Pulsed lasers

As part of a method to study photoinitiated chemical reactions

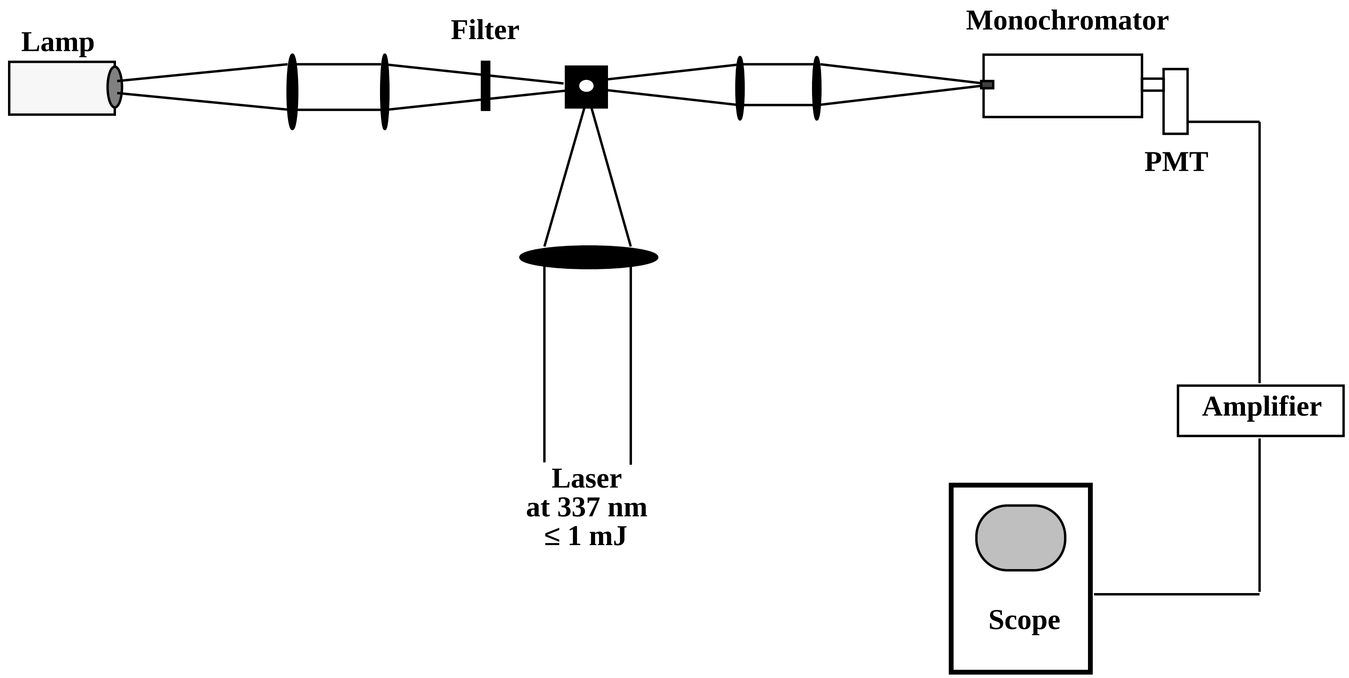
As a light source, to initiate the same chemistry as with conventional sources

To induce new chemistry, different from that initiated by conventional sources

Pulsed nanosecond lasers

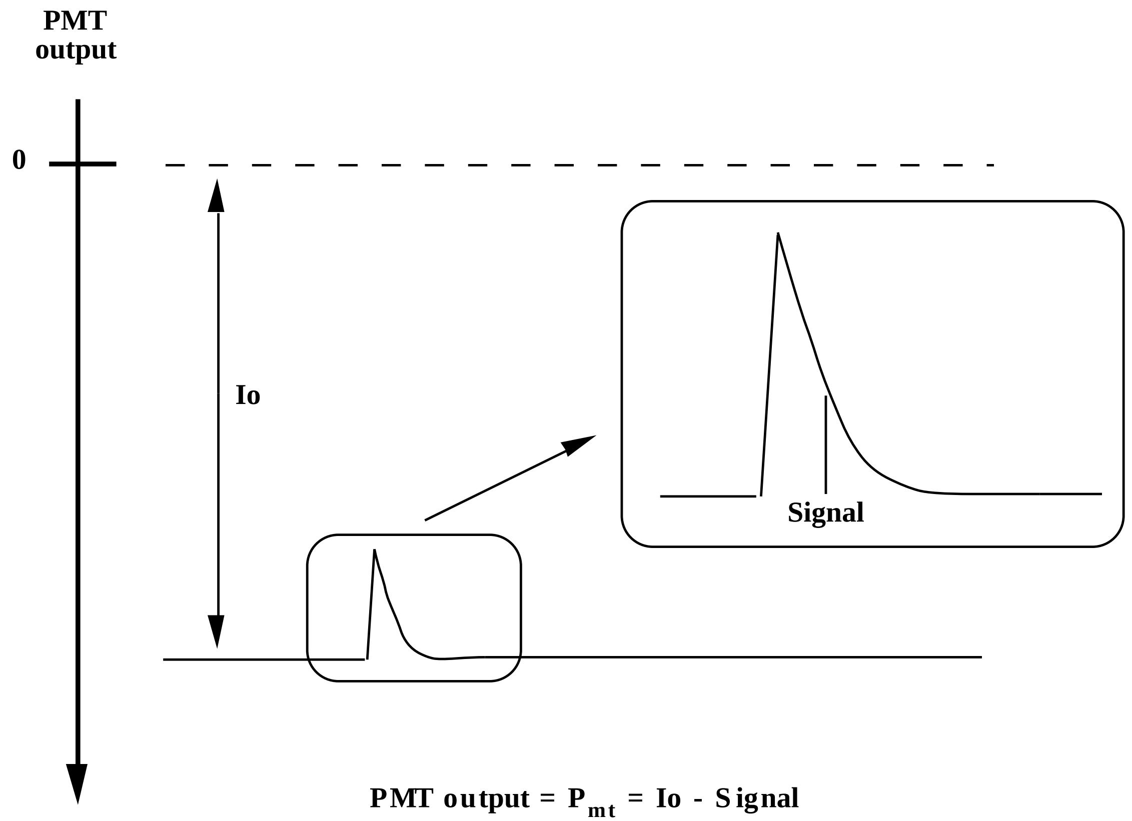
LASER	WAVELENGTH, nm	PULSE
Nitrogen	337	8 ns, ≤ 10 mJ
Excimer	193 (Ar/F)	5-50 ns, ≤300 mJ
	248 (Kr/F)	5-50 ns, ≤ 1J
	308 (Xe/Cl)	5-50 ns, ≤ 500 mJ
	351 (Xe/F)	5-50 ns, ≤ 300 mJ
Ruby	694	≥ 10 ns, 1 J
	347 (x2)	≥ 10 ns, 300 mJ
Nd/YAG	1064	5-10 ns, 0.5-5 J
	532 (x2)	5-10 ns, ≤ 500 mJ
	355 (x3)	5-10 ns, ≤ 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

