Chapter 5
Four-Wave Mixing with Broadband Laser Pulses

Abstract
In this Chapter, we derive a complete equation that describes the signal measured in third-order nonlinear spectroscopy. This equation is applicable to laser pulses down to one optical cycle in duration. We show that even for extremely short pulses the signals obtained in photon echo spectroscopy can be described in the conventional way, provided care is taken of the spectral filtering effect and experimental beam arrangement. The typical four-wave mixing experiments are considered: transient grating, self-diffraction, and pump–probe.
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5.1 Introduction

The use of extremely short 5-fs pulses, described in the preceding three chapters, provides obvious advantages to a spectroscopic experiment. Next to the very high temporal resolution, the broad bandwidth associated with short pulses allows covering an impressive spectral window at once. On the other hand, any experiment with 5-fs pulses is a daunting task. Besides the trivial experimental nuisances such as the pulse lengthening during its propagation before and inside the sample because of group velocity dispersion, there are also more fundamental problems to be addressed.

The conventional description of nonlinear signals applicable to multi-cycle pulses becomes questionable for the pulses that consist merely of a couple of optical fringes. Clearly, in the latter case the conventionally employed slowly varying envelope approximation [1-3] implying that the temporal variation of the pulse amplitude is negligible on the duration of an optical cycle, can no longer be maintained. Furthermore, the phase-matching bandwidth [4,5], which is limited due to dispersion in the nonlinear medium, rapidly gains importance with the broadening of the pulse spectrum. Another point of serious concern is the frequency-dependent variation in the sensitivity of the photodetector employed to register the signal generated in the nonlinear process. In combination, the above listed features of an experiment with broadband pulses result in what is known as a spectral-filter effect [6-8]. On top of that, artificial lengthening of the observed time dependencies is a direct consequence of the noncollinear geometry employed in spectroscopic experiments. Evidently, if a portion of the signal field is filtered out in frequency and/or the signal is artificially “blurred” in time this might crucially influence the measured data [9] and subsequently lead to its erroneous interpretation.

To address these issues, we present a comprehensive theoretical analysis in which the frequency– and time–domain formalism of ultrafast nonlinear spectroscopy is thoroughly reexamined. The complete expressions valid even for single-cycle-pulse applications are derived for the nonlinear signal in the frequency and time domains. Among others, we show that one does not need to invoke the slowly varying envelope approximation in its aforementioned meaning, i.e. rejecting derivatives of the time-domain electric field. We also assert that the influence of geometrical delay smearing does not introduce a significant distortion of the observed traces provided that the geometry is carefully optimized.

This Chapter is organized as follows. In Section 5.2, we discuss the formalism for optical four-wave mixing spectroscopy with extremely short laser pulses that consist of only a few optical cycles. We summarize the experimental conditions required to link the time– and frequency– domain observables. Section 5.3 investigates a particular case in which the spectral-filter effect is shown to jeopardize the outcome of the self-diffraction experiment. In Section 5.4 we discuss the impact of beam geometry on the outcome of the spectroscopic measurements with 5-fs pulses. The formalism for frequency-resolved pump-probe experiment is outlined in Section 5.5. Finally, in Section 5.6, we present our conclusions.
5.2 The formalism for ultrafast spectroscopy with 5-fs pulses

In this Section, we derive the master equation that describes spectroscopic observables and is valid even for single-cycle optical pulses. Using the frequency–domain framework, we consistently include the effects of phase-matching, dispersive pulse broadening, dispersion of the third-order nonlinearity, and frequency dependence of the resulting nonlinear signal. The frequency–domain formalism is then recast in the time–domain, which is conventionally used in the description of transient spectroscopy with short light pulses. We subsequently show that despite the ultrabroad bandwidth associated with 5-fs pulses, the effect of spectral filtering can be disregarded under proper experimental conditions. This allows a straightforward transition from the frequency–domain representation to the time–domain one, with the latter offering a simpler formalism. Most importantly, this simplifies the experimental task by lifting the otherwise unavoidable necessity to frequency-resolve the signals generated by the ultrabroadband pulses.

