This chapter provides a brief introduction into the basic nonlinear-optical phenomena and discusses some of the most significant recent advances and breakthroughs in nonlinear optics, as well as novel applications of nonlinear-optical processes and devices.

Nonlinear optics is the area of optics that studies the interaction of light with matter in the regime where the response of the material system to the applied electromagnetic field is nonlinear in the amplitude of this field. At low light intensities, typical of non-laser sources, the properties of materials remain independent of the intensity of illumination. The superposition principle holds true in this regime, and light waves can pass through materials or be reflected from boundaries and interfaces without interacting with each other. Laser sources, on the other hand, can provide sufficiently high light intensities to modify the optical properties of materials. Light waves can then interact with each other, exchanging momentum and energy, and the superposition principle is no longer valid. This interaction of light waves can result in the generation of optical fields at new frequencies, including optical harmonics of incident radiation or sum- or difference-frequency signals.

5. Nonlinear Optics

5.1 Nonlinear Polarization and Nonlinear Susceptibilities

5.2 Wave Aspects of Nonlinear Optics

5.3 Second-Order Nonlinear Processes

5.4 Third-Order Nonlinear Processes

5.5 Ultrashort Light Pulses in a Resonant Two-Level Medium: Self-Induced Transparency and the Pulse Area Theorem

5.6 Let There be White Light: Supercontinuum Generation

5.7 Nonlinear Raman Spectroscopy

5.8 Waveguide Coherent Anti-Stokes Raman Scattering

5.4.6 Optical Phase Conjugation

5.4.7 Optical Bistability and Switching

5.4.8 Stimulated Raman Scattering

5.4.9 Third-Harmonic Generation by Ultrashort Laser Pulses

5.5 Ultrashort Light Pulses in a Resonant Two-Level Medium: Self-Induced Transparency and the Pulse Area Theorem

5.5.1 Interaction of Light with Two-Level Media

5.5.2 The Maxwell and Schrödinger Equations for a Two-Level Medium

5.5.3 Pulse Area Theorem

5.5.4 Amplification of Ultrashort Light Pulses in a Two-Level Medium

5.5.5 Few-Cycle Light Pulses in a Two-Level Medium

5.6.1 Self-Phase Modulation, Four-Wave Mixing, and Modulation Instabilities in Supercontinuum-Generating Photonic-Crystal Fibers

5.6.2 Cross-Phase-Modulation-Induced Instabilities

5.6.3 Solitonic Phenomena in Media with Retarded Optical Nonlinearity

5.7.1 The Basic Principles

5.7.2 Methods of Nonlinear Raman Spectroscopy

5.7.3 Polarization Nonlinear Raman Techniques

5.7.4 Time-Resolved Coherent Anti-Stokes Raman Scattering

5.8.1 Enhancement of Waveguide CARS in Hollow Photonic-Crystal Fibers
Although the observation of most nonlinear-optical phenomena requires laser radiation, some classes of nonlinear-optical effects were known long before the invention of the laser. The most prominent examples of such phenomena include Pockels and Kerr electrooptic effects [5.1], as well as light-induced resonant absorption saturation, described by Vavilov [5.2, 3]. It was, however, only with the advent of lasers that systematic studies of optical nonlinearities and the observation of a vast catalog of spectacular nonlinear-optical phenomena became possible.

In the first nonlinear-optical experiment of the laser era, performed by Franken et al. in 1961 [5.4], a ruby-laser radiation with a wavelength of 694.2 nm was used to generate the second harmonic in a quartz crystal at the wavelength of 347.1 nm. This seminal work was followed by the discovery of a rich diversity of nonlinear-optical effects, including sum-frequency generation, stimulated Raman scattering, self-focusing, optical rectification, four-wave mixing, and many others. While in the pioneering work by Franken the efficiency of second-harmonic generation (SHG) was on the order of $10^{-3}$, optical frequency doublers created by early 1963 provided 20%–30% efficiency of frequency conversion [5.5, 6]. The early phases of the development and the basic principles of nonlinear optics have been reviewed in the most illuminating way in the classic books by Bloembergen [5.7] and Akhmanov and Khokhlov [5.8], published in the mid 1960s.

Over the following four decades, the field of nonlinear optics has witnessed an enormous growth, leading to the observation of new physical phenomena and giving rise to novel concepts and applications. A systematic introduction into these effects along with a comprehensive overview of nonlinear-optical concepts and devices can be found in excellent textbooks by Shen [5.9], Boyd [5.1], Butcher and Cotter [5.10], Reintjes [5.11] and others. One of the most recent up-to-date reviews of the field of nonlinear optics with an in-depth discussion of the fundamental physics underlying nonlinear-optical interactions was provided by Flytzanis [5.12]. This chapter provides a brief introduction into the main nonlinear-optical phenomena and discusses some of the most significant recent advances in nonlinear optics, as well as novel applications of nonlinear-optical processes and devices.
5.1 Nonlinear Polarization and Nonlinear Susceptibilities

Nonlinear-optical effects belong to a broader class of electromagnetic phenomena described within the general framework of macroscopic Maxwell equations. The Maxwell equations not only serve to identify and classify nonlinear phenomena in terms of the relevant nonlinear-optical susceptibilities or, more generally, nonlinear terms in the induced polarization, but also govern the nonlinear-optical propagation effects. We assume the absence of extraneous charges and currents and write the set of Maxwell equations for the electric, \( \mathbf{E}(\mathbf{r}, t) \), and magnetic, \( \mathbf{H}(\mathbf{r}, t) \), fields in the form

\[
\nabla \times \mathbf{E} = -\frac{1}{c} \frac{\partial \mathbf{B}}{\partial t},
\]

\[
\nabla \times \mathbf{B} = \frac{1}{c} \frac{\partial \mathbf{D}}{\partial t},
\]

\[
\nabla \cdot \mathbf{D} = 0,
\]

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

where \( \mathbf{B} = \mathbf{H} + 4\pi \mathbf{M} \), where \( \mathbf{M} \) is the magnetic dipole polarization, \( c \) is the speed of light, and

\[
\mathbf{D} = \mathbf{E} + 4\pi \int_{-\infty}^t \mathbf{J}(\zeta) \, d\zeta.
\]

Here, \( \mathbf{B} = \mathbf{H} + 4\pi \mathbf{M} \), where \( \mathbf{M} \) is the magnetic dipole polarization, \( c \) is the speed of light, and

\[
\mathbf{D} = \mathbf{E} + 4\pi \int_{-\infty}^t \mathbf{J}(\zeta) \, d\zeta.
\]

where \( \mathbf{J} \) is the induced current density. Generally, the equation of motion for these driven by the electromagnetic field has to be solved to define the relation between the induced current \( \mathbf{J} \) and the electric and magnetic fields. For quantum systems, this task can be fulfilled by solving the Schrödinger equation. In Sect. 5.5 of this chapter, we provide an example of such a self-consistent analysis of nonlinear-optical phenomena in a model two-level system. Very often a phenomenological approach based on the introduction of field-independent or local-field-corrected nonlinear-optical susceptibilities can provide an adequate description of nonlinear-optical processes.

Formally, the current density \( \mathbf{J} \) can be represented as a series expansion in multipoles:

\[
\mathbf{J} = \frac{\partial}{\partial t} (\mathbf{P} - \nabla \cdot \mathbf{Q}) + c (\nabla \times \mathbf{M}),
\]

where \( \mathbf{P} \) and \( \mathbf{Q} \) are the electric dipole and electric quadrupole polarizations, respectively. In the electric dipole approximation, we keep only the first term on the right-hand side of (5.6). In view of (5.5), this gives the following relation between the \( \mathbf{D} \), \( \mathbf{E} \), and \( \mathbf{P} \) vectors:

\[
\mathbf{D} = \mathbf{E} + 4\pi \mathbf{P}.
\]

We now represent the polarization \( \mathbf{P} \) as a sum

\[
\mathbf{P} = \mathbf{P}_L + \mathbf{P}_{NL},
\]

where \( \mathbf{P}_L \) is the part of the electric dipole polarization linear in the field amplitude and \( \mathbf{P}_{NL} \) is the nonlinear part of this polarization.

The linear polarization governs linear-optical phenomena, i.e., it corresponds to the regime where the optical properties of a medium are independent of the field intensity. The relation between \( \mathbf{P}_L \) and the electric field \( \mathbf{E} \) is given by the standard formula of linear optics:

\[
\mathbf{P}_L = \int \chi^{(1)}(t - t') \mathbf{E}(t') \, dt',
\]

where \( \chi^{(1)}(t) \) is the time-domain linear susceptibility tensor. Representing the field \( \mathbf{E} \) and polarization \( \mathbf{P}_L \) in the form of elementary monochromatic plane waves,

\[
\mathbf{E} = \mathbf{E}(\omega) \exp(i\mathbf{k} \cdot \mathbf{r} - \omega t) + \text{c.c.}
\]

and

\[
\mathbf{P}_L = \mathbf{P}_L(\omega) \exp(i\mathbf{k} \cdot \mathbf{r} - \omega t) + \text{c.c.},
\]

we take the Fourier transform of (5.9) to find

\[
\mathbf{P}_L(\omega) = \chi^{(1)}(\omega) \mathbf{E}(\omega),
\]

where

\[
\chi^{(1)}(\omega) = \int \chi^{(1)}(t) \exp(i\omega t) \, dt.
\]

In the regime of weak fields, the nonlinear part of the polarization \( \mathbf{P}_{NL} \) can be represented as a power-series expansion in the field \( \mathbf{E} \):

\[
\mathbf{P}_{NL} = \int \chi^{(2)}(t - t_1, t - t_2) : \mathbf{E}(t_1) \mathbf{E}(t_2) \, dt_1 \, dt_2
\]

\[
+ \int \int \int \chi^{(3)}(t - t_1, t - t_2, t - t_3) \cdot \mathbf{E}(t_1) \mathbf{E}(t_2) \mathbf{E}(t_3) \, dt_1 \, dt_2 \, dt_3 + \ldots,
\]

where \( \chi^{(2)} \) and \( \chi^{(3)} \) are the second- and third-order nonlinear susceptibilities.

Representing the electric field in the form of a sum of plane monochromatic waves,

\[
\mathbf{E} = \sum_i \mathbf{E}_i(\omega_i) \exp(i\mathbf{k}_i \cdot \mathbf{r} - \omega_i t) + \text{c.c.},
\]

we take the Fourier transform of (5.14) to arrive at

\[
\mathbf{P}_{NL}(\omega) = \mathbf{P}^{(2)}(\omega) + \mathbf{P}^{(3)}(\omega) + \ldots,
\]
where
\[ P^{(2)}(\omega) = \chi^{(2)}(\omega; \omega_1, \omega_2) : E(\omega_1)E(\omega_2), \] (5.17)
\[ P^{(3)}(\omega) = \chi^{(3)}(\omega; \omega_1, \omega_2, \omega_3) : E(\omega_1)E(\omega_2)E(\omega_3), \] (5.18)
\[ \chi^{(2)}(\omega; \omega_1, \omega_2) = \chi^{(2)}(\omega = \omega_1 + \omega_2) \]
\[ = \int \int \chi^{(2)}(t_1, t_2) \exp[i(\omega t_1 + \omega_2 t_2)] \, dt_1 \, dt_2 \] (5.19)
is the second-order nonlinear-optical susceptibility and
\[ \chi^{(3)}(\omega; \omega_1, \omega_2, \omega_3) = \chi^{(3)}(\omega = \omega_1 + \omega_2 + \omega_3) \]
\[ = \int \int \int \chi^{(3)}(t_1, t_2, t_3) \exp[i(\omega t_1 + \omega_2 t_2 + \omega_3 t_3)] \, dt_1 \, dt_2 \, dt_3 \] (5.20)
is the third-order nonlinear-optical susceptibility.

The second-order nonlinear polarization defined by (5.17) gives rise to three-wave mixing processes, optical rectification and linear electrooptic effect. In particular, setting \( \omega_1 = \omega_2 = \omega_0 \) in (5.17) and (5.19), we arrive at \( \omega = 2\omega_0 \), which corresponds to second-harmonic generation, controlled by the nonlinear susceptibility \( \chi^{(2)}_{\text{SHG}} = \chi^{(2)}(2\omega_0; \omega_0, \omega_0) \). In a more general case of three-wave mixing process with \( \omega_0 = \omega_1 \neq \omega_2 = \omega_2 \), the second-order polarization defined by (5.17) can describe sum-frequency generation (SFG) \( \omega_{\text{SFG}} = \omega_1 + \omega_2 \) Fig. 5.1 and difference-frequency generation (DFG) \( \omega_{\text{DFG}} = \omega_1 - \omega_2 \), governed by the nonlinear susceptibilities \( \chi^{(2)}_{\text{SFG}} = \chi^{(2)}(\omega_1; \omega_1, \omega_2) \) and \( \chi^{(2)}_{\text{DFG}} = \chi^{(2)}(\omega_2; \omega_1, -\omega_2) \), respectively.

The third-order nonlinear polarization defined by (5.18) is responsible for four-wave mixing (FWM), stimulated Raman scattering, two-photon absorption, and Kerr-effect-related phenomena, including self-phase modulation (SPM) and self-focusing. For the particular case of third-harmonic generation, we set \( \omega_1 = \omega_2 = \omega_3 = \omega_0 \) in (5.18) and (5.20) to obtain \( \omega = 3\omega_0 \). This type of nonlinear-optical interaction, in accordance with (5.18) and (5.20), is controlled by the cubic susceptibility \( \chi^{(3)}_{\text{THG}} = \chi^{(3)}(3\omega_0; \omega_0, \omega_0, \omega_0) \). A more general, frequency-nondegenerate case can correspond to a general type of an FWM process. These and other basic nonlinear-optical processes will be considered in greater details in the following sections.

### 5.2 Wave Aspects of Nonlinear Optics

In the electric dipole approximation, the Maxwell equations (5.1–5.4) yield the following equation governing the propagation of light waves in a weakly nonlinear medium:

\[ \nabla \times (\nabla \times E) - \frac{1}{c^2} \frac{\partial^2 E}{\partial t^2} = \frac{4\pi}{c^2} \frac{\partial^2 P_{\text{NL}}}{\partial t^2} = \frac{4\pi}{c^2} \frac{\partial^3 P_{\text{NL}}}{\partial t^3}. \] (5.21)

The nonlinear polarization, appearing on the right-hand side of (5.21), plays the role of a driving source, inducing an electromagnetic wave with the same frequency \( \omega \) as the nonlinear polarization wave \( P_{\text{NL}}(r, t) \). Dynamics of a nonlinear wave process can be then thought as a result of the interference of induced and driving (pump) waves, controlled by the dispersion of the medium.

Assuming that the fields have the form of quasi-monochromatic plane waves propagating along the \( z \)-axis, we represent the field \( E \) in (5.21) by

\[ E(r, t) = \text{Re} \left[ e^A(z, t) \exp(ikz - \omega t) \right] \] (5.22)

and write the nonlinear polarization as

\[ P_{\text{NL}}(r, t) = \text{Re} \left[ e^A P_{\text{NL}}(z, t) \exp(i\omega t - k\cdot r) \right], \] (5.23)

where \( k \) and \( A(z, t) \) are the wave vector and the envelope of the electric field, \( k_{\text{NL}} \) and \( P_{\text{NL}}(z, t) \) are the wave vector and the envelope of the polarization wave.

If the envelope \( A(z, t) \) is a slowly varying function over the wavelength, \( |\partial^2 A/\partial z^2| \ll |k\partial A/\partial z| \), and \( \partial^2 P_{\text{NL}}/\partial t^2 \approx -i\omega^2 P_{\text{NL}} \) (5.21) is reduced to (5.9)

\[ \frac{\partial A}{\partial z} + \frac{1}{k} \frac{\partial A}{\partial t} = \frac{2\pi k^2}{k^2 c^2} P_{\text{NL}} \exp(i\Delta k z), \] (5.24)
where \( u = (\Delta k / 3\omega)^{-1} \) is the group velocity and \( \Delta k = k_p - k \) is the wave-vector mismatch.

In the following sections, this generic equation of slowly varying envelope approximation (SVEA) will be employed to analyze the wave aspects of the basic second- and third-order nonlinear-optical phenomena.

5.3 Second-Order Nonlinear Processes

5.3.1 Second-Harmonic Generation

In second-harmonic generation, a pump wave with a frequency of \( \omega \) generates a signal at the frequency \( 2\omega \) as it propagates through a medium with a quadratic nonlinearity (Fig. 5.1). Since all even-order nonlinear susceptibilities \( \chi^{(n)} \) vanish in centrosymmetric media, SHG can occur only in media with no inversion symmetry.

Assuming that diffraction and second-order dispersion effects are negligible, we use (5.24) for a quadratically nonlinear medium with a nonlinear SHG susceptibility \( \chi_{\text{SHG}}^{(2)} = \chi^{(2)}(2\omega; \omega, \omega) \) to write a pair of coupled equations for the slowly varying envelopes of the pump and second-harmonic fields \( A_1 = A_1(z, t) \) and \( A_2 = A_2(z, t) \):

\[
\begin{align*}
\frac{\partial A_1}{\partial z} + \frac{1}{u_1} \frac{\partial A_1}{\partial t} &= i\gamma_1 A_1^2 A_2 \exp(i\Delta k z), \\
\frac{\partial A_2}{\partial z} + \frac{1}{u_2} \frac{\partial A_2}{\partial t} &= i\gamma_2 A_1^2 \exp(-i\Delta k z),
\end{align*}
\]

(5.25)

(5.26)

where

\[
\gamma_1 = \frac{2\pi\omega_1^2}{k_1 c^2} \chi^{(2)}(\omega; 2\omega, -\omega)
\]

(5.27)

\[
\gamma_2 = \frac{4\pi\omega_1^2}{k_2 c^2} \chi_{\text{SHG}}^{(2)}
\]

(5.28)

are the nonlinear coefficients, \( u_1 \) and \( u_2 \) are the group velocities of the pump and second-harmonic pulses, respectively, and \( \Delta k = 2k_1 - k_2 \) is the wave-vector mismatch for the SHG process.

If the difference between the group velocities of the pump and second-harmonic pulses can be neglected for a nonlinear medium with a given length and if the intensity of the pump field in the process of SHG remains much higher than the intensity of the second-harmonic field, we set \( u_1 = u_2 = u \) and \( |A_1|^2 = |A_10|^2 = \text{const.} \) in (5.25) and (5.26) to derive in the retarded frame of reference with \( z' = z \) and \( t = \tau + z / u \):

\[
A_2(L) = i\gamma_2 A_{10}^2 \sin \left( \frac{\Delta k L}{2} \right) L \exp \left( i\Delta k L \right). \tag{5.29}
\]

where \( L \) is the length of the nonlinear medium.

The intensity of the second-harmonic field is then given by

\[
I_2(L) \propto \gamma_2^2 I_{10}^2 \left( \frac{\sin \left( \frac{\Delta k L}{2} \right)^2}{\Delta k L} \right)^2 L^2, \tag{5.30}
\]

where \( I_{10} \) is the intensity of the pump field.

Second-harmonic intensity \( I_2 \), as can be seen from (5.30), oscillates as a function of \( L \) Fig. 5.2 with a period \( L_c = \pi / |\Delta k| = \lambda_1 (n_1 - n_2) \), where \( \lambda_1 \) is the pump wavelength and \( n_1 \) and \( n_2 \) are the values of the refractive index at the frequencies of the pump field and its second harmonic, respectively. The parameter \( L_c \), defining the length of the nonlinear medium providing the maximum SHG efficiency, is referred to as the coherence length.

![Fig. 5.2 Second-harmonic intensity as a function of the length L of the nonlinear medium normalized to the coherence length Lc for two values of Lc: (dashed line) Lc1 and (solid line) Lc2 = 2Lc1](image-url)
Although the solution (5.29) describes the simplest regime of SHG, it is very instructive as it visualizes the significance of reducing the wave-vector mismatch $\Delta k$ for efficient SHG. Since the wave vectors $k_1$ and $k_2$ are associated with the momenta of the pump and second-harmonic fields, $p_1 = \hbar k_1$ and $p_2 = \hbar k_2$, with $\hbar$ being the Planck constant, the condition $\Delta k = 0$, known as the phase-matching condition in nonlinear optics, in fact, represents momentum conservation for the SHG process, where two photons of the pump field are required to generate a single photon of the second harmonic.

Several strategies have been developed to solve the phase-matching problem for SHG. The most practically significant solutions include the use of birefringent nonlinear crystals [5.13, 14], quasi-phase-matching in periodically poled nonlinear materials [5.15, 16] and waveguide regimes of nonlinear interactions with the phase mismatch related to the material dispersion compensated for by waveguide dispersion [5.7]. Harmonic generation in the gas phase, as demonstrated by Miles and Harris [5.17], can be phase-matched through an optimization of the content of the gas mixture. Figure 5.3 illustrates phase matching in a birefringent crystal. The circle represents the cross section of the refractive-index sphere $n_0(\omega)$ for an ordinary wave at the pump frequency $\omega$. The ellipse is the cross section of the refractive-index ellipsoid $n_e(2\omega)$ for an extraordinary wave at the frequency of the second harmonic $2\omega$. Phase matching is achieved in the direction where $n_0(\omega) = n_e(2\omega)$, corresponding to an angle $\theta_{pm}$ with respect to the optical axis $c$ of the crystal in Fig. 5.3.

When the phase-matching condition $\Delta k = 0$ is satisfied, (5.29) and (5.30) predict a quadratic growth of the second-harmonic intensity as a function of the length $L$ of the nonlinear medium. This scaling law holds true, however, only as long as the second-harmonic intensity remains much less than the pump intensity. As $|A_2|$ becomes comparable with $|A_1|$, depletion of the pump field has to be taken into consideration. To this end, we introduce the real amplitudes $\rho_j$ and phases $\varphi_j$ of the pump and second-harmonic fields, $A_j = \rho_j \exp(i\varphi_j)$, with $j = 1, 2$. Then, assuming that $u_1 = u_2 = u$ and $\gamma_1 = \gamma_2 = \gamma$, we derive from (5.25) and (5.26)

$$\rho_1(\eta, z) = \rho_{10}(\eta) \text{sech} [\gamma \rho_{10}(\eta) z], \quad (5.31)$$

$$\rho_2(\eta, z) = \rho_{10}(\eta) \tanh [\gamma \rho_{10}(\eta) z]. \quad (5.32)$$

The solutions (5.31) and (5.32) show that the entire energy of the pump field in the phase-matching regime can be transferred to the second harmonic. As the pump field becomes depleted Fig. 5.4, the growth of the second-harmonic field saturates.

Effects related to the group-velocity mismatch become significant when the length of the nonlinear medium $L$ exceeds the length $L_g = \tau_1/|u_2^{-1} - u_1^{-1}|$, where $\tau_1$ is the pulse width of the pump field. The length $L_g$ characterizes the walk-off between the pump and second-harmonic pulses caused by the group-velocity mismatch. In this nonstationary regime of SHG, the amplitude of the second harmonic in the constant-pump-
field approximation is given by

\[ A_2 (z, t) = i \gamma_2 \int_0^z A_{10}^2 \left( -z/u_2 + \xi \left( u_2^{-1} - u_1^{-1} \right) \right) \times \exp \left( -i \Delta k \xi \right) \, d \xi. \]  

(5.33)

Group-velocity mismatch may lead to a considerable increase in the pulse width of the second harmonic \( \tau_2 \). For \( L \gg L_0 \), the second harmonic pulse width, \( \tau_2 \approx |u_2^{-1} - u_1^{-1}|z \), scales linearly with the length of the nonlinear medium and is independent of the pump pulse width.

### 5.3.2 Sum- and Difference-Frequency Generation and Parametric Amplification

In sum-frequency generation Fig. 5.1, two laser fields with frequencies \( \omega_1 \) and \( \omega_2 \) generate a nonlinear signal at the frequency \( \omega_3 = \omega_1 + \omega_2 \) in a quadratically nonlinear medium with a nonlinear susceptibility \( \chi^{(2)}_{\text{SFG}} \). In the first order of dispersion theory, the coupled equations for slowly varying envelopes of the laser fields \( A_1 = A_1(z, t) \) and \( A_2 = A_2(z, t) \) and the nonlinear signal \( A_3 = A_3(z, t) \) are written as

\[ \frac{\partial A_1}{\partial z} + \frac{1}{u_1} \frac{\partial A_1}{\partial t} = i \gamma_1 A_3 A_1^* \exp \left( i \Delta k z \right), \]  
\[ \gamma_1 = \frac{2 \pi \omega_1^2}{k_1 c} \chi^{(2)}_{\text{SFG}} (\omega_1; \omega_3, -\omega_2), \]  
\[ \frac{\partial A_2}{\partial z} + \frac{1}{u_2} \frac{\partial A_2}{\partial t} = i \gamma_2 A_3 A_2^* \exp \left( i \Delta k z \right), \]  
\[ \gamma_2 = \frac{2 \pi \omega_2^2}{k_2 c} \chi^{(2)}_{\text{SFG}} (\omega_2; \omega_3, -\omega_1), \]  
\[ \frac{\partial A_3}{\partial z} + \frac{1}{u_3} \frac{\partial A_3}{\partial t} = i \gamma_3 A_1 A_2^* \exp \left( -i \Delta k z \right), \]  
\[ \gamma_3 = \frac{2 \pi \omega_3^2}{k_3 c} \chi^{(2)}_{\text{SFG}}, \]  

(5.34) (5.37) (5.35) (5.38) (5.36) (5.39)

are the nonlinear coefficients, \( u_1, u_2, \) and \( u_3 \) and \( k_1, k_2, \) and \( k_3 \) are the group velocities and the wave vectors of the fields with frequencies \( \omega_1, \omega_2, \) and \( \omega_3, \) respectively, and \( \Delta k = k_1 + k_2 - k_3 \) is the wave-vector mismatch for the SFG process.

