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Cross-phase modulation in visible-pump/mid-infrared-probe spectroscopy

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ABSTRACT

One of the most powerful tools to investigate the structural dynamics of electronically excited molecular systems is visible-pump/mid-infrared-probe spectroscopy. When performing this kind of experiments one must be aware of the artifacts deriving from the non-linear response of the solvent and of the sample cell itself. Cross-phase modulation (XPM) is observed when a strong visible-pump pulse modulates the refraction index seen by the mid-infrared-probe. The effect is enhanced when the probe pulse is chirped and causes the distortion of the transient signal in both the frequency and the time domains. We undertook a detailed simulation of XPM in the mid-infrared region where a visible pulse modulates the MIR pulse by XPM and in close conditions to the experimental ones. Our simulation takes into account the different group velocities of the pump and probe pulses and includes the influence of the linear chirp of the mid-infrared pulse and its asymmetry. The results of our numerical calculations fit very well the experimental signals measured in a 2 mm thick CaF_2 window.

1. Introduction

When an ultrashort pulse propagates through a medium, it distorts the electronic distribution of atoms and molecules and as a consequence modify temporarily the refractive index seen by the pulse itself [1]. This process induces a time modulation of the pulse phase and generates new frequencies. The pulse phase modulation can be generated by the pulse itself and the phenomenon is defined self-phase modulation (SPM) [2]. It can be also generated by a copropagating pulse and cross-phase modulation (XPM) is observed [2–7]. The first observation of XPM was called induced phase modulation (IPM) [8]. In a typical transient absorption experiment, two ultrashort laser pulses (pump and probe) overlap spatially and temporally into a sample. The response, developed by the excited sample, is monitored by measuring the relative absorption changes of a broadband probe pulse as a function of the time delay between the pump and the probe pulses. In experiments with middle infrared (MIR) probe pulses the sample thickness is a fraction of that of the windows and the length of the spatial overlap between pump and probe is greater than that. Therefore signals originates mainly from the cell windows rather than from the sample contained within them. XPM, as any other off resonance signals, produced during the temporal overlap of the two pulses, may have an intensity comparable or even stronger than the signal itself, thus seriously modifying the spectral and temporal profiles of the signal to be measured. If one needs to analyze in the first picosecond the spectral evolution due to the sample itself, it is necessary to evaluate the contribution of SPM and XPM. Being off-resonance processes, the total energy of the probe remains constant during the propagation but it is distributed on different frequencies. The probe spectrum is broadened and the pulse envelope develops an oscillatory structure. We utilize a simplified model where SPM can be neglected because the probe pulse is less intense than the pump. Coded information can be transferred from the visible to MIR using XPM.

2. Theory

The propagation of an optical wave through a non-linear medium is described by the wave equation, that is a scalar equation if both pulses are linearly polarized [2,9,5,10]:

$$\nabla^2 E' - \frac{1}{c^2}\frac{\partial^2}{\partial t^2}(n^2 E') = 0 \tag{1}$$

where E' is the total electric field and c is the light velocity in vacuum. The refractive index, as function of the frequency, presents a linear part n_0 and a non-linear part that depends on the intensity of the total electric field impinging on the sample [2,9]:

$$n(\omega) = n_0(\omega) + n_2 I \tag{2}$$

where $n_2 = 3\chi^{(3)}/8n_0$ is the non-linear refractive index [11]. The frequency dependence of the linear part of the refractive index is responsible for the group velocity dispersion (GVD). If we represent the electric field of a pulse as:

$$E(x,y,z,t) = \Re(F(x,y)A(z,t)e^{i(\omega t - kz)}) \tag{3}$$

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we can define the group velocity as:

$$v_g = \left[\frac{dk}{d\omega}\right]^{-1} \tag{4}$$

and the GVD coefficient as:

$$\beta^{(2)} = \frac{d^2k}{d\omega^2} \tag{5}$$

The GVD effect comes out from the frequency dependence of the linear part of the refractive index. The non-linear effects are included through the parameter n_2 that in general can be considered as a constant in respect to the frequency. The intensity is the squared module of the total electric field $I = |E'|^2$, where the total electric field is:

$$E'(x,y,z,t) = \Re(F_{pu}(x,y)A_{pu}(z,t) \times exp[i(k_{pu}z - \omega_{pu}t)] + F_{pr}(x,y)A_{pr}(z,t) \times exp[i(k_{pr}z - \omega_{pr}t)]) \tag{6}$$

