PLEXCHEM Technologies

ULTRAVIOLET CROSSLINKING;

AN ALTERNATIVE TO CROSSLINKING OF PE AND HFFR COMPOUNDS

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Topics

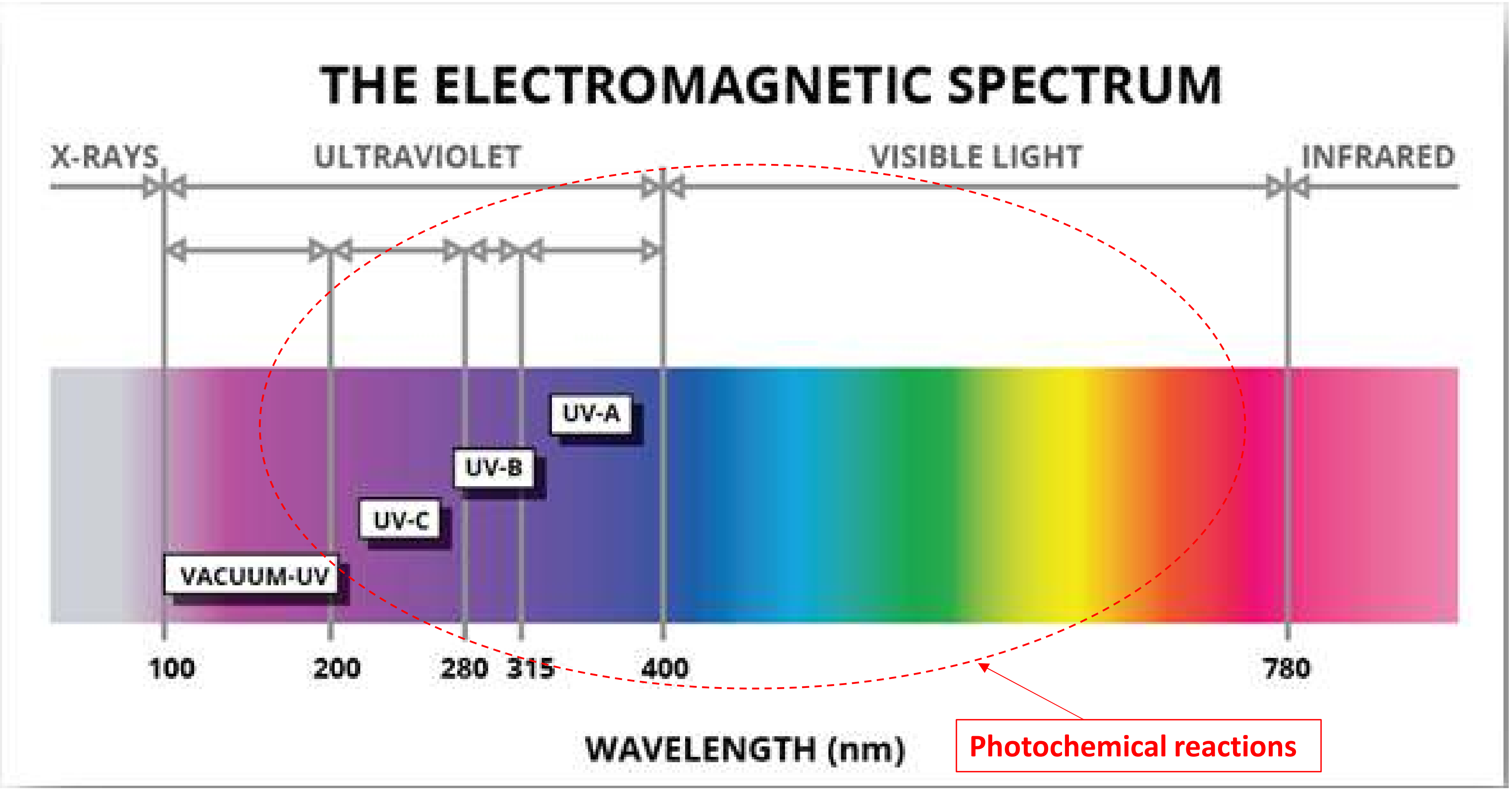
- Problems in chemical crosslinking extrusion
- Definition of photochemistry
- Theoretical concepts
- Photochemical induced reactions
- Equipment profile with short video
- Some results

Crosslinked cables: what crosses your mind?