We consider the case of non-collinear geometry in which three beams $E_i(z,t)$ ($i=1\text{-}3$) intersect at small angles in a nonlinear medium (Fig.5.1.). The corresponding configurations for two types of non-collinear third-order experiments are depicted in Fig.5.1b and 5.1c. The self-diffraction (SD, Fig.5.1b) and transient grating (TG, Fig.5.1c) signals are equivalent to the two- and three-pulse stimulated photon-echo signals originating from the systems with phase memory.

**Fig.5.1:** (a) Schematic representation of the pulse sequence in a three-pulse nonlinear spectroscopic experiment. $E_{1,2,3}$ are the input fields, and $E_4$ is the signal due to the third-order nonlinear process. $t_{12}$ and $t_{23}$ are the delay between pulses $E_1-E_2$ and $E_2-E_3$, respectively. (b) Self-diffraction (two-pulse photon echo) configuration. Two conjugated signal are emitted in the directions $k_4$ and $k'_4$. (c) Transient grating in a “box” geometry.
Focusing conditions of the beams are chosen such that the confocal parameter [5] and the longitudinal beam overlap of the fundamental beams are considerably longer than the interaction length. For simplicity, we assume that neither of the fields is absorbed in the nonlinear medium and that the nonlinear response is purely third order. The input beams then induce a third-order nonlinear polarization \( P^{(3)}(z,t) \) that serves as a source for the signal field \( E_d(z,t) \). The approach used here is similar to the treatment of second-order nonlinear polarization in Section 3.4 (see Eq.3.13). By writing both \( P^{(3)}(z,t) \) and \( E_d(z,t) \) as a Fourier superposition of monochromatic waves, one obtains an equation that governs propagation of the signal wave in the +z direction inside the nonlinear medium [10]:

\[
\frac{\partial^2}{\partial z^2} \tilde{E}_4(z,\Omega) + k_{4z}^2(\Omega) \tilde{E}_4(z,\Omega) = -\mu_0 \Omega^2 \tilde{P}^{(3)}(z,\Omega),
\]

where \( \tilde{E}_4(z,\Omega) \) and \( \tilde{P}^{(3)}(z,\Omega) \) are Fourier transforms of \( E_4(z,t) \) and \( P^{(3)}(z,t) \), respectively. \( \Omega \) is the frequency and \( k_{4z}(\Omega) \) is projection of the wave-vector of signal field \( k_4(\Omega) = \Omega^2 \varepsilon_0 \mu_0 \tilde{\varepsilon}(\Omega) \) onto the z-axis, with \( \tilde{\varepsilon}(\Omega) \) being the Fourier-transform of the complex relative permittivity \( \varepsilon(t) \).

To simplify the left part of Eq.(5.1), we write the signal field as a plane wave propagating along z axis:

\[
\tilde{E}_4(z,\Omega) = \tilde{E}_4(\Omega) \exp[i k_{4z}(\Omega)z],
\]

and substitute it into Eq.(5.1):

\[
2ik_{4z}(\Omega) \frac{\partial}{\partial z} \tilde{E}_4(z,\Omega) + \frac{\partial^2}{\partial z^2} \tilde{E}_4(z,\Omega) = -\mu_0 \Omega^2 \tilde{P}^{(3)}(z,\Omega) \exp[-i k_{4z}(\Omega)z]
\]

Identically to the application of non-equality (3.16), we now neglect the second-order derivative over the signal electric field [5,10]:

\[
\left| \frac{\partial}{\partial z} \tilde{E}_4(z,\Omega) \right| \ll \left| 2k_{4z}(\Omega) \tilde{E}_4(z,\Omega) \right|
\]

on the grounds that were discussed in Section 3.4. Equation 5.3 then has a simple solution by integration:
where $n_d(\Omega) = \sqrt{\varepsilon(\Omega)}$ is the refractive index for the signal wave and $L$ is the thickness of the nonlinear medium.