ω_{pu} and ω_{pr} are the optical frequency of the pump and probe pulses, $k_{pu} = n_{pu}\omega_{pu}/c$ and $k_{pr} = n_{pr}\omega_{pr}/c$ are the wave vectors and $n_{pu} = n(\omega_{pu})$ and $n_{pr} = n(\omega_{pr})$ the linear refractive index at the carrier frequencies. $F_{pu}(x,y)$ and $F_{pr}(x,y)$ describes the transverse distributions of the two fields, they play a role in calculating the overlap integral. This transverse distributions are in general different for two pulses because of the difference in the center wavelengths, nevertheless the differences among various overlap integrals are small and an effective cross sectional area A_{eff} is introduced [2].

At this point, we can substitute the expression of the total field into the wave equation. In order to make life simpler it is possible also to apply the slowly-varying-envelop approximation and expand k_j in a Taylor series around the respective central frequencies up to the second order. In this contest, the derivation of the coupled-amplitude equation is easy:

$$\begin{aligned}
&\frac{\partial}{\partial z}A_{pu}(z,t) + \frac{1}{v_{g_{pu}}}\frac{\partial}{\partial t}A_{pu}(z,t) + \frac{i}{2}\beta^{(2)}_{pu}\frac{\partial^2}{\partial t^2}A_{pu}(z,t) = i\gamma_{pu}(|A_{pu}(z,t)|^2 \\
&\quad + 2|A_{pr}(z,t)|^2)A_{pu}(z,t) \\
&\frac{\partial}{\partial z}A_{pr}(z,t) + \frac{1}{v_{g_{pr}}}\frac{\partial}{\partial t}A_{pr}(z,t) + \frac{i}{2}\beta^{(2)}_{pr}\frac{\partial^2}{\partial t^2}A_{pr}(z,t) = i\gamma_{pr}(|A_{pr}(z,t)|^2 \\
&\quad + 2|A_{pu}(z,t)|^2)A_{pr}(z,t)
\end{aligned} \tag{7}$$

where the non-linearity coefficients $\gamma_j = \frac{n_2\omega_j}{cA_{eff}}$ are introduced [2]. The first terms in the right-hand side of the equations represents respectively the SPM of the pump and of the probe, while the second terms are respectively the XPM induced into the pump by the probe and vice versa.

In the case of a pump-probe configuration, it is possible to reduce the equations making some approximations: (i) when weak probe pulses are used, their SPM contribution can be neglected as well as the XPM induced into the pump by the probe, (ii) the sample thickness (a 2 mm thick calcium fluoride window) is short in respect to the dispersion length, this mean that the GVD effects are negligible [12], $\beta^{(2)}_{pu} = \beta^{(2)}_{pr} = 0$. The equations are then reduced:

$$\begin{aligned}
&\frac{\partial}{\partial z}A_{pu}(z,t) + \frac{1}{v_{g_{pu}}}\frac{\partial}{\partial t}A_{pu}(z,t) = i\gamma_{pu}|A_{pu}(z,t)|^2A_{pu}(z,t) \\
&\frac{\partial}{\partial z}A_{pr}(z,t) + \frac{1}{v_{g_{pr}}}\frac{\partial}{\partial t}A_{pr}(z,t) = i2\gamma_{pr}|A_{pu}(z,t)|^2A_{pr}(z,t)
\end{aligned} \tag{8}$$