As long as the intensity of the sum-frequency field remains much less than the intensities of the laser fields, the amplitudes of the laser fields can be assumed to be given functions of \( z, A_1(z, t) = A_{10}(t) \) and \( A_2(z, t) = A_{20}(t) \), and the solution of (5.36) yields

\[ A_1 (z, t) = i \gamma_1 \int_0^z A_{10} \left[ t - z/u_1 + \xi \left( u_1^{-1} - u_3^{-1} \right) \right] \times \exp \left( -i \Delta k \xi \right) \, d \xi. \]  
\[ A_3 (z, t) = i \gamma_3 \int_0^z A_{20} \left[ t - z/u_3 + \xi \left( u_3^{-1} - u_1^{-1} \right) \right] \times \exp \left( -i \Delta k \xi \right) \, d \xi. \]  

(5.40)

The efficiency of frequency conversion, as can be seen from (5.40), is controlled by the group delays \( \Delta_{21} \approx |u_2^{-1} - u_1^{-1}|L, \Delta_{31} \approx |u_1^{-1} - u_3^{-1}|L, \) and \( \Delta_{32} \approx |u_3^{-1} - u_2^{-1}|L \) between the pulses involved in the SFG process. In particular, the laser fields cease to interact with each other when the group delay \( \Delta_{21} \) starts to exceed the pulse width of the faster laser pulse.

In difference-frequency generation (DFG), two input fields with frequencies \( \omega_1 \) and \( \omega_2 \) generate a nonlinear signal at the frequency \( \omega_3 = \omega_1 - \omega_2 \). This process is of considerable practical significance as it can give rise to intense coherent radiation in the infrared range. In the limiting case of \( \omega_1 \approx \omega_2 \), this type of nonlinear-optical interaction corresponds to optical rectification, which has been intensely used over the past two decades for the generation of terahertz radiation.

If the field at the frequency \( \omega_1 \) is strong and remains undepleted in the process of nonlinear-optical interaction, \( A_1(z, t) = A_{10}(t) \), the set of coupled equations governing the amplitudes of the remaining two fields in the stationary regime is written as

\[ \frac{\partial A_2}{\partial z} + \frac{1}{u_2} \frac{\partial A_2}{\partial t} = i \gamma_2 A_1 A_2^* \exp \left( i \Delta k z \right), \]  
\[ \frac{\partial A_3}{\partial z} + \frac{1}{u_3} \frac{\partial A_3}{\partial t} = i \gamma_3 A_1 A_2^* \exp \left( -i \Delta k z \right), \]  

(5.41) (5.42)

where,

\[ \gamma_2 = \frac{2 \pi \omega_2^2}{k_2 c} \chi^{(2)}_{\text{DFG}} (\omega_2; \omega_1, -\omega_2), \]  
\[ \gamma_3 = \frac{2 \pi \omega_3^2}{k_3 c} \chi^{(2)}_{\text{DFG}}, \]  

(5.43) (5.44)

are the nonlinear coefficients and \( \Delta k = k_1 - k_2 - k_3 \) is the wave-vector mismatch for the DFG process.

With no signal at \( \omega_3 \) applied at the input of the nonlinear medium, \( A_3(0, t) = 0 \), the solution to (5.41) and (5.42) in the stationary regime is given by [5.12]

\[ A_2 (z) = A_{20} (0) \left[ \cosh \left( \Delta k z \right) + i \Delta k \frac{\sinh \left( \Delta k z \right)}{\Delta k} \right], \]  
\[ A_3 (z) = i A_{20} (0) \sinh \left( \Delta k z \right). \]  

(5.45) (5.46)
where
\[ \kappa^2 = 4\gamma_2 \gamma_3 |A_1|^2 - (\Delta k)^2. \] (5.47)
Away from the phase-matching condition, the amplification of a weak signal is achieved only when the intensity of the pump field exceeds a threshold,
\[ I_1 > I_{th} = \frac{n_1 n_2 n_3 c^3 (\Delta k)^2}{32\pi^3 |\chi^{(2)}_{DFG}|^2 \omega_2 \omega_3}, \] (5.48)
where we took
\[ \chi^{(2)}(\omega_2; \omega_1, -\omega_3) \approx \chi^{(2)}(\omega_3; \omega_1, -\omega_2) = \chi^{(2)}_{DFG}. \]
Above, this threshold, the growth in the intensity \( I_2 \) of a weak input signal is governed by
\[ I_2(z) = I_2(0) \left[ \frac{\gamma_2 \gamma_3 |A_{10}|^2}{\kappa^2} \sin^2(\kappa z) + 1 \right]. \] (5.49)
This type of three-wave mixing is often referred to as optical parametric amplification. A weak input field, referred to as the signal field (the field with the amplitude \( A_2 \) in our case), becomes amplified in this type of process through a nonlinear interaction with a powerful pump field (the undepleted field with the amplitude \( A_1 \) in the case considered here). In such a scheme of optical parametric amplification, the third field (the field with the amplitude \( A_3 \)) is matched in its group velocities.

We now consider the regime of optical parametric amplification \( A_{10} = \omega_2 + \omega_3 \) where the pump, signal, and idler pulses are matched in their wave vectors and group velocities. Introducing the real amplitudes \( \rho_j \) and phases \( \varphi_j \) of the pump, signal, and idler fields, \( A_j = \rho_j \exp(i \varphi_j) \), where \( j = 1, 2, 3 \), assuming that \( \gamma_2 = \gamma_3 = \gamma \) in (5.35) and (5.36), \( A_1(z, t) = A_{10}(t) \) and \( A_3(0, t) = 0 \), we write the solution for the amplitude of the signal field as \([5.18]\)
\[ A_2(\eta, z) = A_{20}(\eta) \cosh [\gamma \rho_{10} (\eta) z]. \] (5.50)
The idler field then builds up in accordance with
\[ A_3(\eta, z) = A_{30}(\eta) \exp[i \varphi_{10}(\eta)] \sinh [\gamma \rho_{10}(\eta) z]. \] (5.51)
As can be seen from (5.50), optical parametric amplification preserves the phase of the signal pulse. This property of optical parametric amplification lies at the heart of the principle of optical parametric chirped-pulse amplification \([5.19]\), allowing ultrashort laser pulses to be amplified to relativistic intensities. It also suggests a method of efficient frequency conversion of few-cycle field waveforms without changing the phase offset between their carrier frequency and temporal envelope, making few-cycle laser pulses a powerful tool for the investigation of ultrafast electron dynamics in atomic and molecular systems.

In the nonstationary regime of optical parametric amplification, when the pump, signal, and idler fields propagate with different group velocities, useful and important qualitative insights into the phase relations between the pump, signal, and idler pulses can be gained from energy and momentum conservation, \( \omega_1 = \omega_2 + \omega_3 \) and \( k_1 = k_2 + k_3 \). These equalities dictate the following relations between the frequency deviations \( \delta \omega_j \) in the pump, signal, and idler fields \( (j = 1, 2, 3) \):
\[ \delta \omega_1 = \delta \omega_2 + \delta \omega_3 \] (5.52)
and
\[ \delta \omega_1/u_1 = \delta \omega_2/u_2 + \delta \omega_3/u_3. \] (5.53)
In view of (5.52) and (5.53), we find
\[ \delta \omega_2 = q_2 \delta \omega_1 \] (5.54)
and
\[ \delta \omega_3 = q_3 \delta \omega_1, \] (5.55)
where \( q_2 = (u_1^{-1} - u_3^{-1})/(u_2^{-1} - u_1^{-1}), q_3 = 1 - q_2, \) and \( q_m = \alpha_m t^2/2, (\Delta m = q_m \alpha_1, m = 2, 3). \) In the case of a linearly chirped pump, \( \varphi_1(t) = \alpha_1 t^2/2 \), the phases of the signal and idler pulses are given by \( \varphi_m(t) = \alpha_m t^2/2 \), where \( q_m = \alpha_m \alpha_1, \) \( m = 2, 3. \) With \( q_m \gg 1 \), the chirp of the signal and idler pulses can thus considerably exceed the chirp of the pump field.

### 5.4 Third-Order Nonlinear Processes

Optical nonlinearity of the third order is a universal property, found in any material regardless of its spatial symmetry. This nonlinearity is the lowest-order nonvanishing nonlinearity for a broad class of centrosymmetric materials, where all the even-order nonlinear susceptibilities are identically equal to zero for symmetry reasons. Third-order nonlinear processes include a vast variety of four-wave mixing processes, which are extensively used for frequency conversion of laser radiation and as powerful methods of nonlinear spectroscopy. Frequency-degenerate, Kerr-effect-type phenomena constitute another important class of third-
order nonlinear processes. Such effects lie at the heart of optical compressors, mode-locked femtosecond lasers, and numerous photonic devices, where one laser pulse is used to switch, modulate, or gate another laser pulse. In this section, we provide a brief overview of the main third-order nonlinear-optical phenomena and discuss some of their practical applications.

5.4.1 Self-Phase Modulation

The third-order nonlinearity gives rise to an intensity-dependent additive to the refractive index:

\[ n = n_0 + n_2 I(t) \].  

(5.56)

where \( n_0 \) is the refractive index of the medium in the absence of light field, \( n_2 \) is the nonlinear refractive index, \( \chi^{(3)}(\omega; \omega, -\omega) \) is the third-order nonlinear-optical susceptibility, referred to as the Kerr-type nonlinear susceptibility, and \( I(t) \) is the intensity of laser radiation. Then, the nonlinear (intensity-dependent) phase shift of a pulse at a distance \( L \) is given by

\[ \Phi(t) = \frac{\omega}{c} n_2 L \frac{\partial I(t)}{\partial t} \].  

(5.57)

Due to the time dependence of the radiation intensity within the light pulse, the nonlinear phase shift is also time-dependent, giving rise to a generally time-dependent frequency deviation:

\[ \Delta \omega(t) = \frac{\omega}{c} n_2 L \frac{\partial I(t)}{\partial t} \].  

(5.58)

The resulting spectral broadening of the pulse can be estimated in the following way:

\[ \Delta \omega = \frac{\omega}{c} n_2 L \frac{I_0}{\tau} \],  

(5.59)

where \( I_0 \) is the peak intensity of the light pulse and \( \tau \) is the pulse duration.

The first-order dispersion-theory equation for the slowly varying envelope \( A(t, z) \) of a laser pulse propagating in a medium with a Kerr-type nonlinearity is written as [5.9]

\[ \frac{\partial A}{\partial z} + \frac{1}{u} \frac{\partial A}{\partial t} = i \bar{\gamma} |A|^2 A \],  

(5.60)

where \( u \) is the group velocity of the laser pulse and

\[ \bar{\gamma} = \frac{3\pi\omega}{2n_0^2 c^3} \chi^{(3)}(\omega; \omega, -\omega, \omega) \].  

(5.61)

is the nonlinear coefficient.

In the retarded frame of reference, \( z' = z - \eta \) and \( \eta = t - z/u \), the solution to (5.60) is written as

\[ A(\eta, z) = A_0(\eta) \exp \left[ i \bar{\gamma} |A_0(\eta)|^2 z \right] \].  

(5.62)

where \( A_0(\eta) \) is the initial field envelope.

Since the group-velocity dispersion was not included in (5.60), the shape of the pulse envelope remains unchanged as the pulse propagates through the nonlinear medium. The intensity-dependent change in the refractive index gives rise to a nonlinear phase shift

\[ \varphi_{NL}(\eta, z) = \gamma_{SPM} I_0(\eta) z \].  

(5.63)

where \( \gamma_{SPM} = 2\pi n_2/\lambda \) and \( I_0(\eta) \) is the initial intensity envelope.

The deviation of the instantaneous frequency of the pulse is given by

\[ \delta \omega(\eta, z) = - \frac{\partial \varphi_{NL}(\eta, z)}{\partial t} = - \gamma_{SPM} \frac{\partial I_0(\eta)}{\partial \eta} z \].  

(5.64)

A quadratic approximation of the pulse envelope,

\[ I_0(\eta) \approx I_0(0) \left( 1 - \frac{\eta^2}{\tau_0^2} \right) \],  

(5.65)

where \( \tau_0 \) is the pulse width, which is valid around the maximum of the laser pulse, gives a linear chirp of the

![Fig. 5.5](image-url) Self-phase-modulation-induced spectral broadening of a sech-shaped laser pulse with an initial pulse width of 30 fs in a fused-silica optical fiber with \( n_2 = 3.2 \times 10^{-16} \text{ cm}^2/\text{W} \). Curve 1 presents the input spectrum of the pulse. The input pulse energy (2) 0.1 nJ, (3) 0.2 nJ, and (4) 0.5 nJ.
Basic Principles and Materials

5.4 Part A

Modulation and pulse compression may take place in the propagation of the pulse. In certain regimes of pulse propagation, self-phase modulation and pulse compression are now widely used for the purposes of pulse compression. Systems of diffraction gratings and, recently, multilayer chirped mirrors [5.20] are now widely used for the purposes of pulse compression. This can be achieved by designing a dispersive element with the required sign of dispersion and appropriate dispersion relation. Systems of diffraction gratings and, recently, multilayer chirped mirrors [5.20] are now widely used for the purposes of pulse compression. In certain regimes of pulse propagation, self-phase modulation and pulse compression may take place in the same medium.

5.4.2 Temporal Solitons

The nonlinear phase shift acquired by a laser pulse propagating through a medium with a Kerr nonlinearity can be balanced by group-velocity dispersion, giving rise to pulses propagating through the nonlinear dispersive medium with an invariant or periodically varying shape: optical solitons.

Optical solitons is a special class of solutions to the nonlinear Schrödinger equation (NLSE)

\[ i \frac{\partial q}{\partial t} + \frac{1}{2} \frac{\partial^2 q}{\partial \tau^2} + |q|^2 q = 0. \]  

(5.68)

The NLSE can describe the evolution of optical wave packets including the dispersion \( \beta(\omega) \) of optical waves in a bulk material or in a waveguide structure through the power series expansion

\[ \beta(\omega) \approx \beta(\omega_0) + \frac{1}{u} (\omega - \omega_0) + \frac{1}{2} \beta_2 (\omega - \omega_0)^2 + \ldots, \]  

(5.69)

where \( \omega_0 \) is the central frequency of the wave packet, \( u = (\beta(\omega)/\beta(\omega_0))^{-1} \) is the group velocity, and \( \beta_2 = \partial^2 \beta/\partial \omega^2 |_{\omega=\omega_0} \). Thus, with the NLSE (5.68) projected on laser pulses propagating in a nonlinear medium, \( q \) is understood as the normalized pulse envelope, \( q = A/(P_0)^{1/2} \), with \( \xi \) being the normalized propagation coordinate, \( \xi = z/L_d \), \( L_d = \tau_0^2/|\beta_2| \) being the dispersion length, \( P_0 \) and \( \tau_0 \) defined as the pulse width and the pulse peak power, respectively, and \( \tau = (t-z/u)/\tau_0 \).

The canonical form of the fundamental soliton solution to (5.68) is [20]

\[ q(\xi, \tau) = \text{sech}(\tau) \exp \left( \frac{i \xi}{2} \right). \]  

(5.70)

The radiation peak power required to support such a soliton is given by

\[ P_0 = |\beta_2|/(\gamma \tau_0^2). \]  

(5.71)

Solitons retain their stable shape as long as their spectrum lies away from the spectrum of dispersive waves that can propagate in the medium. High-order dispersion perturbs solitons, inducing Cherenkov-type wave-matching resonances between solitons and dispersive waves [5.21, 22]. Under these conditions solitons tend to lose a part of their energy in the form of blue-shifted dispersive-wave emission. For low pump-field powers, the generic wave-matching condition for such soliton–dispersive wave resonances is written [5.22]

\( \Omega = 1/2\epsilon, \) where \( \Omega \) is the frequency difference between the soliton and the resonant dispersive wave and \( \epsilon \) is the parameter controlling the smallness of perturbation of the nonlinear Schrödinger equation, which can be represented as \( \epsilon = |\beta_3/6\beta_2| \) for photonic-crystal fibers.
(PCFs) with second-order dispersion \( \beta_2 = \partial^2 \beta / \partial \omega^2 \) and third-order dispersion \( \beta_3 = \partial^3 \beta / \partial \omega^3 \). This dispersive wave emission of solitons is an important part of supercontinuum generation in nonlinear optical fibers, including photonic-crystal fibers.

### 5.4.3 Cross-Phase Modulation

Cross-phase modulation (XPM) is a result of nonlinear-optical interaction of at least two physically distinguishable light pulses (i.e., pulses with different frequencies, polarizations, mode structures, etc.) related to the phase modulation of one of the pulses (a probe pulse) due to the change in the refractive index of the medium induced by another pulse (a pump pulse).

The cross-action of a pump pulse with a frequency \( \omega_1 \) on a probe pulse with a frequency \( \omega_2 \) gives rise to a phase shift of the probe pulse, which can be written as [5.23].

\[
\Phi_{\text{XPM}}(\eta, z) = -\frac{3\pi n_0^2}{c^2 k_2} \chi^{(3)}(\omega_1, \omega_1, \omega_p, -\omega_p) \int_0^z \left| A_p \left( \eta - \frac{\xi}{\sigma}, 0 \right) \right|^2 d\xi ,
\]

where \( \chi^{(3)}(\omega_1, \omega_1, \omega_p, -\omega_p) \) is the third-order nonlinear-optical susceptibility of the medium; \( 1/\sigma = 1/u_1 - 1/u_2; u_1 \) and \( u_2 \) are the group velocities of the pump and probe pulses, respectively; and \( k_2 \) is the wave number of the pump pulse. Taking the time derivative of the nonlinear phase shift, we arrive at the following expression for the frequency deviation of the probe pulse

\[
\delta \omega_{\text{XPM}}(\eta, z) = -\frac{3\pi n_0^2}{c^2 k_2} \chi^{(3)}(\omega_1, \omega_1, \omega_p, -\omega_p) \times \sigma \left[ \left| A_p (\eta, 0) \right|^2 - \left| A_p \left( \eta - \frac{z}{\sigma}, 0 \right) \right|^2 \right] .
\]

Similarly to self-phase modulation, cross-phase modulation can be employed for pulse compression. The dependence of the chirp of the probe pulse on the pump pulse intensity can be used to control the parameters of ultrashort pulses [5.24]. Cross-phase modulation also opens the ways to study the dynamics of ultrafast nonlinear processes, including multiphoton ionization, and to characterize ultrashort light pulses through phase measurements on a short probe pulse [5.25].

#### 5.4.4 Self-Focusing

Self-focusing is a spatial counterpart of self-phase modulation. While SPM originates from the time-dependent change in the refractive index induced by a laser pulse with an intensity envelope \( I(\tau) \) varying in time, self-focusing is related to a nonlinear lens induced by a laser beam with a spatially nonuniform intensity distribution \( I(r) \). Given a transverse intensity profile \( I(r) \), the nonlinear additive to the refractive index is written as

\[
n(r) = n_0 + n_2 I (r) .
\]

If the field intensity peaks at the center of the beam at \( r = 0 \), the nonlinear change in the refractive index also reaches its maximum at \( r = 0 \), yielding a focusing or defocusing lens, depending on the sign of \( n_2 \).

The stationary regime of self-focusing is governed by [5.9]

\[
2\kappa \frac{\partial A}{\partial z} + \Delta \perp A = -2k_2 \frac{n_1}{n_0} A ,
\]

where \( \Delta n = n_2 I = \bar{n}_2 |E|^2 \), \( \Delta \perp \) is the transverse part of the Laplacian.

We consider a Gaussian beam and assume that this beam retains its profile as it propagates through the nonlinear medium,

\[
A(r, z) = \frac{A_0}{f(z)} \exp \left[ -\frac{r^2}{2a_0^2 f^2(z)} + i\psi(z) \right] ,
\]

where \( a_0 \) is the initial beam size, \( f(z) \) characterizes the evolution of the beam size along the propagation coordinate \( z \) \( f(0) = 1 \), and the function \( \psi(z) \) describes the spatial phase modulation of the field.

In the paraxial approximation, \( r \ll a_0 f(z) \), (5.75) and (5.76) give [5.18]

\[
\frac{d^2 f}{dz^2} = \frac{L_{\text{NL}}^2 - L_{\text{diff}}^2}{f^3(z)} ,
\]

where \( L_{\text{diff}} = 2\pi a_0^2 / \lambda \) and \( L_{\text{NL}} = a_0 [2n_0 / (n_2 |A|^2)]^{1/2} \) are the characteristic diffraction and nonlinear lengths, respectively.

Solving (5.77), we arrive at

\[
f^2(z) = 1 + \left( \frac{z}{L_{\text{diff}}} \right)^2 \left( 1 - \frac{P_0}{P_{\text{cr}}} \right) ,
\]

where \( P_0 \) is the total power of the laser beam and

\[
P_{\text{cr}} = \frac{c\kappa^2}{16\pi^2 n_2}
\]

is the critical power of self-focusing. The focal length of the nonlinear lens is given by

\[
L_{\text{diff}} = \frac{L_{\text{diff}}}{\left( \frac{P_0}{P_{\text{cr}}} - 1 \right)^{1/2}} .
\]
With $P_0 > P_{cr}$, the nonlinear lens leads to a beam collapse. In reality, beam collapse can be arrested by the saturation of optical nonlinearity occurring at high field intensities.

Beyond the paraxial approximation, the scenario of self-focusing is much more complicated. The beam does not collapse as a whole, as the focal length of the nonlinear lens for peripheral beams differs from the one for paraxial beams. In the quasistationary regime, i.e., when the pulse duration $\tau_0$ is much larger than the characteristic response time of optical nonlinearity $\tau_{nl}$, the length of self-focusing is a function of time, giving rise to moving foci [5.26]. In the nonstationary regime, i.e., on time scales less than $\tau_{nl}$, the leading edge of the pulse experiences no focusing, but induces a nonlinear lens that focuses the trailing edge of the pulse. As a result, the beam becomes distorted, evolving to a hornlike pattern [5.27].

The equation of self-focusing (5.75) allows a waveguide solution [5.28, 5.29], which corresponds to the regime where the nonlinear lens exactly compensates for the diffraction of the laser beam. This solution is, however, unstable with respect to infinitely small fluctuations, which either give rise to a diffraction divergence or lead to a beam collapse. Such nonlinear waveguides can be stabilized, as shown by Fibich and Gaeta [5.29], by reflections of light from guiding boundaries in optical waveguides. To illustrate this regime of nonlinear beam dynamics, we consider a cylindrical gas-filled hollow waveguide and define nondimensional cylindrical coordinates $r$ and $z$ as $r = R/r_0$ ($R$ is the inner radius of the hollow fiber) and $z = Z/L_{df}$ ($Z$ is the dimensional longitudinal coordinate). The radial profiles $Q_{\beta}(r)$ of light intensity distribution in the waveguide solutions $\psi \propto \exp(i\beta z)Q_{\beta}(r)$ to the NLSE governing self-focusing (i.e., waveguides induced through the Kerr nonlinearity along the $z$-axis on a bounded domain with a circular symmetry) are described [28, 29] by solutions to the ordinary differential equation
\[
\Delta_{\perp} Q_{\beta} - \beta Q_{\beta} + Q_{\beta}^3 = 0 \quad (\Delta_{\perp} = \partial^2/\partial r^2 + (1/r)\partial/\partial r),
\]
subject to the boundary conditions $Q_{\beta}(0)/dr = 0, Q_{\beta}(1) = 0$. Although this model neglects the fields outside the fiber core (e.g., radiation modes), it provides useful physical insights into the spatial self-action in hollow PCFs. This differential equation has an infinite number of solutions $Q_{\beta}^{(n)}$, $n = 0, 1, 2, \ldots$. The Hamiltonians for all the guided modes $Q_{\beta}^{(n)}$ are positive, preventing the blowup of the profiles $Q_{\beta}^{(n)}$ in the presence of small fluctuations, thus stabilizing the nonlinear waveguides in a hollow fiber. The ground-state solution $Q_{\beta}^{(0)}$ is a monotonically decreasing function of $r$, tending to a zeroth-order Bessel function in the case of low field amplitudes $Q_{\beta}^{(0)} \propto \varepsilon J_0(2.4r)$, where $\varepsilon$ is a small parameter controlled by the field intensity and the nonlinearity of the gas filling the fiber.

Although the modes $Q_{\beta}^{(n)}$ are stable with respect to small perturbations, these solutions are centers, rather than attractors, in a conservative system [5.30]. However, mode solutions corresponding to Kerr nonlinearity-induced waveguides may become attractors in systems with dissipation, e.g., in hollow waveguides.
with losses. The circularly symmetric field distribution is then formed at the output of the hollow waveguide regardless of the initial beam profile [30]. As demonstrated by Moll et al. [5.31], collapsing light beams tend to form universal, Townesian profiles [5.28] while undergoing self-focusing on an infinite domain in bulk materials. Unlike Townesian beam profiles, which are known to be unstable in free space, the ground-state waveguide modes observed in hollow photonic-crystal fibers [5.32] remain stable with respect to small fluctuations, in agreement with the theory of self-focusing on bounded domains [5.29, 30], resulting in no blowup until the critical power of beam collapse is reached.

5.4.5 Four-Wave Mixing

In general-type four-wave mixing (Fig. 5.6a), three laser fields with frequencies \(\omega_1\), \(\omega_2\), and \(\omega_3\) generate the fourth field with a frequency \(\omega_{\text{FWM}} = \omega_1 + \omega_2 + \omega_3\). In the case when all three laser fields have the same frequency (for example, when all the three pump photons are taken from the same laser field), \(\omega_{\text{FWM}} = 3\omega\) (Fig. 5.6b), and we deal with third-harmonic generation (THG), which is considered in greater detail for short-pulse interactions in Sect. 5.4.9. If the frequency difference \(\omega_1 - \omega_2\) of two of the laser fields is tuned to a resonance with a Raman-active mode of the nonlinear medium (Fig. 5.6c), the FWM process \(\omega_{\text{FWM}} = \omega_1 - \omega_2 + \omega_1 = \omega_1\text{CARS is referred to as coherent anti-Stokes Raman scattering (CARS). An FWM process involving four fields of the same frequency (Fig. 5.6d) with } \omega_{\text{DFWM}} = \omega = -\omega + \omega \text{ corresponds to degenerate four-wave mixing (DFWM). The FWM field in this nonlinear-optical process is the phase-conjugate of one of the laser fields, giving rise to another name of this type of FWM – optical phase conjugation.}

For the general-type FWM \(\omega_{\text{DFWM}} = \omega_1 + \omega_2 + \omega_3\), we represent the pump interactions as

\[
E_j = A_j \exp \left[ i \left( k_j z - \omega_j t \right) \right] \text{c.c.},
\]

where \(j = 1, 2, 3\) and \(k_j = k_{jFWM} + i\alpha_j\) are the complex wave vectors of the pump fields.

