

High-resolution four-photon spectroscopy with chirped pulses

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Abstract. We propose new schemes of high-resolution coherent four-photon spectroscopy where chirped pulses are employed for the Raman excitation of a nonlinear medium. The use of linearly chirped pulses in coherent anti-Stokes Raman scattering spectroscopy allows the spectra of nonlinear susceptibility to be studied with a terahertz resolution by measuring the intensity of the signal emerging from four-wave mixing as a function of the delay time between the pump pulses. This approach can be also employed for single-pulse spectroscopy of nonlinear susceptibility.

1. Introduction

Femtosecond four-photon spectroscopy is currently one of the most promising and exciting directions in nonlinear optics. An impressive conceptual and methodological progress achieved in this field in recent years [1–11] is associated, on the one hand, with a rapid development of femtosecond lasers and, on the other hand, with extensive applications of femtosecond four-photon spectroscopy for the investigation of ultrafast processes in molecular dynamics and real-time monitoring of photochemical reactions.

Importantly, the use of femtosecond pulses in four-photon spectroscopy enables one to pump and probe molecular vibrations within a broad spectral range. Simultaneously, this approach allows the investigation of the dynamics of different vibrational molecular subsystems and the study of wave-packet evolution with the use of time-domain measurements (analysis of beats in the impulse response of a system [1]) or frequency-domain methods (by tuning the wavelength of signal detection [8]).

In the context of extensive studies in femtosecond four-photon spectroscopy and broad opportunities associated with the application of such methods for the investigation of the physics of vibrational relaxation and the dynamics of quantum-chemical systems, it is of considerable interest to discuss new approaches and methods in femtosecond four-photon spectroscopy. In this paper, we propose a method of four-photon spectroscopy based on the use of chirped short light pulses. The advantages of four-wave mixing with chirped pulses as a method for the investigation of

ultrashort time dynamics and the structure of energy levels of molecular systems have been demonstrated in [12]. Currently, chirped pulses are employed for controlling molecular dynamics and photochemical processes and for the solution of quantum-control problems [13–16]. Dogariu and Hagan [17] implemented an experimental scheme where chirped pulses were used to measure the gain in stimulated Raman scattering.

In what follows, we will consider two schemes of coherent four-photon spectroscopy with chirped pulses. In one of the schemes discussed in this paper, the detuning of the difference of instantaneous frequencies of chirped pump pulses from the frequency of the studied Raman resonance is a linear function of the delay time between the pump pulses. This approach allows a high-resolution four-photon spectroscopy to be implemented through the measurement of the intensity of the nonlinear signal as a function of the delay time between the pump pulses. In the second scheme proposed in this paper, one of the incident light pulses is linearly chirped, while the other two are transform-limited. Then, tuning the difference of instantaneous frequencies of pump pulses around a Raman resonance, one can perform single-pulse spectroscopic measurements on the medium under study.

2. Basic relations

Consider the generation of an anti-Stokes wave through coherent anti-Stokes Raman scattering (CARS) $\omega_4 = \omega_1 - \omega_2 + \omega_3$ involving plane light waves propagating along the z -axis,

$$E_i = A_i(t - z/v_i, z) \exp[i(k_i z - \omega_i t)] + \text{c.c.}, \quad (1)$$

where A_i , ω_i , k_i , and v_i are the slowly varying amplitude, the frequency, the wave number, and the group velocity for the i th wave ($i = 1, 2, 3, 4$), respectively.

The equation for the slowly varying amplitude of the CARS signal in the first order of dispersion theory is written as [18]

$$\left(\frac{\partial}{\partial z} + \frac{1}{v_4} \frac{\partial}{\partial t} \right) A_4 \left(t - \frac{z}{v_4}, z \right) = - \frac{2\pi\omega_4^2}{ik_4 c^2} P^{\text{NL}} \exp[-i(k_4 z - \omega_4 t)], \quad (2)$$

where

$$P^{\text{NL}}(t, z) = \int_0^\infty \int_0^\infty \int_0^\infty \chi(t_1, t_2, t_3, z) E_1(t - t_1, z) \times E_2(t - t_2, z) E_3(t - t_3, z) dt_3 dt_2 dt_1 \quad (3)$$

is the nonlinear polarisation of the medium cubic in the light field [18] and $\chi(t_1, t_2, t_3, z)$ is the time-domain nonlinear-optical cubic susceptibility responsible for the considered CARS process.

