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# Noise Correlation Spectroscopy

## Spettroscopia a correlazione di fluttuazioni

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Le aquile non volano a stormi, ma una rondine non fa primavera.

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## Introduction

The detection of nonlinear optical signals is severely hampered by their weakness relative to the linear contributions. Random noise, intrinsic to the measurement of every physical quantity, further complicates the detection, leading to a blurring of the signal.

The common way to deal with these experimental challenges, is to work in an integrated mode, namely consider the mean-value signal, properly averaged over several stroboscopic repetitions. When working with femtosecond laser sources, this approach relies strongly on pulse-to-pulse consistency and has thus motivated significant efforts in pursuit of perfect experimental stability.

By contrast, we propose a novel spectroscopic technique, named *Noise Correlation Spectroscopy* (NCS), which radically flips this well-established paradigm and identifies noise as a powerful asset to be exploited rather than mitigated.

As its name suggests, NCS is based on the investigation of photon correlations and the understanding of what kind of significant information can be retrieved from the measurement of the noise obtained in repeated experiments. To do so, a single shot frequency resolved acquisition of each pulse that has interacted with the sample is required. In this way, it is possible to uncover the correlations between the noises at different frequencies and therefore accessing non-classical photon correlations introduced by the light-matter interaction.

This innovative approach requires equally innovative analysis tools. The typical mean-value method consists in repeating several times the same experiment and clearly in this situation the most reasonable choice is to use simply the mean to achieve the desired signal-to-noise ratio. The new path we want to chart can be thought of as a situation in which each single pulse coming from the laser can be regarded as a new experiment, taking place in different conditions with respect to the previous one and therefore carrying different information. Acquiring single shot spectra and then performing a mean over them, would inevitably flatten all the features peculiar to each pulse. A more proper way to enhance these intrinsic fluctuations rather than wipe them out, would be choosing a statistical tool able to search the random noise and extract the hidden information. NCS identifies covariance as a good candidate to accomplish such kind of task.

Femtosecond nonlinear optical spectroscopies are particularly suitable for such approach. Indeed, ultrafast pulsed sources are typically characterized by a large number of amplification stages, whose presence inevitably leads to a noisy output which jeopardizes the reliability of the mean-value approaches. In this connection, we stress that, in the NCS framework, pulse-to-pulse consistency is no longer an essential requirement, but has instead a detrimental impact on the success of the technique. Stable laser systems deliver in fact highly coherent pulses, whose high degree of correlation covers all the potential correlated fluctuations intrinsic to each pulse. Furthermore, it is of paramount importance that also the Fourier components within the same pulse are statistically independent. Should there be non-zero correlations among the photon modes of the incident pulse, they would obscure the ones encoded by the nonlinear process. In order for the light pulses to fulfil these requirements, stochastic fluctuations must be manually introduced across their spectrum. While this can be achieved in several ways, we use a programmable liquid crystal Spatial Light Modulator (SLM) based pulse shaper to randomly modulate either the phase or the amplitude of the spectral components.

The conceptual framework we have developed so far is totally general and can be applied to many femtosecond nonlinear optical processes. My thesis project aims to apply NCS to the study of vibrational modes in a sample of crystalline quartz through Impulsive Stimulated Raman Scattering (ISRS).

### Noise Correlation Spectroscopy applied to Impulsive Stimulated Raman Scattering

ISRS is a nonlinear process which takes place whenever a sufficiently short laser pulse passes through a Raman-active medium [1]. The result of this interaction is the excitation of coherent lattice or molecular vibrations. By coherent, we mean that the induced vibrations are not chaotic (like those due to thermal disorder), but they imply a precise correlation between all the atomic positions, i.e. all the atoms in the crystal oscillate in phase. Collective excitations of this kind are called *coherent phonons*.

In a Raman process, a photon of frequency  $\omega_1$  is annihilated and a new one is created at frequency  $\omega_2$ , where  $\omega_2 - \omega_1 = \pm \Omega$  and  $\Omega$  is the characteristic frequency of the phonon involved (Figure 1a). If the phonon has been created (+ sign) and the radiation has lost energy, the process is called Stokes. Conversely, if the phonon has been absorbed and the radiation has gained energy, we refer to the process as Anti-Stokes. The process described is an inelastic scattering, through which the number of photons is conserved, but not their energy. The stimulated character of the Raman processes pertains to the way the Raman resonance is created. If a single off-resonance incident electromagnetic field is involved, the Raman resonance is established in a spontaneous, low-efficient manner. If we instead employ two impinging fields, tuned such that their energy difference matches the phonon one, the process is said to be stimulated. In this connection, it should be noted that a spontaneous Raman scattering can be also regarded as a process stimulated by the quantum vacuum field.

When dealing with ultrashort light pulses, ISRS dominates the interaction between light and matter. Due to the Heisenberg uncertainty principle, the temporal



Figure 1: a) Depiction of Stokes and Anti-Stokes processes involving a pair of photons of frequencies  $\omega_1$  and  $\omega_2$ , and a phonon of frequency  $\Omega$ . b) The grey curve indicates the distribution of the modes within the bandwidth of an ultrashort pulse. For simplicity, only Stokes process is considered. The Raman process involving  $\omega$  as the "up" photon will result in a shift of spectral weight to  $\omega - \Omega$ ; the same process will also involve a shift of spectral weight to  $\omega$  from  $\omega + \Omega$ . Doing this calculation for all frequencies in the pulse, we get the shifted spectrum (red curve) as output. The shift depends on both the phonon frequency and the scattering cross section of the process.

features of femtosecond pulses affect their chromatic properties, so that ultrashort pulses are characterized by a broad spectral content. The duration of each pulse is generally much shorter than the vibrational period of characteristic phonons and therefore the spectral bandwidth necessarily exceeds the vibrational frequency. This in turn means that for the ISRS to take place it is not necessary to excite the material using two distinct fields, but any pair of frequencies within the bandwidth of the ultrashort pulse can actually play the role of  $\omega_1$  and  $\omega_2$ . Moreover, multiple of such pairs can be found within a single light pulse.

The overall effect of the ISRS process consists in a shift of spectral weight in the transmitted pulses (Figure 1b, red curve). Nevertheless, the energy of the vibrational modes involved in the excitation of the material cannot be directly obtained from the spectral shift experienced by the outgoing pulse. The entity of such shift depends indeed not only on the energy of the phonon modes involved, but also on the scattering cross section of the process. This difficulty is easily overcome using the NCS approach.

In order to understand the crucial role of noise in such approach, let us consider a Gaussian pulse in which a narrow fluctuation localized at a specific frequency  $\omega$  has been introduced (Figure 2). The ISRS process will induce similar fluctuations also at frequencies  $\omega \pm \Omega$  within the transmitted pulse. If we repeat the measurement many times involving different unique fluctuations, this will induce a correlation between these frequencies.

If stochastic fluctuations (be they either in phase or in amplitude) are introduced across the whole pulse spectrum, this process takes place for every  $\omega$  within the laser bandwidth. Each transmitted pulse is then embedded with a unique pattern of correlations which, if properly analyzed, can ultimately shed light on the



**Figure 2:** A localized narrow fluctuation is introduced in the incoming pulse (grey curve). It will imprint distinguishable features at the frequencies involved in the Stokes process in the transmitted pulse (red curve).

complete Raman spectrum of the target sample.

In this thesis, we prove the feasibility of the NCS approach. An experimental setup suitable for its implementation has been assembled in the T-ReX laboratory at Elettra-Sincrotrone Trieste.

The thesis is organized as follows:

- Chapter 1 provides an overview of the standard theory of nonlinear optical processes. After giving a simple classical picture to help intuition, we introduce the density operator formalism in Liouville space and provide the basis for a fully quantum description of optical signals.
- In Chapter 2 we develop the theoretical model of our experiment. We describe Raman scattering stimulated by ultrashort stochastic light pulses. The model is the result of a collaboration with the group of Shaul Mukamel (University of California, Irvine).
- Chapter 3 focuses on the experimental realization of our technique. We pay particular attention to the pulse shaper, through which arbitrary manipulation of the laser pulses is achieved.
- In Chapter 4 we present the outcomes of the static measurements performed on a crystalline quartz sample. After proving the feasibility of the method, we explore the parameter space of the technique by investigating different experimental configurations.
- Chapter 5 is dedicated to time-resolved measurements in which we combine NCS to a standard pump and probe scheme. A selective polarization geometry is implemented for studying vibrational symmetry properties.

## Chapter 1

# Theory of nonlinear optical processes

Optical excitation of coherent lattice vibrations in Raman-active materials is commonly described by Impulsive Stimulated Raman Scattering (ISRS) [1]. The impulsive nature of the process lies in the fact that the ultrashort laser pulses involved, being shorter than the typical vibrational lifetimes, act as an instantaneous perturbation and can force a coherent oscillation of the atoms around their equilibrium positions. Its stimulated character relates instead to the way the excitation is established. Precisely, in a stimulated process, a Raman-active molecule is driven into resonance by two photons whose frequency difference is tuned to resemble that of a specific vibrational transition, whose occurrence is thus resonantly enhanced. Since femtosecond pulses have a broadband spectrum due to the uncertainty principle, both frequencies involved in the stimulated process can be found within the pulse bandwidth and coherent phonon excitation can occur through optical mixing of the Fourier components within the incoming pulse. Therefore, only a single, sufficiently short laser pulse is required for the ISRS to take place.

ISRS belongs to the extremely broad class of Raman spectroscopies. Raman spectroscopies encompass a large number of techniques, that, at least at first sight, may appear significantly different in both experimental and theoretical approach. However, they can all be described as nonlinear optical techniques related to the third-order polarization.

In this chapter we present the standard theory of nonlinear optics. The aim of this discussion is to build the conceptual background and the mathematical formalism necessary to the development of the theoretical model of our experiment, which will be presented in Chapter 2. After putting the basis to understand what the branch of nonlinear optics deals with [2], we briefly give an intuitive picture of nonlinear optical processes based on a simple classical description [3]. We then present the widely-used semiclassical approach [4], by introducing the density operator formalism. Finally, we develop a fully quantum treatment of nonlinear optical signals that will be the starting point of our model.

#### **1.1** Introduction to Nonlinear Optics

Optical phenomena, be they linear or nonlinear, can be interpreted as the result of the interaction between the electric field component of the impinging electromagnetic radiation and the charged particles inside the target material. When dealing with visible and near-infrared radiation, the driving frequencies of the electric field are typically in the  $10^3$  THz range, namely they are far too high for the nuclei to follow the oscillation adiabatically [3]. For this reason, in this frequency range, optical effects are mainly due to the motion of the electrons in the material.

As a result of the interaction, electrons, still bound to the nuclei, are displaced by their equilibrium positions so that a tiny electric dipole moment  $\mu(t)$  is established:

$$\mu(t) = -e \cdot r(t) \tag{1.1}$$

where e is the electron charge and r(t) the displacement experienced by the electron. The magnitude of the dipole moment varies according to the strength of the bond between electrons and nuclei: the stronger the bond, the less significant will be the displacement. For electrons close to the nuclei, the binding potential is usually approximated by a harmonic potential.

This simple microscopic picture can easily be mapped into observable macroscopic effects. By adding up all N electric dipoles per unit volume, we get what is called the *macroscopic polarization*:

$$P(t) = N\mu(t) \tag{1.2}$$

So far, no assumptions have been made on the intensity of the applied field and this treatment has general validity. The distinction between linear and nonlinear effects becomes clear as soon as we define how the driving electric field and the induced dipole moment are related.

In the limit of weak applied fields (weak with respect to the field that binds the electrons to the nuclei), the resulting electronic displacement can be thought to be directly proportional to the impinging electric field <sup>1</sup>:

$$P(t) = \epsilon_0 \chi E(t) \tag{1.3}$$

where  $\epsilon_0$  is the electric permittivity in the vacuum and  $\chi$  is the susceptibility of the material. This relation, while highlighting the linear relationship between the magnitude of the electric field applied and the macroscopic polarization of the material, offers the key to understanding the conventional (i.e. linear) optics.

In the daily life, Equation 1.3 would be enough to explain all the optical phenomena we experience. Typically, only laser light is indeed sufficiently intense to break the hypothesis of weak field we have made.

<sup>&</sup>lt;sup>1</sup>We assume that the polarization at time t depends only on the instantaneous value of the electric field strength. The assumption of instantaneous response implies that the medium is loss-less and dispersionless. Consequently, the susceptibilities considered in this section are frequency independent. In a more rigorous analysis,  $P(t) = \epsilon_0 \int \chi(t - t') E(t') dt'$ .



Figure 1.1: Third-order nonlinearity between the driving field and the induced polarization due to anharmonic contributions. Weak and strong electric fields are indicated by black and green solid lines, respectively. When intense electric field are applied, the polarization profile no longer matches the sinusoidal profile of the incoming field. Adapted from [3].

When an intense laser beam is shined on a material, electrons are farther displaced from their equilibrium positions. Under these conditions, the binding electronic potential can no longer be considered harmonic and anharmonic effects have to be taken into account. As long as the anaharmonic corrections are small, the displacements of the electrons can be expanded as a power series in the field. Consequently, Equation 1.3 can be generalized to include nonlinear contributions:

$$P(t) = \epsilon_0 \left[ \chi^{(1)} E(t) + \chi^{(2)} E^2(t) + \chi^{(3)} E^3(t) + \ldots \right]$$
  
$$\equiv P^{(1)}(t) + P^{(2)}(t) + P^{(3)}(t) + \ldots$$
(1.4)

where  $\chi^{(n)}$  is the  $n^{th}$ -order susceptibility and  $P^{(n)}$  is the  $n^{th}$ -order contribution to the macroscopic polarization. For simplicity, we have taken P(t) and E(t) to be scalar quantities and we will use this approximation throughout the chapter. However, we should bear in mind that, in a more complete picture, the vector nature of the fields must be considered; in such a case  $\chi^{(n)}$  becomes a (n+1)-rank tensor.

Different orders in the nonlinear polarization are responsible for different nonlinear optical effects. The second-order nonlinear polarization gives rise to three-wave mixing processes (sum and difference frequency generation), the third-order nonlinear polarization is instead related to four-wave mixing (FWM) processes (such as Stimulated Raman Scattering (SRS)) and Kerr-effect-related phenomena. Peculiar symmetry properties of the material play an important role in determining which kind of nonlinear processes are allowed. It can be easily proved that  $\chi^{(2)}$  vanishes for centrosymmetric crystals (that is, crystals that display inversion symmetry)[2]. This means that, in such media, the lowest order nonlinear contribution is due to  $\chi^{(3)}$ . A third-order nonlinear relationship between the driving field and the polarization is depicted in Figure 1.1. The effects we are going to discuss throughout this thesis and that are relevant to our experiment can all be understood as resulting from the third-oder contribution to the nonlinear polarization  $P^{(3)}$ . The magnitude of these effects thus depends on both the product of the incoming fields and the amplitude of the third-order nonlinear susceptibility  $\chi^{(3)}$ . The aim of the following analysis is to obtain an expression of  $\chi^{(3)}$  or, equivalently,  $P^{(3)}$ . Once this expression is computed, directly observable features can be predicted.

#### **1.2** Classical description of matter and field

The classical model we present here provides an intuitive framework for qualitatively interpreting some properties of third-oder nonlinear effects [3]. We shall pay particular attention to coherent Raman Scattering processes and build a simple picture able to describe them.

Let us first clarify a crucial point which will be extensively used in the following. We have already stressed that visible and near-IR driving fields can only set electrons in motion. However, this might be surprising, having in mind that Raman processes disclose information about vibrational modes. Nevertheless, electrons do carry information about nuclear motions as adiabatic electronic potentials effectively depend on nuclear coordinates. Hence, Raman scattering can be interpreted as originating from a perturbation in the electronic polarizability due to the presence of the nuclear modes. Assuming that the driving frequency is far from any electronic resonances, we can express the electric dipole moment in terms of the polarizability  $\alpha(t)$  and then expand the latter in a Taylor series of the nuclear coordinate Q:

$$\mu(t) = \alpha(t)E(t)$$
  
=  $\left[\alpha_0 + \left(\frac{\delta\alpha}{\delta Q}\right)_0 Q(t) + \dots\right]E(t)$  (1.5)

where the magnitude of the first-order correction to the polarizability  $\frac{\delta \alpha}{\delta Q}$  can be interpreted as the coupling strength between the nuclear and the electronic coordinates.

The classical description of a stimulated Raman process can be easily divided into two steps. First, two impinging electric fields perturb the electron cloud, whose oscillations exert a force along the nuclear coordinate, thus exciting the nuclear modes. Second, the refractive properties of the material are coherently modulated by the excited vibrational modes, so that a third field propagating through the medium will develop sidebands shifted by the modulation frequency. The amplitude of the sidebands is maximed when the resonance condition in fulfilled, namely the frequency difference of the driving fields matches the vibrational one.

In order to work out a simple expression for the resulting polarization, we shall now assume that the vibrational motion in the molecule can be described by a damped harmonic oscillator with a resonance frequency  $\omega_{\nu}$ . For the sake of simplicity, we shall consider a single harmonic nuclear mode per molecule, but the extension to multiple modes is straightforward.



**Figure 1.2:** a) Frequency components of the two incoming fields. b) Each fundamental frequency gives rise to two sidebands shifted by  $\Omega$ . Adapted from [3].

The two incoming electric field can be modelled as plane waves,  $E_i(t) = A_i e^{-i\omega_i t} + c.c.$ , where i = (1, 2). We also assume that  $\omega_1, \omega_2 \gg \omega_{\nu}$  (so that the nuclear mode will not be efficiently driven into resonance by the fundamental frequencies) and that  $\omega_1 > \omega_2$ . If the fields are sufficiently intense, nonlinear effects will take place and the electron cloud will experience oscillations not only at the fundamental frequencies  $\omega_1$  and  $\omega_2$ , but also at combination frequencies, including the difference frequency  $\Omega = \omega_1 - \omega_2$ . The nuclear coordinate Q(t) is sensitive to the driving force exerted by the combined optical fields and so the process is ruled by the following equation of motion:

$$\begin{cases} \frac{d^2Q(t)}{dt^2} + 2\gamma \frac{dQ(t)}{dt} + \omega_{\nu}Q(t) = \frac{F(t)}{m} \\ F(t) = \left(\frac{\delta\alpha}{\delta Q}\right)_0 \left[A_1 A_2^{\star} e^{-i\Omega t} + c.c.\right] \end{cases}$$
(1.6)

where  $\gamma$  is the damping constant and m the reduced mass of the nuclear oscillator.

The analytic solution of Equation 1.6 yields the time-varying nuclear displacement:

$$Q(t) = \frac{1}{m} \left(\frac{\delta\alpha}{\delta Q}\right)_0 \frac{A_1 A_2^*}{\omega_\nu^2 - \Omega^2 - 2i\Omega\gamma} e^{-i\Omega t} + c.c.$$
(1.7)

Equation 1.7 summarises all the effects we have discussed. It is clear indeed that the nuclear mode is driven into resonance by the combined action of the two incoming fields. The amplitude of the nuclear displacement is directly proportional to the amplitudes of the driving fields and to the coupling strength between the electronic and the vibrational degrees of freedom. Furthermore, nuclear oscillation are resonantly enhanced when  $\Omega = \omega_{\nu}$ .

The modulation of the nuclear coordinate affects the optical properties of the material, namely its polarizability. Combining eqs. 1.2, 1.5 and 1.7, we can compute

the resulting polarization:

$$P(t) = N \left[ \alpha_0 + \left( \frac{\delta \alpha}{\delta Q} \right)_0 Q(t) \right] \left[ E_1(t) + E_2(t) \right]$$
  
=  $P_L + \underbrace{P(\omega_{cs})e^{-i\omega_{cs}t} + P(\omega_2)e^{-i\omega_2t} + P(\omega_1)e^{-i\omega_1t} + P(\omega_{as})e^{-i\omega_{as}t}}_{P^{(3)}} + c.c.$  (1.8)

where

 $\omega_{cs} \equiv 2\omega_2 - \omega_1$  is called Coherent Stokes frequency

 $\omega_{as} \equiv 2\omega_1 - \omega_2$  is called Coherent Anti-Stokes frequency

We have also called  $P_L$  the linear contribution to the polarization due to the constant polarizability  $\alpha_0$  and  $P^{(3)}$  the third-order nonlinear term due to the driven Raman mode (i.e. proportional to  $\left(\frac{\delta\alpha}{\delta Q}\right)_0$ ).

The physical interpretation of Equation 1.8 is clear. The evanescing light oscillates not only at the fundamental frequencies, but also at the new frequencies  $\omega_{cs}$  and  $\omega_{as}$ . These additional contributions constitute the Raman sidebands, as depicted in Figure 1.2. It is worth to underline once again that in our experiment broadband ultrashort pulses are involved. This means that the process we have just described, which is stimulated by only two incoming fields, takes place for multiple pairs of frequencies within the bandwidth of the pulse. The resulting transmitted pulse has therefore a profile that is not as simple as that shown in Figure 1.2. In general, this makes difficult the retrieving of the vibrational frequency from the measured spectrum.

The relative intensities of the detected Raman components in Figure 1.2 may vary due to interference effects [3], but this discussion goes beyond the scope of the simple picture we want to give. It will suffice to know that the classical model actually provides a qualitative description of the stimulated Raman process and a justification for the rise of the Stokes and Anti-Stokes sidebands. The main failure of the classical description is that it does not recognize the quantized nature of the nuclear oscillations. To overcome this limitation and get quantitatively more meaningful nonlinear susceptibilities, a semiclassical approach is required.

# **1.3** Semiclassical description: quantum matter and classical fields

The semiclassical approach is named after the dualism that characterizes it, that is the description of the electromagnetic fields remains classical, whereas the medium is treated quantum mechanically [4]. The final aim of this discussion is, as in the previous section, to obtain an expression of the macroscopic polarization which is the quantity that encodes all the optical properties of the material.

In order to develop the theory required to accomplish our goal, let us first briefly review some basic quantum mechanical concepts which will help us justify the adoption of the so-called *density matrix* formalism [3].

It is well known that, in the quantum mechanical description, the state of a material can be completely defined in terms of molecular wavefunctions, which are typically written as:

$$\Psi(r,t) = \sum_{n} c_n \Psi_n(r,t)$$
(1.9)

where  $\Psi_n$  constitute a basis of molecular eigenstates of the unperturbed Hamiltonian of the system  $\hat{H}_0$  and  $c_n$  the projections of  $\Psi$  along them.

As usual, the time-dependent Schrödinger equation rules the temporal evolution of the wavefunction:

$$i\hbar \frac{d\Psi}{dt} = \hat{H}_0 \Psi \tag{1.10}$$

When the system interacts with the impinging electromagnetic radiation, a new interaction term must be added to the hamiltonian, which reads:

$$\hat{H}(t) = \hat{H}_0 + \hat{V}(t) 
= \hat{H}_0 - \hat{\mu} \cdot E(t)$$
(1.11)

where we have assumed that the magnetic degrees of freedom are negligible and the coupling happens only through the electric charges. We have also introduced the electric dipole operator  $\hat{\mu}$  which, in the dipole approximation<sup>2</sup>, is defined as follows:

$$\hat{\mu} = \sum_{\alpha} e_{\alpha} \hat{r}_{\alpha} \tag{1.12}$$

where the summation is over both electrons and nuclei.

The solution of the Schrödinger equation for the new Hamiltonian would return the state of the system  $\Psi(r, t)$  and thereby allow the calculation of all the meaningful observables. In particular, the polarization could be evaluated as the expectation value of dipole operator:

$$P(t) = N\langle \hat{\mu}(t) \rangle = N\langle \Psi(r,t) | \hat{\mu} | \Psi(r,t) \rangle$$
(1.13)

However, in most cases, finding  $\Psi(r, t)$  is not trivial. The common strategy to overcome this difficulty is to adopt a new formalism whose key element is no longer the vector state  $|\Psi\rangle$ , but a new object, called *density matrix*, able to describe a statistical ensemble of different state vectors.

In the following, we will adopt the formalism developed by Shaul Mukamel [4].

#### **1.3.1** Density operator

Let us consider a statistical ensemble of equally prepared physical states and suppose that the probability  $P_k$  for the system to be in the  $k^{th}$  normalized state  $|\Psi_k(t)\rangle$  is known. The expectation value of a generic observable  $\hat{A}(t)$  is then given by:

$$\langle \hat{A}(t) \rangle = \sum_{k} P_k \langle \Psi_k(t) | \hat{A} | \Psi_k(t) \rangle$$
(1.14)

 $<sup>^{2}</sup>$ This approximation holds as long as the optical wavelength is much greater than the sample dimensions, so that the field can be considered homogeneous in the affected area.

The physical message encoded in Equation 1.14 is that, since we do not know the exact state of the system, we can only access the statistical average value of the observable. The statistical mixture can be obtained by introducing what is called the *density operator*, defined as the weighted average of the projectors on the states  $|\Psi_k(t)\rangle$ :

$$\hat{\rho}(t) \equiv \sum_{k} P_{k} |\Psi_{k}(t)\rangle \langle \Psi_{k}(t)| \qquad (1.15)$$

where  $P_k$  are non-negative  $(P_k \ge 0)$  and normalized  $(\sum_k P_k = 1)$ .

The density operator allows to write 1.14 in a new and more compact form:

$$\langle \hat{A}(t) \rangle = \sum_{k} P_{k} \langle \Psi_{k}(t) | \hat{A} | \Psi_{k}(t) \rangle$$

$$= \sum_{m} \sum_{n} P_{k} \langle \Psi_{k}(t) | \hat{A} | m \rangle \langle m | \Psi_{k}(t) \rangle$$

$$= \sum_{m} \langle m | \hat{\rho} \hat{A} | m \rangle$$

$$= Tr \left( \hat{\rho} \hat{A} \right)$$

$$(1.16)$$

where we have introduced the completeness condition  $\sum_{m} |m\rangle \langle m|$  and denoted with  $Tr(\hat{O})$  the trace of a generic operator  $\hat{O}$ , namely the sum of all its diagonal elements in any complete set of states.

The last equality in 1.16 will be extensively used in the following, as it represents the standard way of computing expectation values within the density operator formalism. Moreover, Equation 1.16 clearly highlights the possibility of adopting a more explicit matrix approach, instead of the more cryptic operator one.

In analogy with the definition of the density operator  $\hat{\rho}(t)$ , we can indeed define the density matrix as the set of the matrix elements of  $\hat{\rho}(t)$  calculated on any basis, namely  $\rho_{nm} = \langle n | \hat{\rho} | m \rangle$ . The diagonal terms of the density matrix,  $\rho_{nn}$ , give the probability that the system is in the eigenstate  $|n\rangle$  and are called *populations*. The off-diagonal terms imply instead that the system is in a coherent superposition of the eigenstates  $|n\rangle$  and  $|m\rangle$  with  $n \neq m$  and provide the amplitude of what is called the *coherence* of the two states.

**Properties of the density operator** In order to gain a greater understanding of the power of this new formalism, we summarise here a few important properties of the density operator.

• The density matrix has unitary trace, as a direct consequence of the normalization condition. Equivalently, this means that the probability to find any state should be unity.

• The density matrix is hermitian and its diagonal terms (in any representation) are non-negative.

• When all  $P_k = 0$  except for one (which will be thus equal to one), the density operator is simply the projector on the only state having probability 1, namely  $\hat{\rho}(t) = |\Psi_k(t)\rangle \langle \Psi_k(t)|$ . Only in this case, the vector state is sufficient to completely characterize the system and the density operator formalism, even if still correct, becomes superfluous. In such a case, the system is said to be in a *pure state*. The general case identifies instead a *mixed state*, whose description necessarily requires the density operator.

• A simple way to recognize if a given density matrix corresponds to either a pure or a mixed state is to compute the trace of its square:

$$Tr\left(\hat{\rho}^{2}\right) = \sum_{k} P_{k}^{2} \le \sum_{k} P_{k} = 1$$

$$(1.17)$$

Only if all  $P_k$  vanish except for one, the equality can be reached and the density matrix identifies a pure state.

**Time evolution of the density operator** In analogy with the state vector, we can consider the time evolution of the density operator and derive its equation of motion. Let us first consider a pure state and calculate the time derivative of its density operator:

$$\frac{\partial \hat{\rho}}{\partial t} = \left(\frac{\partial}{\partial t} |\Psi(t)\rangle\right) \langle \Psi(t)| + |\Psi(t)\rangle \left(\frac{\partial}{\partial t} \langle \Psi(t)|\right)$$
(1.18)

Using now the time-dependent Schrödinger equation (Equation 1.10 with a generic Hamiltonian  $\hat{H}$ ) and its Hermitian conjugate, we obtain:

$$\frac{\partial \hat{\rho}}{\partial t} = -\frac{i}{\hbar} \hat{H} |\Psi\rangle \langle \Psi| + \frac{i}{\hbar} |\Psi\rangle \langle \Psi| \hat{H} 
= -\frac{i}{\hbar} \left( \hat{H} \hat{\rho} - \hat{\rho} \hat{H} \right)$$
(1.19)

The last equality in Equation 1.19 has been specifically worked out for pure states. However, since pure and mixed states are related by a linear transformation (namely, the density operator describing a mixed state is a superposition of pure state density operators), Equation 1.19 can be also extended to mixed states and has, therefore, general validity. In a more compact notation,

$$\frac{\partial \hat{\rho}}{\partial t} = -\frac{i}{\hbar} \left[ \hat{H}, \hat{\rho} \right] \tag{1.20}$$

The previous relation is known as *Liouville-Von Neumann equation* and rules the time evolution of the density operator.

The density operator formalism we have developed, while allowing the description of systems whose state vector is unknown, helps us reformulate the problem exposed in Equation 1.13 as follows:

$$P(t) = N\langle \hat{\mu}(t) \rangle = N \operatorname{Tr} \left( \hat{\mu} \hat{\rho}(t) \right)$$
(1.21)

Equation 1.21 contains all the contributions, both linear and nonlinear, to the macroscopic polarization. As we have repeatedly stated, our interest is in working

out an expression for the third-order nonlinear contribution, since we are willing to describe stimulated Raman scattering processes. We thus need to isolate  $P^3(t)$  from Equation 1.21. Similar to solving for the system's wavefunction, this can be done by performing a perturbative expansion<sup>3</sup> of  $\hat{\rho}(t)$  in powers of the electric field:

$$\hat{\rho}(t) = \rho^{(0)}(t) + \rho^{(1)}(t) + \rho^{(2)}(t) + \rho^{(3)}(t) + \dots$$
(1.22)

where  $\rho^{(n)}$  is the *n*<sup>th</sup>-order contribution in the electric field and  $\rho^{(0)}(t) = \rho(-\infty)$  is the unperturbed (at thermal equilibrium) density matrix.

The purpose of the next sections is to obtain an expression for  $\rho^{(3)}(t)$  and consequently for  $P^{(3)}(t)$ . The perturbative approach we shall take will require the introduction of the time evolution operator and the expansion of the density operator in the interaction picture. However, before starting this discussion, let us first introduce a slightly different notation that will be very useful in writing these expressions in a more compact and insightful form.

#### 1.3.2 Liouville representation

The Liouville-Von Neumann equation, as the Schrödinger equation in the standard quantum mechanical approach, constitutes the starting point for the development of the time-dependent perturbation theory. Nevertheless, the two equations, though conceptually very similar, are formally very different at this level: the former describes the time evolution of a matrix through the action of a commutator, the latter the time evolution of a vector ruled by a Hilbert operator. In order to make Equation 1.20 formally isomorphous to Equation 1.10, we redefine the notation on the basis of the following points:

• the density matrix will be no longer represented by a matrix, but by a column vector. For a N-level system, this means that the  $N \times N$  density matrix will be represented by a column of  $N^2$  elements.

• we introduce the so-called *Liouville space operators*  $\mathbb{H}$  and  $\mathbb{V}$ , also known as *superoperators*. The action of these superoperators on an ordinary Hilbert operator  $\hat{A}$  is defined through:

$$\mathbb{H}\hat{A} \equiv \begin{bmatrix} \hat{H}, \hat{A} \end{bmatrix}$$
(1.23)

$$\mathbb{V}(t)\hat{A} \equiv \begin{bmatrix} \hat{V}(t), \hat{A} \end{bmatrix}$$
(1.24)

where  $\hat{V}(t)$  has been defined in Equation 1.11. Liouville space operators can be represented by a  $N^2 \times N^2$  matrix.

The latter two points represent the basis for the construction of the *Liouville space*, a vectorial space that is the result of the cartesian product of two Hilbert spaces and whose elements are the density operators  $\hat{\rho}(t)$ .

<sup>&</sup>lt;sup>3</sup>By taking a perturbative approach, we are assuming that the radiation fields are sufficiently weak to allow an expansion order by order. Typically, the weak field approximation holds even for powerful lasers as the radiation fields must be compared to the internal electric fields  $(10^{17}W/cm^2)$  in the hydrogen atom).

