

Wavelength shifters

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Abstract

Wavelength shifters as a specific application of the broader optical fibers technique are discussed. The physical mechanisms responsible for their working are explored. Applications to physics and engineering are proposed.

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I. INTRODUCTION

Wavelength shifters are polymers designed specifically to absorb light of a certain frequency and re-emit a fraction of it at a different one. The transmission of this re-emitted light along the material is through internal reflection. Wavelength shifting fibers are a type of flexible scintillating material and most of the light is kept inside the scintillating environment, which makes them superior to rigid scintillating materials in that they can adapt to intricate geometrical set-ups and avoid light loss from the medium.

II. SPECTRAL SHIFTERS

A. The Franck-Condon principle

The reason for the capacity of a molecule to absorb photons with a certain frequency and emit others at a different one is the Franck-Condon principle.[11] Upon the absorption of a photon, the molecule vibrates. To be more specific, when a new electronic configuration occurs, such as when a molecule is excited, the electronic transition happens faster than the nuclei can respond. When the nuclei realign respect to each other according to the new electronic configuration, the vibrational energy of the molecule is changed,[12] which, as shown in Figure 1, will give an emission of a photon with a lower frequency than the one that was initially absorbed by the molecule. The excess energy is carried in the form of phonons.[11]

The Franck-Condon principle states that the probability of a vibrational transition to occur is determined by the Franck-Condon overlap integral:[12]

$$\begin{aligned} P_{i \rightarrow f} &= \left(|\langle \Psi_{final}^* | \mu | \Psi_{initial} \rangle| \right)^2 \\ &= \left(\left| \int \Psi_{final}^* \mu \Psi_{initial} d\tau \right| \right)^2, \end{aligned} \quad (1)$$

where μ is the molecular dipole operator (or transition operator). We can write:

$$\begin{aligned} \langle \Psi_{total,f} | \mu | \Psi_{total,i} \rangle &= \langle \Psi_{nuc,f}^* | \langle \Psi_{el,f}^* | \mu | \Psi_{el,i} \rangle | \Psi_{nuc,i} \rangle \\ &= \langle \Psi_{nuc,f}^* | \Psi_{nuc,i} \rangle \langle \Psi_{el,f}^* | \mu | \Psi_{el,f} \rangle, \end{aligned} \quad (2)$$

where $S_{if} = \langle \Psi_{nuc,f}^* | \Psi_{nuc,i} \rangle$ is the coefficient of transition. The more the vibrational configurations overlap, the more likely it is for the vibrational transition to occur, creating a “displacement” of

