An Introduction to the Technique and Applications of Pump-Probe Spectroscopy

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INTRODUCTION:

Many processes in the natural world occur on very fast time scales including atomic motion during chemical reactions, molecular vibrations, photon absorption and emission, and many scattering phenomena. Some of these processes even occur on time scales as short as a few picoseconds (10^{-12} s) or femtoseconds (10^{-15} s). Observation of these fast processes is essential to fully understanding the dynamics of various excitations in matter, which has provided motivation for great advancements in the accuracy of time-resolved measurements in the past several decades.

To accurately measure ultrafast processes, the uncertainty in timing must be smaller than the time scale of the process, requiring temporal resolution on the order of 10^{-15} s. Early time-resolved measurements reached a temporal resolution on the order of milliseconds through use of the stopped-flow method [1]. This method was used to study chemical reactions and involved letting a solution flow into an observation cell for short time periods. The next generation of time-resolved experiments improved the resolution up to the order of microseconds by use of a flash photolysis method [2]. However, in the mid-twentieth century, the time-resolution of fast dynamical studies plateaued due to limiting factors of detectors such as fast photodiodes and stroboscopic oscilloscopes, which only posses temporal resolution on the order of 10^{-10} s [3].

To circumvent the limitations of detectors, a fundamentally different approach toward time-resolved measurements was conceived. The technique, know as pump-probe spectroscopy, involves observing the state of a process indirectly through observation of a "probe" laser pulse. Pump-probe spectroscopy has become a prominent method for time-resolved studies and has lead to advancements in many scientific fields.

EXPERIMENTAL TECHNIQUE

The first step in performing pump-probe measurements is to use a beam splitter to split a laser pulse into a 'pump' pulse and a 'probe' pulse (Fig. 1). Each of the two pulses approach the sample on different paths determined by the experimenter through placement of mirrors.
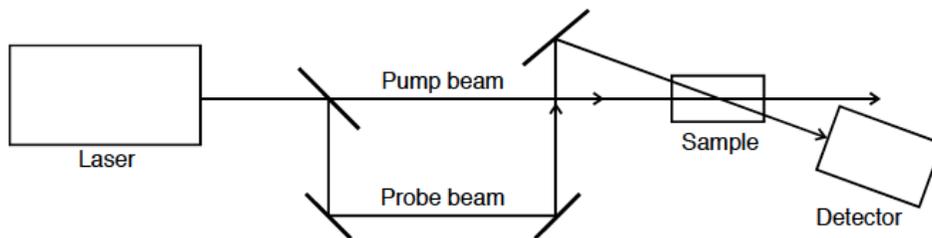
Figure 1: Pump-probe spectroscopy setup. The laser is split to pump and probe beam. The pump beam excites the sample. The probe beam interacts with the sample and then is detected. [3]

As pump-probe spectroscopy is a tool to study dynamical processes, the physical system must be perturbed from an equilibrium state. This is accomplished through the pump pulse,

which must travel along a shorter path in order to reach the sample first. The pump pulse interacts with the sample and can be manipulated in many ways including energy, intensity, polarization and duration in order to excite the sample in the desired way. As an example of this process, consider electron energy levels in an atom. If the pump pulse energy is equal to the energy difference between two levels, the atoms in the sample will absorb photons in the pump pulse causing an increase in the population of electrons in the higher energy level.

Some time after the pump pulse has perturbed the sample, the probe pulse reaches the sample. The delay between the pump and probe pulse is controlled by changing the path length difference between the pump and probe pulse, giving a delay described by $dT = dX/c$, where dX is the path length difference. The optical mirrors can be mounted on translation stages to allow easy variation of path length difference.

The probe pulse is measured with a detector after it has interacted with the sample (Fig. 1). Observing the modulation of the probe pulse after it has interacted with the sample is key to deducing the physical state of the sample as it decays back to an equilibrium state after the perturbation from the pump pulse. In the example of excited electrons in the atom, if many electrons are still in the excited state by the time the probe pulse arrives, most of the probe pulse will be transmitted rather than absorbed. However, if many of the electrons that were previously excited by the pump pulse have already decayed by the time the probe pulse arrives, most of the probe pulse will be absorbed since many electrons reside again in the lower energy state. Thus, measuring the intensity modulation of the probe pulse as a function of delay will describe the population dynamics of the electron energy levels.

