CXS Project on Carotenoids with Ultrafast Spectroscopy

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You are to write a media article or a presentation to parliament about the work of the physics and laser laboratories at Swinburne, to explain how the study of light responsive molecules can be beneficial and important to understanding the process of photosynthesis. Furthermore the document should include how understanding the nature of the interactions between light and matter can help in developing future energy solutions.

Introduction

Research is being undertaken at Swinburne University, into photosynthesis and its properties. To do this they require a detailed understanding of how photosynthesis works, in particular how light energy is absorbed, transferred and converted into chemical energy. Physicists are using state of the art laser facilities in conjunction with the knowledge biologists have of photosynthesis to further understand the relaxation mechanisms within light harvesting molecules called carotenoids. With this we will have a deeper understanding of the photosynthetic process and may be able to harness these properties to manufacture efficient green energy resources.

Carotenoids
Photosynthesis is a process that occurs in plants, algae and photosynthetic bacteria. It is where sunlight provides the energy for carbon dioxide and water to react and produce glucose and oxygen.

It is displayed as: \[ 6\text{CO}_2 + 6\text{H}_2\text{O} \xrightarrow{\text{Sunlight}} \text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2 \]

Carotenoids play a vital role in the photosynthetic process as they are able to capture the sun’s energy. The first publication of carotenoid discovery was in 1914. Since the 1980’s we have been developing technology which has allowed us to observe the individual energy states within carotenoids. Even now the technology is being refined to improve the clarity of results.

Carotenoids are long molecules comprised of carbon, hydrogen and sometimes oxygen, and are connected to chlorophyll (which is another significant component of photosynthesis) by proteins. Carotenoids are crucial to the process of photosynthesis where with nearly 100% efficiency, they can transport captured light energy to the chlorophyll.
The optical properties of carotenoids are due to alternating single and double bonds between carbon atoms; this is called conjugation. This formation of double bonds lets electrons move freely along the whole conjugation length. This freedom of the electrons is due to the delocalised electrons. Variety in structure can alter its properties.

Carotenoids are able to absorb a wide range of wavelengths.

Carotenoids have the ability to absorb light over a broad spectrum, which usually extends beyond the range of chlorophyll. This light absorption gives carotenoids their colour pigment properties.
As the light effects the electrons, in the carotenoid, the electrons receive energy and are excited. This excitation elevates the electron from their ‘ground energy state’ (called 1Ag) to the 1Bu⁺ state which is an excited state. From here the energy is transferred on to the chlorophyll.

Because the energy levels for the states vary according to sample preparation, mapping the energy levels becomes difficult. Before the relaxation mechanism can be studied, the energy gap between the states for the carotenoid must be defined. A specific carotenoid being used in research is Lycopene, its results display a relaxation mechanism.

Through further experiments a possible relaxation mechanism has been proposed. From the excited 1Bu⁺ state the electrons relax into the 1Bu⁻ state. These two states have very short lifetimes, of about 50-300 femtoseconds. The next state in the relaxation mechanism is the 2Ag⁻ state, which lasts much longer: around 4.1 picoseconds. The exact relaxation pathway is not fully understood. This is why more experiments need to be conducted.
From the results that have been found there is a relaxation mechanism, which is where the energy is transferred to the chlorophyll. A better grasp on the relaxation mechanism will make the rest of the process easier to uncover.

In an attempt to mirror the efficiency of nature, scientists are observing the process of photosynthesis. Developments in this area will pave the way for an efficient, eco-friendly energy source, such as solar panels. Further knowledge in this area may also shed light on new advancements in medical technology. For example, it is known that carotenoids contain anti-oxidants, which also fight cancer- and heart disease-causing free-radicals.
Lasers

Lasers are a vital part of the experiments. But what are lasers?

A laser is a directional light that emits light of a specifically chosen wavelength. These tools are incredibly intricate, and allow optical experiments to be carried out in a very precise manner.

Lasers solve these problems because they only emit one wavelength of light. This allows experiments to be tailored to transitions of interests.

