Ultrafast photoinduced dynamics in an Heisenberg antiferromagnet probed by Femtosecond Stimulated Raman Scattering

Relatore: prof. Tullio Scopigno

Candidato: Nicola Di Palo
Matricola: 1206071

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Nicola Di Palo

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Chapter 1

Introduction

Modern physics moved forward in leaps and bounds thanks to impressive technological progress in the last decades. The introduction of laser sources as powerful tools to study the world around us paved the way to the comprehension and the observation of many physical processes in lots of different research areas, from the solid state or particle physics, to biology, chemistry and so on.

One of the principal targets of modern science is the observation of dynamics which are not perceptible by eye. The most part of physical, chemical or biological processes manifesting on macroscopic time scale are mainly the results of elementary phenomena like interaction between electrons or atoms, formation or breaking of chemical bonding and so on. These processes take place on the atomic length scales ($\approx 1 \times 10^{-10} m$), with atoms moving at $\approx 1000 m/s$, resulting on effects taking place on the femtosecond time scale ($1 fs = 10^{-15} s$).

The experimental approach used for this time-resolved studies is the so called Pump-Probe technique, in which the system usually interacts with two light pulses. The first, called pump, prepares the system in a non-equilibrium state, while the second probes it at controlled time delays (that is why it is called probe).

In order to follow sub-picosecond dynamics with an acceptable resolution, methods based on electronic synchronization of different pulses are too slow, since they do not exceed the $\mu s$ timescale. The introduction of ultrafast pulsed lasers, which pulse duration can reach the femtosecond time scale for commercial laser sources, led to the implementation of methods based on the optical synchronization of such ultrafast light pulses. Processes such as isomerization, bond breaking and recombination, energy redistribution upon excitation of short living intermediates are only some examples of all the possible ultrafast phenomena studied in the recent times.
In solid state physics, for example, one of the most active research fields is the so called ultrafast magnetism. The manipulation of the macroscopic phases of solids by means of ultrashort light pulses has resulted in spectacular phenomena, like laser-induced metal to insulator transition [1, 2], superconductivity [3] and sub-picosecond modification of the magnetic order [4]. The comprehension and the development of this research area depend strongly on the understanding of the optical control of fundamental interactions in condensed matter.

Some of the processes mentioned above, for example bond breaking and recombination in organic compounds or magnetic order modification in crystals, are strictly related to variations of the system structure out of equilibrium states, often related to vibrational dynamics. One of the most used experimental techniques to study vibrational features is the Raman Spectroscopy, which is based on the anelastic scattering of light with vibrating atoms or molecules when passing through a medium. The comprehension of temporal evolution of transient Raman spectra often allows the understanding of structural dynamics.

I developed my thesis project in Femtoscopy lab at Physics Department of University "La Sapienza" of Rome, in collaboration with Opto-Magnetism group of Radboud University in Nijmegen led by prof. A. Kimel. The aim of this work was to study the presence of sub-picosecond photoinduced dynamics in an antiferromagnetic system, a crystal of Potassium-Nickel-Fluoride compound. The study was led by means of an experimental technique developed in the last ten years called Femtosecond Stimulated Raman Scattering (FSRS). This is a pump-probe Raman-based technique which is able to follow vibrational dynamics with very high temporal and spectral resolution.

This work is structured as follows:

In the first Chapter there is description of the general scheme of FSRS and the presentation of the sample with its main features.

In Chapter 2 theoretical background for Femtosecond Stimulated Raman Scattering is provided.

In Chapter 3 there is the description of the experimental setup.

In Chapter 4 experimental results of FSRS on $KNiF_3$ are shown.

In Chapter 5 an interpretation of the main results will be given.
1.1 The Raman effect

The Raman effect is an inelastic scattering of incident light photons which involves the generation of new output frequencies due to light-matter interaction. It was first discovered by Sir C. V. Raman [5] and G. Landsberg and L. Mandelstam [6] independently. When light is incident on matter, the majority of photons are scattered elastically and do not change their frequency. This process is known as Rayleigh scattering. However, a very small fraction of the incident photons are scattered inelastically, increasing or lowering their energy in the interaction with matter, and so changing their output frequencies (i.e. colors). The latter is known as Raman scattering [7].

![Figure 1.1: A graphical representation of the Raman effect: a portion of the incident light can be reemitted with different colors!](image)

The nature of this effect can be explained, in first approximation, on a classical base. Suppose to have a single molecule interacting with an external monochromatic field of given frequency $\omega$, expressed by $E(t) = E_0\cos(\omega t)$. This field will induce in the molecule a dipole moment given by:

$$P(\omega, t) = \alpha(\omega)E_0\cos(\omega t), \quad (1.1)$$

where $\alpha(\omega)$ is the polarizability tensor of the molecule. This oscillating dipole moment will emit electromagnetic radiation with an average intensity

$$I \propto |\frac{d^2P}{dt^2}|^2 = \omega^4\alpha^2(\omega)|E|^2. \quad (1.2)$$

Generally, the molecule is in motion because of the activation of its internal motions, i.e. vibrations, rotations. If we now consider only the possibility to have vibrational motion for this molecule, it will modify the polarizability
tensor, that can be expanded in power series of vibrational coordinates $Q_i$:

$$\alpha = \alpha_0 + \sum_k \left( \frac{\partial \alpha}{\partial Q_k} \right)_0 Q_k + \frac{1}{2} \sum_{k,l} \left( \frac{\partial^2 \alpha}{\partial Q_k \partial Q_l} \right)_0 Q_k Q_l + \cdots$$  \hspace{1cm} (1.3)

where 0 subscript indicates equilibrium configuration. Using the harmonic approximation, equation of motion for vibrational variables $Q_k$ is

$$\frac{d^2 Q}{dt^2} + 2\gamma \frac{dQ}{dt} + \omega_k^2 Q = 0$$  \hspace{1cm} (1.4)

whose solution, without the damping term, is $Q_k = Q_{k0} \cos(\omega_k t + \delta_k)$, with $\omega_k$ being the frequency of the k-th vibrational mode of the molecule. In the linear approximation, first order of the series, we get for the polarizability tensor

$$\alpha_k = \alpha_0 + \alpha'_k Q_{k0} \cos(\omega_k t + \delta_k),$$  \hspace{1cm} (1.5)

where $\alpha'_k = \left( \frac{\partial \alpha}{\partial Q_k} \right)_0$. Inserting last expression in 1.1, using prosthaphaeresis formulas, it is possible to write for the induced dipole moment

$$P_{TOT}(\omega) = \alpha_0(\omega) E_0 \cos(\omega t) + \frac{1}{2} \alpha'_k Q_{k0} [\cos(\omega t + \omega_k t + \delta_k) + \cos(\omega t - \omega_k t + \delta_k)].$$  \hspace{1cm} (1.6)

It is clear from the last expression that the induced dipole moment has different oscillating contributions:

- $P(\omega)$, which produces radiation at the incident light frequency $\omega$ corresponding to Rayleigh scattering;
- $P(\omega - \omega_k)$, producing radiation at a frequency lower than the incident, which accounts for Stokes Raman scattering;
- $P(\omega + \omega_k)$ which produces radiation at an higher frequency, accounting for Anti-Stokes Raman scattering.

All molecules exhibit Rayleigh scattering, because all the molecules are polarizable to a greater or lesser extent, $\alpha_0$ will always have some non-zero components. The corresponding necessary condition for Raman scattering associated with a molecular frequency $\omega_k$ requires that at least change in one of the tensor components of the derived polarizability tensor $\alpha_k$ with respect to the normal coordinate of the vibration $Q_k$, must be non-zero at the equilibrium position. It should be noted that induced dipoles $P(\omega \pm \omega_k)$ are shifted in phase relative to the incident field by $\delta_k$, this quantity being different for each molecule.
Figure 1.2: Typical example of Spontaneous Raman spectrum: at the center there is the Rayleigh signal, at the incident laser frequency. At higher and lower frequencies very sharp vibrational peaks are visible. Stokes lines (red) show higher peaks respect to Anti-Stokes lines (blue) for the linear dependence on the concentration, ruled by the Boltzmann factor.

Although classical theory discussed above provides qualitative information about Raman scattering, it is unable to provide quantitative informations on the magnitude of $\alpha_k$ as well as the vibrational frequencies related to the properties of the scattering molecule. The quantum mechanical theory provides this information and forms the basis for a complete treatment of all aspects of Raman scattering. This treatment reveals Raman scattering as a tool for spectroscopy.

Both Stokes Raman scattering and anti-Stokes Raman scattering are called Spontaneous Raman scattering. In Stokes scattering, the population of the ground state is transferred into excited states, whereas in anti-Stokes scattering, the population of vibrational excited states (for high temperature samples that have considerable population in these states) is transferred to the ground state. The intensity of spontaneous Raman scattering is linearly proportional to the concentration of the sample and reflects the population of the energy states.

Because the position of the vibrationally excited states determines the frequency-shift between the incident light and Raman scattering photons, the spectrum of spontaneous Raman contains informations about the energy level structures of the sample. This spectroscopic method is called Raman
Spectroscopy. And the frequency difference between incident and scattered radiation is called Raman shift. Raman shift is independent of the frequency of the incident light, it is constant and characteristic of the sample molecule.

1.1.1 Spontaneous vs Coherent processes

To understand at all limits and strengths of this spectroscopic technique, it is useful to list pros and cons of using Spontaneous Raman [7]. Among the advantages, there are:

- the possibility to use it as a chemical selective tool, because it addresses directly to the vibrational structure of the system;
- both polar and non-polar molecules exhibit Raman transitions, while it is not possible to study the latter with absorption spectroscopy, since the latter is related to electric dipole transitions;
- the range of frequencies used for Raman experiments is arbitrary, since the output signal frequency depends only on the excited vibrational frequency;
- to get higher spatial resolution, Raman spectroscopy usually involves radiation in the UV-visible range rather than the infrared region.

On the other side, Raman spectroscopy has to face some annoying issues. The main disadvantage is that it is a process with a very small cross section, producing very weak signals. Its cross section is in general several orders of magnitude smaller than the fluorescence emission, another optical process occurring in the same range of frequency that can easily overwhelm Raman signals. Furthermore, it is an incoherent process: each emitting dipole bear an arbitrary value of the phase \( \delta_k \), the system being an assembly of molecules emitting light with random phases. The output signal will be an incoherent radiation spread in a \( 4 \pi \) steradian solid angle.

Finally, this technique has a serious limitation in time resolved spectroscopy. When studying ultrafast dynamics, it is necessary to have probing pulses whose duration must be quite shorter than the time scale of the physical processes involved. If on one side it is now possible to use pulsed lasers with very short time duration (tens of fs), in Raman spectroscopy you have to face the Fourier transform limit, which relates temporal and spectral resolution of the spontaneous Raman spectra with

\[
\Delta E \cdot \Delta t \geq 15 cm^{-1} ps, \quad (1.7)
\]
so, it is not possible to go below the picosecond time scale without facing a really bad spectral resolution.

It is possible to overcome these issues by means of Coherent Raman spectroscopy. Coherent techniques are based either on the coherent excitation of the target atoms or molecules or on the superposition of coherently scattered light from the target atoms or molecules [8]. Laser pulses can excite coherently and establish a definite phase relationship among the amplitudes of atomic or molecular wavefunctions of the target atoms or molecules. Such a definite phase relationship in turn determines the total amplitude of the scattered, emitted or absorbed radiation. In addition the spatial coherence of the incident laser pulse also creates a definite spatial distribution of the coherently excited molecules. This ends up with a spatial coherence in the scattered signal leading to a directional signal. Such property constitutes the main difference between Coherent Raman process and its incoherent counterpart, Spontaneous Raman.

Coherent Raman Spectroscopy (CRS) techniques can be considered as twostep processes. In the first step, a set of multiple laser pulses centered at different optical frequencies, but whose combination matches the vibrational frequency of the target molecules, is incident on the sample and generates a vibrational coherence state in the molecules. These coherent collective induced vibrations in the first step prepare the sample for the second step.

Figure 1.3: Macroscopical difference between incoherent (left) and coherent (right) process: randomly oriented waves produce a much weaker signal respect to a coherent superposition.
Under this criterion the difference between spontaneous Raman and CRS is that in spontaneous Raman, the target molecules are vibrating randomly in phase, while in CRS, after the first step, target molecules are vibrating coherently.

In analogy with the spontaneous Raman effect, in the second step of CRS, another laser pulse usually called probe pulse, either at the same frequency of one of the first-step laser pulses or at a different frequency, interacts with the sample and modulates the vibrational coherence generated in the first step. At the output we detect the beat frequencies between the vibrational resonance frequency and the probe pulse frequency to identify the presence of the target molecules. Thus, in CRS, at least two laser photons, called pump ($\omega_p$) and Stokes ($\omega_s$) respectively, whose frequency difference ($\omega_p - \omega_s$) matches a molecular vibration, are needed in the first step, and a third laser photon, either degenerate or not with respect to the former pair, is needed as a probe ($\omega_{pr}$) in the second step. The whole mechanism generates fourth photon ($\omega_p - \omega_s + \omega_{pr} = \omega_{CRS}$). It implies that CRS processes are a kind of four-wave mixing (FWM) process, driven by non-linear response of the material. In the second chapter a theoretical treatment of non-linear optical processes is presented, with a strong accent on four wave mixing and the case of Stimulated Raman Scattering, introduced in the next lines.

Figure 1.4: Overview of most known coherent Raman Scattering processes.
1.1.2 Broadband Stimulated Raman Scattering

Among the different Coherent Raman processes, a particular mention goes to *Stimulated Raman Scattering* process (SRS), which constitutes the core of our experimental technique. In this process, two different light pulses, namely a *Raman pump* and a *Stokes pulse*, are incident on the sample, whose frequency difference usually matches at least one vibrational frequency of the system, \( \omega_R - \omega_S = \omega_{\text{vib}} \).

The reason of the adjective *Stimulated* stands for the fact that the total electric field interacting with the sample

\[
E(r, t) = E_{\text{Raman}}(r, t) + E_{\text{Stokes}}(r, t)
\]

participates to the Raman process as a driving force in the equation of motion for the oscillating molecules 1.4

\[
\frac{d^2Q}{dt^2} + 2\gamma \frac{dQ}{dt} + \omega_k^2 Q = \alpha_k |E(r, t)|^2,
\]

whose solution gives the output signal of SRS process. In the next chapter a semi-classical approach will be shown to calculate the response of SRS.

As all the CRS processes, it is a third order optical process in which there are two interacting fields and the output signal occurs at the same frequency of the probe (Stokes), because of energy conservation. The process is said to be self phase-matched, for the momentum conservation, and the output signal is emitted collinearly to the probe, so the detection occurs in a small solid angle. The result is an higher cross-section respect to the Spontaneous case, which is no more overwhelmed by the fluorescence emission.

A particularly powerful implementation of SRS is the so called *Broadband Stimulated Raman Scattering*. It is obtained by broadband Stokes pulse *(short in time)* and a narrowband Raman pump *(long in time)*. The Raman pump has usually a time duration of few picoseconds and a very narrow spectral width \((0.1 \div 1 \text{ cm}^{-1})\); when \(\omega_R\) is tunable, it can be set in correspondence of an electronic resonance to exploit significant enhancement of the *Resonant Raman Scattering*. The Stokes pulse is usually a white light continuum *(sometimes called WLC)* with a time duration of tenth of femtosecond. In the third chapter the generation of similar pulses will be explained in details.