In order to familiarize with the new notation, let us consider a two-level system, with energy levels  $\epsilon_1$  and  $\epsilon_2$  [5]. Its density matrix has four elements:

$$\hat{\rho}(t) = \begin{pmatrix} \rho_{11} & \rho_{12} \\ \rho_{21} & \rho_{22} \end{pmatrix}$$

We can now rewrite Equation 1.20 in the Liouville representation as follows <sup>4</sup>:

$$\frac{d}{dt} \begin{pmatrix} \rho_{11} \\ \rho_{12} \\ \rho_{21} \\ \rho_{22} \end{pmatrix} = -\frac{i}{\hbar} \underbrace{\begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & (\epsilon_1 - \epsilon_2) & 0 & 0 \\ 0 & 0 & (\epsilon_2 - \epsilon_1) & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}}_{\mathbb{H}} \begin{pmatrix} \rho_{11} \\ \rho_{12} \\ \rho_{21} \\ \rho_{22} \end{pmatrix}$$

that can be put in the following more compact form:

$$\frac{d\hat{\rho}}{dt} = -\frac{i}{\hbar} \mathbb{H}\hat{\rho} \tag{1.25}$$

Thanks to the Liouville representation, the Liouville-Von Neumann equation recast into Equation 1.25 is formally equivalent to the Schrödinger equation in the Hilbert space. The advantage of this isomorphism is that the solution to Equation 1.25 (i.e. the time evolution of  $\hat{\rho}(t)$ ) can now be obtained for free, by simply translating in the Liouville representation the known results in the Hilbert one.

Finally, it is worth to notice that, when expanded in a basis set, Equation 1.25 becomes:

$$\frac{d\rho_{jk}}{dt} = -\frac{i}{\hbar} \sum_{m,n} \mathbb{H}_{jk,mn} \rho_{mn}$$
(1.26)

that is, as expected for a  $N^2 \times N^2$  matrix, superoperators matrix elements are labeled by four indices. The notation used to distinguish the Liouville space from the Hilbert one is therefore called *tetradic notation*. Without entering into the mathematical details of it, we summarise in Table 1.1 only a few points that will be useful in the next.

Object	Hilbert space	Liouville space
State of the system	$ \Psi angle$	ho angle angle
Scalar product	$\langle \Psi   \Phi  angle$	$\left< \left< A   B \right> \right> \equiv Tr \left[ A^{\dagger} B \right]$

**Table 1.1:** Fundamental features of the tetradic notation in comparison with the Hilbert one.

#### **1.3.3** Time evolution operator in Liouville space

In close analogy with the Schrödinger equation, we can write down the solution to the differential equation 1.25 as follows:

$$\rho(t) = \mathbb{U}(t, t_0)\rho(t_0) \tag{1.27}$$

 $<sup>{}^{4}</sup>$ The precise order of the elements in the column vector is arbitrary, but once chosen it must be kept.

where we have introduced the Liouville space propagator  $\mathbb{U}(t, t_0)$ .

By substituting Equation 1.27 in Equation 1.25, we find out that  $\mathbb{U}$  satisfies the Liouville-Von Neumann equation:

$$\frac{\partial \mathbb{U}(t,t_0)}{\partial t} = -\frac{i}{\hbar} \mathbb{H} \mathbb{U}(t,t_0)$$
(1.28)

with the initial condition  $\mathbb{U}(t_0, t_0) = 1$ .

By integrating Equation 1.28 and solving iteratively, it is possible to get an explicit expression for the superoperator  $\mathbb{U}(t, t_0)$ .

For a time-independent Hamiltonian (and hence, a time-independent Liouville operator  $\mathbb{H}$ ), the solution is simply given by:

$$\mathbb{U}(t,t_0) = e^{-\frac{i}{\hbar}\mathbb{H}(t-t_0)} \tag{1.29}$$

whose action is defined by:

$$\mathbb{U}(t,t_0)\rho(t_0) \Leftrightarrow e^{-\frac{i}{\hbar}\hat{H}(t-t_0)}\rho(t_0)e^{\frac{i}{\hbar}\hat{H}(t-t_0)}$$
(1.30)

where we cannot write the equality sign as on the left-hand side  $\rho$  is considered as a vector, while on the right-hand side as a matrix. However, although represented in different spaces, the two objects are, physically speaking, equivalent. For this reason, we shall use the equality sign in the following.

When the Hamiltonian is time-dependent, the formal solution for the time evolution superoperator becomes:

$$\mathbb{U}(t,t_0) = \mathcal{T}e^{-\frac{i}{\hbar}\int_{t_0}^t d\tau \mathbb{H}(\tau)}$$
(1.31)

where  $\mathcal{T}$  is the time ordered exponential in Liouville space, namely an abbreviated notation for:

$$\mathbb{U}(t,t_{0}) = 1 + \sum_{n=1}^{\infty} \left(-\frac{i}{\hbar}\right)^{n} \int_{t_{0}}^{t} d\tau_{n} \int_{t_{0}}^{\tau_{n}} d\tau_{n-1} \dots \int_{t_{0}}^{\tau_{2}} d\tau_{1} \times \\
\times \mathbb{H}(\tau_{n}) \mathbb{H}(\tau_{n-1}) \dots \mathbb{H}(\tau_{1})$$
(1.32)

It is worth to notice that, without the operator  $\mathcal{T}$  Equation 1.31 would be just a naive (and incorrect) solution to Equation 1.28, obtained by simply treating  $\mathbb{H}$  as a number instead of an operator. The expansion of Equation 1.31 without  $\mathcal{T}$  would be very similar to Equation 1.32, but with a crucial difference: in Equation 1.32 the  $\tau_k$  time variables are all fully time ordered  $t \geq \tau_n \geq ... \geq \tau_1 \geq t_0$ , while in the expansion of 1.31 without  $\mathcal{T}$  all time orderings would contribute, and this would be a problem if the Hamiltonians do not commute.

As in Equation 1.30, we can write explicitly the action of the superoperator  $\mathbb{U}(t, t_0)$  in its general and expanded form:

$$\mathbb{U}(t,t_{0})\rho(t_{0}) = 1 + \sum_{n=1}^{\infty} \left(-\frac{i}{\hbar}\right)^{n} \int_{t_{0}}^{t} d\tau_{n} \int_{t_{0}}^{\tau_{n}} d\tau_{n-1} \dots \int_{t_{0}}^{\tau_{2}} d\tau_{1} \times \left[\hat{H}(\tau_{n}), \dots \left[\hat{H}(\tau_{2}), \left[\hat{H}(\tau_{1}), \rho(t_{0})\right]\right] \dots\right] \tag{1.33}$$

where we have used the definition of superoperator in Equation 1.23.

#### The interaction picture

The expression obtained in Equation 1.32 is not very useful, as it treats the total Hamiltonian (that cannot be considered weak in general) perturbatively. This implies that the perturbative expansion we have made so far only holds for short times, while breaking down for longer times. An immediate solution to this problem is to derive another expansion for  $\mathbb{U}(t, t_0)$  which treats the interaction Hamiltonian( $\hat{V}(t)$ , in Equation 1.11) perturbatively and the free Hamiltonian  $\hat{H}_0$  exactly. As in the usual Hilbert space, this can be accomplished by reformulating the time evolution superoperator in the interaction picture.

The interaction picture is an intermediate picture between the Schrödinger and the Heisenberg ones, in the sense that the time-dependence of the states is only partially moved to the observables. As a consequence, the interaction picture in the Hilbert space is defined as follows:

$$\begin{aligned} |\Psi_I(t)\rangle &= e^{\frac{i}{\hbar}\hat{H}_0 t} |\Psi_S(t)\rangle \\ \hat{O}_I(t) &= e^{\frac{i}{\hbar}\hat{H}_0 t} \hat{O}_S e^{-\frac{i}{\hbar}\hat{H}_0 t} \end{aligned} \tag{1.34}$$

where the subscripts S and I denote the Schrödinger and the interaction picture, respectively.

In a similar fashion, we can introduce the interaction picture in the Liouville space by splitting the superoperator  $\mathbb{H}$ , as Equation 1.11 suggests:

$$\mathbb{H} = \mathbb{H}_0 + \mathbb{V} \tag{1.35}$$

So we can rewrite the time evolution superoperator as the following product:

$$\mathbb{U}(t,t_0) = \mathbb{U}_0(t,t_0)\mathbb{U}_{int}(t,t_0)$$
(1.36)

with

$$\begin{cases} \mathbb{U}_0(t,t_0) = \mathcal{T}e^{-\frac{i}{\hbar}\int_{t_0}^t d\tau \mathbb{H}_0(\tau)} \\ \mathbb{U}_{int}(t,t_0) = \mathcal{T}e^{-\frac{i}{\hbar}\int_{t_0}^t d\tau \mathbb{V}_{int}(\tau)} \end{cases}$$
(1.37)

where we have defined  $\mathbb{V}_{int}(\tau) = \mathbb{U}_0^{\dagger}(\tau, t_0)\mathbb{V}(\tau)\mathbb{U}_0(\tau, t_0)$ , namely the superoperator  $\mathbb{V}$  in the interaction picture.

We can now express the superoperator in Equation 1.36 in its time-ordered expanded form:

$$\mathbb{U}(t,t_{0}) = \mathbb{U}_{0}(t,t_{0}) + \sum_{n=1}^{\infty} \left(-\frac{i}{\hbar}\right)^{n} \int_{t_{0}}^{t} d\tau_{n} \int_{t_{0}}^{\tau_{n}} d\tau_{n-1} \dots \int_{t_{0}}^{\tau_{2}} d\tau_{1} \times \\
\times \mathbb{U}_{0}(t,\tau_{n})\mathbb{V}(\tau_{n})\mathbb{U}_{0}(\tau_{n},\tau_{n-1})\mathbb{V}(\tau_{n-1}) \dots \\
\dots \mathbb{U}_{0}(\tau_{2},\tau_{1})\mathbb{V}(\tau_{1})\mathbb{U}_{0}(\tau_{1},t_{0})$$
(1.38)

which is equivalent, using the  $\mathcal{T}$  operator, to:

$$\mathbb{U}(t,t_0) = \mathbb{U}_0(t,t_0)\mathcal{T}e^{-\frac{i}{\hbar}\int_{t_0}^{t}d\tau \mathbb{V}_{int}(\tau)}$$
(1.39)

Finally, we have all the tools to perform the expansion of the density operator in powers of the electric field (Equation 1.22) and get the nonlinear optical polarization.

#### **1.3.4** Nonlinear optical polarization

In analogy with the expansion of the wavefunction in the standard time-dependent perturbation theory, we can write down the perturbative expansion of the density operator. Using Equation 1.33 and Equation 1.38, we get:

$$\rho^{(n)}(t) = \left(-\frac{i}{\hbar}\right)^n \int_{t_0}^t d\tau_n \int_{t_0}^{\tau_n} d\tau_{n-1} \dots \int_{t_0}^{\tau_2} d\tau_1 \times \\ \times \mathbb{G}(t-\tau_n) \mathbb{V}(\tau_n) \mathbb{G}(\tau_n-\tau_{n-1}) \mathbb{V}(\tau_{n-1}) \dots \times \\ \times \mathbb{G}(\tau_2-\tau_1) \mathbb{V}(\tau_1) \mathbb{G}(\tau_1-t_0) \rho(t_0)$$

$$(1.40)$$

where the time variables  $\tau_n$  are fully time ordered and represent the actual times of the interactions. We have also introduced the **Liouville space Green's function**, defined by:

$$\mathbb{G}(\tau) \equiv \theta(\tau) e^{-\frac{i}{\hbar} \mathbb{H}\tau} \tag{1.41}$$

where  $\theta(\tau)$  is the Heavyside step function.  $\mathbb{G}(\tau)$  describes the time propagation of the material in the absence of radiation; it thus rules the free evolution of the system in between the light-matter interactions.

The expression for  $\rho^{(n)}$  has a rather intuitive form when read from the right to the left [3] the system starts at thermal equilibrium  $\rho(t_0)$  and then is repeatedly perturbed by the subsequent application of light fields, described by the operators  $\mathbb{V}$ . In the interval between two perturbations, the system evolves according to the Green's function  $\mathbb{G}$ .

We can now recast Equation 1.40 in a new form, by explicitly writing the electric fields involved. To do so, keeping in mind the expression of the interacting Hamiltonian  $\hat{V}$  in Equation 1.11, we can define a new superoperator  $\mathbb{M}$ , whose action on a generic operator  $\hat{A}$  is:

$$\mathbb{M}\hat{A} = \begin{bmatrix} \hat{\mu}, \hat{A} \end{bmatrix}$$
(1.42)

where  $\hat{\mu}$  is the electric dipole operator. From the latter equation, it follows that  $\mathbb{V}(t) = -E(t)\mathbb{M}$ . Furthermore, we can simplify Equation 1.40 by noticing that, since  $\rho(t_0)$  is the equilibrium density operator and it does not evolve in time,  $\mathbb{G}(\tau_1 - t_0)\rho(t_0) = \rho(t_0)$ . Equation 1.40 then becomes:

$$\rho^{(n)}(t) = \left(\frac{i}{\hbar}\right)^n \int_{t_0}^t d\tau_n \int_{t_0}^{\tau_n} d\tau_{n-1} \dots \int_{t_0}^{\tau_2} d\tau_1 E(\tau_n) E(\tau_{n-1}) \dots E(\tau_1) \times \\ \times \mathbb{G}(t-\tau_n) \mathbb{M}\mathbb{G}(\tau_n-\tau_{n-1}) \mathbb{M} \dots \mathbb{G}(\tau_2-\tau_1) \mathbb{M}\rho(t_0)$$
(1.43)

Finally, we can write the expansion of the density operator in its final and most insightful form by performing a change of variables. Precisely, we define  $t_k \equiv \tau_{k+1} - \tau_k$ . A further simplification can be made by defining the superoperator  $\mathbb{M}(\tau) = e^{\frac{i}{\hbar} \mathbb{H} \tau} \mathbb{M} e^{-\frac{i}{\hbar} \mathbb{H} \tau}$ , i.e. the dipole superoperator in the interaction picture. In the limit



Figure 1.3: Schematic depiction of the subsequent time-ordered perturbations and the time variables employed in the text. Adapted from [5].

 $t_0 \to -\infty$ , we get:

$$\rho^{(n)}(t) = \left(\frac{i}{\hbar}\right)^n \int_0^\infty dt_n \int_0^\infty dt_{n-1} \dots \int_0^\infty dt_1 E(t-t_n) E(t-t_n-t_{n-1}) \dots \\ \dots E(t-t_n-t_{n-1}\dots-t_1) \mathbb{G}(t_n+t_{n-1}+\dots+t_1) \mathbb{M}(t_{n-1}+\dots+t_1) \dots \\ \dots \mathbb{M}(t_1) \mathbb{M}(0) \rho(-\infty)$$
(1.44)

where now the time variables  $t_k$  run over the interval between the application of a light field incident at  $t_{n-1}$  and one incident at  $t_n$ , as shown in Figure 1.3.

The perturbative expansion of the density operator allows the computation of any observable of the system. As repeatedly stressed, we are interested in getting a perturbative expression for the polarization, whose complete knowledge is sufficient for the interpretation of any time-domain or frequency-domain spectroscopic measurement. The  $n^{th}$ -order contribution to the polarization is given by:

$$P^{(n)}(t) = N Tr \left(\mu \rho^{(n)}(t)\right) = N \left\langle \left\langle \mu | \rho^{(n)}(t) \right\rangle \right\rangle =$$
  
=  $N \int_{0}^{\infty} dt_{n} \int_{0}^{\infty} dt_{n-1} \dots \int_{0}^{\infty} dt_{1} S^{(n)}(t_{n}, t_{n-1}, \dots, t_{1}) E(t - t_{n}) \times (1.45)$   
 $\times E(t - t_{n} - t_{n-1}) \dots E(t - t_{n} - t_{n-1} \dots - t_{1})$ 

with

$$S^{(n)}(t_n, t_{n-1}, ..., t_1) \equiv \left(\frac{i}{\hbar}\right)^n \left\langle \left\langle \mu | \mathbb{G}(t_n) \mathbb{M}\mathbb{G}(t_{n-1}) \mathbb{M} ... \mathbb{G}(t_1) \mathbb{M} | \rho(-\infty) \right\rangle \right\rangle$$
$$= \left(\frac{i}{\hbar}\right)^n \theta(t_1) \theta(t_2) ... \theta(t_n) \times \left\langle \left\langle \mu(t_n + ... + t_1) | \mathbb{M}(t_{n-1} + ... + t_1) ... \mathbb{M}(t_1) \mathbb{M}(0) | \rho(-\infty) \right\rangle \right\rangle$$
(1.46)

 $S^{(n)}$  is the *n*<sup>th</sup>-order response function and contains all the microscopic information

required for the calculation of optical processes  $^{5}$ .

The Heavyside step functions in the second equality of Equation 1.46 guarantee the causality principle, that is the polarization at a given time can depend only on the electric field at earlier times. Should any argument of  $S^{(n)}$  be negative, the response function vanishes.

Finally, we want to highlight that every superoperator  $\mathbb{M}$  in Equation 1.46 represents a commutator. This means that the  $n^{th}$ -order nonlinear response function is actually made up of  $2^n$  terms, each representing a different situation which involves a different number of interactions acting either on the left (i.e. on the ket) or the right (i.e. on the bra) of the density matrix. Each contribution is called **Liouville space pathway**.

#### 1.3.5 Double-sided Feynman diagrams

The nonlinear optical response function we have worked out in Equation 1.46 contains all the information necessary to the formal description of any kind of nonlinear optical processes. However, its expression, even for low-order processes, may be not immediately obvious. We shall now introduce a graphic representation that is definitely more helpful than equations in visualizing the actual processes involved. The core objects of this representation are the so-called *double-sided Feynman* (ds-F) diagrams. Each diagram is related to a certain Liouville pathway and it thus describes a certain combination of the incoming fields that gives rise to the emitted one. Moreover, ds-F diagrams are particularly useful in building up a picture of the pulse ordering and the state of the system at each interaction.

In order to translate each independent term of the nonlinear response function into a diagram, we need to define the following fundamental rules [5]

- 1. The diagram takes the form of a ladder, in which the vertical lines represent the time evolution of the ket (left line) and the bra (right line) of the density matrix. The system must start and end in either a ground state population or an excited state population (i.e. both ket and bra are in the same quantum state).
- 2. Time is running from the bottom to the top. The rungs of the ladder indicate the timing of the light-matter interactions. The spacing between the rungs is the time delay between interactions.
- 3. The arrows represent the interactions with the incoming light fields. Arrows pointing to the right stand for contributions of the form  $e^{+ikr-i\omega t}$ , while arrows

$$P^{(n)}(\omega) = N \int d\omega_n \int d\omega_{n-1} \dots \int d\omega_1 \chi^{(n)} (-\omega; \omega_1, \dots, \omega_{n-1}, \omega_n) \times E(\omega_1) \dots, E(\omega_{n-1}), E(\omega_n)$$

where  $E(\omega) = \int dt E(t) e^{i\omega t}$  and  $\chi^{(n)}$  is the nonlinear susceptibility mentioned in sec.1.1 that is nothing but the frequency domain counterpart of the response function  $S^{(n)}$ .

<sup>&</sup>lt;sup>5</sup>Alternatively, the nonlinear polarization can be recast in the frequency domain:

pointing to the left stand for  $e^{-ikr+i\omega t}$ . Arrows pointing inwards represent absorption of a photon and so an increasing excitation of the system, while arrows pointing outwards represent emission of a photon and so a de-excitation of the system.

- 4. The last interaction, which originates from the perturbed density matrix, is represented by a wavy arrow. By convention, it points away from the left side of the ladder <sup>6</sup>.
- 5. Each diagram has a sign  $(-1)^{N_R}$ , where  $N_R$  is the number of interactions from the right. This is due to the fact that each interaction from the right in the commutator carries a minus sign. The last interaction has not to be taken into account in this sign-rule, as it is not part of the commutator.

#### 1.3.6 Example: Third-order processes

We shall now restrict our discussion only to the third-order nonlinear processes and give a detailed description of the response function involved and the ds-F diagrams able to graphically depict it.

We start our discussion by rewriting Equation 1.46 for n = 3:

$$S^{(3)}(t_3, t_2, t_1) = \left(\frac{i}{\hbar}\right)^3 \theta(t_1)\theta(t_2)\theta(t_3) \times \\ \times \left\langle \langle \mu(t_3 + t_2 + t_1) | \mathbb{M}(t_3 + t_2 + t_1)\mathbb{M}(t_2 + t_1)\mathbb{M}(t_1)\mathbb{M}(0) | \rho(-\infty) \rangle \right\rangle$$
(1.47)

Since the three  $\mathbb{M}$  superoperators can act either from the left or from the right, there are  $2^3 = 8$  different terms. To evaluate each of them, we can switch back to the Hilbert space:

$$S^{(3)}(t_3, t_2, t_1) = \left(\frac{i}{\hbar}\right)^3 \theta(t_1)\theta(t_2)\theta(t_3) \times \\ \times \langle \mu(t_3 + t_2 + t_1) \left[ \mu(t_2 + t_1), \left[ \mu(t_1), \left[ \mu(0), \rho(-\infty) \right] \right] \right] \rangle$$
(1.48)

where  $\langle ... \rangle$  has to be intended over the unperturbed density matrix.

It is clear that the last interaction  $\mu(t_3 + t_2 + t_1)$  in Equation 1.48 plays a different role in the process. From a mathematical point of view, this is due to the fact that only the first three interactions are part of the commutators, while the last is not. The physical interpretation is that the interactions occurring at times 0,  $t_1$ and  $t_1 + t_2$  are directly linked to the incoming electric fields, whose combined action generates a non-equilibrium  $\rho^{(3)}$ . The perturbed density matrix is then responsible for the emission of a light field at time  $t_3 + t_2 + t_1$ . In general, this means that a  $n^{th}$ -order nonlinear response actually involves n + 1 fields. This is the reason for the apparently misleading association between the third-order nonlinear response and the four-wave mixing techniques.

<sup>&</sup>lt;sup>6</sup>Diagrams in which the last interaction points away from the right are just complex conjugates and will not be explicitly shown.

Equation 1.48 can be conveniently recast in the following form:

$$S^{(3)}(t_3, t_2, t_1) = \left(\frac{i}{\hbar}\right)^3 \theta(t_1)\theta(t_2)\theta(t_3) \sum_{\alpha=1}^4 \left[R_\alpha(t_3, t_2, t_1) - R_\alpha^\star(t_3, t_2, t_1)\right]$$
(1.49)

where we have defined:

$$R_{1}(t_{3}, t_{2}, t_{1}) = \langle \mu(t_{3}, t_{2}, t_{1})\mu(0)\rho(-\infty)\mu(t_{1})\mu(t_{1} + t_{2})\rangle$$

$$R_{2}(t_{3}, t_{2}, t_{1}) = \langle \mu(t_{3}, t_{2}, t_{1})\mu(t_{1})\rho(-\infty)\mu(0)\mu(t_{1} + t_{2})\rangle$$

$$R_{3}(t_{3}, t_{2}, t_{1}) = \langle \mu(t_{3}, t_{2}, t_{1})\mu(t_{1} + t_{2})\rho(-\infty)\mu(0)\mu(t_{1})\rangle$$

$$R_{4}(t_{3}, t_{2}, t_{1}) = \langle \mu(t_{3}, t_{2}, t_{1})\mu(t_{1} + t_{2})\mu(t_{1})\mu(0)\rho(-\infty)\rangle$$
(1.50)

 $R^{\star}_{\alpha}$  are just the complex conjugate of the expressions in Equation 1.50. This means that, out of the eight possible combinations, just four are relevant. This is a general rule, which also holds in the general  $n^{th}$ -case, and which halves the number of the Liouville space pathways  $(2^n \to 2^{n-1})$ .

We can now apply the rules we have previously defined to construct the ds-F diagrams for the four independent terms in Equation 1.50. We show in Figure 1.4 the corresponding ds-F diagrams [5]. Note that, since there are either two interactions or no interactions at all acting from the right, all the contributions come with a plus sign.



**Figure 1.4:** Double-sided Feynman diagrams representing the four relevant contributions to the third-order response function.

It is worth to notice that the four Liouville pathways we have discussed here are just those due to the explicit calculation of the response function. However, also electric fields appear in the expression of the final third-order polarization, which reads (from Equation 1.45):

$$P^{(3)}(t) = \int_0^\infty dt_3 \int_0^\infty dt_2 \int_0^\infty dt_1 E(t-t_3) E(t-t_3-t_2) E(t-t_3-t_2-t_1) S^{(3)}(t_3,t_2,t_1)$$
(1.51)

If we now assume that the emitted light field originates from three distinct laser pulses, each electric field entering in the last equation is actually the sum of the electric fields of the three pulses, namely:

$$E(t) = E_1(t) \cdot (e^{-i\omega_1 t} + e^{+i\omega_1 t}) + E_2(t) \cdot (e^{-i\omega_2 t} + e^{+i\omega_2 t}) + E_3(t) \cdot (e^{-i\omega_3 t} + e^{+i\omega_3 t})$$
(1.52)

which yields 6 distinct terms.

This means that the polarization splits into  $6 \cdot 6 \cdot 6 \cdot 4 = 864$  terms. However, this number can be considerably reduced if the following experimental tricks are considered [5]

• Time ordering: we consider the pulses' duration much shorter than the time separation between them, so that they do not overlap in time and interact with the material in a strict time ordering. In this condition, it is possible to trace back each interaction to a specific electric field. The number of possible pathways is reduced from 864 to  $2 \cdot 2 \cdot 2 \cdot 4 = 32$  terms.

• Rotating Wave Approximation (RWA): we consider a condition in which the applied fields are near resonance with a characteristic transition in the system. It can be proved that terms in the Hamiltonian which oscillate fast can be neglected [5]. As a consequence, only terms containing either  $e^{i\omega t}$  or  $e^{-i\omega t}$  will contribute, but not both. The number of terms is further reduced to  $1 \cdot 1 \cdot 1 \cdot 4 = 4$ .

• Phase matching: so far, we have ignored the wavevectors of the fields. If one includes them, the emitted field will have a resulting wavevector given by  $k = \pm k_1 \pm k_2 \pm k_3$ . If the RWA holds, then only a set of signs will survive. By defining an appropriate experimental geometry, it is then possible to isolate a selected Liouville pathway.

It should be pointed out here that in our experiment, though the last two points remain valid, the time ordering of the interactions, except for the pump-probe measurements, cannot be strictly controlled. We will thus develop our model in the frequency domain, which seems a more natural way to describe the process.

#### **1.3.7** Heterodyne detection of wave mixing

We have repeatedly stressed the key role that the polarization plays in determining the optical properties of a material. We have then worked out the expression of the  $n^{th}$ -order nonlinear polarization and stated many times that, once this expression is known, any kind of nonlinear process can be predicted.

We shall now move a step forward by discussing how the polarization is mapped into directly detectable effects, that is how optical signals can be computed [4]. The calculation of the optical signals requires the solution of the Maxwell's equations, through which the nonlinear polarization acts as a source for the radiation of the signal electric field.

Let us consider a multiwave mixing process involving n electric fields with wave vectors  $\mathbf{k}_1, ..., \mathbf{k}_n$  and frequencies  $\omega_1, ..., \omega_n$ . The interaction will result in the coherent generation of a signal field with wave vector  $\mathbf{k}_s = \pm \mathbf{k}_1 \pm ... \pm \mathbf{k}_n$  and frequency  $\omega_s = \pm \omega_1 \pm ... \pm \omega_n$ . We assume the radiated field to be much weaker than the incoming fields.

By solving the Maxwell's equations (see Appendix A) for a slab-shaped sample, we get:

$$E_s(l,t) = \frac{2\pi i}{n(\omega_s)} \frac{\omega_s}{c} l P_s(t) sinc\left(\frac{\Delta kl}{2}\right) e^{i\frac{\Delta kl}{2}}$$
(1.53)

where l is the thickness of the slab along the direction of  $\mathbf{k}_s$  (fixed by the position of the detector),  $n(\omega_s)$  the frequency-dependent refraction index,  $P_s(t)$  is the nonlinear polarization of a given order along the detection axis, and  $\Delta k = |\mathbf{k}_s - \mathbf{k}'_s|$  with  $k'_s \equiv \frac{\omega_s}{c} n_s$  determined by the frequency dispersion and the geometry of the experiment. Note that the signal field is linear in the polarization. This means that the intensity of the detected field will be proportional to  $|P_s(t)|^2$ .

An important advantage of the wave mixing techniques is that the signal can be generated in a new direction, i.e. a direction different from those of the incoming fields. Typically, this would make the detection much more sensitive, since there is no background. However, nonlinear signals are usually very weak and very difficult to detect. A considerable improvement can be achieved by adopting an interferometric technique, called *heterodyne detection*. In this configuration, an amplification of the signal is obtained by adding an external reference field, called *local oscillator* (LO), which has the same wave vector of the output field <sup>7</sup>. The total detected intensity is thus the superposition of the signal field  $(E_S(t))$  and the local oscillator  $(E_{LO}(t))$ :

$$I(t) = \frac{n(\omega_S)c}{4\pi} |E_{LO}(t) + E_S(t)|^2$$
  
=  $I_{LO}(t) + I_S(t) + 2\frac{n(\omega_S)c}{4\pi} \Re e \left[ E_{LO}^{\star}(t) \cdot E_S(t) \right]$  (1.54)

where  $I_{LO}(t)$  and  $I_S(t)$  are the intensities of the local oscillator and the signal field, respectively.

Since  $E_S(t)$  is usually much weaker than  $E_{LO}(t)$ , the second term in Equation 1.54 can be neglected. Moreover, the intensity of the local oscillator can be easily subtracted, since it is a known field. The heterodyne contribution to the signal can be therefore isolated as follows:

$$I(t) = \frac{n(\omega_S)c}{4\pi} \mathfrak{Re}\left[E_{LO}^{\star}(t) \cdot E_S(t)\right]$$
(1.55)

which is linear rather than quadratic in the polarization and, hence, easier to measure.

**Self-heterodyne detection** We immediately recognize some similarities with our experiment. The stimulated Raman scattering process we observe gives rise to signal fields whose frequencies lie within the bandwidth of the incoming pulse, resulting in a mixing of its Fourier components. Therefore, what we measure in a transmission geometry is not just the intensities of the radiated signal fields, but instead the superpositions between each of them and the corresponding incident fields within the pulse. We are thus performing a heterodyne detection. Moreover, in our particular case in which the local oscillator is not an external field but is instead one of the driving fields, the detection is said to be self-heterodyne. The signal one measures

 $<sup>^{7}</sup>$ *Heterodyne* is opposed to *homodyne* detection. In terms of quantized field, a signal is said to be homodyne when detected at a field mode which is initially vacant and heterodyne when detected at a field mode already occupied.

in this condition is given by:

$$S(t) = \frac{n(\omega_S)c}{4\pi} \operatorname{\mathfrak{Re}} \left[ E_2^{\star}(t) \cdot E_S(t) \right]$$
  

$$\propto -(\omega_2 l) \operatorname{\mathfrak{Im}} \left[ E_2^{\star}(t) P_S(t) \right]$$
(1.56)

where in the first line we have simply replace  $E_{LO}(t)$  with one of the incoming fields (arbitrarily chosen to be that at frequency  $\omega_2$ ) and in the last step we have used Equation 1.53.

#### 1.4 Fully quantum description

In both the classical and semiclassical approaches we have developed so far the optical field has been treated classically. This description, while providing a rather convenient theoretical framework, inevitably prevents the prediction of observables related to the quantum nature of the electromagnetic field. These limitations are clearly more severe if one deals with the response of a single or a few scatterers, when single photon regime can be achieved [3].

This situation, however, would seem very far from our experimental conditions in which a macroscopic sample is examined and, most importantly, the fields involved can be safely considered classical. The fully quantum treatment we are going to introduce, although formally correct, may seem indeed superfluous for the process we are willing to describe.

Nonetheless, there is a compelling reason to prefer such approach to the typical semiclassical one. Precisely, this reason lies in the expression we have derived for a heterodyne detected signal. Indeed, a crucial point in the semiclassical derivation of Equation 1.55 is that the local oscillator does not interact with the material. We have implicitly made this assumption in writing Equation 1.54, where we have considered the interference between the LO and the signal only after the latter has been generated. However, this assumption breaks for self-heterodyned signals in which the LO, being at the same time one of the incoming fields, obviously interacts with the sample [6].

The development of a quantum model for both fields and matter allows to reformulate nonlinear wave mixing processes and naturally leads to a unified description of heterodyne and self-heterodyne detected signals [7]. In this framework, all the n + 1 waves (including the signal) involved in a  $\chi^{(n)}$  process are treated on the same footing and the LO needs not to be spatially separated from the material [6]. Moreover, a fully quantum approach provides a more intuitive definition of the signal that intrinsically includes both spontaneous and stimulated emission events [8]. Finally, this treatment will allow us (Chapter 2) to recast optical signals in terms of transition amplitudes rather than susceptibilities, thus establishing a clearer picture of the underlying molecular processes.