The FWM vector is written as

\[
E_{\text{FWM}} = A_{\text{FWM}} \exp \left[ i \left( k_{\text{FWM}} z - \omega_{\text{FWM}} t \right) \right] + \text{c.c.}
\]

where \(k_{\text{FWM}} = k'_{\text{FWM}} + i\alpha_{\text{FWM}}\) is the complex wave vector of the FWM fields.

The third-order nonlinear polarization responsible for the considered FWM process is

\[
P_{(3)}^{\text{FWM}} = \chi^{(3)} (\omega_{\text{FWM}}; \omega_1, \omega_2, \omega_3) \cdot \exp(i \omega_{\text{FWM}} t) E(\omega_1) E(\omega_2) E(\omega_3).
\]

With no depletion of the pump fields, the SVEA equations give the following expression for the envelope of the \(i\)-th Cartesian component of the FWM field [5.9]:

\[
[A_{\text{FWM}}(z)]_i = -\frac{2\pi i A_{\text{FWM}}^2}{k_{\text{FWM}}^2} \chi^{(3)} (\omega_{\text{FWM}}; \omega_1, \omega_2, \omega_3) \times A_1 A_2 A_3 \exp \left( \frac{i \Delta k z}{2} \right) \times \exp \left( -i \alpha_{\text{FWM}} z \right) \frac{\sin \left( \frac{\Delta k z}{2} \right)}{\Delta k z} \cos z.
\]

where

\[
\Delta k = k_1 + k_2 + k_3 - k_{\text{FWM}} + i(\alpha_1 + \alpha_2 + \alpha_3 - \alpha_{\text{FWM}})
\]

is the \(z\)-component of the wave-vector mismatch.

Phase matching, as can be seen from (5.84), is the key requirement for high efficiency of frequency conversion in FWM. The fields involved in FWM can be phase matched by choosing appropriate angles between the wave vectors of the laser fields and the wave vector of the nonlinear signal or using the waveguide regime with the phase mismatch related to the material dispersion compensated by the waveguide dispersion component.

5.4.6 Optical Phase Conjugation

Optical phase conjugation is generally understood as the generation of an optical field with a time-reversed wave front, or with a conjugate phase. This effect can be used to correct aberrations in certain types of optical problems and systems [5.33]. Suppose that a light beam with an initially plane wave front propagates through an aberrating medium, such as, for example a turbulent atmosphere or a material with inhomogeneities of the refractive index. The wave front of the light beam transmitted through such a medium is distorted. We now use an optical-phase-conjugate process to generate the field with a wave front time-reversed with respect to the wave front of the beam transmitted through the aberrating system. As the phase-conjugate beam now propagates through the aberrating medium in the backward direction, its wave front becomes restored.
A phase-conjugate field can be produced through the degenerate four-wave mixing of light fields

\[ E_j(r, t) = A_j(r, t) \exp \left[ i (k_j \cdot r - \omega t) \right] + \text{c.c.}, \]  

where \( j = 1, 2, 3, 4. \)

The phase-conjugate geometry of DFWM is shown in Fig. 6d. In this scheme, two strong counterpropagating pump fields \( E_1 \) and \( E_2 \) with the same frequency \( \omega \) and wave vectors \( k_1 \) and \( k_2 = -k_1 \) illuminate a medium with a cubic nonlinearity \( \chi^{(3)}_{\text{DFWM}} = \chi^{(3)}(\omega, \omega, -\omega, \omega). \) The DFWM interaction of these two pump fields with a weak signal of the same frequency \( \omega \) and an arbitrary wave vector \( k_3 \) gives rise to a field with a frequency \( \omega \) that propagates in the opposite direction to the signal beam and that is phase-conjugate of the signal field. The phase-conjugate field generated through DFWM can be instructively thought of as a result of scattering of the forward pump field off the grating induced by the backward pump and the signal field or as a result of scattering of the backward pump from the grating induced by the forward pump and the signal field.

The nonlinear polarization responsible for phase conjugation in DFWM is

\[ P^{(3)}_{\text{DFWM}} = 6 \chi^{(3)}_{\text{DFWM}} E_1 E_2 E^*_3. \]  

If the depletion of the pump fields is negligible, the nonlinear propagation equation (5.24) for the considered DFWM process is reduced to the following two equations for the amplitude of the signal field and its phase-conjugate [5.1]

\[ \frac{dA_3}{dz} = i\kappa_3 A_3 + i\kappa_4 A^*_4, \]  

\[ \frac{dA_4}{dz} = -i\kappa_3 A_4 - i\kappa_4 A^*_3, \]  

where

\[ \kappa_3 = \frac{12\pi\omega}{cn} \chi^{(3)}_{\text{DFWM}} \left( |A_1|^2 + |A_2|^2 \right), \]  

\[ \kappa_4 = \frac{12\pi\omega}{cn} \chi^{(3)}_{\text{DFWM}} A_1 A_2. \]  

By introducing

\[ A_3 = B_3 \exp(ik_3 z), \]  

\[ A_4 = B_4 \exp(-ik_4 z), \]  

we reduce the set of equations (5.88) and (5.89) to

\[ \frac{dB_3}{dz} = i\kappa_4 B^*_4, \]  

\[ \frac{dB_4}{dz} = -i\kappa_3 B^*_3. \]  

The solution can now be written as

\[ B_3(z) = -\frac{i}{\kappa_4} \frac{\sin(|\kappa_4| z)}{\cos(|\kappa_4| L)} B_4(L) + \frac{\cos(|\kappa_4| (z - L))}{\cos(|\kappa_4| L)} B_3(0), \]  

\[ B_4(z) = \frac{\cos(|\kappa_4| z)}{\cos(|\kappa_4| L)} B_4(L) - \frac{i\kappa_4 \sin(|\kappa_4| (z - L))}{|\kappa_4| \cos(|\kappa_4| L)} B_3(0), \]  

where \( B_3(0) \) and \( B_4(L) \) are the boundary conditions for the signal and DFWM fields. With \( B_4(L) = 0, \) (5.97) gives

\[ B_4(0) = \frac{i\kappa_4}{|\kappa_4|} \tan(|\kappa_4| L) B_3(0). \]  

This expression visualizes the structure of the phase-conjugate field generated through DFWM. The intensity reflection coefficient of the DFWM medium serving as a phase-conjugate mirror is given by

\[ R_{\text{DFWM}} = \tan^2(|\kappa_4| L). \]  

As can be seen from (5.99), the reflectivity of the DFWM-based phase-conjugate mirror can exceed 100%. This becomes possible due to the energy supplied by the strong pump fields.

### 5.4.7 Optical Bistability and Switching

In optical bistability or multistability, an optical system has two or more than two stable states, most often represented by the intensity at the output of the system as a function of the input intensity. With the level of the output intensity determined by a certain operation on a light beam, a bi- or multistable system makes a decision in which state it will operate, acting as a switch for optical communications or optical data processing.

As an example of an optical bistable system, we consider a Fabry–Perot cavity with a Kerr-nonlinear medium inside. We assume that the cavity mirrors are identical and have an amplitude reflectance \( r \) and transmittance \( t \). Let \( A_1, A_2, \) and \( A_3 \) be the amplitudes of the incident, reflected, and transmitted fields, respectively. The amplitudes of forward and backward waves inside the cavity will be denoted as \( B_1 \) and \( B_2, \) respectively. The amplitudes of the fields inside and outside the cavity are related by the expressions [5.1]

\[ B_2 = r B_1 \exp(2i k L - \alpha L), \]  

\[ B_1 = t A_1 + r B_2. \]
where \( k \) is the wave number and \( \alpha \) is the intensity absorption coefficient.

Solving (5.100) and (5.101), we arrive at the relation

\[
B_1 = \frac{tA_1}{1 - R \exp(i\delta)},
\]

which is known as the Airy equation. When \( k \) or \( \alpha \) is a strongly nonlinear function of the light intensity, (5.102) leads to a bistable behavior of the system in the transmitted field.

Let us assume that the absorption is negligible and rewrite (5.102) as

\[
B_1 = \frac{tA_1}{1 - R \exp(i\delta)},
\]

where \( R = \rho^2 \exp(-i\phi) \) is the intensity reflectance of the cavity mirrors and the phase shift \( \delta \), corresponding to a full round trip around the cavity, is given by

\[
\delta = \delta_0 + \delta_{NL},
\]

where

\[
\delta_0 = \phi = 2n_0^2 \alpha L / c
\]

is the linear phase shift and

\[
\delta_{NL} = 2n_2 I \omega L / c
\]

is the nonlinear phase shift, with \( I = [cn/(2\pi)](|B_1|^2 + |B_2|^2) \approx [cn/(\pi)]|B_1|^2 \).

The ratio of the field intensity inside the cavity \( I_2 = [cn/(2\pi)]|B_1|^2 \), to the intensity of the incident field \( I_1 = [cn/(\pi)]|A_1|^2 \) is now given by

\[
\frac{I_2}{I_1} = F(I_2),
\]

where

\[
F(I_2) = \frac{1}{T + 4R \sin^2(\frac{\delta}{2})},
\]

where \( T \) is the intensity transmittance of the cavity mirrors, and

\[
\delta = \delta_0 + \frac{4n_2 \omega L}{c} I_2.
\]

In Fig. 5.7, we present the function \( F(I_2) \) and the ratio \( I_2/I_1 \), i.e., the left- and right-hand sides of (5.107), plotted as functions of the intensity \( I_2 \) normalized to \( I_0 = \lambda/(n_2 L) \) for different input field intensities \( I_1 \): (1) \( I_1 = I' \), (2) \( I_1 = I'' \), and (3) \( I_1 = I''' \), \( I''' > I'' > I' \). The circles in the Airy-function curve show the range of input intensities where the operation of the Fabry–Perot cavity is unstable.

The circles in the Airy-function curve show the range of input intensities where the operation is unstable. As the input intensity \( I_1 \) is increased, the system displays a bistable behavior and hysteresis. More hysteresis loops and a multistable behavior are observed, as can be seen from Fig. 5.7, with a further increase in \( I_1 \).

In Fig. 5.8, we present the function \( F(I_2) \) and the ratio \( I_2/I_1 \), i.e., the left- and right-hand sides of (5.107), plotted as functions of the intensity \( I_2 \) for different input field intensities \( I_1 \). The points where the straight lines representing the left-hand side of (5.107) cross the plot of the Airy-type function \( F(I_2) \) define the operation points of the nonlinear Fabry–Perot cavity. The circles in the Airy-function curve show the range of input intensities where the operation is unstable. As the input intensity \( I_1 \) is increased, the system displays a bistable behavior and hysteresis. More hysteresis loops and a multistable behavior are observed, as can be seen from Fig. 5.7, with a further increase in \( I_1 \).
Optical switching can now be implemented [5.1] by including a nonlinear medium into one of the arms of a Mach–Zehnder interferometer Fig. 5.8. The intensities at the output ports 1 and 2 are determined by the interference of light fields transmitted through the arms of the interferometer. If there is only one input beam applied to the system with symmetric beam splitters BS1 and BS2, output intensities display an oscillating behavior as functions of the nonlinear phase shift $\Phi_{NL}$ acquired by the light field in one of the arms of the interferometer. When $\Phi_{NL} = 0$, the intensity at output port 1 is at its maximum, while the intensity at output port 2 is at its minimum. An opposite relation between the output intensities is achieved with $\Phi_{NL} = \pi$. The requirement $\Phi_{NL} = \pi$ is typical of a broad class of all-optical switching devices.

### 5.4.8 Stimulated Raman Scattering

Vibrations or rotations of molecules, electronic motions in atoms or collective excitations of matter can interact with light, shifting its frequency through an inelastic scattering process by the frequency $\Omega$ of Raman-active motions (as shown in Fig. 5.6c). This phenomenon was discovered by Raman and Krishnan [5.34] and almost simultaneously by Mandelstam and Landsberg [5.35] in 1928. In an intense laser field, pump laser photons and frequency-shifted photons act coherently to resonantly drive molecular motions, leading to the amplification of the Raman-shifted signal. This effect is called stimulated Raman scattering (SRS). In the SRS regime, Raman-active modes of a material function as optical modulators, forcing the driving laser field to oscillate at new frequencies. An intense laser field under these conditions not only gives rise to photons at new frequencies through interaction with Raman-active modes, but also amplifies the light consisting of those photons.

In the continuous-wave regime, the interaction between the pump field and the frequency-shifted (Stokes) signal is governed by the following set of coupled equations for the intensities of the pump $I_p$ and Stokes $I_s$ fields [5.23]:

\[
\frac{dI_p}{dz} = g_Re_p I_s - \alpha_p I_p , \quad (5.110)
\]

\[
\frac{dI_s}{dz} = -\frac{\alpha_p}{\alpha_s} g_Re_s I_p - \alpha_s I_s . \quad (5.111)
\]

Here, $\alpha_p$ and $\alpha_s$ are the losses at the frequencies of the pump and Stokes fields, $\omega_p$ and $\omega_s$ are the frequencies of the pump and Stokes fields, and $g_R$ is the Raman gain, which is related to the imaginary part of the third-order susceptibility [5.9],

\[
g_R \propto \text{Im} \left[ \chi^{(3)}(\omega_s; \omega_p, -\omega_p, \omega_s) \right] . \quad (5.112)
\]

Neglecting the action of the Stokes field on the pump, i.e., omitting the first term on the right-hand side of (5.111), we arrive at the following solution for the intensity of the Stokes field at the output of a Raman-active medium with a length $L$:

\[
I_s(L) = I_s(0) \exp \left[ g_R I_0 L_{\text{eff}} - \alpha_s L \right] , \quad (5.113)
\]

where $I_0$ is the incident pump intensity at $z = 0$ and

\[
L_{\text{eff}} = \frac{1}{\alpha_p} \left[ 1 - \exp \left( -\alpha_p L \right) \right] . \quad (5.114)
\]

Thus, pump absorption restricts the nonlinear interaction length to $L_{\text{eff}}$.

In the absence of the Stokes field at the input of a Raman-active medium, $I_s(0) = 0$, the Stokes field builds up from spontaneous Raman scattering inside the medium. The power of the Stokes signal at the output of a medium with a length $L$ is then given by

\[
P_s(L) = \tilde{P}_0 \exp \left[ g_R(\omega_s) I_0 L_{\text{eff}} - \alpha_s L \right] , \quad (5.115)
\]

where

\[
\tilde{P}_0 = \hbar \omega_s B_{\text{eff}} ,
\]

\[
B_{\text{eff}} = (2\pi)^{1/2} \left| g_2(\omega_s) I_0 L_{\text{eff}} \right|^{-1/2} ,
\]

and

\[
g_2(\omega_s) = \left( \frac{\partial^2 g_R}{\partial \omega^2} \right)_{\omega=\omega_s} .
\]

With an assumption of a Lorentzian Raman gain band, the critical pump power corresponding to the threshold of SRS effect is given by an approximate formula

\[
P_{ct} \approx \frac{16 S_{\text{eff}}}{g_R L_{\text{eff}}} . \quad (5.116)
\]

where $S_{\text{eff}}$ is the effective mode area of the pump field.

In Sect. 5.6.3, we will consider in greater detail the influence of SRS on the propagation of ultrashort laser pulses in a nonlinear medium. It will be shown, in particular, that the Raman effect in fibers gives rise to a continuous frequency downshift of solitons propagating in optical fibers.
5.4.9 Third-Harmonic Generation by Ultrashort Laser Pulses

Third-harmonic generation (THG) is one of the basic nonlinear-optical processes, which has been intensely studied and employed for numerous applications since the early days of nonlinear optics [5.7–9]. The seminal work by Miles and Harris [5.17] has demonstrated a tremendous potential of direct THG related to the cubic optical nonlinearity $\chi^{(3)}$ of gases for efficient frequency conversion of laser radiation and for the diagnostics of the gas phase. Solid-state strategies of frequency conversion, on the other hand, mainly rely on the quadratic nonlinearity $\chi^{(2)}$ of non-centrosymmetric crystals, with frequency tripling conventionally implemented through cascaded second-order nonlinear-optical processes, phase matched by crystal anisotropy [5.13, 14] or periodic poling of nonlinear materials [5.16].

Photonic-crystal fibers (PCFs) [5.36, 37] – optical fibers of a new type where the solid continuous cladding of standard fibers is replaced by a microstructure with an array of air holes running along the fiber parallel to its core Fig.5.9 – have opened a new phase in nonlinear optics [5.38, 39]. Controlled dispersion of guided modes [5.40] and large interaction lengths provided by these fibers for light fields strongly confined in a small fiber core [5.41] result in a radical enhancement of nonlinear-optical frequency conversion and spectral transformation of laser radiation through self- and cross-phase modulation (SPM and XPM) [5.38], supercontinuum generation [5.42–44], four-wave mixing (FWM) [5.45], third-harmonic generation [5.42–52], modulation instabilities [5.53], and soliton frequency shifting [5.54]. Third-order nonlinear-optical processes enhanced in PCFs now offer a useful alternative to frequency-conversion schemes using $\chi^{(2)}$ nonlinear crystals.

Highly efficient THG has recently been observed in fused silica [5.46–50] and multicomponent glass PCFs [5.51], as well as in tapered fibers [5.52]. These

Fig. 5.9a–d SEM images of photonic-crystal fibers: (a) periodic- and (b) double-cladding fused-silica PCFs, (c) high-index-step birefringent PCF, and (d) hollow-core PCF.
Basic Principles and Materials

5.4 Phenomenon and Materials

In the guided-wave regime, the wave numbers (or the propagation constant) $k$ represent the wave numbers (or the propagation constant) $v$ for the interacting pair of pump and third-harmonic modes. The possibility to tune the frequency of the third harmonic by varying the group-velocity mismatch is a universal intrinsic feature of multimode guided-wave THG. Based on the arguments of the slowly varying envelope approximation (SVEA), we will show that the sign and the absolute value of the third-harmonic frequency shift, observed in many PCF experiments, is controlled by the phase- and group-index mismatch for the interacting pair of pump and third-harmonic fields.

The frequency of the third harmonic $3\omega$ can be identified with no signal produced at the central frequency $\omega_0$ frequency. We start with qualitative arguments illustrating phase matching for third-harmonic generation generalized to include the phase and group-velocity mismatch of the pump and third-harmonic fields, as well as the Kerr effect, broadening the pump spectrum through SPM. We represent the wave numbers (or the propagation constants of guided modes in a waveguide regime) $k_p$ and $k_h$ at the frequencies of the pump field and the third harmonic as

$$k_p(\omega) \approx k(\omega_0) + v_p^{-1}\Omega/3 + \kappa_{\text{SPM}} P,$$  \hspace{1cm} (5.117)

$$k_h(3\omega) \approx k(3\omega_0) + v_h^{-1}\Omega + 2\kappa_{\text{XPM}} P,$$  \hspace{1cm} (5.118)

where $\omega_0$ is the central frequency of the pump field; $v_{ph} = (\partial k/\partial \omega)^{-1}|_{3\omega_0}$ are the group velocities of the pump and its third harmonic; $\Omega = 3\omega - 3\omega_0$; $\kappa_{\text{SPM}} = \kappa_{\text{SPM}}(\epsilon_0 n_2^3/c S_{\text{eff}})$ and $\kappa_{\text{XPM}} = \kappa_{\text{XPM}}(\epsilon_0 n_2^3/c S_{\text{eff}})$ are the SPM and XPM nonlinear coefficients ($S_{\text{eff}}$ is the effective beam, or mode, area); and $n_2$ and $n_3$ are the nonlinear refractive indices at $\omega_0$ and $3\omega_0$, respectively; and $P$ is the power of the pump field. In writing (5.117) and (5.118), we neglect group-velocity dispersion and higher-order dispersion effects, as well as the SPM of the third-harmonic field. With $n_2 \approx n_2$, the phase mismatch $\Delta k$ is then given by

$$\Delta k = k_h - 3k_p \approx \Delta k_0 + \xi \Omega + 3\kappa_{\text{SPM}} P,$$  \hspace{1cm} (5.119)

where $\Delta k_0 = k(3\omega_0) - 3k(\omega_0)$ is the phase mismatch of the pump and third-harmonic wave numbers at the central frequencies of these fields and $\xi = v_h^{-1} - v_p^{-1}$ is the group-velocity mismatch.

As can be seen from (5.119), the group delay of the pump and third-harmonic pulses is an important factor in THG momentum conservation. In this respect, the balance of momenta for THG radically differs from standard phase-matching conditions for parametric FWM processes [5.23], where the first-order dispersion order terms cancel out, reducing the FWM momentum balance to group-velocity dispersion (GVD)-related issues.

The phase-matching condition (5.119) suggests the possibility of substantially frequency shifting the maximum in the spectrum of the third harmonic. However, the amplitude of an $\Omega$-shifted spectral component in the spectrum of the third harmonic and, hence, the efficiency of $\Omega$-shifted peak generation is determined by the spectrum of the pump field. To specify this dependence, we proceed with an SVEA analysis of THG in the field of SPM-broadened pump field by writing SVEA coupled equations for the envelopes of the pump and third-harmonic fields, $A(t, z)$ and $B(t, z)$:

$$\frac{\partial}{\partial t} + \frac{1}{v_p} \frac{\partial}{\partial z} A = i\gamma_1 |A|^2,$$  \hspace{1cm} (5.120)

$$\frac{\partial}{\partial t} + \frac{1}{v_h} \frac{\partial}{\partial z} B = i\beta |A|^3 \exp(-i\Delta k_0 z) + 2i\gamma_2 B |A|^2,$$  \hspace{1cm} (5.121)

where $v_p$ and $v_h$ are the group velocities of the pump and third-harmonic pulses, respectively, and $\gamma_1$, $\gamma_2$ and $\beta$ are the nonlinear coefficients responsible for SPM, XPM, and THG, respectively; and $\Delta k = k_h - 3k_p$ is the phase mismatch (or the difference of propagation constants in the guided-wave regime) in the absence of the nonlinear phase shifts of the pump and third-harmonic fields.

Solution of (5.120) and (5.121) yields [5.24, 55]

$$A(t_p, z) = A_0(t_p) \exp[i\kappa_{\text{SPM}}(t_p), z)],$$  \hspace{1cm} (5.122)

$$B(t_h, z) = i\omega \int_0^z d' A_0^2(t_h + \xi z') \times \exp[-i\Delta \beta_0 z' + 3i\kappa_{\text{SPM}}(t_h + \xi z', z')] + i\kappa_{\text{XPM}}(t_h, z', z')],$$  \hspace{1cm} (5.123)

where $t_p = (t - z/v_p)$ with $l = p, h$ for the pump and the field, respectively; $A_0(t)$ is the initial-condition envelope.
of the pump pulse:

\[ \psi_{\text{SPM}} (t_p, z) = \gamma_1 |A_0 (t_p)|^2 z \]  

(5.124)
is the SPM-induced phase shift of the pump field; and

\[ \psi_{\text{XPM}} (t_h, z', z) = 2\gamma_2 \int \frac{z}{z'} |A_0 (t_h + \xi z')|^2 \, dz' \]  

(5.125)
is the XPM-induced phase shift of the third-harmonic field.

In the regime where the nonlinear phase shifts, given by (5.124) and (5.125), are small, the Fourier transform of (5.123) yields the following expression for the spectrum of the third-harmonic intensity:

\[
I (\Omega, z) \propto \beta \sin^2 \left( \frac{(\Delta k_0 + \Omega \xi) \tau}{\Delta k_0 + \Omega \xi} \right) \\
\times \left| \int_{\infty}^{\infty} \int_{-\infty}^{\infty} A (\Omega - \Omega') A (\Omega' - \Omega'' \xi) \right|^2 \\
\times A (\Omega'') \, d\Omega' \, d\Omega''
\]  

(5.126)

where \( A(\Omega) \) is the spectrum of the input pump field. Analysis of the regime of small nonlinear phase shifts is thus very instructive as it allows phase-matching effects to be decoupled from the influence of the spectrum of the pump field. While the phase matching is represented by the argument in the exponential in the first factor on the right-hand side of (5.126), the significance of the pump spectrum is clear from the convolution integral appearing in this expression. Depending on the signs of the phase and group-velocity mismatch, \( \Delta k_0 \) and \( \xi \), the peak in the spectrum of the third harmonic can be either red- or blue-shifted with respect to the frequency \( 3\omega_0 \). The spectral width of this peak, as can be seen from (5.126), is given by \( \delta \approx 2\pi (|\xi| z)^{-1} \), decreasing as \( z^{-1} \) with the growth in the propagation coordinate \( z \) (see inset in Fig. 5.10).

With low pump powers, the generalized phase-matching condition (5.119), as can be seen also from the exponential factor in (5.126), defines the central frequency \( 3\omega_0 + \Omega_{\text{max}} \). \( \Omega_{\text{max}} = -\Delta k_0 / \xi \), of the peak in the spectrum of the third harmonic. The amplitude of this peak, as shown by (5.126), is determined by the amplitudes of the pump field components with frequencies \( \omega_1 = \omega_0 + \Omega_{\text{max}} - \Omega' \), \( \omega_2 = \omega_0 + \Omega' - \Omega'' \) and \( \omega_3 = \omega_0 + \Omega'' \), which can add up to transfer the energy to the \( 3\omega_0 + \Omega_{\text{max}} \) component in the spectrum of the third harmonic through the \( \omega_1 + \omega_2 + \omega_3 = 3\omega_0 + \Omega_{\text{max}} \) process. The spectrum of the pump field should therefore be broad enough to provide a high amplitude of this peak. In the regime when the SPM-induced broadening of the pump spectrum is small, the tunability range of the third harmonic (i.e., the range of frequency offsets \( \Omega \)) is mainly limited by the bandwidth of the input pump field. This regime of THG is illustrated in Fig. 5.10. As the ratio \( \Delta k_0 \tau / \xi \) changes from \(-2 \) (curve 1) to \(-3 \) (curve 2), the peak in the spectrum of the third harmonic is bound to shift from \( \Omega_{\text{max}} = 2/\tau \) to \( 3/\tau \). A similar spectral shift limited by a field-unperturbed pump spectrum has been earlier predicted by Akhmanov et al. for second-harmonic generation [5.56]. For large \( |\Delta k_0 / \xi| \), however, the pump power density at the wings of the spectrum is too low to produce a noticeable peak with \( \Omega_{\text{max}} = -\Delta k_0 / \xi \) in the spectrum of the third harmonic (cf. curves 2 and 3 in Fig. 5.10).