- Pre-crosslinking - *lumpy surface*
- Punctures - *cable failures*
- Under-crosslinking - *poor hot set*
- Shrinkage - *choosing the right tools*
- Orange Skin - *unacceptable appearance*
- The outcome of extrusion - *finding out too late*
- Operating conditions - *leading to poor test results*
- Special storage conditions - *Shelf life*

An introduction to Photochemistry

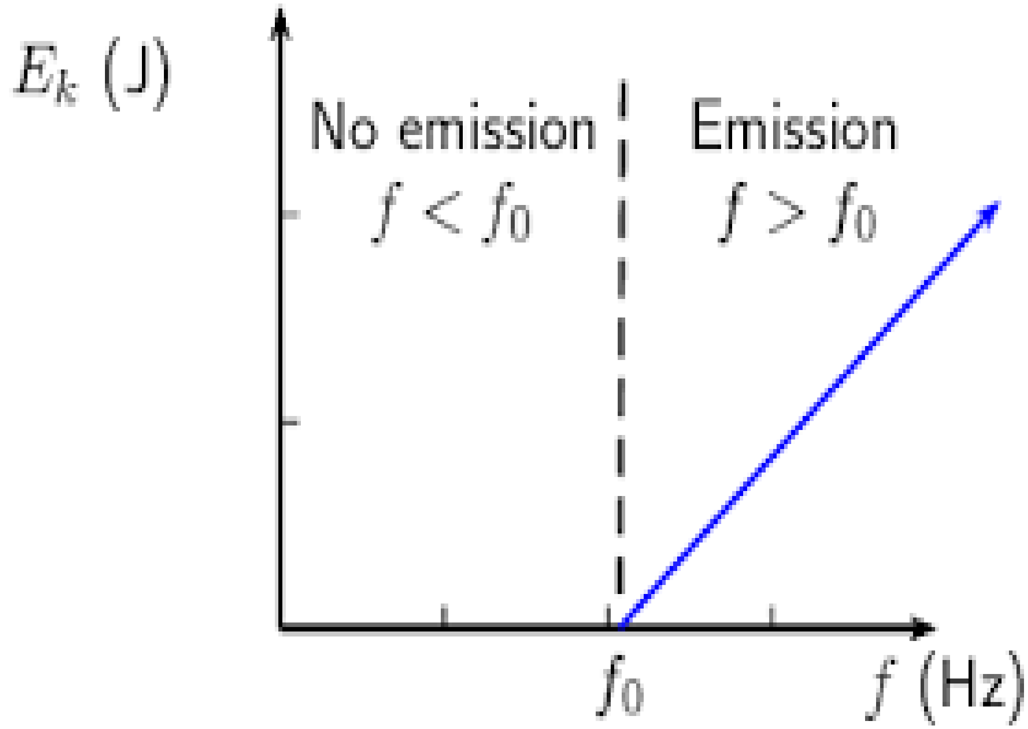
The study of chemical reactions and physical behaviour that may occur under the influence of visible and/or ultraviolet light is called **Photochemistry**


THE ELECTROMAGNETIC SPECTRUM
X-RAYS
ULTRAVIOLET
VISIBLE LIGHT
INFRARED
UV-A
UV-B
UV-C
VACUUM-UV
100
200
280
315
400
780
WAVELENGTH (nm)
Photochemical reactions

