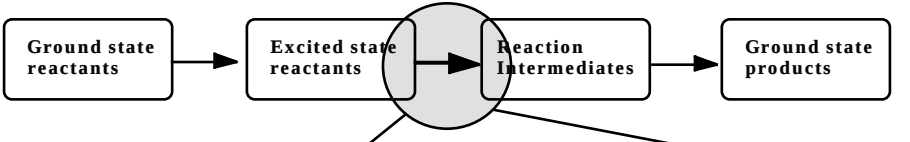
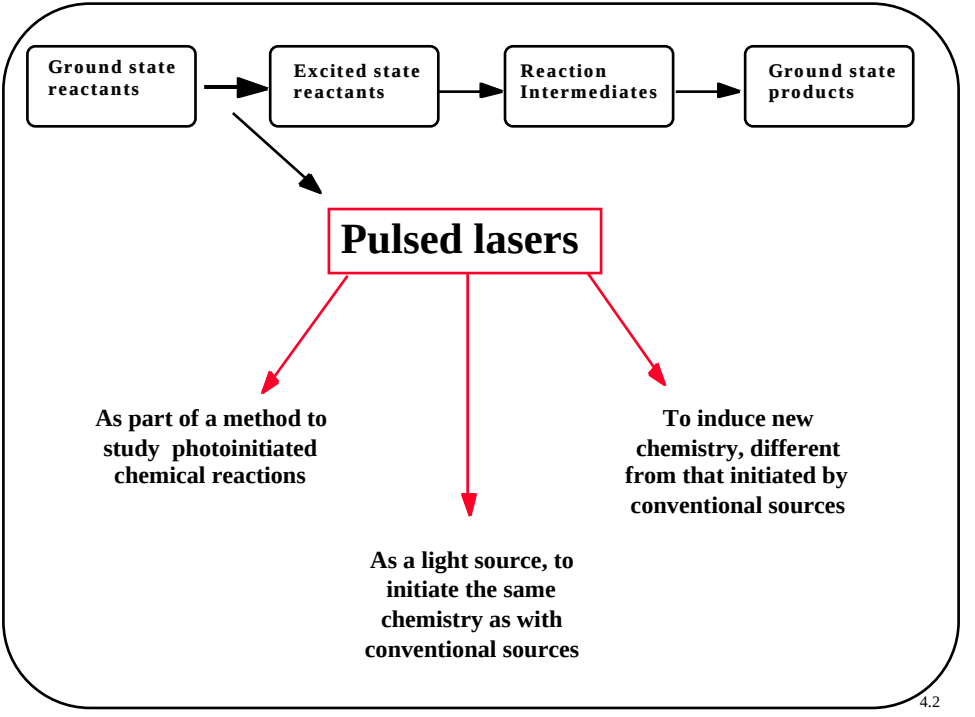
Photochemical techniques



LASER TECHNIQUES

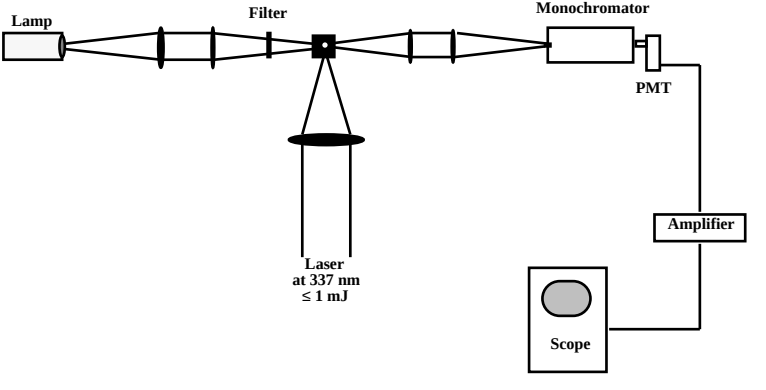
- Luminescence
- Transient absorption (UV, Vis, IR)
- Time resolved diffuse reflectance
- Photoacoustic spectroscopy
- Transient conductivity
- L.I.F. of reaction intermediates
- Mirage spectroscopy
- Time resolved light scattering
- Time resolved resonance Raman


Ground state reactants
Excited state reactants
Reaction Intermediates
Ground state products
Pulsed lasers
As part of a method to study photoinitiated chemical reactions
As a light source, to initiate the same chemistry as with conventional sources
To induce new chemistry, different from that initiated by conventional sources

