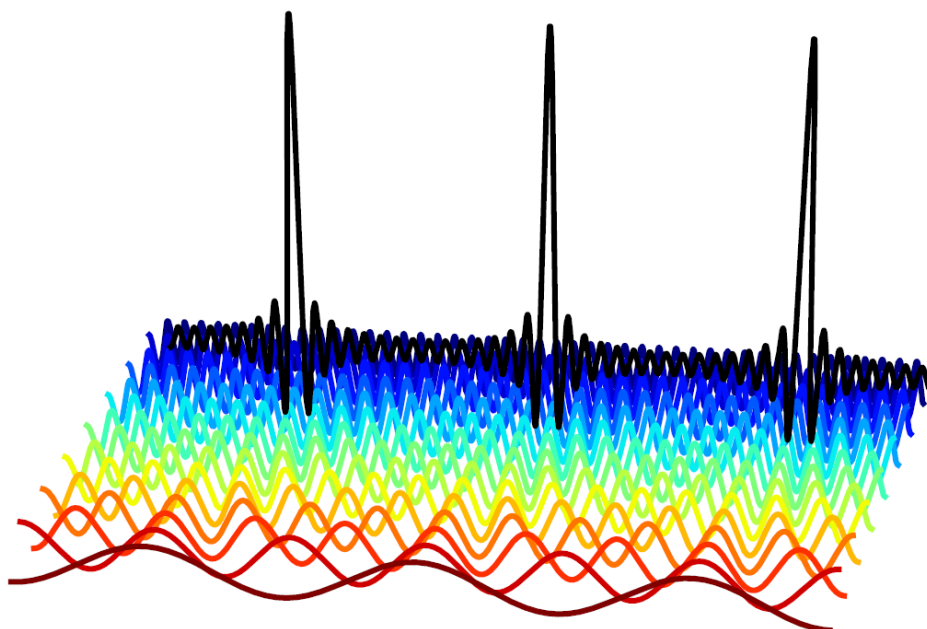


Ultrafast Optics: For Chemists

v1.1

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Preface

This document grew whilst I was preparing to give a short talk to my group about the basic principles of ultrafast optics/lasers that I think are relevant for chemists using 'turn-key' systems. The project rather ran away with me and I ended up producing this as a supplement to the slides, I hope it can be useful as a reference for future students. The idea is to present the key information about ultrafast optics that I wish I had known before embarking on a PhD in a much more physics-based group. Emphasis throughout is placed on qualitative, intuitive, understanding rather than dense mathematics. Hopefully it will allow students to not see lasers as a mysterious 'black box' but rather begin to appreciate the underlying physics.

All figures and herein were made by me, except where explicitly stated in the caption. As source material, I can recommend Hooker and Webb '*Laser Physics*', or Milonni and Eberly '*Laser Physics*'. Physicists are notoriously adventurous with their textbook naming. Another extremely useful resource is the Light Conversion optical toolbox: toolbox.lightcon.com.

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Preamble: Common Terms

- **Photon energy:** I will generally use angular frequency ω to express photon energy ($E = \hbar\omega$), but at times will switch to wavelength λ . Being comfortable converting between these units is essential!
- **Pulse duration:** Generally defined as either the FWHM or $1/e^2$ width of the Gaussian pulse envelope.
- **Bandwidth:** The range of frequencies present in a pulse, with units of frequency or wavelength. Generally is given as a FWHM but the definition can vary.
- **Chirp:** The time-dependent frequency of a pulse. If the frequency does not change during the pulse, it has zero chirp (is 'unchirped'). If red frequencies come first, then it has positive chirp (is 'upchirped'), otherwise it has negative chirp (is 'downchirped').
- **Dispersion:** The spreading out of frequency components in time as a pulse propagates.
- **Propagation direction:** The direction of travel of a laser beam, this is normally the same as the direction of energy flow (the Poynting vector).
- **Polarisation direction:** The direction of the oscillations of the electric field of the laser beam. The polarisation plane is orthogonal to the propagation direction. Light could be linearly, circularly, or elliptically polarised within this plane.
- **Beam waist:** Generally defined as the radius from the centre of the beam at which the intensity is reduced to a factor of $1/e^2$ of the peak intensity.
- **Repetition rate:** How many pulses per second the laser produces.
- **Pulse energy:** The total energy contained within each pulse (number of photons in the pulse \times photon energy).
- **Average Power:** What you measure on a power meter - the pulse energy \times repetition rate.
- **Fluence:** energy per unit area of a given laser pulse - requires that you know the beam waist.
- **Intensity:** power per unit area of a given laser pulse - this requires that you know the beam waist and pulse duration.

Chapter 1

Lasers

'LASER' is an acronym, standing for **L**ight **A**mplified **S**timulated **E**mission of **R**adiation. They are one of, if not the, most widely used experimental tool across a lot of physical chemistry/chemical physics. Fundamentally, a laser is a device which produces highly directional¹ EM radiation. This radiation can have a very well defined energy (with a narrow *bandwidth*, termed '**narrowband** radiation') - which is useful for many kinds of resonant spectroscopy. Alternatively, it can exist as very fast pulses of energy, which necessarily have a poorly-defined energy (a broad bandwidth, or '**broadband** radiation') - useful for time-resolved spectroscopy of ultrafast processes.

¹We say the light has high *Spatial Coherence*.

1.1 Why Lasers?

The utility of lasers for chemists lies in the aforementioned directionality, and in the relative ease with which a wide variety of different wavelengths of EM radiation can be produced. Radiation that is resonant with a wide range of different molecular energy level spacings can be produced, and as such lasers have become the standard weapon in the armoury of the spectroscopist. The high directionality means that almost all of the produced photons can be efficiently directed onto the sample of interest - so there are not a large number of 'wasted' photons which there are if a sample is irradiated using (for example) a discharge lamp.

Lasers are not fixed to run (or 'lase') at a single frequency, but can be very tunable to allow a wide range of molecular resonances to be interrogated using a single laser system. Acquiring a laser system that will run at your desired frequency is (mostly) a matter of finances - although producing high intensity coherent X-rays is difficult in a normal 'tabletop' lab.

1.2 Laser Action

Here we will discuss some of the basic principles of laser action - how lasers work. As the acronym suggests, lasers work via stimulated emission of radiation. Figure 1.1 shows a basic schematic of how a laser functions²

²This is strictly a schematic of 'four-level laser', but this is fine for our purposes. Titanium Sapphire lasers operate in this way, which is what we will largely be concerned with.

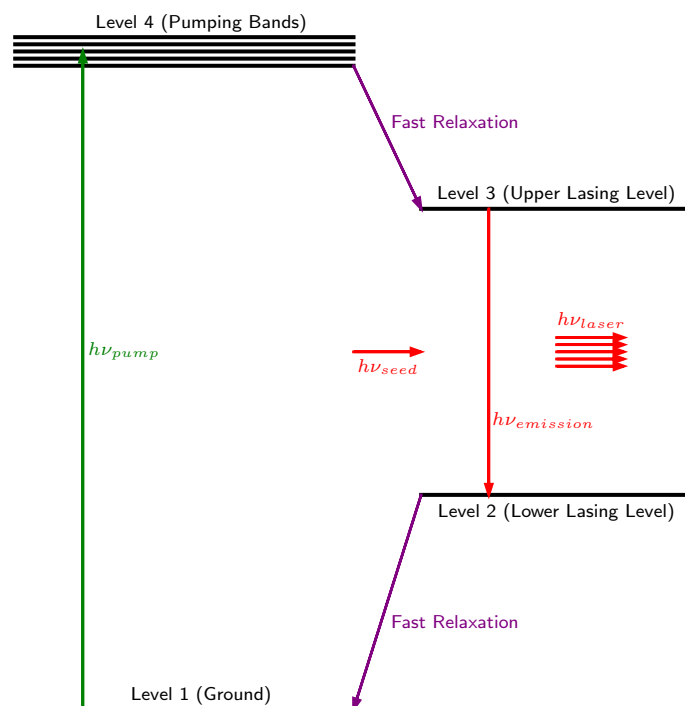


Figure 1.1: A schematic of basic laser action. Lasing is achieved between levels 2 and 3, via excitation from level 1 to level 4.

There are four distinct energy levels in this system. A ground level (1), which is pumped³ into level 4, often via optical pumping with photons of energy $h\nu_{\text{pump}}$ - provided by a flashlamp or another laser (known as a **pump laser**). Level 4 is shown as a broad band of levels, rather than a single level, as this is often the case such that precise frequency matching of the pumping radiation to a specific upper level is not necessary, and allows the use of broadband pump sources.

There is then rapid population transfer from the pumped level(s) 4, into the upper lasing level, level 3. Lasing will occur on the $3 \rightarrow 2$ transition, so a **population inversion** needs to exist between levels 2 and 3. The idea of a population inversion may be familiar from undergraduate courses, and is the situation where there is more population in the upper level (3) than the lower level (2) - non-

³'Pumped' is laser terminology for 'excited'. I suppose it is largely a matter of semantics, but I find 'excited' doesn't give enough of a feel for the wholesale uprooting of ground state population into an upper state that 'pumped' does.

Boltzmann behaviour. This requires that the population of level 3 is kept high, while the population of level 2 is kept low. Stimulated emission from level 3 into level 2 produces the laser radiation. This emission is either stimulated using a **seed laser** with photon energy $h\nu_{seed}$ as shown, or relies on spontaneous emission from level 3 to induce the stimulated emission.

Finally, there is another rapid population transfer from level 2 back to the ground state. This has the effect of ensuring that the population of the lower lasing level remains low, such that a large population inversion can be maintained for efficient lasing.

Clearly, there must be some medium in which all these levels exist, and this is known as the **gain medium** or **laser medium**. It is the spacing between levels 2 and 3 in the medium that determines the wavelength of the laser radiation. There are a huge number of different possible laser media, in the gas, solution, and solid phase. Here we will limit our discussion to solid-state laser media, as these are most common in ultrafast optics. Different laser media have different emission energies (the gap between levels 2 and 3), and different pump energies (the gap between levels 1 and 4). These are tabulated below for some solid-state laser media and common lasing schemes⁴: Titanium-doped Sapphire; Neodymium-doped Yttrium Aluminium Garnet (YAG); and Neodymium-doped Yttrium Lithium Fluoride (YLF).

⁴Many laser media could be pumped to lase at a variety of different wavelengths. For example, Nd:YAG can be pumped to lase at 1440 nm as well.

Laser Medium	Pump Energy (nm)	Emission Energy (nm)
Ti:Sa	400-600	650-1100
Nd:YAG	730-820	1064
Nd:YLF	730-820	1053

Note that the emission energy need not be a single well defined energy, as levels 2 and 3 could just as easily be broader bands that lead to a broader lasing bandwidth - this is indeed necessary for ultrafast laser pulse generation. The pump and emission energies shown are merely selected for illustrative reasons. Titanium Sapphire has the broadest emission bandwidth of any solid-state laser medium, making it exceptional for production of ultrashort pulses. It is often pumped at around 527 nm to produce emission between 770 nm and 830 nm. Nd:YAG and Nd:YLF are commonly used laser media, with Nd:YLF often being used as a pump laser for Ti:Sa - as frequency doubling the 1053 nm output leads to the 527 nm output previously mentioned.