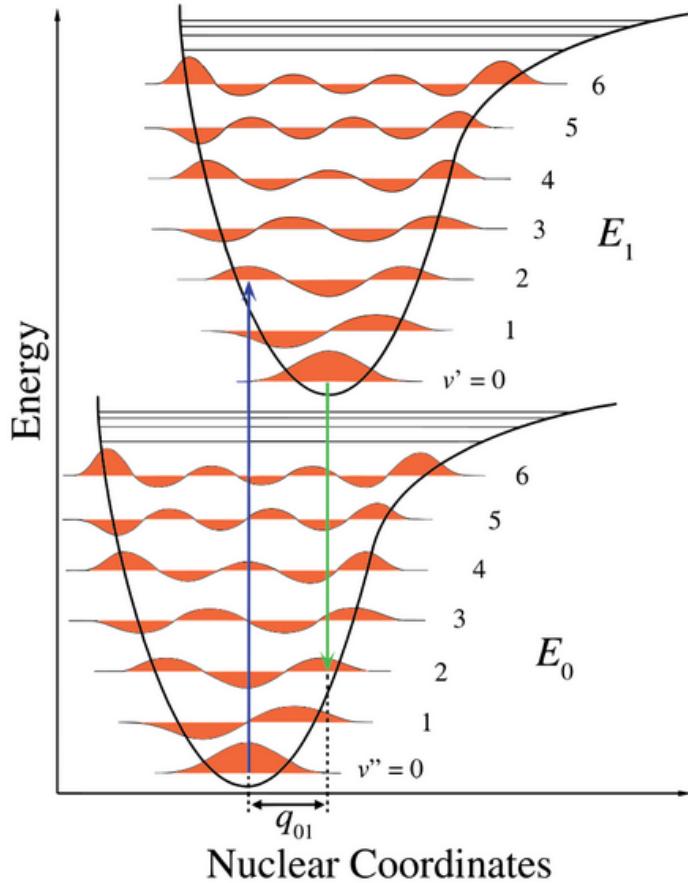


FIG. 1: Franck-Condon principle energy diagram. Three things are observed: 1) an absorption of a photon leads to a higher energy state, 2) the fluorescence leads to a lower energy state, 3) the shift in nuclear coordinates indicates a new equilibrium position in the interaction potential.

Taken from [12].

the emitted photon's frequency, according to the re-configuration of the nuclear coordinates.

We look at the example of a transition from a ground state to first excited state in the context of the harmonic oscillator. The coefficient of nuclear overlap is the following:[12]

$$S_{01} = \sqrt{\frac{\alpha^2}{2}} (R_e - Q_e) e^{-\alpha(R_e - Q_e)^2/4}, \quad (3)$$

where $\alpha = \sqrt{\frac{mk}{\hbar}}$ (m = mass, k = wave-number, \hbar is the [reduced] Plank constant), R_e is the equilibrium bond length in the ground state, and Q_e is the equilibrium bond length in the excited electronic state. The ground state and first excited state wave-functions being, respectively,[12]

$$|\Psi(R)\rangle = \left| \left(\frac{\alpha}{\pi} \right)^{1/4} e^{-\alpha(R-R_e)^2/2} \right\rangle \quad (4)$$

$$|\Psi(R)\rangle = \left| \left(\frac{\alpha}{\pi} \right)^{1/4} e^{-\alpha(R-Q_e)^2/2} \right\rangle \quad (5)$$

and the overlap is given by:[12]

$$\langle \Psi_{nuc,f}^* | \Psi_{nuc,i} \rangle = \sqrt{\frac{\alpha}{\pi}} \int_{-\infty}^{+\infty} e^{-\alpha(R-R_e)^2/2} e^{-\alpha(R-Q_e)^2/2} dR \quad (6)$$

To understand this better, let us look at the case when $S = 1$ and $S = 2$, shown in Figure 2 (a) and (b), respectively. A bigger S means a bigger frequency transition in the fluorescence of the molecule between the absorption and emission frequencies.

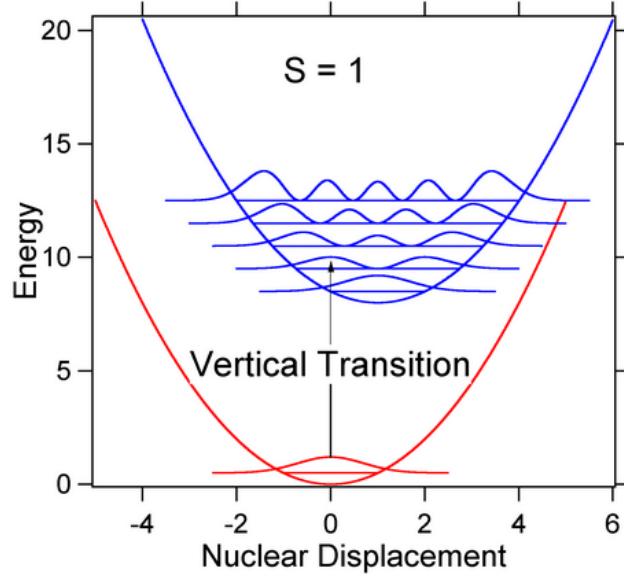
An (efficient) wavelength shifter is any organic compound the presents:[1] 1) a broad absorption cross section, 2) a large Stokes shift, and 3) a high photo-luminescence quantum yield.