Pulsed nanosecond lasers

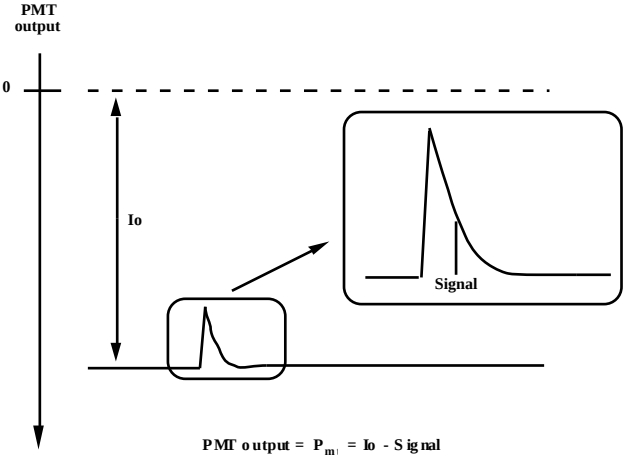
LASER	WAVELENGTH, nm	PULSE
Nitrogen	337	8 ns, ≤ 10 mJ
Excimer	193 (Ar/F)	5-50 ns, ≤300 mJ
	248 (Kr/F)	5-50 ns, ≤ 1J
	308 (Xe/Cl)	5-50 ns, ≤ 500 mJ
	351 (Xe/F)	5-50 ns, ≤ 300 mJ
Ruby	694	≥ 10 ns, 1 J
	347 (x2)	≥ 10 ns, 300 mJ
Nd/YAG	1064	5-10 ns, 0.5-5 J
	532 (x2)	5-10 ns, ≤ 500 mJ
	355 (x3)	5-10 ns, ≤ 300 mJ
	266 (x4)	5-10 ns, ≤ 150 mJ
Diode	> 700 nm	low
Dye	> 300 nm	5-20 % of pump

Lindqvist's 1966 laser set-up



Lindqvist, L. (1966). Utilisation d'un Laser à Émission Ultraviolette Pulsé en Photolyse-Éclairs: Étude de l'état Triplet de l'Acridine. Hebd. Seances Acad. Sci., Ser. C. 263, 852-854.