1.3 Oscillators and Amplifiers

The laser media mentioned in the previous section can be set up in such a way as to function either as laser **oscillators** or as laser **amplifiers**. A detailed discussion

of this is beyond the scope of this document, but it is important to know the qualitative difference.

As laser **amplifier** is a part of a laser which **amplifies** an existing laser beam up to a desired power level. There are a multitude of different geometries of laser amplifier, and we will not discuss in any real detail - save for a description of *regenerative amplification* and *parametric amplification* later on. In all the cases we will discuss in the context of ultrafast optics, an amplifier requires a laser medium, a pump laser⁵, and a weaker seed laser. Energy is dumped into the laser medium by the pump laser, and is then 'picked up' by the seed laser. The effect is that the energy of the pump beam is reduced, whereas the energy of the seed beam is increased.

⁵Some amplifiers can use a flashlamp as a pump radiation source, especially for Nd:YAG lasers.

A laser **oscillator**, then is a part of a laser which *generates the initial, weak, laser pulses*. In a simple case, taking a laser amplifier and applying feedback to it (i.e. returning some of the amplified output to the input of the amplifier) will cause to to **oscillate** at the frequency of the radiation that is fed back. This is practically achieved by building an **optical cavity** around the laser medium, so the laser beam resonates around the cavity passing through the gain medium on each round trip. This is commonly used as a technique to produce low energy pulses that are amplified in subsequent amplifier stages. This weak laser beam may pass through several stages of amplification before it is used for the desired application.

If you are familiar with audio/radio electronics, then this terminology will be familiar to you - think of an oscillator as a guitar string attached to a pickup. This produces a low energy signal which is not powerful enough to drive a loudspeaker. It is then sent through several amplification stages (preamps and power amps) such that the signal level is high enough to efficiently drive a loudspeaker - this is exactly analogous to what we are doing with lasers.

Chapter 2

Laser Light

Having briefly discussed how lasers work, now we turn our attention to the nature of the light that is produced in a laser.

2.1 Pulsed or cw?

Looking back at the diagram in Figure 1.1, we can consider two possibilities. One is that the pump radiation is kept on continuously - this will lead to a continuous laser output, or a **cw-laser**. This means that the laser is (ideally) producing light of a single, well defined frequency - such that the laser output would look like a perfect sine wave.

Alternatively, the pump radiation could be fired in short bursts - this will lead to a laser output that is also in short bursts, and this is called a **pulsed laser**. Many lasers are capable of operating in either pulsed or cw mode, but all ultrafast lasers are pulsed lasers by definition. We will only be discussing pulsed lasers from now on.

2.2 Pulsed Lasers and Time-Bandwidth Products

It is now useful to remind ourselves of the general time-energy uncertainty relation, a recasting of the familiar position-momentum uncertainty relation:

$$\Delta E \Delta t \geq \frac{\hbar}{2} \quad (2.1)$$

This relation tells us that a state that has a very well defined energy (small ΔE) must exist for a very long time (large Δt), and vice versa. This has profound implications for our pulsed laser, as if the laser output is **pulsed**, then by definition it exists for a finite length of time - so Δt is small. This means that for a pulsed laser, ΔE is large - so there is uncertainty in the wavelength of the pulse. **The thing you learnt at school about lasers being monochromatic is a lie!**

Equation 2.1 is true in a general sense, but we need to be a bit more precise about how exactly we define ΔE and Δt for our laser pulses. These depend on the shape that our pulse has, and generally ultrashort laser pulses from Ti:Sa lasers are pretty well described as **Gaussian pulses** - with a Gaussian profile¹ in the time domain. We can then identify the width of our Gaussian pulse in the time domain as $\Delta\tau$ - this is defined as the full-width-at-half-maximum (FWHM) of temporal pulse shape, as illustrated in Figure 2.1 as the blue curve.

¹Different types of laser oscillators produce different pulse shapes. Another common pulse shape is the sech^2 pulse shape.

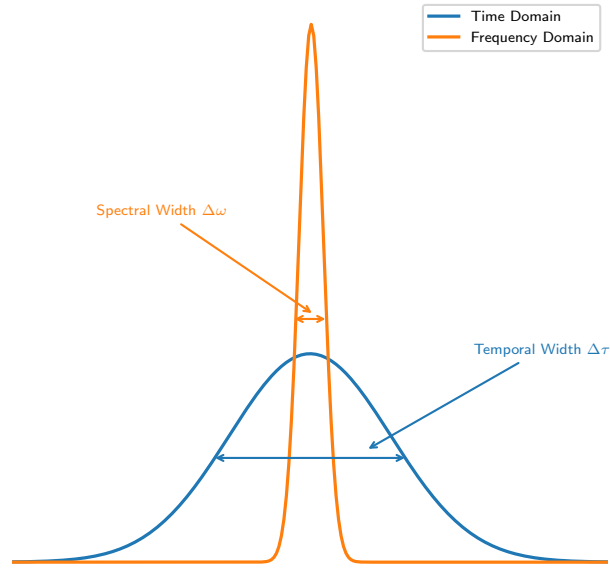


Figure 2.1: A typical Gaussian shaped laser pulse represented in both the time domain (blue) and frequency domain (orange). The frequency domain profile is obtained via Fourier transform of the temporal profile. The definitions of the temporal and spectral width are annotated.

To find the width in the frequency (energy) domain - referred to as the **spectral width** - we take a Fourier transform of our pulse in the time domain to find the shape of the pulse in frequency space. This is the orange curve on Figure 2.1. We then find the FWHM of this to determine the spectral width $\Delta\omega$ ². This spectral width is so named as it is the width of the spectrum that our pulse spans - if there are many colours present in our pulse, then it has a broad spectral width, and vice versa. Commonly, this spectral width is referred to as the **bandwidth**, and we will use this terminology going forward.

²The Fourier transform of a Gaussian is also a Gaussian, so we can find the FWHM in the frequency domain exactly as we did in the time domain

We can then use our new definitions $\Delta\omega$ and $\Delta\tau$ to define a new kind of uncertainty relation in terms of the product $\Delta\omega\Delta\tau$. This is referred to as the **time-bandwidth product** for obvious reasons. For a Gaussian pulse, it is found

that:

$$\Delta\omega\Delta\tau \geq 0.441 \quad (2.2)$$

This means that for a Gaussian pulse with a given bandwidth $\Delta\omega$, the shortest possible pulse is found when this inequality is an equality, and then $\Delta\tau = 0.441/\Delta\omega$. As an rough illustrative example, if we take a typical bandwidth of a Ti:Sa laser of 60 nm (at a central wavelength of 800 nm - corresponding to around 28 THz bandwidth). Then the shortest possible pulse this bandwidth could support is theoretically around 15 fs!³ When the temporal width of the pulse is as short as the bandwidth will allow, we say that the pulse is **transform-limited**, or that it's **at the transform limit**.

³This will seem very short to anyone with experience, and is because not all of this bandwidth can be efficiently compressed, and we also cannot full get rid of higher-order dispersion.

2.3 The Transform Limit

Our time-bandwidth product shows that a laser pulse with a broader bandwidth can have a shorter temporal width than one with a narrower bandwidth. We normally talk about the shortest pulse possible with a given bandwidth as being the shortest pulse that that bandwidth can **support**, and this shortest pulse occurs when the pulse is **transform limited**. A clear question then, is '*are pulses with a broad bandwidth necessarily short?*' - the answer is a resounding **no**, the remainder of this chapter and the next will explore why.

To understand this, it is useful to think about the pulse in the frequency domain. The pulse has a bandwidth $\Delta\omega$ which is spread around a central frequency ω_0 . Within this bandwidth there are many different **spectral components** - for example, in the case of an 800 nm pulse with a bandwidth of 60 nm, we would expect to see components between 770 nm and 830 nm if we looked at the spectrum of our pulse. Each of these components can be considered as a normal sinusoidal wave with electric field $E(t)$:

$$E(t) = E_0 \sin(\omega t + \phi(\omega)) \quad (2.3)$$

Where the frequencies of the wave ω are distributed around ω_0 in accordance with the bandwidth (larger bandwidth \rightarrow larger spread of frequencies). Here $\phi(\omega)$ is the **phase** of the wave with frequency ω . The phase of a wave tells you 'where it starts' - and it is the phase relationship between different frequency components (that is, the difference in their phases $\Delta\phi$) that is critical to understanding ultrafast pulse generation. A simple example is shown in Figure 2.2 - where two waves are interfered. In the top frame, both waves are perfectly in phase and have a phase difference $\Delta\phi$ of zero, leading to constructive interference. In the lower frame, both waves are out of phase by π rad, which leads to destructive interference.

In a typical Ti:Sa laser oscillator, we may have around 250000 colours (waves of different frequencies) all resonating around our cavity. If each wave has a well defined phase relationship to all the other waves, then the waves are said

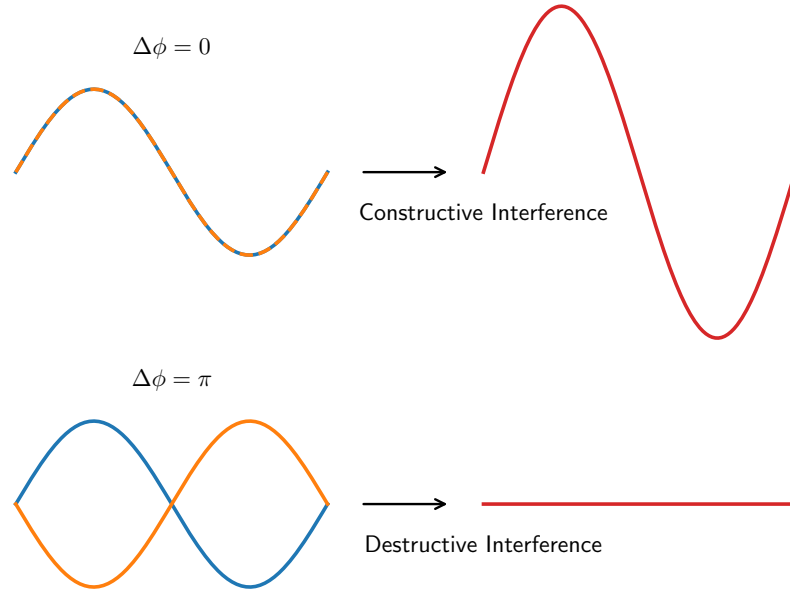


Figure 2.2: Effects of different phase relationships on the interference of two plane waves.

to be **phase-locked**, and the cavity is said to be **mode-locked**. This results in constructive interference and creation of ultrashort laser pulses. Conversely, if all the phases are random, and there is no well defined phase relationship between one wave and the others, then on average there is destructive interference - and no pulse is seen. This is illustrated in Figure 2.3.

