10^{-20}$ m^2/W^{-1} @ λ [nm]	λ_{min}/nm	n_D	Origin of response
CS_2	390 @ 694	380	1.627	Electronic 42% Nuclear 58%[b]
SFL6 Glass	18.9 @ 1060	367	1.796	Electronic
Fused Silica	2.7 @ 1060	165	1.458	Electronic
Benzene	35 @ 694	278	1.501	Electronic 85% Nuclear 15%[c]
Methanol	4.7 @ 530	205	1.328	Electronic
Water	2.8 @ 694	190	1.333	Electronic

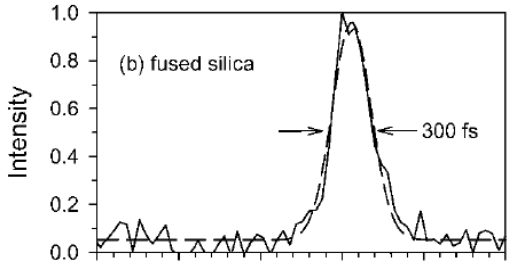
[a] γ is the nonlinear refractive index (intensity coefficient) from Ref. 66.

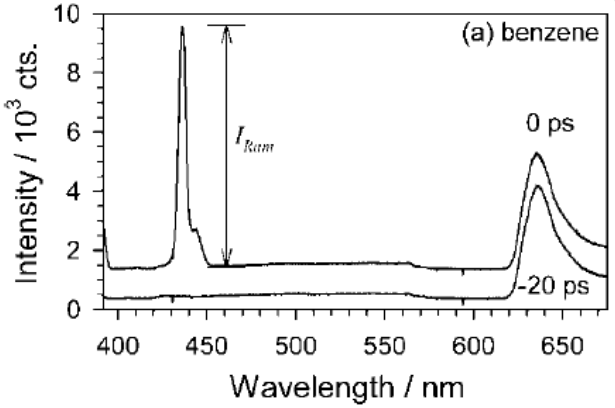
TABLE III. Characteristics of Kerr media observed in use (λ_{gate} = 775 nm).[a]

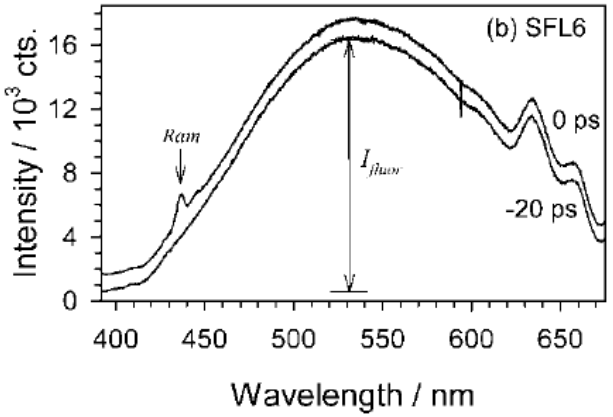
Medium	N_{Ram}	N_{fluor} (530 nm)	Δt/fs
SFL6 Glass	25	250	750
Fused Silica	1	2.5	300
Benzene	125	8	450

[a] All Kerr media are 1 mm thick. Liquids were contained in a quartz cuvette (1.25 mm wall thickness). N_{Ram} and N_{fluor} denote the relative count levels observed with a 1 mm sample of methanol. N_{Ram} measures the relative height of the methanol Raman peak (435 nm) and N_{fluor} gate fluorescence at 530 nm. Δt is the full width at half-maximum intensity of the Raman peak, used as a measure of the instrument response function.