Several advantages occur with these features: the frequency difference between Raman and Stokes now can match more than one vibrational mode, being the Stokes a white light continuum, resulting in simultaneous excitation of different Raman modes. Tuning the Raman frequency and the time delay between the two pulses it is possible to get very sharp Raman spectra with surprisingly high intensities.
In this pulse configuration, Raman features appear as positive or negative gain on the top of the probe pulse, the white light continuum, clearly shown in figure 1.5, 1.6. For every frequency component of the Stokes which satisfy the matching condition with a vibrational mode, a Raman gain appears. To have a clearer view of the Raman peaks, it is usual to calculate a quantity called *Raman Gain*, that is the ratio of the probe intensity in presence and absence of the Raman pump.

Figure 1.5: Left panel: a possible outcome of a Broadband Stimulated Raman Scattering. Intensity profile of Raman pump and Stokes pulse (Raman probe) are shown: on the top of the latter small vibrational features are visible. Right panel: the corresponding Raman Gain spectrum.

Figure 1.6: Left panel: an example of interactions of a pump pulse with a broadband probe, participating with his low and high frequency components. Right panel: simple sketch to show the intensity profile of pump and probe pulse, on top of which gain features on red side or loss features on the blue side are clearly visible.
1.1.3 Time resolved Raman spectroscopy: FSRS

The general scheme adopted for time resolved spectroscopy is the \textit{Pump-Probe} scheme. The main idea is to have two different pulses interacting with the sample: the first, called \textit{pump}, is responsible for photoexcitation of some dynamics in the sample; the second, called \textit{probe}, has to detect these time dependent variations.

To detect ultrafast dynamics, very high time resolution is needed. This is the reason of the massive use of mode-locking laser systems, giving output pulses of $\approx 10\,fs$ time duration. The two pulses are usually obtained by the same laser source, by means of a beam splitter. This is because, on fs-ps timescale, electronic synchronization is too slow, so optical synchronization is required. OPAs are used on the pulse pathways if wavelength tunability is requested, and in general one mechanical delay line is inserted on one of the two pathways to establish time delay between pump and probe (variation of $\mu$m in the pathways produces $1 \div 10\,fs$ time delays).

Figure 1.7: Schematics of a typical pump-probe setup. The output a Ti:Sapphire laser source is split in two pulses: one act as an optical pump, while the second, delayed respect to the pump by means of a delay line, interacts with the sample and probes light-induced variations in the sample.

The photoexcitation of the pump pulse is capable to activate dynamics in the sample. Then the probe pulse is used to detect differential variations of a given quantity, i.e. $\Delta T/T$ where $T$ is the transmittance, registering intensities at different time delays. A mechanical chopper is also used on the pump pathway for the ON-OFF condition of the photoexcitation.
In the last years a new time resolved spectroscopic technique, based on the Coherent Raman process, has been developed, called Femtosecond Stimulated Raman Scattering (FSRS). It is a pump-probe technique capable to study structural changes in ultrafast photophysical and photochemical processes with femtosecond time resolution and high vibrational spectral resolution \cite{9-11}. It involves three different light pulses with different temporal and spectral features, optically synchronized with each other.

In this approach the pump is usually called Actinic pump and it is responsible for the photoexcitation of the sample, preparing it in a specific excited state (i.e. a dynamic wave packet in the excited state surface). Then, the probe part is represented by the two pulses needed for SRS, the Raman pump and the Stokes pulse, as described in the previous section. The combination of a narrowband picosecond Raman pump and a broadband femtosecond Stokes pulse are used to detect high resolution stimulated Raman gain spectrum in the direction of the broadband pulse, with high efficiency and suppression of any (isotropic) fluorescence background. Detection of a photoinduced dynamics is possible by studying the evolution of Raman spectra in presence or absence of the photoexcitation, i.e. the Actinic pump.

![Figure 1.8](image)

Figure 1.8: Illustration of time-resolved femtosecond stimulated Raman spectroscopy. (a) The energy-level diagram for the FSRS experimental setup described. Actinic pump (1) photoinduces some dynamics by promoting the system to an excited state. This dynamics is probed by Raman (2) and Stokes (3) pulses, through stimulated Raman effect. (b) Pulse durations and temporal sequence of the experiment. (c) Energy-level diagrammatic representation of FSRS, discussed in detail in section 2.5.
However, unlike to SRS, FSRS is a spectroscopic technique that provides vibrational structural informations on stationary or transient excited states, with high temporal ($\approx 10 fs$) and spectral ($1 \div 10 cm^{-1}$) resolution, circumventing the Heisenberg uncertainty principle [12]. The reason is based on decoupling of time and frequency resolution by means of two probe pulses. The narrow band Raman pulse produces a spectrum of high frequency resolution, because it binds the energy of Stokes emission at the vibrational properties of sample. The WLC femtosecond pulse allows instead to obtain high time resolution, because the Raman stimulation starts only when there is time overlap between the two beams [13]. Summing up the previous considerations, the spectral resolution depends numerically on the convolution of the vibrational dephasing times ($\gamma_i$) and the spectral resolution of the Raman pulse ($1/\tau_R$), while the temporal resolution is simply given by the time duration of the Actinic pump ($\tau_A$) and the WLC pulse ($\tau_S$).

Because of its unique features, the FSRS technique is the ideal tool for studying ultrafast chemical and biochemical reaction dynamics, allowing previously unattainable insight into the structural dynamics of reactively evolving system with high spectral and femtosecond temporal resolution. In the next chapters we will give the theoretical basis to understand FSRS properties and a description of how a similar setup can be built in lab.

1.2 $KNiF_3$: an Heisenberg antiferromagnet

Recent theoretical developments suggested that the electric field of a light pulse modifies the exchange interaction, $J$, between spins in solid state compounds [14, 15]. An attempt to access the dynamics of the d-f exchange splitting in metals was done via photoemission spectroscopy [16, 17]. However, in these materials ultrafast laser excitation triggers sub-picosecond electronic dynamics and demagnetization [18, 19], which affects the spin correlation function.

In magnetically ordered materials as antiferromagnets, well described by the Heisenberg model 1.2.1, the energy is mostly dominated by the exchange energy, proportional to the exchange interaction $J_{ab}$ and the spin correlation function between spin in sites a and b. Since the dynamics of $J$ is defined by the dynamics of electrons [20], the femtosecond response of the exchange energy in metals to a laser pulse can originate from variations of both $J$ and the spin correlation functions, and disentangling the two contributions is challenging. On the other hand, in dielectrics the scenario is different. In a non-dissipative regime of light-matter interaction the response of the charges is limited to the duration of a femtosecond stimulus, while spin dynamics
are still detectable 100 picosecond later [21]. Nevertheless, an experimental scheme able to isolate the femtosecond dynamics of J, has not been developed yet.

In the first part of this section, a brief description of the Heisenberg model, commonly used to describe magnetic properties of antiferromagnets, is given. Then, the main features of the magnetic sample studied will be presented. Finally, the physical process used to study magnetic behaviour via light-matter interaction is shown.

1.2.1 The Heisenberg model

Magnetism is a purely quantum phenomenon, as demonstrated by the Bohr-van Leeuwen theorem [22]. It is well known that magnetic properties are related to magnetic moments of electrons and nuclei of the considered system. Given the huge number of electrons in a solid, a statistical treatment of the microscopic interactions is necessary to obtain macroscopic informations. Both Bohr-van Leeuwen and Langevin in their works supposed that the interaction between these magnetic moments was ruled by Coulomb forces, i.e. dipole-dipole interaction [23].

Anyway, this kind of interaction is too weak to explain the ferromagnetic behaviour of some materials, like iron oxides even at room temperature. In these materials, magnetic moments act coherently: the understanding of the origin of this coherent behaviour is the core of the Heisenberg model for ferromagnet. Heisenberg understood that an effective interaction between the spins of the electrons, thousands of times larger than the dipolar interaction, was induced by the Pauli principle, i.e., the antisymmetrization of the electronic states.

In a simple system with only two electrons, it is possible to construct antisymmetric states considering that electronic spins can assume two values, \(|\uparrow\rangle\) or \(|\downarrow\rangle\). It comes out to have four combinations, triplet and singlet states, combined with the space-dependent wavefunctions to get all the possible antisymmetric states satisfying the Pauli principle. Coulombian repulsion between electrons is responsible for a small correction of the energy eigenvalues, given by the so called exchange integral

\[
J(r_1 - r_2) \propto \int d\vec{r}_1 d\vec{r}_2 \varphi^*_\lambda(\vec{r}_1)\varphi^*_\mu(\vec{r}_2) \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} \varphi_\mu(\vec{r}_1)\varphi_\lambda(\vec{r}_2).
\] (1.10)

It is manifestly a quantum effect in which one cannot say which electron is in which state. This result is quite remarkable: the interactions that enter in this calculation are purely Coulombian, spin independent, and yet the Pauli principle yields an effective spin-dependent interaction.
This difference of energy between the triplet and singlet states, in a physical situation in which one can neglect the transition to other excited states, may be reproduced by an effective Hamiltonian, written as

\[ H_{\text{eff}} = -J \left( \vec{S}_1 \cdot \vec{S}_2 + \frac{3}{4} \right). \]  

(1.11)

If the exchange integral \( J \) is positive, the energy is lower for two parallel spins and this interaction may potentially lead to a situation in which the spins of a many-body system become ordered at low temperature.

This leads to the Heisenberg model in which one considers localized magnetic moments, i.e., spins, located at the nodes of a periodic crystalline lattice; the exchange integral \( J(\vec{r} - \vec{r}') \) between two sites \( \vec{r} \) and \( \vec{r}' \) is rapidly decreasing with their distance and one can assume that the interactions are limited to nearest neighbours. These considerations led Heisenberg to propose the Hamiltonian

\[ H_{\text{Heis.}} = -J \sum_{(i,j)} \vec{S}_i \cdot \vec{S}_j, \]  

(1.12)

where \((i, j)\) indicate two lattice sites and \( \vec{S}_i \) is the sum of the electronic spins located in those sites.

Anyway, understanding the properties of a large system of spins from this model raises many problems, and only qualitative assumptions on the macroscopic behaviour can be obtained with a statistical approach.

### 1.2.2 Sample features

The object of this study is a cubic sample of Potassium-Nickel-Fluoride (\( K\text{NiF}_3 \)). It is a cubic perovskite with space group of cubic symmetry m\( \overline{3} \)m [24], as it can be clearly seen in the picture 1.9. The magnetic order is established by the two equivalent \( Ni^{2+} \) sublattices, which are antiferromagnetically coupled if the temperature of the sample is well below the Néel temperature, that for \( K\text{NiF}_3 \) is \( T_N = 246K \) [25]. For this purpose, our sample is fixed in a cryostat to keep its temperature down to \( \approx 77K \), temperature of liquid nitrogen. The crystal is a 340\( \mu \)m thick (100) plane-parallel plate. The positive sign of the cubic magnetic anisotropy constant determines the alignment of spins along the [001], [010] or [100] axes. The spontaneous Raman spectroscopy of \( K\text{NiF}_3 \) revealed the two-magnons mode 1.2.3 to be isotropic [21], consistent with the cubic magnetic structure.

The magnetic properties of this sample are well described by the Heisenberg model of an antiferromagnet, assuming in each site of a sublattice a...
Figure 1.9: Crystal structure and spin distribution of $KNI_3$. (a) Crystal structure of the cubic perovskite: in figure, the green atoms are Potassium, the red ones are Fluorine and the blue one at the center is the Nickel, responsible for the antiferromagnetic order. (b) Magnetically ordered spins in the ground and first excited state, occurring in presence of a spin flip.

The total spin $S = 1$. Within this framework, the exchange energy which couples spins is described by the following expectation value

$$\langle \hat{H} \rangle = E_{ex} = \frac{1}{2} \sum_{a \neq b} J_{ab} \langle \hat{S}_a \cdot \hat{S}_b \rangle,$$

where $E_{ex}$ is the exchange energy, $J_{ab}$ is the exchange interaction and the last expectation value is the correlation function between spins on different lattice sites $a$ and $b$.

### 1.2.3 Two magnons light scattering

The goal of this experiment would be to reveal some sub-picosecond dynamics of the exchange interaction $J_{ab}$ when a femtosecond pulse impinge on the antiferromagnetic sample. Two-magnons light scattering constitutes a convenient way to access to possible informations on the exchange interaction of magnetic materials. This section will try to explain the origin of this process and why it is convenient for our aim.

Spin waves, or magnons, are low-lying excitations that occur in magnetically ordered materials. The concept of a spin wave was first introduced by Bloch in 1930. He postulated that electron spins can deviate slightly from their ordered ground-state alignment and the resulting excitation propagates with a wavelike behaviour through the solid. Since the electron spins are described by quantum-mechanical operators, spin waves are also quantized, with the basic quantum excitation being termed the magnon [26].
It is possible to build two-magnon states and to study their energy levels quantum mechanically, but the essential feature is that spin deviations are created at a pair of exchange-coupled magnetic sites on opposite sublattices through virtual electronic transitions to higher states. Thus, in two-magnon scattering in antiferromagnets, two spin deviations with wavevectors $k$ and $-k$ are created in close proximity on opposite magnetic sublattices and are coupled by the exchange interaction. Because the two-magnon density of states peaks at the Brillouin zone boundary, the two-magnon light scattering is expected to be dominated by zone edge magnons $^{27-30}$.

Spontaneous Raman (SR) spectroscopy $^{31-34}$ has been widely used to measure the vibrational frequency of two magnon modes, given by the expression

$$E_{2M} = nJ\langle \hat{S}_i \cdot \hat{S}_j \rangle,$$

where $J$ is the exchange interaction, $\langle \hat{S}_i \cdot \hat{S}_j \rangle$ is the correlation function between spins at sites $i$ and $j$, and $n$ is a factor depending only on the number of nearest neighbours.

Anyway, while SR is an ideal tool to map an equilibrium vibrational structure, it has a critical shortcoming when used as a probe in a time resolved experiment. Specifically, it is subject to a time-energy resolution restriction dictated by the time-bandwidth product of the light pulse, which is limited in the Fourier transform sense ($\Delta E \Delta t \geq 15cm^{-1}ps$).

We try to circumvent this limitation taking advantage of the uncompromised time and energy resolution of Femtosecond Stimulated Raman Spectroscopy (FSRS), which we use to track the vibrational dynamics of the two-magnon line (2ML) of $KNiF_3$ upon ultrashort optical excitation.
Figure 1.11: Raman spectrum of $KNiF_3$: two magnons line clearly visible at $\approx 730 \text{ cm}^{-1}$, with its peculiar asymmetric shape [35].

Figure 1.12: Comparison between Spontaneous Raman spectrum (solid line) and theoretical simulations (dotted line) by Chinn et al. [36] shows an excellent agreement.
Chapter 2

Femtosecond Stimulated Raman theory

A brief presentation of the basic idea of this work has been given in previous chapter, accompanied by a phenomenological description of the physical processes involved and a general view of the experimental technique used. To have a deeper comprehension of these processes, however, a theoretical description of the light-matter interaction and non linear optical effects is necessary, using the quantum mechanics formalism.

In this chapter the theory beyond Femtosecond Stimulated Raman Scattering will be presented. A semiclassical approach will be used for the description of the light-matter interaction, introducing the density operator $\rho$ and the interaction scheme. Then, non linear optical processes will be treated, giving a special emphasis at the Stimulated Raman Scattering, presenting the diagrammatic approach as a useful tool to describe these processes. In the end, the general case of Stimulated Raman Scattering for a three level system will be presented.