#### 1.4.1 Quantum-field description of heterodyne signals

In the quantum-field description of both linear and nonlinear optical processes, the electric field is quantized [3]. In analogy with the material degrees of freedom, the electric field can be completely described by a wavefunction, denoted by  $|\Psi_F\rangle$ . The expectation value of the electric field is then calculated as  $\langle \Psi_F | \hat{E}(\mathbf{r}, t) | \Psi_F \rangle$ , where

$$\hat{E}(\mathbf{r},t) = \hat{\mathcal{E}}(\mathbf{r},t) + \hat{\mathcal{E}}^{\dagger}(\mathbf{r},t)$$
(1.57)

is the optical electric field operator, whose positive-frequency component reads (in cgs units):

$$\hat{\mathcal{E}}(\mathbf{r},t) = \sum_{s} \left(\frac{2\pi\hbar\,\omega_s}{\Omega}\right)^{1/2} \hat{a}_s \, e^{i(\mathbf{k}_s \cdot \mathbf{r} - \omega_s t)} \tag{1.58}$$

where we have indicated by  $\Omega$  the quantization volume and by  $\hat{a}_s$  ( $\hat{a}_s^{\dagger}$ ) the boson annihilation (creation) operators for the mode *s*, which satisfy the boson commutation relation  $\begin{bmatrix} \hat{a}_s, \hat{a}_{s'}^{\dagger} \end{bmatrix} = \delta_{ss'}$ .

The action of the bosonic operators is defined as follows:

$$\hat{a}_{s}^{\dagger}|\Psi_{F}^{s}(n)\rangle = n_{s}^{1/2}|\Psi_{F}^{s}(n+1)\rangle$$

$$\hat{a}_{s}|\Psi_{F}^{s}(n)\rangle = (n_{s}-1)^{1/2}|\Psi_{F}^{s}(n-1)\rangle$$
(1.59)

where  $n_s$  is the photon occupation number of the mode s.

The Hamiltonian of a molecule interacting with an optical electric field (Equation 1.11) has now to be revisited to account for the field quantization [7]

$$\hat{H} = \hat{H}_0 + \hat{H}_F + \hat{H}_{int}$$
(1.60)

where  $\hat{H}_0$  represents the free unperturbed molecule,  $\hat{H}_F$  the field degrees of freedom, and  $\hat{H}_{int}$  the interaction between the molecule and the field.

The latter two contributions are given in the quantum-field model by:

$$\hat{H}_F = \sum_s \hbar \omega_s \hat{a}_s^{\dagger} \hat{a}_s \tag{1.61}$$

$$\hat{H}_{int}(t) = \hat{\mathcal{E}}(t)\hat{V}^{\dagger} + \hat{\mathcal{E}}^{\dagger}(t)\hat{V}$$
(1.62)

where the interacting part has been written in the RWA and we have partitioned the dipole operator  $\hat{\mu}$  as  $\hat{\mu} = \hat{V} + \hat{V}^{\dagger}$ , with  $\hat{V}^{\dagger}$  ( $\hat{V}$ ) being the creation (annihilation) operator for excitation. The dipole operators are of the form  $\hat{V} = \sum_{a} \sum_{b>a} \mu_{ab} |a\rangle \langle b|$ . We recall that, within the RWA, fast oscillating terms are neglected. This condition can be included in the expression of the interaction Hamiltonian by discarding the products  $\hat{\mathcal{E}}(t)\hat{V}$  and  $\hat{\mathcal{E}}^{\dagger}(t)\hat{V}^{\dagger}$ , each containing two positive-frequency oscillating terms.

The expression of the interacting Hamiltonian clearly shows that the light-matter interaction involves a change in both the material and the field degrees of freedom [3]. This point naturally paves the way for a new definition of optical signals. Let us recall that in the semiclassical approach the signal is obtained by calculating the

expectation value of the dipole operator and then using the resulting polarization as a source for the detected radiation. In the quantum approach, the signal is instead calculated in a completely different fashion. By looking at the field degrees of freedom, we can simply relate the signal to the change in the number of photons [7]. When dealing with light pulses, we can define the signal as the *net* change of the photon number between the initial (i) and the final (f) states:

$$S \equiv \int dt \frac{d}{dt} \left( \hat{\mathcal{N}} \right)_{\rho} = \langle \hat{\mathcal{N}} \rangle_f - \langle \hat{\mathcal{N}} \rangle_i \tag{1.63}$$

where  $\hat{\mathcal{N}}$  is the photon occupation number operator:

$$\hat{\mathcal{N}} \equiv \sum_{s} \hat{a}_{s}^{\dagger} \hat{a}_{s} \tag{1.64}$$

where the index s runs over the detected modes. The eigenvalue of  $\hat{\mathcal{N}}$  is the total (all modes) number of photons.

In writing Equation 1.63, we have adopted the following notation, that will be used throughout this section:  $(...)_{\rho}$  denotes the expectation value with respect to the total (molecule + field) density matrix of the system,  $\hat{\rho}(t)$ . Let us recall (section 1.3.1) that an expectation value within the density operator formalism is nothing but a trace with respect to the density matrix. We have also introduced another ensemble average, denoted by  $\langle ... \rangle$ , which indicates the average over the non-interacting ( $\hat{H}_{int} = 0$ ) density matrix. This corresponds to the limit  $t \to -\infty$ .

The time derivative in Equation 1.63 can be evaluated by switching to the Heisenberg picture (in which the density matrix is constant) and using the Heisenberg equations of motion  $^{8}$ 

$$\frac{d}{dt}\left(\hat{\mathcal{N}}\right)_{\rho} \equiv \left\langle \frac{d}{dt}\hat{\mathcal{N}}_{H} \right\rangle = \left\langle \sum_{s} \frac{i}{\hbar} \left[ \hat{H}_{int}(t), \hat{a}_{s,H}^{\dagger} \hat{a}_{s,H} \right] \right\rangle$$
(1.65)

where the subscript H denotes operators in the Heisenberg picture.

By substituting the expression of the interacting Hamiltonian (Equation 1.62) and that of the electric field operator (Equation 1.58), we end up with an equation in which only commutators between bosonic operators are left. Using the boson commutation relation and transforming back to the interaction picture, we get:

$$S = \frac{2}{\hbar} \,\mathfrak{Im} \int dt \left(\hat{\mathcal{E}}^{\dagger}(t)\hat{V}\right)_{\rho} \tag{1.66}$$

Note that if we expand  $\rho(t)$  in power series of the fields (Equation 1.22) in each of the incoming modes, we obtain Equation 1.66 in terms of the nonlinear polarization, rather than the electric dipole operator. Equation 1.66 is thus the quantum counterpart of the semiclassical expression we derived in Equation 1.56 [6].

The signal in Equation 1.66 can be further manipulated to obtain a more explicit expression [6]. This can be done by considering the time evolution of the

<sup>&</sup>lt;sup>8</sup>Note that the Heisenberg equations of motion would involve the total Hamiltonian in the commutators, but in our specific case only the commutator with  $\hat{H}_{int}$  survives.

density operator. Recalling the final expression of the time evolution superoperator  $\mathbb{U}(t, -\infty)$  in the interaction picture (Equation 1.39), we can write:

$$\rho(t) = \left\{ \mathcal{T}e^{-\frac{i}{\hbar} \int_{-\infty}^{t} d\tau \mathbb{H}_{int}(\tau)} \right\} \rho(-\infty)$$
(1.67)

which is the exact solution of the Liouville-Von Neumann equation (Equation 1.25).

It is convenient at this point to slightly change the notation we have used so far. The propagation can be more compactly described in terms of the so-called Liouville space "left" and "right" superoperators (L/R representation), defined as follows:

$$\hat{A}_L \hat{X} \equiv \hat{A} \hat{X}$$
$$\hat{A}_R \hat{X} \equiv \hat{X} \hat{A}$$
(1.68)

where on the right-hand side the operator  $\hat{A}$  and  $\hat{X}$  are in the Hilbert space [7]. The L/R representation is particularly useful to keep trace of all the interactions the sample undergoes, since it clearly tells whether the ket or the bra of the density matrix are involved. Moreover, we can define linear combinations (+/- superoperators) of the L/R superoperators:

$$\hat{A}_{\pm} \equiv \frac{1}{\sqrt{2}} \left[ \hat{A}_L \pm \hat{A}_R \right] \tag{1.69}$$

In particular, the following formal equivalence holds:

$$\hat{A}_{-} \Leftrightarrow \mathbb{A}$$
 (1.70)

By propagating the density matrix as in Equation 1.67, we can now rewrite Equation 1.66 in the L/R representation:

$$S = \frac{2}{\hbar} \Im \mathfrak{m} \int dt \left\langle \hat{\mathcal{E}}_{L}^{\dagger}(t) \hat{V}_{L}(t) \mathcal{T} e^{-\frac{i}{\hbar} \int_{-\infty}^{t} d\tau \sqrt{2} \mathcal{H}_{int-}(\tau)} \right\rangle$$
(1.71)

where  $\mathcal{H}_{int-}$  is the - superoperator corresponding to  $\hat{H}_{int}$  (Equation 1.62) and the time dependence of the dipole superoperator comes from the transformation to the interaction picture.

Equation 1.71 is the general expression for a heterodyne detected signal in the fully quantum approach. Let us highlight the fact that we have explicitly required the detection to be heterodyne when we have defined the signal as the time derivative of the expectation value of  $\hat{\mathcal{N}}$ . Indeed, this definition holds only if no one among the detected modes is initially empty. Moreover, Equation 1.71 has general validity, since neither approximations nor perturbative expansions have been made so far, except for the RWA. The expression we have derived is the exact and compact form of the signal, as it still contains all orders in the fields. It is thus regarded as the starting point for the perturbative calculation of specific optical signals, which can differ both in the order of nonlinearity and the degrees of freedom involved [7].
Finally, it can be proved that Equation 1.71 applies to both spontaneous and stimulated signals, thus providing a unified description of both the processes [8]. In the following, we shall ignore spontaneous emission and consider only stimulated events. We assume that the field is initially in a coherent state [7]:

$$|\Psi_C\rangle = A_0 \, e^{\sum_s \hat{a}_s^{\dagger} \alpha_s} |0\rangle \tag{1.72}$$

where  $A_0 = \exp(-\sum_s |\alpha_s|^2)$  is the renormalization factor such that  $\langle \Psi_C | \Psi_C \rangle = 1$ ,  $\alpha_s$  is the eigenvalue of the photon annihilation operator  $(\hat{a}_s | \Psi_C \rangle = \alpha_s | \Psi_C \rangle)$ , and  $|0\rangle$  is the vacuum state. The expectation value of the field is then:

$$\langle \Psi_C | \hat{E}(\mathbf{r}, t) | \Psi_C \rangle = \mathcal{E}(\mathbf{r}, t) + c.c.$$
 (1.73)

where

$$\mathcal{E}(\mathbf{r},t) = \sum_{s} \left(\frac{2\pi\hbar\omega_s}{\Omega}\right)^{1/2} e^{i(\mathbf{k}_s\cdot\mathbf{r}-\omega_s t)}\alpha_s \tag{1.74}$$

is the field amplitude at space-point **r**, namely the classical expectation value of  $\hat{\mathcal{E}}$ .

# Chapter 2

# Stimulated Raman Scattering with stochastic light

In Chapter 1 we have developed the theory of nonlinear optical processes and the formalism required for their description. In particular, we have introduced the density operator formalism within the semiclassical model and stressed its importance also in the fully quantum approach. As already mentioned above, the quantum description we have discussed in section 1.4 is the starting point for the development of the theoretical model of our experiment.

The key feature of the proposed Noise Correlation Spectroscopy (NCS) is the choice of the incoming pulses interacting with the sample: we use broadband light pulses in which noise is introduced as stochastic narrow fluctuations within the pulse bandwidth (see Figure 2.1). The experimental details on how noisy pulses are generated, will be given in Chapter 3. It will suffice to know for now that our experimental apparatus allows us to introduce both phase and/or amplitude fluctuations at given frequencies within the spectral content of the pulse. Since a nonlinear process can be regarded as a mixing of the Fourier components within the bandwidth of each incoming pulse, the light-matter interaction results in a coupling of the spectral components involved in the process. It is then expected that the noises of the light components at entangled frequencies will be correlated.

In the following, we will prove that this is actually the case. We will start by the definition of heterodyne detected signals we gave in Equation 1.71 and we will adapt it to the description of Stimulated Raman Scattering (SRS) in the frequency domain. We will then introduce the random fluctuations and see what a covariancebased statistical analysis of the spectra which have interacted with the sample can reveal about the SRS process.

The model we present is the result of a collaboration with the theoretical group of Shaul Mukamel.<sup>1</sup> The preliminary version we discuss here is only suitable for the description of phase fluctuations. Moreover, our current model has been tailored to the description of static measurements only, thus ruling out the possibility of studying the relaxation of the system in pump and probe measurements. For the

<sup>&</sup>lt;sup>1</sup>Department of Chemistry, University of California, Irvine (USA).



Figure 2.1: Simulation of an incident pulse used in NCS. The grey pulse represents a pristine gaussian pulse, as it would be delivered by the femtosecond near-infrared laser source we use. The black curve depicts the same pulse after localized narrow fluctuations have been introduced within its spectrum.



Figure 2.2: Depiction of the experimental situation described by our theoretical model.

sake of clarity, we are describing here a situation like that depicted in Figure 2.2. Noisy broadband pulses with uncorrelated pulse-to-pulse phase fluctuations repeatedly interact with a Raman-active medium in its ground state. Each transmitted pulse is acquired by a frequency-resolved detection system and the cross-correlation signal is then obtained by computing the covariance over all the repetitions.

A more complete model, able to include amplitude fluctuations and time-domain measurements as well, is going to be developed soon.

## 2.1 Frequency dispersed signal

Let us first recall the expression of heterodyne detected signals that we have derived in the last section of Chapter 1:

$$S = \frac{2}{\hbar} \Im \mathfrak{m} \int dt \left\langle \hat{\mathcal{E}}_{L}^{\dagger}(t) \hat{V}_{L}(t) \mathcal{T} e^{-\frac{i}{\hbar} \int_{-\infty}^{t} d\tau \sqrt{2} \mathcal{H}_{int-}(\tau)} \right\rangle$$
(2.1)

where  $\hat{\mathcal{E}}_L^{\dagger}$  is the negative frequency component of the electric field operator and  $\hat{V}_L$  the positive frequency component of the electric dipole operator, both expressed in the L/R representation. We also recall that in this notation the single-particle polarization reads:

$$P(t) = \langle \hat{V}(t) \rangle = Tr\left(\hat{\rho}\,\hat{V}(t)\right) = \int d\omega P(\omega)e^{-i\omega t}$$
(2.2)

where  $\rho$  is the density matrix and  $P(\omega)$  the Fourier transform of the polarization.

The signal S in Equation 2.1 has been defined as the net change in the number of photons after the interaction with the material, by considering all the photon modes involved in the process. However, since we acquire shot-to-shot frequencyresolved spectra, we are interested in the frequency dispersed signal  $S(\omega)$ , that is the intensity we expect to measure at frequency  $\omega$ . To do so, we can first Fourier transform the negative-frequency component of the electric field operator and then add a frequency gating  $\delta(\omega - \bar{\omega})$ . By substituting  $\bar{\omega} \to \omega$ , we get:

$$S(\omega) = \frac{2}{\hbar} \Im \mathfrak{m} \int dt \, e^{i\omega t} \left\langle \hat{\mathcal{E}}_L^{\dagger}(\omega) \hat{V}_L(t) \mathcal{T} e^{-\frac{i}{\hbar} \int_{-\infty}^t d\tau \sqrt{2} \mathcal{H}_{int-}(\tau)} \right\rangle$$
(2.3)

By using Equation 1.5, we can write the off-resonant polarization in terms of the polarizability  $\alpha(t)$ . So, if the coupling between the field modes and the matter is off resonance, one can rewrite the signal as:

$$S(\omega) = \frac{2}{\hbar} \Im \mathfrak{m} \int dt e^{i\omega t} \left\langle \hat{\mathcal{E}}_L^{\dagger}(\omega) \hat{\mathcal{E}}_L(t) \alpha_L(t) \mathcal{T} e^{-\frac{i}{\hbar} \int_{-\infty}^t d\tau \sqrt{2} \mathcal{H}_{int-}(\tau)} \right\rangle$$
(2.4)

The last equation still contains all the contributions coming from any order in the electric fields. We can now perform a perturbative expansion of Equation 2.4, by considering the explicit action of the time ordering operator  $\mathcal{T}$ . Since the 0<sup>th</sup>-order contains only one light-matter interaction ( $\alpha_L$ ), it vanishes when traced over the non-interacting density matrix. We thus expand to the first (nontrivial) order as:

$$S(\omega) = \frac{2}{\hbar} \Im \mathfrak{m} \int dt e^{i\omega t} \left\langle \hat{\mathcal{E}}_L^{\dagger}(\omega) \hat{\mathcal{E}}_L(t) \alpha_L(t) \left( -\frac{i}{\hbar} \sqrt{2} \right) \int_{-\infty}^t d\tau \mathcal{H}_{int-}(\tau) \right\rangle$$
(2.5)

By recalling the definition of the - superoperator (Equation 1.69), the first-order contribution to the signal splits into two terms:

$$S(\omega) = \frac{2}{\hbar^2} \Re \mathfrak{e} \int dt e^{i\omega t} \left\langle \hat{\mathcal{E}}_L^{\dagger}(\omega) \hat{\mathcal{E}}_L(t) \alpha_L(t) \left[ \int_{-\infty}^t d\tau \mathcal{H}_{int,R}(\tau) - \int_{-\infty}^t d\tau \mathcal{H}_{int,L}(\tau) \right] \right\rangle$$
  
$$\equiv S_a(\omega) - S_b(\omega)$$
(2.6)



Figure 2.3: CTPL diagrammatic representation of the SRS process. The diagram a) and b) represent the term  $S_a(\omega)$  (Stokes process) and  $S_b(\omega)$  (Anti-Stokes process) in the text, respectively.

The first term  $(S_a)$  involves interactions from both the left and the right, while the second one  $(S_b)$  only interactions from the left. We can describe them using the Closed-Time-Path-Loop (CTPL) representation, a diagrammatic expansion that, although similar to the double-sided Feynman diagrams, is most suitable when the signal is expressed in the frequency domain. By following the rules outlined in Appendix B, we can construct the two diagrams in Figure 2.3, which describe the process we are examining. The diagram on the left represents the energy loss of the electric field (Stokes process), while the one on the right represents the energy gain of the electric field (Anti-Stokes process).

The two contributions can be explicitly evaluated as follows. We start by calculating  $S_a$ :

$$S_{a}(\omega) = \frac{2}{\hbar^{2}} \Re \mathfrak{e} \int dt e^{i\omega t} \left\langle \hat{\mathcal{E}}_{L}^{\dagger}(\omega) \hat{\mathcal{E}}_{L}(t) \alpha_{L}(t) \int_{-\infty}^{t} d\tau \mathcal{H}_{int,R}(\tau) \right\rangle$$
$$= \frac{2}{\hbar^{2}} \Re \mathfrak{e} \int dt e^{i\omega t} \left\langle \hat{\mathcal{E}}_{L}^{\dagger}(\omega) \left[ \int \frac{d\omega_{1}d\omega_{2}}{(2\pi)^{2}} e^{-i(\omega_{1}+\omega_{2})t} \hat{\mathcal{E}}_{L}(\omega_{1}) \alpha_{L}(\omega_{2}) \right] \times \qquad (2.7)$$
$$\times \int_{-\infty}^{t} d\tau \int \frac{d\omega_{3}d\omega_{4}d\omega_{5}}{(2\pi)^{3}} e^{-i(-\omega_{3}+\omega_{4}+\omega_{5})\tau} \hat{\mathcal{E}}_{R}^{\dagger}(\omega_{3}) \hat{\mathcal{E}}_{R}(\omega_{4}) \alpha_{R}(\omega_{5}) \right\rangle$$

where in the second step we have substituted the expression of the interaction Hamiltonian in terms of  $\alpha$  and Fourier transformed both the electric field operators and the polarizabilities.

Since the average  $\langle ... \rangle$  is over the unperturbed density matrix, we can now separate the material degrees of freedom (denoted by  $\mu$ ) from the field ones (denoted

by  $\phi$ ):

$$S_{a}(\omega) = \frac{2}{\hbar^{2}} \Re \mathfrak{e} \iint \frac{d\omega_{1} d\omega_{2} d\omega_{3} d\omega_{4} d\omega_{5}}{(2\pi)^{5}} \langle \hat{\mathcal{E}}_{L}^{\dagger}(\omega) \hat{\mathcal{E}}_{L}(\omega_{1}) \hat{\mathcal{E}}_{R}^{\dagger}(\omega_{3}) \hat{\mathcal{E}}_{R}(\omega_{4}) \rangle_{\phi} \times \\ \times \langle \alpha_{L}(\omega_{2}) \alpha_{R}(\omega_{5}) \rangle_{\mu} \underbrace{\int dt e^{i(\omega-\omega_{1}-\omega_{2})t} \int_{-\infty}^{t} d\tau e^{-i(-\omega_{3}+\omega_{4}+\omega_{5})\tau}}_{\equiv I}$$
(2.8)

We highlight that the average over  $\phi$  does not include the stochastic degrees of freedom over which the our covariance-based analysis is performed, but it refers only to the field density matrix.

We can now separately solve the integrals over t and  $\tau$ :

$$I = \int dt e^{i(\omega - \omega_1 - \omega_2)t} \left( \lim_{\gamma \to 0} \frac{i e^{-i(-\omega_3 + \omega_4 + \omega_5)t}}{-\omega_3 + \omega_4 + \omega_5 - i\gamma} \right)$$
  
$$= i \lim_{\gamma \to 0} \int dt \frac{e^{-i(-\omega_3 + \omega_4 + \omega_5 + \omega_1 + \omega_2 - \omega)t}}{-\omega_3 + \omega_4 + \omega_5 - i\gamma}$$
  
$$= i \lim_{\gamma \to 0} \frac{2\pi \,\delta(\omega_1 + \omega_2 + \omega_4 + \omega_5 - \omega_3 - \omega)}{-\omega_3 + \omega_4 + \omega_5 - i\gamma}$$
(2.9)

Substituting in the expression of  $S_a$ :

$$S_{a}(\omega) = \lim_{\gamma \to 0} \frac{2}{\hbar^{2}} \Im \mathfrak{m} \iint \frac{d\omega_{1} d\omega_{2} d\omega_{3} d\omega_{4} d\omega_{5}}{(2\pi)^{5}} \frac{\langle \hat{\mathcal{E}}_{L}^{\dagger}(\omega) \hat{\mathcal{E}}_{L}(\omega_{1}) \hat{\mathcal{E}}_{R}^{\dagger}(\omega_{3}) \hat{\mathcal{E}}_{R}(\omega_{4}) \rangle_{\phi}}{-\omega_{3} + \omega_{4} + \omega_{5} - i\gamma} \times \langle \alpha_{L}(\omega_{2}) \alpha_{R}(\omega_{5}) \rangle_{\mu} 2\pi \delta(\omega_{1} + \omega_{2} + \omega_{4} + \omega_{5} - \omega_{3} - \omega)$$
(2.10)

We can now span the polarizabilities in the energy eigenstates of the material. We consider here a two-level system (the vibrational ground state is denoted by  $|g\rangle$ , while the excited one by  $|e\rangle$ ) with a single vibrational frequency  $\Omega$ . The term involving the polarizability is then given by:

$$\langle \alpha_L(\omega_2)\alpha_R(\omega_5) \rangle_{\mu} = Tr(\alpha(\omega_2)\rho\,\alpha(\omega_5))$$

$$= Tr(\alpha(\omega_2)|g\rangle\langle g|\alpha(\omega_5))$$

$$= \langle e|\alpha(\omega_2)|g\rangle\langle g|\alpha(\omega_5)|e\rangle$$

$$= |\alpha_{ge}|^2(2\pi)^2\delta(\omega_2 + \Omega)\,\delta(\omega_5 - \Omega)$$

$$(2.11)$$

where in the last step we have expressed the average in the Kramers-Heisenberg (KH) form (a generalized Fermi golden rule), as in [6]. We have denoted by  $\alpha_{ge}$  the polarizability transition amplitude between the two states. The generalized KH form allows to recast heterodyne optical signals in terms of the scattering amplitudes rather than the standard nonlinear susceptibilities. The equivalence of the two formulations is discussed and demonstrated in [6]. We prefer here taking the KH approach since it is more intuitive and, most importantly, it helps in clearly revealing what is really happening to the matter in the course of the process.

By solving the Dirac deltas, we get the final expression for  $S_a$ :

$$S_a = \lim_{\gamma \to 0} \frac{2|\alpha_{ge}|^2}{\hbar^2} \Im \mathfrak{m} \iint \frac{d\omega_1 d\omega_2}{(2\pi)^2} \frac{\mathcal{E}^*(\omega)\mathcal{E}(\omega + \omega_1 - \omega_2)\mathcal{E}^*(\omega_1)\mathcal{E}(\omega_2)}{-\omega_1 + \omega_2 + \Omega - i\gamma}$$
(2.12)

where we have replaced the electric field operators with their expectation values (Equation 1.74), since we detect intense fields (i.e. fields in a classical regime).

The term  $S_b$  can be evaluated in a similar fashion, with the exception that now the polarizability reads:

$$\langle \alpha_L(\omega_2)\alpha_L(\omega_5) \rangle_{\mu} = \langle g | \alpha(\omega_2) | e \rangle \langle e | \alpha(\omega_5) | g \rangle$$
  
=  $|\alpha_{ge}|^2 (2\pi)^2 \delta(\omega_2 - \Omega) \, \delta(\omega_5 + \Omega)$  (2.13)

since all the operators act from the left in  $S_b$ .

By recombining the two terms, we get:

$$S(\omega) = \lim_{\gamma \to 0} \frac{2|\alpha_{ge}|^2}{\hbar^2} \Im \mathfrak{m} \iint \frac{d\omega_1 d\omega_2}{(2\pi)^2} \mathcal{E}^{\star}(\omega) \mathcal{E}(\omega + \omega_1 - \omega_2) \mathcal{E}^{\star}(\omega_1) \mathcal{E}(\omega_2) \times \\ \times \left[ \frac{1}{\omega_2 - \omega_1 + \Omega - i\gamma} - \frac{1}{\omega_2 - \omega_1 - \Omega - i\gamma} \right]$$
(2.14)

We can now use the *Sokhotski-Plemelj theorem* to explicitly calculate the terms within the square brackets. The theorem states that:

$$\lim_{\gamma \to 0} \frac{1}{\omega - i\gamma} = \mathscr{P} \mathscr{P} \frac{1}{\omega} + i\pi \delta(\omega)$$
(2.15)

where the symbol  $\mathscr{PP}$  denotes the principal value.

Equation 2.14 should now split into four distinct integrals, two involving the principal values and two involving the Dirac deltas. However, since  $\mathcal{E}^*(\omega)\mathcal{E}(\omega+\omega_1-\omega_2)\mathcal{E}^*(\omega_1)\mathcal{E}(\omega_2)$  is smooth and even around the poles of the integrand function, the principal values vanish when the integration over  $\omega_{1/2}$  is performed. Therefore, by considering the action of the Dirac deltas only, we get the final expression of the signal:

$$S(\omega) = \frac{|\alpha_{ge}|^2}{\hbar^2} \Re \mathfrak{e} \int \frac{d\omega'}{2\pi} \times [\mathcal{E}^{\star}(\omega)\mathcal{E}(\omega+\Omega)\mathcal{E}^{\star}(\omega')\mathcal{E}(\omega'-\Omega) - \mathcal{E}^{\star}(\omega)\mathcal{E}(\omega-\Omega)\mathcal{E}^{\star}(\omega')\mathcal{E}(\omega'+\Omega)]$$
(2.16)

We stress that the signal above should not be confused with the *total* frequencyresolved intensity we measure in the experiment. Indeed, recalling that we have worked out  $S(\omega)$  starting from Equation 1.63,  $S(\omega)$  does not probe any background. The signal in Equation 2.16 accounts only for intensity fluctuations deviating from the average.

**Temperature dependence** So far, we have neglected the temperature dependence of the system. If the sample has a finite temperature, two more processes must be considered, since the system can be initially either in the ground state or in the vibrationally excited one. These two situations correspond to a Raman Stokes process and a Raman Anti-Stokes process, respectively. The additional Anti-Stokes contributions we have neglected so far, are identical to  $S_a$  and  $S_b$  if one replaces  $\Omega \to -\Omega$ . We thus get the same contributions with a minus sign.

If we assume the system to be at thermal equilibrium of inverse temperature  $\beta$ , the temperature dependence can be included by considering the thermal distributions for the system, given by:

$$\begin{cases} p_g = \frac{1}{1 + e^{-\beta\hbar\Omega}}, & \text{for the ground state} \\ p_e = \frac{1}{1 + e^{\beta\hbar\Omega}}, & \text{for the first excited state} \end{cases}$$

The overall signal, including the two thermal distributions, reads:

$$S(\omega; \Gamma) = \frac{|\alpha_{ge}|^2 p_{ge}(\beta)}{\hbar^2} \Re \mathfrak{e} \int \frac{d\omega'}{2\pi} \times [\mathcal{E}^{\star}(\omega)\mathcal{E}(\omega + \Omega)\mathcal{E}^{\star}(\omega')\mathcal{E}(\omega' - \Omega) - \mathcal{E}^{\star}(\omega)\mathcal{E}(\omega - \Omega)\mathcal{E}^{\star}(\omega')\mathcal{E}(\omega' + \Omega)]$$

$$(2.17)$$

where we have defined the factor  $p_{ge}(\beta) = p_g - p_e$  and introduced the parameter  $\Gamma$ , which includes all the field parameters that can be tuned in the experiment. Note that Equation 2.17 is consistent with the fact that, if the temperature is infinite, the Stokes and Anti-Stokes processes equally contribute and thus the pulse does not change energy. Indeed, in this limit, the signal vanishes because of the factor  $p_{ge}(\beta)$ .

## 2.2 The signal including stochastic phases

Equation 2.17 quantifies the frequency resolved signal one expects to measure after the SRS process has taken place. So far, the only hypothesis we have made on the electric fields, is that they are intense enough to consider only their classical expectation values. No assumptions have been made yet on the phases of the fields. We will now formally introduce the random phase fluctuations that characterize our pulses.

To simplify the expression of the signal, we consider the phase transition to stochasticity relatively slowly, i.e. we choose the stochastic phases to have a Gaussian correlation function:

$$\langle \varphi(\omega_1)\varphi(\omega_2)\rangle \propto e^{-\left(\frac{\omega_1-\omega_2}{\Delta_{corr}}\right)^2}$$
 (2.18)

where  $\varphi(\omega_i)$  is the spectral phase at frequency  $\omega_i$  and  $\langle ... \rangle$  denotes the average over repeated measurements. The quantity  $\Delta_{corr}$  can be experimentally controlled and sets the *correlation length* of the phase fluctuations we introduce. Moreover, since we want to reveal statistical correlations between spectral components whose frequency difference matches the involved vibrational mode, the phonon frequency must be larger than  $\Delta_{corr}$  to be detected. The correlation length thus sets the scale of the spectral resolution of the method. In the following, we will consider  $\Omega \gg \Delta_{corr}$ , such that one may regard  $\varphi(\omega)$  and  $\varphi(\omega \pm \Omega)$  as statistically independent variables. It should be noted, however, that this treatment is not limited to Gaussian correlation functions only. It can be applied to any kind of decaying correlation functions whose scale is defined by a characteristic length.

Under these conditions, we can rewrite the signal by explicitly splitting each field  $\mathcal{E}(\omega)$  into its envelope  $E(\omega)$  and its spectral phase  $\varphi(\omega)$ . By grouping the

phase factors of each four-field product and taking the real part of the formula, we get:

$$S(\omega;\Gamma) = \frac{|\alpha_{ge}|^2 p_{ge}(\beta)}{\hbar^2} \int \frac{d\omega'}{2\pi} \times [E^{\star}(\omega)E(\omega+\Omega)E^{\star}(\omega')E(\omega'-\Omega)\cos\gamma - E^{\star}(\omega)E(\omega-\Omega)E^{\star}(\omega')E(\omega'+\Omega)\cos\beta]$$
(2.19)

where we have defined the following quantities:

$$\begin{cases} \gamma = \varphi(\omega + \Omega) - \varphi(\omega) + \varphi(\omega' - \Omega) - \varphi(\omega') \\ \beta = \varphi(\omega - \Omega) - \varphi(\omega) + \varphi(\omega' + \Omega) - \varphi(\omega') \end{cases}$$

#### 2.2.1 Average signal

We can now compute the average signal, namely the signal one would measure by taking the mean over the subsequent repetitions, each one with different random phases of the electric fields. Since we have assumed that  $\Omega \gg \Delta_{corr}$ , the average values of  $\cos \gamma$  and  $\cos \beta$  vanish (and so does the average value of the signal) unless  $\gamma$  and  $\beta$  are both zero, i.e. unless:

$$\begin{cases} \omega' = \omega + \Omega, & \text{for the first sum} \\ \omega' = \omega - \Omega, & \text{for the second sum} \end{cases}$$

We can thus write the average transmitted signal as:

$$\langle S(\omega;\Gamma)\rangle = \frac{|\alpha_{ge}|^2 p_{ge}(\beta)}{2\pi\hbar^2} \{|E(\omega)E(\omega+\Omega)|^2 - |[E(\omega)E(\omega-\Omega)|^2\}$$
(2.20)

where the average has been taken over the stochastic degrees of freedom, included in the distribution  $\Gamma$ . Equation 2.20 correctly describes the spectral (red or blue) shift due to the inelastic scattering [1] [9]. When the pulse is very broad, as in our case, similar shifts involve all the spectral components within the pulse bandwidth, so that it is not possible in general to retrieve the Raman frequency  $\Omega$ .