In order to calculate the third-order dielectric polarization induced at frequency $\Omega$ by the fundamental fields, we should sum over all possible permutations of fundamental frequencies weighted according to the third-order susceptibility [11]:

$$
\widetilde{P}^{<3>} (z, \Omega) = \int \wedge \int d\omega' d\omega'' \, \tilde{\chi}^{<3>} (\omega_{eg} - \omega', \omega'' - \omega_e + \Omega) \tilde{E}_1 (z, \omega') \times 
\overline{E_2 (z, \omega'' \rangle \tilde{E}_3 (z, \Omega - \omega'' + \omega)} \exp \left[ -i k_{1z} (\omega') + k_{2z} (\omega'') + k_{3z} (\Omega - \omega'' + \omega') \right] \times 
\exp \left[ -i \omega'' t_{12} - i (\Omega - \omega'' + \omega') (t_{12} + t_{23}) \right] \times 
(5.6)
$$

where $\tilde{E}_i (z, \omega'')$ is a Fourier transform of $E_i (z, t)$. Analogously to Eq. (5.2), the phase accumulated as the result of linear propagation, $(k, z)$, is styled into a separate oscillating term. In Eq.(5.6), $t_{12}$ and $t_{23}$ are the delays between pulses $E_1$–$E_2$ and $E_2$–$E_3$, respectively. In the SD case (Fig.5.1b) $t_{23}$ is set to zero and $t_{12}$ is scanned while in the TG experiment (Fig.1c) $t_{12}$ is scanned. Representation of the frequency-dependent third-order nonlinear susceptibility, $\tilde{\chi}^{<3>} (\omega_{eg} - \omega', \omega'' - \omega_e + \Omega)$, is based on the interaction of the input fields with an electronic transition with the frequency $\omega_{eg}$. The inclusion of the third-order susceptibility due to Raman and two-photon processes is also straightforward. The particular expression for $\tilde{\chi}^{<3>}$ will be discussed below.

To calculate the signal field, one should integrate the signal intensity over the longitudinal coordinate $z$ according to Eq.(5.5). This can be performed analytically for a low-efficient nonlinear process ($E_{1,2,3} = \text{const}$), as it is usually the case in spectroscopic applications:

$$
\tilde{E}_3 (\Omega, t_{12}, t_{23}) = \frac{i e^L}{2 n_i (\Omega)} \int \wedge \int d\omega' d\omega'' \, \tilde{\chi}^{<3>} (\omega_{eg} - \omega', \omega'' - \omega_e + \Omega) \times 
\tilde{E}_1 (\omega') \tilde{E}_2 (\omega'') \tilde{E}_3 (\Omega - \omega'' + \omega) \text{sinc} \left( \frac{\Delta \omega_{12}}{2} \right) \times 
\exp \left[ i \Delta \omega_{12} \frac{L}{2} - i \omega'' t_{12} - i (\Omega - \omega'' + \omega') (t_{12} + t_{23}) \right] \times 
(5.7)
$$

The phase mismatch

$$
\Delta \omega_{12} (\Omega, \omega', \omega'') = -k_{1z} (\omega') + k_{2z} (\omega'') + k_{3z} (\Omega - \omega'' + \omega') - k_{4z} (\Omega) \times 
(5.8)
$$
should be calculated for each particular geometry, given in Fig.5.1b,c.

Equation 5.7, which will be extensively used in this Chapter, is valid even for single-cycle optical pulses. The frequency representation allows us to include in a self-consistent way dispersive broadening of interacting pulses and frequency-dependence of the nonlinear susceptibility. Besides, we avoid the introduction of the carrier frequency [12] the definition of which becomes confusing for a few-cycle pulses. We also draw attention to the \( \Omega \) term in front of the integral that follows directly from the Maxwell equations and reflects the fact that higher frequencies are generated more efficiently. It is this term that is responsible for the effect of self-steepening of the pulses propagating in optical fibers [13].

The total spectrally-resolved signal registered by a quadratic detector is written as

\[
\tilde{I}_4(\Omega, t_{12}, t_{23}) = \varepsilon_0 \frac{n_4(\Omega)Q(\Omega)}{c} \left| \tilde{E}_4(\Omega, t_{12}, t_{23}) \right|^2
\]

with \( Q(\Omega) \) being the spectral sensitivity of a monochromator-detector combination.