2.1 Density operator

In the Schrödinger picture, a generic quantum state of a given system is described by its wavefunction $|\psi(t)\rangle$, a vector belonging to the Hilbert space of all the possible states. The expectation value of a given operator evaluated on this state is expressed by

$$\langle A \rangle = \langle \psi(t) | A | \psi(t) \rangle.$$  \hspace{1cm} (2.1)
Expanding the state vector in an arbitrary orthonormal basis set \( \{|n\}\) of the Hilbert space, the previous equation becomes

\[
\langle A \rangle = \sum_{m,n} c_n(t)c^*_m(t) \langle m|A|n \rangle = \sum_{m,n} c_n(t)c^*_m(t)A_{mn}.
\] (2.2)

A quantum state could be also described by its density operator, expressed by

\[
\rho(t) = |\psi(t)\rangle \langle \psi(t)|
\] (2.3)

that, expanded in the same basis set, becomes

\[
\rho(t) = \sum_{m,n} c_n(t)c^*_m(t)\langle n|m \rangle = \sum_{m,n} \rho_{mn}(t)\langle n|m \rangle,
\] (2.4)

where the density matrix \( \rho_{mn}(t) = c_n(t)c^*_m(t) \) has been introduced. In this description, the expectation value of a generic operator is given by

\[
\langle A \rangle = \sum_{m,n} A_{mn}\rho_{mn}(t) = Tr [A \rho(t)].
\] (2.5)

A quantum system that can be described by means of its wavefunctions is said to be in a pure state. These states are represented by a complex vector in an Hilbert space and they are defined by the first postulate of quantum mechanics. However, the description of complex systems like biological or solid state samples is not possible by means of pure states. They are usually described by means of statistical ensembles of pure states, called mixed states, whose description is not possible in terms of wavefunctions, while it is natural in the formalism of the density matrix. Given a statistical ensemble of state \( |\psi_n(t)\rangle \), each one with its probability \( 0 \leq P_n \leq 1 \), the density operator will be expressed by

\[
\rho(t) = \sum_{n} P_n |\psi_n(t)\rangle \langle \psi_n(t)|.
\] (2.6)

From its definition, it is straightforward to derive the following properties for the density operator:

- it is an hermitian operator;
- diagonal terms are real non-negative numbers, while the off-diagonal terms are in general complex;
- \( Tr(\rho) = 1 \);
- \( Tr(\rho^2) \leq 1 \), where the equal stands only for pure states.
Quantum states in which the density matrix contains only diagonal terms are called *population* states, while *coherence* states are described by density matrix with non-zero off-diagonal terms [37].

In the Schrödinger picture, wavefunctions are expressed by time-dependent vectors, whose temporal evolution is governed by the Schrödinger equation

$$
\frac{\partial}{\partial t} |\psi(t)\rangle = -\frac{i}{\hbar} H |\psi(t)\rangle.
$$

(2.7)

It is possible to find a similar equation for the temporal evolution of the density operator, by doing the time derivative of equation 2.3

$$
\frac{d}{dt} \rho = \frac{d}{dt} (|\psi(t)\rangle \langle \psi(t)|),
$$

(2.8)

and then substituting Schrödinger equation in it, to obtain

$$
\frac{d}{dt} \rho = -\frac{i}{\hbar} [H, \rho]
$$

(2.9)

that is the *Liouville - Von Neumann equation.*

This equation is very similar to the Schrödinger one, but the presence of the commutator on the right side generates the action of the Hamiltonian operator both on the bra and the ket side of the density operator. Hence, an initial population state can evolve in a coherence state and vice versa as density matrix terms usually change under the action of the operator $H$.

Equation 2.9 can be also written as

$$
\frac{d}{dt} \rho = -\frac{i}{\hbar} L \rho,
$$

(2.10)

where the Liouville super-operator $L$ has been introduced as a four-index matrix acting on the space of the matrices $\rho$ describing the system. This equation, named the *Liouville equation,* has the same expression of the Schrödinger equation, in the sense that results found in the space of wavefunctions are adaptable for the space of density matrix too.

Liouville equation is really useful when *dephasing* effects are included in the theory. Dephasing is the process in which a coherence state, induced by an external perturbation, decays after a time interval, leading the system in the initial state. This effect can be included in the Liouville equation as an additional term,

$$
\frac{d}{dt} \rho = -\frac{i}{\hbar} L \rho - \Gamma \rho,
$$

(2.11)

where $\Gamma$ is the dephasing superoperator acting on the space of the density matrices [38, 39].
2.2 Interaction scheme and perturbative expansion

Consider a system with a general time-dependent Hamiltonian operator \( H(t) \). The temporal evolution of the system is governed by a propagator defined as

\[
|\psi(t)\rangle = U(t, t_0)|\psi(t_0)\rangle,
\]

which is a unitary hermitian operator depending only on the temporal interval \((t - t_0)\). This expression could be inserted in the Schrödinger equation 2.7 to obtain

\[
\frac{\partial}{\partial t} U(t, t_0) = -\frac{i}{\hbar} H(t) U(t, t_0).
\]

Integrating the last expression, we get

\[
U(t, t_0) = 1 - \frac{i}{\hbar} \int_{t_0}^{t} dt' H(t') U(t', t_0),
\]

which can be iteratively solved to find

\[
U(t, t_0) = 1 + \sum_{n=1}^{\infty} \left( -\frac{i}{\hbar} \right)^n \int_{t_0}^{t} dt_n \int_{t_0}^{t_n} dt_{n-1} \cdots \int_{t_0}^{t_{2}} dt_1 H(t_n) \cdots H(t_1).
\]

A more compact expression can be written introducing the time-ordered product, defined as

\[
T[A(t_1)B(t_2)] = \begin{cases} 
A(t_1)B(t_2), & \text{if } t_1 < t_2, \\
B(t_2)A(t_1), & \text{if } t_1 > t_2
\end{cases}
\]

which allow us to rewrite equation 2.15 as

\[
U(t, t_0) = 1 + \sum_{n=1}^{\infty} \left( -\frac{i}{\hbar} \right)^n \int_{t_0}^{t} \int_{t_0}^{t} \cdots \int_{t_0}^{t} dt_n dt_{n-1} \cdots dt_1 T[H(t_n)H(t_{n-1}) \cdots H(t_1)].
\]

Remembering equation 2.12, we can now write for the wavefunction at a given time \( t \)

\[
|\psi(t)\rangle = |\psi(t_0)\rangle + \sum_{n=1}^{\infty} \left( -\frac{i}{\hbar} \right)^n \int_{t_0}^{t} \int_{t_0}^{t} \cdots \int_{t_0}^{t} dt_n dt_{n-1} \cdots dt_1 T[H(t_n)H(t_{n-1}) \cdots H(t_1)] |\psi(t_0)\rangle.
\]
Analogous expressions can be derived for the density operator too, with
the simple substitutions of $|\psi\rangle$ and $H$ with $\rho$ and $L$. Temporal evolution is
obtained applying the Liouville propagator $U$

$$\rho(t) = U(t-t_0)\rho(t_0), \quad (2.19)$$

where $U$ satisfies Liouville equation 2.10. With the same mathematical op-
erations it is possible to write for the density operator at a given time $t$

$$\rho(t) = \rho(t_0) + \sum_{n=1}^{\infty} \left( -\frac{i}{\hbar} \right)^n \int_{t_0}^{t} dt_n \int_{t_0}^{t_n} dt_{n-1} \cdots \int_{t_0}^{t_2} dt_1$$

$$[H(t_n), [H(t_{n-1}), \cdots [H(t_1), \rho(t_0)] \cdots ]]. \quad (2.20)$$

Anyway, the expansions 2.18,2.20 are valid only at very short times, while
they will always diverge at longer times. The series is divergent because of
the perturbative expansion of the full Hamiltonian, whose terms could be
not so small. In order to obtain a convergent expansion we can adopt a new
picture, called interaction or Dirac picture.

Suppose to express the total Hamiltonian operator of the system as

$$H(t) = H_0 + H'(t), \quad (2.21)$$

where $H_0$ is a simple time-independent Hamiltonian while $H'(t)$, the interaction term, can be considered as a weak perturbation of the first term. This expression is reasonable for many light-matter interaction problems, in which the radiation fields can be treated as a weak perturbation of the strong molecular or crystalline fields. The idea is to find solutions for $H_0$, and then to make a perturbative expansion in powers of $H'(t)$ limited to a finite number of terms.

In the Schrödinger picture, operators are constant in time, while state
vectors evolve according to Schrödinger equation, that is with the action of the operator

$$|\psi_S(t)\rangle = U(t,t_0)|\psi_S(t_0)\rangle = e^{-\frac{i}{\hbar}H(t-t_0)}|\psi_S(t_0)\rangle. \quad (2.22)$$

In the Heisenberg picture, state vector are time-independent, while operators
evolve in time with

$$A_H(t) = U(t, t_0)A_S U(t, t_0) = e^{\frac{i}{\hbar}H(t-t_0)} A_S e^{-\frac{i}{\hbar}H(t-t_0)} \quad (2.23)$$

The interaction picture is a combination of the two mentioned before. Operators evolve in time with $H_0$, while $H'(t)$ rules the evolution of state vectors:

$$\frac{\partial}{\partial t} |\psi_I(t)\rangle = -\frac{i}{\hbar}H'_I(t)|\psi_I(t)\rangle \quad (2.24)$$
\[ H'_I(t) = U_0^\dagger(t, t_0) H'(t) U_0(t, t_0), \quad (2.25) \]
\[ U_0(t, t_0) = e^{-\frac{i}{\hbar}H_0(t-t_0)}. \quad (2.26) \]

Introducing the time-evolution operator of the wavefunction in the Dirac picture as
\[
|\psi_I(t)\rangle = U_I(t, t_0) |\psi_I(t_0)\rangle, \quad (2.27)
\]
we can write equations for \(U_I\) equal to 2.13, 2.15. Hence, we can easily deduce the time-evolution for the wavefunction in the interaction picture
\[
|\psi_I(t)\rangle = |\psi_I(t_0)\rangle + \sum_{n=1}^{\infty} \left( -\frac{i}{\hbar} \right)^n \int_{t_0}^{t} \int_{t_0}^{t} \cdots \int_{t_0}^{t} dt_n dt_{n-1} \cdots dt_1 T [H'_I(t_n) H'_I(t_{n-1}) \cdots H'_I(t_1)] |\psi(t_0)\rangle. \quad (2.28)
\]

Coming back to Schrödinger picture by using eq. 2.26 and
\[
|\psi_S(t)\rangle = U_0(t, t_0) |\psi_I(t)\rangle, \quad (2.29)
\]
we can rewrite the expansion as
\[
|\psi_S(t)\rangle = |\psi^{(0)}(t)\rangle + \sum_{n=1}^{\infty} \left( -\frac{i}{\hbar} \right)^n \int_{t_0}^{t} \cdots \int_{t_0}^{t} dt_n dt_{n-1} \cdots dt_1 T [U_0(t, t_n) H'_I(t_n) \cdots U_0(t_2, t_1) H'_I(t_1) U_0(t_1, t_0)] |\psi(t_0)\rangle, \quad (2.30)
\]
where \(|\psi^{(0)}(t)\rangle = U_0(t, t_0)|\psi(t_0)\rangle\) is the zero-order unperturbed wavefunction, and now the expansion is written in powers of \(H'(t)\). This term is small for definition, so the series is convergent and the perturbative expansion makes sense.

The last expression has an intuitive physical interpretation: from the initial time \(t_0\), the system is subject to a free propagation under the action of \(H_0\) until time \(t_1\), as indicated by \(U_0(t_1, t_0)\). At \(t = t_1\), it interacts with the perturbation term \(H'(t_1)\). Afterwards, there is another free propagation from \(t_1\) to \(t_2\). This sequence has to be repeated for every instant \(t_i\).

Given these results, it is possible to extend them to the density matrix scheme. In the interaction picture, remembering eq. 2.29, the density matrix can be expressed as
\[
\rho(t) = |\psi(t)\rangle \langle \psi(t) | = U_0(t, t_0) \rho_I(t) U_0^\dagger(t, t_0) = U(t-t_0) \rho(t_0). \quad (2.31)
\]
Now, for the linearity in $|\psi(t)\rangle$ of all the previous expressions and for the
direct connection between Hilbert space of wavefunctions and Liouville space
of density matrix, we can deduce

$$\rho(t) = \rho^{(0)}(t) + \sum_{n=1}^{\infty} \left( -\frac{i}{\hbar} \right)^n \int_{t_0}^{t} dt_n \int_{t_0}^{t_n} dt_{n-1} \cdots \int_{t_0}^{t_2} dt_1$$

$$U_0(t-t_0) \left[ \rho^{(n)}(t), [\rho^{(n)}(t-\infty)], \cdots \right] \rho^{(0)}(t-t_0). \quad (2.32)$$

The same physical interpretation of eq. 2.30 can be used, keeping in mind
that, in density matrix scheme, interactions can happen on both bra and ket
side, for example to create or destroy coherence states.

Assuming that at the instant $t_0$ the system is in an equilibrium state,
eigenstate of the Hamiltonian $H_0$, we can consider the limit $t_0 \to -\infty$ and
write:

$$\rho(t) = \rho^{(0)}(-\infty) + \sum_{n=1}^{\infty} \rho^{(n)}(t). \quad (2.33)$$

In the study of light-matter interaction it is usual to express the interaction
term as $H'(t) = E(t) \cdot \mu(t)$, where $E(t)$ is the electromagnetic field interacting
with the sample and $\mu(t)$ is the dipole moment operator. It can be expressed
in the interaction picture as

$$\mu_I(t) = U_0^\dagger(t, t_0) \mu U_0(t, t_0), \quad (2.34)$$

so the n-order term of the density matrix expansion will be

$$\rho^{(n)}(t) = \left( -\frac{i}{\hbar} \right)^n \int_{-\infty}^{t} dt_n \int_{-\infty}^{t_n} dt_{n-1} \cdots \int_{-\infty}^{t_2} dt_1 E(t_n) E(t_{n-1}) \cdots E(t_1)$$

$$U_0(t, t_0) \left[ \mu(t_n), [\mu(t_{n-1}), \cdots [\mu(t_1), \rho(-\infty)], \cdots \right] \rho^{(0)}(t-t_0). \quad (2.35)$$

where the subscript I for the interaction scheme was omitted. The presence
of the commutators in eq. 2.35 generates several contributions for the density
matrix expansion, even at the lowest orders. For this reason, a diagrammatic
approach will be presented in section 2.5 to easily evaluate all the terms
generated by the expansion of the commutators [38, 39].

2.3 Non linear polarization

Once calculated the temporal evolution of a system interacting with an ex-
ternal radiation field through the interaction scheme and the perturbative
expansion, our goal is to understand the nature of non-linear optical phenomena, like SRS, in order to calculate finally the output optical signals recorded in experiments. SRS, like every Raman process, is sensitive to variations of polarization in the sample; in particular, it is the result of several (4, as we will see) interactions with the sample, therefore it requires a non linear optical theory for a detailed description.

In general, an electromagnetic field passing through a system can induce a time-dependent polarization. For quite low intensities, it is not wrong to suppose this polarization to be linearly proportional to the electric field strength,

\[ P = \varepsilon_0 \chi^{(1)} \cdot E, \]  

where \( \chi^{(1)} \) is the linear susceptibility. In the laser physics, very high intensities can be reached by common laser sources, and the linear approximation is no longer correct. In the most general case, the expression of the induced polarization is a power series in the electric field

\[ P = \varepsilon_0 \left( \chi^{(1)} \cdot E + \chi^{(2)} \cdot E \cdot E + \chi^{(3)} \cdot E \cdot E \cdot E + \cdots \right), \]  

where \( \chi^{(n)} \) is the n-order non linear susceptibility, constituted by a rank-n+1 tensor according to the vectorial nature of light. Generally, these tensor elements are strongly dependent on the geometrical structure of the medium, reflecting in this way its symmetries. For example, isotropic media with inversion symmetry have all even-order susceptibilities equal to zero, so the lowest order non linear processes are of the third order, like Stimulated Raman Scattering.