By employing this method, temporal resolution is no longer limited by the detector, but by the duration of the laser pulse: if some of the probe pulse was absorbed by an excitation in the sample, we know that this absorption had to occur during the time the pulse was present in the sample. Thus, if the pulse duration is very short, there is a very short time interval in which the absorption event could have taken place.

TECHNICAL DETAILS

The main technical challenge present in the method of pump-probe spectroscopy and today's limiting factor in improving time resolution lies in the generation of ultrafast laser pulses. In the early 1960's, laser pulses with a duration of 10 milliseconds could be generated. During this time, the Q switching technique was developed and reduced the laser pulse duration by a factor of 10^4, allowing the creating of nanosecond pulses [4]. The technique of Q switching involves controlling the ratio of energy stored to energy loss in the optical cavity of a laser. This technique made great advances, but was limited to pulses of tens of nanoseconds because of required pulse build up time.

In 1964, the generation of shorter laser pulses on the order of femtoseconds was made possible by the development of the mode-locking technique [5]. A description of the principle of mode-locking requires first a basic outline of the design of lasers.

Lasers consist of an 'active medium' that absorbs and emits light, enclosed and each end by two highly reflective mirrors (Fig. 2).
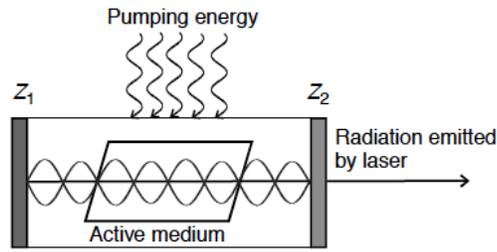
Figure 2: The optical resonator consists of an active medium surrounded by two mirrors, Z_1 and Z_2. The active medium is excited with pumping energy. Certain frequencies of light emitting from the active medium exist as standing waves in the cavity. [3]

The active medium and optical mirrors are called the optical resonator. To create intense, coherent light laser light, electrons within the active medium are first excited to higher energy levels by the application of an energizing pump. This pump is usually another light source and can include a large range of frequencies. The active medium will emit light as electrons drop down to lower energy levels via spontaneous and stimulated emission. Emitted light from the active medium with wavelengths that satisfies equation 1 is reinforced as standing waves between the mirrors where L is the length of the cavity and n is an integer.

$$\lambda = \frac{2L}{n} \qquad (1)$$

These modes that are sustained as standing waves become intensified because the light waves through the active medium results in even more stimulated emission, causing a chain reaction. As a result of this process, laser light is composed of several reinforced, intense optical modes described by equation 1.

The technique of mode-locking involves a manipulation of the phases of the different modes that are present within the optical resonator. Without mode-locking, the emitted laser light is just a statistical time-average of all the modes at random phases, and coherence is just observed within each mode individually. Mode-locking forces all modes to become in phase. As shown in Fig. 3, a superposition of coherent waves of different frequencies results in pulses.
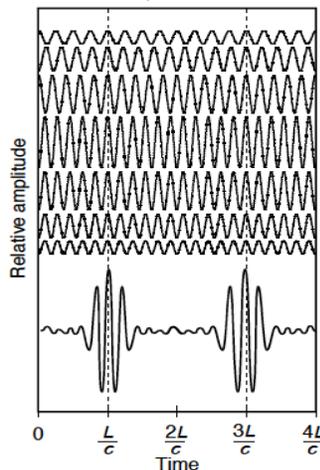
Figure 3: Modes of different frequencies are made to have the same phase and summed to give pulses. [3]

To induce a mode-locked state, parameters of the optical resonator must be modulated at a frequency equal to the difference in frequency of neighboring modes present in the resonator. From equation 1, frequencies of modes in optical resonator are described by

$$\omega_o \pm n\Omega \tag{2}$$

where ω_o is the fundamental frequency, $n = 1$ mode.

There are a number of methods to modulate the optical resonator including the use of saturable absorbers that modulate the amplification factor of active medium and the use of acousto-optic devices that modulate the density of the active medium. To further elaborate on the implementation of mode-locking, the acousto-optic technique will be outlined.