From the point of view of practical application of 5-fs pulses, we now quantify the differences between the complete frequency-resolved signals of TG and SD computed according to Eqs.(5.7–9) with \( \tilde{\chi}^{<3>} = \text{const} \) and the ideal frequency-resolved TG and SD signals for an instantaneous nonlinear response [14]:

\[
I_{4,\text{ideal}}(\Omega, t_{12}, t_{23}) = \left[ \int \int d\omega' d\omega'' \tilde{E}_1^*(z, \omega') \tilde{E}_1(z, \omega'') \left( \tilde{E}_1(z, -\omega'' + \omega') + \tilde{E}_1(z, \omega'' - \omega') \right) \right]^2
\]

The comparison of the respective complete and ideal signals provides us with information on the spectral filter effect, that is, a combined influence of the spectral variations in the generation efficiency of the signal field and in its detection. To simulate the conditions of our experiments on hydrated electrons (see Chapter 6), in the calculation of the complete SD and TG traces we included dispersive properties of a 100-µm layer of water [15,16] and the impact of the non-collinear beam geometry on the phase-mismatch given by Eq.(5.8). The small thickness of the medium is crucial to prevent dispersive broadening of the pulse inside the jet. The lengthening of a 5-fs 800-nm pulse caused by a 100-µm layer of water is less than 0.1 fs and, therefore, is negligible. The ideal frequency-resolved traces were calculated according to Eq.(5.10). The spectral filters for the SD and TG cases, obtained as the ratios of the complete [Eqs.(5.7–9)] vs. ideal [Eq.(5.10)] signals, are presented in Fig.5.2. The dashed and dotted curves correspond to TG and SD, respectively, for the case of a flat spectral response of the detector (\( Q(\Omega) = \text{const} \)). Apparently, both filters are dominated by the \( \Omega^2 \)-dependence that originates from the \( \Omega \)-term in Eq.(5.5). The curve representing the SD filter is somewhat steeper compared with the one in the TG case. This reflects the fact
that the phase mismatch for SD is greater since SD is intrinsically a non-phase-matched geometry [14].

**Fig. 5.2:** Spectral filters for two configurations of photon-echo experiment in water. Shaded contour represents the spectrum of ideal 5-fs pulses. The spectral filter calculated for self-diffraction is shown by a dotted line, and the filter for transient grating is presented by a dashed line. The dash-dotted line depicts the typical spectral sensitivity of a silicon light detector, $Q(\lambda)$. The spectral filter for transient grating corrected by $Q(\lambda)$ is given by a solid curve. The thickness of the water layer is taken 100 µm and the intersection angles of the beams are 4°. Note that the solid curve (the overall spectral filter in the TG case) is nearly flat in the wavelength region up to 900 nm because the photo-detector sensitivity balances off the more efficient generation of the nonlinear signal at higher frequencies.

The taking into account of a typical real spectral sensitivity of a silicon photodiode, $Q(\Omega)$ (dash-dotted curve in Fig. 5.2) results in the overall spectral filter for TG depicted by the solid curve. Noteworthy, the overall spectral filtering effect is nearly frequency-independent throughout most of the spectrum of a 5-fs pulse (shaded contour in Fig. 5.2) because the photo-detector sensitivity balances off the $\Omega^2$-dependence. Therefore, we can disregard the effect of spectral filtering in case it is counterweighed by the proper choice of the spectral response of the detector. This is an important conclusion for the practical purpose of nonlinear spectroscopy with 5-fs pulses since it justifies the use of less cumbersome spectrally unresolved detection of TG and SD signals.

Now we demonstrate how to arrive to the conventionally used time–domain description of ultrafast spectroscopy [4]. As we already pointed out, to match the information obtained in a SD or TG experiment, Eq. (5.9) should be integrated over all frequency components in order to obtain the total energy of the signal field detected by a quadratic detector. According to Parseval’s theorem [17], the amount of energy carried by the signal is the same whether we compute it in the time domain or in the frequency domain. Therefore, the following formula is a time-domain expression for the same signal:
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\[ S(t_{12}, t_{23}) = e_0 \frac{n(\omega_1)}{2\pi c} \int_0^\infty dt_1 |E_1(t, t_{12}, t_{23})|^2 \]  (5.11)

where

\[ E_1(t, t_{12}, t_{23}) = \frac{e \mu_e L}{2n_4(\omega_1)} \int_0^\infty dt_1 dt_2 \int_0^\infty dt_3 \exp \left( t - t_3 - t_2 - t_1 \right) E_2 \left( t - t_{12} - t_3 - t_2 \right) \]