B. Absorption cross section and the Beer-Lambert law

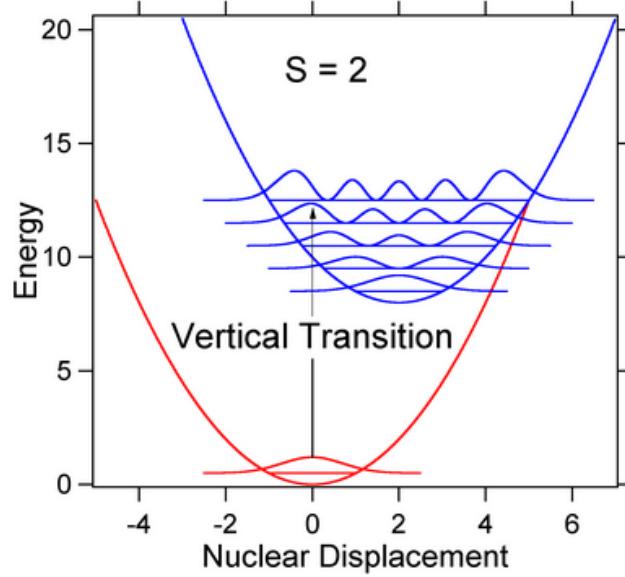
The absorption cross section is better explained by the Beer-Lambert law, which defines the absorbance, or capacity of absorption (of light), of the material in question, as:[2]

$$A = \log_{10} (I_0/I) = \epsilon lc, \quad (7)$$

where I_0 is the initial (incoming) light intensity, I is the intensity of light not absorbed by the material (i.e. the light that is *transmitted* through the material), ϵ is the molar extinction coefficient, c is the concentration of light-absorbing material, and l is the path-length that the light travels through the material. For fibers, which are generally very thin, we would need a large ϵ , mainly, with ϵ itself being a measure of the probability of electronic re-configuration of the atoms via electron excitation. The quantum mechanics of nature are key here, and different materials will absorb accordingly to the most appropriate light frequency (as explained by the photoelectric effect). For example, compounds bearing five-to six-membered heterocycles [1] with pi-configurated systems have maximal spectral characteristics in the violet to red range [1].



(a)



(b)

FIG. 2: wave-functions transitions for a harmonic oscillator with (a) $S = 1$ and (b) $S = 2$ at $T = 0$ kelvin, $8,000 \text{ cm}^{-1}$ in energy, and wave-number vibrational mode $1,000 \text{ cm}^{-1}$. Taken from [12].

C. The Stokes shift

The Stokes shift is just the difference in wave-length between the absorbed photon and the emitted one (See Equation 3). This is explained by the Franck-Condon principle. The molecule

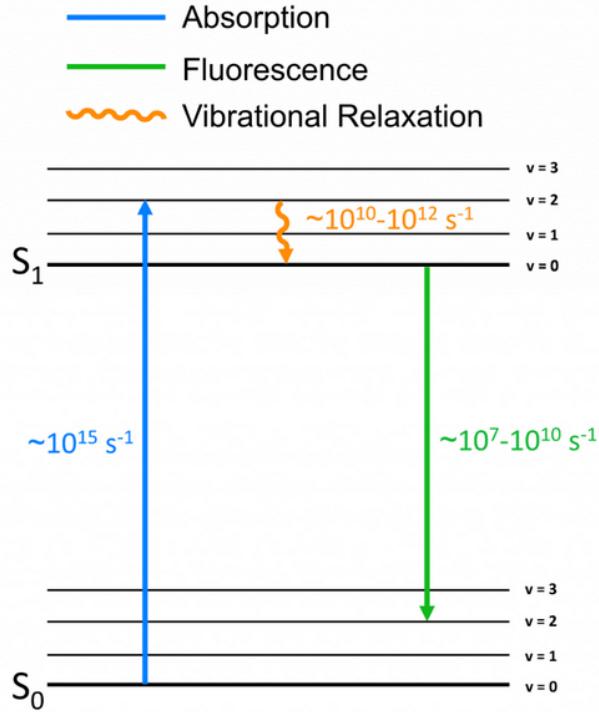


FIG. 3: Franck-Condon principle as the origin of the Stokes shift. The molecule absorbs a photon, it changes its vibrational mode, it relaxes and re-emits a photon at a different frequency.