Provided that the frequency difference $\omega_1 - \omega_2$ is tuned to a resonance with some Raman-active transition in the medium under study, we can write the nonlinear cubic susceptibility as

$$\chi(t_1, t_2, t_3, z) = \chi(t_1, z) \delta(t_1 - t_2) \delta(t_3). \quad (4)$$

In the frequency domain, the nonlinear susceptibility (4) depends only on the frequency difference $\omega_1 - \omega_2$. Substituting (4) into (3) and performing integration in t_1 and t_3 , we derive the following expression for the nonlinear polarisation:

$$P^{\text{NL}}(t, z) = \int_0^\infty \chi(t_1, z) E_1(t - t_1, z) E_2(t - t_1, z) dt_1 E_3(t, z). \quad (5)$$

Expressions (2) and (5) govern Raman-resonant four-wave mixing in plane waves in the case when the effects related to the dispersion spreading of light pulses are negligible.

3. CARS spectroscopy using chirped pulses with a tuneable delay

Suppose that the pump pulses with frequencies ω_1 and ω_2 are linearly chirped and are characterised by equal constant chirps, while the third (probe) pulse is transform-limited. Then, neglecting the differences in the group velocities of the incident light pulses, we can represent the amplitudes of the pump pulses as

$$A_1(\theta, z) = B_1(\theta) \exp(-i\alpha\theta^2), \quad (6)$$

$$A_2(\theta, z) = B_2(\theta - \tau) \exp[-i\alpha(\theta - \tau)^2], \quad (7)$$

$$A_3(\theta, z) = B_3(\theta), \quad (8)$$

where $\theta = t - z/v_j$ is the running time, B_j is the transform-limited envelope of the j th pulse ($j = 1, 2, 3$), α is the chirp, and τ is the delay time between the first and second pulses.

Since the difference of the instantaneous frequencies of the linearly chirped pulses (6) and (7) is a linear function of τ , we can tune the combination of instantaneous frequencies $\Delta\bar{\omega} = \bar{\omega}_1 - \bar{\omega}_2 = \omega_1 - \omega_2 + 2\alpha\tau$ around the Raman resonance under study by varying the delay time between the pump pulses (Fig. 1). In terms of the frequency-domain representation, the possibility of implementing the above-described approach for a high-resolution spectroscopy is associated with the fact that, in the case of linearly chirped pump pulses with equal chirps, the product of the fields $E_1 E_2$ involves a narrow spectral component whose frequency depends on the delay time between the pump pulses and whose bandwidth is determined by the bandwidth of the product $B_1 B_2^*$ of pump envelopes. In other words, the bandwidth of this component depends on the durations of pump

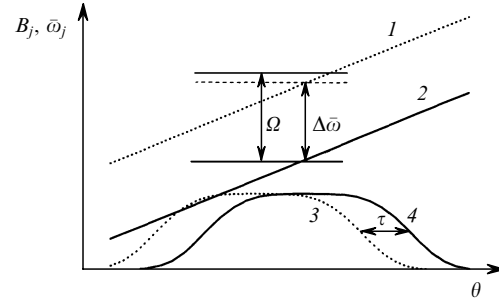


Figure 1. The instantaneous frequencies $\bar{\omega}_j = \omega_j - \partial \arg A_j / \partial \theta$ (1, 2) and the amplitudes B_j (3, 4) of the first (1, 3) and second (2, 4) pump pulses as functions of the running time in CARS spectroscopy using chirped pulses (6)–(8) ($\Delta\bar{\omega} = \bar{\omega}_1 - \bar{\omega}_2$ is the difference of instantaneous frequencies of the first and second pump pulses, Ω is the frequency of the Raman resonance, and τ is the delay time between the pump pulses).

pulses and the delay time between these pulses, but is independent of the chirp of these pulses.

Using expressions (1), (2), and (5)–(8) and introducing the running frame of reference θ, z , we derive the following equation for the amplitude of the CARS signal:

$$\frac{\partial A_4(\theta, z)}{\partial z} = \frac{2i\pi\omega_4^2}{k_4 c^2} \int_0^\infty \chi(t_1, z) B_1(\theta - t_1) B_2^*(\theta - t_1 - \tau) \times \exp(i\Delta\bar{\omega}t_1) dt_1 B_3(\theta) \exp(i\alpha\tau^2 - i\Delta kz), \quad (9)$$

where $\Delta k = k_4 - k_1 + k_2 - k_3$ is the phase mismatch and $\omega_4 = \omega_1 - \omega_2 + \omega_3 + 2\alpha\tau$ is the central frequency of the signal.