\[ \times E_3 \left( t - t_{13} - t_{12} - t_3 \right) R(t_1, t_2, t_3) \exp \left[ -i\omega_e(t_3 - t_2) + i(\omega_3 + \omega_2 - \omega_1)t_3 + i(\omega_2 - \omega_1)t_2 - i\omega_1 t_1 + iT_{12} + iT_{13} + iT_{23} \right] \]  (5.12)

and the so-called nonlinear response function is introduced as a Fourier transform of the nonlinear susceptibility [4]:

\[ R(t_1, t_2, t_3) = \int \int \int \int \hat{\chi}^{(3)}(\omega_1, \omega_2, \omega_3) \exp \left[ -i\omega_1 t_1 - i\omega_2 t_2 - i\omega_3 t_3 \right] dt_1 dt_2 dt_3 \]  (5.13)

In Eq.(5.12) we also extracted the oscillations of electrical fields at the optical frequency \( \omega_1 \):

\[ E_i(t) = E_i(t) \exp(-i\omega_1 t) \]  (5.14)

Note, that in the case of ultrabroadband optical pulses the transition between the frequency–domain description formulated by Eqs.(5.7–9) and the time–domain representation summarized by Eq.(5.11–13) becomes valid only in the case of a flat spectral filter. In other situations when the spectral filtering of the SG or TG signals does occur (regardless of its reason), the correctness of Eq.(5.12) is not warranted and one must use more general Eqs.(5.7–9).

Equation 5.13 provides the link between the nonlinear response function \( R(t_1, t_2, t_3) \) and the third-order susceptibility \( \hat{\chi}^{(3)} \). For the former, extensive formalism of non-Markovian dynamics, based on the pathway propagation in the Liouville space [4] has been developed. Here we restrict ourselves to a simple model of a homogeneously broadened two-level system. In this case, the nonlinear response function is given as

\[ R(t_1, t_2, t_3) = \frac{\mu_{eg}^4 N}{\hbar^3} \exp \left[ -\frac{t_1 + t_3 - t_2}{T_2} \right] \]  (5.15)

where \( \mu_{eg} \) is the transition dipole moment, \( N \) is concentration, \( T_1 \) and \( T_2 \) are the population-relaxation and dephasing times, respectively, and

\[ T_2^{-1} = (T_2^a)^{-1} + (2T_1)^{-1} \]  (5.16)
with $T_2^*$ being the pure dephasing time. Fourier-transformation of Eq.(5.15) yields a well-known result [18]:

$$\chi^{(3)}(\omega - \omega', \omega'' - \omega_\text{eg} + \Omega) =$$

$$-i \frac{\mu_\text{eg}^N}{\hbar^4} \frac{1}{T_1^{-1} - i(\omega' - \omega)} \left[ \frac{1}{T_2^{-1} - i(\omega_\text{eg} - \omega')} + \frac{1}{T_2^{-1} - i(\omega'' - \omega_\text{eg})} \right] \frac{1}{T_2^{-1} + i(\omega_\text{eg} - \Omega)}$$

(5.17)

The second sum term in square brackets in Eq.5.17 is included to account for the fact that $\chi^{(3)}$ possesses symmetry with respect to $\omega'$ and $\omega''$, and the total expression of $\chi^{(3)}$ is a sum of all frequency permutations [5,10]. The situation addressed here is of direct relevance to the experiments described in Chapter 6 and 7. Third-order susceptibilities for different four-photon processes like Raman scattering or two-photon absorption can be calculated in a similar fashion. The two-level system can also be dressed in a vibrational manifold to account for coherent excitation of several Frank-Condon transitions [4].

### 5.3 Case study: Blue pulse characterization by third-order FROG

In the previous Section we demonstrated a fortunate combination of the beam geometry, medium properties, and detector sensitivity. The spectral filter resulting from it is benign and, consequently, it does not seriously affect the correctness of the wavelength-integrated detection of SD and TG traces. Obviously, under less fortunate circumstances the spectral filtering can play a significantly more damaging role.