In a semiclassical approach, with a quantum treatment of the matter and a classical treatment for the radiation fields, it is easy to see how the induced polarization participates to the wave propagation, ruled by the Maxwell equations. These equations, in the case of non magnetic and non conducting media, are

\[ \nabla \times \mathbf{E} = -\mu_0 \frac{\partial \mathbf{H}}{\partial t} \]  

(2.38a)

\[ \nabla \times \mathbf{H} = \varepsilon_0 \frac{\partial \mathbf{E}}{\partial t} + \frac{\partial \mathbf{P}}{\partial t} \]  

(2.38b)

\[ \nabla \cdot \mathbf{E} = -\frac{1}{\varepsilon_0} \nabla \cdot \mathbf{P} \]  

(2.38c)

\[ \nabla \cdot \mathbf{H} = 0. \]  

(2.38d)

Taking the curl of eq. 2.38a and the time derivative of 2.38b, combining the results we get the general wave equation

\[ \nabla \times \nabla \times \mathbf{E} = -\frac{1}{\varepsilon_0} \frac{\partial^2 \mathbf{E}}{\partial t^2} - \mu_0 \frac{\partial^2 \mathbf{P}}{\partial t^2}, \]  

(2.39)
where the relation $c_0^2 = \frac{1}{\mu_0 \varepsilon_0}$ is used. Simplifying the left-member expression and assuming transverse waves only, we obtain the \textit{non linear optics equation}

$$\nabla^2 E - \frac{1}{c_0^2} \frac{\partial^2 E}{\partial t^2} = \mu_0 \frac{\partial^2 P}{\partial t^2}.$$ (2.40)

In this semiclassical approach, the macroscopic polarization is an observable, defined by trace operator (eq. 2.5), which reads:

$$P(t) = Tr [\mu \rho(t)],$$ (2.41)

that is the expectation value of the dipole moment $\mu$ on the density matrix, whose evolution is described in eq 2.32. As in 2.33, polarization can be expanded in series, in order to have for the n-order term

$$P^{(n)}(t) = Tr [\mu \rho^{(n)}(t)].$$ (2.42)

The substitution of expansion 2.35 in 2.42 produces

$$P^{(n)}(t) = \left( - \frac{i}{\hbar} \right)^n \int_{-\infty}^{t_n} dt_n \int_{-\infty}^{t_{n-1}} dt_{n-1} \cdots \int_{-\infty}^{t_1} dt_1 E(t_n) E(t_{n-1}) \cdots E(t_1)

Tr \{ \mu(t) [\mu(t_n), [\mu(t_{n-1}), \cdots [\mu(t_1), \rho(-\infty)] \cdots] \} \}. \quad (2.43)$$

Last equation can be conveniently simplified using a different set of time variables:

$$\tau_1 = t_2 - t_1$$
$$\tau_2 = t_3 - t_2$$
$$\vdots$$
$$\tau_n = t - t_n$$

While times $t$ indicate the instants at which the interaction happens, the new set of times $\tau_i$ are the time intervals during which the density matrix propagates freely.

The last equation for the n-order term of the polarization can be also expressed in terms of n-order non linear response function of the system using these new temporal variables:

$$P^{(n)}(t) = \int_{0}^{\infty} d\tau_n \int_{0}^{\infty} d\tau_{n-1} \cdots \int_{0}^{\infty} d\tau_1 S^{(n)} (\tau_n, \tau_{n-1}, \cdots, \tau_1)

E(t - \tau_n) E(t - \tau_n - \tau_{n-1}) \cdots E(t - \tau_n - \tau_{n-1} - \cdots - \tau_1), \quad (2.44)$$
Figure 2.1: The two temporal reference system used: $t_i$ indicates time of $i-$th light-matter interaction, while $\tau_i$ indicates the temporal interval between $i-$th and $i+1-$th in which the system undergoes free propagation.

that is the convolution between $n$ electric fields and the non-linear response functions, expressed by comparison with the previous relations

$$S^{(n)}(\tau_n, \cdots, \tau_1) = \left( -\frac{i}{\hbar} \right)^n \text{Tr} \{ \mu(\tau_n + \cdots + \tau_1) [\mu(\tau_{n-1} + \cdots + \tau_1), \cdots [\mu(0), \rho(-\infty)] \cdots] \}. \quad (2.45)$$

It is worth to focus the attention on the last interaction term, $\mu(\tau_n + \cdots + \tau_1)$, which has a different role in the evolution, being out of any commutators. The first $n$ interactions prepare a non-equilibrium density matrix $\rho^{(n)}$ whose off-diagonal terms allow the emission of light at time $\tau_n + \cdots + \tau_1$.

As already pointed out, the approach followed to get the $n$-th order polarization $P^{(n)}(t)$ induced in the system is to use a semiclassical theory, which treats the sample as a quantum system, but considers the interaction with classical external fields. Mukamel et al [40, 41] have proposed a quantum electrodynamical (QED) description that uses quantized electrical fields. The Hamiltonian operators are expressed in terms of creation and annihilation operators, both for radiation field and for interaction term. Anyway, the advantages of QED approach arise when dealing with incoherent phenomena of light-matter interaction (like two photon fluorescence or spontaneous Raman), since they are intrinsically related to the quantum nature of the fields involved [38, 39, 42].

2.4 Four wave mixing

The polarization derived in the previous section plays a key role in spectroscopy since it controls the light-matter interaction. Now, the goal of this
section is to evaluate the possible output signals of non linear optical pro-
cesses by replacing the polarization in the wave equation for non linear optics.
That reads, to find a solution of the non linear optics equation

$$\nabla^2 \mathbf{E} - \frac{1}{c_0^2} \frac{\partial^2 \mathbf{E}}{\partial t^2} = \mu_0 \frac{\partial^2 \mathbf{P}}{\partial t^2}. \tag{2.46}$$

The equation can be simplify by splitting $\mathbf{P}$ in its linear and non linear
collections

$$\mathbf{P} = \mathbf{P}_L + \mathbf{P}_{NL}, \tag{2.47}$$

and assuming the case of a plane wave propagating along the $z$ axis (scalar
wave approximation). Hence, it can be rewritten as

$$\frac{\partial^2 \mathbf{E}}{\partial z^2} - \frac{1}{c_0^2} \frac{\partial^2 \mathbf{E}}{\partial t^2} = \mu_0 \varepsilon_0 \chi^{(1)} \frac{\partial^2 \mathbf{E}}{\partial t^2} + \mu_0 \frac{\partial^2 \mathbf{P}_{NL}}{\partial t^2} \Rightarrow \tag{2.48a}$$

$$\frac{\partial^2 \mathbf{E}}{\partial z^2} - \frac{1}{c_0^2} \frac{\partial^2 \mathbf{E}}{\partial t^2} = \mu_0 \frac{\partial^2 \mathbf{P}_{NL}}{\partial t^2} \tag{2.48b}$$

where it is clear how the linear polarization modifies the wave propagation
velocity, from $c_0$ in the vacuum to $c = \frac{c_0}{\sqrt{1 + \chi^{(1)}}}$, while the non linear con-
tribution participates as a driving force in the wave equation.

It is possible to express the electric field $\mathbf{E}$ as

$$\mathbf{E}(z, t) = A(z) e^{i(\omega_0 t - k_0 z)} \tag{2.49}$$

and, similarly, for the polarization

$$\mathbf{P}_{NL}(z, t) = \mathbf{P}_{NL}(z) e^{i(\omega_0 t - k_{P} z)}, \tag{2.50}$$

where $A(z)$ and $\mathbf{P}_{NL}(z)$ are the spatial envelopes of the respective waves and
$k_0$ and $k_P$ are their wavevectors.

Then, inserting the last two expressions in 2.48b and introducing the Slowly Varying Envelope Approximation (SVEA)

$$\frac{\partial^2 A}{\partial z^2} \ll k_0 \frac{\partial A}{\partial z} \tag{2.51}$$

we obtain the non linear propagation equation

$$\frac{\partial A(z)}{\partial z} = -\frac{\mu_0 \omega_0 c}{2 n_0} \mathbf{P}_{NL}(z) e^{-i \Delta k z}, \tag{2.52}$$

where $n_0 = \frac{c_0}{\varepsilon_0}$ is the refractive index and $\Delta k = k_P - k_0$ is the difference
between the wavevectors, usually called phase mismatch vector.
Processes, like SRS, in which there are four interactions with the matter, are called four wave mixing. In order to describe them, the total electric field $E(t)$ must be written as a superposition of four different contributions

$$E(z, t) = \frac{1}{2} [A_1(z)e^{i(\omega_1t-k_1z)} + A_2(z)e^{i(\omega_2t-k_2z)} + A_3(z)e^{i(\omega_3t-k_3z)} + A_4(z)e^{i(\omega_4t-k_4z)} + c.c.]$$

(2.53)

together with the total energy conservation

$$\omega_1 - \omega_2 + \omega_3 = \omega_4.$$  

(2.54)

For media in which the inversion symmetry is satisfied, as we said, the lowest non linear non-zero contribution to the polarization is the third order term. If we stop the series expansion at this order, we obtain

$$P_{NL}(z,t) = 6\varepsilon_0 \chi^{(3)} E_3(z,t)$$

(2.55)

where the 6 factor comes from the possible permutations of the three applied electric fields.

Substituting the last expression in eq. 2.52, with some calculations, for the output field at frequency $\omega_4$ it is possible to write

$$\frac{\partial A_4}{\partial z} = -i\alpha_4 \chi^{(3)} A_1 A_2^* A_3 e^{i\Delta k z},$$

(2.56)

where $\alpha_4 = \frac{3\omega_4}{cn}$, formula that can be the integrated to calculate the output signal at a given position $z$.

The application of this theory to the case of Stimulated Raman Scattering is straightforward. In this process there are two pulses impinging on the sample, so the frequency arguments become

$$\omega_1 = \omega_2 = \omega_R$$

(2.57)

$$\omega_3 = \omega_4 = \omega_S$$

(2.58)

where the subscript R and S are respectively related to the Raman and Stokes (WLC) pulses. In this case, the phase matching condition $\Delta k = k_4 + k_2 - k_1 - k_3 = 0$ is automatically satisfied. Then, eq. 2.56 for SRS becomes

$$\frac{\partial A_S}{\partial z} = -i\alpha_S \chi^{(3)} |A_R|^2 A_S$$

(2.59)

which can be integrated with $z$ ranging from 0 to $L$, assuming $A_R \approx cost$ and $A_S(0) = A_{S0}$, to obtain

$$A_S(L) = A_{S0} \exp \left(-i\alpha_S |A_R|^2 L \right).$$

(2.60)
If the argument of the exponential is much smaller than unity (as usually happens), we can get the first order expansion

\[ A_S(L) \simeq A_{S_0} - i\alpha_S \chi^{(3)}|A_R|^2 A_{S_0} L = A_{S_0} + \Delta A_S. \]  

(2.61)

The quantity \( \Delta A_S \) is a quite small gain (either positive or negative in theory) superimposed to the Stokes signal (i.e. at the same frequency). The detection of a similar output signal is called *heterodyne detection*, because the signal detected contains a mixing term with both incident and emitted radiations; therefore, the emitted field has the same frequency of incident radiation. It is substantially different from *homodyne detection*, in which the emitted signal is detected at an optical frequency totally different from the incident ones.

The physical quantity measured by detectors is the signal intensity, given by the absolute square of the signal field

\[ I_S(L) = |A_S(L)|^2 = |A_{S_0} + \Delta A_S|^2 \approx |A_{S_0}|^2 + 2\Re(A_{S_0}^* \Delta A_S) \]  

(2.62)

that, using the expression for \( \Delta A_S \) becomes

\[ I_S = I_{S_0} + \Re(iA_{S_0} A_{S_0}^* L |A_R|^2 \alpha_S \chi^{(3)}) \]

\[ \Rightarrow I_S = I_{S_0} + 2\Re \left[ i|A_{S_0}|^2 L |A_R|^2 \alpha_S \left( \chi^{(3)'} + i\chi^{(3)''} \right) \right] \]

(2.63)

where \( \chi^{(3)'} \) and \( \chi^{(3)''} \) are the real and imaginary parts of the third order susceptibility.

To get clearer Raman spectra, it is usual to evaluate the *Raman Gain*, defined as

\[ RG = \frac{\Delta I_S}{I_{S_0}} = -\alpha_S \chi^{(3)''} I_R L, \]  

(2.64)

which shows, similarly to Spontaneous Raman case, a Lorentzian shape, being proportional to \( -\chi^{(3)''} \) (see [42]). In general, it is possible to visualize dispersive features in Raman Gain spectra: they could come out from higher order terms of the series expansion of the exponential in 2.60 or when the \( |\Delta A_S|^2 \) term is not neglected [38, 39, 42].

### 2.5 Diagrammatic approach

In the previous section, we got the Raman Gain being proportional to the imaginary part of third order susceptibility, related to the non linear polarization. Next step is to calculate non linear response function of the system in
equation 2.45, that means to explicitly expand the commutators in eq. 2.43. This difficult task is really simplified by the use of diagrammatic approach, a powerful tool useful to list and to calculate all the several contributions arising from expressions 2.43, 2.44, 2.45.

In the first part two different approaches, double-sided Feynman diagrams and FWM energy level diagrams, will be presented. Then, in the second, they will be applied to a three-level system for the Stimulated Raman Scattering.

### 2.5.1 Feynman and FWMEL diagrams

Third order polarization is given by:

\[ P^{(3)}(t) = \int_0^\infty d\tau_3 \int_0^\infty d\tau_2 \int_0^\infty d\tau_1 E(t - \tau_3)E(t - \tau_3 - \tau_2)E(t - \tau_3 - \tau_2 - \tau_1)S^{(3)}(\tau_1, \tau_2, \tau_3) \]

where \( S^{(3)} \) is the response function of the system

\[ S^{(3)}(\tau_1, \tau_2, \tau_3) = \left( -\frac{i}{\hbar} \right)^3 Tr(\mu(\tau_1 + \tau_2 + \tau_3)\mu(\tau_1 + \tau_2), [\mu(\tau_1), [\mu(0), \rho(-\infty)]]). \]

Expanding the commutator we get eight terms

\[ S^{(3)}(\tau_1, \tau_2, \tau_3) = \left( -\frac{i}{\hbar} \right)^3 [R_1 + R_2 + R_3 + R_4 + c.c.] \]

\[ R_1 = Tr[\mu(\tau_1 + \tau_2 + \tau_3)\mu(0)\rho(-\infty)\mu(\tau_1)\mu(\tau_1 + \tau_2)] \]

\[ R_2 = Tr[\mu(\tau_1 + \tau_2 + \tau_3)\mu(\tau_1)\rho(-\infty)\mu(0)\mu(\tau_1 + \tau_2)] \]

\[ R_3 = Tr[\mu(\tau_1 + \tau_2 + \tau_3)\mu(\tau_1 + \tau_2)\rho(-\infty)\mu(0)\mu(\tau_1)] \]

\[ R_4 = Tr[\mu(\tau_1 + \tau_2 + \tau_3)\mu(\tau_1 + \tau_2)\mu(\tau_1)\rho(-\infty)] \]

where \( R_i^* \) terms are hermitian conjugates of \( R_i \) changed in sign. To give a physical interpretation of these terms, we can rewrite them using dipole moments definition in the Dirac scheme 2.34 and properties of the trace. For
example, for $R_i$ it is possible to write (assuming $U(t_i) = U(t_i, t_0)$)

$$
\text{Tr} [\mu(\tau_1 + \tau_2 + \tau_3)\mu(0)\rho(-\infty)\mu(\tau_1)\mu(\tau_2)] = 
$$

$$
= \text{Tr} [U^\dagger(\tau_3)U^\dagger(\tau_2)U^\dagger(\tau_1)\mu\rho(-\infty)\mu(\tau_1)\mu(\tau_2)U(\tau_1)U(\tau_2)] = 
$$

$$
= \text{Tr} \left( \mu U(\tau_3)U(\tau_2)U(\tau_1)\mu\rho(-\infty)U^\dagger(\tau_1)\mu U^\dagger(\tau_2)\mu U^\dagger(\tau_3) \right). \tag{2.68}
$$

Last term of equation 2.68 gives a clear interpretation of the temporal sequence of interactions: starting from $\rho(-\infty)$ describing the system in its initial state, we have

1. first dipole moment on the left, acting as a perturbation on the ket side of density matrix;
2. after the perturbation, free propagation during $\tau_1$ given by $U(\tau_1)$ and $U^\dagger(\tau_1)$;
3. second perturbation with dipole moment from the right acting on the bra side;
4. free propagation during $\tau_2$;
5. third perturbation with dipole moment from the right acting on the bra side;
6. free propagation during $\tau_3$;
7. finally, last dipole moment acting on the ket and then trace calculation.