The advantage of using NCS is that we look at the covariance rather than the mean value. We will now see that, by calculating the cross-correlation signal, these features are actually enhanced.

#### 2.2.2 Cross-correlation signal

In our experiment, the frequency dependent signal is collected shot by shot and the covariance is then calculated with respect to the stochastic degrees of freedom, i.e. averaging over the distribution  $\Gamma$ . This means that the crucial quantity we need to

evaluate is the following one:

$$\langle S(\omega_i; \Gamma) S(\omega_j; \Gamma) \rangle = \frac{|\alpha_{ge}|^4 p_{ge}^2(\beta)}{\hbar^4} \int \frac{d\omega'}{2\pi} \int \frac{d\omega''}{2\pi} \times \\ \times \left\langle \left[ E^{\star}(\omega_i) E(\omega_i + \Omega) E^{\star}(\omega') E(\omega' - \Omega) \cos \gamma_i' - E^{\star}(\omega_i) E(\omega_i - \Omega) E^{\star}(\omega') E(\omega' + \Omega) \cos \beta_i' \right] \times \right. \\ \times \left[ E^{\star}(\omega_j) E(\omega_j + \Omega) E^{\star}(\omega'') E(\omega'' - \Omega) \cos \gamma_j'' - E^{\star}(\omega_j) E(\omega_j - \Omega) E^{\star}(\omega'') E(\omega'' + \Omega) \cos \beta_j'' \right] \right\rangle$$

$$(2.21)$$

where we have used the expression of the signal in Equation 2.19. We have introduced the symbols  $\gamma_r^s$  and  $\beta_r^s$  where the subscripts r = (i, j) refer to the frequencies  $\omega_i$  and  $\omega_j$  for which the cross-correlation is calculated, and the superscripts s = (', '') refer to the corresponding integration variables.

The product within the angle brackets in Equation 2.21 gives rise to four distinct terms involving the averages of the product of two cosines:

a) 
$$\langle \cos \gamma'_{i} \cos \gamma''_{j} \rangle = \frac{1}{2} \langle \cos(\gamma'_{i} + \gamma''_{j}) + \cos(\gamma'_{i} - \gamma''_{j}) \rangle$$
  
b)  $\langle \cos \beta'_{i} \cos \beta''_{j} \rangle = \frac{1}{2} \langle \cos(\beta'_{i} + \beta''_{j}) + \cos(\beta'_{i} - \beta''_{j}) \rangle$   
c)  $\langle \cos \gamma'_{i} \cos \beta''_{j} \rangle = \frac{1}{2} \langle \cos(\gamma'_{i} + \beta''_{j}) + \cos(\gamma'_{i} - \beta''_{j}) \rangle$   
d)  $\langle \cos \beta'_{i} \cos \gamma''_{j} \rangle = \frac{1}{2} \langle \cos(\beta'_{i} + \gamma''_{j}) + \cos(\beta'_{i} - \gamma''_{j}) \rangle$   
(2.22)

where we have used the Werner formula for the product of cosines. Equation 2.21 thus splits into eight terms.

Each term in Equation 2.22 yields delta-functions upon averaging. We focus here only on those terms that can be satisfied simultaneously. Precisely, two of the four terms involving either two  $\gamma$ 's or two  $\beta$ 's (like those in a) and b) ) contribute with the same delta-functions. Analogously, two of the four remaining cross-terms in c) and d) yield the same result. For this reason, we only explicitly calculate just one term for each kind, namely:

$$i) \gamma'_{i} - \gamma''_{j} = \varphi(\omega_{i} + \Omega) - \varphi(\omega_{i}) + \varphi(\omega' - \Omega) - \varphi(\omega') - [\varphi(\omega_{j} + \Omega) - \varphi(\omega_{j}) + \varphi(\omega'' - \Omega) - \varphi(\omega'')]$$
  
$$ii) \gamma'_{i} + \beta''_{j} = \varphi(\omega_{i} + \Omega) - \varphi(\omega_{i}) + \varphi(\omega' - \Omega) - \varphi(\omega') + [\varphi(\omega_{j} - \Omega) - \varphi(\omega_{j}) + \varphi(\omega'' + \Omega) - \varphi(\omega'')]$$
  
$$(2.23)$$

The two contributions in Equation 2.23 are the arguments of two cosines which must be then averaged over the stochastic distribution. They thus yield the following contraction deltas:

$$i) \left\langle \cos(\gamma'_i - \gamma''_j) \right\rangle = \delta(\omega'' - \omega') \,\delta(\omega_j - \omega_i)$$
  

$$ii) \left\langle \cos(\gamma'_i + \beta''_j) \right\rangle = \delta(\omega' - \omega'' - \Omega) \,\delta(\omega_i - \omega_j + \Omega)$$
(2.24)

The terms which contribute with contractions of type i) are trivial, since represent a diagonal term ( $\omega_i = \omega_j$ ) of autocorrelation. Contractions of type ii) are

instead the interesting ones, since give rise to distinct off-diagonal sidebands shifted by the Raman frequency from the diagonal. This means that looking at the crosscorrelated signal is indeed a good way of retrieving the vibrational frequency we are interested in.

We explicitly calculate the signal coming from the contributions of kind ii):

$$\langle S(\omega_i; \Gamma) S(\omega_j; \Gamma) \rangle_{\gamma'_i + \beta''_j} = \frac{|\alpha_{ge}|^4 p_{ge}^2(\beta)}{\hbar^4} \int \frac{d\omega'}{2\pi} \int \frac{d\omega''}{2\pi} \, \delta(\omega' - \omega'' - \Omega) \, \delta(\omega_i - \omega_j + \Omega) \times \\ \times E^*(\omega_i) E(\omega_i + \Omega) E^*(\omega') E(\omega' - \Omega) E^*(\omega_j) E(\omega_j - \Omega) E^*(\omega'') E(\omega'' + \Omega) \\ = \frac{|\alpha_{ge}|^4 p_{ge}^2(\beta)}{\hbar^4} |E(\omega_i) E(\omega_i + \Omega)|^2 \int \frac{d\omega'}{(2\pi)^2} \times \\ \times |E(\omega') E(\omega' - \Omega)|^2 \, \delta(\omega_i - \omega_j + \Omega)$$

$$(2.25)$$

It should be noted that the condition of statistical dependence between two frequencies is satisfied for all the distances smaller or comparable to  $\Delta_{corr}$ : thus the deltas above must be considered to have a finite width, leading to a blurring of the signal around the lines  $\omega_j = \omega_i$  and  $\omega_j = \omega_i \pm \Omega$ .<sup>2</sup>

# 2.3 Characterization of the reference pulse

So far, nothing has been said about the correlation properties of the incident noisy pulses we employ. In the experiment, along with the transmitted pulse, we also record frequency-resolved shot-to-shot copies of the incident pulses, which are routed on a fast spectrometer before interacting with the sample. The analysis of the correlations within these reference pulses is indeed essential to recognize those features that are genuinely due to the interaction with the sample from those that are just artefacts due to the intrinsic properties of the impinging light.

We introduce here a phenomenological model able to characterize the incident pulses and then interpret the results we will discuss in the following chapters.

The crucial point in this treatment lies in correctly modelling the detection procedure. In particular, since we use detectors with a finite frequency resolution, we have to study which effects the frequency discretization is responsible for. To model the finiteness of the spectral resolution, we consider a frequency gating  $G(\omega - \bar{\omega})$ , extending over a spectral region centered around  $\bar{\omega}$ . The spectral extension of the gating is set by the finite size of the pixels of the photodiode arrays we use.

We can thus write the intensity measured by the pixel centered at  $\bar{\omega}$  by considering the superposition of the fields within its spectral content, as:

$$I(\bar{\omega}) = \Re \epsilon \int d\omega' \, d\omega'' \, G(\omega' - \bar{\omega}) \, G(\omega'' - \bar{\omega}) E^{\star}(\omega') E(\omega'') \, e^{-i[\varphi(\omega') - \varphi(\omega'')]}$$
(2.26)

<sup>&</sup>lt;sup>2</sup>The  $\pm$  sign has been considered here since it is expected that the cross-correlation signal is symmetric under the exchange  $i \leftrightarrow j$ . This symmetry can be also retrieved by evaluating the term  $\beta'_i + \gamma''_j$  in Equation 2.22, which yields  $\delta(\omega' - \omega'' - \Omega)\delta(\omega_i - \omega_j + \Omega)$ .

where  $\varphi(\omega')$  and  $\varphi(\omega'')$  are the stochastic phases we introduce in the incident pulses, and the integration variables  $\omega'$  and  $\omega''$  span the spectral size of the pixel.

We assume that the field amplitudes and the spectral phases vary slowly across the gate. Precisely, this assumption corresponds to considering the correlation length of the phase fluctuations ( $\Delta_{corr}$  in Equation 2.18) larger than the detector unit size, so that it is expected that the phase does not change much within a single pixel. We can thus consider only the value of the fields at the central frequency  $\bar{\omega}$  and expand the phase to first order around  $\bar{\omega}$  as:

$$\varphi(\omega'') - \varphi(\omega') \approx (\omega'' - \omega') \frac{\partial \varphi}{\partial \omega}\Big|_{\bar{\omega}} \equiv \Phi(\bar{\omega})$$
 (2.27)

The intensity measured by the pixel centered at  $\bar{\omega}$  can be written as:

$$I(\bar{\omega}) = \Re e \left[ E^{\star}(\bar{\omega}) E(\bar{\omega}) e^{i\Phi(\bar{\omega})} \right] = |E(\bar{\omega})|^2 \cos \left[ \Phi(\bar{\omega}) \right] \equiv I(\bar{\omega}) \cos \left[ \Phi(\bar{\omega}) \right]$$
(2.28)

whose positivity is guaranteed by the fact that we have assumed  $\Phi(\bar{\omega})$  to be a small quantity. Equation 2.28 clearly highlights that phase fluctuations are mapped into amplitude ones, as a consequence of the detection procedure.

We can now write the correlator between the intensities measured at two distinct pixels centered at  $\bar{\omega}_1$  and  $\bar{\omega}_2$  as:

$$\langle I(\bar{\omega}_1)I(\bar{\omega}_2)\rangle = \bar{I}(\bar{\omega}_1)\bar{I}(\bar{\omega}_2)\langle\cos\left[\Phi(\bar{\omega}_1)\right]\cos\left[\Phi(\bar{\omega}_2)\right]\rangle$$
(2.29)

We recall that we have assumed a Gaussian correlation between distinct spectral phases (Equation 2.18), which results in a non-null correlation also between their derivatives  $\Phi(\bar{\omega}_1)$  and  $\Phi(\bar{\omega}_2)$ . We thus expect that the average of the product of the two cosines in Equation 2.29 has a different behaviour according to whether or not  $\bar{\omega}_1$  and  $\bar{\omega}_2$  lie within the correlation length  $\Delta_{corr}$ :

$$\langle I(\bar{\omega}_1)I(\bar{\omega}_2)\rangle - \langle I(\bar{\omega}_1)\rangle\langle I(\bar{\omega}_2)\rangle = \begin{cases} \bar{I}(\bar{\omega}_1)\bar{I}(\bar{\omega}_2)\kappa_{12}^2 & \text{if } |\bar{\omega}_1 - \bar{\omega}_2| \lesssim \Delta_{corr} \\ 0 & \text{if } |\bar{\omega}_1 - \bar{\omega}_2| \gg \Delta_{corr} \end{cases}$$
(2.30)

where, to be consistent with the treatment of the sample beam, we have considered the correlator net of the average intensity of the background and defined  $\kappa_{12}^2 \equiv \langle \cos [\Phi(\bar{\omega}_1)] \cos [\Phi(\bar{\omega}_2)] \rangle - \langle \cos [\Phi(\bar{\omega}_1)] \rangle \langle \cos [\Phi(\bar{\omega}_2)] \rangle$ . Note that spectral phases at frequencies whose difference is greater than the correlation length, can be regarded as independent variables, and so  $\langle \cos [\Phi(\bar{\omega}_1)] \cos [\Phi(\bar{\omega}_2)] \rangle$  can be factorized as  $\langle \cos [\Phi(\bar{\omega}_1)] \rangle \langle \cos [\Phi(\bar{\omega}_2)] \rangle$ , leading to a null degree of correlation.

Equation 2.30 is the key tool to interpret the correlations within the incident light pulses. We stress once again that the crucial step in this approach is to consider the finiteness of the spectral resolution of the detectors.<sup>3</sup> Indeed, in the ideal case of a monochromatic detection, the random phase fluctuations would have no effects on the measured intensities, and no detectable correlations would be expected within the reference beam.

 $<sup>^{3}</sup>$ Note that, even if we have discussed here only the role of the detectors, the results we have obtained can be extended to all non-ideal coarse-grained instruments which are responsible for summations over neighboring spectral modes. It is likely that also the SLM introduces similar effects on the pulses.

# Chapter 3

# Experimental apparatus

In Chapter 2 we have theoretically described the application of the Noise Correlation Spectroscopy (NCS) to the study of Impulsive Stimulated Raman Scattering (ISRS). Here, we provide the description of the experimental realization of our spectroscopic technique. We will first describe the experimental setups we have designed to perform the measurements discussed in Chapters 4 and 5. After briefly outlining the main features of the laser source we have employed, we will focus on the pulse shaper, the experimental component on which the success of NCS relies. We will discuss in detail its working principle and how it can be used to introduce the phase and/or amplitude fluctuations we need. Finally, we will focus on the detection system and see how the pulse shaper can be exploited to calibrate the detectors.

# 3.1 Experimental setups

In order to explore the potential of NCS, we have performed different kinds of measurements, which can be grouped in the three classes mentioned below. Though the arrangement of the optical elements changes according to the requirements of each kind of measurement, the core part of the setup (i.e. the laser source, the pulse shaper and the detectors) stays the same in the three configurations. The three main parts of the setup are shown in Figure 3.1 enclosed by the dashed blocks.

We employ intense ultrashort light pulses, generated by a chirped pulse amplification laser system. After being properly polarized,<sup>1</sup> the output of the laser is routed through a pulse shaper, which enables us to introduce the desired random fluctuations. The detection is then performed by a pair of fast spectrometers, designed to acquire frequency-resolved shot-to-shot pulses. Each spectrometer consists of a diffraction grating which diffracts the beam on a linear array of 256 photodiodes. Pulse by pulse detection is guaranteed by a trigger which synchronizes the pulse acquisition with the laser repetition rate.

 $<sup>^{1}</sup>$ The output of the laser is linearly horizontally polarized. However, as we will see below, our pulse shaper requires as input linearly polarized light in the vertical direction.

#### 3.1.1 Static transmission measurements

When we refer to *static transmission measurements*, we have in mind a configuration like that depicted in Figure 2.2 and described in our theoretical model. We call it *static* since there is only a beam interacting with the sample, which is therefore in its ground state at each new interaction. By *transmission*, we simply refer to the detection geometry; being crystalline quartz a transparent material within the visible/near infrared region, we record the pulses transmitted by the sample.

A scheme of the setup is shown in Figure 3.1. The output of the pulse shaper is splitted into two beams by a beam splitter 90/10. The weakest of them, the reference beam, is recorded as it is. The other one interacts with the sample and is then acquired in a transmission geometry. We stress once again that the detection of a reference pulse is of crucial importance, since its analysis can help us identify the features that are genuinely due to the interaction with the sample.



Figure 3.1: Simplified representation of the experimental setup for performing static transmission measurements.

#### 3.1.2 Pump and probe measurements

Static transmission measurements, while potentially enabling the retrieval of the Raman spectrum, can tell nothing about the lifetimes of the phonon modes. In order to get information about the relaxation dynamics, a time-domain experiment is required. We have therefore implemented the possibility of performing pump and probe measurements.

In this configuration (see Figure 3.2), the laser output is splitted before passing through the pulse shaper to get the pump and probe beams. The former (which is cross-polarized with respect to the probe to minimize interference effects) optically excites the sample, while the latter interacts with the target at a retarded time, which is set by a delay line. The probe, which is still shaped by the pulse shaper, is then recorded after being transmitted by the sample. Along with the transmitted probe, a reference pulse is simultaneously acquired. For each delay time, thousands of pulses, each with a different noisy pattern superimposed by the pulse shaper, interact with the sample. Therefore, this configuration is nothing but a time-resolved version of NCS. The final result is a crosscorrelation signal for each delay time, whose features are expected to vary according to the relaxation dynamics of the vibrational excitations.



Figure 3.2: Simplified representation of the experimental setup for performing timedomain pump and probe measurements.

#### 3.1.3 Polarization dependent measurements

Every phonon has its own symmetry properties. In order to study them, we have designed the polarization selective setup in Figure 3.3.

The configuration is similar to that used in a simple pump and probe measurement, with the only difference being the addition of a polarizing beam splitter after the sample. A polarizing beam splitter is a device able to split the incoming light into two beams, having horizontal and vertical polarization, respectively. The two beams are then separately detected by the spectrometers.

The idea behind this configuration is that the symmetry properties of the phonons result in a well-defined orientation of the excited vibrational modes with respect to the pump polarization. Since the probing process depends on the phonon geometry, this means that the polarization properties of the light transmitted by the sample depend on both the pump and the probe polarizations. Hence, the only parameter which matters is the relative polarization between the two beams, which can be easily modified by rotating the half-wave plate on the pump channel. The measuring procedure is similar to that described for a simple pump and probe measurement: for each time delay, many noisy transmitted pulses are acquired, so that one gets a cross-correlation signal for each step of the temporal scan. This is repeatedly done for different pump and probe relative polarizations.

It is worth to note that the choice of simultaneously acquiring the two transmitted polarizations obviously comes at the cost of losing the reference channel. However, the significant advantage of doing this is the possibility of studying the cross-correlation signal calculated by combining the pulses with different polarizations. If we had simply used a polarizer instead of a polarizing beam splitter, we would have been still able to get the cross-correlation signals independently on the two detectors, but then the combination between the two would have been meaningless, since they would have referred to different statistical sets. However, this calculation may prove a valid method to improve our understanding of the mechanisms underlying the coupling between the photon polarization and the phonon symmetry.



Figure 3.3: Simplified representation of the experimental setup for performing polarization dependent measurements.

## 3.2 Laser system

A schematic representation of the laser system is shown in Figure 3.4. The ultrashort pulses are produced by a Kerr-lens Mode-Locked Ti:Sapphire oscillator (Vitara-T), which is pumped by a green continuous wave laser (Verdi). The oscillator produces nearly Gaussian pulses centered at 800 nm and having a bandwidth of  $\sim$ 50 nm. At this stage, the repetition rate (number of pulses per unit time) is approximately 80 MHz and each pulse carries an amount of energy equal to 6 nJ.

In order to increase the energy per pulse, the output of the oscillator undergoes an amplification stage through a chirped pulse amplifier (Legend Elite Duo). Here, Ti:Sapphire crystals are pumped by a pulsed green laser (Revolution), whose repetition rate (5 kHz) sets that of the final output of the laser system. The amplification is divided in three steps. First, the ultrashort seed pulse coming from the oscillator is temporally stretched. The amplification is then performed and the pulse is shortened again by means of a compressor. The stretching-compressing of the pulse is required in order to avoid nonlinear effects that would instead arise because of the high intensities involved.

The final output of the laser consists of a pulsed beam of transform-limited<sup>2</sup>

<sup>&</sup>lt;sup>2</sup>A pulse is said to be *transform-limited* (or, equivalently, *Fourier limited*) when the product of its energy bandwidth and its temporal length is equal to  $\hbar$ .



Figure 3.4: Scheme of the laser source.

Gaussian pulses centered at 800 nm ( $\sim$ 375 THz), having 2.4 mJ/pulse and a repetition rate equal to 5 kHz. The minimum attainable temporal duration is  $\sim$ 40 fs. However, the duration can be varied by the user to reach few picoseconds at most. Indeed, an external engine is provided, enabling to remotely control the dispersive compressor in the amplifier. We have worked with a pulse duration of  $\sim$ 70 fs, measured through an optical autocorrelator placed in front of the pulse shaper.<sup>3</sup> The polarization of the output light is set to lie in the horizontal plane (i.e. parallel to the optical board). Finally, the total power of the laser output is 12 W, but only its  $\sim$ 8% is isolated by means of a beam splitter and used in our experiment.

Our laser system, as most modern laser sources do, delivers shot-to-shot correlated pulses [9]. While mean-value measurements benefit from this high coherence, NCS requires pulse-to-pulse stochasticity. Moreover, stable sources, being dominated by long-range fluctuations throughout the pulse spectrum, lack the noisy component of localized narrow fluctuations which is essential for the success of NCS. Therefore, fluctuations of this kind have to be manually introduced in the incident pulses. We accomplish this task by using a pulse shaper.

# 3.3 Femtosecond pulse shaping

In order to describe in detail how our pulse shaper works, let us first introduce some basic concepts on which femtosecond pulse shaping techniques rely.

First of all, by the expression *femtosecond pulse shaping*, one usually refers to all the techniques which enable to manipulate ultrafast optical wave forms according to the user requirements.

Although there are several ways of achieving this result, we will focus here on the most widely adopted method, which consists in a spatial masking of the spatially

 $<sup>^3\</sup>mathrm{Note}$  that it is likely that the temporal length of the pulses is somehow modified by the pulse shaper.



(b) 4f scheme

Figure 3.5: Pulse shaping by linear filtering in the frequency domain. (a) Pictorial scheme of the filtering procedure. (b) Experimental configuration for performing a spatial masking of the incoming pulse. This scheme is called 4f, owing to the fact that the spacings of the optical elements match the focal length f of the lenses. The spatial mask is placed in the Fourier plane (FP). Adapted from [10].

dispersed optical frequency spectrum. In this framework, an arbitrary shaping of ultrashort pulses can be achieved by controlling independently both the phases and the amplitudes of (ideally) each spectral component within the pulse bandwidth.

This approach can be conveniently described by using the concept of linear filtering in the frequency domain, as depicted in Figure 3.5(a) [11]. The filter is characterized by its complex frequency response  $H(\omega)$ , which completely describes the pulse shaper. The output pulse can be simply written as:<sup>4</sup>

$$E_{out}(\omega) = H(\omega)E_{in}(\omega) \tag{3.1}$$

The experimental counterpart of the linear filter we have just described, is shown in Figure 3.5(b). It is the most basic pulse shaping apparatus and is commonly called 4f scheme. It consists of a pair of diffraction gratings and lenses, arranged so that they are equally spaced by a distance f (the focal length of the lenses). The frequency components within the incoming pulse are angularly dispersed by the first grating and are then focused by the first lens at the back focal plane (also called *Fourier plane*, FP). Indeed, the first lens basically performs a Fourier transform which maps the angular dispersion from the grating to a spatial separation of the spectral components, which result in small diffraction limited spots at the FP. By

<sup>&</sup>lt;sup>4</sup>Of course, the same process can be equivalently described in the time domain, by considering the convolution between the input signal and the impulsive response characteristic of the filter (i.e. the Fourier transform of  $H(\omega)$ ). However, when dealing with ultrashort pulses, the direct shaping in time cannot be achieved because of the speed limitations of the electronics. Therefore, most devices operate in the frequency domain.



Figure 3.6: Birefringence of nematic liquid crystals. A light beam linearly polarized along the extraordinary axis  $(n_e)$ , experiences different refractive indices according to whether or not a voltage is applied between the electrodes.

placing a mask there, it is possible to selectively act on specific frequency components and thus transfer a precise pattern from the mask to the spectrum. Then, the second pair lens-grating recombines the dispersed light, so that the final output is a properly shaped, collimated beam.

It is clear at this point that the crucial step is the choice of a specific mask capable of introducing the desired features in the outgoing pulse. In principle, every kind of spatial mask can serve this purpose. For instance, if one is interested in modifying the spectral phase of specific frequency components, variations in the individual optical paths can be introduced by simply putting a mask in which micro-structures have been obtained through microlithografic techniques. Similarly, amplitude modifications can be obtained by choosing a mask with a variable transmittivity, in order to filter out a certain quantity of the incoming light.

However, masks of this kind are *static*, in the sense that they need to be replaced if one wants to change the features of the outgoing pulse more than once. In this connection, we recall that our experiment requires a new, randomly generated, noisy pattern at each repetition. Static masks are then clearly unsuitable for our setup. A more appropriate choice would instead be using a programmable mask, whose pattern can be refreshed through software at each repetition. We have fulfilled this requirement by using a liquid crystal spatial light modulator (LC-SLM).

#### 3.3.1 Liquid crystal spatial light modulator (LC-SLM)

An LC-SLM exploits the birefringent properties of the liquid crystals to arbitrarily control the optical path of the light impinging on it. It consists of a pair of electrodes with a thin layer of nematic<sup>5</sup> liquid crystals placed between them, in such a way that their director is parallel to the substrates when no voltage is applied between them.

<sup>&</sup>lt;sup>5</sup>Liquid crystals are said to be in a *nematic phase* when their molecules have no positional order but tend to point in the same direction, identified by the name of *director*.



Figure 3.7: Side view of a LC-SLM operating in a reflection geometry.

In order to clarify the role played by the birefringence of the liquid crystals, we consider a situation like that depicted in Figure 3.6. If the incoming light is linearly polarized in the direction parallel to the director of the liquid crystals, it faces two distinct situations according to whether or not a voltage is applied between the electrodes. In the former case, the beam experiences the greatest possible difference between the extraordinay  $(n_e)$  and the ordinary  $(n_o)$  refractive index. Conversely, when a voltage is applied, molecules realign along the electric field that has been established. In this new configuration, the impinging light sees no difference between the refractive indices along the two directions. Hence, the LC-SLM acts as a waveplate which is responsible for a phase delay  $\varphi$  equal to:

$$\varphi(\omega, V) = \frac{\omega \,\Delta n(\omega, V) \,d_{LC}}{c} \tag{3.2}$$

where V is the voltage applied,  $\omega$  the frequency of the impinging light,  $\Delta n$  the index difference between the ordinary and the extraordinary axes, and  $d_{LC}$  the thickness of the layer.

As a consequence of Equation 3.2, the first outgoing beam in Figure 3.6 is then shifted in phase with respect to the second one. In a more general picture, intermediate voltages can be applied, so that a gradual change in the phase delay can be achieved. Moreover, by independently varying the voltages applied in distinct portions of the layer, one can selectively impose a specific phase delay for a light beam impinging on that specific portion. This is shown in Figure 3.7, where a complete side view scheme of an LC-SLM is depicted.

The fundamental difference between this general configuration and that in Figure 3.6 lies in the pixelation of the bottom electrode. One can thus think of the previous, simple representation as just one single pixel of the more general structure in Figure 3.7. As a result, the four impinging light beams are phase-delayed each in a different amount, according to the voltage applied at the corresponding pixel. Note that, even if the distinction between different pixels is clear in the electrode, the layer of liquid crystals is not effectively partitioned. This means that neighbouring pixels cannot be regarded as completely independent. Furthermore, the presence of a dielectric



Figure 3.8: Our pulse shaper arrangement.

mirror suggests that a reflection geometry rather than a transmission one can be also employed. Recalling the 4f scheme in Figure 3.5(a), a reflection geometry (commonly called *folded 4f scheme*) can be arranged by using only the first grating-lens pair, which acts as both dispersive and collimating element.

A simple LC-SLM thus consists of a pixelated array on which the pulse spectrum is dispersed along the direction of the pixelation (i.e. horizontally in Figure 3.7). By controlling the voltage applied on each pixel through software, it is possible to refresh the matrix at the arrival of each new pulse. The refreshing time (which ultimately affects the speed of the experiment) is set by the time response of the liquid crystals. The frequency resolution is instead limited by both the dispersion and the pixel dimensions: clearly, the more efficient the spatial dispersion and the smaller the size of the pixels, the better the spectral resolution.

#### 3.3.2 Two-dimensional diffraction-based LC-SLM

So far, we have only explored the capabilities of the LC-SLM for manipulating the spectral phase. However, more sophisticated tools based on a similar scheme can be used to achieve a simultaneous shaping of both the phase and the amplitude of femtosecond pulses. We focus here on the method proposed in [12], which is the basis of the pulse shaper arrangement used in our experiment (Figure 3.8).

The method relies on the use of a two-dimensional (2D) LC-SLM (Meadowlark Optics, in our case), instead of a linear one. Our 2D LC-SLM consists of a pixelated matrix of  $512 \times 512$  pixels, which is placed at the focal plane of a folded 4f scheme. The spectral components of the incoming beam are dispersed horizontally by the combined action of a diffraction grating and a cylindrical lens, and each of them hits a specific pixel, as in the previous configuration. However, the advantage of using a 2D matrix is that now we have an additional degree of freedom, that is the choice of the voltages to be applied along the vertical direction. The diffraction-



Figure 3.9: (a) Diffraction of a monochromatic beam by a blazed grating with period d and amplitude A. (b)Amplitude of first-order diffracted light as a function of the sawtooth amplitude A (Equation 3.5).

based method proposed in [12] consists in choosing a proper combination of voltages, whose effect results in the application, to each frequency component, of a sawtooth phase function along the vertical direction of the matrix. The overall result is that every spectral component impinging on the LC-SLM "sees" a blazed grating, by which it will be diffracted according to the *blazed grating diffraction equation*:

$$d\left[\sin(\theta_m) - \sin(\theta_i)\right] = m\lambda \tag{3.3}$$

where d is the period of the grating, m the order of the diffraction,  $\theta_m$  the angle at which the m-order beam is diffracted,  $\theta_i$  the angle of incidence, and  $\lambda$  the wavelength of the impinging light. The diffraction of a monochromatic beam is depicted in Figure 3.9(a).

By properly aligning the pulse shaper, it is then possible to make the first-order diffracted beam go back to the cylindrical lens, in order to finally get a collimated beam out of the pulse shaper.

In this framework, the LC-SLM mask can be regarded as a collection of several blazed gratings (as many as the pixels along the horizontal direction). A full control over the first-order diffracted light can be then achieved by modifying the parameters of each blazed grating. Precisely, the vertical position and the depth of each grating can be varied to modulate the spectral phase and the amplitude, respectively, of the first-order diffracted beam.

This may be understood in terms of Fraunhofer diffraction. For a sawtooth phase modulation  $\phi$  like that in Figure 3.9(a) and formally given by

$$\phi(\omega, y) = \alpha \left\{ \frac{1}{2} + A(\omega)S_d\left[\varphi(\omega), y\right] \right\},\tag{3.4}$$

the amplitude of the first-order of diffraction is:

$$E(\omega) \propto e^{-i\varphi(\omega)} sinc\left[\pi - \frac{\alpha}{2}A(\omega)\right]$$
 (3.5)



**Figure 3.10:** The two-dimensional color maps are selected examples of SLM patterns. The plots below them show the corresponding effects on an incoming Gaussian pulse with a constant spectral phase. Dashed lines in the plots refer to the incoming pulse, solid lines to the shaped, outgoing one.

where  $\alpha$  is the maximum attainable phase shift,  $S_d[\varphi(\omega), y]$  is a sawtooth function of period *d* along the vertical direction *y* and spectral phase  $\varphi(\omega)$ , and  $A(\omega)$  is the amplitude of the sawtooth [12].  $S_d$  is chosen to have peak values  $\pm 1/2$ , while  $A(\omega)$ can be varied from 0 to 1, independently for each spectral component  $\omega$ .

Equation 3.5 clearly shows that by shifting the sawtooth along y (i.e. varying the *spatial phase*), one can control the phase of the diffracted beam. Furthermore, by modifying the efficiency of the grating (which scales as the *sinc* of the sawtooth amplitude, as in Figure 3.9(b)), one can arbitrarily modify the amplitude of the diffracted beam. Recall that all these manipulations consist, in practice, in applying a proper combination (a *pattern*) of voltages at each pixel within the 2D matrix.

In order to gain a deeper understanding of how we communicate with the instrument, we show in Figure 3.10 three examples of simple patterns that can be sent to the 2D LC-SLM and discuss here which are the corresponding effects on the outgoing beam.