Determining transient absorbances

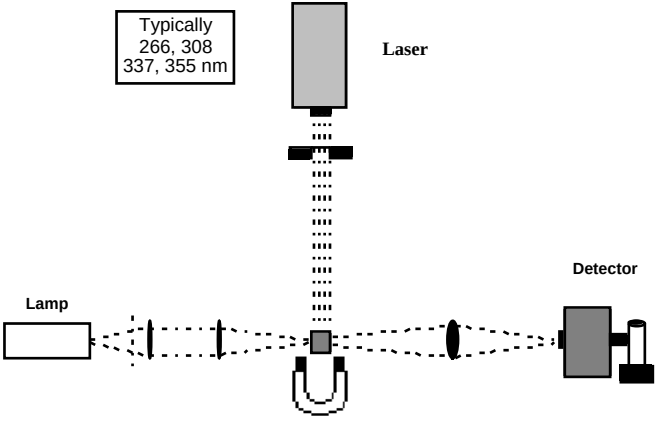


$$\text{PMT output} = P_{mt} = Io - \text{Signal}$$

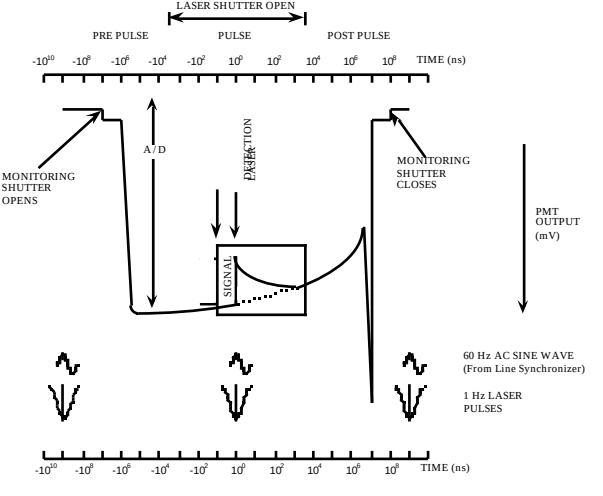
$$T = \frac{P_{mt}}{Io}$$

$$\Delta O.D. = -\log T = \log\left[1 - \frac{\text{Signal}}{Io}\right]$$

Laser flash photolysis technique



Laser photolysis sequence

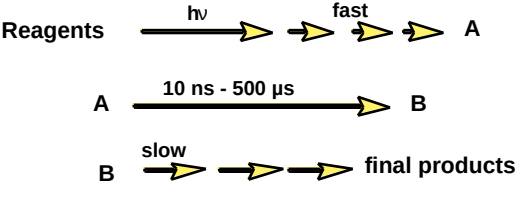


Conditions and capabilities of laser flash photolysis

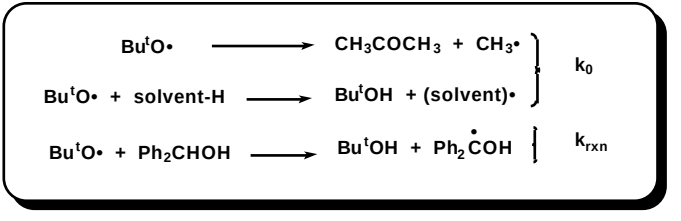
FAST PRECURSOR PROCESSES
SLOW DECAY OF PRODUCTS

Process under study

A → **B**



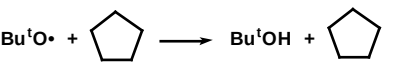
Kinetic analysis for *visible* systems



$$k_{growth} = k_0 + k_{rxn}[Ph_2CHOH]$$

PROBLEM: Most systems of interest do not involve reactants or products that can be readily detected in the UV-Vis region

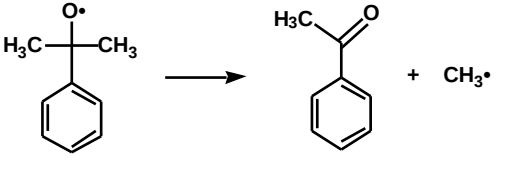
E.g.:



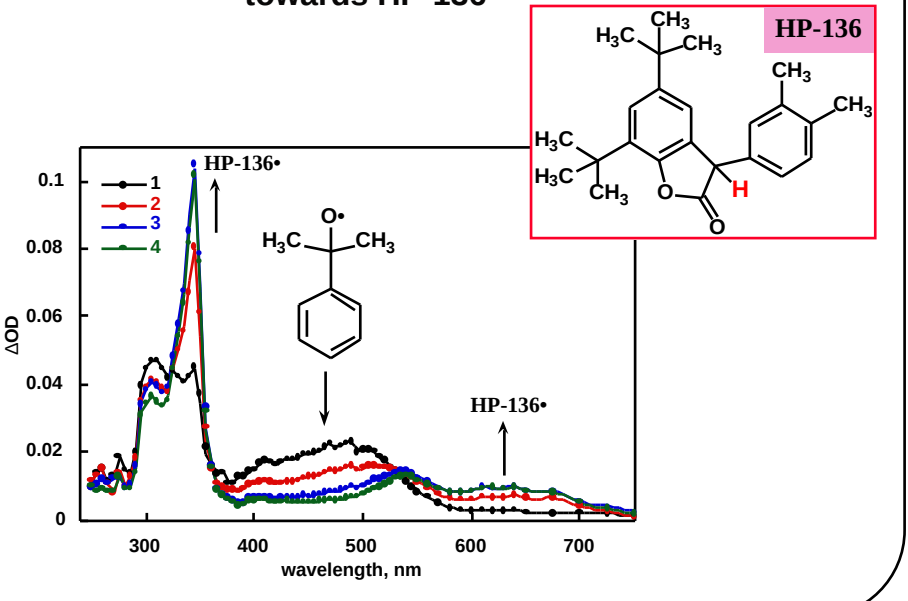
Some background on alkoxyl radicals

Alkoxyl radicals can be readily prepared by thermal or photochemical decomposition of the corresponding peroxide. Typical examples are di-*tert*-butyl peroxide and di-cumyl peroxide. While the excinction coefficients at $\lambda > 300$ nm tend to be small, it is usually possible to use enough peroxide to overcome this. *Tert*-butoxyl radicals are essentially invisible to laser flash photolysis, while cumyloxyl can be detected.

