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Chapter

Fourier Transform in Ultrafast Spectroscopy

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Abstract

Laser technology allows to generate femtoseconds-long pulses of light. These light pulses can be used to learn about the molecules with which they interact. Consequently, pulsed laser spectroscopy has become an important tool for investigating and characterizing electronic and nuclear structure of protein complexes. These spectroscopic techniques can either be performed in the time or frequency domain. Both the time and frequency domain are linked by Fourier Transform (FT) and thus, FT plays a central role in optical spectroscopy. Ultimately, FT is used to explain how light behaves. It is used to explain spectroscopic techniques and enables the development of new techniques. Finally, FT is used to process and analyze data. This chapter thus illustrates the centrality of FT in ultrafast optical spectroscopy.

Keywords: Fourier transform, ultrafast spectroscopy, pulsed laser, wave packet, molecular dynamics

1. Introduction

The theoretical description of light and molecular motion using Fourier Transform (FT) dates back to a century ago, with the development of quantum mechanics and its famous relation to the uncertainty principle [1]. However, it is only since the early 80’s that FT found practical applications in molecular spectroscopy thanks to the development of femto-second pulsed lasers, which enabled the pioneering investigations of molecular dynamics in the femto-second regime by Prof. Zewail [2]. Ever since, the development in ultrafast laser systems has been closely followed by the development of new spectroscopic techniques. For example, lasers are now able to generate high harmonics radiations up to the soft X-ray regime and enables spectroscopies with an atto-second resolution [3].

The developments in lasers and spectroscopy techniques would however not be feasible without the use of FT. Indeed, time-resolved spectroscopy is the study of spectra (i.e. frequencies) over time. Thus, by linking the time domain to the frequency domain, FT provides the theoretical background to conceptualize the spectroscopic techniques. Furthermore, FT is used to describe short pulses of light as well as molecular motions, and how both, light and molecules, interact with each other. FT is consequently at the heart of ultrafast optical spectroscopy.

Optical spectroscopy is not the only type of spectroscopy that uses FT. The most well-known field that has been transformed using FT is probably that of nuclear magnetic resonance (NMR); where FT considerably reduced the acquisition time and resolution, to the point of rendering non-FT NMR techniques obsolete. Similarly, FT enhances optical spectrosopies by increasing the data acquisition...
speed and the amount of information acquired from the sample. In this sense, FT revolutionizes the field of optical spectroscopy.

The goal of this chapter is to appreciate the central role that FT plays in optical spectroscopy. In particular, this chapter focuses on femto-second spectroscopy because such systems are now commercially available and are becoming an essential tool to study molecular dynamics. In this aim, the first section illustrates how FT is used to model and characterize short pulses of light. The second section describes two increasingly common experimental techniques and how they make use of FT. The third section shows how FT is used to extract molecular dynamics from the acquired data. In order to remain accessible to non-specialist, this chapter takes a conceptual approach. The mathematical formalism and technical subtleties are left available in the different cited works.

2. Fourier transform in the experimental setup

With the recent development of laser technology, spectroscopic techniques have reached unprecedented precision. In particular, in the field of optical spectroscopy, the use of pulsed lasers allows to monitor chemical reactions as they are taking place. Commercially available ultrafast spectroscopic systems are now able to generate femto-second-long pulses of light. In this time scale, these setups enable researchers to investigate energy, electronic and nuclear dynamics of specific molecular and atomic structures. Such precision would however not be possible without a complete understanding of light and its manipulation. This section will thus illustrate the role that FT plays in conceptualizing and modeling light pulses.

2.1 Light pulse representation by FT

Light can be considered as an electro-magnetic wave [4]. As shown in Figure 1, a ray of light can be characterized by the amplitude of the (Real part of complex) electric field $E(x, t)$, its wavelength $\lambda$ or period $T$ of oscillation (which defines its color or energy), and phase $\phi$ (which is the shift of the oscillatory pattern of the electric field with respect to an arbitrary reference point).