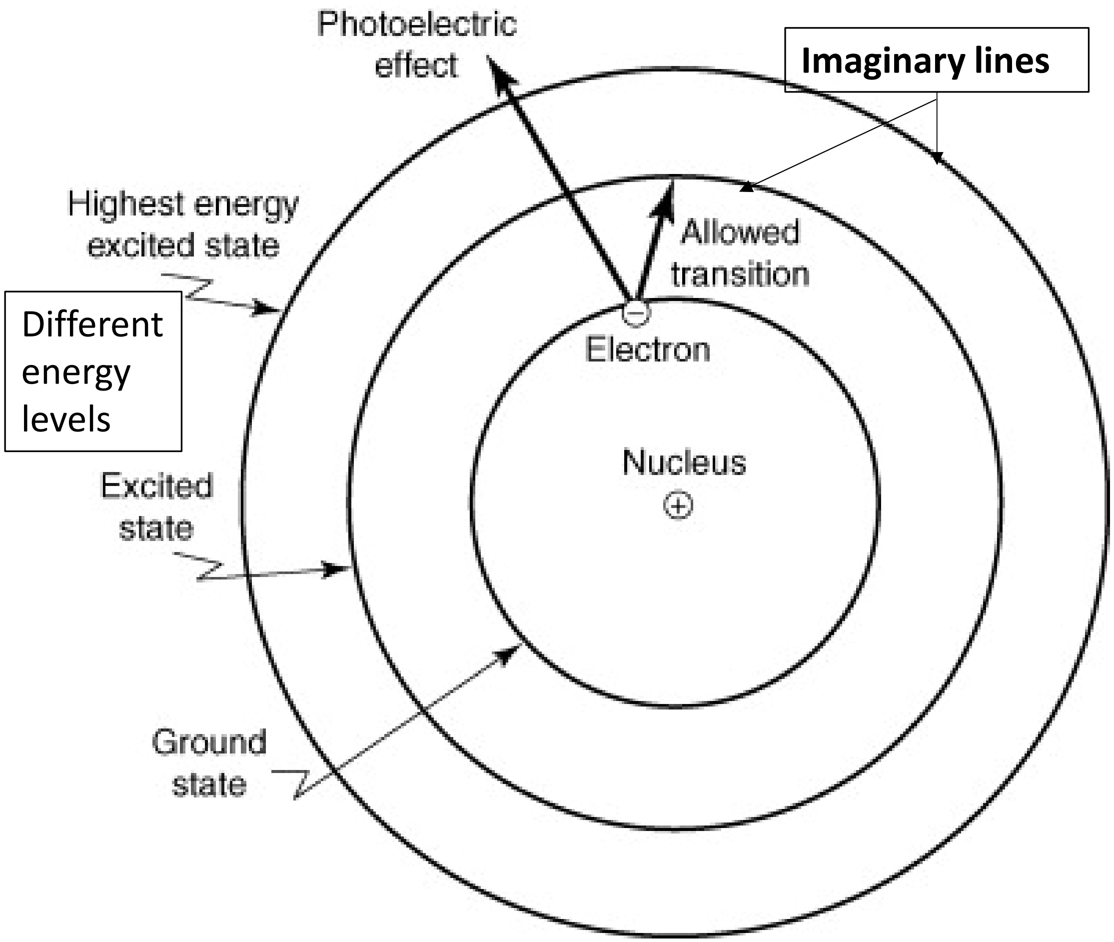
Concept of Threshold frequency

Experiments showed that electrons are dislodged or transition only by the impingement of photons when those photons reach or exceed a threshold frequency (energy).

Below that threshold, no electrons are emitted from the material regardless of the light intensity or the length of time of exposure to the light.