Creating the mode-locked cavity is a key part of ultrashort pulse generation, but the more broad point to take from this is that the more modes we can have that are phase-locked, then the shorter our output pulse can be. When all of the frequency components have a well defined phase relationship⁴, then they will temporally coincide at a certain point, and this is the transform limit. **If all of the colours in the pulse arrive at the same time, the pulse is transform limited.**

⁴This is equivalent to saying that the $\phi(\omega) = k_n\omega$, where k_n is a constant specific to each frequency. Then $\frac{d\phi}{d\omega} = k_n$, and the phase difference between different components does not depend on the frequency.

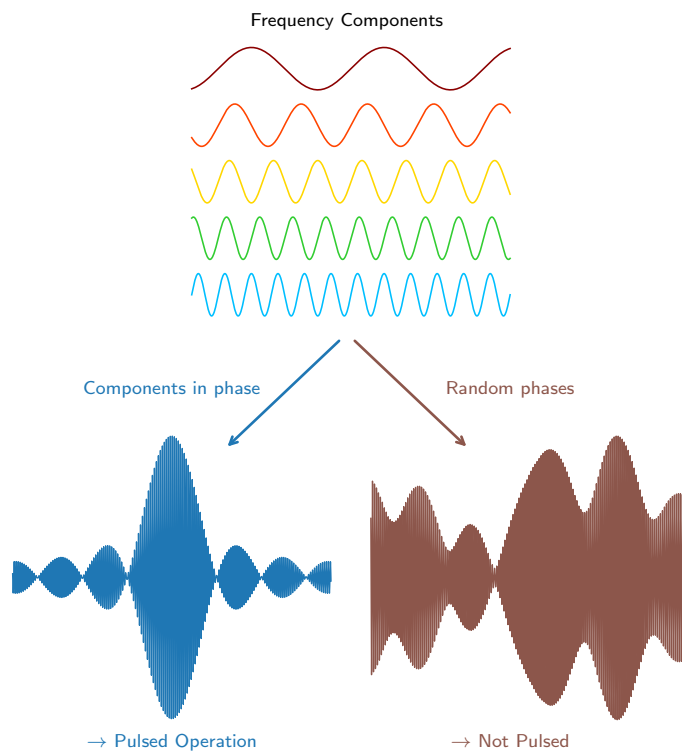


Figure 2.3: Illustration of how adding waves of different frequencies with a well defined phase relationship leads to generation of a pulse, whereas adding waves with random phases does not. The output waveforms are calculated by superimposing ten waves from within a typical 800 nm Ti:Sa bandwidth, whereas the initial plane waves are chosen just for illustrative reasons.

Chapter 3

Dispersion

We didn't really fully answer the question we set out to answer at the beginning of the previous section, which was 'are pulses with a broad bandwidth necessarily short?'. We saw that to have a transform limited pulse (the shortest possible pulse for a given bandwidth), that there had to be a fixed phase relationship between all the frequency components in the pulse, such that at some point all of the different components (different colours) temporally coincide and give us a short pulse.

Dispersion is the phenomenon which stops the different frequency components arriving at the same time, and leads to broadening of the pulse. Dispersion is a problem which is critical in ultrafast optics - and if you are familiar with non-ultrafast optics you may have never really thought about it. Dispersion, unless properly taken care of, can cause your ultrafast pulses to no longer resemble anything close to ultrafast pulses - so it is important to understand!

3.1 Origins of Dispersion

The **refractive index**, n , of a material is defined as:

$$n = \frac{c_0}{c} \quad (3.1)$$

Where c_0 is the speed of light in vacuum, and c is the speed of light in the material. In most materials, $c < c_0$ and therefore $n > 1$ ¹. However, the refractive index of a material depends on the frequency of light you try to send through it - that is, $n = n(\omega)$.

¹Negative refractive indices are possible for reasons to do with relativity which I don't quite understand..

This is the physical origin of dispersion. If different colours of light experience different refractive indices, then (for example) the higher frequency (more blue) colours could travel more slowly through the material than the lower frequency (more red) colours. This situation (higher frequency light travels faster) is

called **normal dispersion**. The inverse, when higher frequency light travels more slowly, is called **anomalous dispersion**. This is summarised in the table below.

Dispersion	Refractive Index	Blue Light	Red Light
Normal	Increases with ω	Travels Slower	Travels Faster
Anomalous	Decreases with ω	Travels Faster	Travels Slower

The wavelength dependence of the refractive index can be calculated easily using the *Sellmeier Equations*, but for practical use it is much more convenient to use the excellent website <https://refractiveindex.info>, which contains wavelength dependent refractive index data for a huge variety of common optical materials. Rearranging Equation 3.1, we can find that in general the speed of a given frequency component is given by:

$$c(\omega) = \frac{c_0}{n(\omega)} \quad (3.2)$$

Which can be helpful to keep in mind when looking at refractive index data.

3.2 Dispersion, Ultrafast Pulses, and Chirp

We have seen that refractive index is frequency (or wavelength) dependent, and this can cause dispersion as different colours of light travel at different speeds through a given medium. For non-ultrafast laser pulses, this is often not an issue - as the bandwidth is sufficiently narrow that the pulse is effectively 'one colour', and therefore the whole pulse experiences the same amount of dispersion. When we start to have ultrafast, **broadband** pulses, though, all bets are suddenly off.

To understand the effect that dispersion can have on an ultrafast pulse, imagine we have a hypothetical transform limited pulse with a very broad bandwidth - it contains frequency components from dark red to deep blue. This pulse is transform limited, so all the different frequency components arrive at the same time. If, however, we pass this pulse through a piece of glass with normal dispersion, then the blue frequency components slow down, but the red frequency components slow down less. If we looked at the pulse after it has gone through the glass, then we would see more red components at the front of the pulse (as they travelled faster through the glass), and more blue components at the back of the pulse (as they travelled more slowly through the glass). Therefore, our pulse is **no longer transform limited!** As the different frequency components have been **dispersed** in time, then the pulse **must** have broadened - we said that the shortest possible pulse arose when all the colours arrive at the same time, this is not the case now - so our pulse must have broadened. This effect is more dramatic for more broadband pulses, or for materials with a higher dispersion.

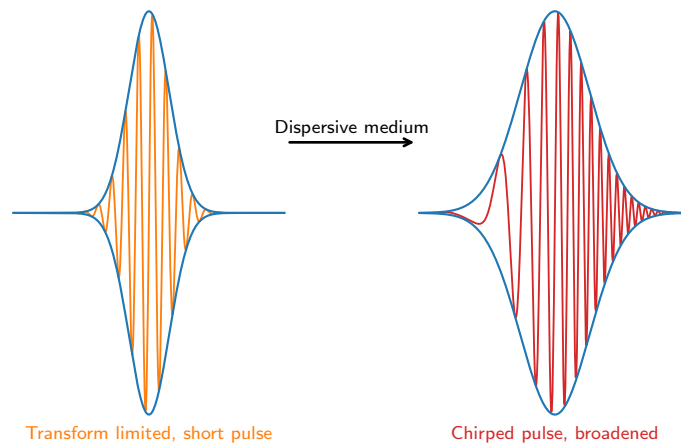


Figure 3.1: Schematic of dispersion of a TL pulse (orange) passing through a dispersive medium, so it becomes chirped and broadened (red). The extent of the chirp has been exaggerated for illustrative reasons.

Following the passage through a dispersive medium, the frequency components are dispersed and (if the material gave positive dispersion), the red components arrive before the blue components - this is the case plotted in Figure 3.1². At this point, we say that the pulse is **chirped**. The reason for this name becomes clear if we look at a spectrogram (plot of frequency against time) for the pulse, as in Figure 3.2.

²It is admittedly impossible to tell this when there is no time axis present, but time runs from left to right as normal - so the higher frequencies arrive later.

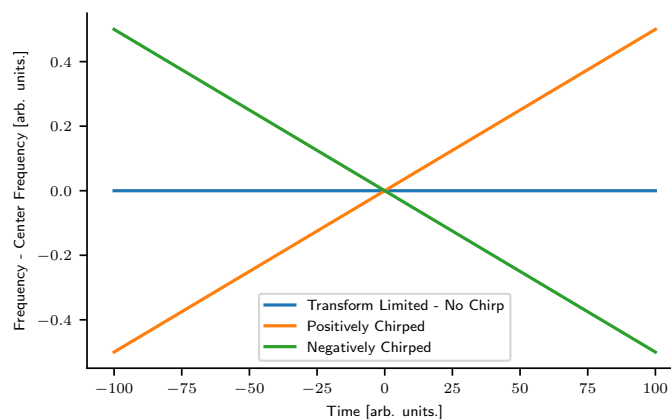


Figure 3.2: Spectrograms for an arbitrary unchirped pulse (blue), positively chirped pulse (orange), and negatively chirped pulse (red). Numerical values are arbitrary and chosen only for illustration.

Clearly for the two chirped pulses, the frequency of the pulse changes during the course of the pulse. For a **positively chirped** pulse, the frequency **increases** during the course of the pulse. For a **negatively chirped** pulse, the frequency **decreases** during the course of the pulse. The name 'chirp' is given, as if you were to downconvert the optical frequencies into audio frequencies, you would hear a rising frequency (for positive chirp) - rather like a bird chirping.

Fine, you say. But how do I know how much this added chirp will broaden my pulses? This requires that we figure out how *much* dispersion is added by a particular optical element. This, in turn, requires that we think more mathematically about what happens when light propagates through a dispersive medium.

3.3 Intermission - Envelopes and Carriers

Before we crack on with the serious business of dispersive media, I will make reference to **envelopes** and **carriers** in the following section, so will explain briefly what they are here. Figure 3.3 shows a sketch of an ultrashort pulse with the pulse envelope and carrier highlighted for a hypothetical transform limited pulse.

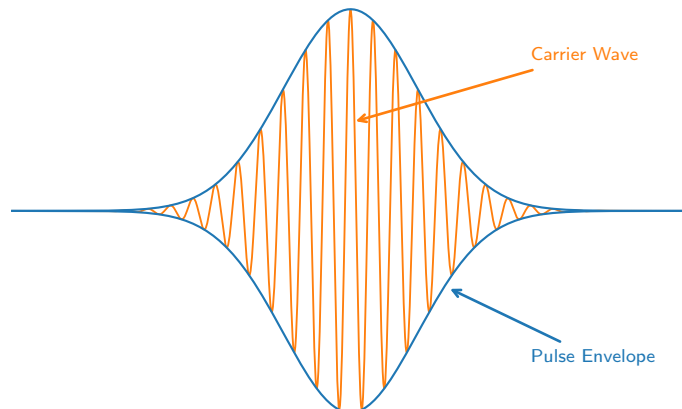


Figure 3.3: A hypothetical transform limited pulse shown with the carrier wave (orange) and pulse envelope (blue).