Laser-light differs from sun light and common light bulbs by the phase and spectrum of the emitted wavelengths. In a laser, all wavelengths have the same

![Figure 1. Representation of light as an electromagnetic (plane) wave. $E_0$ is the amplitude of the electric field component, $\lambda$ is the wavelength in unit distance, $k$ is the wave vector in radiant per unit distance, $T$ is the period in unit time, $\omega$ is the angular frequency in radiant per unit time, $\phi$ is the phase shift in radiant; with $\lambda/T = \omega/k = c$, the speed of light, in vacuum. Re and Im stands for the real and imaginary part of the complex electric field.](image)
phase and belong to a narrow spectral range. Pulsed lasers differ from continuous lasers by the fact that they produced short bursts of light. These pulses are generated when laser-light is trapped in a cavity. The most popular pulsed lasers to date are based on a titanium-doped sapphire (Ti:S) crystal. The crystal is placed between two mirrors, which form a cavity [5]. The titanium atoms are continuously excited (typically, by a frequency-doubled 532-nm Nd:YAG laser) and relax by emitting a range of wavelength around 800 nm. One way to look at the emitted light being trapped in the cavity, of length $L$, is that each generated wavelength $\lambda$ that satisfies the condition $L = m \lambda / 2$, where $m$ is an integer number, creates a standing wave. The different standing waves will interfere with each other. They interfere constructively only in a restricted region of space, and destructively anywhere else, as illustrated in Figure 2. The highly localized oscillations represent a series of wave packets (WP) or pulses of light.

In a typical Ti:S cavity, the number of allowed modes (i.e. wavelengths emitted by a Ti:S crystal that satisfy the above standing wave condition) is in the order of $10^5$, which results in pulse duration of few 10’s of femto-seconds.

The time-evolution of each standing waves will displace the WP within the cavity as if it was traveling back and forth between the two mirrors [6]. Each time the WP goes through the Ti:S crystal, it will trigger the in-phase stimulated emission of the excited titanium atoms, which will add to the magnitude of the WP. From a particle point of view, the WP indicates the region of space where we have the highest chance of finding the actual photons that comprises this pulse of light. The photons travel together and bounce back and forth between the two mirrors of the cavity, and each time they pass through the Ti:S crystal, they stimulate the emission of new photons.

If one of the cavity mirrors is only partially reflective, it will allow the WP to leak out of the cavity, which generates a train of identical and equally spaced pulses. Each WP contains a range of frequencies (defined by the Ti:S crystal, also called the gain medium) that can be resolved via FT. The different frequencies produced within a cavity follow an approximate Gaussian distribution. The time-dependent Gaussian wave packet, $\psi(x,t)$, can be described by the FT of its spectral components as follow (excluding normalization factors):

$$\psi(x,t) = \int_{-\infty}^{\infty} A(k) e^{i(kx-\omega(k)t)} dk$$

(1)
with the Gaussian distribution:

$$A(k) = e^{-(k-k_0)^2/2\sigma^2}$$ (2)

and $\omega(k) = kc/n(k)$ for plane-waves, with $c$, the speed of light and $n(k)$, the index of refraction [4].

The WP, or pulse, is defined by its central frequency $\omega(k_0)$ and variance $\sigma^2$ (full width at half maximum (FWHM) = $2\sqrt{2\ln2} \sigma$). Typical Ti:S lasers produce pulses with a frequency of ~80 MHz and centered around 800 nm with a FWHM of ~35 nm [7].

Technically, in order to resolve the spectral components comprising the pulse, the pulse is passed onto a spectrometer. The spectrometer includes a grating that will reflect each wavelength at slightly different angle, as illustrated in Figure 3.

It is said that the grating performs a FT on the pulse [8] (Ch4.1), i.e. the temporal structure of the pulse's electric field, $E(t)$, is destroyed to allow the monitoring of its spectral components, $E(\omega)$. Both $E(t)$ and $E(\omega)$ are linked by FT as follow: [9].

$$E(\omega) = \int_{-\infty}^{\infty} E(t) e^{i\omega t} dt$$ (3)

2.2 FT limited pulse and characterization

As shown in Eq. (1), the FT links the duration of a pulse with its spectral component. A FT-limited (or bandwidth-limited) pulse is then defined as a pulse that has the minimum possible duration for a given spectral bandwidth. FT-limited pulses have a constant phase across all frequencies.

However, the air and the different optical components, through which the pulse propagates, have an index of refraction, $n(k)$, that affect each frequency differently, as indicated in Eqs. (1) and (2). By traveling through such dispersive medium the pulse broadens [4, 10]. For spectroscopic purposes, in order to achieve the best
temporal resolution, the phase of each wavelength that comprises the pulses must be manipulated so that the FT-limit is obtained at the sample position. As depicted in Figure 1, the relative phase between two light rays is defined as a difference in angle at specific time and position. Hence a phase shift can be introduced either by modulating the distance traveled by one of the rays or the speed at which the ray goes through a given medium. Consequently, different technique can be employed to obtain FT pulses. Most adaptive methods require to spectrally decompose the pulse so that the entire spectrum is split in narrow frequency ranges whose phase can be modified independently. In this aim, the pulse is passed onto a grating, which performs an FT on the pulse, as seen previously. Figure 4 shows that the diffracted beam will be recollimated and either be reflected by a deformable mirror, [11] or passed through a spatial light modulator (SLM) [12].