In the case when the envelopes of the incident pulses vary only slightly within the period of time equal to the characteristic decay time T of the nonlinear polarisation, we have $B_1(\theta - t_1) \approx B_1(\theta)$ and $B_2(\theta - \tau - t_1) \approx B_2(\theta - \tau)$ for $t_1 \leq T$. With these assumptions, equation (9) can be rewritten as

$$\frac{\partial A_4(\theta, z)}{\partial z} = \frac{2i\pi\omega_4^2}{k_4 c^2} \chi'(\Delta\bar{\omega}, z) B_1(\theta) B_2^*(\theta - \tau) B_3(\theta) \times \exp(-i\Delta kz + i\alpha\tau^2), \quad (10)$$

where

$$\chi'(\omega, z) = \int_0^\infty \chi(t, z) \exp(i\omega t) dt$$

is the Fourier transform of the nonlinear-optical cubic susceptibility.

In the case of a spatially uniform medium, where the nonlinear susceptibility is independent of z , the integration of equation (10) yields

$$A_4(\theta, z) = \frac{2i\pi\omega_4^2}{k_4 c^2} \chi'(\Delta\bar{\omega}) B_1(\theta) B_2^*(\theta - \tau) B_3(\theta) \times \exp(i\alpha\tau^2) \frac{\exp(-i\Delta kz) - 1}{-i\Delta k}. \quad (11)$$

Thus, the amplitude of the CARS signal measured as a function of the delay time between linearly chirped pump pulses with equal chirps reproduces the spectral dependence

of the nonlinear-optical cubic susceptibility of the medium under study.

Degenerate four-wave mixing with $\omega_1 = \omega_2 = \omega_3$ is a nonlinear spectroscopic approach that holds much promise for various physical applications. In this case, $\Delta k = 0$, and the integration of equation (10) gives the following expression:

$$A_4(\theta, z) = \frac{2i\pi\omega_4^2}{k_4c^2} \chi'(2\alpha\tau) B_1(\theta) B_2^*(\theta - \tau) B_3(\theta) \exp(i\alpha\tau^2) z^2. \quad (12)$$

As can be seen from formula (12), the proposed scheme of four-photon spectroscopy can be implemented with a single linearly chirped pulse. It seems convenient to split laser radiation into two beams in this case and to employ these beams for the investigation of a medium with a variable delay time.

Consider in greater detail the case of a homogeneously broadened Raman resonance, which is important for many practical applications. In this case, the nonlinear-optical susceptibility of the medium is written as

$$\chi(t, z) = \chi_0 \exp(-i\Omega t - t/T), \quad (13)$$

where χ_0 is a constant and Ω is the frequency of the Raman resonance. The parameter T in this case is understood as the transverse relaxation time, which characterises the spectral line width. The Fourier transform of the nonlinear cubic susceptibility (13) gives an expression for a Lorentzian contour:

$$\chi'(\omega) = \frac{T}{i(\Omega - \omega)T + 1}. \quad (14)$$

Fig. 2 displays the energy of the CARS signal $W = \int |A_4(\theta, z)|^2 d\theta$ calculated with the use of expression (9) as a function of the delay time between the first and second linearly chirped pulses with Gaussian envelopes $B_j(\theta) = B_{0j} \exp(-\theta^2 \tau_j^{-2})$ ($j = 1, 2, 3$) for a two-colour CARS process ($\omega_1 = \omega_2$). For comparison, the dots in Fig. 2 show the spectral dependence of the square nonlinear susceptibility $\chi'(2\alpha\tau)$. The results of calculations presented in Fig. 2 show that the proposed technique allows the frequency dependence of the nonlinear-optical susceptibility of a medium to be measured with a high spectral resolution around a homogeneously broadened Raman resonance.

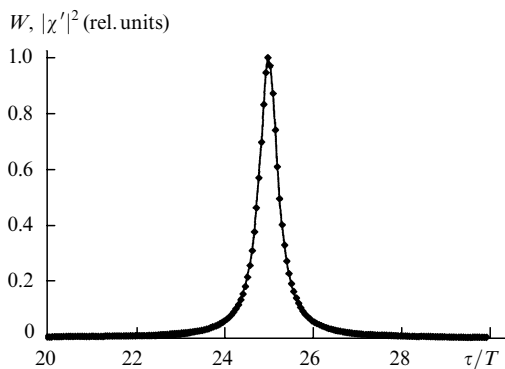


Figure 2. The energy W of the CARS signal as a function of the delay time τ between the pump pulses for $\tau_{1,2} = 60T$, $\alpha T^2 = 2$, and $\Omega T = 100$ (solid curve) and the spectral dependence of the nonlinear susceptibility $\chi'(2\alpha\tau)$ (dots).