In acousto-optic mode-locking, a sound wave is applied to the active medium perpendicular to the incident pumping light source (Fig. 4).
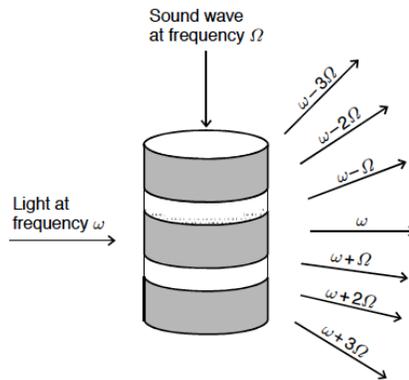
Figure 4: To induce mode-locking, a sound wave penetrates the active medium. The light interacts with the sound in such a way as to emit modes equal to those of the resonant cavity. [3]

The light source interacts with the sound as described by the Debye and Sears effect. The sound wave alters the density of the active medium, which thereby locally alters the index of refraction throughout the medium. The variation of the index of refraction modulates the frequency of the light, and waves of frequencies of equation 2 are emitted. The regions of low density are analogous to slits of a diffraction grating, and the emitted light has an angular dispersion similar to light subject to a diffraction grating. By choosing the sound frequency to be Ω, the new modes generated through interaction with the sound are the same frequency of the optical modes present in the resonant cavity. The light modes that are generated from interaction with the sound overlap and couple to the modes of the optical resonator resulting in coherence among all modes.

Over past decades, the mode-locking has been fine-tuned to allow researchers to now achieve pulses on the order of attosecond (10^{-18}) duration.

THEORETICAL DETAILS

Pump-probe spectroscopy falls under the realm of non-linear optics, which is a field that encompasses optical properties of non-linear materials. In non-linear materials, the optical properties of the material depend on an incident light field. For example, an index of refraction of a material could be specific to properties of the incident light.

In non-linear materials, the dielectric polarization, *P*, responds non-linearly to an electric field, *E*.

$$P = \chi^{(1)}E + \chi^{(2)}E^2 + \chi^{(3)}E^3 + \cdots \tag{3}$$

The electric field of a light wave makes electrons oscillate around the ions in a solid. For small electric fields, the electrons oscillate like harmonic oscillators (linear regime). However, for large electric fields, such as intense laser light, the electrons no longer oscillate in the linear regime.

PUMP PROBE SPECTROSCOPY APPLIED TO INDIRECT EXCITONS

A recent study using pump-probe spectroscopy was completed on a system of direct and indirect excitons [7]. A direct exciton (DX) is a quasi-particle that consists of a bound electron and hole pair, which is formed when a semiconductor absorbs light. An indirect exciton (IX) consists of an electron and hole confined to spatially separated quantum wells (as opposed to DXs which have their electron and hole in the same quantum well) (Fig. 5). Indirect excitons possess several unique properties including a built-in electric dipole moment, long lifetimes, and the ability to form a quantum Bose gas.

This experiment demonstrated the possibility of studying IXs with non-linear optical methods. Studies with non-linear optical methods, such as pump-probe spectroscopy, can only be performed on physical systems possessing high oscillator strength; the oscillator strength characterizes the ability to couple to light, i.e. absorb and emit. Due to the spatial separation of the electron and hole in IXs, they are not easily generated with light and do not easily recombine to create light, resulting in low oscillator strength. However, in DXs the electron and hole are near to each other and the DXs couple well to light. Signals of the probe modulation are proportional to the square of the oscillator strength. Thus, many non-linear optical measurements have been carried out on DXs, but IXs had remained unstudied by these methods due to the difficulty of measuring such small signals.

Recent theoretical work proposed a method for measuring dynamics of IXs with non-linear optical spectroscopy despite the low oscillator strength [6]. The principle of the proposed method lies in the fact that a population of IXs will affect properties of DXs—the experimenter can measure IX population dynamics indirectly by observing the modulation of DX properties that are detectable with pump-probe spectroscopy.

A population of IXs can affect properties of DXs in three ways. The IXs can interact with the DXs through the coulomb interaction, which will result in an increase of the DX energy due to electrical repulsion. IXs can also affect the recombination rate of DXs by phase space filling; IXs take up electron and hole positions in phase space that DXs could otherwise transition to. IXs can also affect non-radiative decay of DXs through scattering effects. The IXs can screen disorder in the sample that DXs would otherwise scatter off of. All of these effects can be calculated quantitatively [6] and be fitted to experimental results to determine which interactions are the most prominent.