The lost energy is in the form of phonons. Taken from [4].

absorbs a photon, it changes its vibrational mode, it relaxes and re-emits a photon at a different frequency. See Figure 3.

$$\Delta\lambda = \lambda_f - \lambda_i. \quad (8)$$

D. Photo-luminescence quantum yield

The quantum yield is given by the number of events occurring per number of photons absorbed. [11] In the case of wavelength shifters, we specifically look at the equation:

$$\Phi = \frac{\text{Number of photons emitted}}{\text{Number of photons absorbed}} \quad (9)$$

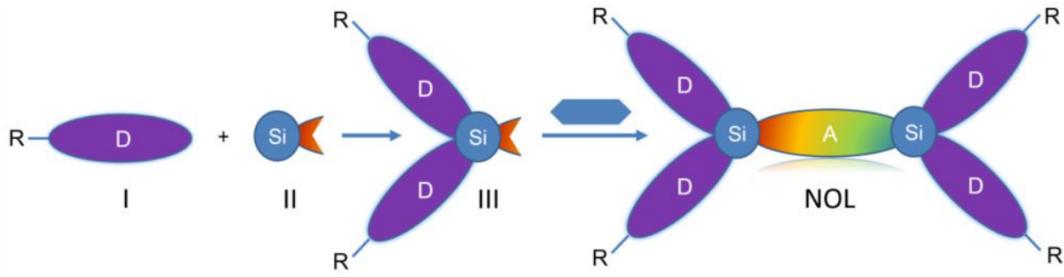


FIG. 4: schematic of a NOL and its main synthetic preparation steps. “Si” is for “silicon”, “D” is for “donor”, and “A” is for “acceptor”. Taken from [1].

E. Nano-structured organosilicon luminophores

Nano-structured organosilicon luminophores (NOLs) have been specially engineered so that they posses a large frequency range of absorption and a narrow emission (or luminescence) range. This property is by virtue of NOLs being able to capture photons and transmit them from the atoms surface to its nucleus in a non-radiative way.[1] In particular, this is achieved by “upgrading” the silicon atoms through the attachment of chromophores, and this is what enables the atom’s (as a whole) absorption of light to proceed according to the Forster mechanism:[1] we create a wider donor (of light) fragment (wider portion of the molecule that will be able to absorb a wide range of light frequencies) and a narrower acceptor fragment (the portion of the molecule that will be emitting the light, at a very narrow frequency range). Figure 4 shows the diagram of a NOL and Figure 5, the plot of the absorption and emission peaks of NOL16.

Different NOL types are formed by attaching a different donor fragment to the silicon atoms. In the same way that we can engineer the molecules so that they emit in a particular, narrow, light frequency range, we can also engineer NOLs that will absorb light at similar (or almost the same) frequency ranges and emit at considerably separated ranges. This property of being able to manipulate the absorption and emission spectra of the NOLs is ideal in the application for detectors that aim at “capturing” different events from say different particles. See Figure 6.