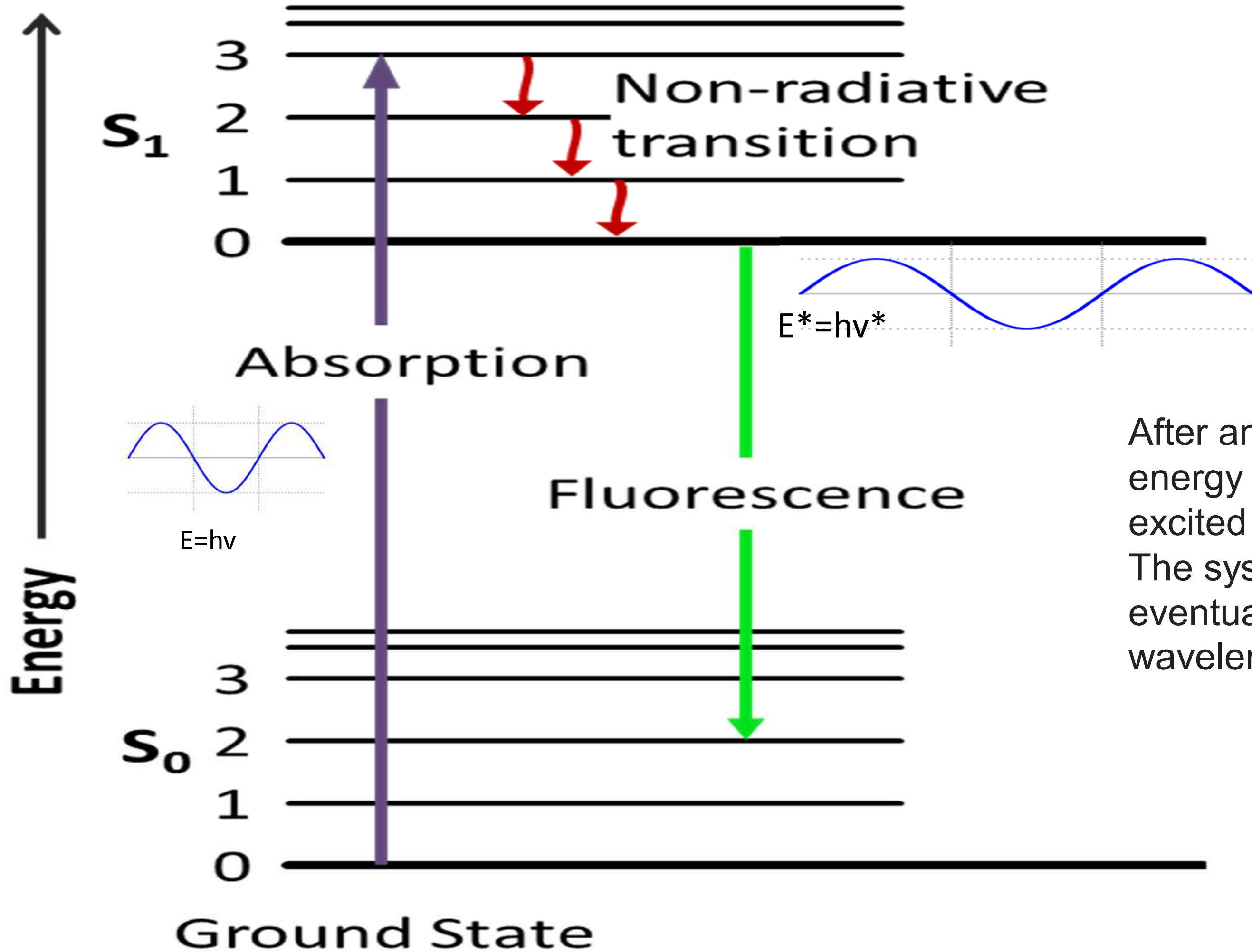


Electronic transitions



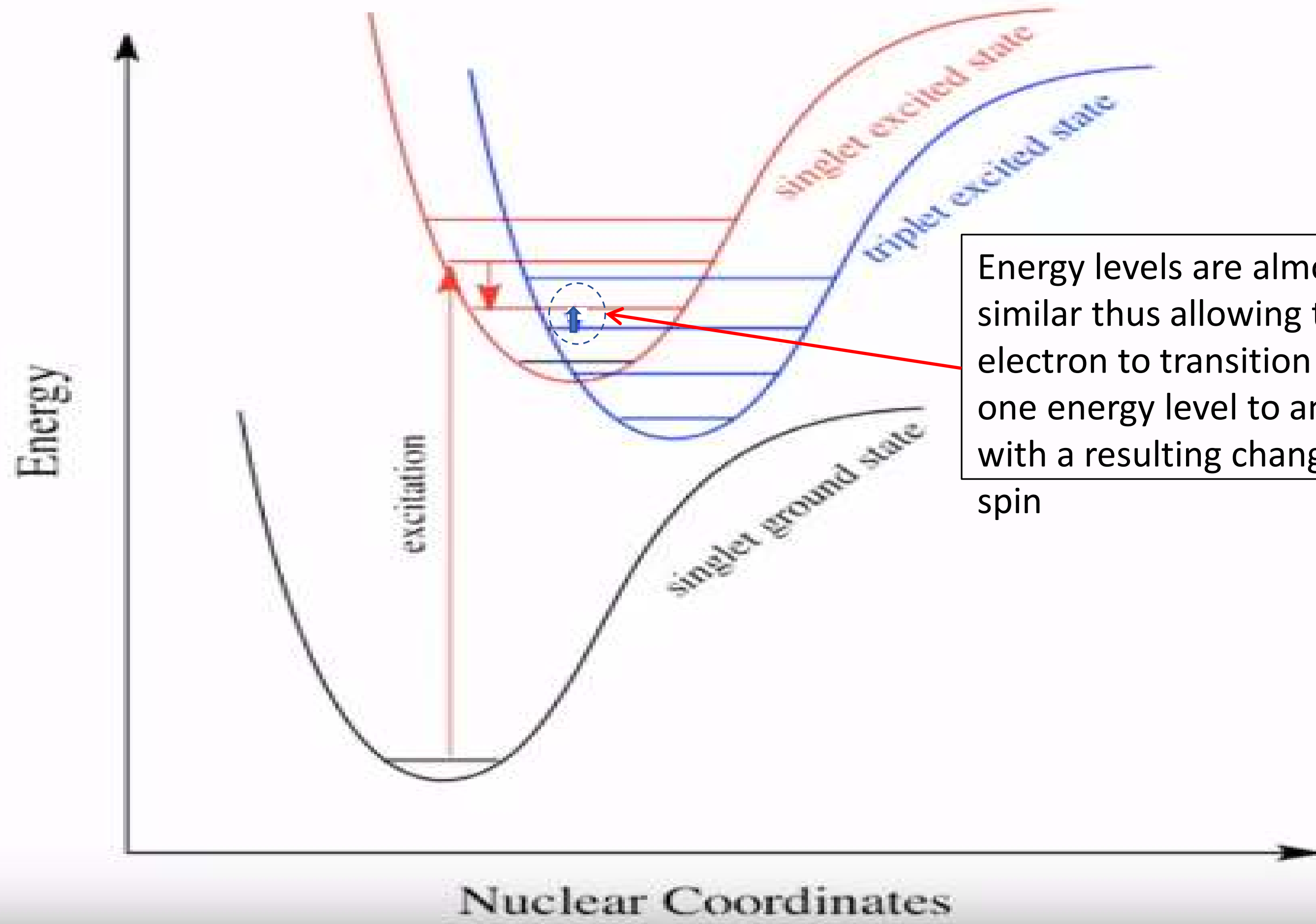
Note: Orbitals represent wave functions that describe the probability of a electron's quantum state as a function of position, time, momentum, and spin.

Fluorescence



After an electron absorbs a high-energy photon, E=hv the system is excited electronically and vibrationally. The system relaxes vibrationally, and eventually fluoresces at a longer wavelength E*=hv*.