4. The spectral resolution of chirped-pulse four-photon spectroscopy

Consider in greater detail the spectral resolution attainable with the above-described modification of four-photon spectroscopy. Expression (9) is, in fact, the Fourier transform of the nonlinear susceptibility χ multiplied by the product of the envelopes of the first and second pump pulses $B_1 B_2^*$. Since the Fourier transform of a product of two functions is equal to the convolution of the Fourier transforms of these functions, the spectral resolution $\Delta\omega_r$ of the considered method in an ideal situation is determined by the bandwidth $\Delta\omega_p$ of the product of pump envelopes $B_1 B_2^*$. In the case under consideration, when the envelopes of the pump pulses B_j do not contain additional phase modulation, the bandwidth of $B_1 B_2^*$ is of the order of the inverse duration of the product of pump-pulse envelopes. In particular, in the case of Gaussian pulse envelopes, we have $\Delta\omega_p \approx 4(\tau_1^{-2} + \tau_2^{-2})^{1/2}$ for delay times $\tau \ll \tau_1, \tau_2$, where τ_1 and τ_2 are the durations of the pump pulses.

Since the spectral resolution of the considered scheme of four-photon spectroscopy is determined by the durations of pump pulses, it seems reasonable to perform such experiments with sufficiently long, subpico- and picosecond laser pulses. In particular, using picosecond pulses, one can achieve a terahertz resolution of spectral measurements carried out in accordance with the technique described above. The spectral range of measurements in this case is determined by the chirps and durations of laser pulses. A femtosecond source can be employed in such experiments as a starting laser. Then, femtosecond pulses produced by this laser should be chirped and stretched up to the required durations.

5. Single-pulse CARS spectroscopy

Physically, the possibility of performing spectral measurements by the methods of time-resolved (nonstationary) spectroscopy with chirped pulses is due to the fact that linearly chirped pulses define a linear relation between the frequency and time variables. In the case of a spatially uniform medium, a similar time-to-space transformation can be introduced by using broad light beams (note that broad-beam FWM methods are currently widely employed for imaging the spatial distributions of physical parameters in gases and plasmas [19]). A smooth variation of the delay time between light pulses along the intersection line of broad beams in this case permits a single-pulse measurement of the CARS signal intensity as a function of the delay time between these pulses. Consequently, this approach allows the CARS spectrum to be measured on a single-pulse basis. One of possible modifications of this approach, implying the use of one broad and two narrow light beams, is shown in Fig. 3.

Single-pulse four-photon spectroscopy with chirped pulses can be also implemented with a fixed delay time between light pulses. To illustrate this possibility, we consider an FWM process where the CARS signal is generated through the interaction of three laser pulses. One of these pulses (for definiteness, the pulse with frequency ω_2) is linearly chirped, while the other two pulses are transform-limited. Let the difference of the frequencies of the pump pulses $\omega_1 - \omega_2$ be tuned to a resonance with some Raman-active transition in the nonlinear medium under study (Fig. 4). Neglecting the difference in the group velocities, we can represent the amplitudes of the incident light pulses as

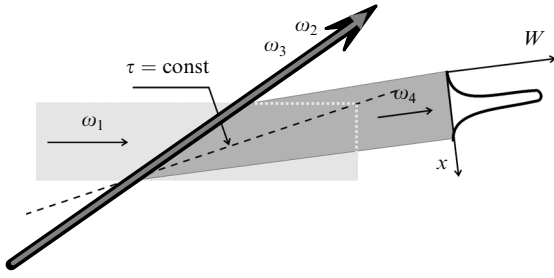


Figure 3. Diagram of light beams in chirped-pulse broad-beam CARS spectroscopy.