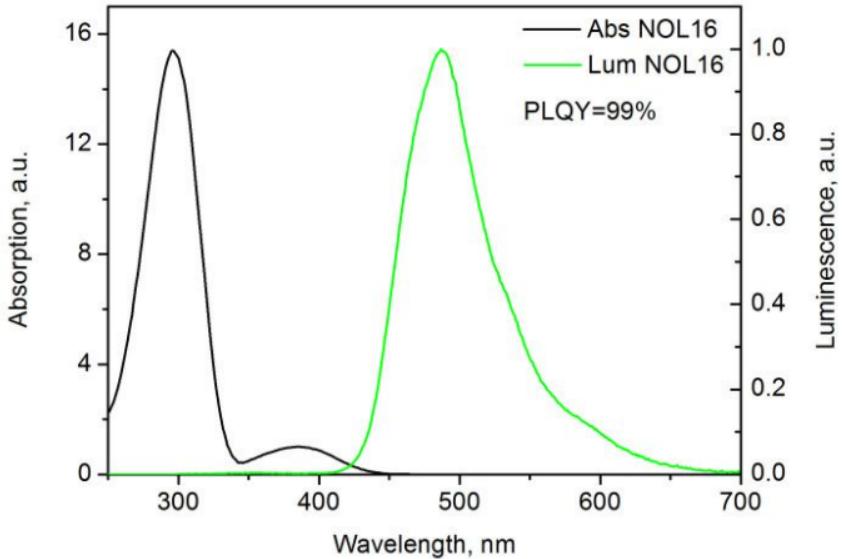


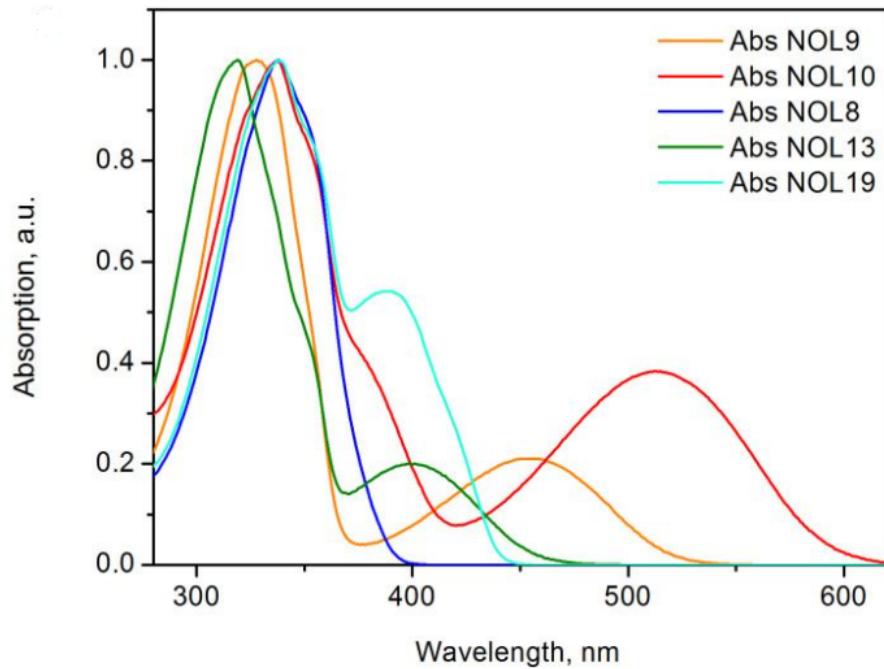
FIG. 5: absorption and emission spectra of NOL16. Taken from [1].