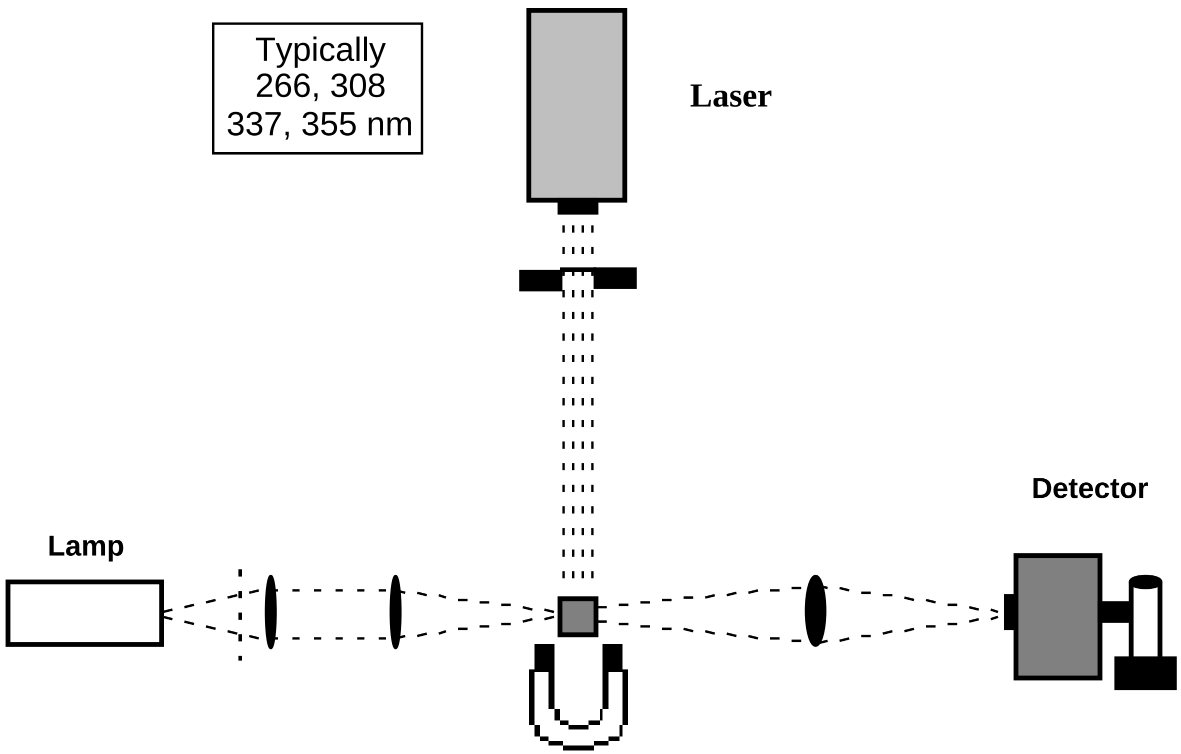


$$\text{PMT output} = P_{mt} = \text{Io} - \text{Signal}$$

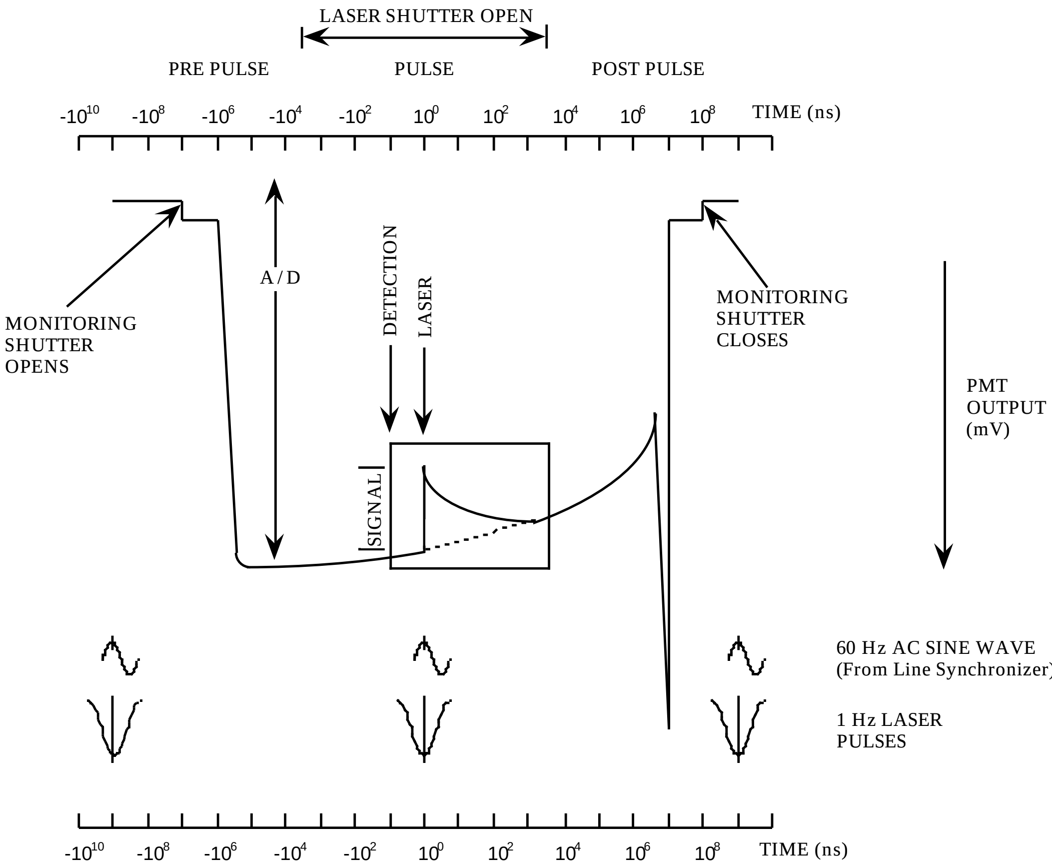
$$T = \frac{P_{mt}}{\text{Io}}$$

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

Laser flash photolysis technique



Laser photolysis sequence



Conditions and capabilities of laser flash photolysis

FAST PRECURSOR PROCESSES
SLOW DECAY OF PRODUCTS

Process under study

$$A \longrightarrow B$$

$$\text{Reagents} \xrightarrow{h\nu} \xrightarrow{\text{fast}} \longrightarrow \longrightarrow A$$

$$A \xrightarrow{10\ \text{ns} - 500\ \mu\text{s}} B$$

$$B \xrightarrow{\text{slow}} \longrightarrow \longrightarrow \text{final products}$$

Kinetic analysis for *visible* systems

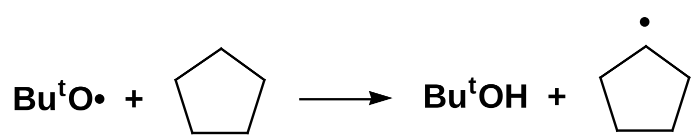
$$\left.\begin{array}{l} Bu^tO\bullet \longrightarrow CH_3COCH_3 + CH_3\bullet \\ Bu^tO\bullet + \text{solvent-H} \longrightarrow Bu^tOH + (\text{solvent})\bullet \end{array}\right\} k_0$$

$$\left.Bu^tO\bullet + Ph_2CHOH \longrightarrow Bu^tOH + Ph_2\dot{C}OH\right\} k_{rxn}$$