So $R_1$ describes three interactions (ket-bra-bra side) on the density matrix, with free propagations between two consecutive interactions. Last dipole moment is the responsible for the emission of light, known as free induction decay, in which the coherence state produced by the previous interactions decays.

A first diagrammatic approach to simplify calculations of $R_i$ terms is due to Feynman. **Feynman double-sided diagrams** consist in two vertical parallel lines representing bra and ket side of $\rho$, while fields interactions are represented by arrows.

They can be read following these rules:
Figure 2.2: Two typical examples of double-sided Feynman diagrams. Blue arrows represent the electric fields interacting on both the bra and ket side of the density matrix, while the green curly arrow is the free induction decay.

1. time runs from the bottom to the top, and vertical lines represent respectively the evolution of the ket and the bra of the density matrix;

2. the initial state is a population state $|i\rangle\langle i|$ which produces a $P(i)$ in the response function;

3. last interaction is the output signal, usually represented by a curly arrow;

4. a sign $(-1)^n$ must be added to each diagram, where $n$ is the number of interactions on bra side, without the last one;

5. an arrow pointing to the right produces a field $E = E(t)e^{-i\omega t + ikr}$, while one pointing to the left produces a field $E = E(t)e^{i\omega t - ikr}$; signal frequency and wave vector are given by energy and momentum conservation;

6. an arrow pointing inwards one of the vertical line represent an excitation, while an arrow pointing outwards is a disexcitation;
7. every free propagation between two consecutive interactions produces a factor $e^{-i\omega_{ij}\tau - \Gamma_{ij}\tau}$, where $i, j$ indicate the density matrix state and $\Gamma$ is the dephasing matrix;

8. last interaction must lead the system in a population state to have a non-zero trace.

An alternative way to visualize these processes is to use *Four wave mixing energy level diagrams* (FWMEL). They are made up of several horizontal lines representing the energy levels of the system and four vertical lines for the interactions.

![Figure 2.3: General example of a Four wave mixing energy level diagram. Vertical lines represent interacting field, where solid lines act on the ket and dashed lines act on the bra side of the density matrix, with the green one being the free induction decay. Horizontal lines are the energy levels of the system.](image_url)

They obey some simple rules:

1. time runs from left to right;

2. arrows pointing to the top represent excitations (higher levels), those pointing to the bottom are disexcitations (lower levels);

3. solid lines represent interactions on ket side, while dashed lines are on the bra side;
4. between two interactions, free propagations occur.

So, we found eight different diagrams for third order expansion; generally, expanding the commutators in the response function, at the order $n$ there are $2^{n-1}$ contributions plus their complex conjugates [38, 39].

**2.5.2 SRS for a three level system**

Consider three energy levels for the system $a$, $c$ and $b$, where $E_a < E_c < E_b$. Levels $a$ and $c$ are two different vibrational levels of the fundamental electronic state, while $b$ is an excited electronic state (or virtual, in non-resonant condition). Suppose $|a⟩⟨a|$ to be the initial population state of the density matrix.

In the case of optical processes with several interactions, the number of diagrams necessary to calculate the whole $P^{(3)}(t)$ is given by all the possible time orderings of electric field interactions satisfying energy and momentum conservations. So, the most general case of a three level system interacting with three different electric fields $E_i(t)$ with frequency $ω_i$, the total number of diagrams is 864 [39]! Fortunately, for the description of Stimulated Raman Scattering we have some constraints that severely reduce the number of possible diagrams:

- we have only two interacting fields, namely $E_R$ and $E_S$;
- because of its femtosecond time duration, it is possible only one interaction with the Stokes pulse;
- the emitted signal has the same frequency of the Stokes field;
- output signal in the same direction of the Stokes, given the phase-matching condition $k_{\text{sig}} = k_R - k_R + k_S$.

Given these constraints, we reduce the number to eight diagrams (plus their complex conjugates). Hence, the total electric field $E$ is the superposition of Raman and Stokes fields

$$E(t) = E_R(t) + E_S(t) = \tilde{E}_R(t)e^{-iω_Rt} + \tilde{E}_S(t)e^{-iω_S} + c.c$$

(2.69)

where the spatial dependence of the envelopes has been omitted.

We can group this eight resulting diagrams in four families: two of these (SRS I e II) represent the direct Raman, with two interactions on the bra and one on the ket side; the other two (IRS I e II) give the inverse Raman, with all the three interactions on the ket. The origin of the adjective direct
and inverse comes from the fact that direct Raman is responsible of positive gain on Stokes pulse profile, while inverse Raman, in non-resonant condition, produces negative gain. Output signals occur at frequency $\omega_R$ (Rayleigh process) or $\omega_R \pm \omega_{vib}$ (like Stokes and Anti-Stokes processes in the spontaneous case), being broad or narrow features depending on the time ordering of the interactions, with $\omega_{vib}$ being to frequency associated to a vibrational mode of the system. Diagrams in which population states, besides the ground state, are involved in the process, are called hot luminescence. From this point we will adopt the FWMEL diagrammatic approach: the Raman pump will be represented by blue arrows, the Stokes pulse by red arrows and the free induction decay will always be the green last arrow.

In SRS(I) there are three different diagrams: two of them, HL(I) and HL(II), are two hot luminescences giving a broad feature in the spectrum. The last one, named RRS(I), is responsible for a sharp peak at $\omega_R$ ($\text{RRS}(I_{aa})$) or $\omega_R - \omega_{vib}$ ($\text{RRS}(I_{cc})$) depending on the Stokes frequency.

![FWMEL diagrams for RRS(I_{cc}) and RRS(I_{aa}) contributions, giving a sharp Gain peak at $\omega_R - \omega_{ac}$ and $\omega_R$ respectively. After each interaction, the density matrix state is expressed.](image)

In SRS(II) there are three diagrams too: two hot luminescences, HL(III) and HL(IV), and RRS(II). They all give a very broad gain in the spectrum.

IRS(I) is another family with only one diagram, whose signal is a negative peak at the frequency $\omega_R$ ($\text{IRS}(I_{aa})$) or $\omega_R + \omega_{vib}$ ($\text{IRS}(I_{ca})$), depending like
Figure 2.5: FWMEL diagrams for HL(I) and HL(II): they involve a population state, namely $|b\rangle\langle b|$, and they produce a large flat baseline centered in $\omega_R - \omega_{ac}$ in the Raman spectrum.

Figure 2.6: FWMEL diagram for RRS(II).
Figure 2.7: FWMEL diagrams for HL(III) and HL(IV), giving large flat baseline around the Raman pump frequency.

Figure 2.8: FWMEL diagrams for IRS($I_{aa}$) on the left and IRS($I_{ca}$) on the right: they both produce a negative peak, centered at $\omega_R$ and $\omega_R + \omega_{vib}$ respectively.
RRS(I) on the Stokes frequency involved (fig. 2.8).

The last family is IRS(II), with only one diagram, giving a very broad loss (negative gain) in the spectrum (fig. 2.9).

\[
\begin{align*}
\text{IRS(II)} \\
\begin{array}{c}
|b><a| \\
\end{array} \\
\begin{array}{c}
\omega_R \\
\end{array} \\
\begin{array}{c}
|b><a| \\
\end{array} \\
\begin{array}{c}
\omega_S \\
\end{array} \\
\begin{array}{c}
|b><a| \\
\end{array} \\
\end{align*}
\]

Figure 2.9: FWMEL diagrams for IRS(II).

It is important to stress that Raman pump is a narrowband pulse, so its frequency (length of the arrow) is well defined, while the Stokes pulse is a white light continuum, carrying on a large number of frequencies, so the length of the arrow is not fixed.

Output signals given by RRS(I) and IRS(I) contribution present a sharp Raman feature respectively on the red or the blue side of the Raman pump frequency (\(\omega_R \mp \omega_{vb}\)). Following the rules of diagrammatic approach, it is possible to write the contribution to the polarization given by these two diagrams: for RRS(I) it gives

\[
P^{(3)}_{\text{RRS(I)}}(t) = \left(-\frac{i}{\hbar}\right)^3 |\mu_{ab}|^2 |\mu_{bc}|^2 \int_0^\infty d\tau_1 \int_0^\infty d\tau_2 \int_0^\infty d\tau_3 E_R^\dagger(t - \tau_3 - \tau_2 - \tau_1) \\
e^{-i(\omega_{ab} - i\Gamma_{ab})\tau_3} E_S(t - \tau_2 - \tau_1) e^{-i(\omega_{ac} - i\Gamma_{ac})\tau_2} E_R(t - \tau_1) e^{-i(\omega_{bc} - i\Gamma_{bc})\tau_1} \quad (2.70)
\]
while, for IRS(I)

\[ P_{RRS(I)}^{(3)}(t) = \left( -\frac{i}{\hbar} \right)^3 |\mu_{ab}|^2 |\mu_{bc}|^2 \int_0^\infty d\tau_1 \int_0^\infty d\tau_2 \int_0^\infty d\tau_3 E_S(t - \tau_3 - \tau_2 - \tau_1) \]

\[ e^{-i(\omega_{ba} - i\Gamma_{ba})\tau_3} E_R^\dagger(t - \tau_2 - \tau_1) e^{-i(\omega_{ca} - i\Gamma_{ca})\tau_2} E_R(t - \tau_1) e^{-i(\omega_{ba} - i\Gamma_{ba})\tau_1} \]  

(2.71)

where \( \mu_{ij} \) is the expected value of the dipole moment \( \langle i | \mu | j \rangle \) on the element \( \rho_{ij} \) of the density matrix.

It is possible to calculate the Raman Gain, i.e. the measured spectrum, by performing the Fourier transform of the previous expressions for third order polarization, and using

\[ RG \propto \omega^3 \left[ \frac{P_{RRS(I)}^{(3)}(\omega)}{E_S(\omega)} \right] \]  

(2.72)

where constant factors have been omitted.

In the next chapters, the behaviour of these two features will be studied thanks to FSRS experiments and numerical methods will be described to simulate numerically third order and fifth order non linear response [38, 39].
Chapter 3

Experimental setup

As explained in section 1.1.3, implementations of FSRS experiments require three synchronized pulses: a narrowband picosecond Raman pump and two broadband femtosecond pulses, the Actinic pump and the Stokes pulse.

In order to obtain high quality Raman spectra exploiting several advantages of such an arrangement, it is desirable to produce an Actinic pump and a Stokes pulse short in time, the second one being a white light continuum practically, but first of all we need the efficient generation of a narrowband picosecond Raman pump with broad wavelength tunability in the UV - visible range to exploit resonance enhancement of Raman response and to extend the great potential of FSRS technique.

In this section the experimental setup for FSRS built by Femtoscopy group will be described, starting from the laser source to the detailed description of the generation of these three pulses.

3.1 Laser source

The laser source is constituted by two main components: a 80 MHz oscillator, acting as the seed of a regenerative amplifier (RGA) with 1 kHz repetition rate. The oscillator (Coherent Micra) operates in a mode-locking regime, generating ultrashort pulses. These pulses are then amplified using the Chirped Pulse Amplification (CPA) technique.

The oscillator employed for our experiments uses a Ti:sapphire crystal as active medium and produces an 80 MHz pulse via a Kerr lens mode locking with an output power of \( \approx 400 \) mW, a wavelength of 800 nm and a bandwidth of 80 nm.

The regenerative amplifier (coherent Legend Elite) is based on a common Ti:sapphire crystal. The optical excitation of the crystal is achieved by
pumping with an Evolution-15 laser, whereas the amplification is achieved by trapping in the resonator a single laser pulse (the seed) from the oscillator by means of two pockels cells. After 10-15 round trips a voltage is applied to the output Pockels cell and the pulse is transmitted outside the resonator. While the pulse is trapped in the resonator, it travels back and forth inside the cavity through the Ti:Sapphire crystal achieving a pulse intensity gain over $10^6$ [43].

The output of the Legend amplifier has the following features:

- a wavelength centered at $\approx 800$ nm;
- a time duration of $\approx 50$ fs;
- a repetition rate of 1kHz;
- an energy of $\approx 3.5$ mJ.

Figure 3.1: Panoramic picture of the optical table used in Femtoscopy lab for FSRS experiments.
3.2 Optical layout

A schematic representation of the experimental setup is reported in figure 3.2, where three beams interacting with the sample are shown:

- a femtosecond Actinic pump (AP) in the visible range responsible for photoexcitation;
- a narrowband picosecond Raman pump (RP) for the stimulated amplification of the probe, with tunable wavelength in order to exploit resonance enhancements;
- a femtosecond white light continuum Stokes pulse (WLC) to detect the Raman spectra in presence or absence of the two pump pulses.

All the beams are simultaneously focused on the sample. Actinic and Raman pump impinge collinearly on the sample, but both are non collinear respect to the WLC in order to allow the detection of the Stokes pulse only. Actinic pump is delayed respect to the WLC to make pump - probe experiments at specific time delays, while the delay line on the Raman pump path controls the efficiency of Stimulated Raman Scattering processes [44]. Typical energies are \( \approx 0.5 - 1 \mu J \) for the AP and \( \approx 1 - 2 \mu J \) for the RP.

As explained in section 1.1.3, to obtain the FSRS response we need a sequence of probe shots with different combinations of the other pulses. To get the Raman Gain (RG) in presence or absence of photoexcitation, we need to acquire single shot detection of four adjacent combinations of pulses as shown in the following table:

<table>
<thead>
<tr>
<th>WLC</th>
<th>ON</th>
<th>ON</th>
<th>ON</th>
<th>ON</th>
</tr>
</thead>
<tbody>
<tr>
<td>RP</td>
<td>ON</td>
<td>OFF</td>
<td>ON</td>
<td>OFF</td>
</tr>
<tr>
<td>AP</td>
<td>ON</td>
<td>OFF</td>
<td>OFF</td>
<td></td>
</tr>
</tbody>
</table>

To record these different pulse combinations, we use two mechanical choppers: one operates on the RP arm at 500Hz (half of the repetition rate), the other operating on the AP arm at 250Hz (a quarter of the repetition rate).