I think it's fairly intuitive as to why these are called the carrier and the envelope. The envelope is the (in our case) Gaussian distribution that dictates the temporal shape of the pulse - shown in blue on the figure. The carrier wave is the superposition of all the frequency components present in the pulse - and represents the electric field of the pulse. Generally speaking, the carrier oscillates much much faster than the envelope - so treating them separately in any mathematical analysis is generally a reasonable assumption.

Note that in this pulse, the peak of the carrier wave coincides with the peak of the envelope - this is because for the pulse shown, there is no **carrier-envelope offset**. This is something of importance to the study of **few-cycle pulses**, where the carrier wave only completes two or three optical cycles in the window provided by the pulse envelope. It takes a bit of work to make few-cycle pulses - so is not something we will consider further.

3.4 Propagation Through a Dispersive Medium

This is very brief as I don't want to get into detailed mathematics at the expense of an intuitive understanding. For more rigour, see (e.g) Hooker and Webb, or Milonni and Eberly. A laser pulse can be considered as a superposition of different frequency components, such that the total electric field $E_{\text{input}}(t)$ can be written as:

$$E_{\text{input}}(t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} a(\omega) e^{-i\omega t} d\omega \quad (3.3)$$

In this equation, the $e^{-i\omega t}$ term is simply a plane wave of frequency ω , and the factor $a(\omega)$ is an amplitude factor that determines how 'much' of each frequency is in the overall pulse³. As the pulse travels through a material, each frequency component will accumulate a phase, $\phi(\omega)$, that is specific to that frequency. The output field after propagation, $E_{\text{out}}(t)$, is therefore:

³This factor can be calculated using basic Fourier theory - see (e.g.) Rob Penfold's lecture notes.

$$E_{\text{output}}(t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} a(\omega) e^{-i(\omega t + \phi(\omega))} d\omega \quad (3.4)$$

If we can find this accumulated phase $\phi(\omega)$, then we can calculate the effect a dispersive medium has on our pulse. To do this, we expand the $\phi(\omega)$ around the central frequency ω_0 as a Taylor series.

$$\phi(\omega) = \phi(\omega_0) + \frac{\partial \phi}{\partial \omega}(\omega - \omega_0) + \frac{1}{2} \frac{\partial^2 \phi}{\partial \omega^2}(\omega - \omega_0)^2 + \dots \quad (3.5)$$

Higher order terms can normally be neglected (although see brief note later). We can now discuss what each of these terms are and what they physically represent. We follow the notation convention in Hooker and Webb, as it seems to be fairly standard.

$\phi(\omega_0) = \phi^{(0)}$. This is the total phase that is accumulated at the central wavelength - this is (partly) responsible for a phenomenon called the '**carrier-envelope offset**', which is interesting but generally only significant for few-cycle pulses, where each pulse only consists of very few optical cycles. This will not be a factor for the laser pulses we will consider.

$\frac{\partial \phi}{\partial \omega} = \phi^{(1)}$. This term is called the **group delay**, with units of time, and gives the time taken for the pulse to propagate through the dispersive medium.

If the dispersive medium has a length L , we can also define the **group velocity**, $v_g = L/\phi^{(1)}$. The group velocity defines the *velocity at which the pulse envelope (i.e. the whole pulse) travels*. This is distinct from the **phase velocity**, which is specific to each frequency (each carrier wave) and defines the velocity of the individual carrier waves. Changing the group delay has the effect of changing the temporal position of the pulse - but does not change the shape of the pulse envelope, so does not lead to broadening.

$\frac{\partial^2 \phi}{\partial \omega} = \phi^{(2)}$. This term is called the **group delay dispersion (GDD)**, and has units of (time)². It is the lowest term responsible for broadening of pulses via dispersion⁴. It is also generally the main source of dispersion that will broaden our pulses. This term represents the **quadratic phase** - and when it is present it implies that the phase difference between components depends on frequency, so it is no longer possible to get the fixed phase relation we need to have all of our frequencies arrive simultaneously and make a transform-limited pulse. **GDD is the main thing that will cause your pulses to broaden!**

⁴One can also calculate the **group velocity dispersion** as GDD/L - the GDD per unit length.

Higher order terms can also play a role, especially **third order dispersion (TOD)**. However, these are much more difficult to compensate for in the lab, so we focus on compensating for the second order terms and pray that the pulses are short...

3.5 Group Delay Dispersion

The quantity $\frac{\partial^2 \phi}{\partial \omega} = \phi^{(2)}$ is the GDD. This quantity has units of (time)², and is generally quoted in units of fs² when you're buying optics and want to assess how much dispersion they will add. The effect of the GDD on a pulse can be assessed as follows. The time taken $T(\omega)$ for a given pulse to propagate through a medium can be expressed as a Taylor expansion around a central frequency as:

$$T(\omega) = T(\omega_0) + \frac{\partial T}{\partial \omega}(\omega - \omega_0) + \dots \quad (3.6)$$

Where the derivatives are evaluated at the central frequency ω_0 . $T(\omega_0)$ is just the group delay $\phi^{(1)}$, from our previous definition (the time it takes the pulse envelope to propagate with no dispersion), and $\frac{\partial T}{\partial \omega}$ is the GDD $\phi^{(2)}$. We can then recast this equation as follows (neglecting higher order terms):

$$T(\omega) = \text{Group Delay} + \text{GDD} \times (\omega - \omega_0) \quad (3.7)$$

So, if GDD is zero, the propagation time is just the group delay, and the pulse is transform limited. However, if the GDD is positive, then the propagation time for frequencies higher than ω_0 is longer - so the 'blue' end of the pulse takes longer to travel through the medium than the 'red' end: we have induced **positive chirp** in the pulse. In contrast, negative GDD leads to a **negative chirp**. Also, it is

clear that a larger bandwidth (larger difference between ω and ω_0) will lead to a longer travel time, and a more pronounced chirp, and a broader pulse.

Hopefully by now you get the basic idea that dispersion (and specifically GDD) is what causes pulses to broaden. As pulses are dispersed away from the transform limit, they become either positively or negatively chirped - this leads to broadening of the pulse.

3.6 Predicting Broadening from Dispersion

Now we consider how we can predict the broadened pulse length of a Gaussian pulse, which will be of considerable practical utility. Assuming that there is only second-order dispersion⁵, then the broadened pulse duration τ of an initially transform-limited Gaussian pulse τ_0 having passed through a medium giving a GDD $\phi^{(2)}$ is:

$$\tau = \tau_0 \sqrt{1 + \left(\frac{4 \ln 2 \phi^{(2)}}{\tau_0^2} \right)^2} \quad (3.8)$$

⁵This is usually reasonable - and most often if there is third-order dispersion we can't do a lot about it anyway.

This equation is plotted for a transform-limited 35 fs input pulse as a function of GDD in Figure 3.4. Clearly, as the initial pulse was transform limited, then any amount of positive or negative GDD added will cause it to broaden. Also, it can be seen from the equation that a shorter input pulse (smaller τ_0) will lead to a broader output pulse - which should make sense, as a pulse with a larger bandwidth will experience a wider range of refractive indices, and the different colours in the pulse will spread out more.

The plot and equation above are both ignoring higher order dispersion - which is normally a reasonable approximation except for the shortest pulses. An additional consideration is to think about *how the GDD added depends on wavelength*. In general, shorter wavelengths (especially in the UV), see higher refractive indices, and experience more severe broadening as they accumulate **much** more GDD than an infrared pulse of similar duration. The table below gives the GVD (simply GDD per unit length) for some common materials.

Substrate	GVD@800nm (fs ² /mm)	GVD@300nm (fs ² /mm)
BK7	44.6	206.1
UV Fused Silica	36.1	155.6
CaF ₂	27.7	103.8
Sapphire	58.1	243.1
Air	0.02	0.08

Clearly the amount of dispersion is higher in the UV for all these materials. Passing a 35 fs TL 300 nm pulse through a 5 mm BK7 window will lead to

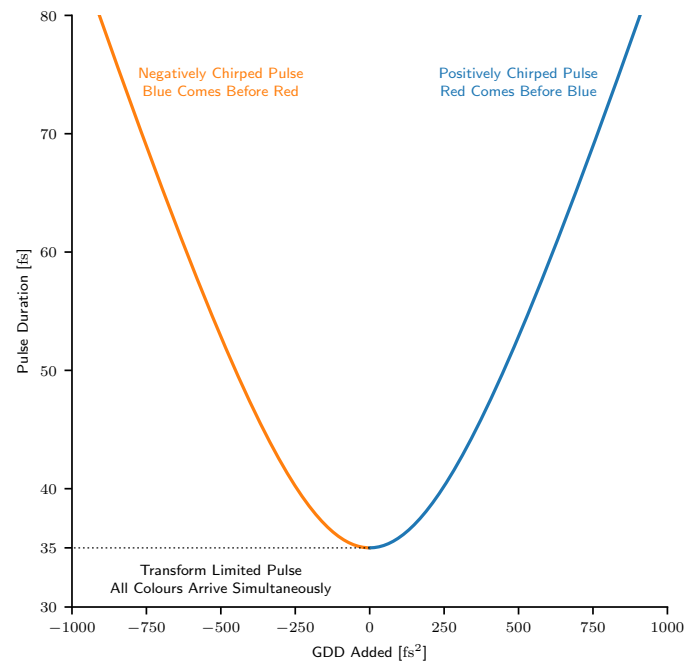


Figure 3.4: Pulse duration of an initially transform limited 35 fs Gaussian pulse as a function of the added GDD. Negative GDD added leads to negative chirp - shown in orange. Positive GDD added leads to positive chirp - shown in blue.

$\sim 1000 \text{ fs}^2$ of added GDD - broadening the pulse from 35 fs to ~ 90 fs - more than a factor of two! It is therefore important to be aware of this, especially in the UV. In the IR it is much less of an issue - as can be seen by performing the same analysis above with different thicknesses of materials, try it and see.

As should now be clear, to avoid pulse broadening, a good rule of thumb is to minimise the amount of transmissive optics you use (so mirrors for steering, not prisms!), especially in the UV.