In Figure 3.10(a), we have chosen a blazed grating which is the same throughout the matrix, as all its parameters (i.e. period, amplitude and vertical position) remain unchanged. Thus, all the spectral components dispersed along the horizontal axis and impinging on the matrix, are identically diffracted by the LC-SLM. In particular, they all preserve their phase relation and their relative amplitudes. Note, however, that the absolute amplitude will change, since we are analyzing only the first-order diffracted beam.

The pattern in Figure 3.10(b) is similar to the first one, with the difference that a gap has been introduced along the horizontal axis, affecting the phase properties of the beam. Precisely, the grating in the second half of the matrix has been shifted by half period with respect to the other one. This means that spectral components within the same portion keep their initial phase relation, but spectral components impinging on different halves of the matrix gain a relative phase delay equals to  $\pi$ . Since the depth of the sawtooth (i.e. its efficiency) has not been modified, the relative amplitudes remain the same along the whole horizontal axis.

In Figure 3.10(c) both the amplitude and the vertical position of the grating have been modified along the SLM horizontal axis. Precisely, the depth of the sawtooth increases going from the left to the right (and so does the efficiency of the diffraction), while the vertical position of the grating follows a quadratic behaviour along the horizontal axis. As a consequence, we get a chirped<sup>6</sup> pulse with a linearly decreasing intensity (from the right to the left).

It is then clear that virtually any modification can be introduced in the outgoing pulse by choosing a proper pattern. The pulse can be temporally broadened or even temporally squeezed (if it is not already transform-limited); its intensity can be selectively attenuated, its single spectral phases can be arbitrarily shifted and much more. However, in order to introduce these variations in a controlled manner, it is essential to calibrate the instrument. In particular, three calibrations are required:

- *frequency calibration*, to know exactly which frequency component impinges on which pixel along the horizontal axis of the LC-SLM;
- *phase calibration*, to know which voltage to apply to get the desired phase shift from the liquid crystals (Equation 3.2). This is essential for correctly constructing the sawtooth phase modulations;
- *amplitude calibration*, to build a functional relation between the depth of the blazed grating and the first-order diffracted amplitude (being Equation 3.5 the theoretically expected one).

The calibration procedures are discussed in detail in Appendix C.

Let us conclude with a final remark. A careful reader might have noticed that we have not mentioned the fact that, according to Equation 3.3, different frequencies would be diffracted in different directions by a grating with a fixed period. Since our aim is to collimate the beam after it has been shaped, we gradually increase the period of the gratings on which higher frequency components impinge. The *grating period calibration* is also discussed in Appendix C.

#### 3.3.3 Introduction of stochastic fluctuations

Although our pulse shaper is suitable for many different applications, we use it with the specific purpose of introducing the stochastic fluctuations required by the NCS.

The most important requirement of the technique is that each new realization must be statistically independent from the previous ones. Therefore, the shaping of the pulse (i.e. the pattern sent to the SLM) has to be refreshed at each new

 $<sup>^{6}\</sup>mathrm{A}$  quadratic phase is commonly called chirp and induces a temporal broadening of the pulse [13].



**Figure 3.11:** (a) Example of a Gaussian smoothing on the  $i^{th}$  pixel. The variance of the Gaussian filter ( $\sigma = 2$  pixels) sets the correlation length of the smoothing. (b) Comparison between the pristine uniform distrubution (light blue) and the Gaussian smoothed one (dark blue). For clarity, we have plot only a portion (ranging from the  $300^{th}$  to the  $400^{th}$  pixels) of the SLM horizontal axis. (c) Distribution (uniform in light blue, Gaussian smoothed in dark blue) of the random numbers generated in a single realization.

measurement. Secondly, the technique requires a proper choice of each of these patterns. In order to clarify this last point, let us recall that the core idea of NCS is to quantify the degree of correlation between light components that might have been entangled by the light-matter interaction. Hence, the pulse must be free from any other possible correlations that may obscure the ones we are interested in. This means that, ideally, any spectral components within the laser pulse must be independent from all the others.

To achieve this result, we build our SLM patterns by generating an array of 512 (as many as the pixels along the SLM horizontal axis) random numbers, uniformly distributed in the range (-0.5, 0.5). However, since neighbouring SLM pixels are not completely uncorrelated due to the coupling of the liquid crystals, a pixel by pixel uniform distribution is not actually meaningful, experimentally speaking. We thus perform a Gaussian smoothing of the uniform distribution, as shown in Figure 3.11(a).<sup>7</sup> Precisely, we replace the uniformly distributed value corresponding to the  $i^{th}$  pixel  $(I_u(i))$  with the sum of the neighbouring values weighted by a Gaussian

<sup>&</sup>lt;sup>7</sup>Note that a Gaussian smoothing of this kind validates the assumption of slowly-varying phases that we have made in our model (Section 2.2).

distribution, namely

$$I_s(i) = \alpha \sum_j I_u(i+j)G[(i+j);\mu_i,\Delta_{corr}]$$
(3.6)

where the subscript s stands for "smoothed",  $\alpha$  is a scale factor, and  $G[(i+j); \mu_i, \Delta_{corr}]$  is a Gaussian distribution centered at the  $i^{th}$  pixel, having a variance equals to  $\Delta_{corr}$  and evaluated at the  $(i+j)^{th}$  pixel. The sum runs over all the horizontal pixels of the SLM.

By performing this calculation for each pixel, we get a smoothing like that in Figure 3.11(b), where we show only a portion of the 512 pixels-wide SLM axis. The smoothing procedure thus maps the initially uniform distribution into a Gaussian one, as shown in Figure 3.11(c). In this connection, it should be said that the scale factor  $\alpha$  in Equation 3.6 is phenomenologically chosen so that the tails of the Gaussian distribution lie, in average, within the extreme values of the original uniform distribution.

After the smoothing, neighbouring pixels can be no longer considered uncorrelated, as a Gaussian correlation function has been indeed introduced (as discussed in Section 2.2). The relevant quantity here is the variance of the Gaussian function that we have used to shape the uniform distribution, for it sets the correlation length ( $\Delta_{corr}$ ) of the fluctuations. Since two frequency components can be regarded as statistically independent only if they impinge on pixels which are farther apart than  $\Delta_{corr}$ , this ultimately sets the spectral resolution of the method.

All the data that will be analyzed in the following chapters, have been acquired by setting  $\Delta_{corr} = 2$  pixels. While taking into account the unavoidable coupling of the liquid crystals, this choice guarantees a reasonable spectral resolution. Since, as estimated in Appendix C.1, the frequency band on each single pixel of the SLM is about 0.1 THz wide, the correlation length is:

$$\Delta_{corr} \simeq 0.2 \,\mathrm{THz} \tag{3.7}$$

Note, however, that the final resolution of the experiment is given by the convolution of  $\Delta_{corr}$  and the spectral resolution of the spectrometers (Equation 3.8).

The Gaussian smoothed array that we obtain by applying Equation 3.6 to each of the 512 SLM pixels, is then used to generate the noisy patterns. Stochastic fluctuations, be they phase or amplitude ones, can be introduced by experimentally controlling two parameters:

- the magnitude of the fluctuations, that we will call *background noise* (BG) in the following
- two pixels  $(p_i, p_f)$  along the SLM horizontal axis between which one desires to apply the noisy fluctuations

These two parameters are then used to adjust the Gaussian distributed array, as depicted in the scheme in Figure 3.12. The distribution is rescaled multiplying by the desired BG; this identifies the range within the fluctuations will be generated.



#### **Generation of random arrays**

Figure 3.12: Conceptual scheme of the generation of the random arrays needed for the construction of the noisy patterns. A detailed discussion is in the text. In the numeric example, we have used BG = 60% and  $\beta = 0.7$ . For the sake of clarity, we have neglected here the correction on the period of the gratings.

Then, the array can be eventually cut from  $p_i$  to  $p_f$ , so that only in that region the modulation will be applied. According to this array, the patterns are then built.

If phase fluctuations are needed, the array is used to vertically shift the blazed grating placed at each horizontal SLM pixel. The amount of each shift is decided by the value of the Gaussian distribution at the corresponding pixel. Since the maximum attainable phase delay is  $2\pi$ , a BG = 100% generates fluctuations within  $\pm \pi$ , BG = 50% within  $\pm \pi/2$ , and so on and so forth. For amplitude fluctuations, the random array sets the depth of the grating at the corresponding pixel. It should be noted that, in this case, the initial efficiency of the grating must be first rescaled by a certain factor  $\beta$  (0 <  $\beta$  < 1), otherwise positive fluctuations would be meaningless. All this information are then encoded in voltages (through both the phase and the amplitude calibrations) and sent to the SLM.

Finally, we recall that this procedure has to be repeated for each new realization (obviously, the parameters  $p_i$ ,  $p_f$  and BG stay the same within the same measurement). A new random array is generated and the matrix of the SLM is refreshed according to it. Since the liquid crystals have a finite temporal response, the speed of the experiment is limited by the time they need to re-orientate and build the new noisy pattern. In our working conditions, the maximum attainable speed is limited



**Figure 3.13:** (a) SLM pattern with a single 1 pixel-wide blazed grating. It diffracts only the frequency components impinging on it. Note that the dimensions of the grating have been enlarged with respect to the SLM matrix size for a better visualization. (b) Normalized intensity spectra acquired by the PDA as function of the position of the blazed grating along the SLM horizontal axis.

to 500 Hz by the SLM. This means that, since the laser repetition rate is 5 kHz, at least 10 pulses are repeatedly shaped by the same SLM pattern. Since they produce the same statistics, we average over them before post-processing the data acquired.

## **3.4** Spectrometer

As mentioned in the description of our setup, we perform single-shot frequencyresolved measurements of the pulses. The beam is routed to the detection area and diffracted by means of a transmission grating. Each spectral component is then spatially separated by a lens and focused on the detector, which consists of a linear array of 256 pixels. Each pixel is a silicon photodiode (Hamamatsu), having a horizontal extension of  $5\mu$ m.

The resolution of the detection is determined by both the diffractive power of the grating and the finite size of the pixels. In order to evaluate it, we can exploit the SLM. Moreover, the SLM can also help us to calibrate the photodiode array (PDA), i.e. assign a specific central frequency to each pixel. In particular, we exploit the fact that, thanks to the frequency calibration of the pulse shaper, we know exactly the matching between each horizontal pixel of the SLM matrix and each frequency within the pulse bandwidth. So, it will suffice to establish a relation between the 512 SLM pixels and the 256 PDA ones to extrapolate the PDA calibration.

A simple way of doing this is to extinguish all the diffracted light, except for the portion of the spectrum impinging on a known, specific SLM pixel. Then, by acquiring the frequency-resolved diffracted beam, it is possible to relate the illuminated PDA pixels to the corresponding SLM one. To isolate only one frequency component, it is convenient to build a 2D pattern like that in Figure 3.13(a), in which only one blazed grating (1 pixel-wide) has been placed at a known position along the horizontal axis. Then, only the spectral component impinging on the grating

will be diffracted back, and the remaining ones will be lost. By iteratively moving this grating, pixel by pixel, along the horizontal axis of the SLM and acquiring the intensity spectrum at each step, one ends up with a map like that in Figure 3.13(b), where the x-axis represents the SLM pixels, the y-axis the PDA ones and the color map the normalized intensity recorded by the detector. Vertical cuts on the map are then the intensity spectra acquired at each position of the grating within the SLM matrix. Note that for a blazed grating placed within both the first and the last chunks of the SLM horizontal axis, the photodiodes detect no intensity. This is because we do not use the entire horizontal axis of the SLM, but only a portion of it. This choice is a compromise between the need of a high spectral resolution and the equally important need of a spectral content wide enough to detect also more energetic vibrational modes. The tilted light vellow stripe in the graph represents the maximum detected intensity, which is a peak moving along the PDA axis. By identifying the PDA pixel corresponding to each peak, it is possible to assign an SLM pixel (and hence a frequency) to each PDA pixel. Note that, since the SLM pixels are twice as many the PDA ones, the easiest way to do this, is to extrapolate the frequencies associated to the first and the last PDA pixels and then linearly interpolate over the 256 pixels of the detector to get the entire frequency scale. By interpolation, we get the following resolution for the spectrometer:

$$\Delta \omega_{\rm PDA} = 0.12 \,\mathrm{THz} \tag{3.8}$$

It should be finally pointed out that, since we use two distinct spectrometers, the procedure we have just discussed must be repeated independently for each of them.

# Chapter 4

# Static transmission measurements

We present the results of the static transmission measurements performed on a sample of crystalline quartz. The experimental setup we will refer to throughout this chapter, is that described in section 3.1.1. In particular, we recall that we acquire two different frequency-resolved spectra at each single repetition: the incident one (*reference beam*) as it has been shaped by the spatial light modulator (SLM) and the one that, after being shaped, is transmitted by the sample (*sample beam*).

We stress that the relevant quantity is the intensity measured at the *i*-th pixel of the photodiodes array, namely  $I(\omega_i)$ . Our aim is to find out whether and to what extent each frequency component is correlated with all the others within the broad spectral content of the pulse. In this connection, the analysis of the reference beam will help us tell the correlations genuinely induced by the Raman process from those intrinsically present in the incident pulse.

After briefly discussing the vibrational properties of the sample examined, we introduce the covariace-based statistical tool on which our approach relies. We then present the results we have obtained and prove the success of the method by comparing the statistical analysis performed on both the reference and the sample beams. A detailed discussion is then given in order to understand how the parameters of the stochasticity we introduce in the pulses affect the visibility of the signal. Finally, we address the nonlinearity of the Raman process via fluence dependent studies.

# 4.1 Phonon modes of crystalline quartz

In order to test the feasibility of our technique for studying ISRS, we have started by examining well-known and relatively simple materials. Crystalline quartz perfectly matches these requirements, as it is characterized by high transparency and high Raman cross section.

Quartz undergoes a phase change at about 848 K. We investigate here the lowtemperature phase, which is called  $\alpha$ -quartz. It has a trigonal structure with  $D_3$ symmetry and N = 9 atoms per unit cell, as shown in Figure 4.1.

Group theory calculations show that the  $3 \times N = 27$  degrees of freedom are divided into 2 acoustic modes of  $A_2 + E$  symmetry and 16 optical modes of  $4A_1 +$ 



**Figure 4.1:** Atomic arrangement in crystalline quartz [14]. a) Crystalline structure of  $\alpha$ -quartz and b) its projection on the plane perpendicular to the c-axis.

 $4A_2 + 8E$  [15]. Of these, the Raman-active vibrations are 4 totally symmetric modes of species  $A_1$  and 8 doubly-degenerate modes of species E. We report in Figure 4.2 the Raman spectra of  $\alpha$ -quartz. In the following analysis, we will often refer to these spectra in order to address the observed phonon modes.

Our sample is 1 mm thick and it is oriented such that the principal symmetry axis of the crystalline structure (c-axis) is parallel to the direction of propagation of the incident beam (assumed to be the z-axis in our coordinate system). In this configuration, we are allowed to limit our analysis to the xy-plane only. Here, the only accessible vibrational modes are those of a system with  $C_3$  rotational symmetry. They are compatible with the vibrations allowed for a triatomic molecule with 3 atoms of equal masses placed at the corners of an equilateral triangle. As shown in Figure 4.3, they consist of one  $A_1$  breathing mode and two double-degenerate Emodes.

In order to relate these symmetry properties to observable effects, let us recall Equation 1.4 and extend now the notation to tensorial quantities to include polarization effects. As widely discussed in Chapter 1, ISRS is a four-wave mixing process ruled by the third-order non linear polarization,  $P^{(3)}(\omega)$ . Its Cartesian components are given by:

$$P_i^{(3)}(\omega) = \sum_{jkl} \chi_{ijkl}^{(3)} \left[ E_1(\omega_1) \right]_j \left[ E_2(\omega_2) \right]_k \left[ E_3(\omega_3) \right]_l$$
(4.1)

The susceptibility tensor  $\chi_{ijkl}^{(3)}$  for quartz in a  $C_3$  rotational symmetry is given by:

$$\chi_{ijkl}^{(3)} = A_{ij}A_{kl} + E_{ij}^T E_{kl}^T + E_{ij}^L E_{kl}^L$$
(4.2)

where each index can assume the values 1,2 associated to the direction x and y, respectively. Following [16], we have denoted by A,  $E^T$  and  $E^L$  the Raman tensors for total-symmetric A modes, transverse E modes and longitudinal E modes, respectively. They are defined as follows:

$$A = \begin{pmatrix} a & 0 \\ 0 & a \end{pmatrix} \qquad E^T = \begin{pmatrix} c & 0 \\ 0 & -c \end{pmatrix} \qquad E^L = \begin{pmatrix} 0 & -c \\ -c & 0 \end{pmatrix} \qquad (4.3)$$

By solving the tensorial product, we get the final expression for the susceptibility:



**Figure 4.2:** Room-temperature Raman spectra of  $\alpha$ -quartz from [15]. a)  $A_1$  modes. b) E modes. "L" and "T" stand for *longitudinal* and *transverse*, respectively. The arrows indicate the most intense  $A_1$  modes that are not completely exstinguished due to imperfect alignment.



Figure 4.3: Normal mode vibrations for a system with  $C_3$  symmetry. A symmetric  $A_1$  breathing vibrational mode and a doubly-degenerate *E*-symmetry vibrational mode [17].

$$\chi_{ijkl}^{(3)} = \begin{pmatrix} \begin{pmatrix} a^2 + c^2 & 0 \\ 0 & a^2 - c^2 \end{pmatrix} & \begin{pmatrix} 0 & c^2 \\ c^2 & 0 \end{pmatrix} \\ \begin{pmatrix} 0 & c^2 \\ c^2 & 0 \end{pmatrix} & \begin{pmatrix} a^2 - c^2 & 0 \\ 0 & a^2 + c^2 \end{pmatrix} \end{pmatrix}$$
(4.4)

where the first index i refers to the polarization of the signal field and the remaining ones to the polarizations of the excitation fields. We will see later in section 5.2 that, by properly choosing the polarizations of the incident fields, it is possible to isolate specific element of the susceptibility tensor in order to discriminate Raman modes with different symmetries.

## 4.2 Pearson correlation coefficient

Our spectroscopic method relies on the use of covariance-based statistical tools rather than the widely-used mean-value approach. We introduce here the main tool that will be extensively used in the following analysis.

Though diverse and more sophisticated covariance metrics could be used, we consider the Pearson correlation coefficient  $\rho$ , which quantifies the degree of linear correlation between two stochastic variables. Here, the variable considered is the intensity  $I(\omega_i)$  at the frequency  $\omega_i$ , namely the signal recorded by the *i*-th pixel of the photodiodes array. By definition, the Pearson correlation coefficient between the intensities of a pair of modes with frequencies  $\omega_i$  and  $\omega_j$  is given by:

$$\rho\left(I(\omega_i), I(\omega_j)\right) = \frac{\langle I(\omega_i) \, I(\omega_j) \rangle - \langle I(\omega_i) \rangle \langle I(\omega_j) \rangle}{\sigma_i \, \sigma_j} \tag{4.5}$$

where the brackets  $\langle ... \rangle$  denote the mean over all repeated single-shot measurements (i.e. the number of noise patterns involved) and  $\sigma$  is the standard deviation over the dataset considered. The numerator of the latter equation is nothing but the covariance between the two variables considered; including the  $\sigma$ 's in the denominator normalizes  $\rho$ , so that it can assume values ranging from -1 (which means that  $I(\omega_i)$  and  $I(\omega_j)$  are anti-correlated) to +1 (which indicates that the two variables are positively correlated); independent variables have a zero-correlation coefficient.


Figure 4.4: Pearson correlation coefficients for datasets having different correlation properties. Uncorrelated variables have  $\rho = 0$ . Variables which either increase or decrease together are positively correlated; negative correlation coefficients relate to variable which have opposite trends. The Pearson coefficient is not defined in the case in which only one of the two variables has a fixed value (central example).

In order to gain a deeper insight into the sign attribute of  $\rho$ , we can rewrite Equation 4.5 by expanding each intensity as  $I(\omega) = \langle I(\omega) \rangle + \delta I(\omega)$ , where  $\langle I(\omega) \rangle$  is simply the average intensity and  $\delta I(\omega)$  is the fluctuation related to each repetition. By substituting in Equation 4.5, we get:

$$\rho\left(I(\omega_i), I(\omega_j)\right) = \frac{\left\langle \delta I(\omega_i) \, \delta I(\omega_j) \right\rangle}{\sigma_i \, \sigma_j} \tag{4.6}$$

where we have used the fact that the fluctuations are centered around zero, namely  $\langle \delta I(\omega) \rangle = 0$ . Note that the numerator in Equation 4.6 is the cross-correlation signal we have worked out in Chapter 2.

By looking at Equation 4.6, it is clear that the sign of the Pearson coefficient can be understood in terms of deviations from the average intensity. If both the intensities considered are higher (or lower) than the corresponding average values,  $\rho > 0$ . Conversely, if they deviate from the corresponding averages in different directions, the fluctuations have opposite signs, resulting in  $\rho < 0$ . The saturated values  $\pm 1$  indicate, respectively, direct and inverse proportionality.

We summarise in Figure 4.4 the possible outcomes. It should be stressed that the Pearson coefficient does not return the slope of the line that fits the distribution, but it is an indicator of the *quality* of the fit (of which, however, it maintains the sign of the estimated slope, as illustrated by the plots in the middle row). It is particularly interesting the case in which  $\rho$  is undefined (central plot). This happens when one of the two variables stays constant, while the other one changes. Finally, we highlight also the limitations of this statistical tool. Indeed, the Pearson coefficient is sensitive only to *linear* correlations. More exotic, nonlinear distributions, like those in the bottom row of Figure 4.4, return  $\rho = 0$ , even if a clear pattern can be discerned.

The calculation of  $\rho$  performed across all the possible combinations of  $I(\omega_i)$  and

 $I(\omega_j)$  within the pulse bandwidth results in a two-dimensional symmetric<sup>1</sup> map: on both axes there is the frequency range, while the colormap indicates the value of the Pearson coefficient for a specific point in the grid, i.e. for a specific pair of spectral intensities. Precisely, since our detectors consist of 256 pixels, we get a  $256 \times 256$ map. For the sake of clarity, we will use the same colormap throughout the chapter: we will indicate a positive correlation with the red, a negative one with the blue, and a null correlation with the white.

#### Pearson maps of simulated datasets

In order to familiarize with the statistical tool we have just introduced, we briefly discuss some simulations performed on an incident laser pulse, as it would look like before interacting with the sample. This preliminary study is particularly useful to characterize the incident pulse and help us understand which features can be traced back to the properties of the incoming pulse, rather than to the interaction with the sample.

We generate Gaussian pulses in which we introduce either correlated or uncorrelated noise. By correlated noise, we denote all the modifications that preserve the Gaussian shape of the pulse and consist only in a random fluctuation of its parameters ( $\delta I_0$  for amplitude fluctuations,  $\delta \omega_0$  for fluctuations in the central frequency of the pulse and  $\delta \sigma_0$  for fluctuations in its width). These three configurations are depicted in Figure 4.5, from a) to c), in which we have indicated with the black line the pulse profile of a single measurement and with the grey line the average over all the repetitions. By uncorrelated noise, we refer instead to a kind of noise which unsettles the Gaussian shape and that is introduced as described in section 3.3.3. In Figure 4.5d) we consider the pulse before adding the Gaussian smoothing, i.e. with pixel-by-pixel random fluctuations. We show in Figure 4.5e) the pulse after the Gaussian smoothing (with a quite large correlation length,  $\Delta_{corr}$ ) has been performed.

The pulse is generated 10000 times for each configuration, each time with different, randomly assigned parameters. On these datasets, we then perform the calculation of the Pearson correlation maps, shown below the corresponding noise configuration in Figure 4.5.

We notice that all the maps show a positive-correlated diagonal line. This line trivially indicates that each frequency is positively correlated with itself. Besides the autocorrelation diagonal, additional features are observable, according to the kind of noise applied. The noise in the pulse amplitude (Figure 4.5a)) corresponds to a positive map because all the modes have the same sign shift with respect to the average pulse. The central frequency shift noise (Figure 4.5b)) returns a map made

<sup>&</sup>lt;sup>1</sup>It should be noted that the Pearson map is symmetric with respect to the diagonal as long as we quantify the correlations between each pulse and itself. This is reasonable since the degree of linear correlation between  $I(\omega_i)$  and  $I(\omega_j)$  is obviously the same of that between  $I(\omega_j)$  and  $I(\omega_i)$ . However, if we are interested in computing the degree of correlation between two *distinct* pulses (A and B, for example), this is no longer true. If a point on the Pearson map will relate  $I^A(\omega_i)$ and  $I^B(\omega_j)$ , the opposite point with respect to the diagonal will relate  $I^B(\omega_i)$  and  $I^A(\omega_j)$ . There is no reason why the two pairs should have the same degree of correlation.



**Figure 4.5:** Case studies of simulated spectra with 10000 repetitions. The black line refers to one random spectrum out of the 10000 simulated ones, while the grey line indicates the average over all spectra. The corresponding Pearson coefficient maps are shown below. a) Spectra characterized by intensity fluctuations. b) Spectra with a jitter in the central frequency position. c) Spectra with fluctuations in the width of the pulse. d) Spectra with random uncorrelated pixel-by-pixel fluctuations. e) Spectra with random, Gaussian-smoothed fluctuations.

of four blocks with different signs: the red blocks link two frequencies that are on the same side of the gaussian profile and that, therefore, experience a shift of the same sign with respect to the mean; conversely, the blue blocks link two different sides of the pulse. Fluctuations in the width of the pulse (Figure 4.5c)) produce a map similar to the one related to the amplitude noise, with the only exception being the behaviour of the central frequency, whose intensity remains unchanged. The uncorrelated noise (Figure 4.5d) and e)) instead produces a map in which only the main diagonal line has a +1 correlation, while the rest of the values are centered around zero. The width of the line is set by the correlation length of the fluctuations manually introduced in the pulse: it is 1 pixel-wide for the not-smoothed noisy pulse, while the line has a finite width in the case of Gaussian smoothed fluctuations.

As repeatedly stressed, the introduction of the pulse shaper in our setup is aimed at overcoming the correlated fluctuations intrinsically present in the laser pulse (such those in Figure 4.5a-c)) that would obscure the nonlinear signal we want to measure, and enhance instead the (properly smoothed) uncorrelated fluctuations.

## 4.3 Noise configurations adopted in this thesis

The programmable nature of the pulse shaper allows great flexibility in how the stochasticity can be applied to the pulse. As described in section 3.3.3, we can both control the magnitude of the random fluctuations and selectively choose the spectral components to which they will be applied. Moreover, since we have arbitrary control on both the phase and the amplitude of each spectral component of the pulse, we can choose to work either in a phase noise or in an amplitude noise modulation. It is thus clear that the parameter space at our disposal is extremely wide.

In this section, we discuss three of the several noise configurations we have explored. Precisely, we consider a situation in which every frequency component within the pulse is modulated (*full modulation*), in which noise is added only to the high-frequency side of the pulse (*partial modulation*), and finally a situation in which the spectral amplitude of the noise-free side is reduced to 0 (*mean value shaping modulation*).

For each of the three configurations, we analyze both the case of a phase and an amplitude modulation. In the former one, we shape the pulse so that each frequency component to which the noise is applied, can have a spectral phase ranging from  $-\pi/2$  to  $\pi/2$ . In the latter case, we make the amplitude of the chosen spectral components randomly vary in the range  $\pm 40\%$ , where the percentage has to be intended with respect to the intensity of the incident pulse (properly attenuated).

All the data shown in this section have been acquired by setting the power of the impinging beam to 1 mW, corresponding to a fluence (see definition in Equation 4.7) equal to  $\sim 10 \text{ mJ/cm}^2$ .



Figure 4.6: Examples of spectra to which a full noisy modulation either in phase (left panel) or in amplitude (right panel) has been applied. The dashed and the solid red lines indicate the pristine pulse and the noisy incident pulse, respectively. The black line indicates the pulse transmitted by the sample. Note that the red curves have been rescaled by an arbitrary factor for a better visualization. Thus, the relative intensity between the incident and the transmitted pulses is not truthful.

#### 4.3.1 Full modulation

The application of a full modulation affects every spectral component within the impinging pulse (approximately 30 THz broad). We show in Figure 4.6 an example of a spectrum shaped according to this configuration. In both panels (phase noise to the left, amplitude noise to the right), we plot the spectral intensity of the pristine laser pulse using a red dashed line. This spectrum is acquired (on both spectrometers) at the beginning of every experiment by applying a simple diffraction grating to the SLM matrix. The importance of having a reference pulse (Not Noisy pulse, in the following) lies in the fact that it allows to monitor the modifications introduced by the pulse shaper. We have indicated with the red solid line the spectrum of the reference beam, after it has been shaped by the SLM. We observe a descrease in the intensity of the noisy pulse with respect to the pristine one. This is due to the fact that we set the average Gaussian amplitude to be 80% of the incident one, in order to allow the application of amplitude random fluctuations centered around 0. Finally, the black line in the plot indicates the spectrum acquired on the sample channel, after it has been transmitted by the quartz. Note that the intensity of the reference beam should be 1/10 of that of the sample beam (they are divided by a 10/90 beam splitter). The red curves in the plot have been rescaled by an arbitrary factor to facilitate the visualization.

For each configuration, we have recorded sample and reference pulse spectra for 50000 different noise patterns. We show in Figure 4.7 the result of the calculation of the Pearson correlation coefficient.<sup>2</sup> The Pearson maps in the first row refer to the

<sup>&</sup>lt;sup>2</sup>Note that the calculation has been performed on a slightly restricted frequency range (from  $\sim 362$  to 385 THz).



Figure 4.7: a-b) Pearson correlation coefficient for all pairs of frequencies within the excitation spectrum (a) after the pulse shaper and (b) after the sample in the case of phase modulation. c) Spontaneous Raman spectrum of  $\alpha$ -quartz, adapted from [18]. d-e) Pearson maps calculated after the pulse shaper (d) and after the sample (e) in the case of amplitude fluctuations.

phase noise configuration (reference pulse in (a) and sample pulse in (b)), while the second row refers to the amplitude noise (reference pulse in (d) and sample pulse in (e)). We clearly observe that the maps of the reference and the sample pulse are unambiguously different, meaning that the interaction with the sample has indeed modified the correlation pattern within the transmitted pulse.

Let us first analyze the reference maps in Figure 4.7(a-d). The reference map in (d) is very similar to that we have shown in Figure 4.5e), obtained by simulating a pulse in which uncorrelated noise had been added. This tells us that the SLM is working correctly and it actually produces a perfectly uncorrelated pulse in which only a trivial autocorrelation survives (diagonal line). Moreover, the width of the diagonal represents a measure of the ultimate frequency resolution of our method, which is set by the convolution of the correlation length of the Gaussian-smoothing we perform (see section 3.3.3) and the frequency resolution of the detectors (see section 3.4). By evaluating the width of the diagonal, we estimate the frequency resolution of the technique to be approximately 1 THz in the selected experimental configuration.<sup>3</sup>

Furthermore, we observe that the reference map in (a) shows a diagonal feature as well. We highlight that this result confirms the validity of our theoretical model (see Equation 2.30), according to which we expect phase fluctuations to be mapped into amplitude ones due to the coarse-grained nature of both the SLM and the detector.

By contrast with the reference maps, the Pearson maps of the pulse that has interacted with the sample are evidently structured. In particular, we observe offdiagonal sidebands whose distances from the diagonal exactly match the Raman shift of the main phonon features, as illustrated in Figure 4.7c). This means that *spectral components whose frequency difference matches the energy of the Raman modes have been entangled by the ISRS process.* This result is consistent with the prediction of our model (see Equation 2.25). More precisely, in the full modulated configuration, we have been able to retrieve the three phonon modes having the highest Raman cross section (3.8, 6.2 and 13.9 THz, by comparison with the Raman spectra in Figure 4.2). The maps in Figure 4.7b-d) show basically the same features, meaning that both the phase and the amplitude noise allow us to retrieve the vibrational spectrum of the sample. However, we observe an enhancement of the signal in the case of phase noise. A complete analysis of the lineshape of the Raman bands is given in section 4.4.

### 4.3.2 Partial modulation

In order to explore the effects related to a partial modulation of the pulse, we have shaped the incident spectra as shown in Figure 4.8. We have added stochastic fluctuations only in the high-frequency side ( $\gtrsim 370$  THz) of the pulse, while we have left unmodulated (just attenuated of the 40%, as in the case of full modulation) the

 $<sup>^{3}</sup>$ The experimental resolution is limited by the correlation length indroduced in the noise. The intrinsic limitation using the hardware described here is a correlation length of 1 pixel which would correspond to 0.1 THz. It is important to note that different hardware configuration could be envisioned and a higher resolution attained.



Figure 4.8: Example of incident (red) and transmitted (black) spectra that have been partially modulated. Precisely, random fluctuations have been applied only to the high-frequency side ( $\gtrsim 370$  THz) of the pulse spectrum, indicated by the light grey box.

remaining spectral content. Note that this choice is arbitrary and we would have obtained the same results even if we had flipped the two sides.