After the interaction with the sample, the WLC pulse is focused on the monochromator slit. A 1200 grooves/mm grating disperses the beam onto a CCD (Charge-Coupled Device) array (Princeton Pixis 400 1340 horizontal and 400 vertical pixels). Reducing the vertical focusing allows to exposure of 20 CCD lines, permitting fast readout, at \( \approx 0 \div 8ms \), thus enabling single shot detection.

In order to record and manipulate the spectra of transmitted probe light a home-built Graphical user interface (GUI) and acquisition software, based
3.2.1 Actinic pump

The Actinic pump pulse is generated by a home-made two-stage optical parametric amplifier (OPA) that uses as input a portion ($\approx 1/2 mJ$) of the laser source output. The OPA input is separated into a seed beam of $\approx 100 \mu J$ and two pump beams for two amplification stages.

The seed beam is attenuated and focused into a 3 mm Sapphire plate that generates a white-light continuum extending from 480 to 1000 nm. The two pump beams are frequency doubled in a 1 mm beta-Barium-Borate (BBO) crystal to generate pulses at 400 nm. The seed and first pump beams are focused and (spatially and temporally) overlapped in a 2 mm BBO crystal to amplify a portion of the white-light continuum. After the first stage of amplification the output power is $\approx 2 \mu J$ and the wavelength is tuned by rotating the last BBO crystal [13]. In the second stage the output of first stage and the second pump beam are focused and overlapped in a different 2 mm BBO crystal. The output energy of the OPA is $40 \mu J$ at 540 nm. A prism
compressor enables us to reach an output beam compression of $\approx 40 - 50 \text{fs}$.

### 3.2.2 Raman pump

There are several methods to synthesize a narrowband picosecond Raman pump from the laser output: one standard implementation is to obtain this picosecond pulse by linear spectral filtering of a femtosecond pulse like the output of a common Ti:sapphire system. If on one side you can reach very narrow pulses with this operation, on the other you have to face very high energy loss and a limited tunability around 800 nm. These are two big problems because we want an intense pump with high tunability in the UV-visible range to exploit resonance enhancement of the Raman response. For this purpose, Femtoscopy group developed some years ago [44] a protocol to efficiently generate a Raman pump with these features.

For the efficient synthesis of tunable picosecond pulses starting from femtosecond pulses in our lab we take advantage of a simple technique that we call *Spectral Compression* (SC) acting on the output of a commercial two-stage OPA (TOPAS-C), similar to the one used for the Actinic pump.

SC is based on a second-harmonic generation (SHG) process in the presence of large group-delay-mismatch (GDM) between the fundamental frequency (FF) and the second harmonic (SH) pulse [45, 46], which results in a narrow SH bandwidth given essentially by the inverse of GDM. The high efficiency of this process is explained by the fact that SH photons are generated not only by direct SHG, but also by an intra-pulse sum frequency generation between FF spectral components that are symmetric with respect to the SHG phase-matching frequency [46, 47], leading to an efficient energy transfer from the broadband FF to the narrowband SH pulse. In our laboratory second harmonic spectral compression (SH-SC) is realized by BBO crystals $\approx 2\text{cm}$ long.

To achieve wavelength tunability for our RP, we perform SC on the output of TOPAS. It takes as input a portion of the laser output of $\sim 1.7\mu\text{J}$ and after two stage of amplification produces an output energy of $\sim 60\mu\text{J}$ (at 880nm). These pulses are then focused in the BBO crystal for the SC to create narrowband picosecond pulses in the $330 - 520 \text{nm}$ range. Second harmonic spectral compression of an OPA output is a particularly promising technique because of its relative simplicity, efficiency, and potentially broad tunability.

However, if the output of the BBO crystal is used for SRS experiments, an annoying issue comes out. Because of the temporal envelope of the picosecond pulses at the end of the SC (an asymmetric "nose" shape), Raman spectra present spectral ringing in each features due to the sharp cut-off
Figure 3.3: On the left side, high Raman pump tunability shown in Cyclohexane spectra for Raman pump wavelengths of 521, 602 and 688 nm (top to bottom), with a pulse energy of \( \approx 0.5 \mu J \). Scale bars show corresponding probe wavelengths. On the right, schematic representation of 2f setup.

of the Raman pulse. This issue has been circumvented by spectrally filtering these picosecond pulses produced by SH-SC. For this purpose we use a double-pass (2f) spectral filter with a single grating (1800 lines/inch, 410 nm blaze) and an adjustable slit in the collimated region of the spectrally dispersed beam \[44\]. This operation suppresses the spectral wings while the temporal envelope evolves to a broader, most symmetric profile. The results are decreasing spectral ringing, due to a more regular temporal profile, with an improved resolution, because of a broader temporal envelope.

3.2.3 Stokes pulse

The Stokes pulse is a femtosecond continuum generated by White Light Generation (WLG) in a Sapphire plate to cover the spectral range from \( \approx 430 \text{ nm} \) to the NIR, though with Si detection based systems there is a cut off at 1.1 \( \mu m \). Alternatively, we can generate the WLG in a CaF2 plate to reach the lower wavelength range. Translating the CaF2 plate over the beam at \( \approx 10 \text{ mm/s} \), we can avoid causing damage to the crystal.

This continuum is then focused on the sample to detect Raman features, appearing as gains or losses on the top of its profile. Using the interface on MATLAB we are able to extrapolate Raman spectra from Stokes pulse and then to study eventual temporal variations in presence of the Actinic pump.
3.3 Calibration and background subtraction

To get clear Raman spectra an important procedure to follow before running the measurements is calibration of the optical layout, which means to find the proper spatial and temporal overlap between Raman and Stokes pulse to get sharp Raman features and to establish time overlap between the two femtosecond pulses.

To obtain the correct calibration of Raman line, we can follow two different procedures. One possibility is measuring exactly the wavelength position of Raman pump (RP), but has the disadvantage that the RP is not collinear with the WLG and therefore has to be redirected each time to monochromator slit. An alternative is to collect diffuse RP onto the monochromator slit but distortion of collected spectrum can occur, due to isotropic emission and non perfect alignment with the optical axis of the monochromator. The most accurate solution is the calibration with a standard Raman spectrum well-known in literature. In our case we use the Cyclohexane, an organic solvent with very strong Raman cross section.

When performing a pump - probe experiment in which is crucial to know as precise as you can which pulse is coming first, a temporal calibration between AP and SP is necessary. In our lab this is achieved using the optical
Kerr effect (or a Kerr gate) between these pulses. According to this effect, the time overlap is estimated as the time window in which a portion of the Stokes pulse passes through two crossed polarizers because of the change in the refractive index caused by the Actinic pump. Then, we use to fix the time $t = 0$ as the inflection point of the transmitted intensity (fig 3.6).

As explained in section 1.1.2, in Stimulated Raman scattering the vibrational features appears on top of the probe profile (white light continuum) as gains or losses. As we already said, the quantity recorded in our experiment is the Raman Gain, given in equation 2.64: even if the probe profile has been subtracted, Raman Gain spectra still show the presence of background, coming from other effects, like fluorescence or coherent artifacts. So, in order to extract a clear and sharp Raman spectrum, it is necessary to perform a background subtraction. For these experiments this procedure was done by means of software MATLAB, fitting the baseline with a polynomial fit around the Raman peaks and then to subtract it from the spectra. Sometimes it could be a quite delicate operation, especially when all the three pulses are involved, because of the distortion of the WLC profile caused by the Actinic pump.
Figure 3.6: On the left, schematic setup for an optical Kerr gate. On the right, experimental Kerr effect intensity measured in lab, reported for five different vibrational modes in Cyclohexane.

Figure 3.7: Intuitive representation of background subtraction: in every subplot, red line is the fitted baseline evaluated on the cyan points of the spectrum. From left to right there are: Raman Gain with Actinic off, Raman Gain with Actinic on, Differences between the first two.
Chapter 4

Experimental results

In this chapter I will show the main results of this experiment. First of all, the identification of the two-magnons mode of the sample is presented, together with the temperature dependence of the Stimulated Raman spectrum of $KNiF_3$, to identify the spectral feature. Then, we will see the effects of adding the Actinic pump for the FSRS scheme, as explained in the first chapter. A surprising and unexpected behaviour of the 2M line under photo-excitation of the sample will be shown, together with a study on the dependence on the fluence of the Actinic pump.

4.1 Temperature dependence of 2M line

Before starting the quest for sub-picosecond dynamics with FSRS experiments, our concern was to verify that this approach is sensitive to the two-magnon mode. For this, we performed Stimulated Raman Scattering spectroscopy on the sample (that means using only Raman and Stokes pulses for our setup) and compared it with Spontaneous Raman data found in literature. Raman pump was set at 490 nm with a bandwidth of $\approx 0.1\,nm$ and a time duration of $\approx 4\,ps$, while the Stokes was the femtosecond white light continuum of about $50\,fs$. In fig 4.1 is reported the comparison between literature data and the spectrum recorded in lab. We correctly measured an excitation at the proper energy of this magnetic feature [21], with a slightly asymmetric shape on the blue side as expected because of the dispersion curve of 2M mode [49]. The temperature was quite below the Néel temperature to get a sharper feature and the two pulses had parallel polarizations to reduce coherent artifacts.

Another important check was to study the temperature dependence of the 2M line. It is known from literature [36] that the energy tend to decrease
Figure 4.1: Comparison between measured Stimulated Raman spectrum (black line) and the Spontaneous spectrum found in literature [21], both registered at 77K, reproducing the peculiar lineshape of 2M mode. Excellent agreement is shown, considering that SRS data are not background subtracted.

and the feature gets broader with increasing temperature because of thermal disorder approaching the Néel temperature. So, changing the temperature of the thermocouple inside the cryostat, we registered the Stimulated Raman spectra at different temperatures, shown in fig 4.2.

To complete the analysis, we studied variations of 2M energy and FWHM (full width half maximum) of the line on temperature. The trends reported are in excellent agreement with Spontaneous Raman data. This evidence leaves no doubt about the two-magnon nature of the observed mode.

4.2 FSRS on $KNiF_3$

Once verified that Stimulated Raman Scattering is sensitive to two-magnons mode in $KNiF_3$, we went through the core of this project that is an FSRS experiment aimed at detecting possible sub-picosecond variations at the exchange interaction $J$ induced by a laser pulse. In a scheme where the pump is the Actinic pulse and the probe is the combination of Raman and Stokes pulses, we performed pump-probe experiments at different time delays searching possible variations of the spectral features observed in the SRS
Figure 4.2: Temperature dependence of 2Magnons line. On the left, SRS spectrum recorded at different temperatures, from 77 to 256K, where the feature is almost disappeared. On the right, colormap clearly shows how the lineshape evolves with increasing temperature. The peak position moves towards lower frequencies, while the lineshape gets broader.

Figure 4.3: Temperature dependence of peak position (left) and FWHM (right) of 2ML and comparison with spontaneous Raman data from literature [36].
spectra.

It is known from recent works that light, through the electric field, is capable to variate the exchange interaction $J$ \cite{14, 15}, related to electronic dynamics that usually take place on femtosecond time scale. However, there was no expectation for the outcome, giving both the absence of similar experiments in literature (FSRS mostly used for proteins...) and the lack of theoretical model to predict quantitatively this variation.

Given the absorption spectrum from the literature \cite{21}, shown in figure 4.4, we fixed the Actinic energy at 1.9\,eV with $\approx 60\,mJ/cm^2$ of fluence and 80\,fs of time duration to be in an almost-zero resonant condition, because our aim is not to induce electronic transitions, leaving the Raman and Stokes pulses as for SRS measurements.

![Figure 4.4: Spectral dependence of the absorption coefficient in KNiF\textsubscript{3} at room temperature. Adapted from \cite{21}.](image)

Several sequence of Raman spectra were recorded ad different time delays, both for the gain feature appearing on the red side, respect to the Raman pump, and the loss feature on the blue side. Negative and positive time delays were scanned, with particular attention to the window of few hundreds of femtoseconds, where positive time delays mean AP coming before the SP, vice versa for negative time delays.
4.2.1 Peak Shift

Comparing Raman Gain spectra in presence and absence of Actinic pump at different time delays, the 2M line seems to be unaffected by the photo-excitation for the most part of the scanned time delays. Only for very short time delays, some tens of femtoseconds, the spectral feature seems to undergo a slight rigid peak shift, as it can be seen in figure 4.5.

Figure 4.5: Left panel: sketch of 2ML in presence (green) and absence (blue) of Actinic pump, showing a slight peak shift. Right panel: colormap shows the evolution of this effect, concentrated in a time window of \( \approx 100 \text{fs} \).

To analyze this effect, we decided to study the differential photoinduced modification of the Raman shift (i.e. the 2ML energy), namely

\[
\frac{\Delta \text{Shift}}{\text{Shift}}(\tau) = \frac{\text{Shift}(\tau)_{\text{AP on}} - \text{Shift}_{\text{AP off}}}{\text{Shift}_{\text{AP off}}},
\]

where \( \tau \) is the time delay between the two femtosecond pulses, while the quantity \( \text{Shift}_{\text{AP on(off)}} \) is the Raman shift in the presence (absence) of the actinic pump. Two-Magnons mode exhibits an asymmetric lineshape, with a little "shoulder" on the higher frequencies side, and there is not a trivial analytical function to fit it. To extrapolate informations on the peak position of 2ML and its variation, a Gaussian fit of the peak was done in a reduced spectral region around it, in order to exclude the asymmetric shoulder from the spectral window of the fit.
Figure 4.6: Quantitative analysis of the peak shift on FSRS spectra. For each time delay, the peak position of 2ML is calculated, in presence or absence of Actinic pump. The position is calculated by fitting the peak with a gaussian function, as it is shown in the inset on the left.

Looking at the plot in figure 4.7, several features come out from the analysis:

- no effect appears for time delays longer than 200 fs, both for gain and loss side;
- a slight rigid peak shift occurs in the first 200 fs, the biggest at the maximum time overlap;
- the duration of this peak shift is similar to the time window where AP and SP are overlapped;
- the magnitude of this effect is comparable between gain and loss, but opposite in sign;
- an unexpected slight peak shift is occurring at negative time delays too, opposite in sign respect to positive time delays and lasting about 500 fs.

If the first two features could be reasonable thinking at electronic dynamics and their timescales, it is not easy to explain these different behaviours
between gain and loss side. Furthermore, no effect was expected at negative time delays, where the SP comes before the AP and so the system probed should not be perturbed.

Figure 4.7: Differential photoinduced modification of the Raman shift for both Gain and Loss features. Clearly opposite behaviour is shown for the two features, together with an unexpected shift at negative time delay. Time zero established by the inflection point of the Kerr profile (fig. 3.6).

4.2.2 Fluence dependence

As already said in section 1.2.2,1.2.3, from Spontaneous Raman experiments performed on KNiF₃ we are sure of the isotropic nature of the two-magnons excitation, because of its cubical structure. Reminding the relation between the energy of 2M line and the exchange interaction $J$, every kind of photo-induced variations is expected to be isotropic as well, depending only on the intensity of the electromagnetic stimulus, i.e. $J(t) \propto |E(t)|^2$.

However, today there is no quantitative theory capable to predict exactly this temporal variation, given all the informations on the incident pulse and the properties of the sample. The only possible estimation is obtained describing the sample with the Hubbard model [50] for a magnetic system with
$S = 1/2$. In this model, for a fluence of $\approx 60 mJ/cm^2$, a differential variation of 2\% is expected for the exchange interaction $J$.