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

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

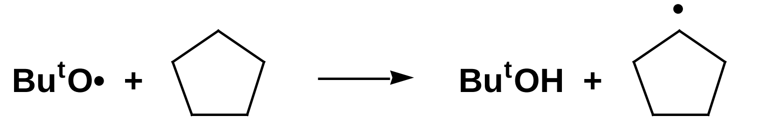
E.g.:



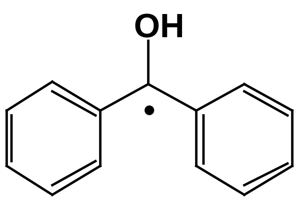
The probe technique

$$Bu^tO\bullet \longrightarrow CH_3COCH_3 + CH_3\bullet$$
$$Bu^tO\bullet + \text{solvent-H} \longrightarrow Bu^tOH + (\text{solvent})\bullet$$
k_0

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



k_{rxn}



signal carrier

λ_{max} 540 nm

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

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

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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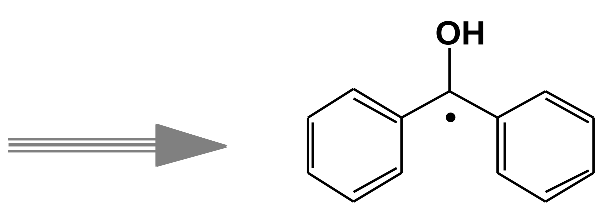
Is there a catch ?

- 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

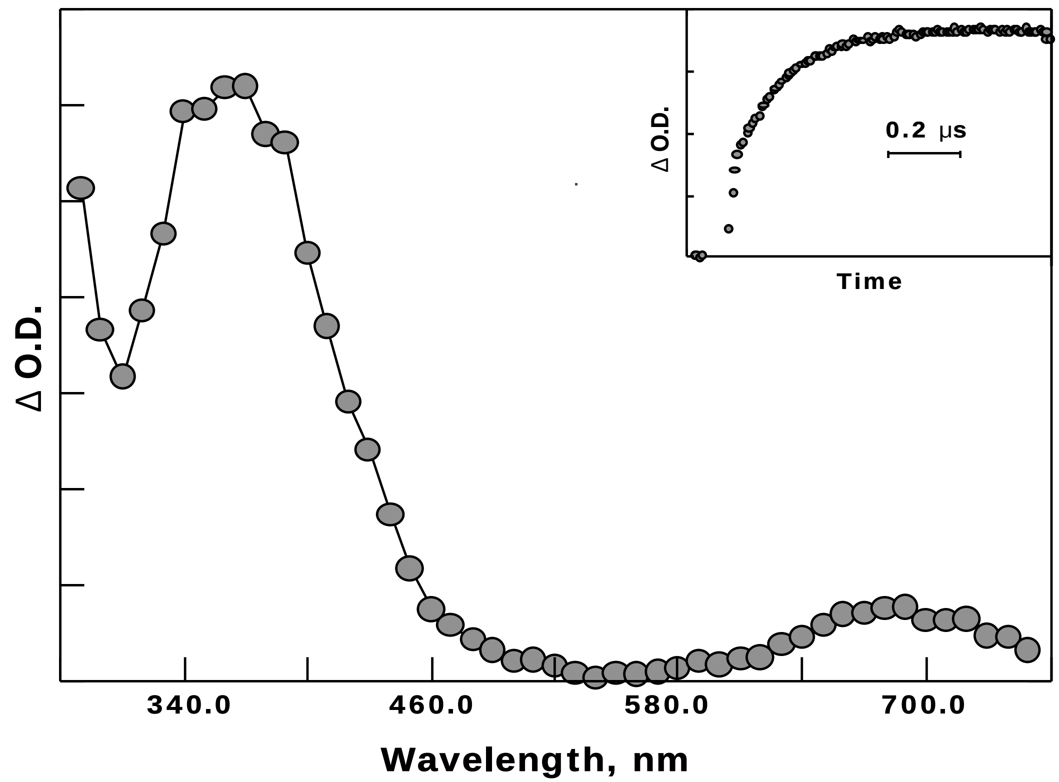
This characteristic also implies that when two spectral bands grow-in with the same kinetics they have the same precursor.

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

$$\mathrm{RCHBr{-}CH_2Br} \xrightarrow{h\nu} \mathrm{Br^\bullet} + \mathrm{R\dot{C}H{-}CH_2Br}$$

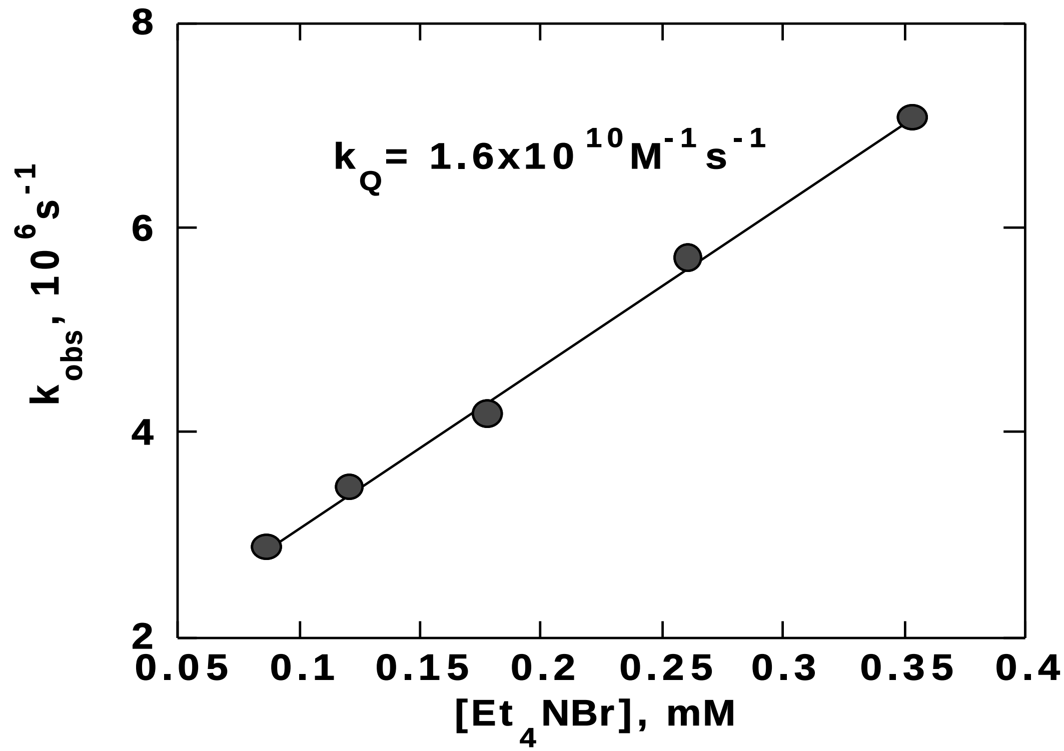
$$\mathrm{R\dot{C}H{-}CH_2Br} \longrightarrow \mathrm{Br^\bullet} + \mathrm{RCH{=}CH_2}$$