In Figure 4.9 we show the Pearson maps computed over 50000 repetitions, in the case of both phase (a-b) and amplitude (c-d) modulation. All the maps exhibit a common structure due to the discontinuity in the pulse modulation that we have placed at  $\sim$ 370 THz. Each map consists of four distinguishable blocks whose features can be traced back to the properties of the portion of the pulse they are related to. More precisely, looking at the reference maps (a-c), the bottom left block diplays the correlations among the unmodulated low-frequency components. In this region, the shot-to-shot coherence of the laser pulses survives, resulting in a positively correlated block. By contrast, the situation in the high-frequency side of the pulse (represented by the top right block) is exactly the same as in the full modulation case, since all spectral components are completely uncorrelated. In the remaining complementary blocks, the degree of correlation between the unmodulated and the noisy parts of the spectrum is shown.

By looking at the sample maps (b-d), we observe that the noisy-noisy block is very similar to the total map we have obtained in the previous section.<sup>4</sup> Surprisingly, the visibility of the signal seems to significantly improve in the mixed blocks. First of all, the Raman features are definitely more intense here than in the upper right block. Moreover, a fourth band appears in this configuration, which can be assigned to the phonon mode at 10.6 THz. It thus seems that in a partially modulated configuration, we are sensitive also to Raman process having a considerably lower cross section.

In conclusion, the technique seems to benefit from the presence of a coherent portion of the pulse. This may be due to the fact that having stochastic fluctuations

<sup>&</sup>lt;sup>4</sup>The Raman bands may appear less intense, but the color scale is different in Figure 4.7 and 4.9.



Figure 4.9: a-b) Pearson maps of the incident and the transmitted pulse, respectively, in the case of phase noise partial modulation. c-d) The same for the amplitude partial modulation.



Figure 4.10: Example of incident (red) and transmitted (black) spectra to which a mean value shaping modulation has been applied (sharp edge at  $\sim$ 370 THz).

in both sides of the spectrum somehow leads to a partial cancellation of the process. For the sake of clarity, let us consider a pair of frequencies ( $\omega_i$  and  $\omega_j$ , with  $|\omega_i - \omega_j| = \Omega_{phonon}$ ) on opposite sides of the spectrum. If we apply a modulation only on  $\omega_j$ , we expect a shift of spectral weight to  $\omega_i$ , which will be imprinted with fluctuations similar to those of  $\omega_j$ . Hence, the two components will be highly correlated. By contrast, if we apply uncorrelated fluctuations on both  $\omega_i$  and  $\omega_j$ , the same process as before will occur, with the only difference that now the fluctuations on  $\omega_i$  induced by  $\omega_j$  will be somehow washed out by  $\omega_i$ 's own fluctuations. This will result in a lower degree of correlation between the two spectral components.

#### 4.3.3 Mean value shaping modulation

In order to exploit the fact that the signal seems to be enhanced by the presence of a coherent part within the spectrum, we have investigated a last noise configuration similar to the partially modulated one, but in which the spectral amplitude of the noise-free side is reduced to 0 so that the the average excitation spectrum has a sharp edge at  $\sim 370$  THz (see Figure 4.10). By comparing the shaped incident (red solid line) and the transmitted (black line) spectrum, one immediately realizes that the interaction with the sample is responsible for scattering events which determine a non-null intensity of the low-frequency side of the transmitted spectrum.

The Pearson maps calculated in this configuration (Figure 4.11) look very similar to the ones obtained in the partially modulated configuration. We observe the same general structure, characterized by the presence of four distinct blocks. Again, the signal in the mixed blocks of the sample maps (Figure 4.11(b-d)) is quite strong. However, a difference that can be easily appreciated is a rather significant modification of the background in the mixed blocks. Moreover, we witness here a change in the sign of the Pearson coefficient along the Raman bands.

Indeed, it should be stressed that, despite the obvious similarities with the



Figure 4.11: a-b) Pearson maps of the incident and the transmitted pulse, respectively, in the case of phase noise mean value shaping modulation. c-d) The same for the amplitude mean value shaping modulation.

partial modulation, the physics underneath the two processes is very different. We will address this question in section 4.4.

Finally, as in the previous case, we observe a slightly better visibility of the signal when a phase modulation, rather than an amplitude one, is applied. Indeed, the phonon with the lowest Raman cross section is not visible in the amplitude noise configuration.



Figure 4.12: a) Pearson maps recorded with phase noise applied across the whole spectrum (full modulation), applied to only the high frequency portion of the spectrum (partial modulation), with a sharp edge to eliminate the low-frequency side of the spectrum (mean value shaping). We have kept the same color scales used in the previous representations in section 4.3. b) Profiles of the three maps obtained by averaging along the frequency vertical axis in the regions indicated by the black dashed lines. Note that the orange and the green profiles have been shifted with respect to the 0 and rescaled.

## 4.4 Lineshape analysis

In this section, we specifically study the Raman features observed in the three noise configurations above. Precisely, we discuss what kind of information can be retrieved from the analysis of the lineshape of the bands.

We examine here the same data shown in section 4.3. Since the absence of any kind of features in the reference Pearson maps has proved the authenticity of the detected signal, we will not show them anymore.

We show in Figure 4.12a) the same Pearson maps reported in the b) panels of Figures 4.7, 4.9 and 4.11. They refer to the application of uniform phase noise in the fully modulated, partially modulated and mean value shaped configuration, respectively. In order to better visualize the ISRS features as function of the Raman shift  $\Delta \omega$ , we recast the maps in a more convenient form, in which we plot the Pearson coefficient as  $\rho(\Delta \omega, \omega)$  instead of  $\rho(\omega_i, \omega_j)$ . This can be regarded as a simple rotation of the previous representation. Note that there should also be a symmetric set of



Figure 4.13: Same as Figure 4.12, but for amplitude noise modulation.

features for negative  $\Delta \omega$  which we discard here for clarity purposes.

The black dashed lines isolate regions of the same kind within each map. In the case of full modulation, the whole map is selected, as there is no discontinuity in the spectra. In both the partial and the mean value shaping modulation, we select only the block that mix the coherent and the incoherent portions of the spectra.

By taking the average  $\Delta \omega$  values along the frequency vertical axis in the selected regions only, we get the three profiles in Figure 4.12b). These profiles can be thought of as a sort of vibrational spectra of the sample. We stress however that care should be taken as they fundamentally differ from the more familiar intensity spectra (see for example Figure 4.2).

The features visible in the maps appear at the same frequencies of the Raman modes (indicated by grey dashed lines in the plot). By comparing the three profiles, it is clear that the lineshape of the resonances actually depends on how the noise is applied. More precisely, we observe in most cases (blue and orange profiles) a dispersive lineshape, in which the Pearson coefficient assumes steeply increasing values as the Raman shift increases. Nonetheless, the profile related to the mean value shaping modulation deviates from this trend, since it has purely positive peak shapes.

First of all, the presence of a dispersive lineshape proves that our technique is sensitive to the phase of the signal. When either a full or a partial modulations are applied, the ISRS signal field spatially and spectrally overlaps with the excitation pulse. Hence, the detected spectrum is the result of a self-heterodyned process (as discussed in section 1.3.7). This means that the measured spectral intensity does depend on the phase shift between the signal field and the excitation pulse (what we called *local oscillator*).

As a consequence, the correlation between spectral intensities which are in phase (out of phase) is expected to be positive (negative), since an increase in the excitation field is expected to induce an increase (decrease) in the signal field due to constructive (destructive) interference effects. Since the ISRS is responsible for a phase shift of  $\pi/2$  of the signal field with respect to the excitation one [3], a dispersive lineshape is consistent with what to expect from a self-heterodyne detection.

The situation is completely different in the case of a mean value shaping modulation (green profile). Here, the photons scattered to the low-frequency side of the spectrum through ISRS, do not self-heterodyne, as the excitation photon modes there are empty. In this case, a homodyne signal is expected, which is not sensitive to the signal phase. This is consistent with the completely positive peak shape observed.

Finally, a similar analysis can be also conducted on the Pearson maps involving amplitude noise. We show the results in Figure 4.13. The overall trend of the vibrational spectra is similar to that discussed for the phase modulation, meaning that the sensitivity to the signal phase is not affected by the typology of noise applied to the spectra.

## 4.5 Mean value shaping dependence

In order to test the validity of the conclusion we have come to in section 4.4, we have performed a set of measurements in which we have gradually moved from a mean value shaped to a partially modulated configuration. The aim of this test is to investigate whether or not the strict positivity of the Raman peaks observed in the mean value shaping configuration (Figure 4.12,4.13b)) can be actually ascribed to the homodyne detection of the signal field. More precisely, we want to rule out the hypothesis that the change in the lineshape may be due to other effects related to the amount of the discontinuity introduced in the pulse spectrum.

We show in Figure 4.14 a selection of transmitted spectra shaped to have different mean-value spectral amplitudes (indicated by the percentage) in the noise-free side of the spectrum: 0% and 100% refer, respectively, to the mean value shaping and the partial configurations previously studied. We have considered both a phase and an amplitude modulation, using the same magnitude of stochastic fluctuations applied before  $(\pm \pi/2 \text{ for phase and } \pm 40\% \text{ for amplitude}).$ 

For each mean-value step, we have acquired 50000 spectra with different noisy patterns and calculated the Pearson map. The profiles in Figure 4.15 have been worked out as described in section 4.4, by averaging only over the mixed blocks in the maps.

In both typologies of noise, we notice that, for percentages ranging from 20% to



Figure 4.14: Transmitted spectra in either a phase (left panel) or an amplitude (right panel) modulation. Different shades of grey refer to intermediate steps moving from a mean value shaped (0%) to a partially modulated (100%) noise configuration.



**Figure 4.15:** Vibrational spectra for different mean value shapings applied to the incident pulses.

100%, neither the visibility of the Raman features nor the lineshape of their peaks seem to be affected by the mean-value spectral amplitude of the low-frequency side of the spectrum. Although a rise in the background is observed as the amplitude increases, the dispersive lineshape of the resonances remains unchanged. The only vibrational spectrum which deviates from this behaviour is the one corresponding to a null spectral amplitude of the noise-free side of the spectrum, for which a positive peak shape is retrieved.

These results show that the relative average amplitude between the noisy and the unmodulated sides of the spectrum does not play any role in determining the lineshape of the Raman resonances. It seems instead that only the total emptiness of the low-frequency photon modes leads to a change in the peak shapes. This validates our interpretation of the processes underlying the properties of the vibrational spectrum. Indeed, while a truly homodyne detection necessarily requires a null amplitude of the local oscillator, for a self-heterodyne one to take place a field



Figure 4.16: Transmitted spectra in either a phase (left panel) or an amplitude (right panel) modulation. Different shades of grey refer to different percentanges of background noise applied to the spectra. As regards phase noise, we recall that BG = 100% corresponds to fluctuations ranging from  $-\pi$  to  $+\pi$ .

superimposed to the signal is needed, no matter how high its intensity is.

## 4.6 Background noise dependence

In this section we address the question whether the magnitude of the stochastic fluctuations - what we called *background noise* (BG) in section 3.3.3 - affects the ISRS signal. In this respect, we have performed a set of measurements, applying either phase or amplitude noise, in which we have systematically increased the magnitude of the fluctuations introduced by the SLM. As shown in Figure 4.16, we have applied noise across the whole spectrum of the pulse. Let us recall that, in the case of phase noise, the percentages have to be intended with respect to a maximum range of  $2\pi$ , so that BG = 100% implies fluctuations ranging from  $-\pi$  to  $+\pi$ .

If we look at the right panel in Figure 4.16, we immediately realize that the detected intensity fluctuations are directly proportional to the amount of background noise applied. This is shown in the insets of the graph, where the standard deviation (calculated over all the repetitions) is plotted as function of the corresponding background noise. The direct proportionality retrieved in the case of amplitude noise is consistent with one would expect, given that we introduce amplitude fluctuations by randomly changing the efficiency of the diffraction grating imprinted on the SLM. Conversely, by looking at the left panel, we see that this proportionality is not preserved in the case of phase noise. Precisely, we observe in the inset that larger intensity fluctuations arise when the spectral phase varies approximately in the range  $\pm \pi/2$  (BG = 50%). It thus seems that the mechanism through which phase stochasticity is mapped into intensity fluctuations is not linear in the phase



Figure 4.17: Vibrational spectra for different amounts of background noise applied to the incident pulses.

background noise.

We show in Figure 4.17 the vibrational spectra obtained by computing the Pearson map and averaging along the frequency axis for each value of background noise. It seems that, except for a slight variation in the background, there are no significant alterations neither in the lineshape nor in the visibility of the Raman resonances as the background noise increases. This suggests that, at least above the minimum percentage of background noise considered, the technique is not sensitive to the magnitude of the stochastic fluctuations. Above this value, it suffices for the process to take place that any kind of random fluctuations are involved, no matter how large their deviation from the average value is. Future investigations will be carried out to study configurations with BG < 20% and determine a possible stochasticity threshold for the success of the method.

## 4.7 Single frequencies modulation

In this section we show and discuss the results of a set of measurements performed by introducing the stochasticity (either in phase or in amplitude) only to selected frequency components of the incident pulse. The aim of these tests is to improve our understanding of the mechanism that activates the Raman process. Precisely, we want to understand which role the stochasticity plays in our method and how it is involved in our measurements.

We explore different configurations in which noisy fluctuations are introduced in a controlled manner to either a single one or a pair of spectral components. This study will enable us to clarify whether the process is a single-frequency effect or it requires a double-frequency modulation to be observed. Moreover, we investigate the possibility that a tuning of the two fluctuating intensities near a Raman resonance could play a role in the amplification of the process.



**Figure 4.18:** A few randomly selected incident spectra having either a fixed (a) or a randomly changing (b) single-peak amplitude modulation.

#### 4.7.1 Single fixed peak

We start by applying stochastic fluctuations only to a fixed spectral component. This means imprinting a diffraction pattern on the SLM matrix in which only a single column (at a given horizontal position) is repeatedly modified. We show in Figure 4.18a) a few incident spectra to which noise has been applied at approximately 377 THz. Keeping fixed the position of the noisy spectral component, we acquire thousands of transmitted pulses, each one having a randomly assigned magnitude of fluctuation.

Figure 4.19 shows the result of two experiments performed by applying a phase modulation in the range  $\pm \pi$  (Pearson map in Figure 4.19a)) and an amplitude modulation of  $\pm 40\%$  (Pearson map in Figure 4.19c)). Both maps are almost totally positive-valued. This is reasonable since most of the spectrum is unshaped and thus preserves the pulse-to-pulse coherence of the laser source. However, the single peak modulation is responsible for a vertical and a horizontal lines which are mainly white, meaning that most of the frequencies within the spectrum are uncorrelated with the randomly fluctuating peak. Therefore, if there is any coupling between photon modes whose frequency difference matches the energy of the phonons, it should be searched in those lines. Since the Pearson map is symmetric with respect to the diagonal, we consider only the horizontal line and take the average over the regions delimited by the green and the yellow lines.

The average profiles are shown in Figure 4.19b) and d) for phase and amplitude noise, respectively, as function of the frequency distance from the diagonal. The yellow cut, which should have negative frequency differences, has been mirrored to be displayed on the same axis. The dashed grey lines in the plot indicate the nominal energy of the Raman modes we usually detect. We observe that the cuts undergo either a shift or a modulation in the vicinity of the expected frequency differences. The peaks corresponding to the most energetic phonon seem to be a bit shifted with respect to the expected value. This shift could be due to the integration procedure, but in any case its amount is within the estimated frequency resolution of our method.



Figure 4.19: Pearson maps and corresponding horizontal cuts for both phase (a) and b)) and amplitude modulation (c) and d)).

Of course, the features that we observe are not as strong as the ones in which either a partial or a full modulation is present. However, these results suggest that a stochasticity applied to a single mode is enough to faintly observe the Raman process. Moreover, since these effects are visible in both the phase and the amplitude modulation, we reckon that this conclusion is valid for both typologies of noise.

#### 4.7.2 Single random peak

We have then performed a second test in which we have randomly changed, pattern by pattern, both the position and the magnitude of the single modulated spectral component. Examples of incident pulses of this kind are shown in Figure 4.18b), where each color refers to a different repetition.

We have repeated the experiment both in an amplitude and a phase noise configuration, working with the same range of stochasticity as in the previous case. We show in Figure 4.20 the result of the calculation of the Pearson coefficient for the amplitude (a) and the phase modulation (b). Unlike in the previous experiment, the maps are not almost completely red, since the randomly fluctuating peak unsettles the pulse-to-pulse coherence of the spectra. However, intrinsic correlations within the incident pulse are still present and arise as a block structure of the maps. On



**Figure 4.20:** Pearson maps for amplitude (a) and phase (b) modulation for incident spectra having a single randomly fluctuating spectral component.

top of this chequered pattern, a faint feature in correspondence with the phonon at 13.9 THz can be distinguished. This Raman band is visible in both configurations.

This result again suggests that a single fluctuating spectral component is required in order for the Raman process to take place. However, under this condition, the signal is very weak and only the phonon with the highest scattering cross-section is detectable.

#### 4.7.3 One peak fixed, one random

On the basis of the previous tests, we have performed a third one in which we have shaped the incident pulse to have both a fixed and a random fluctuating peak. The aim of this experiment is to understand whether or not the effects we have observed in the previous configurations do affect each other.

We have chosen the fixed fluctuating peak to lie approximately at frequency 371 THz and we have applied the same magnitude of noise (amplitude  $\pm 40\%$  or phase  $\pm \pi$ ) to a second spectral component whose position is randomly assigned at each repetition.

We show in Figure 4.21 the Pearson maps corresponding to the amplitude (a) and the phase (b) modulation. They look very similar to the maps obtained in the case of a single random peak (Figure 4.20), with the only exception being the vertical and the horizontal lines for which the addition of the fixed peak is responsible. As in the previous case, only the Raman band at 13.9 THz is slightly visible. We can carry out an analysis similar to the one we have performed in section 4.7.1 on the regions in the map delimited by the green and the yellow lines. We plot the average cuts in Figure 4.22. Again, distinguishable features appear in the vicinity of the expected Raman resonances, especially near the phonons at 6.2 and 13.9 THz. It is



Figure 4.21: Pearson maps of two datasets in which amplitude (a) and phase (b) noise has been introduced by shaping the incident pulse to have both a fixed ( $\sim$ 371 THz) and a random fluctuation.



Figure 4.22: Average horizontal cuts over the regions delimited by the green and the yellow lines in Figure 4.21.



Figure 4.23: Example of Pearson map calculated over thousands of spectra with two fixed randomly fluctuating peaks, whose frequency difference is approximately 7 THz. While the peak at 376 THz has been kept fixed for all the set of measurements, the other one has been scanned from a minimum distance of 3 THz to a maximum one of 12 THz.

likely that the phonon at 6.2 THz, visible in the cuts, is obscured in the remaining regions of the map by the chequered pattern due to the intrinsic correlations of the incident pulse. Indeed, in the slices delimited by the green and yellow lines, these intrinsic correlations are flattened out by the stochasticity of the fixed peak, enabling a better visibility of the Raman signal.

These results show that the overall effect of this mixed configuration can be considered as a combination of the ones we have previously discussed. We can thus conclude that the two fluctuating spectral components are not coupled.

#### 4.7.4 Two fixed peaks with variable distance

Finally, we have performed a last set of measurements in which we have introduced two fixed random fluctuations, whose distance has been gradually increased from 3 to 12 THz. Hence, the frequency range has been chosen to cover two of the Raman resonances (3.8 and 6.2 THz phonons). The aim of this kind of measurements is to explore the possibility of an enhancement of the Raman signal when the distance of the two stochastic spectral components resonates with one of the Raman modes.

We have placed one of the two fixed peaks at about 376 THz and we have moved the second one up to 388 THz in ~0.2 THz steps (2 SLM pixels). Note that the choice of the frequency step is consistent with the estimated frequency resolution of the method. At each step, we have acquired ten thousands of transmitted spectra, so that a Pearson map can be computed at each frequency distance of the two peaks,  $\Delta\omega$ . One of them ( $\Delta\omega = 7$  THz) is shown in Figure 4.23. As expected, the map is similar to one obtained in section 4.7.1, but now there is a pair of vertical and horizontal lines corresponding to both the fluctuating peaks.

Similarly to what we have done in section 4.7.1, we can once again consider the average cuts of the Pearson maps along the horizontal line comoving with the second



Figure 4.24: Maps showing the average cuts of the Pearson maps along the horizontal line comoving with the second peak.

peak. As result, we will get one profile for each frequency step. We plot the final result in a 2D map in which the x-axis is the frequency difference from the diagonal (Raman shift) and the y-axis is the frequency distance between the two fluctuating peaks; the color map quantifies the Pearson coefficient along each cut (see Figure 4.24).

In both the configurations we have studied (amplitude noise  $\pm 40\%$  and phase noise  $\pm \pi$ ), we observe that the Pearson coefficient assumes higher (absolute) values for frequency distances from the diagonal that match the ones of the phonon modes. This result is exactly what we have already discussed in the single fixed peak configuration (section 4.7.1). Furthermore, we observe the presence of other features in the maps. The vertical line centered at 0 THz is of course due to the autocorrelation of the moving peak. But there are also (anti-) diagonal lines that highlight the presence of peaks in the cuts of the Pearson maps that change their position according to  $\Delta\omega$ . In particular, the clearest line of these is directly due to the presence of the fixed peak, which is uncorrelated (white line) to the moving one. Said in another way, the white diagonal line collects all the points of intersection between the comoving horizontal line and the fixed vertical line in the Pearson map (Figure 4.23). We reckon that the other fainter diagonal lines (parallel to the main one) are due to some sort of replicas of this feature.

However, none of the maps show either an enhancement of the signal or a clear change in the lineshape of the Raman bands in the vicinity of the resonances. This leads us to believe that no kind of interaction between the two peaks is present.

Finally, keeping in mind the results obtained in the previous three sections, we can conclude that stochastic noise combined with a Pearson coefficient-based analysis seems to be sensitive to single-frequency stochasticities only.

### 4.8 Fluence dependence

The typical approach to study the order of nonlinearity of nonlinear optical effects, is to perform measurements in which the energy of the incident light is increased step by step. At each step, the signal intensity is recorded, in order to extrapolate its dependence on the intensity of the excitation field.

However, this approach cannot be directly applied to our method. Indeed, even if our measured quantity is the spectral intensity transmitted by the sample, our observable is the covariance of them, calculated over repeated measurements. In this framework, we had to develop another approach to work out the order of the Raman process we study.

Though the Pearson correlation coefficient is a powerful tool to quantify the degree of correlation between two stochastic variables, it is, by definition, a normalized quantity. This means that it is not sensitive to the strength of the signal. This property, while being an asset when dealing with weak nonlinear signals, makes the Pearson coefficient unsuitable for fluence dependence studies. To extrapolate the order of nonlinearity of the process we observe, we have thus to define a more proper statistical tool.

The core idea of the method is to exploit the simultaneous acquisition of the reference pulse. Indeed, a way to keep trace of the strength of the signal as the intensity of the excitation pulse is increased, could be directly relating the intensity fluctuations of the transmitted pulse to those of the shaped pulse before the interaction. Should there be a nonlinearity in the signal, the ratio between the amplitude of the signal field and the one of the excitation field would vary according to the order of the process. For a linear process, the ratio is expected to be independent from the incident pulse energy. A process with a quadratic dependence on the pulse energy, should instead give a linear increase of the ratio as function of the pulse power. We will see in the following how this ratio can be evaluated and study its dependence on the incident pulse energy.

Before discussing the details of the measurements, let us define a quantity which is commonly used in this typology of analysis, the *fluence* (f). It is typically ex-



Figure 4.25: Reference and transmitted pulses in a mean value shaping configuration, in which amplitude noise has been added. Both spectra have been divided by the corresponding not-noisy spectra; the intensity (Noisy/NotNoisy, N/NN) is thus centered around 1. The blue markers indicate the intensity of the spectral components for which a linear fit is performed in Figure 4.26.

pressed in  $mJ/cm^2$  and defined as

$$f\left[\mathrm{mJ/cm}^{2}\right] = \frac{P\left[mW\right]}{r[\mathrm{Hz}]A\left[\mathrm{cm}^{2}\right]}$$
(4.7)

where P is the measured power of the beam, r the repetition rate of the laser and A the area of the beam impinging on the sample. In our setup, r = 5 kHz and the spot has a diameter of  $\sim 50 \ \mu$ m.

#### 4.8.1 Slope map

In order to evaluate the order of nonlinearity of the process, we have performed two sets of measurements in a mean value shaping configuration: the first by adding amplitude noise, the second by applying a stochasticity in the spectral phase of the pulse. We will consider in the following analysis only the amplitude modulation. The same applies also in the case of phase noise, for which we will show only the final result.

We have defined a set of powers for the incident pulse and, for each of these value, we have repeated the measurement 50000 times. Precisely, we have scanned a range of powers from 0.5 to 2.6 mW (fluences ranging from 5.4 to  $26.3 \text{ mJ/cm}^2$ ).

We show in Figure 4.25a) both the incident and the transmitted spectra for a single realization and for a specific choice of fluence. We stress that it is particularly important here to consider the noisy spectra normalized over their corresponding not-noisy ones. This is because we have placed a filter wheel in front of the spectrometer to attenuate the beam in the high-power range. Hence, if they were not normalized, spectra acquired in different conditions would not be comparable.



Figure 4.26: Scatter plot of the spectral intensities of the sample beam  $(I_{sam}(\omega_j))$  as function of the intensities of the reference beam  $(I_{ref}(\omega_i))$ . The pair of frequencies  $\omega_i$  and  $\omega_j$  considered is identified by the markers in Figure 4.25.

As mentioned above, we are interested in establishing a relation between the transmitted spectra and their corresponding reference pulses. To do this, let us, for the sake of clarity, consider only the spectral intensities marked by the blue circles in Figure 4.25. Precisely, we want to evaluate the relation between the intensity of the reference pulse at the frequency  $\omega_i$   $(I_{ref}(\omega_i))$  and that of the transmitted one at frequency  $\omega_j$   $(I_{sam}(\omega_j))$ . By considering all the 50000 spectra acquired, we can construct a plot like that in Figure 4.26, in which the spectral intensities of the sample beam are plotted as function of the intensities of the reference beam and each marker refers to each single repetition. We observe that the markers are uniformly distributed in the plane, meaning that the two spectral components selected are uncorrelated.

By calculating the central value and the standard deviation  $\sigma$  of the distribution, we can identify those points that are farther away than  $3\sigma$  from the mean (indicated by solid rather than transparent markers) and reject them. On the remaining points, we perform a linear fit (dashed yellow line in the figure) to estimate the slope and the intercept of the distribution. While the intercept does not contain much information, the slope is exactly the quantity we need to estimate the ratio between the spectral amplitude of the signal field and that of the excitation field.

Though only a single pair of frequencies has been considered here, the same calculation has to be performed considering all the possible combinations of  $\omega_i$  and  $\omega_j$  within both pulses in Figure 4.25. Since each spectrum is provided with 256 frequency channels, we end up with a  $256 \times 256$  map. Each point in the grid of



**Figure 4.27:** Slope maps cross-correlating the sample and the reference beam for different powers of the incident pulse.

coordinates  $(\omega_i, \omega_j)$  displays the estimated slope between  $I_{ref}(\omega_i)$  and  $I_{sam}(\omega_j)$ . We shall refer to this map as *slope map*.

Finally, let us point out that in the specific case of a mean value shaping configuration (like the one considered here), an additional care should be taken, as the reference spectrum has null spectral amplitude on the noise-free side. Hence, the linear fit between low-frequency modes of the incident pulse and any mode of the transmitted pulse would result in an infinite slope. We shall discard these points and consider only the spectral components of the reference pulse above the sharp edge ( $\sim$ 372 THz).

#### 4.8.2 Power exponent map

By following the procedure described above, we can construct a slope map for each fluence value. The result of the calculation is shown in Figure 4.27. It is clear that the slope map does change as function of the fluence. In particular, we notice that the Raman sidebands are fairly visible for low-energy impinging light and become more and more intense by increasing the fluence of the incident beam. Furthermore, as always, the signal seems to be much stronger in the mixed block, where the incoherent part of the incident beam is coupled to the unmodulated chunk of the transmitted spectrum.



Figure 4.28: Slope map (a) for the maximum power of the incident pulse. The green circle indicates a point within the map for which the slope value is plotted as function of the power in linear scale (b) and in logarithmic scale (c). A linear fit of the data is performed and shown in c) by the dashed red line. P is the slope estimated by the fit.

We have now all the tools to estimate the power law through which the slope value scales with the fluence. For the sake of clarity, we illustrate the fitting procedure for one selected point in the slope map, marked with a green circle in Figure 4.28a). If we consider the value of the slope in that specific point in all the maps in Figure 4.27 and plot it as function of the fluence, we will get the behaviour shown in Figure 4.28b). We want to fit these data with a function of the kind:

$$y = A(x - x_0)^P (4.8)$$

with the constraint that  $x_0 = 0$ , since we expect the signal to be zero with no incident light. The quantity that we need in order to determine the degree of nonlinearity of the process is the power exponent P.

In order to evaluate it, we can switch to a logarithmic scale (Figure 4.28c)) and perform a linear fit of the data to get the slope of the line and thus the power exponent P.

We can apply the same procedure to all the points within the slope maps in Figure 4.27, to get a *power exponent map*. It is worth to note that we perform this fit on the *absolute value* of the slope maps. This is because it does not matter whether the correlation between the modes is positive or negative. We are only interested in how the degree of correlation scales with the fluence of the impinging light.

At the end of the fitting procedure (applied to both the amplitude and the phase modulation datasets), we get the power exponent maps shown in Figure 4.29.



Figure 4.29: Power exponent maps for both amplitude (a) and phase (b) noise.

We observe that in the upper block, which relates the incoherent part of both the reference and the sample beams, the maps are rather noisy (except for the diagonal which remains constant as function of the fluence, P=0). Moreover, it seems that in this region the Raman bands fade into the background, meaning that there is not an obvious distinction in the fluence dependence of the signal.

Conversely, in the mixed block the Raman bands are clearly distinguishable, especially in the case for which amplitude noise has been introduced. They arise out of the background as white lines, meaning that their strength increases quadratically (P=2) with the fluence. This result is consistent with a  $\chi^{(3)}$  (third-order) nonlinear process such stimulated Raman scattering.

The poor visibility of the Raman features in the phase noise configuration may be due to inteference effects which we expect to occur among the spectral components of the pulse. Moreover, we recall that we also expect amplitude fluctuations to be introduced by the SLM even when only phase stochasticity has been applied (section 2.3). One might expect that these fluctuations contribute to the process in a way similar to the case of pure amplitude modulation (as in Figure 4.28a)), thus expecting a quadratically increasing function also in the case of phase modulation. However, this cannot be taken for granted, as we do not know how the mechanism that maps phase noise into amplitude modulations scales with the fluence.

# Chapter 5

# **Time-resolved** measurements

The time evolution of the lattice vibrations is usually addressed by means of pump and probe experiments. In this framework, an intense laser pulse (the pump) impulsively injects coherent oscillations in the target material and a second one (the probe), properly delayed in time, measures how the response of the material evolves on ultrashort time scales. Since the optical response is expected to oscillate at the frequencies of the phonon modes excited by the pump, the Fourier-transform of the time-domain signal ultimately provides the energy and the lifetime of the oscillations.

In standard pump and probe experiments, the measured quantity is the transmitted/reflected average intensity of the probe as function of the time delay. More precisely, the measurement is stroboscopically repeated at each delay and then an integration is performed to work out the average signal.

We propose a radically different method that combines Noise Correlation Spectroscopy (NCS) with the traditional pump-probe approach. Here, the relevant quantity is no longer the average intensity over repeated measurements, but, rather, the covariance of them. In particular, we use the Pearson correlation coefficient (section 4.2) to quantify it and thus get a Pearson map at each pump-probe time delay.

At this point, a fundamental difference between the standard pump-probe approach and the proposed method should be underlined. While the standard approach *requires* a temporal scan to work out the energy of the phonon modes, static transmission measurements via NCS already provide this information, as proved in Chapter 4. Our main interest in performing a time-resolved NCS by combining the two techniques, lies in studying the relaxation dynamics of the lattice and thus determining the lifetimes of the phonons, to which static experiments are blind.

In the first section, we focus on the implementation of the method and discuss a preliminary time-resolved measurement performed by adopting the experimental setup in section 3.1.2. We use Fourier analysis to understand whether the time evolution of the covariances can disclose information on the transient pump-induced state of the material.

We then switch to polarization dependent measurements by using the setup described in section 3.1.3. Following [18], we explore different experimental configurations by properly choosing the polarization of the pump and probe beams. We finally address the question whether the technique is sensitive to the symmetry properties of the phonons.