It is convenient to evaluate the solutions of Eq. (8) in a new coordinate system (z, τ) moving with the group velocity of the probe pulse and normalized to its time duration τ_{pr} [2]:

$$\tau = \frac{t}{\tau_{pr}} - \frac{1}{\tau_{pr}}\frac{z}{v_{g_{pr}}} \tag{9}$$

In this reference frame the coupled-amplitude equations take the following form:

$$\begin{aligned}
&\frac{\partial}{\partial z}A_{pu}(z,\tau) = i\gamma_{pu}|A_{pu}(z,\tau)|^2A_{pu}(z,\tau) \\
&\frac{\partial}{\partial z}A_{pr}(z,\tau) + \frac{\epsilon}{L_W}\frac{\partial}{\partial t}A_{pr}(z,\tau) = i2\gamma_{pr}|A_{pu}(z,\tau)|^2A_{pr}(z,\tau)
\end{aligned} \tag{10}$$

where $\epsilon = sgn(v_{g_{pu}} - v_{g_{pr}})$ and $L_W = \frac{\tau_{pr}}{|v^{-1}_{g_{pu}} - v^{-1}_{g_{pr}}|}$ is the walk-off length. For such a system it is possible to calculate an analytical solution. XPM and group velocity mismatch are taken into account while higher order effect due to GVD broadening are not considered. The general solution evaluated at the end of the sample $z = L$ is [2]:

$$\begin{aligned}
&A_{pu}(L,\tau) = A_{pu}\left(0, \tau - \epsilon\frac{L}{L_W}\right)e^{i\phi_{pu}} \\
&A_{pr}(L,\tau) = A_{pr}(0,\tau)e^{i\phi_{pr}} \\
&\phi_{pu}(\tau) = \gamma_{pu}L|A_{pu}(0,\tau)|^2 \\
&\phi_{pr}(\tau) = 2\gamma_{pr}\int_0^L |A_{pu}(0, \tau - \epsilon\frac{z}{L_W})|^2dz
\end{aligned} \tag{11}$$

The XPM contribution changes along the sample because of the group velocity mismatch (GVM) and it is obtained by integrating along the sample length L.

In order to perform the integration it is necessary to give a specific shape to the two pulses. These are the initial conditions. Simulations have been performed for different initial conditions. The pump pulse in all the cases is represented by an unchirped Gaussian pulse delayed in time in respect to the probe pulse:

$$A_{pu}(\tau) = A_{0_{pu}}e^{-\frac{4log2}{\tau^2_{pu}}(\tau+\Delta T)^2} \tag{12}$$

ΔT is the delay time between pump and probe. In the calculus two types of probe pulses have been considered: a chirped symmetric Gaussian pulse and a chirped asymmetric pulse.

3. Experimental details

The collection of the signals has been performed on a typical pump-probe set-up. The laser system is based on a commercial Ti:Sapphire oscillator and regenerative amplifier (Coherent Legend Elite HE USP) producing a 1 kHz train of 40 fs pulses at 800 nm. A fraction of the total output (700 μJ) is utilized to generate both the

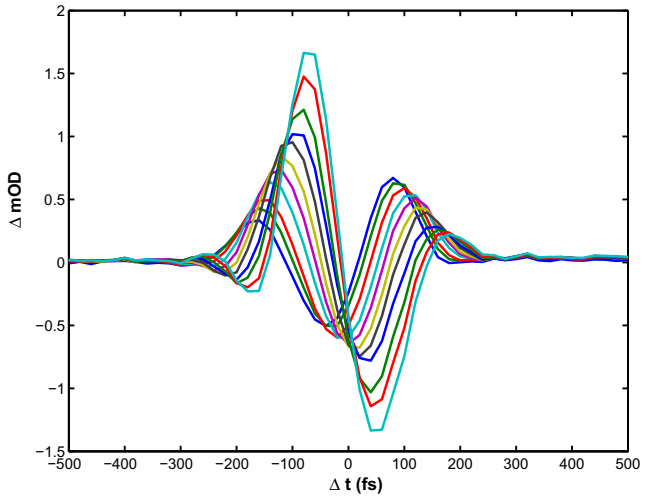

Fig. 1. Signals obtained on a 2 mm thick CaF_2 window at 6 μm. Time profiles are relative to different frequency components, between 1608 cm^{-1} and 1736 cm^{-1}, separated by ≈5 cm^{-1}.