There are several different types of lasers, including solid state, gas, liquid and diode lasers. SOLL labs make use of most of these types of lasers, although they all have subtle differences. All these lasers work in essentially the same way. Lasers work by “pumping” a medium of gas, solid, or liquid to force the medium to emit photons, which make up light. These are then trapped between two mirrors in a cavity. The mirrors reflect the light back and forth, through the lasing medium. Eventually the light becomes more concentrated, and is all going in the same direction. One of the mirrors is deliberately slightly transparent, so light can escape through the mirror, and come out of the cavity as laser light. This is explained in the pictures below.
The laser in the ultrafast spectroscopy differs somewhat form a continuous wave (CW) laser. A CW laser emits a constant stream of light at a constant intensity. Ultrafast spectroscopy uses a special technique that requires them to use a pulsed laser.

A small amount of time in this perspective is called a femtosecond. A femtosecond is the equivalent of $10^{-15}$ seconds. To illustrate how small this amount of time is, in one second, light can travel from Earth to the moon. In 100 femtoseconds, light will only travel the breadth of a human hair. This incredibly short pulse of light is created using several systems.

The pulsed laser is sent through a system called a regenerative amplifier. This amplifier overcomes yet more problems posed by the incredibly short pulse of light. A pulse as short as 100 femtoseconds is also very intense, and a pulse of this
length will destroy the laser crystal used to amplify it. To solve this problem, the pulse is first stretched, amplified, and finally compressed. This allows them to reach impressively high peak powers, in the region of $10^{10}$ watts; in an area the size of a match head. This is equivalent to just over 13 million times the output of a standard light globe. This is also immense power when compared to the 5600 W/h of energy per square meter per day that originates from the sun.

All the steps in this process take less than the time it takes to blink an eye. This special system allows the scientists to see things that they weren’t able to see using slower systems. Even this system could go through improvements, though. The shorter the pulse they are able to use, the better time resolution they can achieve.
Ultrafast Spectroscopy

Swinburne University utilise an Ultra-fast laser system in its 2-colour 3-pulse experiments. They are employing this experiment method to determine how Carotenoids work. The laser system is actually quite complex. The process of pumping a laser involves a smaller laser sending light into a larger laser. The light is absorbed and then awaits stimulated emission. Light is then amplified within the laser cavity. One of the mirrors will release a percentage of the photons, resulting in a laser beam.

The Millennia is the first stage of the ultrafast laser system. It is pumped by a diode laser. The Millennia emits a continuous green beam into the tsunami (the next laser) in order to pump it. The tsunami has a titanium sapphire crystal (Ti:Sapphire) inside it which is used to generate a laser beam. The Tsunami gets pumped by the millennia laser, resulting in the emission of a pulse beam of 7.2nJ at
800nm and it is 80fs in duration. The Tsunami runs at a frequency of 82MHz, therefore releasing 82 million pulses a second!

Furthermore, the pulse is then directed to the stretcher and compressor. Here, the pulse is stretched in time so that the intensity of the pulse is lowered. Stretching the pulse out in turn brings down the intensity. If this step was omitted the Ti:Sapphire crystal in the regenerative amplifier (Spitfire) would be damaged.

Once the pulse has been stretched in time by the stretcher and compressor, it is directed to the spitfire. The spitfire is pumped by a nano-second pulse laser (Evolution).

The spitfire amplifies the pulse, and the pulse moves to the compressor side of the stretcher and compressor. The pulse is then compressed to 100fs in duration which makes the pulse a lot shorter. The pulse has now finished the power up stage and has 1mJ of energy compared to the original 7.2nJ. Additionally, it runs at a frequency of 1 kHz compared to the original 82 MHz.

Following this, the pulse is split in two and enters into optical parametric amplifier (OPA) 1 and 2.

The output wavelength (colour) is adjusted within the two OPAs, exploiting non-linear processes to achieve this result.