Intersystem Crossing

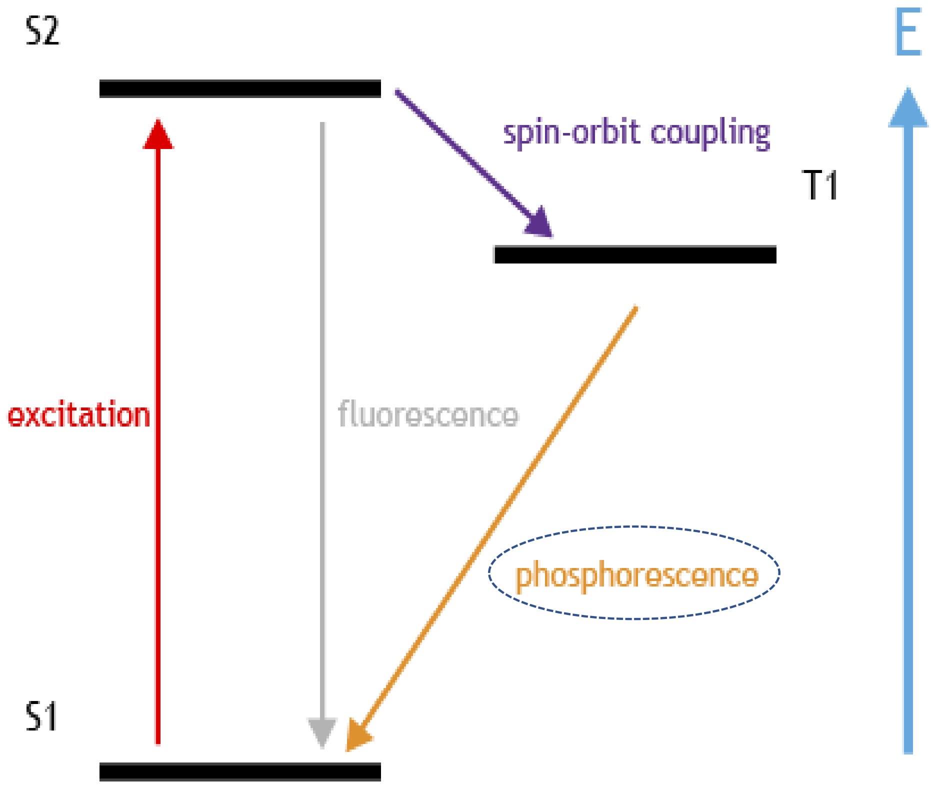


Energy levels are almost similar thus allowing the electron to transition from one energy level to another with a resulting change of spin

Inter System Crossing

- **Inter System Crossing (ISC) is the process in which spin of an excited electron is reversed which results in a change in the multiplicity of the molecule involved (eg, from Singlet to triplet state)**
- **This is enhanced if the vibrational level of the two states overlap**

Phosphorescence



signage

Process	Transition	Timescale (sec)
Light Absorption (Excitation)	$S_0 \rightarrow S_n$	10^{-15} (instantaneous)
Internal Conversion	$S_n \rightarrow S_1$	10^{-14} to 10^{-11}
Vibrational Relaxation	$S_n^* \rightarrow S_n$	10^{-12} to 10^{-10}
Intersystem Crossing	$S_1 \rightarrow T_1$	10^{-11} to 10^{-6}
Fluorescence	$S_1 \rightarrow S_0$	10^{-9} to 10^{-6}
Phosphorescence	$T_1 \rightarrow S_0$	10^{-3} to 100
Non-Radiative Decay*	$S_1 \rightarrow S_0$	10^{-7} to 10^{-5}
	$T_1 \rightarrow S_0$	10^{-3} to 100

The non-radiative decay* may take place by intermolecular energy transfer to a different molecule. This collisional process is termed **quenching**

Photochemical reactions

Carbonyl compounds

-The absorption properties of ketones and aldehydes are convenient for irradiation around 350 nm (n, π^* 330 - 380 nm).