Alkoxyl radicals tend to abstract hydrogen readily; to a lesser extent, they also add to unsaturated systems. In addition, they undergo cleavage reactions which are hery sensitive ty the polarity of the medium (see below)



An example of cumyloxyl reactivity towards HP-136



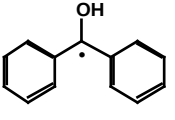
The probe technique

$Bu^tO\bullet \longrightarrow CH_3COCH_3 + CH_3\bullet$

$Bu^tO\bullet + \text{solvent-H} \longrightarrow Bu^tOH + (\text{solvent})\bullet$ } k_0

$Bu^tO\bullet + Ph_2CHOH \longrightarrow Bu^tOH + Ph_2\dot{C}OH$ k_{probe}

$Bu^tO\bullet +$  $\longrightarrow Bu^tOH +$  k_{rxn}



signal carrier

λ_{max} 540 nm

$$k_{growth} = k_0 + k_{probe}[probe] + k_{rxn}[XH]$$

$$k_{growth} = k_0' + k_{rxn}[XH]$$

The technique allows the determination of the absolute rate constant for a reaction where all the reagents and all the products are invisible to the technique employed

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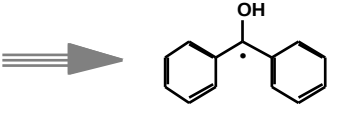
Is there a catch ?

- **The method provides no information on the nature of the reaction; for example the mode or site of attack cannot be established by this method.**
- **The signals observed get weaker as the reactant is added. The rates are largely derived from conditions where the growth is fast and the signal weak.**

It is essential to select probes that overcome the second problem by giving intense, readily detectable signals.



The significance of growth rates

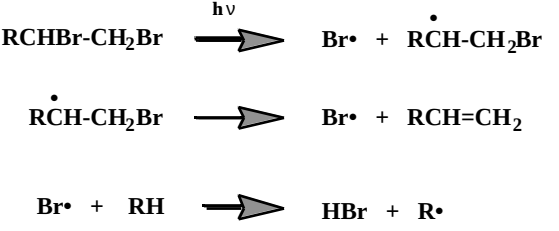
All products from a reaction grow-in with a lifetime that is identical to the decay lifetime of their precursor. It is this characteristic that makes the *probe* technique possible

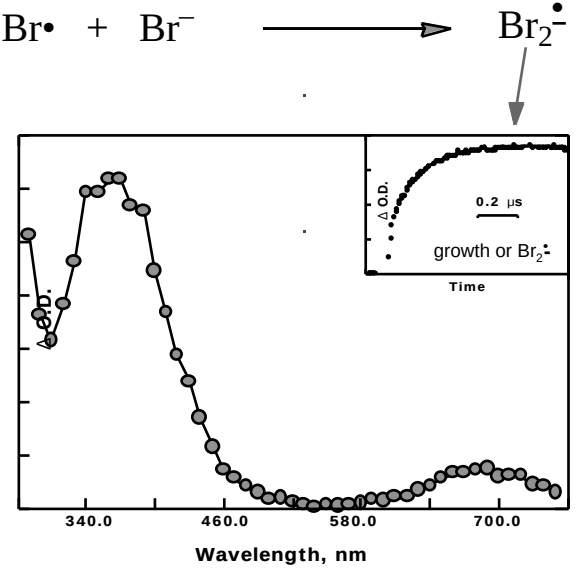
This characteristic also implies that when two spectral bands grow-in with the same kinetics they have the same precursor.

It does not mean that the two bands necesarily belong to the same species.

Studies of atomic species in solution

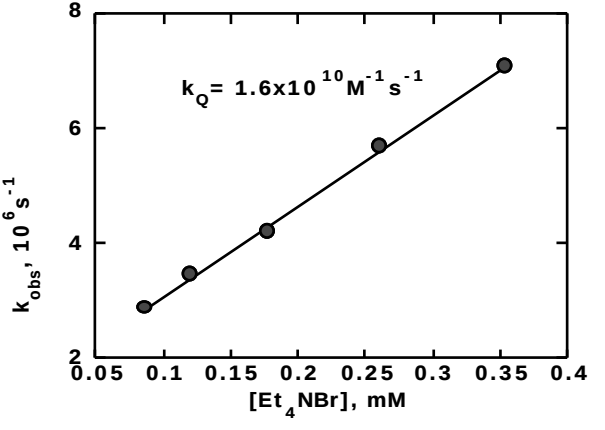
Bromine atoms can be readily generated, but are invisible to the technique of laser flash photolysis