III. APPLICATIONS

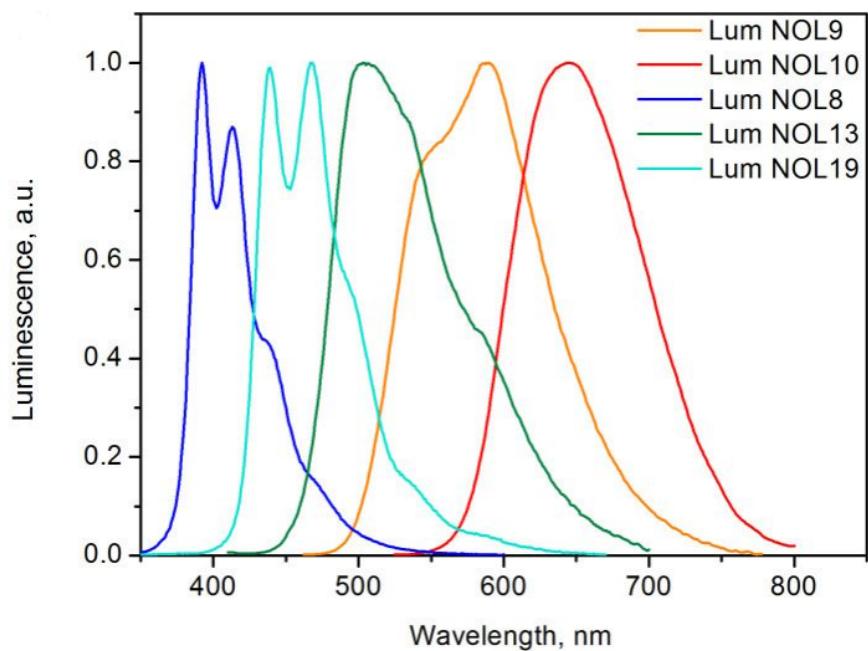
A. High energy physics

It is common in high energy physics to detect *ionizing* particles with the use of scintillating materials. In this case, light is not absorbed by the material, however. Instead, a highly ionizing particle interacts with the plastic molecules as it crosses the body of the material. This interaction process produces electronic excitation in the material, which quickly de-excites to produce light. The detection process itself is usually done with the use of photomultipliers (photomultiplier tubes or silicon photomultipliers, for example), which capture the light emitted from the de-excitation and translates it into a voltage signal.

The application of the wavelength shifters to high energy shifters becomes apparent then when we consider that photodetectors/multipliers are more sensitive at certain light frequencies.[1] We could then embed the scintillating material with wavelength shifting molecules (see Figure 7) that would absorb the light emitted within the scintillator from the interaction of the plastic with the ionizing particles, and then these wavelength shifting molecules would re-emit light at a frequency that maximizes the voltage translation in the photodetector. The main advantage of this is the (possible) reduction of noise in the apparatus, as one could have more freedom in manipulating thresholds to rule out real detections from noise. An easy setup to see how this test could be



(a)



(b)

FIG. 6: (a) absorption and (b) emission spectra for different NOLs. Taken from [1].

conducted is shown in Figure 8, where the scintillating material has fibers embedded into it, which are “connected” to photomultipliers with matching emission/detection frequencies, respectively. The photomultipliers are connected to a coincidence unit, which reduces dark noise arising from the voltage applied to the photomultiplier; it is very unlikely that all the photomultipliers produce a noise signal “simultaneously” in a very small time window, the time window being determined by how long a photon would take to travel a long the scintillator bar. Those signals that fall inside this time window will be then sent to the counter unit, which will indicate the detection of a particle. The plastic, at the same time, would be scanned with two scintillator paddles put in coincidence by themselves and also in coincidence with the photodetectors attached to the fibers; this is to reduce noise even further and to give us a direct way of determining the efficiency of the scintillator. The results of the efficiency of the bar (“real triggers of the coincidence unit”)/“noise plus real triggers of the coincidence unit”) when “dopped” with wavelength shifters would be compared with those results of the scintillator bar alone.

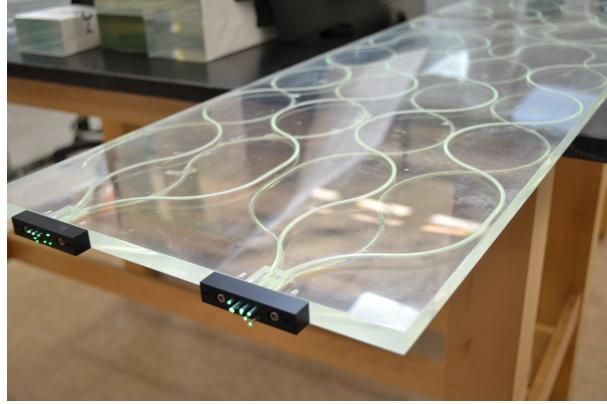
As an example [3] of a possible application to an actual experiment (existing apparatus) is the Sudbury Neutrino Observatory (SNO), responsible for the experimental confirmation of neutrino flavour-oscillation. Part of the SNO’s experiment that looked at the elastic scattering neutral-current reaction,

$$\nu_x + e^- \rightarrow \nu_x + e^-,$$

where ν_x is any flavour type neutrino and e^- is an electron. To observe this interaction, SNO used tanks filled with a mixture of pure heavy water and salt water. The detection of this reaction is through Cherenkov’s radiation.[7] Liquid wavelength shifters could be added to the tank; the light emitted by Cherenkov radiation would be absorbed by the spectral shifters and emitted by the same shifters at a frequency that matches the frequency of maximal capture by the photodetectors in the tank.