Given these informations, we decided to study the dependence of the main effect, the peak shift, on the fluence of the Actinic pump. This analysis has been performed only on the gain side feature, assuming a specular behaviour for the loss side too. Several actinic pump fluences were scanned in the range from $20 \div 100 mJ/cm^2$, recording spectra at different time delays for each of these values of fluence. Higher values of fluence were not considered because distortion of the spectrum due to coherent artifacts becomes significant.

To extrapolate a possible dependence on this parameter, we studied the behaviour of the maximum photoinduced variation of the Raman shift registered at each value of fluence scanned, plotting the result in figure 4.8. The trend seems to be linear with the fluence, as expected.

![Graph showing the dependence of maximum photoinduced variation of the Raman Shift on the Actinic pump fluence. The trend seems to be linear, as expected.]

Since the differential variation of this effect should be equal to the variation of exchange interaction of the sample (equation 4.1), it is possible to compare the theoretical results with our analysis. A factor of 5 between the theoretical estimation and the measured value has come out, the second being the smallest. The reason of this substantial difference could be that the Hubbard model for a magnetic system with $S = 1/2$ is too much simplified for our case, in which the sample is a $S = 1$ magnetic system.
Chapter 5

Interpretation and modelling

The main results of the FSRS experiments on \( KNiF_3 \) shown in the previous chapter are quite surprising, even if there was no expectation on the outcome of the experiment coming from theoretical background. The asymmetry between \textit{Gain} and \textit{Loss} side or the presence of a non-zero effect at negative time delays, when Stokes pulse comes before the Actinic pump, are only two of the features appeared on the Raman spectra.

In this final chapter, I will try to give a possible explanation of these experimental results. First, an interpretation of the photoinduced dynamics will be given, using a comparison with a similar experiment on a totally different sample, namely cyclohexane. Finally, an attempt to model the line-shape variation will be proposed, trying to develop the theoretical framework of non linear optical interactions in the FSRS scheme.

5.1 Asymmetry between Gain and Loss side

With \textit{Gain} and \textit{Loss} side we mean, respectively, the lower (red) and higher (blue) frequency side of the Raman pump frequency. As we saw in sections 1.1.2.2.5.2, Stimulated Raman Scattering with a broadband Stokes pulse produces two sharp vibrational features at frequency \( \omega_R \pm \omega_{vib} \): a positive gain at lower frequencies and a negative gain (loss) at higher frequencies.

These two features are the \textit{ Stimulated counterpart} of the Stokes and Anti-Stokes lines appearing in Spontaneous Raman Scattering. However, while Spontaneous Raman spectra show only positive peaks, in the Stimulated case also negative features can occur. Gain and Loss positions in the spectra are the same of Stokes and Anti-Stokes lines because they satisfy the same resonance condition. So, any kind of photo-induced process affecting the energy level structure of the system, should act on the position of Gain
(Stokes) and Loss (Anti-Stokes) in the same identical way.

In principle, any possible variation of the exchange interaction $J$ of the sample under photo-excitation should bring the same variation on both Gain and Loss features, since the Raman shift is directly related to $J$ according to

$$E_{2M} = nJ \langle \hat{S}_i \cdot \hat{S}_j \rangle.$$  

(5.1)

However, what we obtained by the analysis of 2ML at different time delays, is that Gain and Loss show an opposite behaviour (figure 4.7). For positive time delays the peak position of the Gain undergoes a light induced decrease of its absolute value, and then recoveries its unperturbed position in less than 150 fs. Such a behaviour has to be contrasted with an increase of the Loss position, taking place in the same temporal window.

Together with the unexpected asymmetry, two more peculiar features characterize the photo-induced effect. One is the presence of a non-zero effect at negative time delays: in this time region, Stokes pulse comes before the Actinic pump, so in theory the 2ML should be unperturbed. The second is the time duration of the whole effect: dynamics timescale is comparable with Actinic and Stokes pulse duration.

### 5.2 FSRS on Cyclohexane

In view of these considerations, the effect is highly suggestive of the dominance of a fifth order non linear optical interaction between the three pulses, in which the pump and probe scheme loses significance, as the entire process is exhausted during a time overlap condition among the three pulses. While the SRS is a third order non linear process, as we saw in section 2.4, the presence of the Actinic pump should add at least two more interactions to ensure energy conservation, identifying a truly six-wave mixing process.

The general experimental scheme described in the first chapter is a typical example of fifth order non linear optical processes (or six wave mixing, considering the free induction decay). Thinking in the density matrix description, the pump-probe scheme requires first two interactions with the Actinic pump for the photoexcitation of structural dynamics, and after this three interactions with the probe part, i.e. Raman and Stokes pulse, to have Stimulated Raman process.

This scheme falls down when this temporal sequence is not respected. In overlap condition, with Actinic and Stokes pulse delayed by a $\Delta t$ smaller than the pulse duration ($50 \div 100 fs$), it is not possible to identify which pulse is first interacting with the sample. Finally, when $\Delta t$ change in sign,
Figure 5.1: Temporal sequence of interacting pulses. When the time delay becomes small, i.e. overlap condition, it is no longer correct to talk about Pump-Probe.

that is SP before AP, no photo-excitation is present in the sample and so a fifth order optical interaction theory is needed.

Figure 5.2: On the left the molecular structure of Cyclohexane, made up of Carbon (black) and Hydrogen (red and blue) atoms. Its Raman spectrum is shown on the right.

The idea of involving truly non linear optical processes was corroborated by experimental evidences coming from an FSRS experiment on a totally different sample. We performed similar measurements (that means using the same pulse configuration) on liquid cyclohexane: it is an organic solvent, generally used in our lab at the beginning of each experiment for the optical calibration (section 3.3). This solvent is totally transparent to the light pulses
involved, that is zero absorption occur at the involved wavelengths, so in principle no variation of the SRS spectra is expected under photoexcitation by the Actinic pump.

Following the evolution of four of the most prominent Raman peaks of cyclohexane, we found the same strange effect: also in this organic solvent, totally transparent at AP and RP wavelengths, Gain and Loss features shifts in opposite direction, the effect being observed for all the four Raman modes considered.

Figure 5.3: Analysis of photoinduced effect on Gain and Loss FSRS features for Cyclohexane on the 801 cm$^{-1}$ mode. Black lines are Raman Gain with Actinic off, while cyan lines are taken with Actinic on. They undergo an opposite peak shift: the Loss Raman Shift moves towards the blue (higher frequencies), while the Gain moves towards the red (lower frequencies).

5.3 Photoinduced effect as Loss-Gain difference

The experimental evidences coming from FSRS results on $K\text{NiF}_3$ and cyclohexane are quite strong. A photoinduced effect is observed in both the samples, consisting in a frequency shift of vibrational mode energies (2M line in $K\text{NiF}_3$ and four Raman peaks in cyclohexane), opposite in sign for Gain and Loss side, with a very short time duration ($\approx 150fs$) comparable with AP and SP pulse duration.

This peak shift is a quite small effect, not too far from the spectral and temporal resolution of the FSRS technique used. Anyway, if a comparison is
made between the strength of the photoinduced effect on the Gain and the Loss side, something unexpected appears. As already said in this section, the same identical effect is expected to occur on the Gain and Loss features for both the samples, either for the sign and the strength of the effect.

In the figure representing cyclohexane Gain and Loss behaviours, the quantity \( \omega(t) - \omega_0 \) is plotted for the four different Raman modes considered. As the physical sense would suggest, the detected effect is the same for all the four modes, but in particular, the strength of the effect is practically the same for Gain and Loss side.

![Figure 5.4](image)

Figure 5.4: Photoinduced response as measured by FSRS for 4 distinct vibrational modes in Cyclohexane: losses and gains asymmetrically evolve in the same direction, but sharing the same amplitude (absolute value), as expected in presence of a \( \chi^{(5)} \) optical effect.

If we now consider the same plot for the Gain and Loss features of \( KNiF_3 \), there is a slight but clear difference between the two features in the positive time delay region, the effect being stronger on the blue side. This fact is not predictable by thinking to fifth order non linear optical processes. On the other hand, the absence of this difference on cyclohexane made us thinking to the possible presence of a net, genuine photoinduced increase of \( J(t) \) contributing to the total as a symmetric shift.
This evidence allows identifying in a truly six-wave mixing process, occurring when the three beams are temporally overlapped, the very origin of the whole observed photoinduced effect in cyclohexane. The same effect dominates in $KNiF_3$ over a smaller, but still detectable positive effect of modification of the exchange interaction, expressed by

$$\Delta J(t) \propto \Delta \omega_{\text{apparent}} = \frac{1}{2} [||\Delta \omega_{\text{loss}}|| - ||\Delta \omega_{\text{gain}}||],$$

(5.2)

embodying the light induced modification of the 2ML frequency $\omega_{2ML}$ and, equivalently, of the exchange interaction.

### 5.4 On the effective temporal resolution...

Remarkably, the entire dynamics manifests itself in a temporal window of less than 150 fs, demonstrating the great potential for condensed matter studies brought about by the FSRS time-energy resolution. An important point, however, is the true capability of FSRS to track ultrafast dynamics occurring on a timescale comparable or smaller than the vibrational lifetime, as in the present case.
In 2011, Mukamel and Biggs [51] made a comment on the effective time and spectral resolution of Broadband Stimulated Raman signals. They argued that while it is certainly true that the time precision initiating the vibrational coherence is independent on the spectral resolution, one has to be aware that in presence of a vibrational wavepacket motion the link between the instantaneous frequency and the vibrational lineshape is not straightforward, and the spectral response cannot be considered as sequence of snapshots of vibrational frequencies for each time.

They used a formalism different from the one proposed in section 2 based on the evolution of the density matrix. It is based on the evolution of the wavefunction, ruled by the closed time path loop diagrammatic technique, explained in [40, 41]. The pulse configuration considered consists of a first femtosecond pulse initiating some structural dynamics in the sample at $\tau = 0$, followed by a combination of a long picosecond and another short pulse to obtain Stimulated Raman process at $\tau = T$. The whole process can be considered as a fifth order non linear optical process, with an output signal given by

$$S_{\text{SRS}}(\omega) = 3P^{(5)}(\omega)E_3^*(\omega),$$

where $P^{(5)}(\omega)$ is the fifth order polarization in the frequency domain, and $E_3^*(\omega)$ is the complex conjugate of the third field interacting.

Considering the case where the stimulated vibrational frequency $\omega_{ca}$ varies under the action of the first short pulse, and assuming the picosecond field as monochromatic and the second short field as impulsive, the non linear polarization produced depends on the evolution of the vibrational wavepacket through

$$P^{(5)}(t) \propto \exp \left( i \int_{T}^{t} \omega_{ca}(\tau) d\tau - |t - T| \gamma_{ca} \right),$$

where $t$ is the detection time and $\gamma_{ca}$ is the dephasing rate related to the vibrational transition $c \rightarrow a$. It is clear from this result that the output signals depend on the entire trajectory of the frequency $\omega_{ca}(\tau)$ between the stimulation time $T$ and the detection time $t$, i.e. it may not simply be related to a single snapshot of $\omega_{ca}(T)$.

Some insight into the effective time resolution of these measurements can be obtained by considering a model system of a single vibrational mode whose frequency changes according to

$$\omega_{ca}(t) = \begin{cases} \omega_{ca}^{\text{final}} + e^{-t/t'} (\omega_{ca}^{\text{initial}} - \omega_{ca}^{\text{final}}) & \text{if } t \geq 0 \\ \omega_{ca}^{\text{initial}} & \text{if } t < 0 \end{cases},$$

where $t'$ is the timescale of the vibrational wavepacket dynamics. This expression can be used to simulate the output signal, including reasonable values.
for dephasing rates and dynamics timescales.

Figure 5.6: FSRS spectra at several time delays (black lines) and real vibrational frequency \( \omega_{ca}(T) \) in two different situations. Dephasing time is fixed at \( \gamma_{ca}^{-1} = 620 \text{ fs} \). (a) Frequency changes very slowly (\( t' = 5 \text{ ps} \)), FSRS is able to detect this variation. (b) Very fast modification of frequency (\( t' = 300 \text{ fs} \)), FSRS is no longer capable to follow the dynamics. Adapted from [51].

In figure 5.6 two different cases are presented: in the first one, on the left panel, the dynamics timescale is longer than the dephasing time (\( \gamma^{-1} \)), where the peak position in the detected polarization is in quite good agreement with the nominal vibrational frequency (red dots). In the other case, the frequency changes rapidly with respect to the dephasing time, and the result is that only for the very slow reaction the vibrational frequency is well resolved. So, it is not correct to state that FSRS in principle circumvent Fourier transform limit [11], because the detected signal is intrinsically related to photoinduced structural dynamics and their timescales.

Given these considerations, our idea was to extend this argument to the case of \( KNiF_3 \). Photoinduced modification of the exchange interaction \( J \) by the Actinic pump would be responsible for the variation of 2M line frequency, \( \omega_{2M} \), hence activating a vibrational dynamics. 2M line has a frequency of \( 735 \text{ cm}^{-1} \) and a Raman linewidth \( \gamma_{2M}^{-1} \) of \( \approx 60 \text{ cm}^{-1} \), but there is not any theoretical estimation of the photoinduced shift (\( \Delta \omega_{2M} \)) and the dynamics timescale \( \tau \) in presence of the Actinic pump.
However, we took as an upper limit the temporal window where AP and SP are overlapped, given by the duration of the optical Kerr effect, described in section 3.3. The whole effect takes place in \( \approx 150\,\text{fs} \), so it seemed reasonable to assume a timescale \( \tau \simeq 80\,\text{fs} \) for this dynamics. Referring to Mukamel’s work, we are in the condition \( \tau_{\text{dynamics}} < \gamma_2^{-1} \), i.e. vibrational frequency varies faster than the Stimulated Raman process. Using these numbers, we performed numerical simulations on the Gain feature using expression 5.5 to generate the output FSRS signal, reported in figure 5.7.

![Figure 5.7: Measured and simulated FSRS response of the system with femtosecond dynamics. (a) FSRS response evaluated for a model system consisting of a vibrational mode with an exponentially varying frequency (from \( \omega_0 = 753\,\text{cm}^{-1} \) to \( \omega_F = 743\,\text{cm}^{-1} \) with \( \tau = 80\,\text{fs} \)) for different time delays: the red triangles indicate the instantaneous vibrational frequency \( \omega(t) \), while the red dashed line indicates the asymptotic peak position. (b) Colormap inset of the FSRS spectrum: the two black lines indicate the 2ML frequency \( \omega(t) \) (dashed), the much smaller apparent peak shift \( \omega_{\text{app}}(t) \) (solid). (c) Values of the photoinduced 2ML shift \( \Delta \omega = \omega_f - \omega_0 \) for different values of the relaxation time \( \tau \) compatible with the observed shift \( \Delta \omega_{\text{app}}(t) \).](image-url)
We found that a variation \( \Delta \omega = \omega^f - \omega^i \approx 10 \text{ cm}^{-1} \) combined with a dynamics timescale of 80 fs produces an apparent shift, \( \Delta \omega_{\text{app}} \), much smaller than the real \( \omega_{2ML}(t) \) evolution, as explained by Mukamel’s work and clearly visible in the left panel of figure 5.7. The peak position of the simulated signal is in good agreement with the measured gain peak position, as it is shown in the right upper panel. Unfortunately, as we said, we don’t have theoretical basis to justify these numbers; so we also calculated the pairs of value for \( \Delta \omega \) and \( \tau \) which reproduces the observed shift \( \Delta \omega_{\text{app}} \), resulting in the right bottom plot of the same figure.