$$\mathrm{Br^\bullet} + \mathrm{Br^-} \longrightarrow \mathrm{Br_2^{\bullet-}}$$



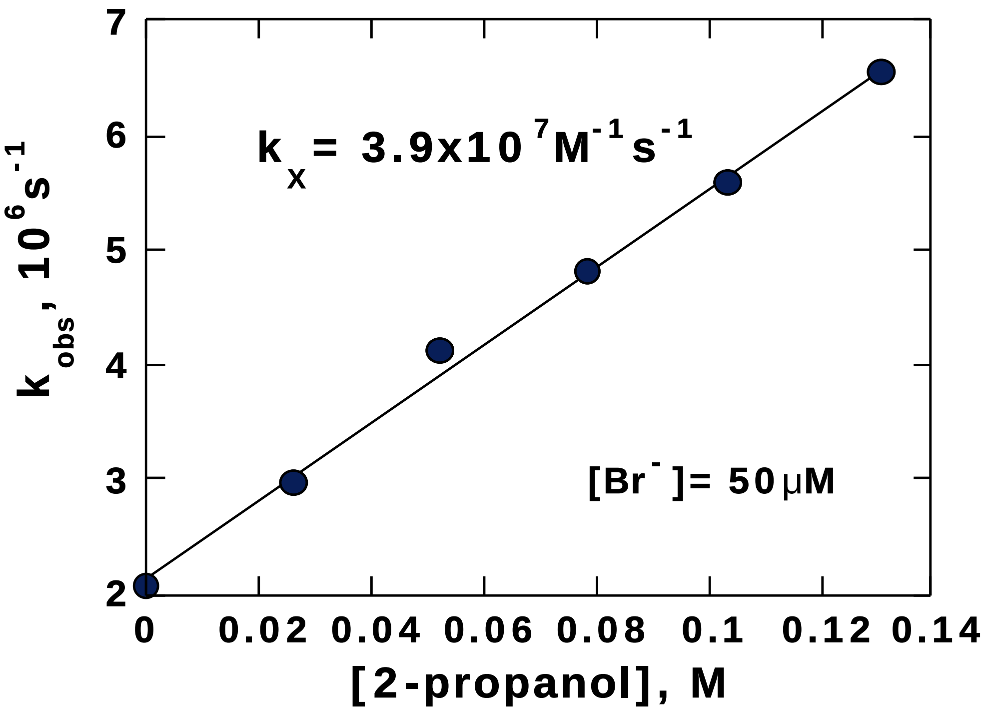
Analysis of the growth kinetics for $Br_2^{\bullet-}$

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



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

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

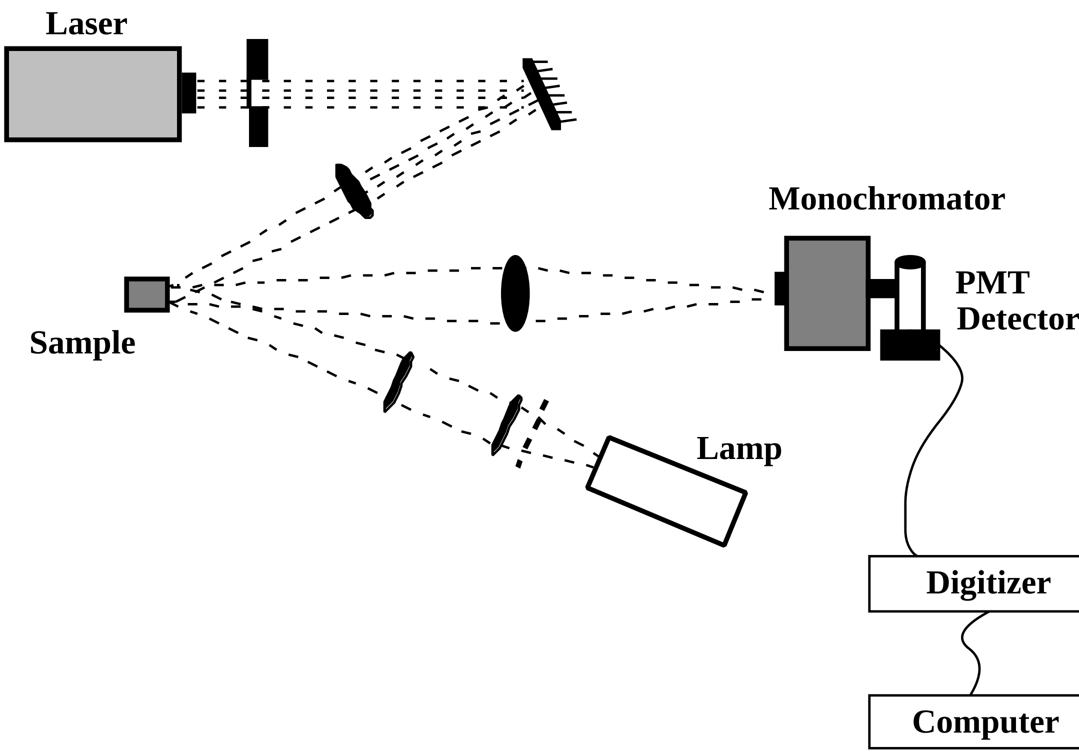


Reate constants for reactions of bromine atoms

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

Time resolved diffuse reflectance

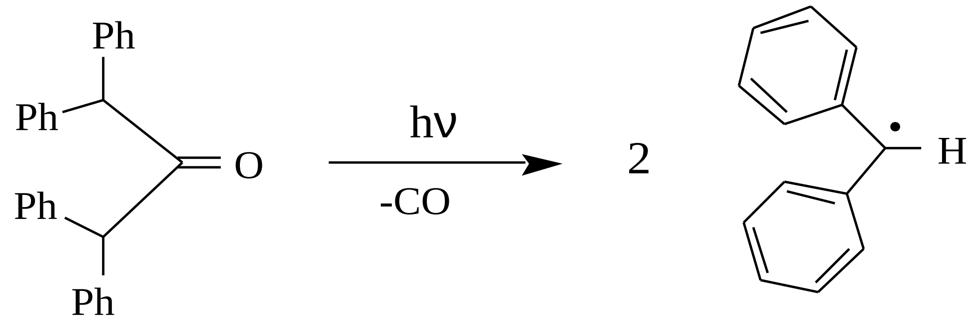
an alternate approach for opaque samples