In the general case of non-negligible nonlinear phase shifts, phase-matching effects cannot be decoupled from the influence of the pump spectrum, and we resort to approximate integration methods to identify the main features of the THG process. For a pump pulse with a Gaussian envelope, \( A_0(t_p) = A \exp[-t_p^2/(2\tau^2)] \), where \( A \) and \( \tau \) are the amplitude and the initial duration.

**Fig. 5.10** Spectra of the third harmonic generated in the regime of weak self-phase modulation of the pump field with \( \Delta k_0 \tau / \xi = -2 \) (curve 1), \(-3 \) (2) and 0 (3). The inset illustrates narrowing of the main peak in the spectrum of the third harmonic with \( \Delta k_0 \tau / \xi = -1 \) and \( \xi L / \tau = 2 \) (1), 4 (2), and 10 (3).
of the pump pulse, the spectrum of the third harmonic, in view of (5.123), is given by
\[
B(\Omega, z) = i \beta \hat{A}^3 \int_{-\infty}^{\infty} dz' \exp \left[ -\frac{3}{2\tau^2} \left( \frac{h_{0} + \xi z'}{\tau} \right) \right. \\
\times \left. \exp \left( -\frac{(h_{0} + \xi z')^2}{\tau^2} \right) \right] \\
\times \exp \left( -\frac{(h_{0} + \xi z')^2}{\tau^2} \right) \\
\times \exp \left( -\frac{(h_{0} + \xi z')^2}{\tau^2} \right) + i \Omega t_h \right)
\]
(5.127)

Changing the order of integration in (5.127), we apply the saddle-point method to estimate the integral in \(dt_h\):
\[
B(\Omega, z) \propto i \beta \hat{A}^3 \int_{0}^{\infty} dz' \\
\times \exp \left[ -i \left( \Delta k_0 + \Omega \xi - 3\gamma_1 |\hat{A}|^2 \right) z' \right. \\
\left. + 2i\gamma_1 |\hat{A}|^2 \frac{\Phi}{\xi} \left[ (z - z') \frac{\xi}{\tau} \right] \right]
\]
(5.128)

where \(\Phi(x) = \int_{0}^{x} \exp(-x^2) dx\).

With \(\xi/z/\tau \gg 1\) and \(\Phi((z - z')/\xi)\) constant, the phase matching is controlled by the factor
\[
F(\Omega, z) = \frac{\sin^2 \left( \frac{\Delta k + \Omega \xi + 3\gamma_1 |\hat{A}|^2 z}{2} \right)}{\left( \Delta k + \Omega \xi + 3\gamma_1 |\hat{A}|^2 z \right)}
\]
(5.129)

Thus, the saddle-point estimate of the SVEA integral for the third-harmonic field recovers the generalized phase-matching condition in the form of (5.119). The frequency offset \(\Omega_{\text{max}}\) providing the maximum efficiency of THG is now determined by the dispersion of the material, its nonlinear properties, and the intensity of the pump field.

Spectral broadening of the pump field due to SPM radically expands the tunability range of the third harmonic (Fig. 5.11). With \(\gamma I_0 L = 1\) (\(L\) is the interaction length and \(I_0\) is the pump-field peak intensity), the spectrum of the pump field is broad enough to produce a high-amplitude peak at \(\Omega_{\text{max}} = -6/\tau\). The peak becomes narrower as the length of the nonlinear medium increases (cf. curves 2 and 3 in Fig. 5.11), suggesting a convenient way for an efficient generation of short-wavelength radiation with a well-controlled spectrum for spectroscopic and metrological applications. In the time domain, the third harmonic tends to break up into two pulses, as shown in the inset to Fig. 5.11 for \(\gamma I_0 L = 1\) (curve 1) and 2 (curve 2) with \(\xi L/\tau = 20\). The first peak at \(t_h = -20\) represents a third-harmonic pulse that propagates with the pump pulse and that is phase-matched to the pump field in the sense of (5.119). The second pulse propagates with the group velocity of the third harmonic and is group-delayed in our case with respect to the pump field. Due to the phase matching, the ratio of the amplitudes of the first and second peaks increases with the growth in \(\gamma I_0 L\) (cf. curves 1 and 2 in the inset to Fig. 5.11).

Examples of frequency-shifted THG can be found in the recent literature on nonlinear optics of PCFs and tapered fibers [548–52]. Interesting collinear and Cherenkov-type intermode phase-matching options [550, 51] have been highlighted. The nature of the frequency shift has been identified in [557, 58]. Generation of an asymmetrically broadened and spectrally shifted third harmonic is the most frequently encountered situation, observed in nonlinear-optical ex-
The two most striking recent experimental findings include the observation of a 260 nm spectral component generated by Ti:sapphire laser pulses in high-delta PCFs [5.49] and the generation of a spectrally isolated third harmonic in an air-clad fused-silica fiber with a core radius of 0.9 μm. The pump wavelength is 1.25 μm. The vertical dashed line shows the wavelength λ = 383 nm, where Δk₀ + ξΩ = 0. The insets show a typical experimental spectrum of blue visible emission (1) and the spectrum of the Cr:forsterite laser pump field (2) at the output of a photonic-crystal fiber with a length of 10 cm (after [5.57]).

We have shown that third-harmonic generation in PCFs [5.49–51] and tapered fibers [5.52]. The two most striking recent experimental findings include the observation of a 260 nm spectral component generated by Ti:sapphire laser pulses in high-delta PCFs [5.49] and the generation of a spectrally isolated frequency component at 380 nm by femtosecond pulses of 1.25 μm Cr:forsterite laser radiation [5.59]. In the former case, the central wavelength of the ultraviolet (UV) component remained stable [5.49] as the central pump wavelength was tuned from 770 to 830 nm [which seems to agree well with the phase-matching condition of (5.119)]. In the latter case, generation of a blue-shifted third harmonic allowed a highly efficient frequency conversion of pump radiation over the frequency interval exceeding 540 THz [5.59]. The spectral peak of visible blue emission was shifted from the frequency 3ω₀ in these experiments by 34 nm (a typical spectrum is presented in the inset to Fig. 5.12), with no signal produced at 3ω₀.

To identify the main features of the dramatic frequency shift in the spectrum shown in the inset to Fig. 5.12, we consider the dispersion of guided modes in an air-clad fused-silica thread as a generic example of PCF dispersion. In Fig. 5.12, we plot the phase and group-velocity mismatch, Δk₀ and ξ, as well as the effective phase mismatch Δk_eff passes through zero at the wavelength of 383 nm, corresponding to a frequency shift of about 63 THz relative to 3ω₀, which agrees well with the typical spectrum of blue emission from a PCF [5.59] presented in inset 1 to Fig. 5.12. The main features and dominant tendencies of the third-harmonic spectrum are adequately described by (5.119) and (5.127). Comparison of the pump (inset 2 to Fig. 5.12) and third-harmonic spectra presented in Fig. 5.11 also suggests that a blue shifting of the main peak in the spectrum of the third harmonic by more than 60 THz becomes possible due to a strong broadening of the pump field, which is, of course, not only due to SPM in realistic conditions of PCF experiments.

Fig. 5.12 The phase mismatch Δk₀ (1), group-velocity mismatch ξ (2), and the effective phase mismatch Δk_eff + ξΩ (3) for third-harmonic generation in an air-clad fused-silica fiber with a core radius of 0.9 μm. The pump wavelength is 1.25 μm. The vertical dashed line shows the wavelength λ = 383 nm, where Δk₀ + ξΩ = 0. The insets show a typical experimental spectrum of blue visible emission (1) and the spectrum of the Cr:forsterite laser pump field (2) at the output of a photonic-crystal fiber with a length of 10 cm (after [5.57]).
5.5 Ultrashort Light Pulses in a Resonant Two-Level Medium: Self-Induced Transparency and the Pulse Area Theorem

5.5.1 Interaction of Light with Two-Level Media

The phenomenological approach based on nonlinear-optical susceptibilities does not include nonstationary phenomena related to a dynamic modification of the nonlinear medium by the laser field. Interaction of a resonant laser field with a two-level system is a physically interesting and methodologically important regime where the equations governing the evolution of the laser field in a nonlinear medium can be solved self-consistently with the equations of motion for the quantum system interacting with the field. Such a self-consistent analysis reveals the existence of a remarkable regime of nonlinear-optical interactions. A resonance laser pulse whose amplitude and pulse width are carefully matched to the two-level system can propagate in a two-level medium with no absorption-induced attenuation of the pulse amplitude, a phenomenon known as self-induced transparency.

The interaction of laser radiation with a two-level system is a classic problem of laser physics [5.60]. It has been extensively studied with the use of various approximate analytical approaches and numerical procedures over four decades, revealing important aspects of the interaction of laser radiation with a two-level system and, generally, laser–matter interactions. The standard approach based on the slowly varying envelope approximation (SVEA) and rotating-wave approximation gives Maxwell–Bloch equations in the case of a two-level atom [5.60, 61]. These equations provide an adequate description of the Schrödinger equation for the wave functions should be solved without any assumptions that are usually employed in the SVEA approach. In the one-dimensional case, the FDTD algorithm involves step-by-step integration of two Maxwell curl equations

\[
\frac{\partial D_z(x,t)}{\partial t} = \frac{\partial H_y(x,t)}{\partial x}, \\
\frac{\partial H_y(x,t)}{\partial t} = \frac{\partial E_z(x,t)}{\partial x}.
\]  

To perform this integration, we have to define the relation between the components of the electromagnetic induction and the electromagnetic field. This can be done through the equation for the polarization of the medium. In our case of a two-level medium, this involves the solution of the Schrödinger equation for the wave functions of the energy levels.

Hughes [5.67, 68] has employed the FDTD approach to demonstrate the possibility of generating sub-femtosecond transients in a two-level medium.

Tarassishin et al. [5.69] have applied FDTD technique to integrate jointly the Maxwell and Schrödinger equations for an ultrashort light pulse propagating in a two-level medium. Below in this section, we explain the FDTD-based algorithm [5.69] solving the Maxwell and Schrödinger equations to model the interaction of ultrashort laser pulses with an ensemble of two-level atoms. FDTD simulations presented below reveal interesting regimes of short-pulse propagation and amplification in two-level media, including the evolution of the pulse to a 2π soliton, amplification of a single-cycle pulse in a medium with a spatially modulated distribution of dipole moments of resonant transitions, and amplification of chirped light pulses.

5.5.2 The Maxwell and Schrödinger Equations for a Two-Level Medium

We shall start with the extension of the standard FDTD procedure to the case of short pulses propagating in a two-level medium, when the Maxwell equation for the fields and the Schrödinger equation for the wave functions should be solved without any assumptions that are usually employed in the SVEA approach. In the one-dimensional case, the FDTD algorithm involves step-by-step integration of two Maxwell curl equations

\[
\frac{\partial D_z(x,t)}{\partial t} = \frac{\partial H_y(x,t)}{\partial x}, \\
\frac{\partial H_y(x,t)}{\partial t} = \frac{\partial E_z(x,t)}{\partial x}.
\]
We will consider an ensemble of noninteracting two-level atoms or molecules whose wave functions can be represented as superpositions of two basis states 1 and 2:

$$\psi(t) = \psi_1(x, t) \psi_1 + b(x, t) \psi_2,$$

(5.132)

where $\psi_1$ and $\psi_2$ are the eigenfunctions of an unperturbed system corresponding to the states with energies $E_1$ and $E_2$ (we assume for definiteness that $E_1 > E_2$), respectively, and $a(x, t)$ and $b(x, t)$ are complex coefficients. Then, the Schrödinger equation for the wave function yields the following set of differential equations:

$$i \hbar \frac{da(x, t)}{dt} = E_1 a(x, t) - \mu E_z(x, t) b(x, t),$$

(5.133)

$$i \hbar \frac{db(x, t)}{dt} = E_2 b(x, t) - \mu E_z(x, t) a(x, t),$$

(5.134)

where $\mu$ is the dipole moment of transition between the levels 1 and 2. Following Feynman et al. [5.68], we introduce real combinations of the complex quantities $a(x, t)$ and $b(x, t)$:

$$r_1(x, t) = a(x, t) b^*(x, t) + a^*(x, t) b(x, t),$$

(5.135)

$$r_2(x, t) = i [a(x, t) b^*(x, t) - a^*(x, t) b(x, t)],$$

(5.136)

$$r_3(x, t) = a(x, t) a^*(x, t) - b(x, t) b^*(x, t),$$

(5.137)

$$r_4(x, t) = a(x, t) a^*(x, t) + b(x, t) b^*(x, t).$$

(5.138)

The physical content of the parameters defined by (5.135–5.138) is well known from classic textbooks on coherent optics [5.60, 61]. It can be easily verified using the set (5.133) and (5.134) that $r_2(x, t)$ is independent of time and can be interpreted as the probability to find the system in either state 1 or state 2. The quantities $r_1(x, t)$ and $r_3(x, t)$ play an especially important role. Depending on the sign of $r_3(x, t)$, resonant electromagnetic radiation can be either amplified or absorbed by a two-level system. The quantity $r_1(x, t)$ controls the polarization of the medium in the case of a linearly polarized light field:

$$P_z(x, t) = 4 \pi \mu r_1(x, t) N,$$

(5.139)

where $N$ is the volume density of two-level atoms or molecules. Thus, the quantity $r_1(x, t)$ defines the sought relation between the components of the electromagnetic induction and the electromagnetic field.

Using (5.133) and (5.134), we arrive at the following set of equations for the quantities defined by (5.135–5.137):

$$\frac{dr_1(x, t)}{dr} = -\omega_0 r_2(x, t),$$

(5.140)

$$\frac{dr_2(x, t)}{dr} = \omega_0 r_1(x, t) + 2 (\mu / \hbar) E_z(x, t) r_3(x, t),$$

(5.141)

$$\frac{dr_3(x, t)}{dr} = -2 (\mu / \hbar) E_z(x, t) r_2(x, t),$$

(5.142)

where $\omega_0 = (E_1 - E_2) / \hbar$. Differentiating (5.141), using (5.140) for $d r_2(x, t) / dr$, and taking into consideration that $r_1(x, t) = P_z(x, t) / (\mu N) = [D_z(x, t) - E_z(x, t)] / (4 \pi \mu N)$, we find that

$$\frac{d^2 D_z(x, t)}{dt^2} - \frac{d^2 E_z(x, t)}{dt^2} + \omega_0^2 [D_z(x, t) - E_z(x, t)]$$

$$+ 2 \pi \mu^2 \omega_0 N \frac{d}{dt} E_z(x, t) r_3(x, t) = 0,$$

(5.143)

$$\frac{dr_3(x, t)}{dr} = \frac{2}{4 \pi \hbar \omega_0 N} \left( \frac{d D_z(x, t)}{dt} - \frac{d E_z(x, t)}{dt} \right).$$

(5.144)

The FDTD approach involves difference approximation [5.66] of time and spatial derivatives involved in (5.130) and (5.131):

$$D_{z, i}^{n+1} = D_{z, i}^n + \frac{\Delta t}{\Delta x} \left( H_{z, j=i+1/2}^n - H_{z, j=i-1/2}^n \right),$$

(5.145)

$$H_{z, j=i+1/2}^n = H_{z, j=i+1/2}^{n+1/2} + \frac{\Delta t}{\Delta x} (E_{z, i}^{n+1} - E_{z, i}^n),$$

(5.146)

where $i$ and $n$ indicate the values of discrete spatial and temporal variables, respectively, $x = i \Delta x, t = n \Delta t$, $\Delta x$ and $\Delta t$ are the steps of discretization in spatial and temporal variables. This approach yields the following set of difference equations:

$$E_{z, i}^{n+1} = D_{z, i}^{n+1} + D_{z, i}^{n-1} - E_{z, i}^n$$

$$+ \left( 4 E_{z, i}^n - 4 D_{z, i}^n - 4 \Delta t^2 2 \pi \mu^2 \omega_0 N E_{z, i}^{n-1} \right) \frac{1}{2 + \Delta t^2 \omega_0^2},$$

(5.147)

$$r_{3, i}^{n+1} = r_{3, i}^{n-1} + 0.5 \frac{2}{4 \pi \hbar \omega_0 N} \left( E_{z, i}^{n+1} + E_{z, i}^n \right)$$

$$\times \left( D_{z, i}^{n+1} - D_{z, i}^{n-1} - E_{z, i}^{n+1} + E_{z, i}^{n-1} \right).$$

(5.148)

Thus, we arrive at the following closed algorithm of numerical solution:

1. substitute $D_{z, i}^{n+1}$ determined from (5.145) for the current value of the discrete-time variable into the set
of (5.147) and (5.148) and determine the values of $r_{3}^{(+)}$ and $E_{c,t}^{(+)}$.

2. substitute the quantities thus determined into (5.146) and determine the values of the magnetic field $H_{c,t}^{(+)}$.

3. substitute these values of the magnetic field into (5.145) and repeat the procedure for the next value of the discrete-time variable.

### 5.5.3 Pulse Area Theorem

To test the FDTD-based procedure of simulations described in Sect. 5.5.2, we model the propagation of light pulses

$$E(x,t) = A(x,t)e^{i\phi_{kz}-\omega t} + c.c.,$$

where $A(x,t)$ is the pulse envelope, in a two-level medium and compare the results of these simulations with the predictions of the McCall–Hahn area theorem [5.62, 63]. This plan can be accomplished by keeping track of the pulse area

$$\theta(x) = \int_{-\infty}^{\infty} \Omega(x, t) \, d\tau,$$

where $\Omega(x,t) = 2\mu \Omega A(x,t)$ is the real Rabi frequency.

The SVEA equation for the pulse envelope $A(x,t)$ can be represented as

$$\frac{\partial A(x,t)}{\partial x} + \frac{n}{c} \frac{\partial A(x,t)}{\partial t} = i \frac{2\pi\omega}{nc} P(x,t),$$

where $n$ is the refractive index of the medium, $P(x,t)$ is the slowly varying amplitude of the polarization induced in the medium. As shown by McCall and Hahn [5.62, 63], on exact resonance, $P(x,t) = i\mu N \sin[\theta(x,t)]$, with

$$\theta(x,t) = \int_{-\infty}^{\infty} \Omega(x, t) \, d\tau.$$ Hence, (5.151) yields

$$\frac{\partial A(x,t)}{\partial x} + \frac{n}{c} \frac{\partial A(x,t)}{\partial t} = -\frac{2\pi\omega N}{nc} \sin[\theta(x,t)].$$

The celebrated solution to (5.152) is a pulse with a hyperbolic-secant shape, which propagates in a resonant two-level medium with no changes in its envelope:

$$A(x,t) = \frac{\hbar}{\mu \tau} \text{sech} \left( \frac{t-x/V}{\tau} \right),$$

where $V$ is the pulse velocity in the medium,

$$V = \left( \frac{4\pi\mu^{2}\omega N^{2}}{\hbar c} + \frac{n}{c} \right)^{-1}.$$
and $2.09\pi$, respectively. Thus, the results of FDTD simulations agree very well with the predictions of the area theorem, indicating the adequacy of the numerical approach.

### 5.5.4 Amplification of Ultrashort Light Pulses in a Two-Level Medium

Since the numerical algorithm based on the FDTD technique is intended to simulate the evolution of very short pulses, it enables one to explore many important aspects of short-pulse amplification in a two-level medium, providing a deeper understanding of the problems arising in the amplification of short pulses and the ways that can be employed to resolve these problems.

Propagation of $\pi$ pulses seems to provide optimal conditions for amplification in a two-level system, since such pulses transfer atoms (or molecules) in an initially inverted medium to the lower state. However, the Rabi frequency increases as a light pulse propagates through the medium and its amplitude increases due to the amplification. Because of this change in the Rabi frequency, the pulse now cannot transfer inverted atoms or molecules to the lower state, but leaves some excitation in a medium, which reduces the gain and leads to pulse lengthening due to the amplification of the pulse trailing edge in a medium with residual population inversion. Thus, some precautions have to be taken to keep the area of the pulse constant in the process of pulse amplification. Thus, some precautions have to be taken to keep the area of the pulse constant in the process of pulse amplification. Below, we use the FDTD technique to explore two possible ways to solve this problem: (i) modulation of the spatial distribution of the dipole moments of resonant transitions in a two-level medium and (ii) amplification of a frequency-detuned chirped pulse.

#### Modulation of the Spatial Distribution of the Dipole Moment

First, let us explain why we expect that the modulation of the spatial distribution of the dipole moment may improve the efficiency of amplification of an ultrashort light pulse in a two-level medium. To do this, we multiply (5.152) by $\partial \Phi(x,t) / \partial x$ and integrate the resulting expression in time. Then, introducing the pulse energy, $\Phi(x) = \int_{-\infty}^{\infty} A^2(x,t)dt$, and taking into consideration that the pulse energy remains constant if $\theta(x_0) = 0, 2\pi, \ldots$, we arrive at the following equation relating the pulse energy and area:

$$\frac{\partial \Phi(x)}{\partial x} = \frac{2\pi \omega N h}{\hbar c} [\cos \theta(x) - 1] \ .$$  

(5.158)

Thus, if the pulse area is kept equal to $\pi$, as the pulse propagates through an inverted two-level medium, then the energy of such a pulse would grow linearly as a function of the distance:

$$\Phi(x) = (1 + \beta x) \Phi(0) \ ,$$  

(5.159)

where $\beta = \frac{3\pi \omega N h}{\Phi(0) \hbar c}$ and $\Phi(0)$ is the initial energy of the pulse.

By looking at (5.150) and (5.159) and taking into consideration that $\Phi(0) = 2\pi E_0^2 = 2\pi \hbar / \mu(0)$ for a hyperbolic-secant pulse (5.157), we find that the pulse area can be kept equal to $\pi$ by modulating the spatial distribution of the dipole moment in accordance with

$$\mu(x) = \frac{\mu_0}{\sqrt{1 + \beta x}} \ .$$  

(5.160)

Such a modulation of the spatial distribution of dipole moments can be achieved, for example, by preliminarily orienting molecules in the medium.

In accordance with the area theorem, the evolution of the amplitude of a $\pi$ pulse propagating in an inverted two-level medium with a spatial profile of the dipole moment described by (5.160) is governed by

$$E(x) = E_0 \sqrt{1 + \beta x} \ .$$  

(5.161)

This growth of the pulse amplitude is exactly compensated by the decrease in the dipole moment of transitions in the two-level medium. The net effect is that the pulse area remains constant and equal to $\pi$.

Figures 5.13a–d present the results of FDTD simulations for the amplification of a light pulse with a duration $T = 2\pi / \omega$ corresponding to a single optical cycle in an inverted two-level medium with a uniform distribution of the dipole moment (Figs. 5.13a,b) and in an inverted two-level medium where the spatial distribution of dipole moments of resonant transitions is modulated in accordance with (5.160) (Figs. 5.13c,d). Simulations were performed for the case when $\Omega = 2\mu_0 E_0 / 2\hbar = 0.159\omega_0$, $4\pi \mu N \Omega T(0) = 0.12 E_0$, and $\omega = \omega_0$. The time in these plots is measured from the moment when the center of the pulse passes through the entrance boundary of the medium.

Figures 5.13a,b display the evolution of a $\pi$ pulse in an inverted uniform two-level medium and the population difference in this medium at the distances $0, 3\beta^{-1}$ and $6\beta^{-1}$. These plots show that a two-level medium with a uniform distribution of the dipole moment of transitions cannot ensure an efficient amplification of a transform-limited resonant $\pi$ pulse. Figures 5.13c,d present the results of FDTD simulation for a $\pi$ pulse
propagating through a medium with a spatial evolution of the dipole moment described by (5.160). These simulations illustrate the possibility of efficient amplification of a single-cycle pulses in such a medium. Note that the pulse amplitude in Figs. 5.13c and 5.13d increases linearly with the propagation coordinate $x$ (the deviation from the linear dependence does not exceed $10^{-4}$). This result agrees very well with the predictions of the area theorem and can also be considered as another test of the reliability of the developed algorithm.
Frequency-Detuned Chirped Pulses
The second idea of keeping the area of the amplified pulse unchanged is to use chirped pulses whose frequency is detuned from the exact resonance. Such a pulse experiences compression as it propagates in the considered two-level medium. With an appropriate choice of pulse parameters, this decrease in pulse duration may serve to preserve the area of the light pulse undergoing amplification.

The Rabi frequency in this case is written
\[ \Omega = \frac{1}{2} \sqrt{\Delta^2 + \left( \frac{2 \mu_0 E_0}{\hbar} \right)^2}, \]
where \( \Delta = \omega - \omega_0 \) is the detuning of the central frequency of the pulse from the resonance.

Figures 5.13c,f present the results of FDTD simulations for a single-cycle pulse with a quadratic initial chirp
\[ E(0, t) = E_0 \frac{2 \cos (\omega t + k r^2 / T^2)}{\exp (-r / T) + \exp (-r / T)}, \]
with \( k = 1.4 \), propagating in a uniform two-level medium with the same parameters as in Figs. 5.13a,b. The distance covered by the pulse in the medium is \( 6 \beta^{-1} \), and the frequency detuning is \( \Delta = \omega - \omega_0 = -0.02 \omega_0 \).

As can be seen from Figs. 5.13e,f, although higher-order dispersion effects noticeably distort the waveform of the pulse, the peak intensity of an initially chirped pulse at the output of an amplifying uniform medium is nearly twice as high as the output energy of a transform-limited pulse. Furthermore, comparison of Figs. 5.13a,b,e,f shows that, chirping a light pulse, one can avoid undesirable pulse-lengthening effects.