Br• + Br⁻
Br2•⁻
△ O.D.
0.2 μs
growth or Br2•⁻
Time
△ O.D.
340.0
460.0
580.0
700.0
Wavelength, nm

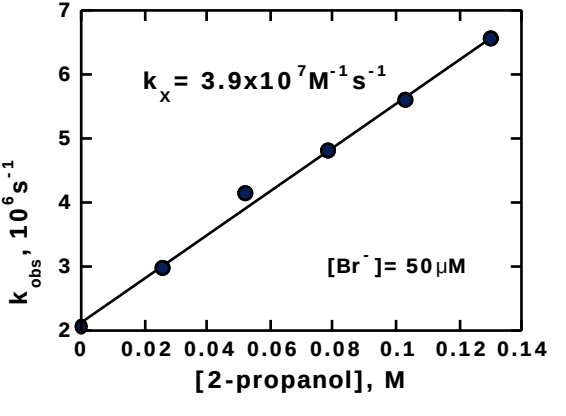
Analysis of the growth kinetics for $Br_2^{\bullet-}$

$$k_{growth} = k_0 + k_{rxn}[Rt_4NBr]$$



The kinetics for *invisible reactions* can be determined by using the absorption from $Br_2^{\bullet-}$ as a probe

$$k_{growth} = k_0 + k_{Br^-}[Br^-] + k_X[X]$$



Reate constants for reactions of bromine atoms

Quencher	k_Q , 10^6 M^{-1} s^{-1}
Methanol	0.93
Ethanol	16
1-Pentanol	11
1-Octanol	12
2-Octanol	35
2-Propanol	39
3-Pentanol	12
2-Methil-1-propanol	17
Dioxane	1.2
Ether	17
Toluene	66
Triethilamina	29000
p-Cresol	30000

One step further in the probe technique
Examining triethylsilyl radicals

$Bu^tO\bullet \longrightarrow CH_3COCH_3 + CH_3\bullet$

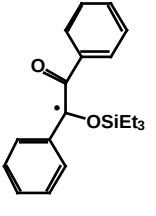
$Bu^tO\bullet + \text{solvent-H} \longrightarrow Bu^tOH + (\text{solvent})\bullet$

} k_0

$Bu^tO\bullet + Et_3SiH \longrightarrow Bu^tOH + Et_3Si\bullet$ $(k=5.7\times10^6 M^{-1}s^{-1})$

$Et_3Si\bullet + \text{Probe} \longrightarrow \text{Signal carrier}$ } k_{probe}

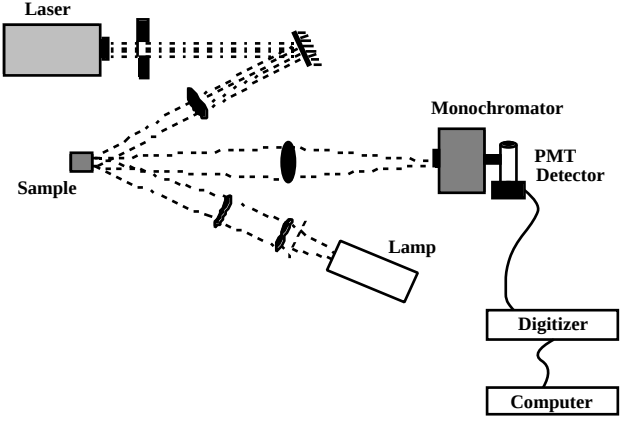
$Et_3Si\bullet + \text{R-Br} \longrightarrow Et_3SiBr + R\bullet$ } k_{rxn}