In the case of the deformable mirror, the phase of the light is modulated by displacing the surface of the mirror backward or forward by means of piezo-electric components, therefore retarding or advancing certain wavelength with respect to others. In the case of the SLM, the phase of the light is modulated by changing the relative orientation of each liquid crystal domains. The changes in orientation induce changes in refractive index of the medium, which, in turns, affects the speed at which the light travels through. Once modulated, the different spectral components are recombined by means of a second grating, which thus performs an inverse FT. Such adaptive methods are useful when the actual phase of the pulse in not known. When governed by (genetic or evolutionary) algorithms, they can achieve FT-limit by iteration, automatically [13]. Other passive methods will make use, for example, of grating and prism pairs, or chirp-mirrors to induce or compensate a pre-defined phase structure.

In order to characterize the actual pulse, any diffractive method will distort the actual phase and temporal structure. Hence, to retrieve these characteristics, a reference pulse is used, and both are made to interfere. The interference signal, which can be clearly distinguished from any background signals, contains information about both pulses. If the reference pulse is well-defined, the spectral components and relative phase of the other pulse can be deduced by means of FT. One of the most common methods employed is the frequency-resolved optical gating (FROG) [14]. FROG is a type of autocorrelation in the sense that the reference is played by the replicate of the actual pulse. However, the autocorrelation method implies that the reference is unknown and that the solution has to be guessed. In order to monitor the complex electric field of the pulse and its replicate in FROG, both are made to interact into a non-linear crystal (BBO). The response signal is then passed onto a spectrometer which performs a FT, as shown in Figure 5, so that the signal can be resolved spectrally.
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A spectrogram of the response signal is recorded for each time delay, $\tau$, to build a so-called FROG trace: a 2D time-frequency map of the non-linear signal intensity. In the case where the non-linear signal is the second harmonic (SHG FROG), the frequency and time dependent signal, $I_{\text{SHG FROG}}(\omega, \tau)$, can be fully written in the time domain via the FT expression as follow:

$$I_{\text{SHG FROG}}(\omega, \tau) = \left| \int_{-\infty}^{\infty} E(t) E(t-\tau) e^{-i\omega t} dt \right|^2$$  \hspace{1cm} (4)

with $E(t)$ and $E(t-\tau)$ being the time-dependent electric field of the pulse and that of its delayed duplicate (reference).

As mentioned, the reference is unknown and the exact solution for $E(t)$ and $E(t-\tau)$ that reproduces the specific FROG trace is retrieved by iterative algorithm guesses [14]. Fortunately, a typical FROG trace contains many more data points (and thus equations) than unknown variables, which means that the guesses are well informed. The conversion of the algorithm results in the retrieved spectral, temporal and phase information of the initial pulse. There exists variations of the FROG and other ways to characterize the temporal structure, phase and spectral component of ultrashort pulses of light, all of which will make use of FT [15, 16].

3. Fourier transform in data processing

Whenever a molecule is investigated by light, whether it is in the X-ray, ultra-violet, visible or infra-red regime, the desired information is often extracted by means of FT. In the field of spectroscopy, FT is either performed by using optical components, often through a grating, and/or numerically, after acquisition of the signal. In this section we will describe two types of UV-visible spectroscopy techniques in which FT plays a central role: absorption spectroscopy and 2D-FT electronic spectroscopy, also called photon echo or four wave-mixing spectroscopy.

3.1 Linear absorption spectroscopy

In (steady-state) absorption spectroscopy, the continuous probe beam acquires information about the sample by passing through it. The probe is modulated by
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the sample’s absorption. In order to visualize these spectral modulations, the probe beam is diffracted by a grating and the full spectrum is compared to a reference spectrum, as illustrated in Figure 6a. The comparison (log of the ratio) of both beams yields the absorption spectrum of the sample.