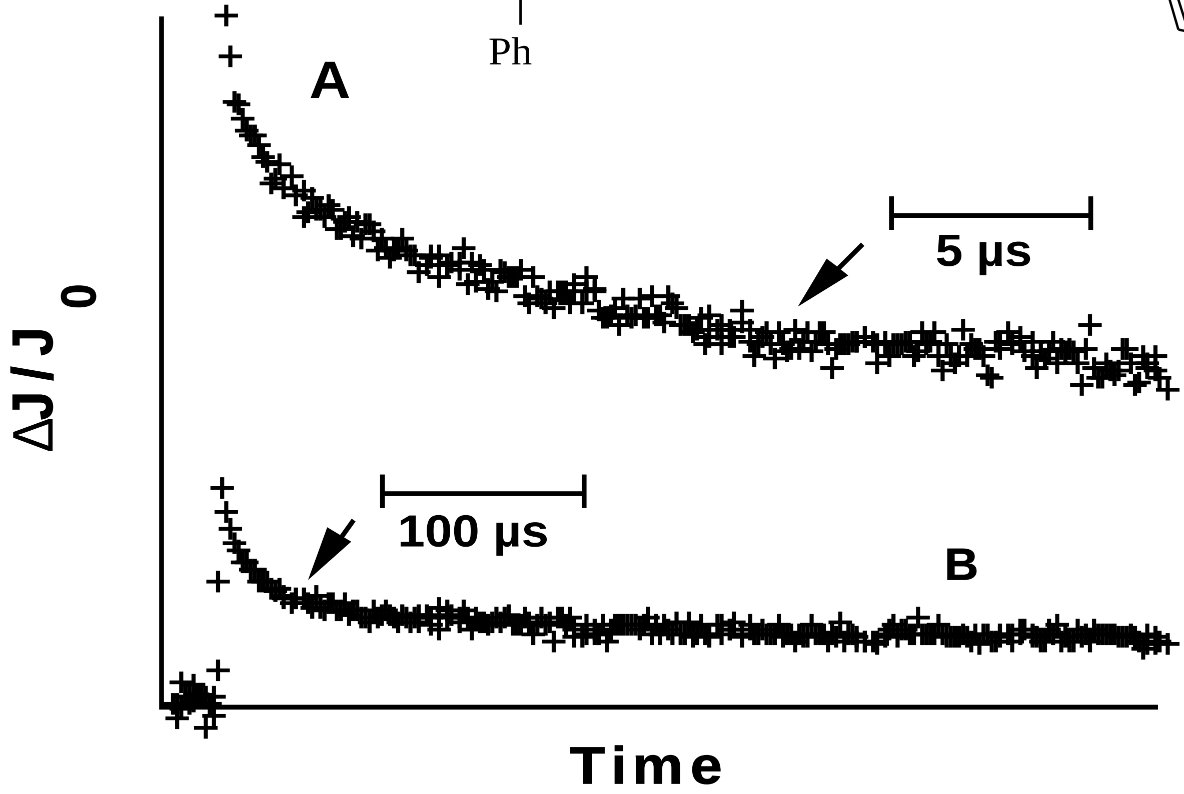


Decay of diphenylmethyl on silicagel

Diffuse reflectance

under nitrogen





Pulsed lasers

As part of a method to study photoinitiated chemical reactions

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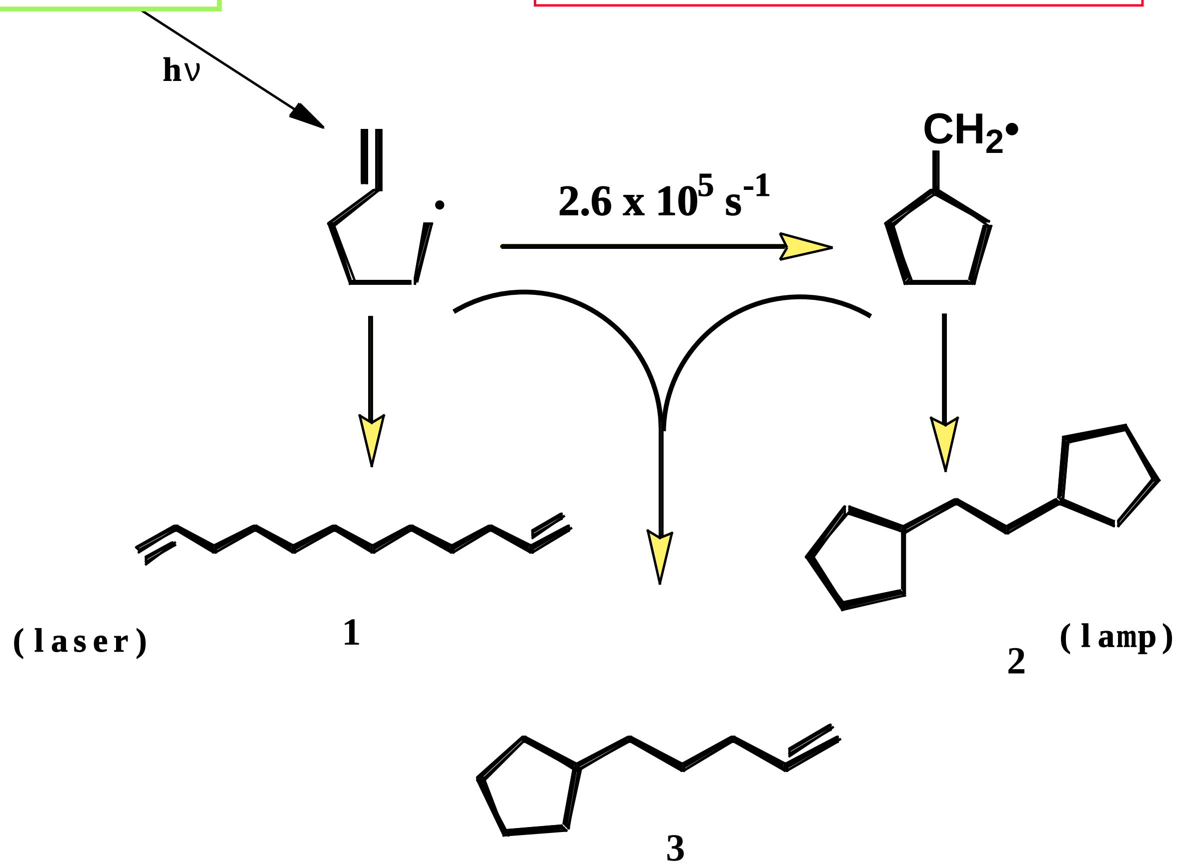
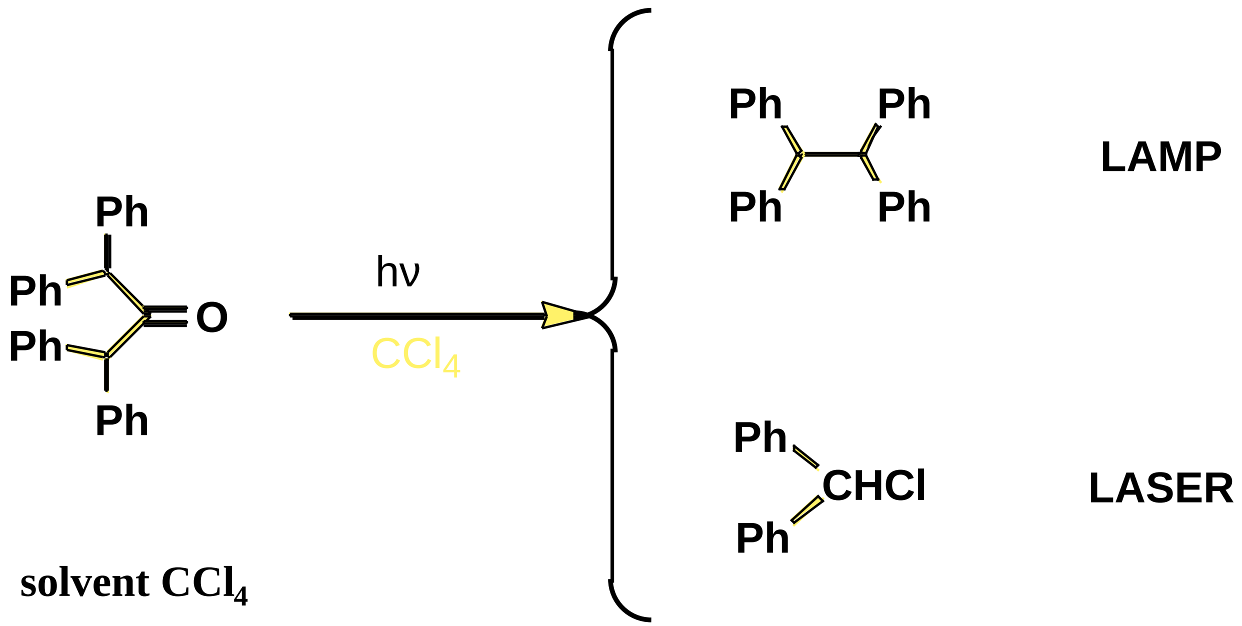
To induce new chemistry, different from that initiated by conventional sources