Signal carrier derived from benzil

Time resolved diffuse reflectance

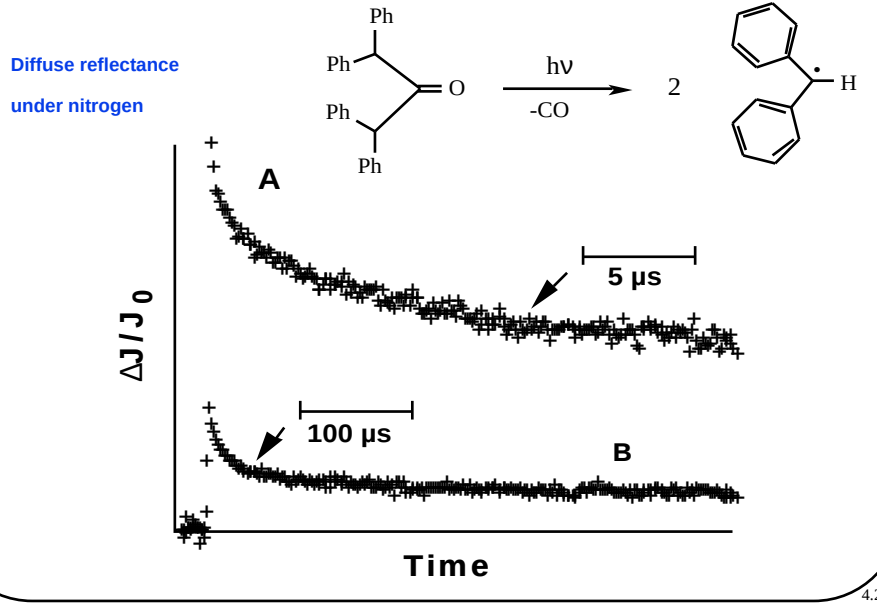
an alternate approach for opaque samples



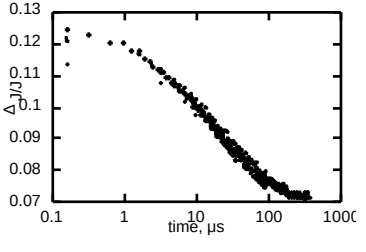
Decay of diphenylmethyl on silicagel

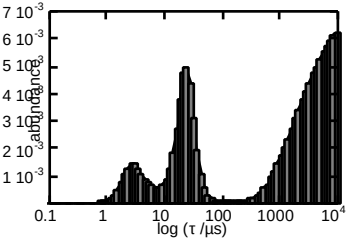
Diffuse reflectance

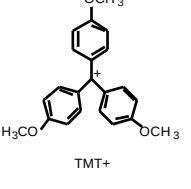
under nitrogen



Complex kinetics are common in heterogeneous systems

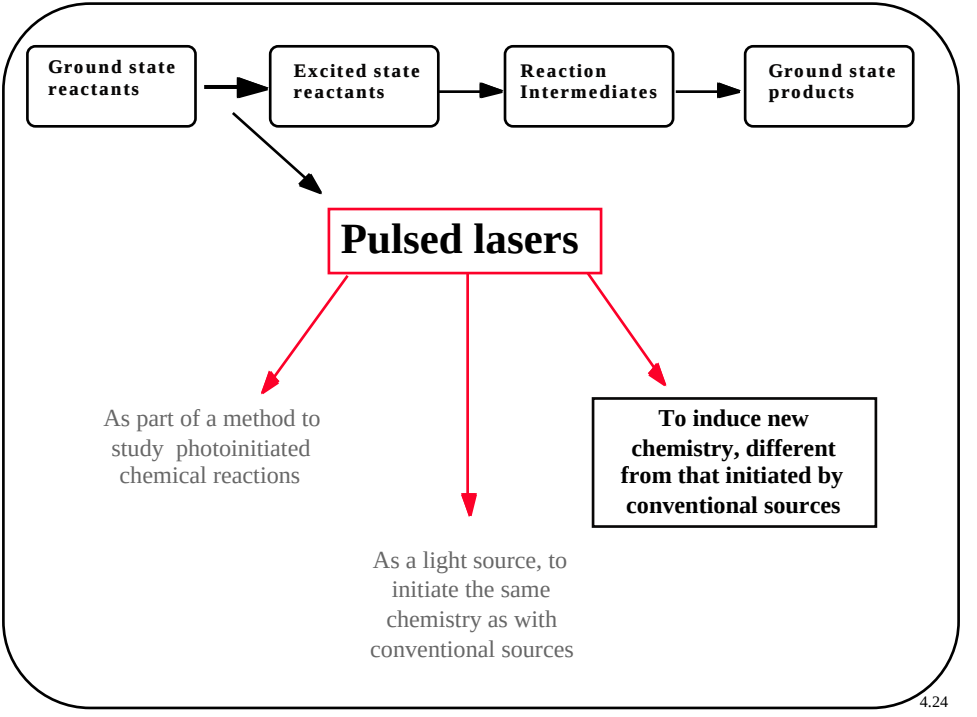






TMT+

(LEFT) Decay trace in different time domains of TMT+/HY film. The traces were monitored at 350 nm and the 2, 5, 10 and 20 µs time scales were used. Note the logarithmic time scale. (RIGHT) Distribution analysis of the TMT+/HY film.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