Similarly, in ultrafast transient absorption spectroscopy, the sample is probed by a short pulse of light, after excitation by the pump pulse, [17] as shown in Figure 6. Each probe pulse thus contains information about the excited states of the sample. If the duration of the pump and probe pulses is shorter than the relaxation or chemical reaction taking place, the probe will contain the information about that specific transient molecular state. The pulses are then FT by means of a grating and spectrally resolved. By varying the delay between pump and probe, we can spectrally resolve all intermediate states, from the instant of the excitation all the way to the recovery of the ground state. Since the delay between pump and probe can be precisely controlled (sub-femto-second precision) by simple elongation of the path of light (via a delay stage), the temporal resolution of the technique is limited by the duration of the pulses themselves (10’s of femto-seconds). In these time scales, we can monitor intra- and inter-molecular energy transfers, electronic transitions, charge transfer and molecular vibrations [18].

3.2 2D-FT spectroscopy

In comparison to pump-probe spectroscopy, which has only one excitation pulse, the desired photon echo in 2D-FT electronic spectroscopy is a result of three consecutive laser interactions with the sample. The photon echo is consequently called a third order signal, as shown in Figure 7a. The 2D-FT electronic spectroscopy is the ultimate third order experiment in the sense that it harvests the maximal amount of information about the sample given the number of excitation pulses [19]. In such experiment, the data is acquired, and the information is retrieved by a series of FTs.

The generation of the photon echo is conceptually similar to that of the free induction decay in pulsed NMR spectroscopy. However, due to the slow response of the detectors, direct recording of the photon echo would result in integrating its fast...
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oscillating electric field over time. This is called homodyne or integrated detection [19]. However, such configuration would not allow to retrieve the time and phase structure of the photon echo. Furthermore, the amplitude of the photon echo is typically weak and comparable to the noise amplitude [20]. In order to properly resolve the photon echo, it is made to interfere with a reference pulse called local oscillator (LO). The condition for interferences to take place is that both, the photon echo and the LO, are colinear, have similar spectrum and are within pico-second from each other. In such configuration, the photon echo is said to be heterodyned.

The heterodyned photon echo is then passed onto a spectrometer, which performs the first FT (via a grating) and is imaged, in the frequency domain, as depicted in Figure 7b. While the signal is FTed by the spectrometer, the detector does an intensity measurement, which corresponds to the square of the signal’s electric field. The monitored signal is now composed of 3 components: the (negligible) spectral intensity of the photon echo, that of the LO and the interference term that contains the desired information: the autocorrelation function [16] or spectral interferogram [19]. Once acquired, the interferogram signal is FTed from the frequency back to the time domain, as shown in Figure 7c: the FT of the spectral intensities of photon echo and LO gives signal around 0, while the interferogram gives signal at \( t_{LO} \) - the time delay between the two pulses.

By selecting the non-zero signal at positive times only (for causation), one can filter out most of the noise and retrieve, via FT, the phase and intensity of the photon echo at particular coherence time \( \tau \) and population time \( T \), as illustrated in Figure 7d. Incrementing the coherence time \( \tau \) enables to acquire the desired full 2D spectrum, for particular population times \( T \). The experience is then repeated for different population times in order to monitor the evolution of the 2D spectrum (Figure 7e).

In summary, the heterodyned FT technique allows to monitor weak signals, such as a photon echo, to filter out most noise contributions and to retrieve the desired temporal and phase information of the signal.

Figure 7.
(a) Scheme of a 2D-FT electronic spectroscopy in a so-called box-CARS geometry [21] with \( \tau \) being the coherence time, \( T \) the population time and \( t_{LO} \) the delay between the third pulse that triggers the emission of the photon echo and the local oscillator (LO). (b) Typical data acquired (from dye molecule). (c)–(e) Signal processing. FT\(^{-1}\) stands for inverse FT.
4. Fourier transform in data analysis

FT-based laser spectroscopic techniques enable to acquire first and third order responses, as seen previously, and even up to the fifth order optical response [22]. But the use of FT is not bound to the acquisition of the signals. Once the optical response signal of the sample is resolved over time, FT can also help analyze and extract the dynamics of the sample. In particular, when the duration of the laser pulses used are shorter than the oscillation period of the molecular vibration, one can resolve, using these techniques, the optical modulations caused by the vibration of the molecule. The use of FT thus helps distinguish between the different modes of vibration present in the optical signal, as illustrated in Figure 8.