The experiment carried out in [7] is a realization of this proposed method. In this experiment, two measurements were performed: intensity modulation of the probe pulse (photoinduced reflectivity) and polarization modulation of the probe pulse (kerr rotation) after reflection. The sample used was a layered semiconductor with two quantum wells (Fig 5).
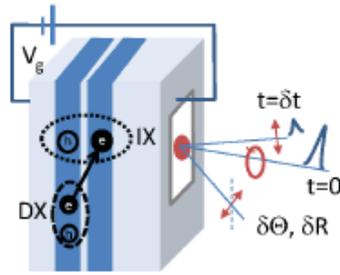
Figure 5: A pump pulse is applied to a layered semiconductor sample. IXs and DXs interact with a probe pulse and the reflectivity and kerr rotation are measured. [7]

In addition to demonstrating the possibility of applying non-linear optical spectroscopy to IXs, this experiment also aims to measure the population and spin dynamics of optically active (bright) and optically inactive (dark) IXs. The reflectivity of the probe pulse as a function of time was measured to describe the population of IXs and DXs. The polarization of the probe pulse was measured to describe the spin polarization of the IXs and DXs (Fig. 6).
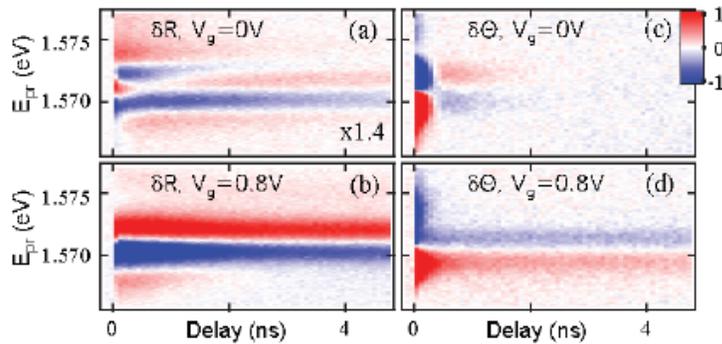
Figure 6: Reflectivity and kerr rotation of probe pulse as a function of probe pulse energy for many delays at two gate voltages. [7]

In Fig. 6, red corresponds to a probe signal higher than if there were no pump pulse and purple corresponds to a probe signal lower than if there were no pump pulse. V_g corresponds to a voltage applied across the sample which changes the energy of IXs as IXs are oriented dipoles. For each delay, the reflectivity and kerr rotation amplitudes for different probe energies can be analyzed (Fig. 7).
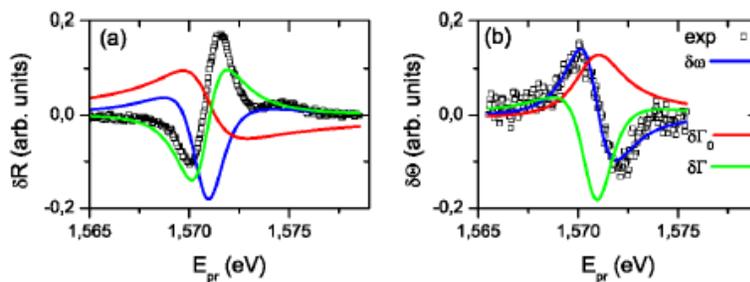
Figure 7: The experimental data is fit to theoretical calculations to determine which interactions between IXs and DXs are the most prominent. [7]

The experimental data is fitted to the theoretical calculations of the reflectivity and kerr rotation due to each of the three possible interactions between IXs and DXs. The blue curve represents interactions due to coulomb repulsion. The red curve represents interactions due to phase-space filling. The green curve represents interactions due to scattering effects.

This experiment demonstrated a proof of the theoretical concept of measuring IXs via DXs in non-linear optical spectroscopy. This result is of interest to scientist in this field because it provides a method of studying optically inactive IXs, which are normally difficult to detect.

CONCLUSION

The high temporal resolution that is reached by the method of pump-probe spectroscopy has opened doors to new experiments describing the dynamics of ultrafast processes. Ultrafast lasers developed for the purpose of time-resolved studies are also finding applications in other fields of research such as energy production and astrophysics. It is even thought that ultrafast intense laser pulses could mimic conditions inside star centers [3]. Ultrafast lasers continue to be improved and pump-probe spectroscopy remains a useful tool to study ultrafast dynamics of physical systems.

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