3.7 Calculating Dispersion of Optical Elements

This was largely explained in the previous section - it is really a matter of looking up the value of the GDD or GVD for the material that you're using. Most optics suppliers will give this information readily on websites. It's also important that you don't **only** consider transmissive optics when you're thinking about pulse broadening - mirrors will also contribute some GDD, and especially so if you're not using mirrors that are specially coated for ultrafast pulses. Generally an 'ultrafast' mirror will have a GDD of $< 30 \text{ fs}^2$ per bounce. Figure 3.5 shows this information for a standard ultrafast mirror from Thorlabs - note that the GDD

Item #	UM05-45A	UM10-45A	UM15-45A	UM20-45A
Design Wavelength Range	700 - 930 nm			
Diameter	1/2"	1"	1.5"	2"
Diameter Tolerance	+0.00 / -0.10 mm			
Clear Aperture ^a	Minor Diameter	0.28"	0.57"	0.85"
	Major Diameter	0.4"	0.8"	1.2"
Thickness	6.4 mm	9.5 mm	12.0 mm	12.0 mm
Thickness Tolerance	±0.20 mm			
Reflectance	R _s > 99% (700 - 930 nm) R _p > 99% (730 - 870 nm)			
Angle of Incidence	45°			
Group Delay Dispersion	GDD _s < 30 fs ² (700 - 930 nm) GDD _p < 30 fs ² (730 - 870 nm)			
Laser Induced Damage Threshold ^b	0.40 J/cm ² (800 nm, 52 fs FWHM, S-Pol, 1000 Pulses)			
Substrate	Fused Silica			
Front Surface Flatness ^c	<λ/4	<λ/6	<λ/4	<λ/2
Front Surface Quality	15-5 Scratch-Dig			20-10 Scratch-Dig
Parallelism	≤3 arcmin			≤5 arcmin
Back Surface	Polished			Fine Ground

Figure 3.5: Screenshot from Thorlabs' page for ultrafast mirrors - GDD information highlighted.

can depend on polarisation⁶ (although not much in this case). The physical origin of GDD from a mirror is that broadband dielectric mirrors are constructed of a number of different layers of coatings which each reflect a different wavelength in the total reflected bandwidth. Therefore, when a pulse bounces on such a mirror, different colours in the pulse travel through subtly different path lengths - leading to dispersion. In a metallic mirror, there are no such layers, and the GDD is (ideally) zero - however metallic mirrors often have much lower reflectivity and are more easily damaged.

A very useful resource for finding GDD for a large number of materials is Light Conversion's online Optical Toolbox: toolbox.lightcon.com. This contains a huge number of helpful calculators, and under 'Dispersion Calculators' there are applets to calculate arbitrary dispersion, pulse broadening, and many other things. They also include third-order dispersion, so this can be useful if you're concerned as to whether this can be neglected for your application.

⁶Note the 's/p' notation for polarisation. This comes from the German for 'perpendicular' and 'parallel'. An s-polarised wave is polarised perpendicular to the plane the wave travels in before and after reflection from an interface. Generally, s-polarisation is vertically polarised in our case.

3.8 Pulse Compression - Compensating for Dispersion

Finally, we end this chapter on dispersion by considering how we can remove unwanted dispersion and make our pulses short again. As may be evident from Figure 3.4, we want to push our pulse back down this curve towards the transform limit - towards having zero chirp. How we achieve this depends on whether the pulse has accumulated net positive or negative GDD - whether it is positively or negatively chirped. If we can establish this, then we simply have to add GDD of the opposite sign to get it back towards the transform limit.

What you will find on looking into this, is that there aren't really any materials in the UV-near IR region⁷ which exhibit negative GDD. This means two things:

⁷Which we are interested in because we're using Ti:Sa lasers

1. If our pulses start life as transform limited pulses, they will almost inevitably end up gaining only positive GDD, so ending up positively chirped after some propagation and needing negative GDD to recompress them back to the transform limit.
2. Adding said negative GDD is a pain because just finding a material which has negative GDD is very difficult/impossible.

So, we can't just get another piece of exotic glass and send the pulse through it to recompress it. This can be possible in the IR/far IR, where some common optical materials (such as BK7) add negative GDD⁸, but generally is not possible for the 200 nm-800 nm pulses we will use.

⁸As these materials have both positive and negative GDD, there is generally a wavelength where they exhibit zero GDD - the zero dispersion wavelength.

Happily, there is a way we can add this negative GDD, by using a **compressor** - which is generally made using prisms or gratings. These devices are constructed in a geometry that means that an initially positively chirped pulse will enter (red comes before blue), but in the compressor the red components are delayed relative to the blue components. This means that the blue components have time to 'catch up' to the red components. Two common geometries are shown in Figure 3.6.

To discuss how each individual type of compressor works, we look at Figure 3.6. Initially, the grating compressor (top), works by making the blue components of the pulse travel over a shorter distance than the red components - so they have time to catch up, and negative GDD is added. The prism compressor (bottom) is similar, but the red components do **not** have a longer path length, but they travel through more of the prism (as the blue components pass nearer the apex). This means that they experience more material dispersion and slow down relative to the blue components - allowing the blue components time to catch up. Grating compressors generally can produce larger amounts of negative GDD than prism compressors - but are more expensive⁹.

⁹If you need to add large amounts of GDD, then using a **chirped mirror** can be a good idea - these have a large (positive or negative) GDD per bounce, and can be combined with a grating or prism for fine dispersion control.

There are a few final points to make about compressors. Firstly, none of the compressors above can compensate for third-order dispersion - to do this you need to use a 'GRISM', which is a grating etched into a prism. Secondly, the compressors can also be aligned to introduce positive GDD, which can either compensate for negatively chirped pulses, or enable it to function as a **pulse stretcher** as well as a pulse compressor. This can be very useful in some circumstances - as we will see later when we discuss chirped-pulse amplification.

Finally, inside most Ti:Sa lasers is a compressor which compresses the final output pulses - this compressor can generally be adjusted to produce negatively

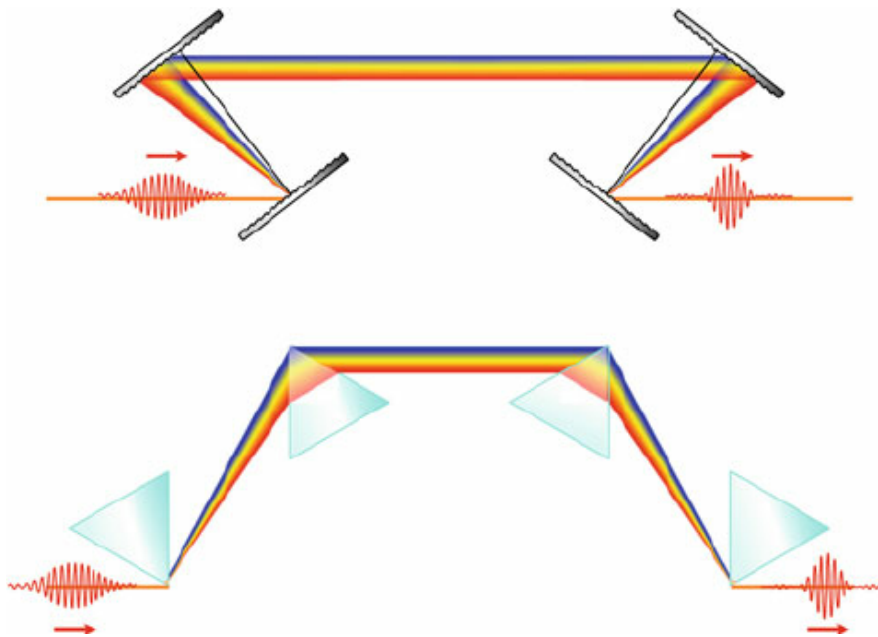


Figure 3.6: Schematic of a grating compressor (top) and prism compressor (bottom). Figure taken from Evans and Mazur, *Nanophotonics: Linear and Nonlinear Optics at the Nanoscale*.

chirped pulses from the laser output, which will then steadily gain positive chirp as the propagate through your optical system. Careful choice of this compression can enable you to effectively *pre-compensate* for the positive GDD added by your optical components, so that the initial negative chirp exactly matches the accumulated positive chirp. In this way, you end up with a transform limited pulse at the end of the line (where you want it). **Pre-compensating for the positive dispersion** in this way is a very useful tool.

Chapter 4

Non-linear Optics

In this final section, before we summarise and look at how all of the optical phenomena previously discussed combine to guide what we do in the lab, we will briefly discuss **non-linear optics**. Non-linear optics are not exclusively an 'ultrafast' thing, but ultrafast pulses necessarily have a very high *intensity*, so non-linear effects can be very significant.

The physics and mathematics behind a lot of non-linear optics quickly become quite dense, and I think would get in the way of the (somewhat superficial) understanding we need as chemists when using these pulses day-to-day. Most books on laser physics will have a more rigorous treatment than what is described here, if desired.

4.1 Nonlinear Material Response

As discussed previously, a laser pulse can be effectively described as an oscillating electric field (the carrier wave), inside a more slowly varying envelope. When a medium (air, glass, anything) is subjected to an electric field \mathbf{E} , the material response is given by the **polarisation** \mathbf{P} , of the medium. Polarisation has units of 'dipole moment per unit volume', so if the applied electric field produces a large dipole moment, then the medium is said to be **polarisable**¹. The polarisation \mathbf{P} can be expressed as follows:

$$\mathbf{P} = \epsilon_0 \chi^{(1)} \mathbf{E} + \epsilon_0 \chi^{(2)} \mathbf{E}^2 + \epsilon_0 \chi^{(3)} \mathbf{E}^3 + \dots \quad (4.1)$$

¹Note that this is not the same thing as the polarisation **of** the electric field, which is the orientation of the field oscillation.

Where $\chi^{(n)}$ is the n^{th} order electric susceptibility², and ϵ_0 is the vacuum permittivity. For weak fields, all terms apart from the first term in Equation 4.1 can be considered to be zero. However, for intense fields (like we generally have with ultrafast pulses), then the higher order susceptibilities become important. It turns out that in isotropic media (a lot of things we will use), then this gives rise to an

²i.e. How effected by the applied field the medium is

intensity dependent refractive index:

$$n(I) = n_0 + n_2 I(t) \quad (4.2)$$

³The second order susceptibility is zero unless the medium is anisotropic - see later.

The first term in this equation, n_0 , arises from the first order susceptibility, and is responsible for the normal frequency dependent refractive index we are familiar with. The second term arises from the *third order* susceptibility³, and this means that the refractive index seen by a particular frequency within our laser pulse will be different at the peak of the pulse compared to at the edges. The extent of this difference depends on the magnitude of n_2 - which is material dependent. n_2 is normally positive, so the refractive index is higher for areas of high intensity (at the centre of a Gaussian beam, and at the peak of a Gaussian pulse).

This dependence of n on intensity is known as the **Kerr Effect**, and leads to a couple of important phenomena we need to know a bit about.

4.2 Self-Focussing and Self-Phase Modulation

We first consider the phenomenon of **self-focussing**. Self-focussing occurs when an intense laser pulse passes through a medium and experiences an intensity dependent refractive index via the Kerr effect (Equation 4.2). Most laser beams we look at can be well described as **Gaussian beams**, which means that the transverse intensity across the face of the beam is described by a 2D Gaussian function, such that the intensity in the center of the beam is higher than that at the edges - as shown in Figure 4.1.

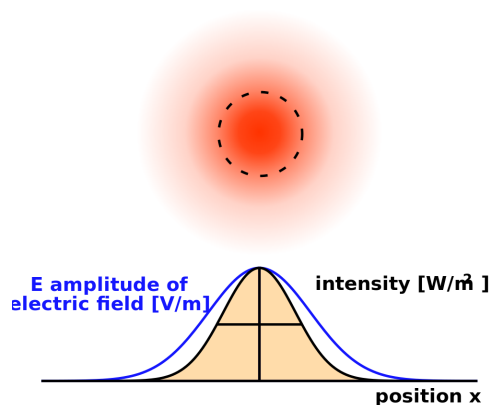


Figure 4.1: The 2D transverse intensity profile of a Gaussian beam, with the 1D intensity along the x direction plotted below. Figure from Wikipedia.