The pulse travels through a crystal resulting in two things; a horizontally polarised signal pulse with a wavelength range of 1.1-1.6\_m, and a vertically polarised idler pulse with a wavelength range of 1.6-2.93\_m. The wavelengths of the idler and signal pulses are tuned by changing the angle of the crystal.
The two pulses are then sent to another crystal where one of them is mixed with some 800nm residual to make pulses with a wavelength range of 460-630nm.

After this the pulses then travels out of the OPA and into the experiment.
The Experiments

OPA’s have the ability to tune the laser over a wide variety of wavelengths. Changing wavelengths changes the colour of the laser pulses used in the experiment. In one colour experiments the light produced by both OPA’s are the same wavelength. In two colour experiments the OPA’s are tuned to different wavelengths.

In the experiments, we can see from figure 3.3 a pulsed laser beam originate from each OPA, which may have the same or different wavelengths. One of these pulses is split into two using a beam splitter. The beam splitter in this experiment lets 50% of the pulse through and directs the other 50% in the direction chosen. This effectively creates three pulses. Pulse 1($K_1$) and pulse 3 ($K_3$) go through a delay stage. The delay stage consists of carefully placed mirrors which can be moved back and forth to change the relative path length to be longer or shorter. Pulse 2 is not delayed. Using a series of mirrors, the three pulses are directed into a lens which focuses the three pulses so that they spatially overlap in the sample. By stepping the delay stages, it allows a scan to be taken of the sample through time.

![Figure 7](image-url)
Due to laser pulse overlap in the sample, a 3rd order polarisation occurs, resulting in the extra emission of light at different angles to the excitation beam. Three of these beams are of interest and are called $K_4$, $K_5$ and $K_6$. These three extra emissions are spread in space away from the incident laser pulses. This allows the result to isolate and therefore measured in the spectrometer free from any background signals. The spectrometer spectrally divides the light and passes the information onto a computer for further analysis and storage.

From what’s collected in the spectrometer the results can be analysed and the results for a one colour experiment show us that one colour stimulates one state. The one colour graph shows us that the lifetime of the excited state last for quite a long time. The results for the two colour experiment show two states are being excited. The graph shows us how long in time the excited states are affecting each other.
The Future

With the aid of lasers, carotenoids and a dedicated team of researchers, scientists are becoming closer to unlocking the secrets of photosynthesis. Even so, we have much to learn.

At this moment in time, most experiments use a selection of carotenoid molecules suspended in hexane, a substance comprised of carbon and hydrogen. To complete only experiments using hexane would leave the results subject to error. In order to isolate the carotenoid, using different solutions throughout multiple experiments allows the effect of the solution to be disregarded, and solely the carotenoid studied. Solutions with different polarity and studies of different types of carotenoids will provide this diversity.

Aims at the moment revolve around locating the states which couple between the carotenoid and the chlorophyll. Coupling states are those which correspond to one another, which are the key to energy transfer. Another major goal is to observe the carotenoid in the light-harvesting complex as a whole. This will allow a fuller understanding of how the carotenoid’s positioning affects its functionality.

Explaining the relaxation mechanism (the gain and distribution of energy through electrons) is a long-term goal: knowledge of this will lead to greater understanding of the whole of photosynthesis.

By studying carotenoids, we will further our knowledge of both carotenoids and photosynthesis in general. This is the main incentive, as with it will come new possibilities and solutions. Already proposed benefits of studying this area include a more efficient solar energy source – perhaps even one to rival natural
photosynthesis – and medical advantages. Carotenoids, which contain antioxidants, may one day be used as a way to prevent and combat cancer and heart disease. Though the task is great, with time and adequate equipment, incredible things can come from this study.
Media Article

OUR BRIEF

You are to write a media article or a presentation to parliament about the work of the physics and laser laboratories at Swinburne, to explain how the study of light responsive molecules can be beneficial and important to understanding the process of photosynthesis. Furthermore the document should include how understanding the nature of the interactions between light and matter can help in developing future energy solutions.