## 5.1 NCS applied to pump and probe experiments

We have first performed time-resolved measurements on the quartz sample within a simple pump and probe scheme, without adopting polarization selective geometries. We recall that in our setup (section 3.1.2) the probe is the beam which is shaped by the SLM, while the pump is an unshaped, intense beam previously beam-splitted from the laser output. The desired pump-probe time delay is achieved by means of a translation stage which properly modifies the optical path of the pump. Then, the two beams spatially overlap within the sample. We highlight that the pump is almost collinear with the probe, so that we are still allowed to assume the quartz sample to have a  $C_3$  rotational symmetry. Finally, we recall that we acquire only the transmitted probe. More precisely, we record thousands of spectra per delay, each one with a different noisy pattern superimposed by the SLM. The pump beam is instead properly blocked after the sample.

We present in this section a preliminary dynamical measurement to investigate the feasibility of the method. Since the typical lifetime of the optical phonon modes is approximately a few picoseconds long, we have scanned time delays up to 3.5 ps in 20 fs steps. We have also recorded data for negative delays (up to -300 fs) to have reference measurements of the system before the excitation induced by the pump. In order to enhance the Raman signal, we have shaped the probe to have a null spectral amplitude on the noise-free side of the pulse spectrum (mean value shaping configuration, section 4.3.3). Moreover, since we usually observe a stronger signal when a phase (rather than an amplitude) stochasticity is injected in the pulse, we have worked in a phase noise configuration ( $\pm \pi/2$ ). We have set the pump power to be much greater than the probe one. Precisely, we have worked with powers of the order of 200 and 20 mJ/cm<sup>2</sup>, respectively.

The analysis has been carried out by computing a Pearson map for each set of spectra acquired at a fixed delay. We show in Figure 5.1 a selection of maps corresponding to significant pump-probe delays. To better visualize the Raman resonances (indicated by the grey dashed lines in the figure), we have plotted the Pearson map as function of the frequency shift from the diagonal line, as described in section 4.4.

First of all, we observe that distinguishable Raman features are present in all the mixed blocks of the maps. The strongest ones are those corresponding to the phonons at 13.9 and 6.2 THz, which have the highest scattering cross sections. We particularly stress that the signal is also present at negative time delays, where there should not be any pump to excite the sample. We reckon that this is probe-related effect: it is likely, in fact, that the probe of its own also contributes to the rise of the Raman bands, exactly as if we were performing a static transmission measurement.

Besides the Raman lines, the Pearson maps present other visible structures, completely absent in the maps analyzed in Chapter 4. The upper triangle (which



Figure 5.1: Preliminary time-resolved NCS measurements on quartz. Pearson maps are shown for selected time delays. The grey dashed lines indicate the nominal Raman resonances expected.



Figure 5.2: Pearson map (a) for  $\tau = -300$  fs. The green marker indicates the point in the map whose temporal dependence and Fourier transform are shown in (b) and (c), respectively. The black line indicates the points whose Pearson coefficient is plotted as function of the pump-probe delay in Figure 5.3.

correlates two spectral modes both within the noisy side of the spectrum) is dominated by stripes having positive-negative Pearson coefficient, which are also present (although much weaker) in the mixed block. The spacing of these stripes varies according to the pump-probe delay: it stretches in the proximity of the temporal overlap, and it gets shorter as the delay increases, until the stripes completely disappear approximately at  $\tau = 2$  ps. The presence of these stripes prevents the observation of Raman features in the upper triangle of the maps, but it also partially obscures them in the mixed block. We believe that these stripes are due to a coherent coupling between the pump and the probe [19]. When the two beams interfere in the sample, a spatial modulation of the optical properties of the material is established. A fraction of the pump light can be scattered off this induced transient grating and be deflected in the probe direction, to which it adds coherently onto the detector. Even if we have cross-polarized the pump and the probe to minimize these effects, they are unavoidable when the two beams come from the same laser output and thus share the same spectral content. In this condition, the pump and the probe are said to be *degenerate*.

In order to partially get rid of the interference, we consider in the following analysis only the mixed blocks of the Pearson maps.

#### 5.1.1 Fourier analysis

In order to determine whether the covariance can reveal information about the lifetime of the lattice excitations, we have performed a dynamical analysis.

For the sake of clarity, we illustrate the procedure for just one point within the Pearson map, marked by a green circle in Figure 5.2a). We have chosen this point to lie on the Raman band corresponding to the phonon at 6.2 THz and plotted in

Figure 5.2b) the Pearson coefficient corresponding to it as function of the pumpprobe delay. The Pearson coefficient exhibits a periodically oscillating behaviour, which seems to slowly decay after approximately 2 ps.

To evaluate the oscillation frequency, we have then performed the Fourier transform of the Pearson coefficient (Figure 5.2c)), which clearly shows a peak right on top of the characteristic frequency of the Raman resonance marked by the green circle.

We have extended this analysis to all the points lying on the black line in Figure 5.2a) to get the 2D map in Figure 5.3. For each point considered, we retrieve a periodically oscillating dependence on the pump-probe delay (horizontal cuts in the map), whose frequency gets higher as the the frequency distance from the diagonal (i.e. the frequency difference between the two spectral components for which the Pearson coefficient is evaluated) increases. We observe a discontinuity in the amplitude of the oscillations at about 6 THz. By looking at the Pearson maps in Figure 5.1, this threshold seems to match the border of the region within which the stripes due to the pump-probe interference are more prominent.

By Fourier transforming along the delay axis, we get the 2D map in Figure 5.4. The line which clearly arises out of the background shows that what we have observed by picking a single point on the 6.2 THz Raman line, holds for *all* the points in the Pearson map, no matter whether or not they lie on the Raman bands. The line in Figure 5.4 is indeed a bisector, meaning that the degree of correlation between two spectral modes of the probe oscillates in time according to their frequency separation. We report that this is not affected by the choice of the points in the Pearson map (black line in Figure 5.2a)). This result suggests that, at least under the experimental conditions investigated, the Pearson correlation coefficient seems to not be sensitive to the lattice relaxation dynamics.

The physical meaning of this evidence has not yet been understood. The most obvious guess is that it could be related to the pump-probe coherent coupling. For this reason, we are currently setting up a non-degenerate scheme to get rid of the interference effects.



Figure 5.3: Pearson correlation coefficient as function of the time delay for the points lying on the black line in Figure 5.2a).



Figure 5.4: Fourier transform of Figure 5.3 along the delay axis.
### 5.2 Polarization dependent pump and probe

In this section, we focus on the symmetry properties of the system. Following [18], we use a pump-probe flexible geometry to separately analyze nuclear oscillatory modes having different symmetry.

We recall that in our setup the pump beam is almost collinear with the probe, so that the susceptibility of the sample is still ruled by the fourth-rank tensor in Equation 4.4. This equation is read with the outer level rows and columns (indices i,j) corresponding to the signal and the probe polarizations, respectively. The inner level row and columns (indices k,l) refer instead to the polarization of two modes within the pump bandwidth. The element of the tensor indicate whether or not in a particular configuration (i.e. for a particular choice of the polarization of the beams involved) specific Raman modes are observable. We highlight that, in order to select the polarization of the signal field, the essential requirement is to place an analyzer after the sample<sup>1</sup> (the polarizing beam splitter in Figure 3.3).

As proved in [18], though four indices are formally involved in the susceptibility, there are only two true degrees of freedom. If we consider as reference axis the polarization of the pump beam, we get that the most general detected signal is:

$$\operatorname{signal} = c^2 \cos(\alpha + \delta) + a^2 \cos(\alpha - \delta) \tag{5.1}$$

Pump-probe angle $(\alpha)$	Pump-analyzer angle $(\delta)$	Susceptibility tensor element
$\pi/2$	0	0
$\pi/2$	$+\pi/2$	$a^2 - c^2$
0	0	$a^2 + c^2$
0	$-\pi/2$	0
$\pi/4$	$+\pi/4$	$a^2$
$\pi/4$	$-\pi/4$	$c^2$

where  $\alpha$  is the angle between the pump and the probe polarizations and  $\delta$  is the angle between the pump axis and the analyzer. We summarise in Table 5.2 the expected Raman signal for a set of polarization geometries.

 Table 5.1: Elements of the susceptibility tensor for selected polarization geometries.

We observe that only in a configuration in which  $\alpha$  is equal to  $\pi/4$  it is possible to independently detect either the total-symmetric A<sub>1</sub> modes ( $a^2$ ) or the doubledegenerate E modes ( $c^2$ ). The former one can be isolated by considering the polarization component of the signal parallel to the polarization of the incoming probe beam, while the latter by looking at the component orthogonal to the probe polarization. In all the other cases the signal should either vanish or be due to the contributions of both symmetries.

<sup>&</sup>lt;sup>1</sup>Since the quartz is optically active, the axis of the analyzer must be corrected to take into account the additional rotation for which the sample is responsible. We have estimated such rotation to be of the order of  $\sim 10^{\circ}$  for our 1mm-thick quartz sample.

In the following, we consider the case in which the pump and the probe are co-polarized and the one in which their polarizations form an angle of  $45^{\circ}$ . We recall that the polarizing beam splitter after the sample allows us to simultaneously acquire both the polarization components of the transmitted probe. The aim of the study is to investigate whether or not the selection rules in Table 5.2 (valid for standard pump-probe studies) also apply to our covariance-based technique. As in the previous section, we have worked with powers of the order of 200 mJ/cm<sup>2</sup> for the pump and 20 mJ/cm<sup>2</sup> for the probe.

### 5.2.1 Co-polarized pump and probe

As in the time-resolved study discussed in section 5.1, we work in a mean value shaping configuration to enhance the signal. For the same reason, we introduce phase, rather than amplitude, stochasticity  $(\pm \pi/2)$  across the probe pulse.

At each step of the temporal scan, we acquire thousands of noisy spectra of the transmitted probe. More precisely, we acquire both the parallel ( $\delta = 0$ ) and the orthogonal ( $\delta = -\pi/2$ ) component of the transmitted pulse (with respect to the incoming probe polarization). We show in Figure 5.5 a selection of Pearson maps calculated for both the parallel (a) and the orthogonal (b) channel. Although the temporal scan considered extends up to a few picoseconds, we have neglected time delays larger than 100 fs as the presence of the interference fringes (see section 5.1) compromises the visibility of the signal.

By reference to the Raman spectra of  $\alpha$ -quartz in Figure 4.2, we assign the correct symmetry to each phonon mode detected. In particular, all the three more energetic Raman resonances (marked with the cyan lines) have A<sub>1</sub> symmetry, while the phonon at 3.8 THz (black line) is the only E-mode.

We observe that, although the theory predicts a vanishing signal for  $\delta = -\pi/2$  (Table 5.2), Raman bands are clearly visible in both the polarization geometries analyzed. More specifically, the Pearson maps in Figure 5.5a) are consistent with the theoretical prediction, as phonons having both A<sub>1</sub> and E symmetry are retrieved. Nonetheless, the same features are also distinguishable in the covariances of the orthogonal component of the transmitted pulse. Here, however, the phonons at 3.8 and 10.6 THz are only very faintly visible.

Our guess is that, in this condition, also the probe, along with the pump, is contributing to the activation of the ISRS process. Hence, the transmitted pulse would be the result of the addition of two processes: the one we would expect in a simple pump-probe scheme (that is polarization selective for a proper polarization geometry), and the one we have studied in Chapter 4 in a static transmission geometry where only a single noisy pulse is involved. In the latter case, the probe on its own behaves as a pump and excites all the vibrational modes without distinction. Consequently, a truly polarization selective geometry seems to be not achievable in this configuration.

Since the latter one is not sensitive to the symmetry properties of the vibrational modes,



Figure 5.5: Pearson maps computed for a specific set of time delays. The pump and the probe are co-polarized ( $\alpha = 0$ ) and we consider both the parallel (a) and the orthogonal (b) component of the transmitted pulse (with respect to the incident probe polarization).

### **5.2.2** Pump and probe at $45^{\circ}$

We have repeated the same measurement discussed in section 5.2.1 after setting the pump polarization to form an angle of  $45^{\circ}$  with the probe polarization. We recall that, according to the theoretical predictions, this configuration should allow to independently observe the two rotational symmetries.

In Figure 5.6 the Pearson maps calculated over the parallel (a) and the orthogonal (b) component are shown for a few selected time delays.

We observe that the maps in (a) are consistent with what we would expect. Indeed, only the Raman modes having  $A_1$  symmetry are visible.

On the other hand, the most remarkable feature in the maps in Figure 5.6b) is the phonon at 3.8 THz, having E symmetry. The rise of this mode (completely absent in the parallel configuration) is in agreement with the theoretical predictions. However, along with the E-mode, also the most intense  $A_1$  Raman resonances are visible (6.2 and 13.9 THz), whose presence is probably due to an imperfect extinction of the polarization component parallel to the probe. In this connection, we highlight the strength of the method, able to reveal correlations even within a pulse as weak as an extincted one.

The results in Figure 5.6 prove that NCS applied to a polarization selective pump-probe scheme can be actually used to perform symmetry studies of the sample. Though a complete isolation of the E-symmetry modes has not been accomplished owing to imperfect alignment, the total absence of this symmetry in the polarization component parallel to the probe beam suggests that different physical processes take place in the two configurations and that our technique is sensitive to them.

### 5.2.3 Cross-correlation analysis

The Pearson maps discussed so far have been computed as described in section 4.2, namely by evaluating the Pearson coefficient between a pair of frequencies *within* the same spectrum and then extending the calculation to all the possible frequency pairs. We shall refer to this kind of Pearson maps as *autocorrelators*.

However, our polarization selective setup has been designed to perform also another kind of analysis, aimed at revealing correlations *between the two polarization components* that undergo the light-matter interaction. Using 4.6, we evaluate the degree of correlation between the two components as:

$$\rho\left(I^{\perp}(\omega_i), I^{\parallel}(\omega_j)\right) = \frac{\langle \delta I^{\perp}(\omega_i) \, \delta I^{\parallel}(\omega_j) \rangle}{\sigma_i^{\perp} \, \sigma_j^{\parallel}} \tag{5.2}$$

where the superscripts refer to the polarization components orthogonal and parallel to the polarization of the incident probe. The Pearson maps resulting from this calculation will be dubbed *cross-correlators*. In order for this analysis to be meaningful, the two polarization components are simultaneously acquired and come from the same statistical set of incident pulses. More precisely, since the two components are splitted after the sample, they have been imprinted with same noisy patterns by the SLM.



Figure 5.6: Pearson maps computed for a specific set of time delays. The pump and the probe form an angle  $\alpha = 45^{\circ}$  and we consider both the parallel (a) and the orthogonal (b) component of the transmitted pulse (with respect to the incident probe polarization).

In this section, we investigate whether this approach can shed light on the mechanism which couples the phonon symmetry to the photon polarization. In particular, what we are interested in, is to understand whether the cross-correlator keeps trace of the rotation of the polarization of the light interacting with the double-degenerate (non-totalsymmetric) phonon modes. We shall conduct this analysis both in the 0° and 45° pump-probe angle configurations, in order to determine if the pump orientation plays any role. Since it seems that (at least at this stage) a dynamical analysis cannot bring additional information on the process (section 5.1.1), we shall restrict our cross-correlation analysis only to a fixed pump-probe delay. In particular, we choose the condition of temporal overlap since it seems to minimize the interference effects.

We show in Figure 5.7 the result of the calculation. To make it easier for the reader to appreciate the difference between the autocorrelators and the corresponding cross-correlator, we show again the maps for null time delay discussed in the previous two sections. The simple scheme below the Pearson maps clarifies which polarization component has been considered. We highlight that the cross-correlator, being calculated over two distinct pulses, is no longer a symmetric map. Therefore, we plot the entire map (without neglecting the negative frequency shift) as  $\rho(\omega_i^{\perp}, \omega_i^{\parallel})$ .

In Figure 5.7a) we compare the autocorrelators and the corresponding crosscorrelator calculated for a co-polarized pump and probe configuration. By looking at the cross-correlator, we observe that the mixed blocks show strong positive features in correspondence with the expected Raman resonances. In particular, both  $A_1$ - and E- modes are visible in the mixed blocks. The upper right block contains instead only a weak signal corresponding to the 6.2 and 13.9 THz phonons. By comparing the cross-correlator with the two autocorrelators, the former one seems to be a mere superposition of the other two maps. We thus conclude that, in this configuration, no additional information can be retrieved from the study of the correlations between the two polarization components.

We propose the same analysis in Figure 5.7b), where we consider the configuration in which the pump and probe polarizations form an angle of  $45^{\circ}$ . Here, the two mixed blocks appear different with respect to the corresponding autocorrelators. More precisely, we observe that the bands with A<sub>1</sub>-symmetry (which have positive sign in both the autocorrelators) become negative in both the mixed blocks of the cross-correlator. Conversely, the E-mode in the upper left block of the crosscorrelator preserves its positive sign (beware of the different color scales used in the three maps). Also the upper right block is significantly different from the autocorrelators. The main (and somehow anomalous) difference lies in the sign of the diagonal, which is negative. Since this effect is not present in the cross-correlator in a), we reckon that it is due to some pump-related processes. Moreover, it seems that, in the upper right block, only spectral components (belonging to different polarizations) whose frequency difference matches the E-mode energy are coupled. This evidence could be somehow related to the fact that only the E-symmetry phonons are involved in the rotation of the polarization of the incident light.

Though these results are very promising, they still lack a comprehensive interpretation. For this reason, polarization dependent cross-correlations will be subject of further analysis in the future.



**Figure 5.7:** Autocorrelation and cross-correlation maps for the  $0^{\circ}$  (a) and  $45^{\circ}$  (b) pumpprobe angle configurations.

## Summary and outlook

In the traditional, widely-used approaches to nonlinear optical spectroscopy, the signal is worked out as the average over subsequently repeated experiments, performed under unchanged experimental conditions. We flip this paradigm by proposing a novel spectroscopic technique, named *Noise Correlation Spectroscopy* (NCS), which combines a noise-assisted approach to a covariance-based detection.

The main objective of the work described in this thesis was to investigate its feasibility to the study of coherent lattice vibrations through Impulsive Stimulated Raman Scattering (ISRS). To test the method, we examined a benchmark material such as  $\alpha$ -quartz, whose Raman spectrum has been extensively studied through more standard approaches.

To coherently excite the lattice, we employed a femtosecond pulsed near-infrared laser source. The temporal features of the pulses involved are crucial to the implementation of the technique. First, because fields strong enough to induce a nonlinear process as ISRS are required. Secondly, because femtosecond light pulses, due to the uncertainty principle, have a broad spectral content. When such pulses interact with the sample, the ISRS process results in a coupling, within each pulse, of the Fourier components whose energy difference matches the energy of the phonon modes that have been created/annihilated through the inelastic scattering. The process thus imprints each pulse with a correlation pattern that encodes the Raman spectrum of the target material. When the experiment is repeated many times, the statistical dataset becomes large enough to allow the retrieval of this information.

To enhance the correlations established by the nonlinear process, we used a programmable liquid crystal Spatial Light Modulator (SLM) based pulse shaper. At each repetition, the SLM independently modulates each spectral component to overcome pulse-to-pulse laser coherence and introduces instead stochastic, spectrallynarrow fluctuations (either in phase or amplitude). Properly shaped pulses interact with the sample and their transmitted spectra are acquired by a fast photodiodebased spectrometer, which allows a single-shot frequency-resolved detection. Along with the transmitted pulse, also a beam-splitted copy of the incident spectrum is acquired as reference, to help discriminate interaction features only.

The data analysis was conducted by using covariance-based statistical tools to reveal photon correlations over a set of repeated measurements. In particular, we used the Pearson correlation coefficient, which quantifies the degree of linear correlation between two stochastic variables.

The calculation of the Pearson coefficient clearly showed that the transmitted beam is characterized by features that are completely absent in the reference one and are thus genuinely due to the interaction with the sample. The comparison of our results with the Raman spectrum of quartz known from literature proved the feasibility of the NCS approach.

The success of the experimental implementation of the technique was substantiated by the development of a phenomenological model able to describe Raman scattering from stochastic radiation. The model, so far suitable for phase stochasticity only, was derived using a fully quantum approach to the calculation of nonlinear optical signals.

The great flexibility of the pulse shaper allowed us to explore different experimental configurations with the purpose of examining the potential of the technique. We outline in the following the main results achieved:

- the technique seems to benefit from the presence of a coherent portion within the spectrum of the incident pulse. Indeed, when a noisy-free region is present, we observe an enhancement of the Raman signal.
- the technique is sensitive to the phase of the nonlinear signal field. This is supported by the fact that, under proper experimental conditions, we are able to discriminate between a heterodyne and a homodyne detection.
- a systematic study conducted by applying noise only to single selected spectral components showed that the technique relies on single-frequencies stochasticities. It suffices to apply random fluctuations to only one Fourier component to induce correlations among the photon modes entangled by the process.

These results were obtained by carrying out static measurements, where radiation is inelastically scattered by a sample which is initially in its ground state.

To study the dynamics of the lattice relaxation, we combined the NCS approach with a standard pump degenerate and probe scheme. A dynamical analysis showed that, at least in the experimental configuration adopted, the time-resolved correlation map of the transmitted probe does not bring any information about the lifetime of the vibrational eigenmodes. Indeed, the time evolution of the degree of correlation seems to be dominated by features probably due to the coherent coupling between the pump and the probe. We are currently implementing a non-degenerate scheme to get rid of this effect and test the feasibility of the method in this new configuration.

A polarization selective pump and probe setup was also designed to perform symmetry studies on the phonon modes using the NCS approach. We showed that the technique is sensitive to different polarization geometries. While total-symmetric  $A_1$  modes were successfully isolated, the double-degenerate E mode was not separately detected due to imperfect alignment. Further investigations will be carried out using more sophisticated statistical tools to clarify the role of the E modes in coupling the photon polarization to the phonon symmetry.



**Figure 1:** Preliminary analysis of third-order correlations in crystalline quartz. The 2D correlation map is compared with the spontaneous Raman spectrum of quartz adapted from [18].

### Outlook

Though the preliminary studies discussed so far are very encouraging, the potential of the NCS is still far from being properly explored.

Future efforts will certainly go in developing more tailored analysis tools. We are indeed confident that the transmitted pulses are embedded with a great depth of information that the statistical analysis used so far misses. While being sensitive to two-frequency correlations, a Pearson coefficient-based framework may not in fact be the most complete way to study a four-wave mixing process such as ISRS, which is expected to imprint higher-order photon correlations in the transmitted pulses.

We have taken the first steps along this path by extending the study to thirdorder correlations. The aim of such analysis is to investigate whether the excitation of a given phonon mode is somehow affected by the presence of another lattice vibration. Should there be a non-null correlation between two phonon modes having characteristic frequencies  $\Omega_i$  and  $\Omega_j$ , spectral components at frequencies  $\omega$ ,  $\omega + \Omega_i$ and  $\omega + \Omega_j$  should be coupled. A preliminary analysis has been carried out by defining the following third-order correlator:

$$\rho_{ij}^{(3)} = \int d\omega \, \frac{\langle I(\omega + \Omega_i) I(\omega + \Omega_j) I(\omega) \rangle}{\langle I(\omega + \Omega_i) I(\omega + \Omega_j) \rangle \langle I(\omega) \rangle}$$

where the integration is performed across the pulse bandwidth. The result of the calculation thus consists in a 2D map as function of the frequency shifts  $\Omega_i$  and  $\Omega_j$ .

We show in Figure 1  $\rho_{ij}^{(3)}$  calculated for one of the static transmission measurements dataset discussed in Chapter 4. While distinct features are present in

correspondence with the Raman resonances, a clear interpretation of the map is not straightforward. According to the definition of the correlator, if two phonons were correlated, we would expect off-diagonal points in the map whose coordinates should indicate the frequencies of the two phonon modes coupled. What we observe instead is the presence of continuous horizontal and vertical lines which seem to suggest that the excitation of a particular phonon mode is not preferentially affected by a given  $\Omega_{i,j}$ . Therefore, at least in the sample examined, this correlator contains no more information than the two-frequency Pearson coefficient.

The third-order correlator mentioned here is just a preliminary exploration of what we expect to be a wide array of covariance-based analysis tools. Computing even higher-order correlators may be an efficient way of addressing the anharmonicities of the crystalline potential and investigate the intricate interplays among different degrees of freedom in strongly correlated materials.

Furthermore, we have so far tested the technique only in the near-infrared regime, by using table-top pulsed laser sources. However, there is no reason why it should not work also in other frequency ranges. Self-amplified spontaneous emission (SASE) free electron laser (FEL) sources, which operate in the X-Ray regime, are particularly suitable for this purpose [20]. Indeed, the uncorrelated fluctuations that we introduce in the pulses through the pulse shaper, are intrinsically present in the SASE FEL radiation because the self-amplified spontaneous emission is a stochastic process. Being such fluctuations unavoidable in this type of sources, NCS could establish a new paradigm for FEL-based nonlinear spectroscopies.

It is thus clear that we have just started to scratch the surface of what we expect to be a breakthrough for both equilibrium and non-equilibrium spectroscopies.

# Appendix A

## Multiwave mixing signal

A (n + 1)-wave mixing process involves n incoming fields which interact with the sample. The interaction results in the establishment of a macroscopic polarization which acts as a source in the Maxwell's equations for the generation of the detected field.

We shall now solve the Maxwell's equations to get an expression of the radiated field (Equation 1.53). We will then be able to compute the general expression of multiwave mixing signals within the semiclassical approach [4].

The Maxwell's equations in a neutral system are (in cgs units):

$$\begin{cases} \nabla \cdot \mathbf{D} = 0 \\ \nabla \cdot \mathbf{B} = 0 \\ \nabla \times \mathbf{E} = -\frac{1}{c} \frac{\partial \mathbf{B}}{\partial t} \\ \nabla \times \mathbf{H} = \frac{1}{c} \frac{\partial \mathbf{D}}{\partial t} \end{cases}$$
(A.1)

where we have neglected the coupling of the molecular translational motion to the polarization field by considering a null Röntgen current. We have indicated by  $\mathbf{D}$  and  $\mathbf{H}$  the electric and the magnetic displacement fields, respectively, which are defined ad follows:

$$\begin{cases} \mathbf{D} = \mathbf{E} + 4\pi \mathbf{P} \\ \mathbf{H} = \mathbf{B} - 4\pi \mathbf{M} \end{cases}$$
(A.2)

where  $\mathbf{P} = \mathbf{P}_L + \mathbf{P}_{NL}$  is the polarization and  $\mathbf{M}$  is the magnetization.

By taking the curl of the third equation and substituting the fourth one, we get the general wave equation:

$$\nabla \times \nabla \times \mathbf{E} + \frac{1}{c^2} \frac{\partial^2 \mathbf{E}}{\partial t^2} = -\frac{4\pi}{c^2} \frac{\partial^2 \mathbf{P}}{\partial t^2}$$
(A.3)

where we have considered a non-magnetic medium ( $\mathbf{M} = 0$ ). The latter equation bridges the gap between the quantities we have derived in section 1.3 and the optical signals one actually measures in the experiment. Equation A.3, together with the following key equations of the density operator formalism

$$\mathbf{P}(\mathbf{r},t) = Tr\left(\hat{\mathbf{P}}(\mathbf{r}), \hat{\rho}(t)\right)$$

$$\frac{\partial \hat{\rho}(t)}{\partial t} = -\frac{i}{\hbar} \left[ \hat{H}, \hat{\rho}(t) \right]$$

constitutes the Maxwell-Liouville equations.

Equation A.3 can be further manipulated by explicitly writing the linear polarization according to what we have done in section 1.3.4:

$$\mathbf{P}_{L}(\mathbf{r},t) = \int d\mathbf{r}_{1} \int_{0}^{t} dt_{1} S^{(1)}(\mathbf{r}-\mathbf{r}_{1},t-t_{1}) \mathbf{E}(\mathbf{r}_{1},t_{1})$$
(A.4)

where  $S^{(1)}$  is the linear response function.

Combining Equation A.4 with Equation A.3, we get:

$$\nabla \times \nabla \times \mathbf{E} + \frac{1}{c^2} \frac{\partial^2}{\partial t^2} \int d\mathbf{r}_1 \int_0^t dt_1 \varepsilon (\mathbf{r} - \mathbf{r}_1, t - t_1) \mathbf{E}(\mathbf{r}_1, t_1) = -\frac{4\pi}{c^2} \frac{\partial^2 \mathbf{P}_{NL}}{\partial t^2} \quad (A.5)$$

where  $\varepsilon$  is the *dielectric function* and is given by:

$$\varepsilon(\mathbf{r} - \mathbf{r}_1, t - t_1) \equiv \delta(t - t_1)\delta(\mathbf{r} - \mathbf{r}_1) + 4\pi S^{(1)}(\mathbf{r} - \mathbf{r}_1, t - t_1)$$
(A.6)

Now we have all the tools to compute the expression of the field generated in a *n*-wave mixing process. We assume that the signal field is outside the absorption spectrum of the sample, so that absorptive losses are avoided and the dielectric function can be considered real. Furthermore, we assume that the linear response is local in space for all relevant frequencies, so that, from Maxwell's equations, we get:

$$\varepsilon(\omega_j) \equiv \varepsilon(\mathbf{k}=0,\omega_j) = \frac{k_j^2 c^2}{\omega_j^2} = n_j^2$$

where  $n_j$  is the refractive index of the medium for a mode of frequency  $\omega_j$ .

From Equation A.5, we obtain:

$$\nabla \times \nabla \times \mathbf{E} + \frac{n^2}{c^2} \frac{\partial^2 \mathbf{E}}{\partial t^2} = -\frac{4\pi}{c^2} \frac{\partial^2 \mathbf{P}_{NL}}{\partial t^2}$$
(A.7)

The total electric field of the incoming n modes can be written, in a scalar form, as:

$$E(\mathbf{r},t) = \sum_{j=1}^{n} \left[ E_i(\mathbf{r},t) e^{i(\mathbf{k}_j \cdot \mathbf{r} - \omega_j t)} + c.c. \right]$$
(A.8)

 $\mathbf{P}_{NL}$  in Equation A.7 is the nonlinear polarization that we have derived within the density operator formalism in section 1.3.4. For the sake of simplicity, we consider here its expanded scalar form:

$$P_{NL}(\mathbf{r},t) = \sum_{n\geq 2} \sum_{s} P_s^{(n)} e^{i(\mathbf{k}_s \cdot \mathbf{r} - \omega_s t)}$$
(A.9)

where  $\mathbf{k}_s$  and  $\omega_s$  are any combination of the impinging wave vectors and frequencies:

$$\mathbf{k}_s = \pm \mathbf{k}_1 \pm \mathbf{k}_2 \pm \ \dots \ \pm \mathbf{k}_n$$

$$\omega_s = \pm \omega_1 \pm \omega_2 \pm \dots \pm \omega_n$$

We shall solve Equation A.7 for a sample having the shape of a slab of length l, oriented along the z-axis. Moreover, we assume that  $\mathbf{k}_s$  lies in the z-direction and that  $k_s l \gg 1$ .

We shall focus only on a single contribution to the nonlinear polarization, i.e. we fix the order of nonlinearity of the process (index n) and the geometry of the detection (index s):

$$P_{NL}(z,t) = P_s(t)e^{i(k_s z - \omega_s t)}$$
(A.10)

We seek for a solution of the form:

$$E(\mathbf{r},t) = E_s(z,t)e^{i(\mathbf{k}'_s \cdot \mathbf{r} - \omega_s t)} + c.c.$$
(A.11)

where

$$k_s' \equiv \frac{\omega_s}{c} n_s$$

differs from  $k_s$  as a result of the frequency dispersion of  $n(\omega)$ .

We shall also assume that  $P_s(t)$  varies slowly with respect to the optical period:

$$\left|\frac{\partial}{\partial t}P_s(t)\right| \ll |\omega_s P_s(t)|$$

Inserting now Equations A.10 and A.11 in the wave equation A.7, we get a firstorder differential equation for the electric field that, integrated over z from 0 to l, gives:

$$E_s(l,t) = \frac{2\pi i}{n(\omega_s)} \frac{\omega_s}{c} l P_s(t) sinc\left(\frac{\Delta kl}{2}\right) e^{i\frac{\Delta kl}{2}}$$
(A.12)

where  $\Delta k \equiv |k_s - k'_s|$  is the difference between the combination of the incoming wave vectors and the wave vector of the emitted field.

Note that the function  $sinc(\Delta kl/2)$  is large only when  $\Delta kl \ll \pi$  and eventually becomes a Dirac delta for  $l \to \infty$ . This limit is known as *phase matching condition* and has to be satisfied to increase the magnitude of the signal.

Finally, we can compute the optical signal generated by the wave mixing process:

$$I_s(t) = \frac{n_s c}{8\pi} |E_s|^2$$

$$= \frac{\pi}{2n_s} \frac{\omega_s^2}{c} l^2 |P_s(t)|^2 sinc^2 \left(\frac{\Delta kl}{2}\right)$$
(A.13)

which is proportional to  $|P_s(t)|^2$ .

It should be highlighted here that the expression we have derived applies only in the assumption that the signal field is much weaker than the incoming fields, so that they are not affected by the wave mixing process and the wave equation can be solved exactly.