If we imagine that a pulse with Gaussian intensity profile passes through a medium, it could (if the intensity is high enough) induce an intensity dependent

refractive index in the medium. This effectively leads to a lens being imprinted on the material by the laser beam - this 'induced lens'⁴ leads to focussing of the beam as a conventional lens would. So the beam focusses as it passes through the material - this is **self-focussing**, and is illustrated in Figure 4.2.

⁴Sometimes known as **Kerr Lens**.

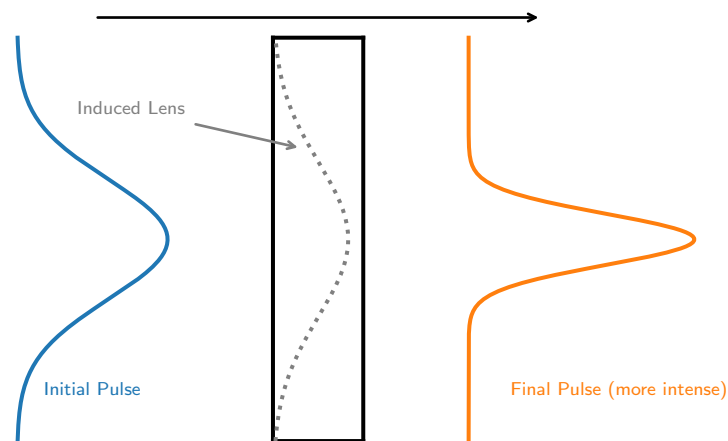


Figure 4.2: Schematic of the self-focussing process. An initial pulse (blue) passes through a dispersive medium (black box) and imprints a transient 'lens' on it via the Kerr effect (grey dashed line). This leads to focussing and the final pulse (orange) has a higher transverse intensity. The extent of this effect has been exaggerated here for illustrative purposes.

This process is important for us, as if we are not careful we can have parasitic self focussing in our optics which will cause us to inadvertently focus the beam, which can damage or destroy optics that are further down the beamline! Aligning optics at low power and then slowly increasing the power can avoid this issue (and is much safer anyway) - you do not want to accidentally focus the beam onto an autocorrelator or inadvertently drill a hole in your vacuum window! Self-focussing is also important in the phenomenon of **Kerr-Lens Modelocking**, discussed briefly later.

The second effect, self-phase modulation, we will treat much more briefly. This is again a result of the Kerr effect. As the intensity of the pulse varies with time (peak intensity at the peak of the pulse envelope), the pulse will 'see' a time-dependent refractive index as it travels through the medium. This causes a phase shift in the pulse which results in a change in the instantaneous frequency. This results in spectral broadening of the pulse, creating new frequencies. This spectral broadening can be important when creation of very short pulses is desired, as effectively you are creating 'extra bandwidth' via the self-phase modulation. Compression of this will then lead to a shorter pulse. This effect is commonly

used in hollow-core fibre broadening, and in **white light generation** - which is important in transient absorption spectroscopy and also in optical parametric amplification (see later).

4.3 Non-linear Frequency Mixing

One of the most important non-linear effects to be aware of is that of **non-linear frequency mixing**. If we consider mixing of only two photons with frequencies ω_1 and ω_2 , then frequency mixing occurs when a third photon ω_3 is produced such that:

$$\omega_3 = \omega_1 \pm \omega_2 \quad (4.3)$$

That is, the frequency of the third photon is either the sum or the difference of the frequencies of the two initial photons. In the case where $\omega_3 = \omega_2 + \omega_1$, this is called **sum-frequency generation (SFG)**, and if $\omega_3 = \omega_2 - \omega_1$, then this is called **difference-frequency generation (DFG)**. These are the most general cases, but there are other possibilities with unique names which are summarised below:

Input Photons	Output Photon	Name
ω_1, ω_1	$\omega_1 + \omega_1 = 2\omega_1$	Second Harmonic Generation (SHG)
ω_1, ω_2 (where $\omega_2 = 2\omega_1$)	$\omega_1 + \omega_2 = 3\omega_1$	Third Harmonic Generation (THG)

So the question becomes, how do we perform this mixing? We will illustrate this using the example of second harmonic generation (SHG) - i.e. frequency doubling.

To do this, we have to combine the photons in a way that conserves momentum and energy, that is:

$$\omega_1 + \omega_2 = \omega_3 \quad (4.4)$$

For energy conservation. We write the momentum of a wave in terms of the **wave vector**, \mathbf{k} , where the wave vector in medium i , $k_i = n_i \omega_i / c$. Then we write the momentum conservation criterion as:

$$\mathbf{k}_1 + \mathbf{k}_2 = \mathbf{k}_3 \quad (4.5)$$

This is known as the **phase-matching condition**. The vector sum of the momenta of the two input photons must be equal to the momentum of the output photon. If this is satisfied, then we can effectively add our input photons together to produce output photons at double the frequency. In the case of SHG, we can write the phase-matching condition in terms of refractive indices as:

$$n_1 + n_2 = 2n_3 \quad (4.6)$$

Which reduces to:

$$n_\omega = n_{2\omega} \quad (4.7)$$

On substitution of $n_1 = n_2 = n_\omega$ and $n_3 = n_{2\omega}$.

When this equation is satisfied, the output second harmonic travels with the same *phase velocity* as the input fundamental. Therefore, any second harmonic created by the fundamental at the start of the crystal will be in phase with any second harmonic created at the end of the crystal - these second harmonic waves then constructively interfere to give the maximum possible second harmonic output. Satisfying ?? is generally not trivial, as for most materials the refractive index depends on the frequency as we have seen many times! However, there are ways to achieve this, and one way is using a **birefringent crystal**.

A crystal that is birefringent has a refractive index which depends on the polarisation and propagation direction of the light incident on it. A 3D crystal will have three refractive indices, n_x , n_y , and n_z . If these are all the same the crystal is **isotropic**. If one of these is different from the other two, then the crystal is **uniaxial**, if they are all different, then the crystal is **biaxial**. From now on we will only consider uniaxial crystals as an illustrative case.

In a uniaxial crystal, there is one axis which has a different refractive index to the other two, this axis is called the **optical axis** of the crystal. If a wave is polarised *along the optical axis*, then it will experience a different refractive index to a wave polarised perpendicular to it. A ray that propagates along the optical axis experiences the same refractive index regardless of its polarisation state, and this is called the **ordinary ray**. Conversely, a wave that is polarised parallel to the plane formed by the propagation direction and the optical axis is called the **extraordinary ray**⁵. When a wave propagating at an angle θ to the optical axis is incident on a crystal, the refractive index it sees $n(\theta)$ is given by:

$$\frac{1}{n(\theta)^2} = \frac{\cos^2(\theta)}{n_o^2} + \frac{\sin^2(\theta)}{n_e^2} \quad (4.8)$$

⁵The names arise because the ordinary ray refracts according to Snell's law, whereas the extraordinary ray does not - hence it is extraordinary!

Where n_o and n_e are the refractive indices experienced by the ordinary and extraordinary rays respectively. $\theta = 90^\circ$ corresponds to propagation purely orthogonal to the optical axis ($n(\theta) = n_e$), whereas $\theta = 0^\circ$ corresponds to propagation along the optical axis ($n(\theta) = n_o$). Given the right crystal, we can then tune the angle θ such that:

$$n_\omega(\theta) = n_{2\omega} \quad (4.9)$$

And we have efficient phase matching, and therefore efficient SHG! There are extra complexities that I have deliberately omitted here regarding the phase matching - there are differences that depend on the relative polarisation states of the input and output waves. At some point I may relegate this information to an appendix, but any standard text on laser physics will give more detail. The fundamental

point is: **to have efficient phase matching, we have to ensure that the fundamental and second harmonic wave experience the same refractive index.**

To do this in practice we need a crystal (as stated), and helpfully for people who grow optical crystals, no one crystal will work for all desired frequency mixing schemes. The most common crystal we use with Ti:Sa systems is β -**barium borate, or BBO**. This crystal can be cut for efficient SHG and THG of 800 nm beams, has a high transparency, and a high damage threshold, so is ideal for use in a lab.

When you buy a crystal, you will see that it is pre-cut for a specific type of frequency mixing - such as SHG or THG at a specified wavelength. This means that when a wave is incident on the flat surface of a crystal, the optical axis is in the right plane such that rotating the crystal in a rotation mount will allow phase matching to be achieved. Some common mixing schemes and crystals are summarised in the table below. Type I here refers to the polarisation state of the

Process	Crystal	Angle
SHG@800nm, Type I	BBO	29.2°
THG@800nm, Type I	BBO	44.3°

input and output waves - in Type I mixing processes the two input waves have ordinary polarisation and the output wave has extraordinary polarisation. If you want to find a crystal that will allow efficient frequency mixing of different colours, then using the optical toolbox is a good idea - there are many calculators on there to help find the right phase matching angles⁶

⁶Angle tuning is not the only way to ensure phase matching - some crystals have a temperature dependent refractive index, and so the crystal can be housed in an oven and the temperature tuned to match the relevant refractive indices.

4.4 Optical Parametric Amplification

A final non-linear process to mention is that of **optical parametric amplification**. The development of this has been a boon to hapless chemists like us who want to use lots of different colours but don't understand enough of the physics to generate them all from scratch ourselves. At its core, an optical parametric amplifier (OPA) is just doing the frequency mixing that we've discussed at length in the previous section, but generally over a wider range of frequencies and in a way that is tunable. Using an OPA, we can simply type the wavelength of light we want into a computer, and motors move all the crystals and mirrors around so that that wavelengths is produced - convenient!

The fundamental idea of an OPA is that a strong **pump beam** with frequency ω_p amplifies a weaker **signal beam** with frequency ω_s via mixing in a non-linear medium. Energy and momentum conservation during this process requires that

a third beam, the **idler beam** is created, with frequency $\omega_i = \omega_p - \omega_s$. This is illustrated in Figure 4.3.

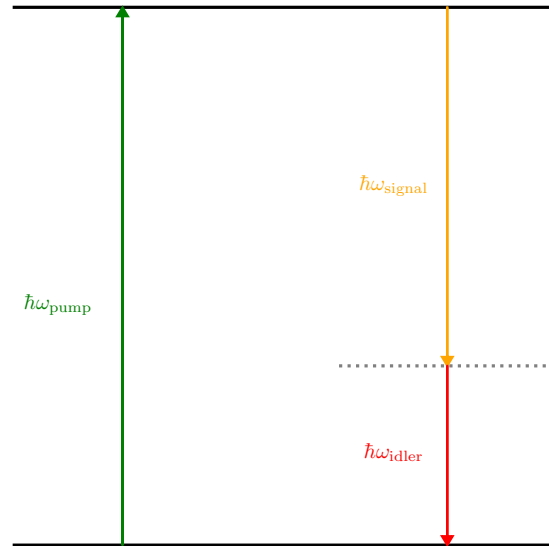


Figure 4.3: Schematic of the optical parametric amplification (OPA) process.