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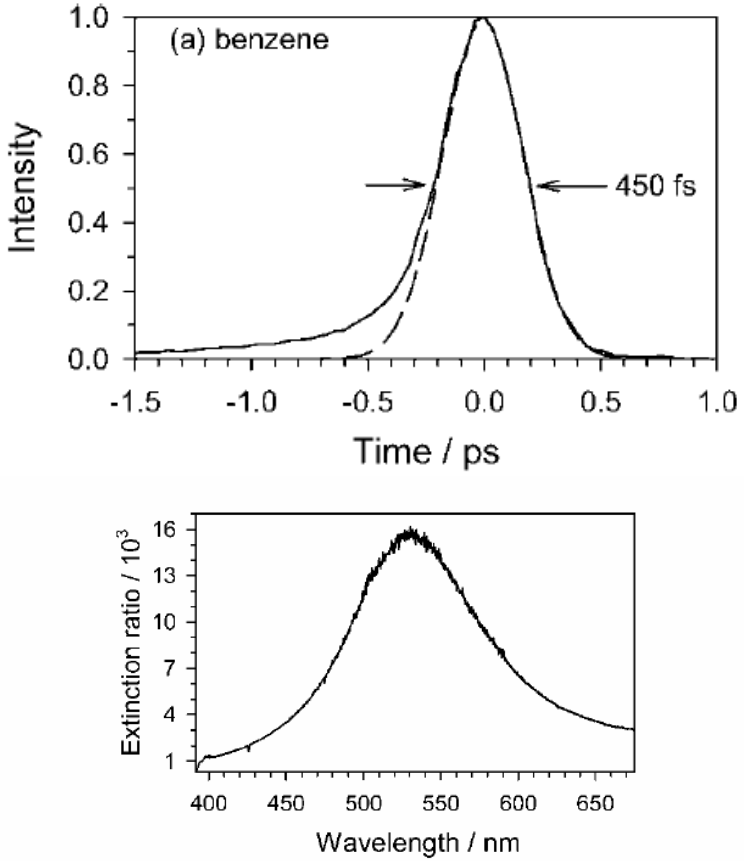
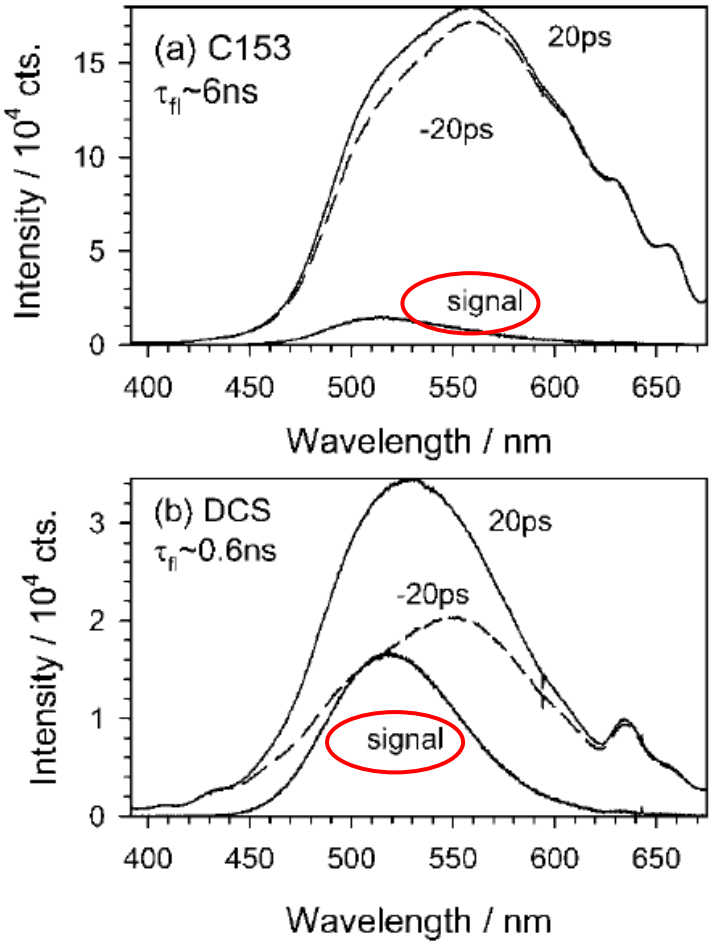


FIG. 5. Approximate extinction spectrum $\varepsilon(\lambda)$ of the Kerr shutter. This curve was determined as the ratio of the emission detected (in the absence of the gate pulse) when polarizer P1 is rotated to provide maximal



IG. 4. Illustration of the relative contributions of gated and ungated mission to the spectra of (**a**) coumarin 153 (C153) and (**b**) 4-dimethylamino-4′-cyanostilbene (DCS) in acetonitrile. The desired signal is the difference between the spectra recorded at 20 ps (gated) and −20 ps (ungated). The latter signal comes primarily from solute emission but the peaks near 630 and 660 nm are scattered gate light. The optical densities and accumulation times for the two samples are: C153 = 0.43, 32 s and DCS = 0.23, 40 s.