Here we address such a situation by exploring the problem of SD and TG FROG measurement of a blue pulse around 400 nm with an ~10-fs duration. Exactly this problem has been recently confronted experimentally in the attempts to characterize tunable pulses around this wavelength generated in gas-filled hollow fibers [19,20]. The severity of the spectral filtering in this wavelength region is aggravated by the steeply rising bulk dispersion in both crystals and glasses because of the proximity of the resonance absorption lying in the UV. The spectral filter calculated for SD and TG measurement configurations in a BBO crystal and quartz (fused silica) is depicted in Fig.5.3.

Here the frequency-dependant conversion efficiency is shown against the spectral content of the pulse. Compared with the SD FROG, the TG FROG (dotted line) provides much wider spectral window that is determined by the self-steepening effect, i.e. more effective generation of blue spectral components. The broadening of the spectral window is a direct consequence of the “box” geometry used in TG FROG [14]. In the SD FROG case, the central frequency components are substantially suppressed while the wings are enhanced. The resulting broader spectrum corresponds to a shorter pulse. To illustrate the latter statement,
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Fig. 5.4 depicts an ideal SD FROG trace of an 11-fs pulse, calculated using conventional expression [14], and the full SD FROG trace calculated according to Eq.(5.7–9).

**Fig.5.3**: Spectral filtering effect in SD and TG FROG techniques. As a nonlinear medium, a 100-µm thick slab of BBO (solid curve, SD) or fused silica (dashed curve, SD, and dotted curve, TG) is used. Angles between interacting beams are set at 4°. A spectrum of a 10-fs spectral-limited pulse is shown as a shaded contour for a comparison.

**Fig.5.4**: Ideal SD FROG trace of a slightly-chirped 11-fs pulse centered around 400 nm. (b): SD FROG trace of the same pulse calculated according to Eq.(5.7–9). (c): Temporal pulse intensities retrieved from ideal (dotted curve) and calculated (solid curve) SD FROG data, i.e. (a) and (b), respectively. A 100-µm BBO crystal is employed as a nonlinear medium. Angles between interacting beams are set at 4°. Note that the trace on (b) appears to belong to a chirp-free pulse.
As is apparent from the ideal trace, the pulse is slightly chirped. However, the full SD FROG trace looks as if the pulse were chirp-free. Moreover, the pulse retrieved from the full trace (Fig.5.4c, solid curve) is noticeably shorter than its counterpart (Fig.5.4c, dashed curve) recovered from the ideal trace. The same applies to the SD autocorrelation traces (not shown), i.e. temporal marginals of the SD traces that would be measured in the experiment using wavelength-integrated detection. This artificial temporal width shortening is mostly the result of phase-matching: signal spectral components with the same frequency but generated from different frequency combinations of fundamental waves have different phase shifts and therefore can interfere constructively or destructively.

In conclusion, we have shown the case of strong spectral filtering in a SD experiment, which severely compromises the correctness of the measured characteristics, – in this case, pulse shape and duration.

5.4 Ultimate temporal resolution of SD and TG experiments

In this Section, we address geometrical smearing – the effect deteriorating the temporal resolution of a nonlinear spectroscopic experiment as a direct consequence of employing non-collinear beam geometry. This type of distortion originates from the fact that in a beam, inclined at an angle to a plane, different transverse components of a pulse travel different distances before reaching the plane. This means that a fixed delay between two pulses propagating in two intersecting beams changes into a range of delays across the waist of the beams in the intersection region. The very same idea of yielding a range of delays simultaneously is utilized in single-shot pulse autocorrelation techniques [21].

The described above “delay blurring” can be of a serious concern dealing with the laser pulses that have duration shorter than 10 fs. This issue has been addressed previously in connection with the temporal resolution of a non-collinear pulse duration measurement via second-harmonic generation [7,8]. Analogously to Section 3.5, here we evaluate the influence of the geometrical smearing on the width of self-diffraction and transient grating traces.