That's kind of it, very simply! The beams are generally overlapped in a non-linear crystal such as BBO to perform the process depicted. There are some similarities and some differences to the prototypical four level laser we discussed at length in section 1. Firstly, you could house the system drawn in Figure 4.3 in an optical cavity, and feedback a certain signal frequency to produce an **optical parametric oscillator**, or **OPO**. Many commercial systems are essentially an OPO followed by an OPA that acts as a power amplifier. Accordingly, we rely on stimulated emission to produce the signal photons - as we did in the four level laser in section 1. By tuning the input signal frequency we can amplify a very wide range of frequencies effectively using OPA.

However, a crucial difference is that **there is no energy stored within the medium the OPA is performed in** - this is in stark contrast to the four level laser where we were dumping huge energy into a crystal and then extracting part of it and relying on fast relaxation between levels to maintain our population inversion. In the four-level case, we would have had to cool the crystal significantly to prevent damage, whereas energy conservation means no energy is actually stored in the (e.g.) BBO crystal we do our OPA in - so cooling is not necessary.

We will discuss briefly how a TOPAS OPA works in the following section, but

fundamentally the process is quite simple:

1. Pump a non-linear medium with a high energy pump beam.
2. Overlap a weak signal beam with the pump (with $\omega_s < \omega_p$) in the non-linear medium.
3. Watch and enjoy as parametric amplification occurs and the signal beam is amplified while the pump beam is depleted. You also get a bonus amplified beam, the idler, with frequency $\omega_i = \omega_p - \omega_s$.

Chapter 5

Practical Ultrafast Optics

Welcome to the final section of this document. Here we will collate all the information we've previously discussed and identify things of key importance to take away, together with some other things that are generally useful but that didn't fit anywhere else.

5.1 Special Considerations with Ultrafast Pulses

Hopefully you've got the impression now that an ultrafast laser pulse is an altogether different beast from a more conventional nanosecond laser pulse (or cw beam). Summarised here are some of the special considerations we have to be aware of when dealing with ultrafast pulses.

5.1.1 Dispersion

Dispersion - the broadening of the pulse as the different colours within it spread out - is a key thing to be aware of, especially with UV pulses. The broadened pulse duration of τ of an initially transform limited pulse with duration τ_0 , having gained a GDD $\phi^{(2)}$ is given by:

$$\tau = \tau_0 \sqrt{1 + \left(\frac{4 \ln 2 \phi^{(2)}}{\tau_0^2} \right)^2} \quad (5.1)$$

Temporal broadening produced by some typical scenarios are summarised in the table below. The pulse durations have been chosen to reflect what we can expect to get out of the Ti:Sa system and TOPAS with no extra compression. This table should make clear a number of points.

1. Shorter pulses (broader bandwidth) are a lot more susceptible to broadening than longer pulses.

Input Pulse	Propagates Through	Output Pulse Duration
800nm, 35fs, TL	1cm UVFS	45fs
800nm, 35fs, TL	10m Air	38fs
800nm, 35fs, TL	10 bounces on ultrafast mirrors	42fs
800nm, 150fs, TL	1cm UVFS	150.1fs
266nm, 70fs, TL	1cm UVFS	105fs
266nm, 70fs, TL	10m Air	80fs
266nm, 70fs, TL	10 bounces on Al mirrors	~70fs

2. UV pulses are a lot more susceptible to broadening than IR pulses.
3. Air propagation isn't generally a huge problem.
4. Minimising transmissive optics is the most important thing to do if you want to keep pulses short.
5. Bouncing on metallic mirrors or ultrafast-coated mirrors is generally OK¹. Metallic mirrors are much more easy to burn and have lower reflectivity though, so generally are only used in the UV where dielectric coatings are less available. Non-ultrafast coated mirrors should be avoided (they don't even give the GDD numbers on these mirrors, so you can imagine that means it's bad...).

¹Although you can lose a lot of power this way

Finally, be aware that often things may have reasonable GDD numbers but result in large power loss over time (e.g. metal mirrors) - you may find that the power you lose travelling through air or other optics is more problematic than the dispersion it incurs, especially in the UV.

5.1.2 Damaging Things

Whilst I wholeheartedly encourage students to be bold and not be petrified into not doing any lab work in case they break something, it is also best to avoid breaking things where you can. This is all the more possible with ultrafast pulses and their very high intensities. The main cause of burnt optics is dirty optics - some dirt on a mirror will absorb the laser radiation and burn the coating of the optic. **Keep your optics clean!**

The other possibility which is especially probable with ultrafast optics is things like self-focussing or diffraction leading to areas of very high local intensity that can burn optics. The following are useful principles to follow.

1. Keep your optics clean!

2. Align new optics at a very low power (also for your own safety), and turn the power up gradually. Watch out for any optics with bright spots on them, or hearing the characteristic 1 kHz whine of your optic having a hole drilled in it. If you see this, turn down the power, clean the optic, and try again.
3. In the event of self-focussing (especially problematic if you're putting very high intensities through relatively thick pieces of glass), your beam may start to weakly focus but not actually reach a focal point until a long distance away from where the self-focussing is happening. I have seen this first hand and at best, it's very annoying for your experiment, and at worst it burns a hole in your £2000 grating.
4. If you do burn an optic, blame it on your supervising postdoc.

5.2 Characterising Ultrafast Pulses

Characterising an ultrafast pulse means measuring a few things about it:

- The pulse energy.
- The pulse duration.
- The size of the beam at the region of interest.

These three parameters will allow the total pulse intensity (power per unit area) to be calculated, which is generally the parameter people report when writing up their work.

To measure the pulse energy, all you need is a power meter and to know the repetition rate of your laser system. The power meter will measure the **average power** coming out of your laser (in Watts - Joules per second). If your laser operates at 1 kHz (1000 pulses per second), and the average power is 5 W, then each pulse contains 5 mJ of energy. In general:

$$\text{Pulse Energy (J)} = \frac{\text{Average Power (W)}}{\text{Repetition Rate (Hz)}} \quad (5.2)$$

Measuring the pulse duration of an ultrafast pulse is more complex as you cannot simply look at it on an oscilloscope like you can for a nanosecond pulse, as the fastest oscilloscopes can only see pulses of around 10 ps duration - and these are prohibitively expensive. A thorough description of ultrafast pulse measurement is beyond the scope of what we're doing here, but some general principles are outline below. I can highly recommend www.swampoptics.com as a place to get some nice descriptions of different kinds of pulse measurement.

We must measure the pulse duration optically, and this is done by somehow interfering the pulse either with itself, or a different pulse, and recording the interference signal. Doing this by interfering the pulse with itself is called doing an **autocorrelation** - and will (after some processing) yield the pulse envelope which tells you the temporal width of the input pulse. You can buy commercial autocorrelators with associated software, or build your own without too much hassle. These are good for telling you if your pulse is short or not, but do not tell you the **sign** of the chirp - so you don't know if the pulse is positively or negatively chirped when trying to work out how to recompress it - and also contain no spectral information. A better step is to use techniques such as **Frequency-Resolved Optical Gating (FROG)** or **Spectral Phase Interferometry for Direct Electric field Reconstruction (SPIDER)**. These essentially produce spectrally resolved autocorrelations which contain much more information (like the phase of each frequency component), so can help you find the sign of the chirp and other things.

When we know the pulse duration and pulse energy, we can work out the **peak power** as:

$$\text{Peak Power (W)} = \frac{2 \times \text{Pulse Energy (J)}}{\text{Pulse Duration (FWHM) (s)}} \times \sqrt{\frac{\ln 2}{\pi}} \quad (5.3)$$

The peak power is the power delivered in each pulse. The additional constants arise due to the Gaussian temporal shape of the pulse - but taking Energy/Duration gives a reasonable first estimate. Peak powers on the order of 1×10^{14} W are not uncommon when using ultrafast pulses.

Finally, we must also measure the size of the beam at the location of interest. Possibly you are using an unfocussed beam in your experiment, so you could even just put some paper in the beam and draw some marks to estimate the size. More often, though, you will be using a focussed beam. The beams will generally have a transverse intensity profile that is well described by a 2D Gaussian function. You can measure this profile using a commercial beam profiler, or you can make a beam profiler out of a webcam - or you can scan a small pinhole or knife edge across the beam and measure the transmitted intensity. This last method gives the most accurate measurements in my experience.

As the intensity follows a Gaussian profile, defining the point where the beam 'stops' is important, as in reality it tails off gradually. Generally, this is taken to be the point where the peak intensity falls to $1/e^2$ of it's maximum value - this radius is the **beam waist**. Numbers for this are generally quoted as radii rather than diameters. Measuring this in both the x and y directions (for a beam travelling along z) will fully characterise the spot size. Typically an 800 nm beam focussed by a 300 mm focal length lens will focus down to a 35 μm beam waist. When you know the beam waist, then you can calculate the **fluence** (energy per unit area)

of the pulse:

$$\text{Fluence (Jm}^{-2}\text{)} = \frac{2 \times \text{Pulse Energy (J)}}{\pi \times (\text{beam waist})^2} \quad (5.4)$$

Again the additional constants arise due to the Gaussian pulse shape (temporal and spatial). Having found the fluence, we can finally calculate the **intensity** (power per unit area) of the pulse:

$$\text{Intensity (Wm}^{-2}\text{)} = \frac{2 \times \text{Fluence (J)}}{\text{Pulse Duration (FWHM) (s)}} \times \sqrt{\frac{\ln 2}{\pi}} \quad (5.5)$$

In a manner similar to the calculation of the peak power. This Gaussian intensity is generally what is reported in papers when people quote their laser intensities.

5.3 How Things Work

The last thing we will do is give a brief overview of how some of the laser systems used day-to-day in B2 work, so you know what you're talking about when an engineer comes or Michael asks you to check the oscillator spectrum.

5.3.1 Solstice Ace

The Spectra-Physics Solstice Ace is best regarded as a **laser system** rather than a single laser. Key specs of this laser are given in the table below. This laser

Central Wavelength	Bandwidth	Pulse Duration	Average Power	Rep Rate
800nm	60nm	35fs	5W	1kHz

system consists of a number of different individual lasers (at least four..) and other things too. A schematic of the overall system is shown in Figure 5.1.

Initially, very short, broadband pulses at 800 nm central wavelength are generated by the MaiTai, which is the **oscillator** in this laser system². This generates femtosecond pulses with a broad (60 nm) bandwidth, but which have a very low (~10 nJ) energy, so need to be amplified before they become useful. The laser medium is a Ti:Sa crystal, and the oscillator runs at a repetition rate of 80 MHz, and produces femtosecond pulses via a technique called **modelocking**.

²This oscillator is itself pumped by another laser!