Normal modes of vibrations in a molecule, in either the ground or excited electronic states, can be represented by Morse-like potential curves along the reaction coordinate [25]. In the inflection of each potential curve lies a stack of vibrational levels. In this picture, the molecule can be described by a time-dependent wave function. The amplitude of the square of that wave function forms a wave packet, as illustrated in Figure 8c. In this context, the spread of the WP represents the uncertainty of finding the molecule at a particular position along the reaction coordinate at a certain time [10].

We can picture this wave packet as traveling on a particular energy level back and forth along the reaction coordinate, as delimited by the Morse-like potential curve, i.e. the molecule vibrates [6, 10].

Typical UV–vis (steady state) spectroscopy probes all (vertical) transitions that can take place in between two vibronic (e.g. that involve vibrational and electronic) levels. Similarly, in ultrafast transient spectroscopy, the probe pulse interrogates the excited molecules and “sees” all transitions that are available to the traveling wave packet, at a specific time. The energy of a particular electronic transitions (e.g. from excited to ground state) thus fluctuates in time, as depicted in Figure 8c for the emission of an excited molecule. Similarly, the absorption of an excited molecule will also be modulated, depending on the relative position between the different electronic states.

Figure 8.
(a) Kinetic trace (for free-based tetraphenyl porphyrin excited by a 500-nm 40-fs pulse) and (b) its FT and corresponding Raman analysis. Possible representation of (c) wave packet (d) nuclear dynamics. * and **, the frequencies reported from transient absorption and resonance Raman experiments are taken from, [23, 24] respectively.
In molecules, it is often the case that a single laser pulse excites many normal modes of vibrations [25]. Accordingly, the amplitude of the probe signal reflects the oscillations of all WPs. The frequencies of each normal mode of vibration present in the probe signal can be extracted by means of FT.

In the case of molecules, the solvent and other molecular interactions imply that each molecule has slightly different vibrational energy levels, thus slightly different oscillation frequencies. Furthermore, each excited molecule will lose energy over time, which can be depicted by the WP going down the vibrational ladder within a particular electronic state. Differences in environment and vibrational relaxation will also modulate the frequency of oscillation. Hence, specific normal modes of vibration will lose their coherence and the oscillations present in the probe signal will be damped (Figure 8a). Competing with decoherence is the exponential decay of the excited state population. Both, the life time of the excited state and decoherence mechanisms restricts the monitoring of the wave packet dynamics, generally, to the first few picoseconds after excitation.

In practice, the oscillatory pattern is first extracted from the usually much larger population state signal via exponential fit of the kinetic trace. FT of the first few picoseconds is then performed on the residual signal to retrieve the different frequencies present (Figure 8b). The phase associated with each normal mode of vibration is indicative of the electronic state from which the oscillation originates [23]. Alternative fitting method such as the Linear Predictive Singular Value Decomposition (LPSVD) can also be used to extract damped oscillations [26]. The resulting amplitude spectrum of the FT or LPSVD power spectrum can then be compared to the low frequency Raman spectrum in the region around 200–400 cm\(^{-1}\) [23, 24]. It is worth mentioning that Raman spectroscopy usually does not resolve vibrations bellow 100 cm\(^{-1}\). Thus, the advantage of using kinetic traces to retrieve the normal modes of oscillations is to resolve vibration in the frequency range from 0 to 100 cm\(^{-1}\).

5. Conclusion

In conclusion, this chapter illustrates how FT helps conceptualize light and helps to characterize laser pulses. It is the use of these well characterized laser pulses that opens the door to time-resolved optical spectroscopy. FT is especially important in the field of ultrafast spectroscopy because it enables new types of molecular dynamic investigations. In brief, FT allows to resolve the spectral, temporal and phase information of optical response signals. While FT allows spectroscopic techniques to develop, from typical pump-probe to multi-pulse experiments, the data analysis is also enhanced by FT. In the case of molecules, for example, FT enables retrieval of the phase and frequency of molecular wave packets in a frequency range that is not accessible by other common tools. Furthermore, FT helps to distinguish between the different normal modes of vibration and assign them to specific electronic states. Because FTs are present in all stages of ultrafast spectroscopy, from conception to data acquisition and data analysis, FT is inherent to the field of ultrafast spectroscopy. Accordingly, FT helps to better understand and control the world in which we live.

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Conflict of interest

The author declares that there is no conflict of interest.

Other declarations

This chapter is dedicated to Dr. Joseph Salomon, who first introduced me to Fourier Transforms by showing me the diffraction pattern of a street lamp-post through the grid of my bedroom's curtains, while I was a child.

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