# Appendix B

## Closed-time-path-loop diagrams

The perturbative expansion of Equation 1.71 can be performed analytically. However, when dealing with higher order nonlinearities or, even more importantly, with multilevel systems, a different approach could be significantly helpful. In a similar fashion to what we did with the double-sided Feynman (ds-F) diagrams (section 1.3.5), we can diagrammatically calculate quantum optical signals by expanding Equation 1.71. Precisely, each term coming from the expansion of the exponential in Equation 1.71 can be represented by a diagram, whose imaginary part contributes to the signal [7]. There is a large number of diagrams that can serve this purpose, according to the features of the process involved. Double-sided Feynman diagrams are particularly suitable for time-domain measurements, in which the time-ordering of the interactions can be controlled. Since the time runs from the bottom to the top for both the ket and the bra of the density matrix, ds-F diagrams are fully time ordered, i.e. they keep a chronological trace of all the interactions the system has experienced. However, things change when the arrival of the pulses cannot be strictly decided (so that two or more pulses may overlap) or when, as in our case, one is interested in the frequency dispersed signal (the number of photon in a particular mode, rather than the total number of photons as function of time). Since in this situation time-ordering is not maintained, the ds-F diagrams are redundant, as a few distinct diagrams can actually represent the same undistinguishable physical situation.

A more proper way of representing frequency dispersed signals is to introduce a new typology of diagrams, which are called *closed-time-path-loop* (CTPL) diagrams in Quantum Field Theory [7]. Each loop represents a state vector in the Hilbert space, which propagates circularly along a closed path. CTPL are not read in real (i.e. physical) time, but clockwise along the loop. This means that the time runs forward on the left branch of the diagram (which still represents the ket of the density matrix) and backward on the right one (the bra). For this reason, CTPL are said to be *partially time ordered*, as only interactions in each branch are ordered in time. Conversely, interactions on the left and the right branches are not timeordered relative to each other. Typically, CTPL diagrams give a more compact (n+1terms) representation than the ds-F diagrams  $(2^n \text{ terms})$  of a  $n^{th}$ -order nonlinear process [21]. From a single CTPL diagram, distinct ds-F diagrams can be retrieved by exploring all the possible permutations between the left and right interactions.

We give in the following paragraph the rules required for the construction of the CTPL diagram [7]. We shall limit our discussion only to the frequency domain.

#### Rules for the CTPL diagrams in the frequency domain

- 1. The diagram takes the form of a closed pathway, in which the time runs clockwise from the bottom left to the bottom right.
- 2. Each wavy line represents an interaction with the electic field.
- 3. The arrow associated to each wavy line indicates the field. An arrow pointing to the right is associated to the field annihilation operator  $\hat{\mathcal{E}}(\mathbf{r},t)$ , which involves the factor  $e^{i(\mathbf{k}_s \cdot \mathbf{r} \omega_s t)}$ . Conversely, an arrow pointing to the left stands for the field creation operator  $\hat{\mathcal{E}}^{\dagger}(\mathbf{r},t)$ , accompanied by the factor  $e^{-i(\mathbf{k}_s \cdot \mathbf{r} \omega_s t)}$ .
- 4. Within the RWA approximation, the action of  $\hat{\mathcal{E}}(\mathbf{r}, t)$  is always linked to the application of the dipole operator  $V^{\dagger}$ , which determines the excitation of the material. This means that an arrow pointing to the right (left) always represents absorption (emission), regardless on whether it occurs with the left or the right branch.
- 5. The interaction occurring at the observation time t is the last one and involves the detected mode. By convention, it occurs on the left branch of the diagram.
- 6. In each loop, wavy lines (interactions) and vertical solid lines (intervals of free evolution) alternate. The formers can be described by the action of the dipole operator, the latters by the frequency-domain counterpart  $G(\omega)$  of the Liouville space Green's function (Equation 1.41). Free evolutions on the left branch (forward in time) are described by  $i G(\omega)$ , whereas free evolutions on the right branch (backward in time) are described by its hermitian conjugate  $-i G^{\dagger}(\omega)$ .
- 7. The frequency arguments of the propagators are cumulative, namely they are given by the sum of all "earlier" interactions along the loop. The ground state frequency must be added to all arguments of the propagators.
- 8. A diagram representing a (n + 1)-wave mixing is preceded by the factor  $i^n (-1^{N_R})$ , where  $N_R$  is the number of interactions occurring from the right.

### B.1 Example: Frequency-domain four-wave mixing signal

We shall now analyze a simple case in order to understand how the CTPL diagrams look like and what kind of significant information can be retrieved from them [6]. We shall apply the rules we have presented in the previous section to compute the fourwave mixing signal at  $\mathbf{k}_s = -\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3$ . After depicting all the diagrams consistent



Figure B.1: Three-level ladder model system with sequential dipole couplings.



Figure B.2: CTPL diagrams for a four-wave mixing signal at  $\mathbf{k}_s = -\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3$ .

with the CTPL rules, we will be able to explicitly write down the expression of the third-order susceptibility which rules the process.

It immediately follows from rule 3, that the fields  $\mathbf{k}_2$  and  $\mathbf{k}_3$  are absorbed (and then represented by wavy arrows pointing to the right) and that field  $\mathbf{k}_1$  and  $\mathbf{k}_s$ are emitted (arrows pointing to the left). We consider a three-level ladder system, shown in Figure B.1. We can then construct the allowed diagrams by placing these four arrows along the close loop, having in mind the following restrictions:

- the interaction with  $\mathbf{k}_s$  is fixed to the top left branch;
- since the time runs clockwise, the system must start and end in the ground state  $(t = -\infty)$ . This implies (if the RWA holds) that the first interaction must be an absorption, while the last one an emission.

We show in Figure B.2 all the allowed CTPL diagrams for the examined process. We stress once again that the order along the loop does not necessarily correspond to an ordering in real time. By using rules 6, 7 and 8, the diagrams can be translated into the third-order nonlinear susceptibility as follows:

$$\begin{split} \chi^{(3)}(-\omega_s;\omega_3,\omega_2,-\omega_1) = & \langle VG(\omega_3+\omega_2-\omega_1+\omega_g)VG(\omega_3+\omega_2+\omega_g)V^{\dagger}G(\omega_3+\omega_g)V^{\dagger}\rangle + \\ & \langle VG^{\dagger}(\omega_2+\omega_3-\omega_s+\omega_g)VG(\omega_2+\omega_3+\omega_g)V^{\dagger}G(\omega_2+\omega_g)V^{\dagger}\rangle + \\ & \langle VG(\omega_2-\omega_1+\omega_3+\omega_g)V^{\dagger}G(\omega_2-\omega_1+\omega_g)VG(\omega_2+\omega_g)V^{\dagger}\rangle + \\ & \langle VG(\omega_3-\omega_1+\omega_2+\omega_g)V^{\dagger}G(\omega_3-\omega_1+\omega_g)VG(\omega_3+\omega_g)V^{\dagger}\rangle + \\ & \langle VG(\omega_2+\omega_3-\omega_1+\omega_g)VG(\omega_2+\omega_3+\omega_g)V^{\dagger}G(\omega_3+\omega_g)V^{\dagger}\rangle + \\ & \langle VG^{\dagger}(\omega_3+\omega_2-\omega_s+\omega_g)VG(\omega_3+\omega_2+\omega_g)V^{\dagger}G(\omega_3+\omega_g)V^{\dagger}\rangle + \\ & \langle VG^{\dagger}(\omega_3-\omega_s+\omega_3+\omega_g)V^{\dagger}G^{\dagger}(\omega_2-\omega_s+\omega_g)VG(\omega_3+\omega_g)V^{\dagger}\rangle + \\ & \langle VG^{\dagger}(\omega_3-\omega_s+\omega_2+\omega_g)V^{\dagger}G^{\dagger}(\omega_3-\omega_s+\omega_g)VG(\omega_3+\omega_g)V^{\dagger}\rangle + \\ & \langle VG^{\dagger}(\omega_3-\omega_s+\omega_g)V^{\dagger}(\omega_3-\omega_s+\omega_g)V^{\dagger}\rangle + \\ & \langle VG^{\dagger}(\omega_3-\omega_s+\omega_g)V^{\dagger}(\omega_3-\omega_s+\omega_g)V^{\dagger}(\omega_3-\omega_g)V^{\dagger}\rangle + \\ & \langle VG^{\dagger}(\omega_3-\omega_s+\omega_g)V^{\dagger}(\omega_3-\omega_g)V^{\dagger}(\omega_3-\omega_g)V^{\dagger}\rangle + \\ & \langle VG^{\dagger}(\omega_3-\omega_g)V^{\dagger}(\omega_3-\omega_g)V^{\dagger}(\omega_3-\omega_g)V^{\dagger}\rangle + \\ & \langle VG^{\dagger}(\omega_3-$$

Equation B.1 underlines the strength of the diagrammatic representation we have built. Once the CTPL diagrams are depicted, it actually allows to directly write the susceptibility (and hence the polarization) of whatever nonlinear process one is willing to describe, without using at all the pedantic mathematical formalism that the semiclassical approach would require.

In this connection, it should be said that the current example has been provided for didactic purposes only. The approach we have taken here differs from the one we have adopted in our model (Chapter 2). The main difference lies in the fact that we have exploited CTPL diagrams not to compute the nonlinear susceptibility, but to recast the signal in terms of transition amplitudes. Indeed, this perspective is far more useful if one is interested in revealing the underlying material processes.

# Appendix C

## Calibrations of the pulse shaper

In this appendix we describe in detail how we have carried out the pulse shaper calibrations. The procedures described here must be followed every time the alignment of the pulse shaper is adjusted.

### C.1 Frequency calibration

A frequency calibration is required for having control of the spectral components impinging on the Spatial Light Modulator (SLM) matrix. Since the beam is horizontally dispersed on the SLM (as shown in Figure 3.8), a narrow frequency range is assigned to each column of the matrix. The aim of the frequency calibration is to match each SLM horizontal pixel with the central frequency of its corresponding range and determine the spectral resolution of the pulse shaper, which is set by the diffracting power of the grating in front of the SLM.

To do so, we send to the SLM a pattern like that in Figure C.1a), in which a few 1 pixel-wide diffraction gratings are applied at specific horizontal positions within the illuminated area of the SLM. <sup>2</sup> The result of the application of this pattern is that the first-order diffracted beam contains only those components which have impinged on the gratings.

The outgoing beam is then detected by means of a fiber spectrometer. The beam is channelled through an optical fiber to a calibrated spectrometer which allows to acquire both the spectrum and the background. We show in Figure C.1b) the spectrum (grey solid line) and the background (grey dashed line) of a beam shaped using the SLM pattern in a). To determine the position of the peaks, we perform a fit (red line) of the spectrum after removing the background.

Knowing the exact position of the gratings of the SLM pattern, we can construct the graph in Figure C.1c), in which the central frequencies of the peaks estimated through the fit are plotted as function of their corresponding SLM horizontal pixels.

 $<sup>^{2}</sup>$ We recall that, in our pulse shaper, the chromatic dispersion is not wide enough to cover the whole horizontal axis of the matrix; we thus use only a portion of it and the number of diffraction gratings used in the calibration depends on its horizontal extension.



**Figure C.1:** a) SLM pattern used for the frequency calibration procedure. A few diffraction gratings are applied to known positions within the SLM horizontal axis. b) Spectrum (solid grey) and background (dashed grey) of the first-order diffracted beam shaped by the pattern in a). The spectrum is fitted with a multiple Gaussian function. The red line shows the result of the fit. c) Central frequencies of the peaks in b) as function of their corresponding grating positions along the SLM horizontal axis. The whole frequency scale (grey line) is obtained through a second-order polynomial fit.

By fitting the red points with a second-order polynomial, we get the entire frequency scale (grey line) which assigns a specific frequency to each of the 512 SLM pixels.

The frequency difference between two neighbouring pixels sets the maximum spectral resolution attainable by the pulse shaper ( $\Delta \omega \simeq 0.1$  THz).

### C.2 Phase calibration

As discussed in section 3.3.1, the only degree of freedom of a liquid crystal SLM is the voltage applied to each pixel within the SLM matrix. The choice of the voltage in turn affects the orientation of the liquid crystals and thus the phase delay the impinging light experiences. To have arbitrary control of the spectral components diffracted by the SLM, it is of crucial importance to study the response of the liquid crystals and build a mapping between the voltage applied to them and the final phase shift they are responsible for.

To do so, we exploit the flexibility of the SLM and build a binary phase grating along the SLM vertical axis, as shown in Figure C.2. The pattern is made up of two alternating bars, a "reference bar" that is held constant and the other which is scanned across the whole range of voltages made available by the SLM electronics



**Figure C.2:** SLM patterns (top row) and their corresponding vertical profiles (bottom row) for binary phase gratings having variable depth.



**Figure C.3:** a) Frequency-resolved intensity of the diffracted beam as function of the depth of the binary phase grating, i.e. as function of the voltage applied to the variable bar. b) Expected efficiency of a binary phase grating as function of its phase depth (red curve). Normalized diffracted intensity integrated along the frequency axis (grey curve). Only voltages ranging from -5 V to the red dashed line in a) have been considered. The grey dashed line indicates the linear background of the detected intensity.

(-5 V ÷ 5 V). By changing the voltage applied to the variable bar, we change the phase grating depth and we thus affect its efficiency. Indeed, the expected efficiency of the first-order (m = 1) diffracted by a binary phase grating having a grating depth  $\Delta \phi$  is:

$$I_{m=1} = \frac{4}{\pi^2} \sin^2\left(\frac{\Delta\phi}{2}\right) \tag{C.1}$$

At each different grating depth, we acquire the spectrum of the diffracted beam by means of the photodiode array. The frequency-resolved detected intensity is shown in Figure C.3a) as function of the voltage applied to the variable bar. We observe an extinction of the signal in correspondence of two specific voltages, sym-



**Figure C.4:** SLM patterns (top row) and their corresponding vertical profiles (bottom row) for blazed gratings having variable depth.

metrically from the null-voltage value. This means that the liquid crystals rotate more than once within the whole voltage range. We thus restrict our analysis only to the first portion of the map, delimited by the vertical red line. This region is wide enough to include the first zero of the intensity (at ~ -1 V), which corresponds to a voltage for which  $\Delta \phi = 2\pi$ .

The intensity integrated along the frequency axis and then normalized is plotted in Figure C.3b) with a grey solid line. By contrast, the red curve indicates the expected efficiency of the grating, according to Equation C.1. After removing the linear background indicated by the dashed grey line, we proceed with the interpolation of the measured and the expected efficiency curves to build the function  $V(\phi)$ , which indicates the voltage to apply to a specific SLM pixel to get the light impinging on it phase-delayed by  $\phi$ .

### C.3 Amplitude calibration

The strength of a diffraction-based liquid crystals SLM is the possibility of simultaneously shaping both the phase and the amplitude of the spectral components. As discussed in section 3.3.2, this is achieved by imprinting on the SLM matrix a blazed grating. In this way, the amplitude of a specific Fourier component can be tuned by varying the efficiency of the grating, i.e. varying its depth. Hence, the amplitude calibration allows us to build a function which maps the desired amplitude to be diffracted into a specific blazed grating depth to apply. We highlight that the depth of the grating is determined by a proper choice of voltages which guarantees a sawtooth-like refraction index. The amplitude calibration thus relies on the phase calibration discussed above.

Similarly to the previous case, we build spectrally flat amplitude patterns having



**Figure C.5:** a) Spectral intensity detected by the photodiode array as function of the blazed grating depth. b) Intensity averaged along the diode pixel number axis and normalized. The red line indicates a horizontal cut which defines the relation in c) which converts the desired diffracted amplitude into the depth to apply to the blazed grating.

different grating depths, like those in Figure C.4. The grating depth is scanned across the 512 values made available by the SLM electronics, from 0 to 1. At each depth, the diffracted beam is recorded by the photodiode array. The frequency-resolved spectra as function of the grating depth are shown in Figure C.5a).

Since the efficiency of a blazed grating is weakly dependent on the wavelength of the diffracted light, we average the intensity along the frequency axis and normalize it to get the map in Figure C.5b). By simply considering a horizontal cut of the map, we get the plot in Figure C.5c), which defines the mapping sought. This function is saved as a global variable and read whenever a new SLM pattern is generated.

### C.4 Grating period calibration

As mentioned in section 3.3.2, a correction on the period of the blazed grating is required for properly focusing the beam. In order to justify this correction, we recall the equation of a blazed grating of period d:

$$d\left[\sin(\theta_m) - \sin(\theta_i)\right] = m\lambda \tag{C.2}$$

where m is the diffraction order,  $\lambda$  the wavelength of the diffracted light, and  $\theta_{i,m}$  the incident and the emission angles, respectively.



**Figure C.6:** Spatially chirped (a) and corrected (b) spot acquired by a camera. Note that the scale of the two images is different. c) Example of a spectrally flat amplitude pattern to which the correction on the grating period has been applied.

According to Equation C.2, different wavelengths are diffracted along different directions if d is fixed. In our specific case, the bandwidth of the pulse (~ 30 THz) is wide enough to give rise to macroscopic effects. As shown in Figure C.6a), by using a grating with a fixed period along the horizontal axis, the diffracted beam has an elongated shape. A beam of this kind is said to have a *spatial chirp*, that is its different frequency components are separated in space transverse to the propagation direction.

To correct this dispersion and refocus the beam, we introduce a linear correction on the period of the grating along the SLM horizontal axis. More precisely, higher frequency components are diffracted by a grating having a larger period to compensate the spatial chirp. The entity of the correction is determined phenomenologically: we systematically adjust the correction, while monitoring the spot shape by means of a camera. When the beam assumes a circular, not chirped shape (as in Figure C.6b)), the correction is considered good and used for the generation of all the SLM patterns. An example of a frequency-dependent blazed grating pattern is shown in Figure C.6c).

## Riassunto

La detezione di segnali ottici non lineari è fortemente ostacolata dalla loro scarsa intensità rispetto ai contributi lineari. Il rumore stocastico, intrinsico alla misura di qualsiasi quantità fisica, complica ulteriormente la loro detezione.

Queste difficoltà sperimentali vengono tipicamente affrontate lavorando in una modalità "integrata", cioè considerando il segnale mediato su eventi ripetuti. Questo approccio, quando si lavora con sorgenti laser impulsate, è fortemente condizionato dalla stabilità (impulso per impulso) della sorgente e ha perciò incentivato la realizzazione di apparati sperimentali i più stabili possibile.

Andando controcorrente rispetto a questi tentativi, noi proponiamo una tecnica spettroscopica innovativa, la *Noise Correlation Spectroscopy* (Spettroscopia a correlazione di fluttuazioni, NCS), che, al contrario, identifica il rumore come un vantaggio da sfruttare piuttosto che eliminare.

Come suggerisce il suo stesso nome, la NCS è basata sullo studio delle correlazioni tra fotoni e sull'analisi delle informazioni che possono essere ottenute a partire dalla misura del rumore in misure ripetute. Per fare ciò, è necessario ricorrere a un'acquisizione risolta in frequenza del singolo impulso che ha interagito con il campione. In questo modo, è possibile rivelare le correlazioni tra i rumori che interessano diverse componenti spettrali e perciò accedere alle correlazioni non classiche tra fotoni introdotte dall'interazione luce-materia.

Questo approccio innovativo richiede strumenti di analisi altrettanto innovativi. Il metodo basato sul valore medio consiste nel ripetere diverse volte lo stesso esperimento e chiaramente in questa situazione la media statistica dei dati risulta la scelta più appropriata per ottenere il rapporto segnale/rumore richiesto. Il nuovo metodo che noi proponiamo può essere invece considerato una situazione in cui ogni singolo impulso proveniente dal laser può essere visto come un nuovo esperimento, che avviene ogni volta in condizioni sperimentali diverse e che perciò contiene nuove informazioni. L'acquisizione dei singoli impulsi e il successivo calcolo della media su di essi porterebbe inevitabilmente a perdere tutte le peculiarità del singolo impulso. Un modo per mettere in risalto le fluttuazioni intrinseche ad ogni pulso consiste invece nello scegliere uno strumento statistico capace di analizzare il rumore stocastico e rivelare le informazioni in esso contenute. La NCS vede nella covarianza un buon candidato per svolgere questa funzione.

Le spettroscopie ottiche non lineari che utilizzano sorgenti impulsate al femtosecondo sono particolarmente adatte all'applicazione di questo metodo. Infatti, tali sorgenti sono tipicamente caratterizzate da numerosi stadi di amplificazione, la cui presenza porta inevitabilmente alla produzione di un fascio laser rumoroso che inficia l'affidabilità di un approccio integrato.

A tal proposito, sottolineiamo che la stabilità impulso per impulso della sorgente non è più un requisito fondamentale per la NCS, ma risulta invece dannosa per il successo del metodo. Sorgenti laser stabili producono infatti impulsi di luce altamente coerenti, il cui alto grado di correlazione copre le eventuali fluttuazioni correlate intrinsiche a ciascun impulso. Inoltre, è di fondamentale importanza che anche le componenti di Fourier contenute nello stesso impulso siano statisticamente indipendenti. Se ci fossero infatti correlazioni non nulle tra i modi fotonici dell'impulso incidente, esse oscurerebbero le correlazioni introdotte dal processo non lineare. Perché gli impulsi di luce incidenti soddisfino questi requisiti, é necessario introdurre fluttuazioni stocastiche nei loro spettri.

Lo schema concettuale discusso finora è del tutto generale e può essere applicato a diversi processi ottici non lineari. Il mio progetto di tesi è consistito nel testare l'applicabilità del metodo per lo studio di vibrazioni reticolari coerenti attraverso *Impulsive Stimulated Raman Scattering* (scattering Raman stimolato impulsato, ISRS). Per testare il metodo, abbiamo esaminato un campione di quarzo cristallino, un materiale di riferimento il cui spettro Raman è stato approfonditamente studiato tramite approcci più tradizionali.

Per eccitare il reticolo, abbiamo utilizzato una sorgente laser impulsata al femtosecondo che emette radiazione nel vicino infrarosso. Le caratteristiche temporali degli impulsi utilizzati sono di cruciale importanza per l'implementazione della tecnica. Primo, perché servono campi sufficientemente intensi per poter stimolare un processo non lineare come l'ISRS. Secondo, perché impulsi di luce cosí corti, a causa del principio di indeterminazione, hanno un ampio contenuto spettrale. Quando impulsi di questo tipo interagiscono con il campione, il processo ISRS comporta un accoppiamento (all'interno di ciascun impulso) delle componenti di Fourier la cui differenza in frequenza corrisponde all'energia dei fononi che sono stati creati/distrutti dal processo di scattering anelastico. Il processo perciò imprime in ogni impulso un pattern di correlazioni che codifica lo spettro Raman del materiale. Se l'esperimento è ripetuto un numero elevato di volte, la statistica diventa sufficientemente ampia per poter recuperare questa informazione.

Per facilitare l'individuazione delle correlazioni introdotte dal processo non lineare, abbiamo utilizzato uno *Spatial Light Modulator* (modulatore spaziale di luce, SLM) a cristalli liquidi. Ad ogni ripetizione, l'SLM modula indipendentemente ciascuna componente di Fourier per eliminare gli effetti coerenti del laser e introdurre invece fluttuazioni stocastiche a corto raggio sia nella fase sia nell'ampiezza dei diversi modi spettrali. Gli impulsi cosí modulati interagiscono con il campione e i loro spettri trasmessi vengono acquisiti da uno spettrometro composto da una serie di fotodiodi, sincronizzati con il *repetition rate* del laser (5 kHz). Insieme all'impulso trasmesso, viene acquisita anche una copia dell'impulso incidente come riferimento, allo scopo di discriminare solo gli effetti dovuti all'interazione con il campione.

L'analisi dei dati é stata effettuata utilizzando degli strumenti statistici basati sulla covarianza. In particolare, abbiamo utilizzato il coefficiente di correlazione di Pearson, che quantifica il grado di correlazione lineare tra due variabili stocastiche. Il calcolo del coefficiente di Pearson ha dimostrato che il fascio trasmesso dal campione presenta delle caratteristiche che sono completamente assenti nel fascio di riferimento e che sono perciò riconducibili interamente all'interazione con il campione. Il confronto dei nostri risultati con lo spettro Raman del quarzo noto in letteratura ha provato l'applicabilità della NCS.

Il successo dell'implementazione sperimentale della tecnica è stato corroborato dallo sviluppo di un modello fenomenologico in grado di descrivere lo scattering Raman da radiazione stocastica. Il modello, al momento adatto alla descrizione della sola stocasticità di fase, è stato derivato utilizzando un approccio quantistico per il calcolo dei segnali ottici non lineari.

La grande flessibilità dell'SLM ci ha permesso di esplorare diverse configurazioni sperimentali allo scopo di valutare le potenzialità della tecnica. Elenchiamo di seguito i principali risultati ottenuti:

- la tecnica sembra trarre vantaggio dalla presenza di una porzione coerente nello spettro dell'impulso. Infatti, quando nell'impulso è presente una regione priva di rumore stocastico, si osserva un miglioramento del segnale Raman.
- la tecnica è sensibile alla fase del campo segnale non lineare. Questa conclusione è supportata dal fatto che, in opportune condizioni sperimentali, siamo in grado di distinguere una detezione eterodina da una omodina.
- uno studio sistematico realizzato applicando rumore stocastico solo su singole componenti spettrali ha mostrato che la tecnica si basa solo su stocasticità a singola frequenza. È infatti sufficiente che le fluttuazioni stocastiche siano applicate solo a una componente di Fourier perchè vengano indotte correlazioni tra i modi fotonici accoppiati dal processo ISRS.

Questi risultati sono stati ottenuti realizzando misure statiche, in cui la radiazione è scatterata anelasticamente da un campione che si trova inizialmente nel suo stato fondamentale.

Per studiare la dinamica di rilassamento del reticolo, abbiamo combinato l'approccio della NCS con uno schema *pump and probe* degenere standard. Un'analisi dinamica ha dimostrato che, almeno nella configurazione sperimentale utilizzata, le mappe di correlazione risolte in tempo del *probe* trasmesso non contengono alcuna informazione circa il tempo di vita degli autostati vibrazionali. Infatti, sembra che l'evoluzione temporale del grado di correlazione sia dominata da effetti probabilmente dovuti all'accoppiamento coerente tra il *pump* ed il *probe*. Al momento, stiamo implementando uno schema non degenere per poter eliminare questi effetti e testare l'applicabilità del metodo in questa nuova configurazione.

Abbiamo inoltre messo a punto uno schema *pump and probe* sensibile alla polarizzazione per poter effettuare studi sulla simmetria dei modi fononici utilizzando la NCS. Abbiamo dimostrato in questo modo che la tecnica è sensibile a diverse geometrie di polarizzazione. Mentre i modi total simmetrici sono stati correttamente isolati, i modi doppiamente degeneri non total simmetrici non sono stati separatamente osservati a causa di imperfezioni nell'allineamento. Studi ulteriori verranno effettuati utilizzando strumenti statistici più sofisticati per chiarire il ruolo ricoperto dai modi non total simmetrici nell'accoppiamento tra la polarizzazione dei fotoni e la simmetria dei fononi.

Quella discussa in questa tesi è solo una delle possibili applicazioni della NCS, il cui potenziale è ancora ben lungi dall'essere esplorato appieno.

Lo sviluppo di strumenti statistici più sofisticati sarà sicuramente uno degli obiettivi principali degli studi futuri. Riteniamo infatti che negli impulsi trasmessi ci sia una grande quantità di informazioni che vengono perse dall'analisi statistica utilizzata finora. Il coefficiente di Pearson è infatti sensibile solo a correlazioni tra coppie di modi fotonici e potrebbe non essere lo strumento più idoneo per lo studio di un processo *four-wave mixing* come l'ISRS, che dovrebbe invece imprimere correlazioni fotoniche di ordine successivo. Il calcolo di correlatori in grado di rivelare correlazioni di ordine superiore potrebbe essere un modo efficace per studiare le anarmonicità del potenziale cristallino e le interazioni tra diversi gradi di libertà in materiali fortemente correlati.

Inoltre, finora abbiamo testato la NCS solo nel regime infrarosso, utilizzando sorgenti laser impulsate da tavolo ottico. Non ci sono comunque ragioni di escludere che la tecnica possa anche essere applicata con successo in altri regimi energetici. Le sorgenti laser a elettroni liberi (FEL) basate sull'emissione spontanea auto-amplificata (SASE) che operano nel regime dei raggi X, sono particolarmente indicate a tal proposito. Infatti, le fluttuazioni scorrelate che noi introduciamo negli impulsi con l'SLM, sono intrinsecamente presenti nella radiazione SASE FEL perché la SASE è un processo stocastico. Poiché queste fluttuazioni sono inevitabili in questo tipo di sorgenti, la NCS potrebbe definire un nuovo paradigma per le spettroscopie non lineari basate sull'utilizzo di sorgenti FEL.

È quindi chiaro che per ora abbiamo solo iniziato a scalfire la superficie di quella che, riteniamo, rappresenterà una svolta sia per le spettroscopie all'equilibrio sia per quelle fuori-equilibrio.

# Bibliography

- Yong-Xin Yan, Edward B Gamble Jr, and Keith A Nelson. Impulsive stimulated scattering: General importance in femtosecond laser pulse interactions with matter, and spectroscopic applications. *The Journal of chemical physics*, 83(11):5391–5399, 1985.
- [2] Robert W Boyd. Nonlinear optics. Elsevier, 2003.
- [3] Eric Olaf Potma and Shaul Mukamel. *Theory of coherent Raman scattering*. CRC Press, 2012.
- [4] Shaul Mukamel. Principles of nonlinear optical spectroscopies. Oxford University Press, 1995.
- [5] Peter Hamm. Principles of nonlinear optical spectroscopy: A practical approach or: Mukamel for dummies. University of Zurich, 41(5):77, 2005.
- [6] Oleksiy Roslyak, Christoph A Marx, and Shaul Mukamel. Generalized kramersheisenberg expressions for stimulated raman scattering and two-photon absorption. *Physical Review A*, 79(6):063827, 2009.
- [7] Shaul Mukamel and Saar Rahav. Ultrafast nonlinear optical signals viewed from the molecules perspective: Kramers-heisenberg transition-amplitudes versus susceptibilities. In Advances in atomic, molecular, and optical physics, volume 59, pages 223–263. Elsevier, 2010.
- [8] Christoph A Marx, Upendra Harbola, and Shaul Mukamel. Nonlinear optical spectroscopy of single, few, and many molecules: Nonequilibrium greens function qed approach. *Physical Review A*, 77(2):022110, 2008.
- [9] Filippo Glerean. Noise Correlation Spectroscopy for Impulsive Stimulated Raman Scattering, 2017. Master Thesis (UniTS).
- [10] Antoine Monmayrant, Sébastien Weber, and Béatrice Chatel. A newcomer's guide to ultrashort pulse shaping and characterization. *Journal of Physics B: Atomic, Molecular and Optical Physics*, 43(10):103001, 2010.
- [11] Andrew M Weiner. Femtosecond pulse shaping using spatial light modulators. *Review of scientific instruments*, 71(5):1929–1960, 2000.
- [12] Joshua C Vaughan, Thomas Hornung, T Feurer, and Keith A Nelson. Diffraction-based femtosecond pulse shaping with a two-dimensional spatial light modulator. *Optics letters*, 30(3):323–325, 2005.

- [13] Jean-Claude Diels and Wolfgang Rudolph. Ultrashort laser pulse phenomena. Elsevier, 2006.
- [14] Jim Clark. The structure of silicon dioxide., 2009. http://www.chemguide. co.uk/atoms/structures/giantcov.html.
- [15] JF Scott and SPS Porto. Longitudinal and transverse optical lattice vibrations in quartz. *Physical Review*, 161(3):903, 1967.
- [16] P Umari, Alfredo Pasquarello, and Andrea Dal Corso. Raman scattering intensities in  $\alpha$ -quartz: A first-principles investigation. *Physical Review B*, 63(9):094305, 2001.
- [17] Marc M Wefers, Hitoshi Kawashima, and Keith A Nelson. Optical control over two-dimensional lattice vibrational trajectories in crystalline quartz. *The Journal of chemical physics*, 108(24):10248–10255, 1998.
- [18] Andy Rundquist, Jon Broman, David Underwood, and David Blank. Polarization-dependent detection of impulsive stimulated raman scattering in  $\alpha$ -quartz. Journal of Modern Optics, 52(17):2501–2510, 2005.
- [19] EP Ippen and CV Shank. Ultrashort light pulses. Springer, Berlin, pages 85–88, 1977.
- [20] Victor Kimberg and Nina Rohringer. Stochastic stimulated electronic x-ray raman spectroscopy. *Structural Dynamics*, 3(3):034101, 2016.
- [21] Shaul Mukamel. Partially-time-ordered schwinger-keldysh loop expansion of coherent nonlinear optical susceptibilities. *Physical Review A*, 77(2):023801, 2008.

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