Photochemical source

A laser and a lamp can give different products even if two photon processes do not occur

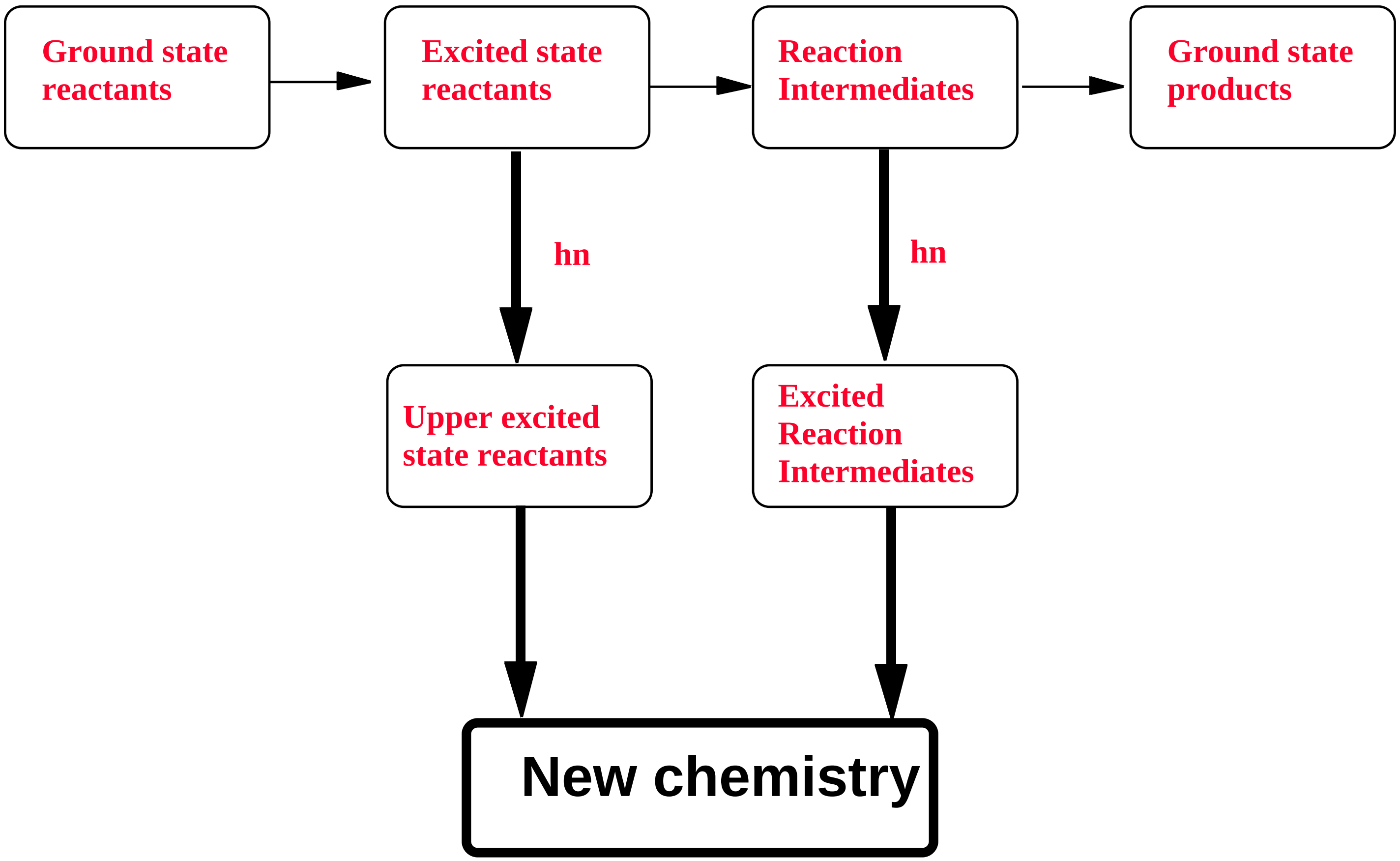


The photochemistry of tetraphenylacetone gives different products depending on the light source