For arbitrary pulses and beam profiles, the shape of the resulting traces should be computed numerically by integrating Eq.(5.9) over each transverse component of the beam. For linearly chirped Gaussian pulses with Gaussian spatial profile, however, these traces can be calculated analytically. Assuming that the nonlinear response of the medium is instantaneous, one can calculate from Eq.(5.10) that the ideal SD or TG trace has a Gaussian intensity profile in time. Its width, $\tau_{0}$, is by a factor of $\sqrt{3/2}$ broader than the pulse duration. The width of the actual signal, $\tau_{meas}$, which has been stretched by geometrical smearing, can be expressed by

$$\tau_{meas}^2 = \tau_{0}^2 + \beta \delta t^2,$$

(5.18)
where $\beta$ is a scaling constant dependent on the employed beam geometry, and $\delta$ is the effective delay smearing given by

$$\delta t = \frac{\alpha d_f}{2c} \quad (5.19)$$

Here $d_f$ is the beam diameter in the focal plane and $\alpha$ is a small intersection angle between the interacting beams (Fig.5.1b,c). As has been stated in Section 3.5, the lowest value of $\delta t$ for Gaussian pulses and beams amounts to 0.4 fs if the central wavelength of the pulse is 800 nm. For the beam profiles other than Gaussian the value of $\delta t$ becomes larger.

![Diagram](image.png)

**Fig.5.5:** Geometrical smearing of transient grating and self-diffraction traces as a function of beam intersection angle. The temporal widths of the observed signals are shown by solid and dashed curves for transient grating and self-diffraction, respectively. The duration of ideal Gaussian pulses is 5 fs and the nonlinear response is assumed instantaneous. The focal length of the focusing optics is 125 mm and the FWHM of the collimated Gaussian beams is 2 mm.

For self-diffraction the constant $\beta$ equals 4/3, while for transient grating in the “Box” beam arrangement $\beta$ takes the value of $\approx 5/3$. The influence of geometrical smearing on the width of the trace observed in these two measurement configurations is illustrated in Fig.5.5. As can be seen from Fig.5.5, the temporal resolution of the self-diffraction experiment is somewhat higher compared to transient grating. This is explained by the fact that the smearing in the case of transient grating takes place in $xz$ and $yz$ planes (Fig.5.1c) simultaneously. In any case, for intersection angles smaller than 10° the lengthening of the detected signal does not exceed 10%.

Therefore, the effect of geometrical smearing on the generated signals is insignificant even for experiments with pulses as short as 5 fs, provided the intersection angle is kept sufficiently small and the beams are properly focused.
5.5 Heterodyned detection and frequency-resolved pump–probe

In the previous sections of this Chapter, we have discussed the implications of third-order nonlinear optical experiments in which the direction of the signal beam differs from that of the input field(s). Therefore, the signal in SD and TG experiments is essentially background-free and proportional to the modulus squared of the nonlinear polarization (see Eqs.(5.6,9)). Despite clear advantages provided by the absence of the background, there are also some inconveniences. These are a typically weak nonlinear polarization; no information on the phase of it; a faster, by a factor of two, decay of the TG traces than the actual decay of induced nonlinear polarization, and square dependence of the signal intensity on the medium length. Therefore, it may be desirable to combine information from such an experiment with the measurement in which the signal can by enhanced by hederodyne detection and is linearly proportional to the nonlinear polarization at the same time.

We now turn our attention to the case of optical pump–probe experiment where the signal wavevector shares its direction with one of the input fields. Thus, the latter field can be viewed as a local oscillator that heterodynes the signal field. A third-order pump–probe experiment involves a double interaction with the pump pulse and a single interaction with a probe pulse. To comply with the notation in Section 5.2, we assume that the field of the pump pulse is $E_1 \equiv E_2$; $t_{23}$ is the delay between pump and probe; and $E_3$ is the field of the probe pulse. The total spectrally-resolved signal registered by a quadratic detector in the direction of the probe pulse wavevector is then [4,11,22-25]:

$$I_{TOTAL}(\Omega, t_{23}) = \varepsilon_0 \frac{n(\Omega)}{c} \left| \tilde{E}_3(\Omega) + \tilde{E}_4(\Omega, t_{23}) \right|^2$$

$$= \varepsilon_0 \frac{n(\Omega)}{c} \left\{ \| \tilde{E}_3(\Omega) \|^2 + 2 \text{Re} \left[ \tilde{E}_4(\Omega, t_{23}) \cdot \tilde{E}_3^*(\Omega) \right] + \| \tilde{E}_4(\Omega, t_{23}) \|^2 \right\} \quad (5.20)$$