**Fig. 5.13** (a)–(d) The evolution of (a), (c) the pulse waveform and (b), (d) the population difference for a single-cycle light pulse propagating in an inverted two-level medium with (a), (b) a uniform distribution of the dipole moment and (c), (d) a spatial distribution of dipole moments of resonant transitions modulated in accordance with (5.160) simulated with the use of the FDTD technique [5.69] for \( \Delta = 2 \mu_0 E_0 / 2h = 0.159 \), \( 4 \pi \mu N \sigma / \hbar = 0.12 E_0 \), and \( \omega = \omega_0 \). The time in these plots is measured from the moment when the center of the pulse passes through the input boundary of the medium. (e), (f) Amplification of a single-cycle chirped laser pulse (5.163) in a two-level medium: (e) the input pulse and (f) the output pulse simulated with the use of the FDTD technique for \( \Delta = 2 \mu_0 E_0 / 2h = 0.159 \), \( 4 \pi \mu N \sigma / \hbar = 0.12 \times 10^4 \), and \( \omega = \omega_0 \).

5.5.5 Few-Cycle Light Pulses in a Two-Level Medium

The results of FDTD simulations, as shown by Taranishtin et al. [5.70], typically agree very well with the predictions of McCall and Hahn theory [5.62, 63] for light pulses propagating in a two-level medium until the pulse duration \( T \) becomes less than the duration \( T_0 \) of a single optical cycle. In agreement with the general predictions of McCall and Hahn, a 2\( \pi \) pulse with \( T = T_0 \), \( 2 \mu_0 E_0 / \hbar = 2.9 \pi \), \( \mu / N E_0 / \hbar = 0.00116 \), for example, is transformed until its area becomes equal to 2\( \pi \). The peak amplitude of the pulse increases by a factor of 1.31 under these conditions, while its duration decreases to 0.55\( T_0 \).

Noticeable deviations from the McCall–Hahn regime were observed for pulses with durations shorter than the duration of a single field cycle. In particular, half-cycle 2\( \pi \) pulses become asymmetric as they propagate through a two-level medium (Fig. 5.14a), and the characteristic length corresponding to the phase shift (5.9) equal to \( \pi \) estimated on the basis of FDTD simulations for such pulses was equal to 9.4 \( \lambda \), which appreciably differs from the SVEA estimate for the characteristic length corresponding to the \( \pi \) phase shift, \( L = (\omega_0 / 4 \alpha^2 \mu^2 T^2 N) = (E_0^2 / \omega_0^2 \pi^2 N \hbar) \). Quarter-cycle 2\( \pi \) pulses display noticeable distortions and lengthening in the process of propagation through a two-level medium (Fig. 5.14b).

Deviations observed in the behavior of very short 2\( \pi \) pulses from the McCall–Hahn scenario are due to the fact that, although, formally, such pulses have an area of 2\( \pi \), the cycle of interaction between light and a two-level system remains incomplete in this case, as the pulses do not even contain a full cycle of the field (Figs. 5.14a,b). As a result, such pulses leave some excitation in a two-level medium (Fig. 5.14d) instead of switching excited-state population back to the ground state, as in the case of longer 2\( \pi \) pulses (Fig. 5.14c).

The amplitude of the leading edge of the pulse becomes higher than the amplitude of its trailing edge, and the pulse waveform becomes noticeably asymmetric (Fig. 5.14a). The group velocity of such very short pulses increases due to this incompleteness of the light-two-level-system interaction cycle, leading to a discrepancy between the SVEA estimate and the FDTD result for the characteristic length corresponding to the \( \pi \) phase shift. The residual population in the medium and the asymmetry of the pulse waveform increase with pulse shortening.

The results of FDTD simulations presented in this section thus show that the general predictions of McCall and Hahn for the evolution of the amplitude and the
phase of short pulses in a two-level medium generally agree reasonably well with the results of numerical simulations until the pulse duration becomes less than the duration of a single optical cycle. Numerical analysis reveals several interesting physical features in the formation of $2\pi$ solitons produced as a result of splitting of single-cycle pulses propagating in a two-level medium. In particular, the resulting pulses may have different amplitudes, durations, and group velocities, allowing the formation of sub-femtosecond pulses and slowing down of the light in two-level media. Noticeable deviations from the McCall–Hahn regime can be observed for pulses with durations shorter than the duration of a single field cycle. Half-cycle $2\pi$ pulses become asymmetric as they propagate through a two-level medium, while quarter-cycle $2\pi$ pulse display considerable distortions and lengthening in the process of propagation through a two-level medium. Deviations observed in the behavior of very short $2\pi$ pulses from the McCall–Hahn scenario are due to the fact that the cycle of interaction between light and a two-level system remains incomplete in this case, and light pulses leave some excitation in a two-level medium instead of switching excited-state population back to the ground state.
5.6 Let There be White Light: Supercontinuum Generation

Supercontinuum (SC) generation – a physical phenomenon leading to a dramatic spectral broadening of laser pulses propagating through a nonlinear medium – was first demonstrated in the early 1970s [5.71, 72] (see [5.73] for an overview of early experiments on supercontinuum generation). Presently, more than three decades after its discovery, supercontinuum generation is still one of the most exciting topics in laser physics and nonlinear optics [5.44], the area where high-field science meets the physics of low-energy unamplified ultrashort pulses in the most amazing way. The advent of photonic-crystal fibers [5.36, 37], capable of generating supercontinuum emission with unamplified, nano- and even sub-nanojoule femtosecond pulses, has resulted in revolutionary changes in frequency metrology [5.74–77] opened new horizons in ultrafast science [5.78, 79] and allowed the creation of novel wavelength-tunable and broadband fiber-optic sources for spectroscopic [5.80] and biomedical [5.81] applications. The rainbow of colors produced by a laser beam Fig. 5.15 has become an optical instrument and a practical tool.

As a physical phenomenon, supercontinuum generation involves the whole catalog of classical nonlinear-optical effects, such as self- and cross-phase modulation, four-wave mixing, stimulated Raman scattering, solitonic phenomena and many others, which add up to produce emission with an extremely broad spectra, sometimes spanning over a couple of octaves. Below, we discuss the basic physical processes contributing to supercontinuum generation in greater detail, with special emphasis made on self-phase modulation, four-wave mixing, and modulation instabilities (Sect. 5.6.1), cross-phase modulation (Sect. 5.6.2), as well as the solitonic phenomena and stimulated Raman scattering (Sect. 5.6.3).

5.6.1 Self-Phase Modulation, Four-Wave Mixing, and Modulation Instabilities in Supercontinuum-Generating Photonic-Crystal Fibers

Propagation of laser pulses in PCFs is always accompanied by SPM-induced spectral broadening. The basic features of SPM are discussed in Sect. 5.4.1. For very short laser pulses and broadband field waveforms, SPM can be thought of as a four-wave mixing

\[ \omega_{p1} + \omega_{p2} = \omega_3 + \omega_4 \]

with frequency components \( \omega_{p1} \) and \( \omega_{p2} \) from the spectrum of the laser field serving as pump photons generating new frequency components \( \omega_3 \) and \( \omega_4 \). In the case of a frequency-degenerate pump, \( \omega_{p1} = \omega_{p2} = \omega_p \), the new frequency components generated through FWM appear as Stokes and anti-Stokes sidebands at frequencies \( \omega_s \) and \( \omega_a \) in the spectrum of the output field. Such FWM processes become especially efficient, as emphasized in Sect. 5.4.4, when phase matching is achieved for the fields involved in the nonlinear-optical interaction. Under certain condi-
tions, the pump fields modify the effective refractive indices of the guided modes involved in the FWM process, inducing the phase matching for the FWM and leading to a rapid growth of spectral sidebands representing the Stokes and anti-Stokes fields. This regime of four-wave mixing, referred to as modulation instability (MI), plays an especially important role in nonlinear-optical spectral transformations of ultrashort pulses in PCFs.

In the simplest, scalar regime of modulation instability, two photons of the pump field with the frequency $\omega_p$ generate Stokes and anti-Stokes sidebands with frequencies $\omega_s = \omega_p - \Omega$ and $\omega_a = \omega_p + \Omega$. To illustrate this regime of MI, we represent the propagation constants of the Stokes and anti-Stokes sidebands as Taylor-series expansions around $\omega_p$,

$$\beta(\omega_p + \Omega) \approx \beta_0(\omega_p) + \frac{1}{\mu_p} \Omega + \frac{1}{2} \beta_2(\omega_p) \Omega^2 + 2\gamma P$$ \hspace{1cm} (5.164)

$$\beta(\omega_p - \Omega) \approx \beta_0(\omega_p) - \frac{1}{\mu_p} \Omega + \frac{1}{2} \beta_2(\omega_p) \Omega^2 + 2\gamma P$$ \hspace{1cm} (5.165)

where $P$ is the peak power of the pump field, $\beta_0(\omega_p)$ is the Kerr-effect-free propagation constant of the pump field mode (i.e., the propagation constant of the pump field corresponding to the regime with $P = 0$), $\mu_p = (\partial^2 \beta / \partial \Omega^2 |_{\omega = \omega_p})^{-1}$ is the group velocity of the pump pulse, $\beta_2(\omega_p) = \partial^2 \beta / \partial \Omega^2 |_{\omega = \omega_p}$, $\gamma = (\partial^2 \beta / \partial \Omega^2 |_{\omega = \omega_p})$ is the nonlinear coefficient, and $S_{\text{eff}} = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} |F(x,y)|^4 \, dx \, dy$ is the effective area of a guided mode with the transverse field profile $F(x,y)$.

With the propagation constant of the pump field written as

$$\beta(\omega_p) = \beta_0(\omega_p) + \gamma P$$ \hspace{1cm} (5.166)

the mismatch of the propagation constants of the fields involved in the FWM process is given by

$$\Delta \beta_{\text{FWM}} = \beta(\omega_p + \Omega) + \beta(\omega_p - \Omega) - 2 \beta(\omega_p) \approx \beta_2(\omega_p) \Omega^2 + 2\gamma P$$ \hspace{1cm} (5.167)

The phase matching can thus be achieved for this type of FWM at

$$\Omega = \pm \left( \frac{2\gamma P}{|\beta_2(\omega_p)|} \right)^{1/2}$$ \hspace{1cm} (5.168)

only when the central frequency of the pump field lies in the range of anomalous group-velocity dispersion, where $\beta_2(\omega_p) < 0$.

Figure 5.16 illustrates typical features of the scalar MI in PCFs observed by Fedotov et al. [5.82]. In those experiments, unamplified 50 fs pulses of 790–810 nm Ti:sapphire laser radiation with a repetition rate of 10 MHz and an energy of 0.1–1.4 nJ were coupled into micro-waveguide channels off the central core of the PCF (the inset in Fig. 5.16). The zero group-velocity dispersion (GVD) wavelength for the micro-waveguide channel used to observe MI is estimated as $\lambda_0 \approx 720$ nm, providing an anomalous GVD for the pump field. With a special choice of the pump pulse power, it is then possible to use the SPM phase shift to induce phase matching for efficient four-wave mixing (Fig. 5.16). This process can be understood as SPM-induced modulation instability, resulting in an exponential growth of spectral sidebands phase-matched with the pump field. In the output spectrum presented in Fig. 5.16, the 795 nm pump field generates sidebands centered at 700 and 920 nm. To understand this result, we use the standard result of MI theory (5.168) for the frequency shift corresponding to the maximum MI gain. With $\gamma \approx 50 \text{ W}^{-1} \text{ km}^{-1}$, $D \approx 30 \text{ ps/(nm km)}$, pulse energy $E \approx 0.5 \text{ nJ}$, initial pulse duration $\tau \approx 50 \text{ fs}$, we find $\Omega_{\text{max}} / 2\pi \approx 50 \text{ THz}$, which agrees well with the frequency shifts of the sidebands observed in the output spectra presented.
in Fig. 5.16. SPM-induced broadening sufficient to seed the considered MI-type FWM process is achieved within a fiber length \( z \approx (2L_d L_{NL})^{1/2} \), where \( L_d = \tau^2/|\beta_2| \) and \( L_{NL} = (\gamma P)^{-1} \) are the dispersion and nonlinear lengths, respectively. For the above-specified parameters of laser pulses and a PCF, we have \( L_d \approx 25 \) cm and \( L_{NL} \approx 0.2 \) cm. SPM-induced broadening can thus provide seeding for sideband generation at a frequency exceeding 3 GHz. Our experimental results thus demonstrate efficient regimes of SPM-induced MI in microchannel waveguides of PCFs, which offer much promise for parametric frequency conversion and photon-pair generation.

5.6.2 Cross-Phase-Modulation-Induced Instabilities

Self-induced MI in PCFs has been shown [5.53, 82] to provide a convenient means for broadband parametric amplification, permitting the creation of compact and convenient all-fiber optical parametric oscillators. Cross-phase-modulation-induced MI, on the other hand, does not require anomalous dispersion [5.23], suggesting convenient and practical control knobs for the frequency conversion of ultrashort pulses in PCFs, allowing the frequency shifts and amplitudes of sidebands in output spectra of the probe field to be tuned by varying the amplitude of the pump field.

Experiments [5.83] were performed with high-index-step fused-silica PCFs having a cross-sectional geometry shown in the inset to Fig. 5.17 with a core diameter of 4.3 \( \mu \)m. Figure 5.17 displays the group velocity and GVD calculated for this PCF using the polynomial expansion technique [5.84]. The standard theory of XPM-induced MI, as presented by Agrawal [5.85], was used to analyze the main features of this phenomenon for fundamental-wavelength and second-harmonic femtosecond pulses of a Cr:forsterite laser co-propagating in a PCF with the above-specified structure. This theory predicts that stationary solutions of this instability can be found by analyzing the dispersion relation

\[
\left[ (K - \Omega \delta g/2)^2 - h_1 \right] \left[ (K + \Omega \delta g/2)^2 - h_2 \right] = C^2, \tag{5.169}
\]

where

\[
h_j = \beta_j^2 \Omega^2 \left( \Omega^2 + 4 \gamma_j P_j g/\beta_j \right)/4, \tag{5.170}
\]

\[
C = 2\Omega^2 \sqrt{\beta_{21} \gamma \gamma P_1 P_2}, \tag{5.171}
\]

\( \gamma_j = n_2 \omega_j / (c S_j) \) are the nonlinear coefficients, \( \delta = (v_g / \nu_g) - 1 \), \( \beta_2 = (d^2 \beta / d \omega^2) \omega_{4\omega}, P_j, \omega_j, v_g, \) and \( \beta_1 \) are the peak powers, the central frequencies, the group velocities, and the propagation constants of the pump \((j = 1)\) and probe \((j = 2)\) fields, \( n_2 \) is the nonlinear refractive index, and \( S_j \) are the effective mode areas for the pump and probe fields. The gain of instabilities with a wave number \( K \) is given by \( G(\Omega) = 2 \text{Im}(K) \).

Fig. 5.17 The group velocity (the solid curve and the right-hand axis) and the group-velocity dispersion (the dashed curve and the left-hand axis) calculated as functions of the radiation wavelength \( \lambda \) for the fundamental mode of the PCF with a cross-sectional structure shown in the inset.
be shown below, this prediction agrees well with our experimental results.

The laser system used in experiments [5.83] consisted of a Cr<sup>4+</sup>:forsterite master oscillator, a stretcher, an optical isolator, a regenerative amplifier, and a compressor. The master oscillator, pumped with a fiber ytterbium laser, generated 30–60 fs light pulses of radiation with a wavelength of 1.23–1.25 µm at a repetition rate of 120 MHz. These pulses were then transmitted through a stretcher and an isolator, to be amplified in a Nd:YLF-laser-pumped amplifier and recompressed to the 170 fs pulse duration with the maximum laser pulse energy up to 40 µJ at 1 kHz. A 1 mm-thick β barium borate (BBO) crystal was used to generate the second harmonic of amplified Cr:forsterite laser radiation.

Figure 5.16, the pump wavelength falls within the area of anomalous dispersion for the fundamental mode of the PCF, while the second-harmonic probe lies in the range of normal dispersion. The faster pump pulse Fig. 5.17 was delayed in our experiments with respect to the slower probe pulse at the input of the PCF by a variable delay time of \( \tau \).

Figure 5.18 presents the results of experimental measurements performed with 170 fs pump pulses (the fundamental radiation of the Cr:forsterite laser) with an energy ranging from 0.2 up to 20 nJ and 3 nJ, 180 fs probe pulses (the second-harmonic output of the Cr:forsterite laser) transmitted through a 5 cm PCF with the cross-sectional structure shown in the inset to Fig. 5.17. For delay times \( \tau \) around zero, the slower probe pulse sees only the trailing edge of the faster moving pump pulse. In such a situation, XPM predominantly induces a blue shift of the probe field. For \( \tau \approx 6L \approx 750 \) fs, where \( L = 5 \) cm is the PCF length, the leading edge of the pump pulse catches up with the probe field closer to the output end of the fiber, which results in a predominant red shift of the probe. To symmetrize the interaction between the pump and probe fields with respect to the XPM-induced frequency shift, we choose the delay time \( \tau = \delta L/2 \approx 375 \) fs. In the regime of low peak pump powers (less than 3 kW), the output spectrum of the probe field displays only slight broadening due to self-phase modulation (Fig. 5.18a). Pump pulses with higher peak powers lead to radical changes in the output spectra of the probe field, splitting the central spectral component of the probe field and giving rise to intense symmetric sidebands around the central frequency \( \omega_2 \) (Figs. 5.18b–d).

The general tendencies in the behavior of the output spectrum of the probe field as a function of the pump power agree well with the prediction of the standard theory of XPM-induced MI. In view of the splitting and slight blue-shifting of the central spectral component of the probe field (Figs. 5.18b–d), we define the effective central wavelength of the pump-broadened probe spectrum as 605 nm. As the pump power changes from 5 kW up to 42 kW in our experiments, the shift of the short-wavelength sideband in the output spectrum of the second harmonic increases from 80 nm up to approximately 90 nm. The theory predicts the wavelength shifts of 76 nm and 90 nm, respectively, indicating the predominant role of XPM-induced MI in the observed spectral transformations of the probe field. The ampli-
uld of sidebands generated by pump pulses with a peak power of about 40 kW, as can be seen from Fig. 5.18d, become comparable or may even exceed the amplitude of the spectral components at the central part of the probe spectrum. The maximum frequency shift of the probe-field sidebands achieved in our experiments with 45 kW pump pulses is estimated as 80 THz, which is substantially larger than typical frequency shifts resulting from XPM-induced MI in conventional fibers [5.23]. With pump powers higher than 50 kW, both the central spectral components of the probe field and its sidebands featured a considerable broadening (Figs. 5.18c,f) and tended to merge together, apparently due to the cross-phase modulation induced by the pump field.

XPM-induced instabilities thus open an efficient channel of parametric FWM frequency conversion in photonic-crystal fibers. Fundamental-wavelength femtosecond pulses of a Cr:forsterite laser were used in our experiments as a pump field to generate intense sidebands around the central frequency of co-propagating second-harmonic pulses of the same laser through XPM-induced MI in a PCF. This effect leads to efficient pump-field-controlled sideband generation in output spectra of the second-harmonic probe field.

### 5.6.3 Solitonic Phenomena in Media with Retarded Optical Nonlinearity

Optical solitons propagating in media with noninstantaneous nonlinear response experience reshaping and continuous frequency down-shifting due to the Raman effect phenomenon, called soliton self-frequency shift (SSFS) [5.86, 87]. Photonic-crystal fibers substantially enhance this nonlinear-optical process due to strong field confinement in a small-size fiber core and the possibility to tailor dispersion of guided modes by varying the fiber structure. Liu et al. [5.54] have shown that 200 fs input pulses of 1.3 μm laser radiation can generate sub-100 fs soliton pulses with a central wavelength tunable down to 1.65 μm through the SSFS in a tapered PCF. Photonic-crystal fibers with the wavelength of zero group-velocity dispersion (GVD) shifted to shorter wavelengths have been used for the soliton frequency downshifting of 800–1050 nm laser pulses [5.88, 89]. Abedin and Kabotya [5.90] have employed a PCF to demonstrate a 120 nm SSFS for 10 GHz-repetition-rate picosecond pulses. In recent experiments [5.91, 92], PCFs with a special dispersion profile have been shown to provide an efficient spectral transformation of chirped sub-6 fs Ti:sapphire laser pulses through SSFS, leading to the generation of a well-resolved solitonic spectral component centered at 1.06 μm. Red-shifted soliton signals formed by sub-6 fs laser pulses in PCFs have been demonstrated to allow to a synchronized seeding of a picosecond Nd:YAG pump laser, permitting a considerable simplification of a few-cycle optical parametric amplification (OPCPA) scheme [5.79].

With many of the key tendencies in the evolution of ultrashort pulses in PCFs analyzed in the extensive literature, we focus here on the possibility of using the SSFS phenomenon for widely tunable frequency shifting of few-cycle laser pulses. Our theoretical analysis is based on the numerical solution of the generalized nonlinear Schrödinger equation [5.93]

$$\frac{\partial A}{\partial z} = i \sum_{k=2}^{6} \frac{(i)^k}{k!} \beta^{(k)} \frac{\partial^k A}{\partial \tau^k} + i \gamma \left( 1 + \frac{i}{\alpha_0} \frac{\partial}{\partial \tau} \right) \times \left[ A(z, \tau) \int_{-\infty}^{\infty} R(\eta) |A(z, \tau - \eta)|^2 d\eta \right].$$

(5.172)

where $A$ is the field amplitude, $\beta^{(k)} = \partial^k \beta/\partial \alpha_0^k$ are the coefficients in the Taylor-series expansion of the propagation constant $\beta$, $\alpha_0$ is the carrier frequency, $\tau$ is the retarded time, $\gamma = (n_2 \omega_0)/c S_{eff}$ is the nonlinear coefficient, $n_2$ is the nonlinear refractive index of the PCF material,

$$S_{eff} = \frac{\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} |F(x, y)|^2 dx dy}{\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} |F(x, y)|^4 dx dy}$$

(5.173)

is the effective mode area [$F(x, y)$ is the transverse field profile in the PCF mode], and $R(t)$ is the retarded nonlinear response function. For fused silica, we take $n_2 \approx 3.2 \times 10^{-16} \text{cm}^2/\text{W}$, and the $R(t)$ function is represented in a standard form [5.93, 94]:

$$R(t) = (1 - f_R) \delta(t) + f_R \Theta(t) \frac{\tau_t^2}{t_1^2} e^{-\frac{t}{\tau_1}} \sin \left( \frac{t}{\tau_2} \right),$$

(5.174)

where $f_R = 0.18$ is the fractional contribution of the Raman response; $\delta(t)$ and $\Theta(t)$ are the delta and the Heaviside step functions, respectively; and $\tau_1 = 12.5$ fs and $\tau_2 = 32$ fs are the characteristic times of the Raman response of fused silica.

We now apply (5.172) and (5.174) to compute the evolution of ultrashort pulses in two types of PCFs (Figs.
5.19, 5.20). PCFs of the first type consist of a fused silica core with a diameter of 1.6 μm, surrounded with two cycles of air holes (inset in Fig. 5.20a). To find the parameters $\beta^{(k)}$ for these fibers, we numerically solved the Maxwell equations for the transverse components of the electric field in the cross section of a PCF using a modification of the method of polynomial expansion in localized functions [5.84]. Polynomial approximation of the frequency dependence of the propagation constant $\beta$ for the fundamental mode of the PCF computed with the use of this numerical procedure with an accuracy better than 0.1% within the range of wavelengths 580–1220 nm yields the following $\beta^{(k)}$ coefficients for the central wavelength of 800 nm:

$$\beta^{(2)} \approx -0.0293 \text{ ps}^2 / \text{m}, \quad \beta^{(3)} \approx 9.316 \times 10^{-5} \text{ ps}^3 / \text{m}, \quad \beta^{(4)} \approx -9.666 \times 10^{-7} \text{ ps}^4 / \text{m}, \quad \beta^{(5)} \approx 1.63 \times 10^{-10} \text{ ps}^5 / \text{m},$$

$$\beta^{(6)} \approx -3.07 \times 10^{-13} \text{ ps}^6 / \text{m}.$$

For the fundamental mode of such PCFs, the GVD, defined as $D = -2\pi c \lambda^{-2} \beta^{(2)}$, vanishes at $\lambda_z \approx 690$ nm. Fibers of the second type are commercial NL-PM-750 PCFs (from Crystal Fibre). The core diameter for these PCFs was equal to 1.8 μm. The parameters $\beta^{(k)}$ for these PCFs were defined as polynomial expansion coefficients for the dispersion profile of the fundamental mode of these fibers provided by the manufacturer. The group-velocity dispersion for PCFs of this type vanishes at $\lambda_z \approx 750$ nm.

In the case studied here, the laser field at the input of a PCF has the form of a few-cycle pulse (the upper panel in Fig. 5.19a) with a broad spectrum (the upper panel in Fig. 5.19b) and a complicated chirp [5.79, 92]. For both types of PCFs, the short-wavelength part of the spectrum lies in the range of normal dispersion, while the wavelengths above $\lambda_z$ experience anomalous dispersion. A typical scenario of spectral and temporal evolution of a few-cycle laser pulse in PCFs of the considered types is illustrated by Figs. 5.19a,b. The initial stage of nonlinear-optical transformation of a few-cycle pulse involves self-phase modulation, which can be viewed as four-wave mixing of different frequency components belonging to the broad spectrum of radiation propagating through the fiber. Frequency components lying near the zero-GVD wavelength of the PCF then serve, as shown in the classical texts on nonlinear fiber optics [5.23], as a pump for phase-matched FWM. Such phase-matched FWM processes, which involve both frequency-degenerate and frequency-nondegenerate pump photons, deplete the spectrum of radiation around the zero-GVD wavelength and transfer the radiation energy to the region of anomalous dispersion (spectral components around 920 nm for $z = 2$ cm in Fig. 5.19b). A part of this frequency-downconverted radiation then couples into a soliton, which undergoes continuous frequency downshifting due to the Raman effect (Fig. 5.19b), known as soliton self-frequency shift [5.23,85,86]. In the time domain, the red-shifted solitonic part of the radiation field becomes

![Fig. 5.19](image-url) Temporal (a) and spectral (b) evolution of a laser pulse with an initial energy of 0.25 nJ and an input temporal envelope and chirp shown in Fig. 5.1b propagating through the second-type PCF (shown in the inset)
delayed with respect to the rest of this field (Fig. 5.19a) because of the anomalous GVD of the fiber. As a result of these processes, the red-shifted soliton becomes increasingly isolated from the rest of the light field in both the time and frequency domains, which reduces, in particular, the interference between the solitonic and nonsolitonic part of radiation, seen in Fig. 5.19b.