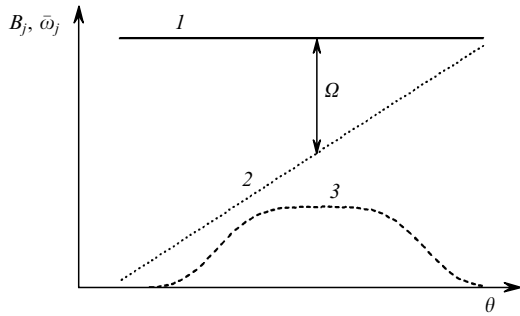


Figure 4. The instantaneous frequencies $\bar{\omega}_j$ of the first (1) and second (2) pump pulses and their envelopes B_j (3) as functions of the running time in CARS spectroscopy using chirped pulses (15)–(17).

$$A_1(\theta, z) = B_1(\theta), \quad (15)$$

$$A_2(\theta, z) = B_2(\theta) \exp(i\alpha\theta^2), \quad (16)$$

$$A_3(\theta, z) = B_3(\theta). \quad (17)$$

Using expressions (1), (2), (5), and (15)–(17) and introducing the running frame of reference θ, z , we arrive at

$$\frac{\partial A_4(\theta, z)}{\partial z} = \frac{2i\pi\omega_4^2}{k_4c^2} \int_0^\infty \chi(t_1, z) B_1(\theta - t_1) B_2^*(\theta - t_1) \times \exp\left\{i\left[\Delta\omega t_1 - \alpha(\theta - t_1)^2 - \Delta kz\right]\right\} dt_1 B_3(\theta), \quad (18)$$

where $\Delta\omega = \omega_1 - \omega_2$ and the central frequency of the CARS signal is equal to $\omega_4 = \omega_1 - \omega_2 + \omega_3$.

In the case of a spatially uniform medium, where the nonlinear susceptibility is independent of z ($\chi(t_1, z) = \chi(t_1)$), under conditions when the envelopes of the incident pulses vary only slightly within the period of time corresponding to the characteristic decay time T of the nonlinear polarisation, we have $B_1(\theta - t_1) \approx B_1(\theta)$ and $B_2(\theta - \tau - t_1) \approx B_2(\theta - \tau)$ for $t_1 \leq T$. Then, the integration of equation (18) yields

$$A_4(\theta, z) = \frac{2i\pi\omega_4^2}{k_4c^2} K(\Delta\omega + 2\alpha\theta, \alpha) B_1(\theta) B_2^*(\theta) B_3(\theta) \times \exp(-i\alpha\theta^2) \frac{\exp(-i\Delta kz) - 1}{-i\Delta k}, \quad (19)$$

where

$$K(\omega, \alpha) = \int_0^\infty \chi(t_1) \exp(i\omega t_1) \exp(-i\alpha t_1^2) dt_1. \quad (20)$$

Provided that the inequality $\alpha T^2 \ll 1$ is satisfied, we find that

$$K(\omega, \alpha) = K(\omega, 0) = \chi'(\omega). \quad (21)$$

Thus, detecting the waveform of the CARS pulse, i.e., measuring the amplitude of the CARS signal as a function of the running time θ in the considered experimental scheme, we can determine the spectrum of the relevant resonant third-order susceptibility of the medium. Note that the spectrum of the CARS signal, $S = |\int A_4(\theta, z) \exp(i\omega\theta) d\theta|^2$, under these conditions generally differs from the spectrum of the relevant nonlinear susceptibility due to the frequency dependence of the phase of the nonlinear susceptibility.

The spectral resolution of the considered scheme of four-photon spectroscopy is determined by the method employed to measure the pulse waveform. Frequency-resolved optical gating (FROG) seems to hold much promise for pulse characterisation in this scheme. The FROG technique allows the envelopes of ultrashort light pulses to be measured with a very high temporal resolution, thus, permitting a high spectral resolution to be achieved with the above-described method of chirped-pulse four-photon spectroscopy.

6. Conclusions

The new schemes of high-resolution coherent four-photon spectroscopy proposed in this paper imply that chirped light pulses are used for the Raman excitation of a nonlinear medium. In one of the considered schemes, the detuning of the difference of instantaneous frequencies of chirped pump pulses from the frequency of the studied Raman resonance is a linear function of the delay time between the pump pulses. Measuring the intensity of the CARS signal as a function of the delay time between the pump pulses under these conditions, one can analyse the spectrum of the relevant nonlinear-optical susceptibility of the medium. The spectral resolution of this method is determined by the durations of the incident light pulses. The use of picosecond pulses allows a terahertz resolution to be achieved with such a spectroscopic approach. The spectral range of measurements in this case is determined by the chirps and durations of laser pulses.

In the second scheme proposed in this paper, one of the incident light pulses is linearly chirped, while the other two are transform-limited. Then, tuning the difference of instantaneous frequencies of pump pulses around a Raman resonance, one can perform single-pulse spectroscopic measurements on the medium under study. A high spectral resolution can be achieved with this approach due to the high resolution of time-domain measurements attainable with modern methods of ultrashort-pulse characterisation.

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