Introduction

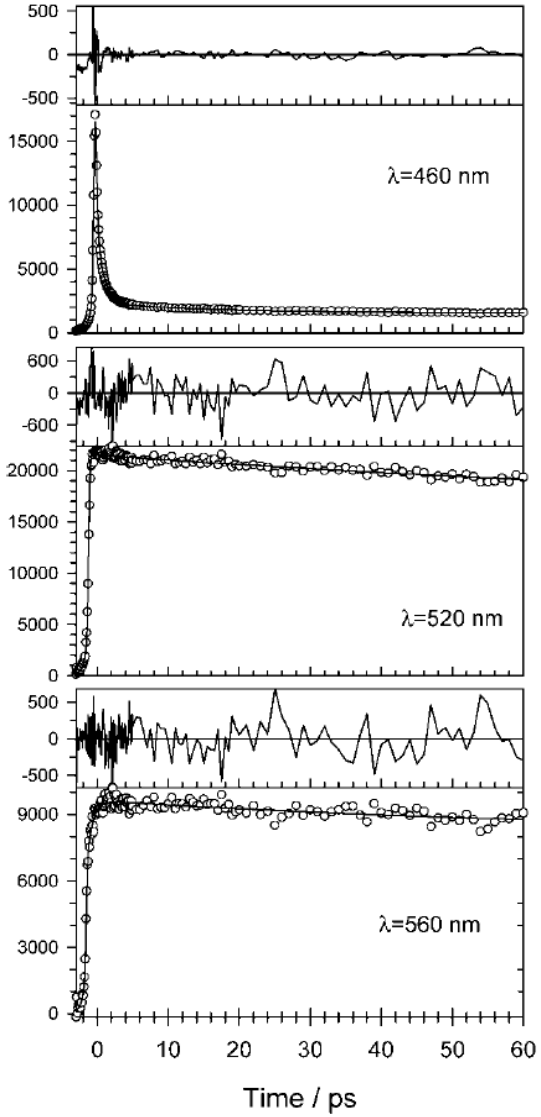


FIG. 10. Time-resolved decays of C153 in acetone at selected wavelengths (points) and 3-exponential fits to these data (smooth curves). Above each decay are shown the unweighted residuals of the fit. The vertical scale in each case shows the accumulated count (averaged over 5 wavelength points in the original data set).