High-order fiber dispersion induces soliton instabilities, leading to Cherenkov-type emission of dispersive waves [5.21, 22] phase-matched with the soliton, as discussed in the extensive literature (see, e.g., [5.95, 96]).

This resonant dispersive-wave emission gives rise to a spectral band centered around 540 nm in Fig. 5.19b. As a result of the above-described nonlinear-optical transformations, the spectrum of the radiation field for a PCF with a characteristic length of 20 cm typically features four isolated bands, representing the remainder of the FWM-converted pump field (the bands centered at 670 and 900 nm in Fig. 5.19b), the red-shifted solitonic part (reaching 1.06 μm for z = 24 cm in Fig. 5.19b), and the blue-shifted band related to the Cherenkov emission of dispersive waves in the visible. In the time domain, as

![Image of intensity envelopes and spectral intensities for different propagation distances](image)

**Fig. 5.20** Temporal (a), (b) and spectral (c), (d) evolution of laser pulses with an initial energy of (a), (c) 0.15 nJ and (b), (d) 0.5 nJ and an initial pulse width of 6 fs in the first-type PCF (shown in the *inset*). The input pulses are assumed to be transform limited.
can be seen from Fig. 5.19a, only the solitonic part of the radiation field remains well localized in the form of a short light pulse, the remaining part of the field spreading out over a few picoseconds.

In Figs. 5.20a–d, we illustrate tunable frequency shifting of few-cycle laser pulses through SSFS in PCFs by presenting the results of simulations performed for an idealistic input pulse with an initial pulse width of 6 fs and a Gaussian pulse shape. For the first-type PCF (shown in the inset to Fig. 5.20a), almost the entire spectrum of the input pulse falls within the range of anomalous dispersion, and the pulse tends to form solitons, observed as well-resolved prominent spikes in the time domain (Figs. 5.20a,b). In the frequency domain, the Raman effect leads to a continuous frequency downshifting of the soliton (Figs. 5.20c,d). The rate of this frequency shift \( d\nu/dz \), where \( \nu \) is the carrier frequency and \( z \) is the propagation coordinate, rapidly grows with a decrease in the pulse duration \( \tau_0 \). With a linear approximation of the Raman gain as a function of the frequency, the integration of the nonlinear Schrödinger equation, as shown by Gordon [5.97], yields \( dv/dz \propto \nu_0^{-2} \). Although high-order dispersion and deviations of the Raman gain curve from the linear function generally make the relation between \( dv/dz \) and \( \tau \) in soliton dynamics much more complicated [5.98], the soliton pulse width remains one of the key parameters controlling the soliton frequency shift for a given Raman gain profile. In the case considered here, the short duration of 6fs input pulses provides a high rate of soliton-frequency shifting at the initial stage of pulse propagation through the PCF. As the spectrum of the soliton is shifted toward the spectral range with larger values of GVD, the pulse width increases, which slows down the frequency shift.

It is instructive to illustrate the main tendencies in the spectral and temporal evolution of few-cycle laser pulses in PCFs using the results of analysis of ideal solitons, i.e., solitons governed by the nonlinear Schrödinger equation [(5.68) in Sect. 5.4.2]. The NLSE (5.68) is recovered from (5.172) by setting \( \beta^{\text{eff}} = 0 \) for \( k \geq 3 \), taking \( f_k = 0 \), and keeping only the term representing the Kerr effect, i.e., the term proportional to \( i\gamma A |A|^2 \), in the nonlinear part of the equation. In normalized, soliton units, the energy carried by a soliton \( j \) is [5.98] \( E_j = 4\xi_j \), where \( \xi_j = W - j + 0.5 \) is the soliton eigenvalue, controlled by the input pulse energy \( 2W^2 \). The soliton pulse width is given by \( \tau_0 = \tau_0/2\xi_j \), where \( \tau_0 \) is the input pulse width. The soliton pulse width can thus be reduced, leading to higher SSFS rates, by increasing the energy of the input pulse.

In the case of solitary waves evolving in fibers with high-order dispersion and retarded nonlinearity, the results of NLSE analysis for the soliton energy and the soliton pulse width are no longer valid. In particular, as the soliton spectrum is shifted toward larger values of GVD, the soliton pulse width is bound to increase, while the soliton amplitude decreases (Figs. 5.20a,b). These changes in the soliton pulse width and amplitude are dictated by the balance between the dispersion and the nonlinearity, necessary for the existence of the soliton. On the qualitative level, however, being applied to short sections of a fiber, these simple relations provide important clues for the physical understanding of the evolution of Raman-shifted solitons in a PCF. Indeed, as can be seen from the comparison of the results of simulations performed for input pulses with the same initial pulse width (6 fs), but different energies, the SSFS rate in the case of higher energy pulses can substantially exceed the frequency-shift rate of solitons produced by lower energy pulses. A pulse with an input energy of 0.15 nJ, as can be seen from Fig. 5.20c, is coupled into a soliton, which undergoes a permanent red-shift as it propagates through the fiber. At \( z = 30 \) cm, the spectrum of this soliton peaks at 1.06 \( \mu \)m. A similar input pulse that has an initial energy of 0.5 nJ forms a soliton that exhibits a much faster frequency downshift. The central wavelength of this soliton reaches 1.12 \( \mu \)m already at \( z = 5 \) cm.

![Fig. 5.21 Temporal envelopes of red-shifted solitons (close-up of the peaks labeled with boxes in Figs. 5.20a,b) generated by laser pulses with an initial pulse width of 6 fs and an initial energy of (1) 0.15 nJ and (2) 0.5 nJ in a PCF at \( z = 30 \) cm (1) and 3 cm (2)](image)
To provide illustrative physical insights into the observed behavior of red-shifted solitons in PCFs as a function of the input pulse energy, we plot in Fig. 5.21 the snapshots of temporal envelopes of the solitonic part of the field corresponding to the input energies of 0.15 nJ (curve 1) and 0.5 nJ (curve 2). We take these snapshots of solitons, representing close-up views of intensity envelope sections labeled with boxes in Figs. 5.20a,b, for two different values of the propagation coordinate, \( z = 30 \text{ cm} \) in the case of a 0.15 nJ input pulse and \( z = 3 \text{ cm} \) for the 0.5 nJ input energy. With the spectra of red-shifted solitons centered around 1.06 \( \mu \text{m} \) in both cases (Figs. 5.20c,d), these values of the propagation coordinate allow a fair comparison of SSFS dynamics in terms of the dependence of the frequency shift rate on the soliton pulse width. As is seen from Fig. 5.21, the SSFS rate correlates well with the soliton pulse width. While the soliton produced by a pulse with an initial energy of 0.15 nJ has a pulse width of about 50 fs (curve 1 in Fig. 5.21), the pulse width of the soliton emerging from the 0.5 nJ laser pulse is about 20 fs. In qualitative agreement with predictions of Gordon [5.97] and Lucek and Blow [5.98], this shorter soliton in Figs. 5.20b,d displays a faster downshifting as compared with the longer soliton in Figs. 5.20a,c. In the following section, this dependence of the SSFS rate on the energy of the pulse launched into the fiber will be used for the experimental demonstration of widely tunable soliton frequency shift of 6 fs pulses produced by a Ti:sapphire oscillator.

At higher input powers, the spectral features originating from FWM, SSFS, dispersive-wave emission of solitons experience broadening due to SPM and XPM effects, merging together and giving rise to a broadband white-light emission (Figs. 5.15, 5.22). This supercontinuum radiation generated in PCFs has been intensely employed through the past few years to measure and control the offset between the carrier and envelope phases of ultrashort laser pulses, as well as for the creation of novel broadband sources for nonlinear spectroscopy, biomedical applications, and photochemistry. Examples of applications of PCF light sources based on enhanced nonlinear-optical interactions of guided modes will be given in Sect. 5.9.

### 5.7 Nonlinear Raman Spectroscopy

Nonlinear Raman spectroscopy is one of the most powerful techniques of nonlinear spectroscopy, which has found numerous applications in condensed- and gas-phase analysis, plasma diagnostics, investigation of molecular relaxation processes, temperature and concentration measurements, condensed-phase studies, and femtochemistry. While many of modifications of nonlinear Raman spectroscopy have become a routine tool of modern optical experiments, giving rise to many successful engineering applications, some of nonlinear Raman experiments carried out in the last decade have shown that the potential of this technique for many topical and sometimes interdisciplinary problems of modern physics, chemistry, and biology is far from being completely realized. Similar to frequency-tunable sources of coherent radiation, which revolutionized nonlinear optics in its early days, allowing many delicate spectroscopic experiments, including nonlinear spectroscopic studies, to be performed, the impressive progress of femtosecond lasers in the 1990s has resulted in the breakthrough of the nonlinear Raman spectroscopy to new unexplored areas, giving rise to several elegant new ideas and approaches, permitting more-complicated systems and problems to be attacked, and leading to the measurements of fundamental importance. This new phase of nonlinear Raman spectroscopy also promoted...
the development of new spectroscopic concepts, including time-resolved schemes, broadband spectroscopy, polarization measurements, and CARS generalizations based on higher-order nonlinear processes. This conceptual and technical progress achieved in the last decade shows us some very important features of what nonlinear Raman spectroscopy is going to be in the nearest future, encouraging the application of new ideas, techniques, and methods in this area of spectroscopy.

This section provides a brief introduction to the main principles of nonlinear Raman spectroscopy, giving a general idea of how the measurements are performed and the spectroscopic data are extracted from the results of these measurements. Following this plan, we will first give a brief introduction to the basic concepts of nonlinear Raman spectroscopy. Then, we will consider various modifications of coherent Raman four-wave mixing (FWM) spectroscopy, including the standard CARS scheme, stimulated Raman scattering, Raman-induced Kerr effect, degenerate four-wave mixing (DFWM), and coherent hyper-Raman scattering. We will also briefly describe polarization techniques for nonlinear Raman spectrometry and coherent ellipsometry, allowing selective investigation of multicomponent molecular and atomic systems and permitting the sensitivity of nonlinear Raman spectrometry to be radically improved. Finally, in the context of the growing interest in the applications of short-pulse spectroscopy for the investigation of ultrafast processes, we will provide an introduction to time-resolved nonlinear Raman spectroscopy.

### 5.7.1 The Basic Principles

Nonlinear Raman spectroscopy is based on nonlinear-optical interactions in Raman-active media. The nonlinear character of light interaction with a medium implies that molecular, atomic, or ionic vibrations in a medium are no longer independent of the light field. Instead, pump light waves with frequencies \(\omega_1\) and \(\omega_2\) modulate Raman-active vibrations in a medium at the frequency \(\Omega \approx \omega_1 - \omega_2\), which can be then probed with another light beam, generally having a frequency \(\omega_3\) (Fig. 5.6c). This wave-mixing process involving the inelastic scattering of the probe wave by molecular vibrations gives rise to coherent Stokes- and anti-Stokes-frequency-shifted signals, whose amplitude \(I\), polarization (the ellipticity \(\chi\) and the tilt angle \(\psi\) of the principal axis of the polarization ellipse), and phase \(\varphi\) carry the spectroscopic information concerning the medium under study. This is the general idea of nonlinear Raman spectrometry, illustrated by Fig. 5.6c.

In practical terms, to undertake a simple three-color CARS experiment, one generally needs three laser sources generating radiation with the frequencies meeting the requirements specified above. In the most popular scheme of two-color CARS, where the anti-Stokes signal is generated through the frequency-mixing scheme \(\omega_a = 2\omega_1 - \omega_2\), the number of lasers required is reduced to two. Light beams have to be brought into coincidence in space to excite Raman-active transitions in a medium and to generate the anti-Stokes signal. Introducing some delay time between pumping and probing pulses, one can also perform time-resolved CARS measurements to keep track of the temporal dynamics of excitation in the system under investigation.

While spontaneous Raman scattering often suffers from the low quantum yield, which eventually results in the loss of sensitivity, coherent Raman scattering allows much more intense signals to be generated, thus allowing very high sensitivities to be achieved. Coherent Raman scattering also offers several other very important advantages that stem from the coherent character of the signal, which is thus well collimated and generated in a precisely known direction.

Generally, the analysis of the amplitude, phase, and polarization of the signal resulting from a nonlinear wave-mixing process in a Raman-resonant medium involves the calculation of the nonlinear response of the medium in terms of the relevant nonlinear susceptibilities and the solution of Maxwell equations for the field of the signal. Below, we restrict our brief introduction to the theory of nonlinear Raman processes to the description of the basic notions and terminology, which will be employed later to explain the main concepts of various nonlinear Raman methods, including frequency- and time-domain CARS, coherent ellipsometry, and the Raman-induced Kerr effect (RIKE).

#### Excitation of Raman Modes

Within the framework of a simple, but physically instructive, semiclassical model of a nonlinear medium consisting of noninteracting molecules with a Raman-active vibration with frequency \(\Omega\), the interaction of light with molecules (atoms or ions) can be described in terms of the electronic polarizability of molecules \(\alpha\) depending on the generalized normal coordinate \(Q\) (e.g., defined as the distance between the nuclei in a molecule) \[5.99\]:

\[
\sigma(Q) = \sigma_0 + \left(\frac{\partial \sigma}{\partial Q}\right)_0 Q + \ldots , \quad (5.175)
\]
where $\alpha_0$ is the equilibrium polarizability of a molecule, $(\partial \alpha / \partial Q)_0$ is the derivative of the electronic polarizability in the normal coordinate taken for the equilibrium position of nuclei, and we restrict our consideration to terms in this expansion linear in $Q$. The term $(\partial \alpha / \partial Q)_0 Q$ in (5.175) is responsible for the modulation of light by molecular vibrations, as it gives rise to new frequency components in the induced polarization of the system, whose frequency shift is determined by the frequency of molecular vibrations. This can be seen from the expression for the polarization of a medium:

$$P = Np,$$  \hspace{1cm} (5.176)

where $N$ is the number density of Raman-active molecules,

$$p = \alpha(Q)E = \alpha_0 E + \left(\frac{\partial \alpha}{\partial Q}\right)_0 Q E + \ldots$$  \hspace{1cm} (5.177)

is the dipole moment of a molecule and $E$ is the electric field strength. The energy of a molecule in a light field is written as

$$H = -pE = -\alpha(Q)E^2.$$  \hspace{1cm} (5.178)

Thus, the light-induced force driving molecular vibrations is given by

$$F = -\frac{\partial H}{\partial Q} = \frac{\partial \alpha}{\partial Q} E^2.$$  \hspace{1cm} (5.179)

As can be seen from (5.179) the force acting on a molecule in a light field may result in a resonant excitation of Raman-active vibrations with a frequency $\Omega$ if the field involves frequency components $\omega_1$ and $\omega_2$ with $\omega_1 - \omega_2 \approx \Omega$.

**Wave Mixing in Raman–Active Media**

The propagation of light waves in a nonlinear medium is governed by the wave equation

$$\Delta E - \frac{n_i^2 c^2 E}{\epsilon_0^2} = \frac{4\pi}{c^2} \frac{\partial^2 P_{nl}}{\partial t^2},$$  \hspace{1cm} (5.180)

where $E$ is the field in the light wave, $n_i$ is the refractive index, $c$ is the speed of light, and $P_{nl}$ is the nonlinear polarization of the medium.

Consider for example the CARS process, as an example of a nonlinear Raman process, assuming that it involves plane and monochromatic waves,

$$E(r, t) = E_1 \exp(-i\omega_1 t + ik_1 r)$$
$$+ E_2 \exp(-i\omega_2 t + ik_2 r)$$
$$+ E \exp(-i\omega t + ik r)$$
$$+ E_4 \exp(-i\omega_1 t + ik_4 r) + c.c.$$,  \hspace{1cm} (5.181)

where $\omega_1$ and $\omega_2$ are the frequencies of pump waves, $\omega$ is the frequency of the probe wave, $\omega_a = \omega + \omega_1 - \omega_2$, the field envelopes $E_1, E_2, E$, and $E_4$ are slowly varying functions of coordinates $r$ and time $t$, $k_1, k_2$, and $k_4$ are the wave vectors of light waves with frequencies $\omega, \omega_1, \omega_2, \omega_a$, respectively, and $c.c.$ stands for a complex conjugate. Then, representing the nonlinear polarization in the medium as a superposition of plane waves, we can write the equation for the amplitude of the anti-Stokes wave as

$$\frac{n_a}{c} \frac{\partial E_a}{\partial t} + \frac{\partial E_a}{\partial z} = \frac{2\pi \omega_a}{cn_a} P_{nl}(\omega_a) \exp(ik_a z),$$  \hspace{1cm} (5.182)

where $P_{nl}(\omega_a)$, $n_a$, and $k_a$ are the amplitude of the nonlinear polarization, the refractive index, and the $z$-component of the wave vector at the frequency $\omega_a$. The pump wave amplitudes will be assumed to be constant. Now, the nonlinear polarization of a medium has to be found with the use of some model of the nonlinear medium.

**Raman–Resonant Nonlinear Polarization and Nonlinear Susceptibilities**

Within the framework of our model of a nonlinear medium, the third-order nonlinear polarization of the medium at the anti-Stokes frequency $\omega_a$ is given by [5.99]

$$P^{(3)}(\omega_a) = \frac{N}{4MD(\Omega, \omega_1 - \omega_2)} \left(\frac{\partial \alpha}{\partial Q}\right)^2_0 EE_1E_2^*,$$  \hspace{1cm} (5.183)

where

$$D(\Omega, \omega_1 - \omega_2) = \Omega^2 - (\omega_1 - \omega_2)^2$$
$$- 2i \Gamma (\omega_1 - \omega_2),$$  \hspace{1cm} (5.184)

derivatives are taken in the equilibrium position, $\Gamma$ is the phenomenologically introduced damping constant, $M$ is the reduced mass of a molecule, $N$ is the number density of molecules, an asterisk indicates a complex conjugate, $Q$ is the amplitude of the Raman-active molecular vibration, which can be expressed in terms of the density matrix $\rho$ of an ensemble of molecules,

$$Q = \text{Sp}(pq) = \rho_{ab}q_{ba},$$  \hspace{1cm} (5.185)

where $\text{Sp}$ is the trace operator and $q$ is the operator of the vibrational coordinate.

Introducing the third-order nonlinear-optical susceptibility of the medium,

$$\chi^{(3)R} = \frac{N}{24MD(\Omega, \omega_1 - \omega_2)} \left(\frac{\partial \alpha}{\partial Q}\right)^2_0,$$  \hspace{1cm} (5.186)
and solving (5.182), we arrive at the following expression for the intensity of the CARS signal \( I_a \):

\[
I_a \propto \left| \chi^{(3)}(\omega_2; \omega, \omega_1, -\omega_2) \right|^2 \times I_1 l_2^2 \left( \frac{\sin \left( \frac{\Delta \omega}{\Delta \lambda} \right)}{\Delta \lambda} \right)^2 ,
\]

where \( I, I_1, I_2 \) are the intensities of the pump and probe beams, \( l \) is the length of the nonlinear medium, and \( \Delta k = |k_2 - k - k_1 + k_3| \) is the wave-vector mismatch. As can be seen from (5.187), the anti-Stokes wave is generated especially efficiently in the direction of phase matching, where \( \Delta k = 0 \).

The cubic nonlinear-optical susceptibility of a medium \( \chi^{(3)} \) is a fourth-rank tensor. The knowledge of the form of this tensor is important, in particular, for understanding the polarization properties of the signal of nonlinear Raman scattering. The form of the \( \chi^{(3)} \) tensor is determined by the symmetry properties of a medium. For an isotropic medium, only 21 of 81 tensor components of \( \chi^{(3)} \) are nonvanishing. Only three of these components are independent of each other, as the relations

\[
\begin{align*}
\chi_{1111}^{(3)} &= \chi_{2222}^{(3)} = \chi_{3333}^{(3)}, \\
\chi_{1122}^{(3)} &= \chi_{1133}^{(3)} = \chi_{2211}^{(3)} = \chi_{1122}^{(3)} = \chi_{3311}^{(3)} = \chi_{3322}^{(3)}, \\
\chi_{1112}^{(3)} &= \chi_{1133}^{(3)} = \chi_{2211}^{(3)} = \chi_{1122}^{(3)} = \chi_{3311}^{(3)} = \chi_{3322}^{(3)}, \\
\chi_{1122}^{(3)} &= \chi_{1133}^{(3)} = \chi_{2211}^{(3)} = \chi_{1122}^{(3)} = \chi_{3311}^{(3)} = \chi_{3322}^{(3)}, \\
\chi_{1111}^{(3)} &= \chi_{1122}^{(3)} = \chi_{1122}^{(3)} = \chi_{1221}^{(3)}.
\end{align*}
\]

hold true for an isotropic medium [5.9, 99]. The form of the \( \chi^{(3)} \) tensor for all the crystallographic classes can be found in many textbooks on nonlinear optics [5.9, 10].

**Phase Matching of Focused Beams**

Generally, in the case of focused beams, phase-matching effects in nonlinear Raman scattering are taken into account through the phase-matching integral. In particular, for Gaussian beams, the expression for the overall power of the two-color CARS signal occurring in accordance with the scheme \( \omega_a = 2\omega_1 - \omega_2 \) is written as [5.11, 100, 101]

\[
P_a = \left( \frac{3\pi^2 \omega_a}{c n_2} \right)^2 |\chi^{(3)}|^2 \\
\times P_1^2 P_2 \frac{2}{\pi} \left( \frac{b}{w_0} \right)^2 \int_0^\infty 2\pi r |J|^2 \, dr .
\]

Here, \( P_1 \) and \( P_2 \) are the powers of the pump beams with frequencies \( \omega_1 \) and \( \omega_2 \), respectively, \( w_0 \) is the waist size of the focused pump beams, \( b \) is the confocal parameter,

\[
J = \frac{C_2}{(1 + i\xi'')(k'' - ik'' \xi'')} H \, d\xi' ,
\]

where \( -C_1 \) and \( C_2 \) are the coordinates of the boundaries of the nonlinear medium,

\[
H = \frac{1 + \xi''^2}{k'' - ik'' \xi'} - \frac{i}{k''} \xi' - \frac{\xi}{3} ,
\]

\( k'' = 2k_1 + k_2, k' = 2k_1 - k_2, \xi = 2(z - f)/b \) is the normalized coordinate along the \( z \)-axis (\( f \) is the coordinate of the beam waist along the \( z \)-axis).

Equations (5.193–5.195) show that the information on the nonlinear cubic susceptibility in the CARS signal may be distorted by phase-matching effects. This problem has been analyzed both theoretically and experimentally for different modifications of nonlinear Raman spectroscopy [5.102]. The influence of absorption at the wavelength of pump and probe waves and at the frequency of the FWM signal can be taken into account by including the imaginary parts of the relevant wave vectors. The integral in (5.194) can be calculated in an analytical form for several particular cases, giving a clear physical understanding of the role of phase-matching and absorption effects in coherent FWM spectroscopy and imaging [5.103].

### 5.7.2 Methods of Nonlinear Raman Spectroscopy

In this section, we will briefly consider standard and widely used schemes for nonlinear Raman spectroscopy (Fig. 5.2), including coherent Raman scattering, stimulated Raman scattering, and the Raman-induced Kerr effect and provide a brief introduction into the vast area of DFWM.

**Stimulated Raman Scattering**

The idea of using stimulated Raman scattering (SRS) as a spectroscopic technique is based on the measurement
of the frequency dependence of the SRS small-signal gain, which is proportional to the imaginary part of the nonlinear cubic susceptibility of a Raman-active medium [5.9, 99]. The power of the pump wave in such measurements has to be chosen in such a way as to avoid uncontrollable instabilities and to obtain noticeable SRS gain. The SRS-based approach was successfully employed, in particular, for high-resolution spectroscopy of Raman transitions [5.104].

Limitations of SRS as a spectroscopic technique are due to instabilities arising for light intensities exceeding the threshold SRS intensity. These instabilities build up under conditions when several nonlinear processes, including self-focusing and self-phase modulation, compete with each other, often rendering the SRS method impractical for spectroscopic applications.

**Coherent Anti-Stokes Raman Scattering**

Instead of measuring the gain of one of two waves, as is done in SRS, Maker and Terhune [5.105] have demonstrated a spectroscopic technique based on measuring the frequency dependence of the intensity of a new wave generated at the anti-Stokes frequency \( \omega_a = 2\omega_1 - \omega_2 \) in the presence of two light waves with frequencies \( \omega_1 \) and \( \omega_2 \) chosen in such a way as to meet the condition of a Raman resonance with a Raman-active transition in a medium: \( \omega_1 - \omega_2 \approx \Omega \) (Fig. 5.6c). This approach, called coherent anti-Stokes Raman scattering, has become one of the most widespread nonlinear Raman methods, allowing many urgent spectroscopic problems to be successfully solved and stimulating numerous engineering applications of nonlinear laser spectroscopy (so-called three-color CARS with \( \omega_a = \omega_1 - \omega_2 + \omega_3 \) is shown in Fig. 5.6c). Similar to the SRS process described in the previous section, CARS involves the stimulated scattering of light in a Raman-active medium. However, in contrast to the standard SRS scheme, where a Stokes wave is generated or amplified, the CARS process gives rise to the appearance of a new frequency component, suggesting a spectroscopic approach that is free of instabilities typically arising in SRS due to the competition of different nonlinear processes.

Due to its high spatial, temporal, and spectral resolution, the possibilities of studying highly luminous objects, and a rich variety of polarization methods, the CARS technique has gained a wide acceptance for temperature and concentration measurements in excited gases, combustion, and flames [5.99, 106–108], gas-phase analysis [5.99, 109, 110], high-resolution molecular spectroscopy [5.111, 112]. Short-pulse CARS gives an access to ultrafast processes and wave-packet dynamics in molecular systems [5.113]. The nonlinear nature and the spectral selectivity of CARS make this method an ideal tool for nonlinear spectroscopy [5.114, 115]. The most recent advances in nonlinear Raman techniques include coherence-controlled CARS [5.116], enhancing the potential of CARS microscopy [5.117], and CARS in photonic-crystal fibers [5.118, 119].