The first term of the sum in Eq.(5.20) is delay-independent and, therefore, it acts as a constant background that can be readily subtracted (e.g., employing a lock-in or synchronous detection). The second term is a heterodyned signal. The last (homodyne) term in Eq.(5.20) is negligibly small compared to the second one provided the conversion efficiency was low enough. After consulting Eqs.(5.6,7), for the heterodyned signal we obtain:

$$I_{HET}(\Omega, t_{23}) = \varepsilon_0 \frac{2n(\Omega)}{c} \text{Re} \left[ \tilde{E}_4(\Omega, t_{23}) \cdot \tilde{E}_3^*(\Omega) \right]$$

$$\propto (\Omega L) \text{Im} \left[ \tilde{E}_3^{<3b}(\Omega, t_{23}) \cdot \tilde{E}_3^*(\Omega) \right] \quad (5.21)$$

In order to construct transient absorption spectra, in assumption that actual optical density change, which is due to nonlinear response, is very small, one computes a ratio
where $\Delta T(\Omega, t_{23})$ denotes the induced change in the sample transmission, $T^0(\Omega)$ is a steady-state transmission. The spectral sensitivity of the detector, omitted in Eq.(5.20), cancels out in Eq.(5.22). Unlike the steady-state absorption spectrum that is invariant to the light source which was used to measure it, the pump-probe spectrum, in general, depends on the actual properties of both the pump and probe pulse. The dependence on the spectral width and frequency of the pump is very well known from the transient hole burning spectroscopy [11] where the first laser pulse creates a spectral “hole” in the absorption spectrum of an inhomogeneously broadened transition. The width of the hole in this case is mostly determined by the homogeneous line-width [4,11]. One cannot, however, neglect the relation between the specific shape of $S_{FRPP}(\Omega, t_{23})$ and the amplitude and phase of the pump and probe pulses even for completely homogeneously broadened absorption lines, especially if the population (longitudinal) relaxation time, $T_1$, is not significantly longer than the duration of the pump pulse, $\Delta \tau$. Indeed, if $T_1 >> \Delta \tau$ in a two-level homogeneously broadened transition, then the memory about specific details of the excitation will be lost upon the complete thermalisation of the excited state. In the opposite case, $S_{FRPP}(\Omega, t_{23})$ can still bear modulation imprinted on it by the laser pulse even at pump-probe delay times that are substantially longer than the duration of the pulse(s) and electronic dephasing, given by the value of $T_3$. We will return to the problem of modulation on the pump–probe spectra in the discussion on our experimental results on the hydrated electron in Chapter 7.

5.6 Conclusions

To solve the non-trivial fundamental issues related to nonlinear spectroscopy with the optical pulses that consist of 2.5 optical cycles, we developed a general formalism describing the generated signal field in both the time– and frequency–domain. The frequency–domain representation is found to be more powerful since it allows a consistent account of a variety of effects, such as phase-mismatch, self-steepening, dispersive pulse broadening, etc. Additionally, the use of the frequency–domain formalism removed the necessity to invoke a number of approximations such as, for example, the slowly varying envelope approximation. The derived formulation also avoids the use of parameters that are ill–defined for broadband optical pulses such as, for instance, the carrier frequency of the pulse. Equations 5.7–10 constitute the backbone of the general description of a third-order nonlinear experiments. Importantly, these equations remain valid and could be directly applied even for single-cycle pulses.

We have developed a general procedure for calculating the spectral-filter effect. Such a routine should be employed to optimize the experimental configuration for any third-order spectroscopic experiment that utilizes laser pulses shorter than 10 fs. In particularly, one can
design a compensating filter to account for spectral-filtering effects, and place it in front of the light detector. Notably, a careful choice of the beam geometry and selection of a photodetector with the suitable spectral sensitivity, as has been done in our experiments, can illuminate the need for a separate compensating filter. We next have demonstrated that the ability to defeat the damaging role of the spectral-filter effect legitimizes a transition to the typically employed for the multi-cycle pulses time–domain formulation. Importantly for the weak-signal applications, the absence of spectral filtering eliminates otherwise unavoidable requirement to frequency-resolve the signals.
References

15. Release on the Refractive Index of Ordinary Water Substance as a Function of Wavelength, Temperature and Pressure (The International Association for the Properties of Water and Steam, Erlangen, Germany, 1997).