B. Application to photovoltaic devices

The efficiency of photovoltaic cells used to convert solar energy into electrical energy could be improved by including luminescent down-shifting (LDS) layers in the apparatus.[1] The incident high-frequency radiation can be down-shifted to lower frequencies at which the energy converter



(a)



(b)

FIG. 7: (a) scintillating plastic with wavelength shifting fibers embedded in it. (b) In this case, the fibers shift the absorbed light spectrum towards the green region. I found this plate with fibers in L2 in CCIS; I think it belongs to Dr. Hallin!

works. Figure 9 shows how the quantum efficiency of a device is improved using this method.

C. Everyday illumination devices

It seems [1, 5, 6, 10] that the transition from incandescent sources of light to LEDs has increased insomnia and retinal damage in the general population. The reason for this is because LEDs have high transmittance in the blue portion of the light spectrum (see Figure 10). Blue light has a lower threshold for retinal damage and negatively affects the production of melatonin, the hormone that causes sleepiness in humans. One could implement wavelength shifters to move the emission spectrum towards redder hues, more specifically, wavelength shifters could peak in the green region

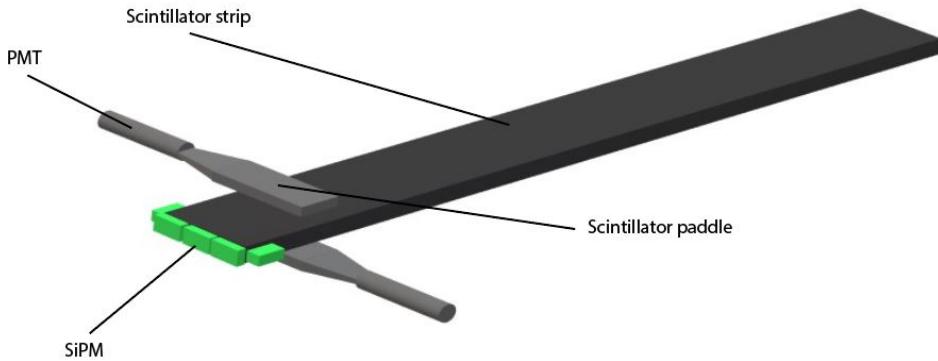


FIG. 8: test setup. In on run of the test, the scintillator strip has wavelength shifting fibers embedded in it; in another run, the scintillator would not me dopped with fibers. The strip is scanned with scintillating paddles to determine the efficiency of the scintillator. PMT is for “photomultiplier tube” and SiPM is for “silicon photomultiplier”. Taken (and for more information) see [9].