The widely employed geometry of nonlinear Raman measurements implies the use of collinear focused laser beams. While focusing allows the intensity sufficient to ensure a reliable detection of the nonlinear Raman signal to be achieved, the collinear geometry of wave mixing increases the length of nonlinear interaction. However, such an approach is reasonable as long as the spatial resolution along the propagation coordinate is not important. The scheme of nonlinear Raman spectroscopy becomes resolvable along the propagation coordinate as soon as collinear beams are replaced by a noncollinear one (Fig. 5.6c). In CARS, this technique is called the boxcars geometry [5.120]. The interaction area is confined in this case to the region where the beams intersect each other, allowing a high spatial resolution to be achieved.

In the broad-beam CARS geometry Fig. 5.23, focused laser beams are replaced with broad or sheetlike beams. This approach allows the nonlinear Raman signal to image the whole areas of a nonlinear medium.
on a charge-coupled device (CCD) camera. The idea of broad-beam CARS imaging, which was discussed by Regnier and Taran [5.121] in 1973, has later proved to be efficient for the solution of many problems of gas-phase and plasma diagnostics [5.102, 122, 123]. Significant progress in extracting the data concerning parameters of a gas medium was achieved, allowing CARS signals from molecules of different types to be simultaneously detected, with the development of a dual broadband CARS scheme [5.124, 125] and angularly resolved CARS [5.126].

Figure 5.23 illustrates the application of the broad-beam folded CARS geometry for the investigation of excited and ionized gases [5.122, 123]. In this scheme, a pair of cylindrically focused coplanar broad light beams with frequencies \( \omega_1 \) and \( \omega_2 \) and wave vectors \( k_1 \) and \( k_2 \), forming a small angle \( \theta \), irradiate a thin plasma layer in a plane parallel to the plane of the target (Fig. 5.23a). A cylindrically focused or a collimated nonfocused laser beam with frequency \( \omega_3 \) and wave vector \( k_3 \), which makes an angle \( \alpha \) with the plane of the \( k_1 \) and \( k_2 \) vectors (Fig. 5.23b), irradiates the laser-produced spark from above. The FWM signal is generated in the direction \( k_{\text{FWM}} \) determined by phase-matching conditions, forming an angle \( \beta \) with the plane of the target (Figs. 5.23a,b). Imaging the one-dimensional FWM signal onto a CCD array, we were able to map the spatial distribution of resonant particles in the plasma line by line. The use of a collimated unfocused beam \( \omega_3 \) enables slice-by-slice plasma imaging [5.102].

### Raman–Induced Kerr Effect

The Raman-induced Kerr effect (RIKE) [5.9] is understood as an optical birefringence induced in an initially isotropic medium due to an anisotropic Raman-resonant third-order polarization of a medium. In this scheme, a nonlinear medium is irradiated with a pair of light beams with frequencies \( \omega_1 \) and \( \omega_2 \) whose difference is tuned, in accordance with the general idea of probing Raman-active vibrations, to a resonance with Raman-active transitions in a medium. Then, the polarization of a probe wave at the frequency \( \omega_1 \) becomes perturbed due to the anisotropic nonlinear polarization induced in the Raman-active medium, which can be detected with the use of a polarization analyzer and a detector. The RIKE technique provides us with a convenient method for measuring the frequency dependence of the cubic susceptibility \( \chi^{(3)} \) around a Raman resonance. The transmission coefficient \( T \) of a polarization analyzer aligned in such a way as to block the probe beam in the absence of the pump beam is given by [5.99]

\[
T (\omega_1 - \omega_2) \propto \sin^2 2\gamma \left| \chi^{(3)}_{1122} (\omega_1; \omega_2, \omega_1, -\omega_2) \right|^2 + \left| \chi^{(3)}_{1212} (\omega_1; \omega_2, \omega_1, -\omega_2) \right|^2 I_2^2
\]

in the case of a linearly polarized pump (\( I_2 \) is the intensity of the pump beam and \( \gamma \) is the angle between the polarization vectors of the pump and probe waves) and

\[
T_c (\omega_1 - \omega_2) \propto \left| \chi^{(3)}_{1122} (\omega_1; \omega_2, \omega_1, -\omega_2) \right|^2 - \left| \chi^{(3)}_{1221} (\omega_1; \omega_2, \omega_1, -\omega_2) \right|^2 I_2^2
\]

in the case of a circularly polarized pump. As can be seen from (5.197), the coherent background is completely suppressed in the case of a circularly polarized pump.

Importantly, RIKE is one of the four-wave mixing processes where the phase-matching condition is satisfied automatically regardless of the arrangement of the wave vectors of pump and probe waves, since the phase-matching condition \( k_3 = k_2 + k_1 - k_2 \) becomes an identity in this case.

### Degenerate Four-Wave Mixing

Although, rigorously speaking, degenerate four-wave mixing does not employ Raman transitions and the models used to describe DFWM may sometimes differ from the standard ways of CARS description [5.9, 10], it is reasonable to briefly introduce DFWM as a nonlinear technique here, as it very frequently offers a useful alternative to CARS, allowing valuable data on a medium to be obtained in a convenient and physically clear way. DFWM is closely related to CARS as both processes are associated with the third-order nonlinearity of a medium. The main difference between these methods is that CARS implies the use of a two-photon Raman-type resonance (Fig. 5.6c), while DFWM is a frequency-degenerate process (Fig. 5.6d), involving either four one-photon resonances or a pair of two-photon resonances. With modern lasers capable of generating very short pulses, having large spectral widths, the DFWM signal can be detected simultaneously with CSRS and CARS in the same experimental geometry with the same molecular system by simply tuning the detection wavelength [5.127]. The combination of these nonlinear-optical approaches allows a more elaborate study of molecular relaxation and photochemistry processes, providing a much deeper insight.
into the ultrafast molecular and wave-packet dynamics [5.127, 128].

The main advantages of DFWM as a spectroscopic technique are associated with the technical simplicity of this approach, which requires only one laser source and allows phase-matching conditions to be automatically satisfied regardless of the dispersion of the medium under study. Broadband DFWM [5.129] makes it possible to measure the temperature of excited gases, including atomic gases [5.130], with a single laser pulse. Folded broad-beam DFWM schemes are employed in several convenient and elegant methods for two-dimensional imaging of spatial distributions of gas parameters [5.131, 132].

5.7.3 Polarization Nonlinear Raman Techniques

Methods of polarization-sensitive four-photon spectroscopy provide an efficient tool for the solution of many problems arising in the investigation of Raman resonances. In particular, the polarization technique is a standard method to suppress the coherent background in CARS measurements [5.99, 106], which makes it possible to considerably improve the sensitivity of spectroscopic measurements [5.99] and improves the contrast in CARS microscopy [5.115]. Polarization techniques in FWM spectroscopy can separately measure the real and imaginary parts of the relevant third-order nonlinear-optical susceptibility [5.133, 134], resolve closely spaced lines in FWM spectra of molecules [5.99, 135] and atoms [5.102], and improve the contrast of cubic-susceptibility dispersion curves near Raman resonances [5.136, 137]. Polarization methods in nonlinear Raman spectroscopy [5.138–140] help to analyze the interference of vibrational Raman resonances with one- and two-photon electronic resonances in CARS spectra [5.141], and can be used to determine invariants of atomic and molecular Raman and hyper-Raman scattering tensors [5.102] and to perform conformational analysis for complex organic molecules [5.141]. A comprehensive review of polarization techniques employed for molecular spectroscopy was provided by Akhmanov and Koroteev [5.99].

Polarization Properties of the Coherent FWM Signal

When analyzing polarization properties of the FWM signal, one has to take into account the interference of resonant components of FWM related to various (molecular or atomic) transitions in the medium and the nonresonant coherent background. In particular, it is the interference of the resonant FWM component with the nonresonant coherent background that ensures the possibility to record complete spectral information concerning the resonance under study, including the data on the phase of resonant FWM.

The polarization ellipse of a Raman-resonant FWM signal is characterized by its ellipticity \( \chi \) (which is defined as \( \chi = \pm \arctan(b/a) \), where \( \arctan \) stands for the arctangent function, \( b \) and \( a \) are the small and principal semiaxes of the polarization ellipse, respectively) and the tilt angle \( \psi \) of its principal axis (Fig. 5.24a). These parameters are related to the Cartesian components of the third-order polarization of a medium \( P_x \) and \( P_y \) by the following expressions [5.99]:

\[
\tan(2\psi) = \tan(2\beta) \cos(\delta) ,
\]

\[
\sin(2\chi) = \sin(2\beta) \sin(\delta) .
\]

Fig. 5.24a,b Polarization technique of nonlinear Raman spectrometry: (a) coherent ellipsometry and (b) polarization suppression of the nonresonant background in CARS spectroscopy
where \( \beta \) and \( \delta \) are defined as

\[
\tan (\beta) = \frac{|P_{r}|}{|P_{n}|},
\]
\[
\delta = \arg (P_{r}) - \arg (P_{n}).
\]

The frequency dependencies of the FWM polarization ellipse parameters, as can be seen from (5.198) and (5.199), provide information concerning the phase of the resonant FWM component, allowing a broad class of phase measurements to be performed by means of nonlinear Raman spectroscopy.

### Suppressing the Nonresonant Background

Polarization suppression of the nonresonant background in CARS is one of the most useful, practical, and widely employed polarization techniques in nonlinear Raman spectroscopy. Physically, the possibility of suppressing the nonresonant background in coherent Raman spectroscopy is due to the fact that the resonant and nonresonant components of the nonlinear polarization induced in a Raman-active medium are generally polarized in different ways. Let us illustrate this technique for the CARS process \( \omega_a = 2\omega_1 - \omega_2 \), where \( \omega_a \) is the frequency of the anti-Stokes signal and \( \omega_1 \) and \( \omega_2 \) are the frequencies of pump waves, in the case of an isotropic medium. The third-order polarization responsible for the generation of the signal with the frequency \( \omega_a \) is then written as

\[
P^{(3)} = [P_{r} + P_{nr}] E_1^2 E_2^2.
\]

where \( E_1 \) and \( E_2 \) are the amplitudes of the light fields, \( P_{r} \) and \( P_{nr} \) are the resonant and nonresonant components of the third-order polarization induced in the Raman-active medium.

In the case of an isotropic medium, relations (5.188–5.192) are satisfied for both resonant and nonresonant components of the nonlinear-optical susceptibility. However, only the nonresonant part of the cubic susceptibility satisfies the Kleinman relations [5.9, 99],

\[
\chi^{(3)}_{1111} = 3\chi^{(3)}_{1222} = 3\chi^{(3)}_{1221} = 3\chi^{(3)}_{1122},
\]

while the resonant part of the cubic susceptibility is usually characterized by a considerable dispersion near a Raman resonance, which implies that the resonant cubic susceptibility tensor components are not invariant with respect to the permutation of their frequency arguments. Taking into account relations (5.203) for the nonresonant part of the cubic susceptibility, we arrive at the following expression for the nonresonant and resonant components of the third-order polarization of a Raman-active medium:

\[
P_{nr} = \chi^{(3)nr}_{1111} [2e_1 (e_1 e_2^* + e_1^* e_2)],
\]
\[
P_{r} = 3\chi^{(3)r}_{1111} [(1 - \bar{\beta}) e_1 (e_1 e_2^* + \bar{\beta} e_2^* (e_1 e_2))],
\]

where \( \bar{\beta} = \chi^{(3)r}_{1221}/\chi^{(3)nr}_{1111} \) and \( e_1 \) and \( e_2 \) are the unit polarization vectors of the light fields with frequencies \( \omega_1 \) and \( \omega_2 \), respectively (Fig. 5.24b).

Suppose that the pump fields with frequencies \( \omega_1 \) and \( \omega_2 \) are linearly polarized and their polarization vectors \( e_1 \) and \( e_2 \) are oriented at an angle \( \mu \) with respect to each other, as shown in Fig. 5.24b. The vectors \( P_{nr} \) and \( P_{r} \), in accordance with (5.204) and (5.205), generally have different orientations in space making a nonzero angle \( \theta \) with each other. Therefore, by orienting the polarization analyzer in such a way as to suppress the nonresonant component of the CARS signal (by setting the angle \( \epsilon \) measured from the direction perpendicular to the vector \( P_{nr} \) equal to zero, see Fig. 5.24b), one can analyze background-free CARS spectra.

In many situations, nonlinear Raman study of Raman-active media would be simply impossible without this technique. This is the case, for example, when the CARS signal from a resonant gas under investigation is too weak to be reliably detected against the nonresonant CARS signal from the windows of a gas cell. Another example is the CARS spectroscopy on low concentrations of complex biological molecules, when the coherent background due to solvent molecules may be so strong that it leaves no way to detect the CARS signal from the molecules being studied without polarization suppression of the nonresonant nonlinear Raman signal. Even small deviations of the orientation of the polarization analyzer from the background-suppression position may be crucial, leading to dramatic changes in the signal-to-noise ratio. Another important conclusion that can be made from (5.204) and (5.205) is that, measuring the ratio of the CARS signals for different polarization arrangements is a convenient way of determining the properties of the nonlinear susceptibility tensor and, thus, characterizing the symmetry properties of molecular transitions under investigation.

### Coherent Ellipsometry

Coherent ellipsometry, i.e., the measurement of the parameters of the polarization ellipse corresponding to the FWM signal, is one of widely used modifications of polarization-sensitive four-photon spectroscopy. Below,
we consider the main physical principles and discuss the main ideas of coherent ellipsometry.

The possibility of reconstructing the real and imaginary parts of the nonlinear-optical susceptibility of a medium as functions of frequency and time is due to the interference of the resonant FWM component with the nonresonant coherent background, which ensures the recording of the phase information for the resonance being studied. For a broad class of problems, the nonlinear polarization of a medium responsible for coherent FWM processes can be represented as a sum of the nonresonant and resonant components described by a real vector \( P_{\text{nr}} \) and a complex vector \( P_r \), respectively. Choosing the x-axis along the vector \( P_{\text{nr}} \) (Fig. 5.24b), we can write the Cartesian components of the total polarization of a medium cubic in the external field as

\[
P_x = P_{\text{nr}} + P_r e^{i\psi} \cos(\theta), \quad (5.206)
\]

\[
P_y = P_r e^{i\psi} \sin(\theta), \quad (5.207)
\]

where \( \psi \) is the phase of the resonant component of the nonlinear polarization and \( \theta \) is the angle between the resonant and nonresonant components.

Knowing the parameters of the polarization ellipse from ellipsometric measurements, we can reconstruct, with the use of (5.198), (5.199), (5.206), (5.207), the real and imaginary parts of the resonant nonlinear polarization as functions of frequency and time from the experimental data of coherent ellipsometry.

In the important particular case when the resonant component of the FWM signal can be considered as a small correction to the nonresonant component, the general procedure of separating the real and imaginary parts of the nonlinear polarization of a medium becomes especially simple. One can easily verify that the relations [5.99]

\[
\psi = \beta \cos(\phi) \propto \text{Re}(P) \quad (5.208)
\]

\[
\chi = \beta \sin(\phi) \propto \text{Im}(P) \quad (5.209)
\]

are satisfied in this case, showing that the spectral or temporal dependencies of the parameters \( \psi \) and \( \chi \) of the FWM polarization ellipse respectively reproduce the spectral or temporal dependencies of the real and imaginary parts of the resonant component of the nonlinear polarization of a medium.

Thus, the data obtained by means of coherent ellipsometry enable one to extract complete information concerning the resonant component of the nonlinear polarization of a medium, including information on its phase [5.134]. Note that no assumptions regarding the shape of the line observed in a nonlinear Raman spectrum was made in our consideration, which means that this approach can be applied to a broad class of spectral lines. This procedure can be also extended to the time domain, allowing not only the spectra but also the time dependencies of the real and imaginary parts of the nonlinear polarization of a medium to be reconstructed. Finally, close molecular and atomic lines unresolvable in amplitude nonlinear Raman spectra can be also resolved in certain cases with the use of the phase information stored in coherent nonlinear spectra.

### 5.7.4 Time-Resolved Coherent Anti-Stokes Raman Scattering

The method of time-resolved FWM spectroscopy implies that information on the parameters of atomic or molecular systems is extracted from an impulse response of a coherently excited system rather than from the frequency dispersion of nonlinear susceptibilities, as is done in frequency-domain FWM spectroscopy. The original idea of time-resolved CARS is that a light pulse with a duration shorter than the characteristic transverse relaxation time \( T_2 \) induces coherent molecular vibrations with amplitude \( Q(t) \), and the decay kinetics of these vibrations is analyzed with the use of another, probe light pulse, which is delayed in time with respect to the pump pulses. The complete set of equations governing the processes related to time-domain CARS includes the SVEA wave equation (5.182) and the equations for the amplitude of coherent molecular vibrations \( Q(t) \), defined in accordance with (5.185), and the normalized population difference between the levels involved in the Raman resonance, \( n = \rho_{aa} - \rho_{aa} \):

\[
\frac{\partial^2 Q}{\partial t^2} + 2 \frac{\partial Q}{\partial t} + \Omega^2 Q = \frac{1}{2M} \frac{\partial \alpha}{\partial t} E^2, \quad (5.210)
\]

\[
\frac{\partial n}{\partial t} + \frac{n - 1}{T_1} = \frac{1}{2\hbar \Omega} \frac{\partial Q}{\partial t} \frac{\partial^2 Q}{\partial t^2}, \quad (5.211)
\]

where \( T_1 \) is the population relaxation time.

In many cases, (5.182), (5.210), and (5.211) can be simplified with the use of the slowly varying envelope approximation. In this approximation, the energy of the CARS signal as a function of the delay time \( \tau \) of the probe pulse in the scheme of time-resolved CARS with short light pulses and \( \Delta k = 0 \) is given by [5.99]

\[
W_\Delta(\tau) \propto \int_{-\infty}^{\infty} |Q(t)|A(t-\tau)|^2 \, dt. \quad (5.212)
\]
Since the intensity of the CARS signal in such a scheme is determined by (5.212), the use of sufficiently short probe pulses makes it possible to measure the kinetics of $Q(t)$. Experiments by Alfano and Shapiro [5.142] and von der Linde et al. [5.143] have demonstrated the possibility of using the time-domain CARS technique to directly measure the $T_2$ time for Raman-active modes in crystals and organic liquids.

Formulas (5.185–5.187) and (5.212) show the relation between the information that can be obtained by frequency- and time-domain CARS spectroscopy. In fact, this information is essentially the same, and frequency- and time-domain CARS methods can successfully complement each other in studies of complex inhomogeneously broadened spectral bands. For example, in frequency-domain CARS spectroscopy, the phase information on molecular resonances can be extracted through polarization measurements and coherent ellipsometry (see the discussion above), and the level of coherent nonresonant background can be suppressed by means of the relevant polarization technique [see (5.204), (5.205) and Fig. 5.24b]. In time-domain CARS, on the other hand, the nonresonant background appears only at zero delay time between the pump and probe pulses, having no influence on the transient signal, while the impulse-response measurements may directly provide the information not only on the amplitude, but also on the phase of a molecular or atomic resonance. The development of femtosecond laser systems resulted in the impressive technical and conceptual progress of time-domain FWM spectroscopy, allowing photochemistry processes and molecular dynamics to be monitored in real time (see [5.109, 110, 113] for a review).

5.8 Waveguide Coherent Anti-Stokes Raman Scattering

5.8.1 Enhancement of Waveguide CARS in Hollow Photonic-Crystal Fibers

The general idea of waveguide CARS [5.144–149] is to improve the efficiency of four-wave mixing by increasing the interaction length and increasing the intensity of pump waves with given pump powers by reducing the transverse size of the wave-guiding layer in planar waveguides or the core diameter in optical fibers. CARS spectroscopy of the gas phase leaves no alternative to hollow waveguides and fibers. Since the refractive index of the core in such waveguides is lower than the refractive index of the cladding, the modes guided in the hollow core are always characterized by nonzero losses. The magnitude of these losses scales [5.150, 151] as $\lambda^2/a^2$ preventing fibers with small inner diameters to be used in nonlinear-optical experiments, which limits the waveguide CARS enhancement factors attainable with such fibers. In hollow-core photonic-crystal fibers [5.36, 152, 153], which guide light due to photonic band gaps, optical losses can often be kept low even in the case of small core diameters. Hollow PCFs with an inner diameter of $\approx 15 \mu m$ demonstrated by Benabid et al. [5.154] have the magnitude of optical losses on the order of 1–3 dB/m. We will show below that this property of hollow-core microstructure fibers makes them very attractive for waveguide CARS spectroscopy.

We start with the expression [5.11] for the power of the three-color CARS signal generated at the frequency $\omega_s = \omega_0 + \omega_1 - \omega_2$ by pump fields with frequencies $\omega_0$, $\omega_1$ and $\omega_2$:

$$P_{\text{CARS}} = \frac{1.755 \times 10^{-5} \omega_0^2 k_0 k_1 k_2}{c^2 k_2^2 k'} D^2 \left| \chi^{(3)} \right|^2 P_0 P_1 P_2 F_2.$$  \hspace{1cm} (5.213)

where $k_0, k_1, k_2, k_s$ are the wave numbers of light fields with frequencies $\omega_0, \omega_1, \omega_2, \omega_s$, respectively; $P_0, P_1, P_2$ are the powers of the fields with frequencies $\omega_0, \omega_1, \omega_2$, respectively; $\chi^{(3)}$ is the effective combination of cubic nonlinear-optical susceptibility tensor components corresponding to the chosen set of polarization vectors of pump and signal fields: $D$ is the frequency degeneracy factor of the four-wave mixing process defined after Maker and Terhune [5.105];

$$F_2 = \frac{2k'}{\pi b} \int_0^\infty 2\pi R dR \left| \frac{\exp \left( \frac{ik' \xi}{2} \right)}{(1 + ik' \xi)} \left( k'' - ik' \xi \right) H \exp \left( \frac{R^2}{bH} \right) \right|^2.$$  \hspace{1cm} (5.214)

is the phase-matching integral, $\Delta k = k_s - (k_0 + k_1 - k_2)$, $k' = k_0 + k_1 - k_2, k'' = k_0 + k_1 + k_2, \xi = 2(\varepsilon - f)/b, \xi = 2f/b, b = n_R q / \omega_0^2 / c$ is the confocal parameter, $\omega_0$ is the
beam waist diameter,
\[ H = \frac{(1 + \xi')^2}{(k'' - 1ik''\xi)} - \frac{1 - \xi'}{k'} \]  
(5.215)

In the limiting case of tight focusing, when the confocal parameter \( b \) is much less than the length of the nonlinear medium \( l \), \( b \ll l \), no increase in the CARS power can be achieved by reducing the pump-beam waist radius because of the simultaneous decrease in the interaction length. Mathematically, this well-known result is a consequence of the tight-focusing limit existing for the action length. Mathematically, this well-known result is written in this limiting case as
\[ F_2 = \frac{4\pi^2}{(1 + \frac{k}{k''})^2}. \]  
(5.216)

In the opposite limiting case of loosely focused pump beams, \( b \gg l \), weak absorption and negligible phase mismatches, the phase-matching integral is reduced to
\[ F_2 = \frac{k'}{k''} \frac{4l^2}{b^2}. \]  
(5.217)

Since the latter regime is exactly the case of waveguide CARS, we can use (5.216) and (5.217) to estimate the enhancement of waveguide CARS with respect to the regime of tight focusing. Phase mismatches in waveguide CARS should be understood as difference of propagation constants of waveguide modes involved in the wave-mixing process, and the mode-overlapping integral should generally be included to allow for the contribution of waveguide effects, in particular, the influence of higher-order waveguide modes.

Assuming that the beam waist radius of focused pump beams is matched to the inner radius of a hollow fiber, \( a \), we find from (5.216) and (5.217) that the waveguide CARS enhancement factor scales as \( \lambda^2 l^2/a^4 \). The length \( l \) can be made very large in the case of fibers, but the fundamental limitation of waveguide CARS in hollow fibers comes from optical losses, whose magnitude scales as \( \lambda^2/a^4 \). The influence of optical losses and phase-mismatch effects on the CARS process in the loose-focusing regime can be included through the factor
\[ M \propto \exp[-(\Delta\alpha + \Delta\lambda)l] \times \left( \sin^2\left(\frac{\Delta\alpha l}{2}\right) + \sin^2\left(\frac{\Delta\lambda l}{2}\right) \right) l^2, \]  
(5.218)

where \( \Delta\alpha = (\alpha_1 + \alpha_2 + \alpha_3 - \alpha_4)/2 \), \( \alpha_1, \alpha_2, \alpha_3, \alpha_4 \) are the magnitudes of optical losses at frequencies \( \omega_0, \omega_1, \omega_2, \omega_3 \), respectively.

It is straightforward to see from (5.218) that the amplitude of the CARS signal in a lossy waveguide reaches its maximum at some optimal length \( l_{\text{opt}}^{\text{CARS}} \), which is given by
\[ \mu_{\text{CARS}}^{\text{opt}} = \frac{1}{\Delta\alpha} \ln \left( \frac{\alpha_1 + \alpha_2 + \alpha_3}{\alpha_4} \right). \]  
(5.219)

With \( \alpha_1 \approx \alpha_2 \approx \alpha_3 \approx \alpha_4 = \alpha \), (5.219) yields
\[ \mu_{\text{CARS}}^{\text{opt}} = \frac{\ln 3}{\alpha}. \]  
(5.220)

Then, setting \( \Delta k = 0 \) for phase matching and \( w_0 = 0.73a \) for the best matching of input beams with the fiber mode radius, assuming that the refractive index of the gas filling the fiber core is approximately equal to unity, and taking into consideration that \( M = (3^{1/2} - 3^{-1/2})^2/(3 \ln 3)^2 \approx 0.123 \) for \( \Delta k = 0 \) and \( l = l_{\text{opt}}^{\text{CARS}} = \ln 3/\alpha \), we arrive at the following expression for the waveguide CARS enhancement factor:
\[ \mu = 1.3 \times 10^{-3} \left( \frac{k + k''}{k''} \right)^2 \frac{\lambda^2}{\alpha^2 a^4}. \]  
(5.221)

We can now see from (5.221), that the waveguide CARS enhancement factor scales as \( \lambda^2/a^4 \) and is limited by fiber losses. We will show in the next section that, due to the physically different mechanism behind light guiding, hollow microstructure fibers allow CARS enhancement factors to be substantially increased with respect to standard, solid-cladding hollow fibers. We will examine also the CARS enhancement factors as functions of the core radius for the fibers of both types and investigate the influence of the phase mismatch.