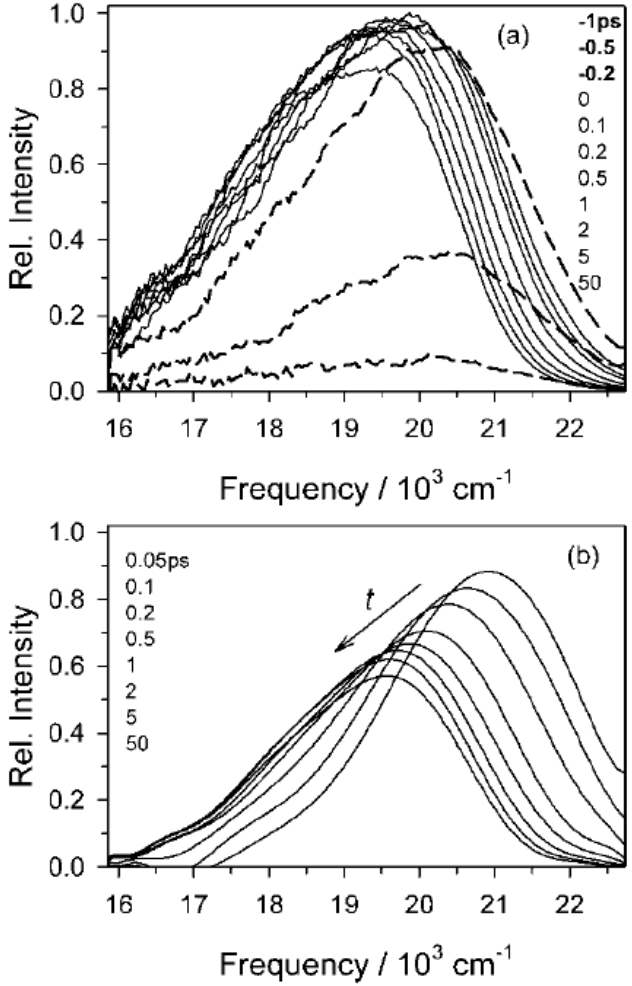


FIG. 11. Spectra of C153 in acetone (**a**) after all processing and (**b**) after fitting to remove the effects of instrumental broadening.

Introduction

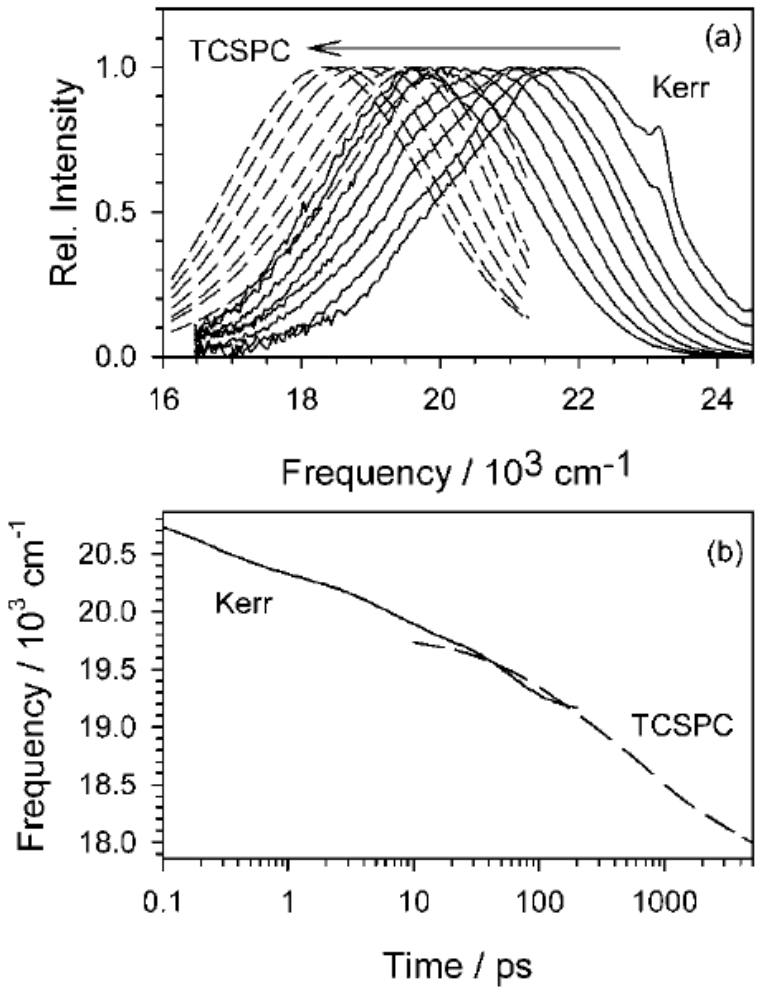


FIG. 14. (**a**) Spectra and (**b**) peak frequency response of DCS in the ionic liquid [bmim$^+$][PF_6^-]. In both panels the solid curves denote data recorded with the Kerr-gated emission spectrometer and the dashed curves denote data obtained from spectral reconstruction of time-correlated single-photon counting data. Times illustrated in the top panel are: 0, 0.2, 0.5, 1, 2, 5, 20, 50, and 100 ps (Kerr data) and 0, 0.1, 0.2, 0.5, 1, 2, and 4 ns (TCSPC data).