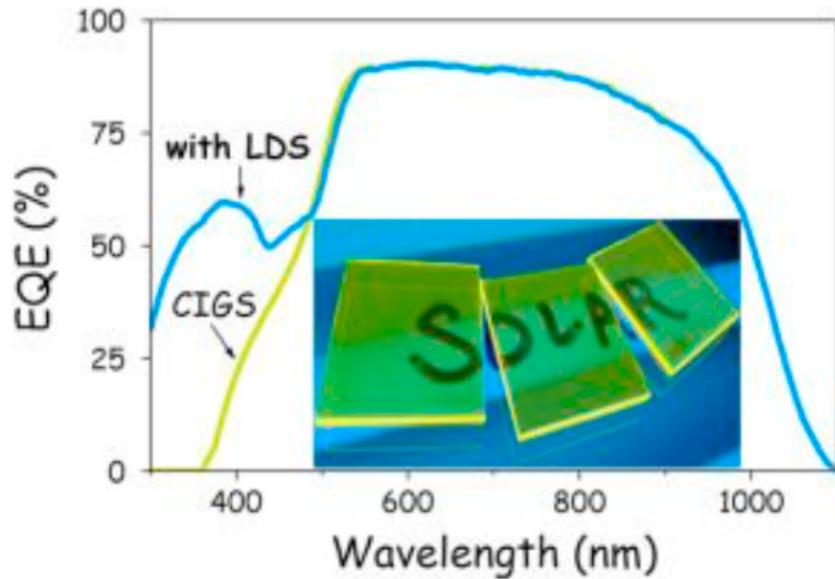


FIG. 9: polymeric films used for the modification of copper-indium-gallium-(di)selenide (CIGS) solar cells that show low efficiency in the UV spectrum. The additive of NOL15 with quantum yield 80% to 92% down-shifted wavelengths in the range 300-400 nm to 500-700 nm. The external quantum efficiency of the device at 360 nm was increased from 1% to 55%. Taken from [1].

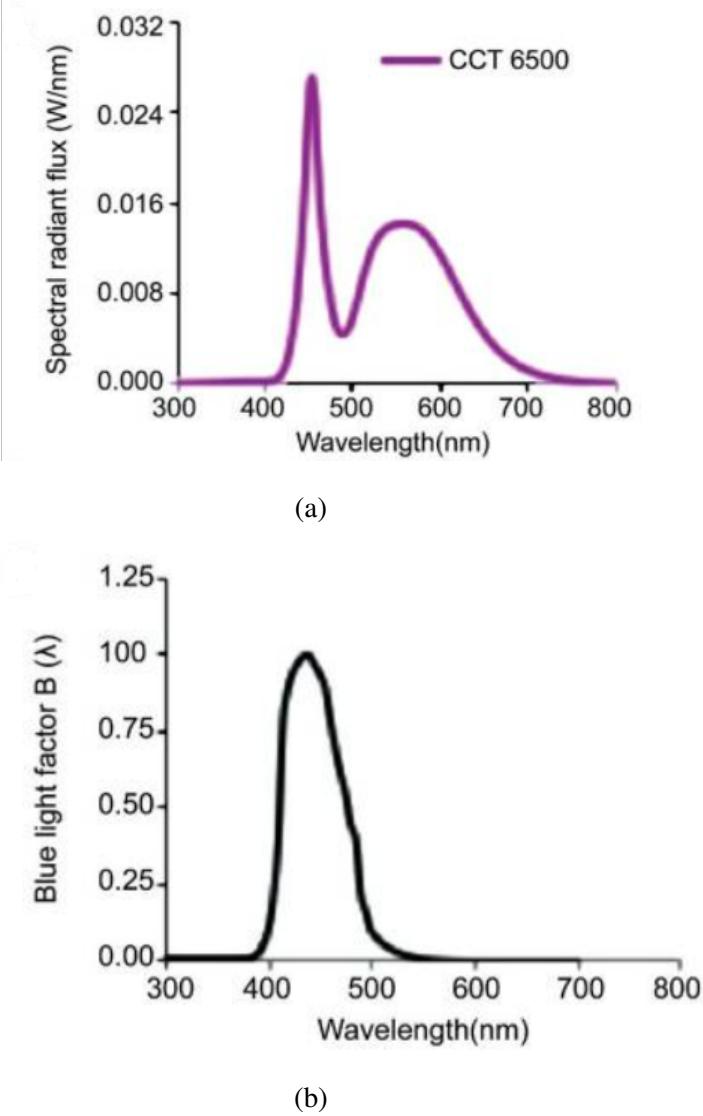


FIG. 10: (a) yellow phospor covered white LED to exhibit color temperature (CCT) at 6500 K. The first peak shows blue content; the second peak shows yellow content. (b) Blue light factor $B(\lambda)$ distribution. Taken from [10].

of the visible spectrum, rather than the blue region, as the human eye evolved to see better in the green area of the spectrum [8]. Since the absorbed photons can only be re-emitted at longer wavelengths, this makes the wavelength shifters ideal for this application.

IV. CONCLUSION

Wavelength shifting molecules are a versatile technology with a range of applications in experimental physics and engineering, specially in renewable sources of energy and information transmission for the latter. The availability of spectral shifters in the form of fibers and liquid makes them ideal for applications that require the manipulation of light (and energy) in devices with complicated geometries.

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