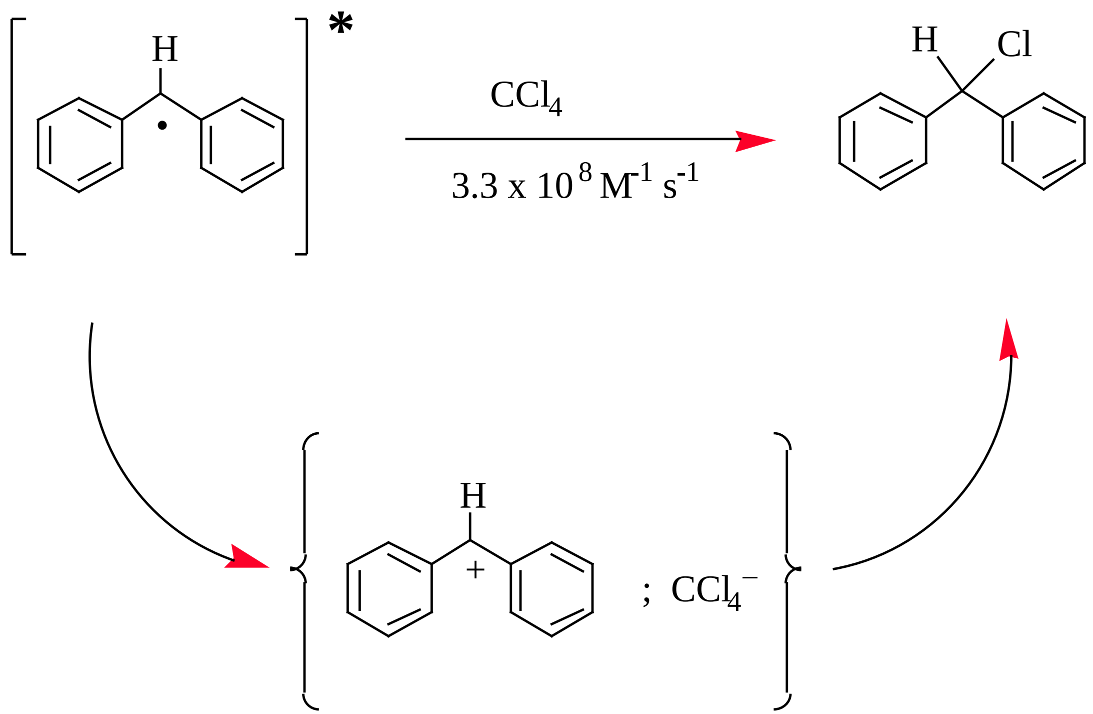
solvent CCl_4

Laser initiated two-photon processes

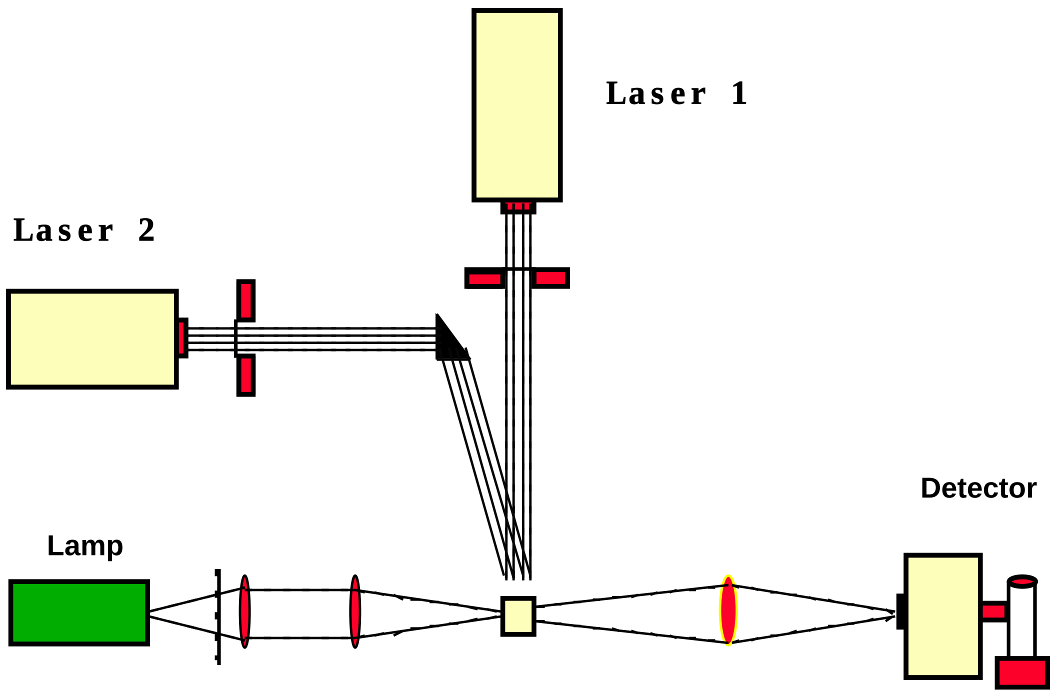


Halogen abstraction reactions of excited diphenylmethyl radicals are quite common.

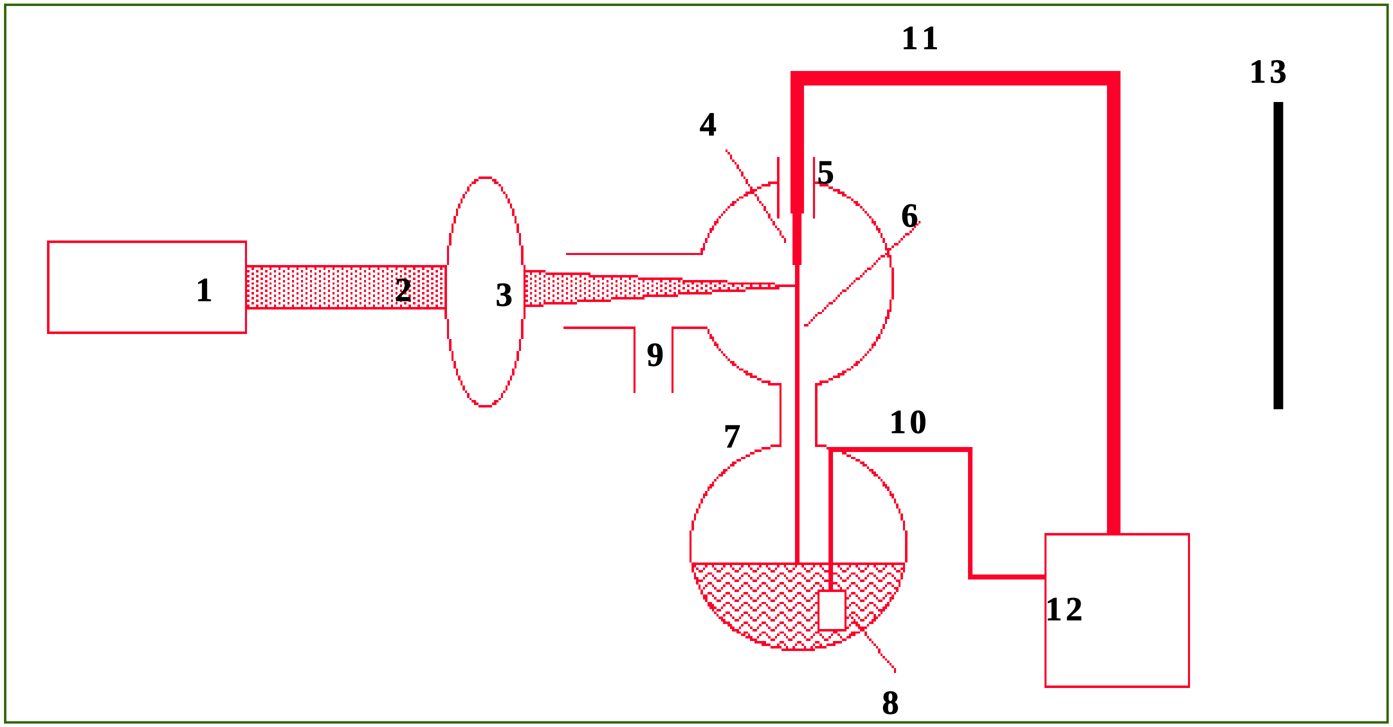
They are known to involve a charge transfer mechanism