5.5 Modelling non linear optical effects

Results obtained by FSRS experiments on two different samples, a cubic sample of \( KNiF_3 \) and liquid Cyclohexane, turned out to be really original. We found in both the sample a not negligible photoinduced effect when the Actinic pump was added to the combination of Raman and Stokes pulse used for SRS. The effect is manifesting as a small perturbation of the peak position, i.e. a peak shift, in both of the samples, with a slight difference between the two. Only in the solid state sample we found a very small difference between Gain and Loss side of the SRS spectrum, which can be ascribed to photoinduced modification of the exchange energy interaction \( J \), directly proportional to the energy of 2 Magnons line, reduced by means of a limited temporal resolution of the experimental scheme adopted (see previous section).

However, it is reasonable to ascribe the most part of the effect in \( KNiF_3 \) and the whole effect in Cyclohexane to non linear optical interaction processes between overlapping light pulses. The order of this effect should be (at least) the fifth, because of it is acting as a perturbation of the Stimulated Raman process, acknowledged as a third order non linear optical process.

In the second chapter the theory of Stimulated Raman Scattering is reported, describing this optical process as an example of Four Wave Mixing, and giving the general expressions to calculate the non linear polarization of the sample. For the really interesting case of SRS we calculated the expression of the Raman Gain, starting from non linear propagation equation, introducing a useful tool to describe all the contributions to the output signal, that is the diagrammatic technique.

During the second half of my thesis project, I developed numerical methods to simulate Stimulated Raman response and to evaluate fifth order corrections to this signal, trying to describe FSRS results. In this section the main results of this methods on both \( KNiF_3 \) and cyclohexane will be pre-
5.5.1 Simulations of SRS signals

In section 2.5.2 we studied the case of SRS for a general three level system. We listed all the possible contributions to the signal, that in terms of diagrams means all the possible time orderings of the interactions observing energy and momentum conservation. Among these, there are two diagrams, namely RRS(I) and IRS(I), which give sharp Raman features on the red and blue side of the Raman pump frequency, respectively. They are the contributions responsible for the Gain and Loss features we studied in the FSRS experiments on KNiF$_3$ and cyclohexane. At the end, we gave the expressions for the third order non linear polarization for RRS(I)

$$P^{(3)}_{\text{RRS}(I)}(t) = \left(-\frac{i}{\hbar}\right)^3 |\mu_{ab}|^2 |\mu_{bc}|^2 \int_0^\infty d\tau_1 \int_0^\infty d\tau_2 \int_0^\infty d\tau_3 E_R^\dagger(t - \tau_3 - \tau_2 - \tau_1)$$

$$e^{-i(\omega_{ab} - i\Gamma_{ab})\tau_3} E_S(t - \tau_2 - \tau_1) e^{-i(\omega_{ac} - i\Gamma_{ac})\tau_2} E_R(t - \tau_1) e^{-i(\omega_{bc} - i\Gamma_{bc})\tau_1} \quad (5.6)$$

and for IRS(I)

$$P^{(3)}_{\text{IRS}(I)}(t) = \left(-\frac{i}{\hbar}\right)^3 |\mu_{ab}|^2 |\mu_{bc}|^2 \int_0^\infty d\tau_1 \int_0^\infty d\tau_2 \int_0^\infty d\tau_3 E_S(t - \tau_3 - \tau_2 - \tau_1)$$

$$E_R^\dagger(t - \tau_2 - \tau_1) e^{-i(\omega_{ba} - i\Gamma_{ba})\tau_2} E_R(t - \tau_1) e^{-i(\omega_{bc} - i\Gamma_{bc})\tau_1} \quad (5.7)$$

which are directly related to the quantity usually measured in the lab, the Raman gain, given by

$$RG \propto \omega^3 \left[ \frac{P^{(3)}(\omega)}{E_S(\omega)} \right]. \quad (5.8)$$

The complete knowledge of the energy level structure of the system and the parameters of the light pulses involved allow the calculation of the previous expression through numerical integration methods. This would be highly helpful because, firstly, it would give a theoretical overview of how the Raman spectra should be and would give analytical expression for the lineshape which can be used for data analysis. These are the reason which led us to study these expressions by a numerical point of view.

By means of MATLAB editor software, I implemented numerical integrations for the calculation of third order non linear polarization, then inserted in the Raman Gain expression. To perform numerical simulation of the expressions 5.6,5.7,5.8, some particular instructions were followed:
• It is not easy to give an estimation for the absolute square value of the transition dipole moments $\mu_{ij}$; since they are numbers, they were included in numerical prefactors.

• For $\omega_{ij}$ and $\Gamma_{ij}$ were chosen values as close as possible to the real ones, measured in lab or found in literature.

• For the field envelopes present in the time integrals $E_i(t - \tau_i)$ a Gaussian shape is chosen, in order to simplify the calculation without loss of generality.

• Time integration in $d\tau_i$ requires a really dense lattice for numerical integration, because of the rapidly oscillating exponential in the expressions; a possible shortcut we exploited is to perform a Fourier transform on the field envelopes, and then to calculate analytically the time integrals in order to simplify the expression for the numerical simulation.

So, the field envelopes were expressed by

$$ E_j(t - \tau_i) = e^{-\frac{(t - \tau_i)^2}{2\sigma_j^2}}, $$

(5.9)
\( \sigma_j = \tau_j^{-1} \), and the following convention was used for Fourier transform:

\[
E_j(\omega) = FT(E_j(t)) = \int_{-\infty}^{+\infty} dt E_j(t)e^{i\omega t}.
\] (5.10)

In the case of cyclohexane, given the spectrum in figure 5.2, we choose to analyze the sharp Raman peak at 801 cm\(^{-1}\), both for the Gain and the Loss side. The following parameters were used:

- Raman pump with \( \omega_R = 20000 \text{ cm}\(^{-1}\) and time duration \( \tau_R = 4 \text{ ps} \);
- Stokes pulse with \( \omega_S = 19000 \text{ cm}\(^{-1}\) and \( \tau_S = 50 \text{ fs} \);
- for the energy levels, \( \omega_{ac} = 800 \text{ cm}\(^{-1}\) with a dephasing \( \Gamma_{ac} = 2.3 \text{ cm}\(^{-1}\) (from vibrational lifetime), \( \omega_{ab} = 50000 \text{ cm}\(^{-1}\) (real electronic excited state), \( \omega_{bc} = \omega_{ab} - \omega_{ac} \), \( \Gamma_{ab} = \Gamma_{bc} \simeq 500 \text{ cm}\(^{-1}\).\)

The results of the simulation are two Lorentzian-like spectral features, centered in the right frequency position, which are in excellent agreement with Stimulated Raman spectra recorded in lab.

![Figure 5.9: Simulated Gain and Loss Raman peaks of Cyclohexane. Frequency values are centered at the Raman pump frequency, so the Gain is redshifted and the Loss is blueshifted. Simulations practically overlap the experimental data.](image-url)
In the case of $KNiF_3$ there is a particular issue: the 2Magnons mode present an asymmetric lineshape $1.11,4.1$ because of the frequency of this mode comes out of a dispersion curve, given by the specific magnons density of states. Even if the "shoulder" on the higher frequencies side is neglected, the lineshape is not properly a Gaussian or a Lorentzian curve.

To fit this lineshape there are two possibilities:

1. To use a pseudo-Voigt function, described by

$$p(\omega) = \mu L(\omega) + (1 - \mu)G(\omega),$$  \hspace{1cm} (5.11)

where $\mu$ is a numerical weight, $L(\omega)$ and $G(\omega)$ are a Lorenztian and a Gaussian function respectively, both having a FWHM frequency dependent to account for asymmetry.

2. It is possible to reproduce the peculiar lineshape of 2ML as a sum of two RRS(I) Raman signals (i.e. Lorenztian contributions), with different amplitudes and FWHMs, which can be simulated as we did for cyclohexane case.

![Figure 5.10: Simulated SRS response for the Gain side for $KNiF_3$. The simulation fits very well 2M lineshape, apart from the asymmetric shoulder on higher frequencies.](image-url)

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Following the second method, I considered only the Gain feature of 2ML. Summing the two contributions with frequencies and spectral width close to the measured ones ($\omega_{2ML} \simeq 735 \text{ cm}^{-1}, \Gamma_{2ML} \simeq 60 \text{ cm}^{-1}$), the simulated signal is able to reproduce 2ML lineshape very well in a quite large spectral region around the peak, as it is clearly shown in figure 5.10.

### 5.5.2 Fifth order corrections on Cyclohexane

In the previous section, a simple method to estimate numerically the third order non linear polarization as well as the Raman Gain has been presented. It was applied to two really different cases, cyclohexane and $KNiF_3$, obtaining an excellent agreement with experimental data. This numerical tool is a real candidate for the data analysis of SRS spectra in the future.

However, in FSRS experiments with three different pulses, higher order effect should be taken into account, and the lowest possible order is the fifth. By comparison of FSRS results on both the samples, we deduced the presence of a not negligible non linear optical effect, which now we want to reproduce starting from the non linear optics and Raman theory.

In the case of $KNiF_3$, the photoinduced effect observed in FSRS spectra can be ascribed to a combination of non linear optical effect and light-induced modification of the exchange interaction $J$. Unfortunately, theory cannot help us in giving an estimation of this modification and the reciprocal strength of these two effects. For this reason, we tried to estimate fifth order polarization in the case of cyclohexane. As already mentioned in section 2.5.2, considering three different fields $E_i$ with their frequencies $\omega_i$ interacting with three level system, the number of possible time orderings of interactions, i.e. possible diagrams, is 864. It is easy to imagine how fast this number will diverge considering more than three energy levels for the system.

However, we considered only a small fraction of all the possible diagrams. Focusing the attention on the redshifted side of the spectrum (Gain side), we considered fifth order contribution as a small perturbation of the third order Raman response. So, starting from RRS(I) diagram, we considered all the possible time orderings adding two interactions with the Actinic pump with a four level system, i.e. considering two vibrational excited states. It turned out there are 22 possible diagrams, which can be divided into three families according to the output response they produce:

- **Gain/Loss** peak lineshape, centered at $\omega_R - \omega_{ac}$;
- **Broad baseline** lineshape, giving a flat contribution over a large spectral region;
Dispersive lineshape.

Figure 5.11: Two examples of possible time orderings in fifth order non linear processes involving three interacting field and four energy levels. Curly arrow is, as usual, the free induction decay.

If the \( P^{(5)} \) contribution represent a small perturbation of the \( P^{(3)} \) Raman signal, peak or baseline lineshapes can not be responsible for the peak shift observed in our FSRS spectra, so the only possible candidate is the dispersive lineshape. Considering possible cancelations between signals opposite in sign, in the dispersive lineshape family there is a surviving diagram not canceled out by the others, represented in figure 5.12. It participates to the overall signal with a contribution given by:

\[
P^{(5)}(t) = \left( -\frac{i}{\hbar} \right)^5 |\mu_{ab}|^2 |\mu_{bc}|^2 |\mu_{bd}|^2 \int_0^\infty d\tau_1 \int_0^\infty d\tau_2 \int_0^\infty d\tau_3 \int_0^\infty d\tau_4 \int_0^\infty d\tau_5 

E_{R}^\dagger(t - \tau_5 - \tau_4 - \tau_3 - \tau_2 - \tau_1) e^{-i(\omega_{ab} - i\Gamma_{ab})\tau_5} 

E_A(t - \tau_4 - \tau_3 - \tau_2 - \tau_1) e^{-i(\omega_{ad} - i\Gamma_{ad})\tau_4} E_A^\dagger(t - \tau_3 - \tau_2 - \tau_1) 

e^{-i(\omega_{ab} - i\Gamma_{ab})\tau_3} E_S(t - \tau_2 - \tau_1) e^{-i(\omega_{bc} - i\Gamma_{bc})\tau_2} E_R(t - \tau_1) e^{-i(\omega_{bc} - i\Gamma_{bc})\tau_1}. \tag{5.12}
\]

Adding this fifth order contribution to the SRS Gain signal, the result is a peak shifting in the same direction of the experimental data, even becoming slightly dispersive at very short times. It is so possible to use these simulated
Figure 5.12: Top panel: FWMEL surviving diagram, involving an excited vibrational state $d$. Bottom panel: corresponding $P^{(5)}$ contribution, calculated numerically from the equation 5.12, for different time delays between Actinic and Stokes pulse.
signals to try to reproduce the FSRS spectra at different time delays, considering the total FRSR signal as the sum of third and fifth order contribution, each one with its numerical prefactor.

Figure 5.13: Numerical fit of experimental FSRS data on Cyclohexane with simulated Raman signal, calculated as sum of third order and fifth order response, each one with a numerical amplitude factor. Different time delays are reported, showing always an excellent agreement. Red vertical lines indicate the real Raman peak position, $801 \text{ cm}^{-1}$.

The simulated signals seem to be in excellent agreement with the experimental data, for different time delays. However, it should be stressed that some shortcuts have been used in these simulations: for example, transition dipole moments were considered as pure numerical factors, while in lots of cases their values are responsible for the presence or absence of specific transitions. The most important thing, anyway, is that all the possible contributions, both for third and fifth order, have to be taken into account to reconstruct the overall FSRS signal. This work is now in progress, with the aim to find a practical protocol to simulate all the possible contributions and then to use them to fit the experimental spectra recorded in lab.
Chapter 6

Conclusions

Generation and manipulation of ultrafast laser pulses on the picosecond-femtosecond time scale paved the way to the comprehension of elementary phenomena which constitutes the foundations of every physical, biological, chemical process in the world around us. Several protocols of time resolved experiments were developed, with the aim to access structural dynamics in many research fields, from the biology to chemistry and physics.

In the last years, several efforts were done in the condensed matter physics. Suggestive phenomena resulted from optical manipulation of macroscopic phases in the ultrafast opto-magnetism research field, like laser-induced metal to insulator transition \[1, 2\], superconductivity \[3\] and sub-picosecond modification of the magnetic order \[4\], have been studied via transient absorption or time resolved photoemission spectroscopy for example.

In this work we suggested a new experimental technique, developed in the last years, called Femtosecond Stimulated Raman Scattering, to study light induced dynamics in a cubic perovskite of \(KNiF_3\), an antiferromagnet well described by the Heisenberg model. The goal was to exploit unique temporal and spectral resolution of FSRS to check the presence of sub-picosecond dynamics of the exchange interaction \(J\), directly related to the energy of two-magnons light scattering mode.

We presented here experimental evidence for sub-100 fs photoinduced dynamics of coherent magnons, direct expression of a positive light induced modification of the exchange energy. Our results provide a quantification of the two magnon line dissipative dynamics in a range of relaxation times, setting an experimental benchmark for theoretical descriptions of light induced magnetism.

Moreover, it testifies to the ability of FSRS to track ultrafast vibrational dynamics occurring on the timescale down to those of the pump and probe pulses, although elucidates the need for correctly taking into account for the
complexity of the spectral response. This latter embeds purely optical six-wave mixing processes and transcend the simplified view of a light-induced peak shift of the Raman line, important aspects to be taken into account for similar future studies of ultrafast dynamics in condensed matter. For this reason, implementation of numerical methods is working now, with the aim to estimate contributions from non-linear optical effects.

We believe that this work could be extremely interesting in the study of ultrafast dynamics and opto-magnetism in condensed matter physics. Implementation of experimental protocols like the one adopted by Femtoscopy lab and reported here, combined with consistent numerical estimations of non-linear optical processes, could become a powerful tool for the understanding of the optical control of fundamental interactions in condensed matter.
Bibliography


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