A team of Coherent X-ray science (CXS) researchers and PhD students at Swinburne University aim to further understand how light energy is transferred from carotenoids to the chlorophyll as chemical energy.

Photosynthesis is a complex process which plants, algae and photosynthetic bacteria use to produce a chemical energy source. This procedure involves absorbing the sun's light and transferring this light to chemical energy to produce glucose. Carotenoids play a fundamental part in photosynthesis. These natural, fat-soluble pigments harness the sun's light and transfer the energy onto the chlorophylls. Carotenoids consist of long molecules comprised of carbon, hydrogen and sometimes oxygen.

Part of the carotenoids structure is made of alternating single, double bonds between carbon atoms; this is called conjugation. Because of this conjugation, the carotenoid has valuable optical properties. The conjugation length depends on the type of carotenoid. The formation of the carotenoids double bonds allows electrons to move freely along the whole conjugation length. By the delocalisation these electrons they can then carry and transfer energy. The energy can be transferred from the carotenoid to the chlorophyll.

Scientists have a strong understanding of photosynthesis, but there are still some steps in the process that aren’t fully explored. We know the basics; Sunlight provides energy for Carbon dioxide and water to react and produce glucose and oxygen. But exactly how light is transferred to the chlorophyll as chemical energy from after being captured in the carotenoid is still not well understood. Through experiments a possible relaxation mechanism has been proposed, results have
located certain energy levels, but more time is needed to prove these accurate. Somewhere during the relaxation mechanism after receiving light and being excited, the carotenoid transfers this energy over to the chlorophyll for the next step in photosynthesis. At what point and energy level this occurs at needs more research. Once this mechanism can be mapped out there will be more understanding of this process.

Lasers are a fundamental part of this kind of research. Lasers work by a process known as “stimulated emission”. This usually takes place within a gas or a solid, which is located within an optical cavity. Laser light then exits the cavity out through a semi silvered mirror at one end. The lasers can emit monochromatic light, at chosen wavelengths. The wavelengths dictate what form of light comes out. Short wavelengths create high energy, Ultra Violet light; whereas longer wavelength, lower energy light comes in the form of microwaves and radio.

The ultrafast spectroscopy laser system is complex system made up of several laser stages. From the final stage of the system (the two OPA’s) the output beam is pulsed and has a variable wave length to allow two color experiments.

From the OPA’s, one of the pulses is split resulting in three pulses for this experiment. Two of these pulses go through a delay stage which changes the time each pulse reaches the sample, these pulses are pulse 1 and pulse3, pulse 2 is not delayed. The time pulse 2 reaches the sample is called zero time. This is zero time so that the other two pulses can be compared to this time. In the sample, the pulses are overlapped in space. Using the delay stages, the pulses can also be overlapped in time. These three extra emissions are due to what is called a third order polarisation. These extra pulses are analysed by a spectrometer and are used to examine various properties of the sample including life time of the state and the lifetime of the coherence of two states.

This research is a current work-in-progress: there are many obstacles yet to overcome, and many disputes arising over new ideas and previously accepted known. To ensure that correct conclusions are drawn from information, experiments must be carefully scrutinized. As data may be inaccurate or corrupt in one instance, repeats of experiments are crucial. This study is taking place worldwide, so findings are cross-checked with those from other universities, groups
within varying countries around the world. One of the experiments at the moment is using varying solvents (the liquid in which the carotenoid molecules are suspended) are underway: this ensures that results are accurate. The Swinburne researchers hope to locate the states which couple (or correspond) to those in the chlorophyll, as well as to observe carotenoids in relation to the entire light-harvesting complex – where it sits and how this affects its efficiency. These studies will primarily provide better understanding, which will shed light on new possibilities, but will perhaps provide the means by which we may create efficient, clean energy.