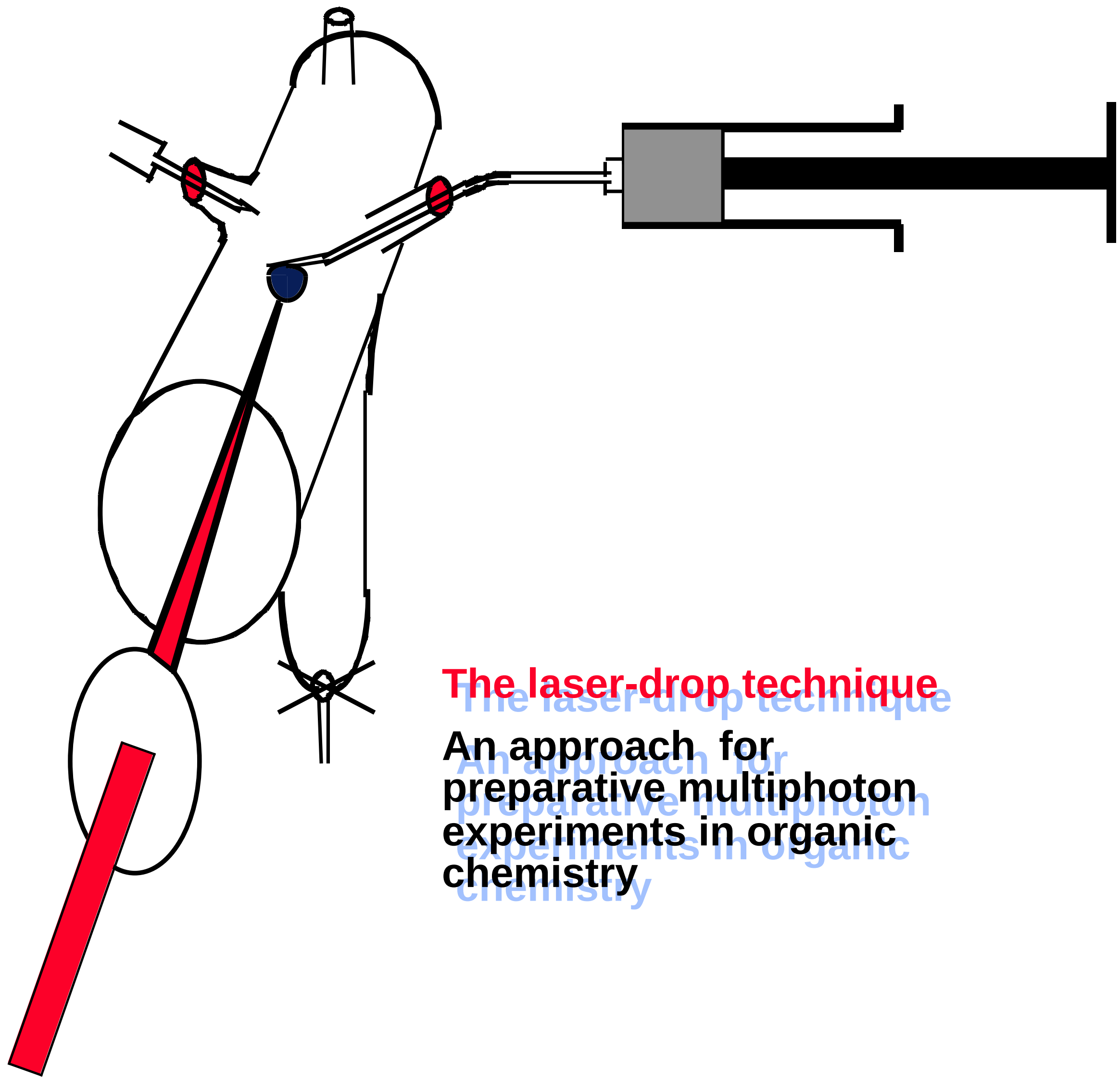
Laser Flash Photolysis
Employing two-color two-laser techniques



The Laser Beam - Liquid Jet



1 - Argon Ion Laser
2 - Laserbeam
3 - Lens on Motor Positioner
4 - Capillary
5 - Glass Bulb
6 - Jet Stream
7 - Collecting Flask
8 - Filter
9 - Inert Gas Supply
10 - Low Pressure Tubing
11 - High Pressure Tubing
12 - HPLC Pump
13 - Projection Screen



The laser-drop technique

An approach for preparative multiphoton experiments in organic chemistry

The laser-drop technique
An approach for preparative multiphoton experiments in organic chemistry

SINGLET OXYGEN EMISSION

$$O_2(^1\Delta_g) \longrightarrow O_2(^3\Sigma_g)$$

1269 nm

1588 nm

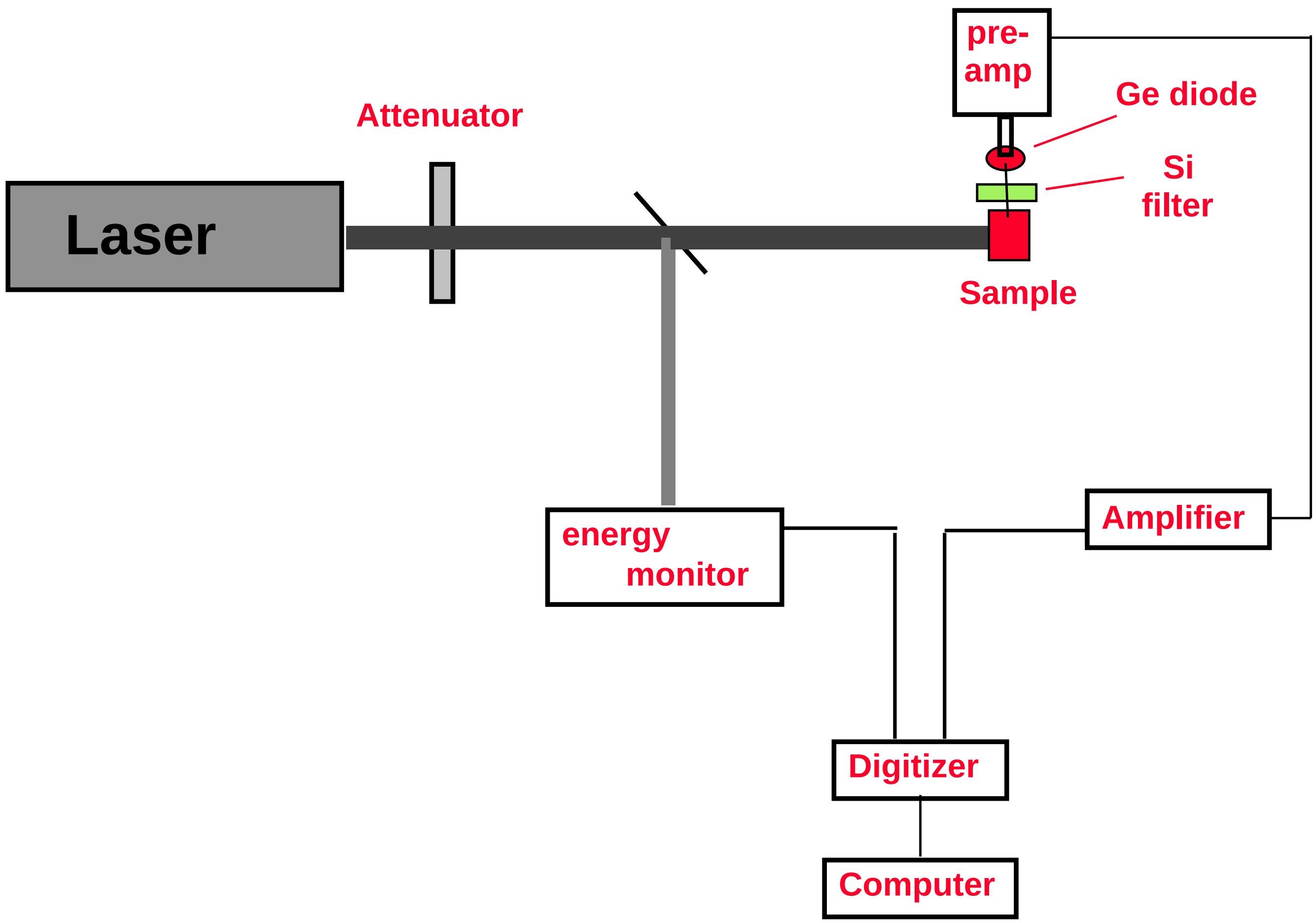
$$O_2(^1\Delta_g) + O_2(^1\Delta_g) \longrightarrow O_2(^3\Sigma_g) + O_2(^3\Sigma_g)$$

"dimol emission"

634 nm

703 nm

Singlet oxygen time resolved detection



CONDUCTIVITY SET-UPS