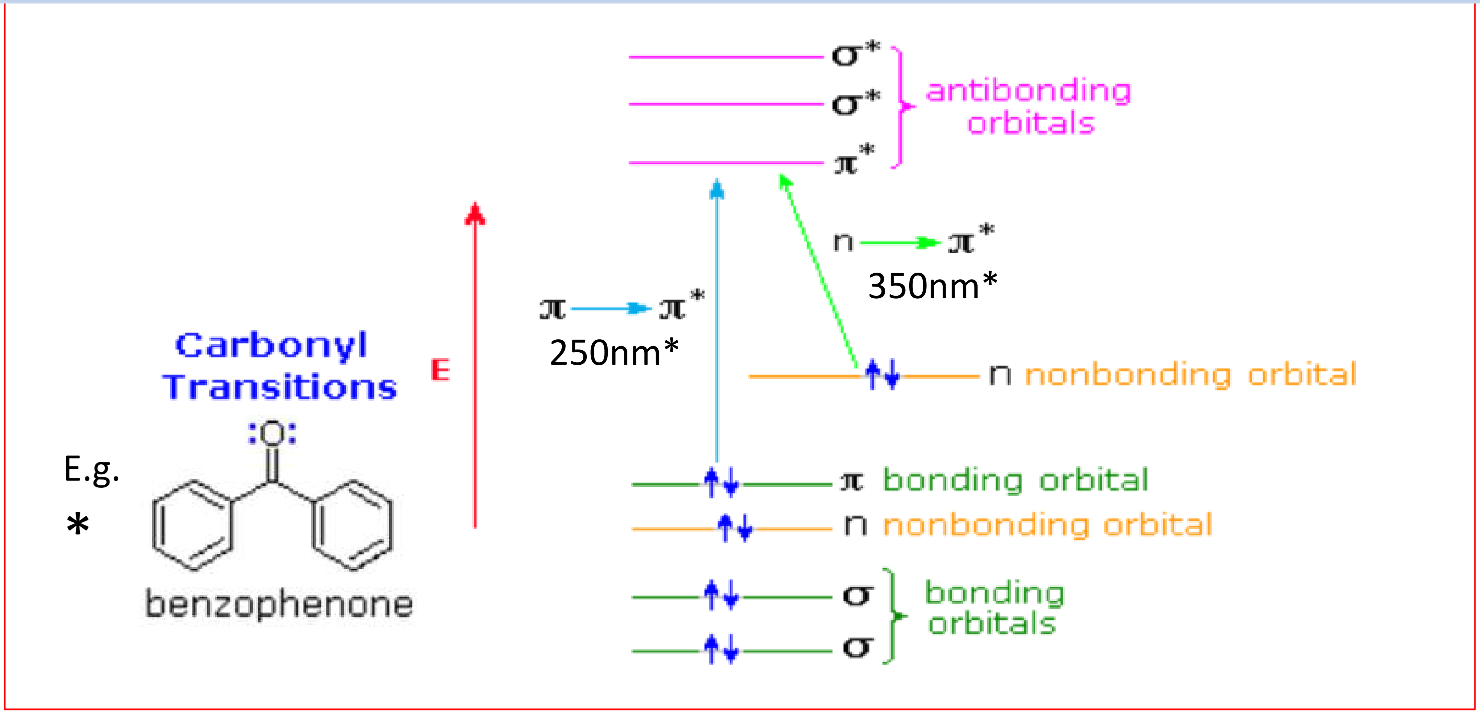
-Triplet-singlet energy gap is small (20-70 kJ/mol).

-Intersystem crossing rates are high.

-Lifetime of first excited singlet state is in the nanosecond region for aliphatic aldehydes and ketones; in the sub-nanosecond region for aromatic aldehydes and ketones.

-Singlet photochemistry can be detected with aliphatic aldehydes or ketones, while aromatic substrates, such as benzophenone or acetophenone, react exclusively from their corresponding triplet states and are excellent triplet sensitizers.

From the standpoint of electronic transitions



Bonding orbitals contain electrons that are used in bonding with electrons from another atom Non boding orbitals contain electron that do not participate in the bonding process but remain paired within the atom Electrons in the antibonding molecular energy levels cause dissociations of molecules.

How is chemical and radiation crosslinking similar?

-Both require the formation of free radicals that extract hydrogen atoms from polymers to be crosslinked

-After hydrogen extraction, the polymeric free radicals will react with other polymers to form crosslink chains

- Mechanistically only the initiation process is dissimilar

Main UV crosslinking equipment

UV Radiator

Purpose: To provide the required amount (intensity) of the threshold frequency (UV radiation) that will promote Electrons to the anti bonding energy level in order to produce free radicals