This article was written by Year 10 students of Padua College: Holly Whitfield, Juliette Milili, Mitch Chasemore, Andrew Taylor, Lachlan Theobold and Christy Dimitrakas, along with Alisdair McDougal from Scotland, with the assistance of the ultrafast spectroscopy group at Swinburne University as part of an Akorn Educational Services Science Students@Work Program.
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Figure 1
<http://ellerbruch.nmu.edu/classes/cs255w52/c5255/students/teabbott/p4/pics/photosynthesis.jpg>

Figure 2
<Femtosecond nonlinear coherent spectroscopy of carotenoids.
By My Thi Tra Do>

Figure 3
<plantphys.info/plantphysiology/lightrxn.shtml>

Figure 4
<With thanks to Koyama et. al>

Figure 5
<With thanks to Lachlan Theobold>

Figure 6
<Femtosecond nonlinear coherent spectroscopy of carotenoids.
By My Thi Tra Do>

Figure 7
<Femtosecond nonlinear coherent spectroscopy of carotenoids.
By My Thi Tra Do>

Figure 8
<With thanks to Evelyn Cannon>
CXS Project on Carotenoids with Ultrafast Spectroscopy

Padua College Pupils
- Lachlan
- Andrew
- Christy
- Holly
- Mitch
- Juliette

Intro

Photosynthesis
- The very existence of human life on this planet relies on this process.
- Plants, algae, and photosynthetic bacteria use this process.
- Harnesses the sun’s light and transfers it into a chemical energy source.
- \( \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{CH}_2\text{O} + \text{O}_2 \)
- Carbon dioxide and water with the aid of sunlight produce glucose and oxygen.

Carotenoids
- Living things get their colour through different absorption and reflection of light.
- From natural pigments.
- Important biological function.
- Most important natural pigments that have carotenoids.
- Natural fat-soluble pigments found mostly in plants, algae, and photosynthetic bacteria.

Swinburne Applied Sciences Building
Physics and Laser Laboratories

Padua SS@W at CXS-Swinburne University
CXS Project on Carotenoids with Ultrafast Spectroscopy

The milliamper is the smallest law on the device.

The pulse is then compressed in time. The pulse is then amplified by the amplifier.

The pulse is then counteract by the glass mirror and coherent mirror (GMA).

The pulse then passes through a segmented interferometer (SPI).

The pulse then travels the CPM and insert into the instrument.

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CXS Project on Carotenoids with Ultrafast Spectroscopy

- Long molecules comprised of carbon, hydrogen and oxygen groups.
- Carotenoids have optical properties.
- The conjugation length depends on the type of carotenoid.
- Formation of these allow electrons to move freely along conjugation lengths.
- Delocalisation of electrons
- Can then carry and transfer energy.

- Electrons are excited by sunlight.
- They elevate from a ground state (1→2) to an excited state (1→3).
- Electrons undergo a relaxation mechanism through other states (1→4 and 2→3).
- Energy is transferred to chlorophyll as chemical energy.

Lasers

- Pump
- Chopped
- Laser
- Photons
- Cycle of Decay

The Electromagnetic Spectrum

- The electromagnetic spectrum is a range of wavelengths.
- Different regions of the spectrum correspond to different types of electromagnetic radiation.

The Ultrafast Laser System

- These lasers are ultrafast spectroscopy lasers.
- They use it in an experiment to study the dynamics of a purely optical system.

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CXS Project on Carotenoids with Ultrafast Spectroscopy

- One colour
- Looking at one state
- Shows lifetime of state
- Two colour
- Looking at two states
- Shows coherence between two states

The Future of Ultrafast Spectroscopy
- This is all new research; it is constantly being developed, questioned and checked.

Current Objectives include:
- Testing a range of carotenoids
- Testing with varying solvents
  - Different polarity
- Locating coupling states
- Observing the carotenoid within the light-harvesting complex
  - How position affects function
- Explaining the relaxation mechanism

Benefits of this study include:
- More efficient solar energy
- Medical advantages
  - May help fight cancer and heart disease
- Greater knowledge
  - New possibilities and solutions

Thank you for coming

Padua SS@W at CXS-Swinburne University