A detailed description of modelocking is beyond the scope of this document, but it can be qualitatively understood as follows. We know that to produce a short pulse, we have to have many different frequencies oscillating with a fixed-phase relationship to one another. A laser oscillator is an optical cavity in which all of these frequencies resonate. If the laser is not modelocked, all of the different frequencies oscillate independently, and the laser does not emit short pulses. However, it is possible (through techniques such as *Kerr Lens modelocking*)³ to

³This essentially amounts to making sure that the cavity gain for the modelocked operation is greater than that for non-modelocked operation.

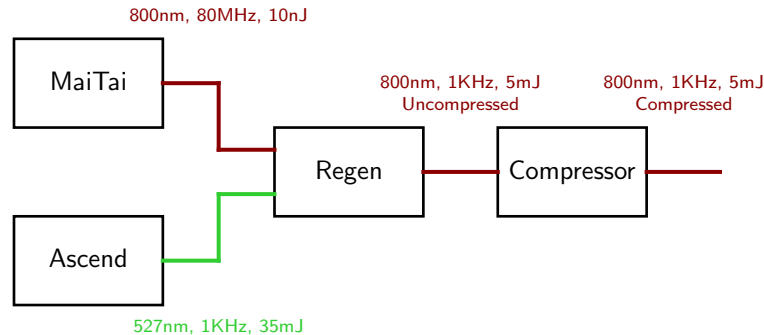


Figure 5.1: A schematic of the Solstice Ace system, showing the MaiTai (oscillator); Ascend (pump laser); regenerative amplifier; and compressor.

force the laser to operate such that the components have a fixed phase relationship. When this happens, the laser is said to be **mode locked**, and the output of the oscillator is a train of ultrashort pulses - as has been discussed previously and is shown on the cover of this document.

These pulses need to be amplified to be useful, and this is accomplished using a **pump laser**. In the Solstice, this is the 'Ascend' laser, which is a Diode-Pumped Solid State (DPSS) laser. This laser works largely as the four-level laser described in Chapter 1. The active medium is a rod of Nd:YLF⁴, and this rod is pumped by a laser diode, which produces laser emission at 1053 nm. These pulses are then frequency doubled to produce 527 nm pulses (this is the blinding green light you will see if you open the Solstice while it is on⁵). These pulses have a very high energy (35 mJ), but the pulses are very long (tens of nanoseconds).

These pulses are used as pump pulses in the main stage of amplification of our oscillator pulses, which happens in the **regenerative amplifier**, or **regen**. Initially the oscillator pulse is stretched in time (so it is no longer transform limited). The crystal is then pumped with green light to create the population inversion, and this is where the amplification takes place. The amplifier is placed in an optical cavity, so that when an oscillator pulse is injected it will resonate around the cavity making multiple passes through the (pumped) crystal, extracting more energy with each trip. At some point, it is then coupled out of the cavity using a thing called **Pockels cell**⁶. This is illustrated in Figure 5.2.

We mentioned that the pulse was stretched before entering the amplifier - this is because if the compressed pulse was amplified it would rapidly reach an

⁴Nd:YLF is preferred to Nd:YAG as it allows higher power and better beam quality - but is more fragile.

⁵Not advised.

⁶A Pockels cell is basically like an electrically controlled optical 'gate' which can let pulses in or out of the regen cavity.

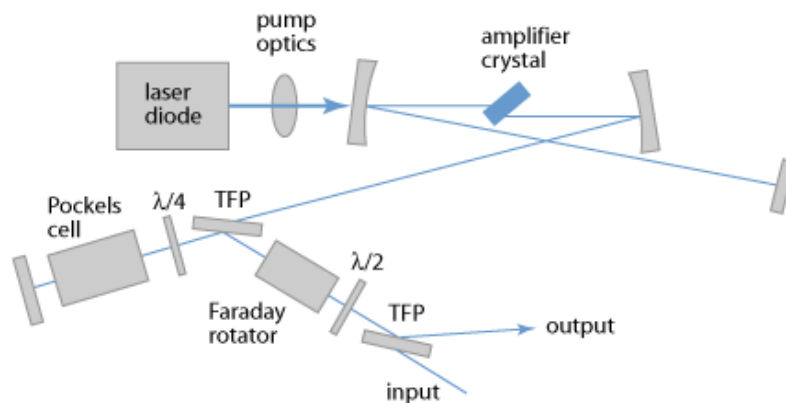


Figure 5.2: Schematic of a regenerative amplifier. The oscillator pulse is injected at the input, and the optics around there are to control the pulse injection/ejection. The cavity is formed between the TFP, the two curved mirrors, and the mirror on the far right. Figure from RP Photonics.

intensity where it would destroy all the amplifying optics! Stretching the pulse before amplification and recompressing it afterwards is the underlying principle of **chirped-pulse amplification**, which is what Donna Strickland and Gerard Mourou won the Nobel Prize for in 2018. Figure 5.3 illustrates the process.

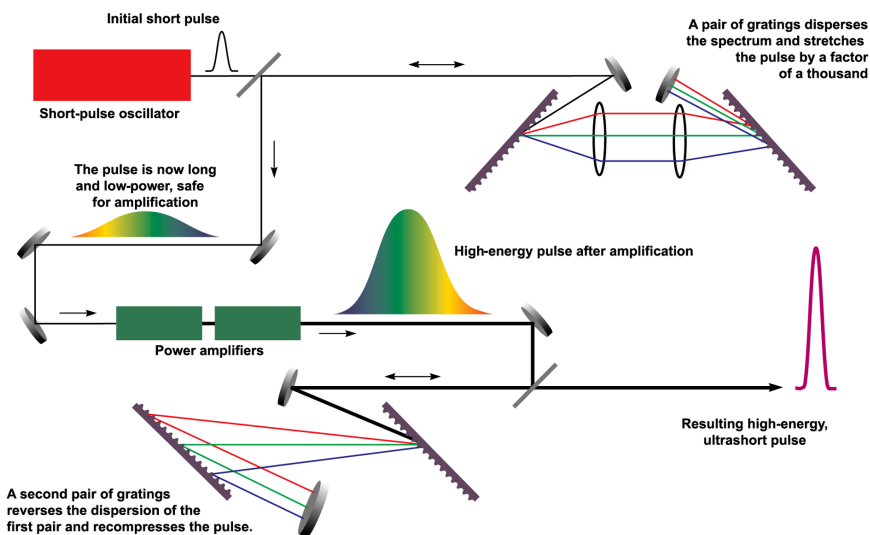


Figure 5.3: Schematic explaining the process of chirped pulse amplification. Figure from Wikipedia.

Then, it is fairly clear why we have a compressor after the regenerative am-

plifier - to recompress the long pulses to short pulses that we can use in our experiments. We can control the effect of the final compression gratings, so that the dispersion can be pre-compensated for. The final result is that we have a train of 800 nm, 35 fs pulses at a rep rate of 1 kHz.

5.3.2 TOPAS Prime and NirUVis

The other large part of the laser systems in B2 is the TOPAS OPA and NirUVis extension. The purpose of this system is to create tunable UV light from part of the Solstice output. The TOPAS itself generates output in the mid IR between 1160 nm and 2600 nm directly via optical parametric amplification (as discussed in Chapter 5). Following this, external frequency mixing of the signal/idler/both beam(s) permits a huge range of other colours to be created, ranging (in theory) from 190 nm to 20 μm . The tuning curves (pulse energy obtainable from a chosen output wavelength) are shown in Figure 5.4.

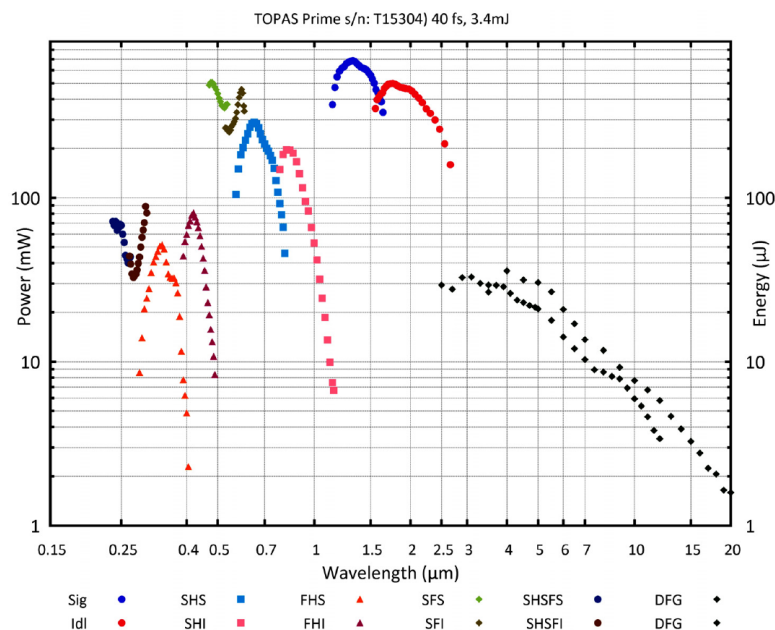


Figure 5.4: TOPAS tuning curves. Acronyms as follows: Sig = signal; Idl = idler; SHS = Second Harmonic Signal; SHI = Second Harmonic Idler; FHS = Fourth Harmonic Signal; FHI = Fourth Harmonic Idler; SFS = Sum Frequency Signal + Pump; SFI = Sum Frequency Idler + Pump; SHSFS = Second Harmonic of SFS; SHSFI = Second Harmonic of SFI; DFG = Difference Frequency Generation. Figure from TOPAS manual.

The inner workings of the TOPAS are comparatively simple compared to the Solstice - as it is not in itself generating laser pulses, but is pumped by 3.4 mJ

pulses supplied from the Solstice Ace. Essentially the TOPAS consists of a white-light generation (WLG) and two OPA stages based on BBO crystals. Initially, the input pump beam is split by an 95:5 beamsplitter, and the smaller fraction is directed onto an 80:20 beamsplitter. The smaller fraction of this is focussed into a sapphire plate which results in WLG via self-phase modulation - this white light has a very broad bandwidth. The white light is then focussed into the first OPA stage and overlapped with the larger fraction of pump beam from⁷. This results in parametric amplification of one of the colours in the white-light spectrum - and this colour is preferentially phase matched by tuning crystal angles.

⁷This overlap is non-collinear to allow easy separation and aid in tunability.

The weak beam of the desired colour is then directed into the second OPA stage, where the remaining 95% of the pump beam from is also directed⁸. This acts as a power amplifier and a signal and idler are produced at their final output power. The phase matching in the second stage is such that the signal and idler are polarised orthogonal to one another, which aids in separation of them in later stages.

⁸Now the overlap is collinear to maximise amplification

Having created the signal and idler beam, the NirUVis box is essentially just a big box of non-linear crystals that allows all kinds of frequency mixing of signal and idler beams to create the dizzying array of colours previously mentioned. In theory, this could all be accomplished using a relatively simple homemade setup, but the ease of tunability and separability of different colours make the NirUVis box a useful tool.