Auxiliary UV crosslinking equipment

Chiller

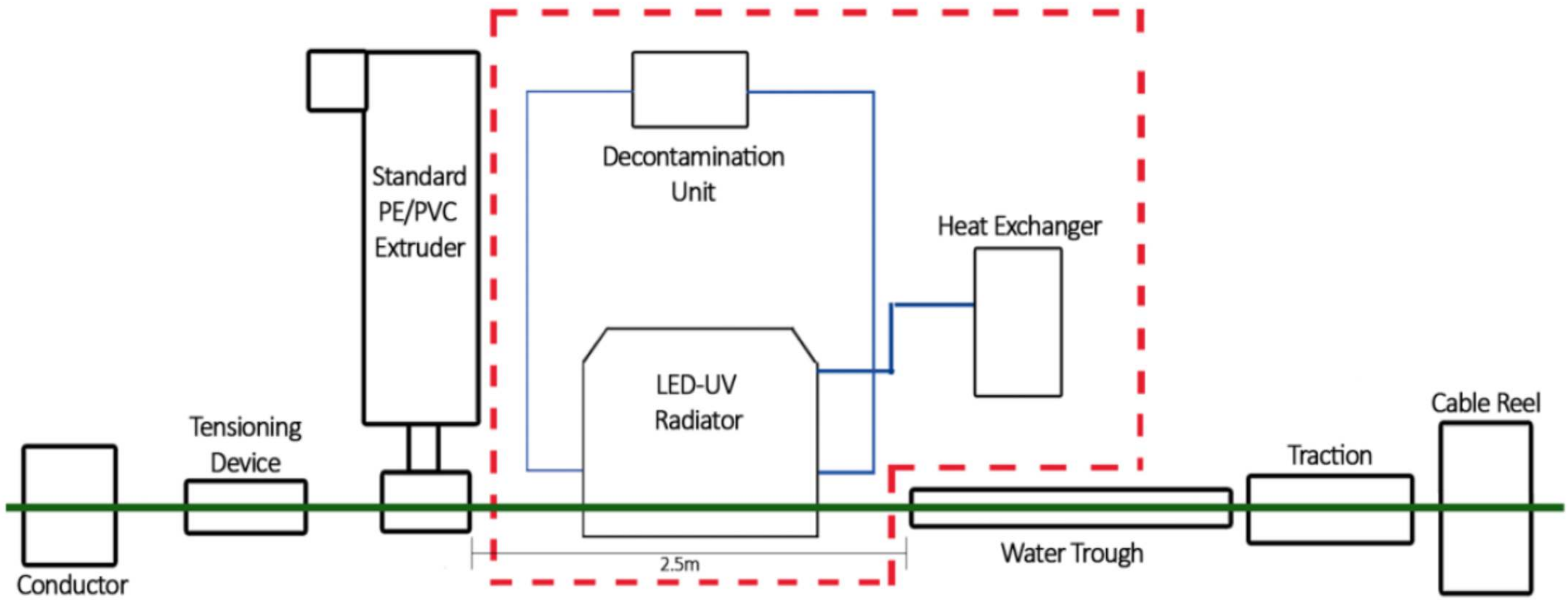
Purpose: The amount of heat generated would eventually lead to the damage of the LED lamps and the electronic components. It is imperative that the system be kept below 50° C.

Extractor

The excitation of electrons into free radicals would produce trace amount of toxic gases e.g. Ozone, Oxides of N2, Carbon monoxide. Such gases are harmful to the operators as well as the equipment.

Complete system Setup

Equipment setup in Extruder Line



Advantages

- **Low cost of equipment**
- **Ease of processing and cleaning**
- **Inexpensive cost of compound with long shelf life**
- **Low energy consumption. Only 20KW**
- **No need for extensive modification of production facility**
- **High draw down = reduced material consumption**
- **Post production operations could be done immediately**
- **Processing XL-HFFR cables**

Testing data for XL-LV cables

	Test	Results	Units	Requirement
Mechanical	Tensile strength	21.7	N/mm2	12.5
	Elongation at break	520	%	250
Thermal	(i) Tensile retention	93	%	25<
	(ii) Elongation retention	87	%	25<
	Hot set (200 ˚C, 15 min)	>40	%	175<
	Permanent elongation	+5	%	15<
	Shrinkage (130˚C 1hr)	1.5	%	4<
Chemical	Gel	78	%	>75
electrical	Volume resistivity 90˚C	3.2 X E16	Ω cm	
	Withstand voltage test	Pass	2.4kV, 5hr	

Next Step Development

- **UV protected cables (2.5% carbon black content or anti UV additives).**

High concentration of carbon black; blocks UV penetration and special formulation for compound is required.

- **Speed adaptation of equipment especially for thin insulation where speeds of 300 - 500m/min**
- **Limitation on high insulation thickness (more than 6 mm)**
- **Difficult for coextrusion**

Safety Requirements

- Irradiation. Never look into the beam of a high power LED; the lights very high intensity damage your eyes.

- Ozone generation: Short wavelength light may generate ozone from oxygen. Always perform reactions in a well ventilated fume hood.

- Lamps: Most lamps operate at high temperature and at high vapour pressure. Never move or touch lamps during operation.

Thank you for your attention

The good news under quantum rules, if you understood nothing you have understood everything

I'm ready for your questions and will apply the quantum rules