We start with the case of standard, solid-cladding hollow fibers. The magnitude of optical losses for \( EH_{mn} \) modes in such fibers is given by [5.150]
\[ \alpha = \left( \frac{\mu_{\text{opt}}}{2\pi} \right)^2 \frac{\lambda^2}{\alpha^3} \frac{n^2 + 1}{\alpha^3 \sqrt{n^2 - 1}}, \]  
(5.222)

where \( \mu_{\text{opt}} \) is the eigenvalue of the characteristic equation for the relevant hollow-fiber mode (the mode parameter), \( n \) is the refractive index of the fiber cladding, and the refractive index of the gas filling the fiber core is set equal to unity.

Plugging optical losses into the CARS enhancement factor by substituting (5.222) into (5.221) with \( \mu_{\text{opt}} = 2.4 \) for the limiting eigenvalue of the \( EH_{11} \) mode of a hollow fiber, we derive the following expression for the factor of CARS enhancement in a solid-cladding hollow fiber.
relative to the tight-focusing regime in the case of exact phase matching:

\[ \rho = 6.1 \times 10^{-2} \left( \frac{k' + k''}{k} \right)^2 \left( \frac{a}{\lambda} \right)^2 \left( \frac{n^2 - 1}{(n^2 + 1)^2} \right)^2. \]  

(5.223)

Optical losses, which grow with decreasing inner radius \( a \), limit the CARS enhancement, with the factor \( \rho \) rapidly lowering with decreasing \( a \) for small values of the fiber inner radius. The situation radically changes in the case of a microstructure fiber. The magnitude of optical losses for such fibers, as mentioned above, may be on the order of 1–3 dB/m in the case of fibers with a hollow core diameter of about 15 \( \mu \)m [5.154]. In the case of small inner radii, microstructure fibers provide much higher CARS enhancement factors than solid-core hollow fibers. The CARS enhancement factor in hollow microstructure fibers with the magnitude of optical losses equal to 0.1 and 0.01 cm\(^{-1}\) starts to exceed the CARS enhancement factor in a solid-cladding hollow fiber for core radii less than 20 and 45 \( \mu \)m, respectively. For hollow fibers with small core radii, the factor \( \mu \) may be several orders of magnitude higher than the enhancement factor \( \rho \).

An additional source of radiation losses in hollow fibers is related to radiation energy transfer to higher-order waveguide modes. The efficiency of this nonlinear-optical mode cross-talk process depends on radiation intensity and the mismatch \( \Delta k \) of propagation constants of waveguide modes involved in energy exchange. Starting with the standard expression for the propagation constants of \( EH_{mn} \) modes in a hollow fiber, we arrive at the following formula for the coherence length \( l_c = \pi (2|\Delta k|)^{-1} \) of the mode cross-talk process:

\[ l_c = \frac{2\pi^2}{\lambda} \frac{a^2}{|u_2^2 - u_1^2|}. \]  

(5.224)

where \( u_2 \) and \( u_1 \) are the parameters of cross-talking fiber modes. The coherence length \( l_c \), as can be seen from (5.224), becomes very small for guided modes of high orders, making the efficiencies of energy transfer from the fundamental to very high order modes negligible. For the cross-talk between the lowest order \( EH_{11} \) and \( EH_{12} \) modes, with \( u_1 \approx 2.4 \) and \( u_2 \approx 5.5 \), the coherence length can be estimated as \( l_c \approx 0.8a^2/\lambda \). The coherence length of such a cross-talk process is typically much smaller than the optimal length for the wave-mixing process (5.220). However, for high-intensity pump beams, the efficiency of this cross-talk process increases [5.155], and the energy lost from the fundamental mode due to the excitation of higher-order modes may become comparable with radiation energy leakage with the characteristic length governed by (5.222).

Importantly, the scaling law of the waveguide CARS enhancement factor as a function of the magnitude of optical losses, fiber inner radius, and radiation wavelength differs from a similar scaling law of the waveguide SRS enhancement factor [5.23], \( \eta = \lambda/a\pi^2 \). Physically, this difference stems from differences in scattering mechanisms involved in SRS and CARS, with SRS and CARS signals building up in different fashions as functions of the interaction length and pump field amplitudes. The difference in waveguide enhancement factors for SRS and CARS suggests different strategies for optimizing fibers designed to enhance these processes.

Phase mismatch, resulting from the difference in propagation constants of guided modes involved in the CARS process, is another important factor limiting the efficiency of CARS in a hollow fiber. In the case of nonzero phase mismatch \( \Delta k \), the optimal length for the CARS process can be found from a transcendental equation that immediately follows from (5.218):

\[ \Delta \alpha \sinh \left( \Delta \alpha \beta_{\text{opt}}^{\text{CARS}} + \Delta k \frac{CARS}{\text{opt}} \right) + (\Delta \alpha + \alpha) \times \left[ \cos \left( \Delta k \beta_{\text{opt}}^{\text{CARS}} \right) - \cosh \left( \Delta \alpha \beta_{\text{opt}}^{\text{CARS}} \right) \right] = 0. \]  

(5.225)

Phase mismatch reduces the maximum waveguide CARS enhancement attainable with a hollow microstructure fiber, with the power of the CARS signal becoming an oscillating function of the fiber length. The characteristic period of these oscillations is determined by the coherence length. Oscillations become less pronounced and then completely flatten out as optical losses build up. No oscillations is observed when the attenuation length becomes less than the coherence length. An important option offered by hollow microstructure fibers is the possibility to compensate for the phase mismatch related to the gas dispersion with an appropriate choice of waveguide parameters due to the waveguide dispersion component, scaling as \( a^{-2} \) in the case of a hollow fiber.

We have shown in this section that hollow microstructure fibers offer a unique opportunity of implementing nonlinear-optical interactions of waveguide modes with transverse sizes of several microns in a gas medium, opening the ways to improve the
efficiency of nonlinear-optical processes, including four-wave mixing and coherent anti-Stokes Raman scattering, and suggesting the principle for the creation of highly sensitive gas-phase sensors based on nonlinear spectroscopic techniques. Hollow-core microstructure fibers have been demonstrated to allow the waveguide CARS efficiency to be substantially increased as compared to standard, solid-cladding hollow fibers. The theorem predicting an $I^2/\alpha^4$ enhancement for a waveguide CARS process in a hollow fiber with an inner radius $a$ and length $l$ has been extended to include new solutions offered by microstructure fibers. The maximum CARS enhancement in a hollow microstructure fiber was shown to scale as $\lambda^2/a^4\alpha^4$ with radiation wavelength $\lambda$, radiation losses $\alpha$, and the inner fiber radius, allowing CARS efficiency to be substantially improved in such a fiber. This $\lambda^2/\alpha^4$ ratio, characterizing waveguide SRS enhancement in a hollow microstructure fiber, is related to the difference in the physical nature of SRS and CARS signals and suggests different strategies for optimizing fibers designed to enhance CARS and SRS processes.

### 5.8.2 Four-Wave Mixing and CARS in Hollow-Core Photonic-Crystal Fibers

Hollow-core photonic-crystal fibers (PCFs) [5.36, 152, 153] offer new interesting options for high-field physics and nonlinear optics. Waveguide losses can be radically reduced in such fibers relative to standard, solid-cladding hollow fibers due to the high reflectivity of a periodically structured fiber cladding within photonic band gaps (PBGs) [5.152, 153, 156], allowing transmission of high-intensity laser pulses through a hollow fiber core in isolated guided modes with typical transverse sizes of 10–20 $\mu$m. Due to this unique property, hollow PCFs can substantially enhance nonlinear-optical processes [5.157], including stimulated Raman scattering [5.154, 158, 159], four-wave mixing (FWM) [5.160], coherent anti-Stokes Raman scattering (CARS) [5.118], and self-phase modulation [5.161]. Air-guided modes in hollow PCFs can support high-power optical solitons [5.162, 163], allow transportation of high-energy laser pulses for technological [5.68, 164] and biomedical [5.165] applications.

In this section, we discuss phase-matched FWM of millijoule nanosecond pulses in hollow PCFs with a period of the photonic-crystal cladding of about 5 $\mu$m and a core diameter of approximately 50 $\mu$m. We will show that Raman-resonant FWM in large-core hollow PCFs enhances the potential of waveguide CARS in hollow fibers, providing a convenient sensing tool for condensed-phase species adsorbed on the inner fiber walls and trace-gas detection.

Large-core-area hollow PCFs employed in experiments [5.119, 166] were fabricated using a standard procedure, which involves stacking glass capillaries into a periodic array and drawing this preform at a fiber-drawing tower. Several capillaries have been omitted from the central part of the stack, to produce a hollow core of the fiber. While in standard hollow PCFs, the number of omitted capillaries is seven, PCFs used in our experiments had a hollow core in the form of a regular hexagon with each side corresponding to five cane diameters. The inset in Fig. 5.25 shows an image of a hollow PCF with a period of the cladding of approximately 5 mm and a core diameter of about 50 $\mu$m. The baking of capillaries forming the photonic-crystal structure, as shown in the image, allows a hollow waveguide with a nearly ideal 50 $\mu$m-diameter hexagonal core to be fabricated. It is still to be explored whether this technique can be scaled up to the fabrication of hollow PCFs with even larger core diameters. Transmission spectra of the hollow-core PCF are shown in Fig. 5.25. The inset shows the cross-section view of the PCF with a period of the cladding structure of about 5 $\mu$m.
of hollow PCFs employed in our experiments display well-pronounced passbands (Fig. 5.25), indicating the PBG guidance of radiation in air modes of the fiber.

The laser system used in experiments [5.119, 166] consisted of a Q-switched Nd:YAG master oscillator, Nd:YAG amplifiers, frequency-doubling crystals, a dye laser, as well as a set of totally reflecting dichroic mirrors and lenses adapted for the purposes of CARS experiments. The Q-switched Nd:YAG master oscillator generated 15 ns pulses of 1.064 μm radiation, which were then amplified up to about 30 mJ by Nd:YAG amplifiers. A potassium dihydrogen phosphate (KDP) crystal was used for the frequency doubling of the fundamental radiation. This second-harmonic radiation served as a pump for the dye laser, generating frequency-tunable radiation within the wavelengths ranges 540–560 and 630–670 nm, depending on the type of dye used as the active medium for laser-induced breakdown on PCF walls was judged to be a more careful optimization of the coupling geometry.

FWM processes with the CARS-type frequency-mixing scheme \( \omega_3 = 2\omega_1 - \omega_2 \) (\( \omega_1 \) and \( \omega_2 \) are the frequencies of the pump fields and \( \omega_3 \) is the frequency of the anti-Stokes signal produced through FWM) were studied in our experiments for two different sets of pump and signal frequencies. In the first FWM process, used in our experiments to test phase matching and assess the influence of waveguide losses, two waves with the wavelength \( \lambda_1 = 2\pi c/\omega_1 \) ranging from 630 to 665 nm, provided by the dye laser, are mixed with the fixed-frequency field of the fundamental radiation at \( \lambda_2 = 1064 \) nm, to generate an anti-Stokes signal within the range of wavelengths \( \lambda_3 \) from 445 to 485 nm. The second FWM process, designed to demonstrate the potential of CARS spectroscopy with hollow PCFs, is a standard Nd:YAG-laser CARS arrangement with \( \lambda_1 = 532 \) nm and \( \lambda_2 \) ranging from 645 to 670 nm.

To assess the influence of phase matching and radiation losses on the intensity of the FWM signal generated in a hollow PCF, we use (5.213), (5.218), and (5.225) to write the power of the anti-Stokes signal as \( P_2 \propto |\chi^{(3)}_1|^2 P_1 P_2^2 M \), where \( P_1 \) and \( P_2 \) are the powers of the fields with frequencies \( \omega_1 \) and \( \omega_2 \), respectively; \( \chi^{(3)}_1 \) is the effective combination of cubic nonlinear-optical susceptibility tensor components; and the factor \( M \) includes optical losses and phase-mismatch effects: \( M = \frac{1}{c^3} \frac{4\pi^2}{\omega_1^2} \frac{\Delta \alpha \Delta \beta}{\Delta \beta^2} \frac{1}{\sin^2(\Delta \alpha/2)} \frac{1}{\sin^2(\Delta \beta/2)} \), where \( \Delta \alpha = (2\omega_1 + \omega_2 - \omega_3)/2 \), \( \Delta \beta \) is the mismatch of the propagation constants of waveguide modes involved in the FWM process. In order to provide an order of magnitude estimate on typical coherence lengths \( l_c \), the coherence length is estimated as \( l_c \approx \frac{\pi}{2(\Delta \beta)} \) for FWM processes in hollow PCFs and to choose PCF lengths \( L \) meeting the phase-matching requirement \( L \leq l_c \) for our experiments, we substitute the dispersion of a standard hollow fiber with a solid cladding for the dispersion of PCF modes in these calculations. As shown by earlier work on PBG waveguides [5.167], such an approximation can provide a reasonable accuracy for mode dispersion within the central part of PBGs, but fails closer to the passband edges. For the waveguide FWM process involving the fundamental modes of the pump fields with \( \lambda_1 = 532 \) nm and \( \lambda_2 = 660 \) nm, generating the fundamental mode of the anti-Stokes field in a hollow fiber with a core radius of 25 μm, the coherence length is estimated as \( l_c \approx 10 \) cm. Based on this estimate, we choose a fiber length of 8 cm for our FWM experiments. With such a choice of the PCF length, effects related to the phase mismatch can be neglected as compared with the influence of radiation losses.

Phase matching for waveguide CARS in the PCF was experimentally tested by scanning the laser frequency difference \( \omega_1 - \omega_2 \) off all the Raman resonances (with \( \lambda_1 \) ranging from 630 to 665 nm and \( \lambda_2 = 1064 \) nm)
Fig. 5.26 Intensity of the $\omega_a = 2\omega_1 - \omega_2$ four-wave mixing signal from the hollow PCF with the length of 8 cm versus the wavelength of dye-laser radiation with $\lambda_1$ ranging from 630 to 665 nm and $\lambda_2 = 1064$ nm: (1) the measured spectrum of the FWM signal, (2) fiber transmission for dye-laser radiation, (3) fiber transmission for the FWM signal, and (4) the spectral profile of the factor $M$

and using the above expression for $M(\Delta \alpha L, \alpha_s L, \delta \beta L)$ with $\delta \beta L \approx 0$ to fit the frequency dependence of the FWM signal. Dots with error bars (line 1) in Fig. 5.26 present the intensity of the anti-Stokes signal from hollow PCFs measured as a function of the frequency of the dye laser. Dashed lines 2 and 3 in this figure display the transmission of the PCF for dye-laser radiation and the anti-Stokes signal, respectively. Solid line 4 presents the calculated spectral profile of the factor $M(\Delta \alpha L, \alpha_s L, 0)$. Experimental frequency dependencies of the FWM signals, as can be seen from the comparison of lines 1 and 4 in Fig. 5.26, are fully controlled by the spectral contours of PCF passbands (lines 2 and 3), indicating that phase-mismatch effects are much less significant for the chosen PCF lengths than variations in radiation losses.

The second series of experiments was intended to demonstrate the potential of waveguide CARS in a hollow PCF for the sensing of Raman-active species. For this purpose, the frequency difference of the second-harmonic and dye-laser pump fields was scanned through the Raman resonance, $\omega_1 - \omega_2 = 2\pi c \Delta \Omega$, with O–H stretching vibrations of water molecules, adsorbed on the inner PCF walls. The frequencies $\Delta \Omega$ of O–H stretching vibrations of water molecules typically fall within a broad frequency band of 3200–3700 cm$^{-1}$. The frequency dependence of the FWM signal from the PCF substantially deviates from the spectral profile of the factor $M(\Delta \alpha L, \alpha_s L, 0)$ (cf. lines 1 and 4 in Fig. 5.27), clearly indicating the contribution of Raman-active species to the FWM signal. To discriminate between the CARS signal related to water molecules adsorbed on the PCF walls against the OH contamination of the PCF cladding, we measured the spectrum of the CARS signal from a PCF heated above a burner. Heating by 30 K during 30 min reduced the amplitude of the Raman resonance in the spectrum of the CARS signal by a factor of about seven. The high level of the CARS signal was then recovered within several days. This spectrum of the CARS signal from the dry PCF was subtracted from the CARS spectrum recorded at the output of the hollow PCF under normal conditions. The difference spectrum was normalized to the spectral profile of the factor $M(\Delta \alpha L, \alpha_s L, 0)$. The result of this normalization is shown by line 5 in Fig. 5.27.

Fig. 5.27 Intensity of the $\omega_a = 2\omega_1 - \omega_2$ four-wave mixing signal from the hollow PCF with the length of 8 cm versus the wavelength of dye-laser radiation with $\lambda_1 = 532$ nm and $\lambda_2$ ranging from 645 to 670 nm: (1) the measured spectrum of the FWM signal, (2) fiber transmission for dye-laser radiation, (3) fiber transmission for the FWM signal, (4) the spectral profile of the factor $M$ and (5) the spectrum of the FWM signal corrected for the factor $M$ upon the subtraction of the spectrum of the CARS signal from the heated hollow PCF.
Notably, the contrast of the experimental wavelength dependence of the FWM intensity (squares with error bars) in Fig. 5.26 is higher than the contrast of a similar dependence for the CARS signal in Fig. 5.27. This variation in the ratio of the maximum amplitude of the nonlinear signal correlates well with the behavior of transmission for dye-laser radiation and the nonlinear signal, shown by curves 2 and 3 in both figures. With the dye-laser radiation wavelength set around 650 nm, both the pump and nonlinear signal wavelengths \( \lambda_1 \) and \( \lambda_a \) in Fig. 5.26 are close to the respective maxima of PCF transmission. The CARS signal, on the other hand, is detected away from the maximum transmission for the dye-laser radiation and the nonlinear signal (Fig. 5.27). It is therefore important to normalize the measured CARS spectrum to the wavelength dependence of the \( M \) factor, taking into account wavelength-dependent losses introduced by the PCF. This normalization procedure considerably improves the contrast of the CARS spectrum, as shown by curve 5 in Fig. 5.27.

Experiments presented above demonstrate the potential of waveguide CARS in PCFs to detect trace concentrations of Raman-active species, suggesting PCF CARS as a convenient diagnostic technique. However, CARS signals detected in these experiments do not allow the origin of Raman-active species in the fiber to be reliably identified, as it is not always possible to discriminate between the contributions to the CARS signal provided by the hollow core and PCF walls. As an example of a more easily quantifiable Raman medium, permitting the CARS signal from the PCF core to be separated from the signal from PCF walls, we chose gas-phase molecular nitrogen from atmospheric-pressure air filling the hollow core of a PCF. A two-color Raman-resonant pump field used in these experiments consisted of 15 ns second-harmonic pulses of Nd:YAG laser radiation with a wavelength of 532 nm (\( \omega_1 \)) and dye-laser radiation (\( \omega_2 \)) with a wavelength of 607 nm. The dye-laser frequency was chosen in such a way as to satisfy the condition of Raman resonance \( \omega_1 - \omega_2 = \Omega \) with a \( Q \)-branch Raman-active transition of N2 at the central frequency \( \Omega = 2331 \text{ cm}^{-1} \). Coherently excited \( Q \)-branch vibrations of N2 then scatter off the second-harmonic probe field, giving rise to a CARS signal at the frequency \( \omega_{\text{CARS}} = 2\omega_1 - \omega_2 \) (corresponding to a wavelength of 473 nm). The hollow PCF (shown in inset 1 to Fig. 5.28) was designed to simultaneously provide high transmission for the air-guided modes of the second harmonic, dye-laser radiation, and the CARS signal. With an appropriate fiber structure, as can be seen from inset 2 to Fig. 5.28, PCF transmission peaks can be centered around the carrier wavelengths of the input light fields and the CARS signal (shown by vertical lines in inset 2 to Fig. 5.28). Phase matching for CARS with the chosen set of wavelengths has been confirmed [5.168] (inset 3 in Fig. 5.28) by a numerical analysis of PCF dispersion based on a modification of the field-expansion technique developed by Poladian et al. [5.169].
The resonant CARS signal related to $Q$-branch vibrations of $N_2$ in these experiments can be reliably separated from the nonresonant part of the CARS signal originating from the PCF walls. The spectra of the CARS signal at the output of the PCF Fig. 5.28 are identical to the $N_2 Q$-branch CARS spectrum of the atmospheric air [5.99] measured in the tight-focusing regime. In view of this finding, the CARS signal can be completely attributed to the coherent Raman scattering in the gas filling the fiber core with no noticeable contribution from the nonlinearity of PCF walls.

Results presented here show that large-core-area hollow PCFs bridge the gap between standard, solid-cladding hollow fibers and hollow PCFs in terms of effective guided-mode areas, allowing energy fluence scaling of phase-matched waveguide four-wave mixing of laser pulses. We used hollow PCFs with a core diameter of about 50 $\mu$m to demonstrate phase-matched FWM for millijoule nanosecond laser pulses. Intense CARS signal has been observed from stretching vibrations of water molecules inside the hollow fiber core, suggesting CARS in hollow PCFs as a convenient sensing technique for pollution monitoring and trace gas detection. Hollow PCFs have been shown to offer much promise as fiber-optic probes for biomedical Raman applications, suggesting the way to substantially reduce the background related to Raman scattering in the core of standard biomedical fiber probes [5.170].

5.9 Nonlinear Spectroscopy with Photonic-Crystal-Fiber Sources

5.9.1 Wavelength-Tunable Sources and Progress in Nonlinear Spectroscopy

The progress in wavelength-tunable light sources through the past decades has been giving a powerful momentum to the development of nonlinear laser spectroscopy. Nonlinear Raman spectroscopy, in particular, has benefited tremendously more than 30 years ago from the application of tunable laser sources, as optical parametric oscillators [5.171] and dye lasers [5.172] were demonstrated to greatly simplify measurements based on coherent anti-Stokes Raman scattering (CARS), making this technique much more informative, efficient, and convenient. Broadband laser sources later contributed to the technical and conceptual progress in nonlinear Raman spectroscopy [5.99, 106–110], allowing single-shot CARS measurements. In the era of femtosecond lasers, several parallel trends have been observed in the development of laser sources for nonlinear Raman spectroscopy [5.113]. One of these tendencies was to adapt broadband femtosecond pulses for spectroscopic purposes [5.113, 173, 174] and to use different spatial phase-matching geometries to simultaneously generate coherent Stokes and anti-Stokes, as well as degenerate four-wave mixing signals [5.113, 127, 128]. The rapid progress in nonlinear materials, on the other hand, resulted in the renaissance of optical parametric oscillators and amplifiers (OPOs and OPAs) for nonlinear spectroscopy [5.175]. Chirped pulses were used [5.176, 177] to probe broad spectral regions and large ranges of delay times, suggesting efficient single-shot nonlinear spectroscopic approaches [5.178–180].

In this section, we focus on the potential of photonic-crystal fibers [5.36, 37] as novel efficient sources for nonlinear spectroscopy. PCFs are unique waveguide structures allowing dispersion [5.40] and spatial field [5.181] profiles to be engineered by modifying the design of the fiber structure. Nonlinear-optical PCF components and novel PCF-based light sources have been intensely used through the past few years in frequency metrology [5.74, 77], biomedical optics [5.81], ultrafast photonics [5.78, 79], and photochemistry [5.182].

Coherent nonlinear spectroscopy and microscopy open up a vast area for applications of PCF light sources and frequency shifters. Efficient frequency conversion and supercontinuum generation in PCFs have been shown to enhance the capabilities of chirped-pulse CARS [5.183] and coherent inverse Raman spectroscopy [5.184]. Cross-correlation frequency-resolved optically gated CARS (XFROG CARS) has recently been demonstrated [5.80] using specially designed PCF frequency converters for ultrashort laser pulses. Novel light sources based on frequency shifting in PCFs provide a useful tool for the measurement of second-order optical nonlinearities in organic materials [5.185] and offer interesting new options in CARS microscopy [5.186]. Efficient spectral broadening of ultrashort pulses in PCFs with carefully engineered dispersion profiles [5.42–44] makes these fibers ideal light sources for pump–supercontinuum probe time- and frequency-resolved nonlinear-optical measurements [5.187].

Below in this section, we demonstrate applications of PCF light sources for chirped-pulse CARS...
and nonlinear absorption spectroscopy. We will show that PCFs can provide efficient nonlinear-optical transformations of femtosecond Cr:forsterite laser pulses, delivering linearly chirped frequency-shifted broadband light pulses with central wavelengths ranging from 400 to 900 nm. These pulses were cross-correlated in our experiments with the femtosecond second-harmonic output of the Cr:forsterite laser in toluene solution, used as a test object, in boxcars geometry to measure CARS spectra of toluene molecules (XFROG CARS). The blue-shifted chirped-pulse output of a photonic-crystal fiber with a spectrum stretching from 530 to 680 nm is shown to be ideally suited for the nonlinear absorption spectroscopy of one- and two-exciton bands of thiacarbocyanine J aggregates in a polymer film excited by femtosecond second-harmonic pulses of the Cr:forsterite laser.

5.9.2 Photonic-Crystal Fiber Frequency Shifters

Spectroscopic measurements were performed with multicomponent-glass PCFs [5.51, 188], fabricated with the use of the standard PCF technology [5.36, 37]. In PCFs used in our experiments (Fig. 5.29a), the solid fiber core is surrounded by a single ring of thin-wall capillaries whose outer diameters are equal to the diameter of the PCF core. The outer part of the microstructure cladding consists of 11 rings of capillaries with outer diameters approximately three times larger than the diameter of the PCF core and a high air-filling fraction. Dispersion and nonlinearity of the PCFs were managed by scaling the geometric sizes of the PCF structure. Technologically, this was realized by using the same preform to fabricate PCFs with the same type of the structure, but with different magnifying factors. This procedure allowed to scale the sizes of PCF structure without changing its geometry.

The laser system used in experiments consisted of a Cr4+:forsterite master oscillator, a stretcher, an optical isolator, a regenerative amplifier, and a compressor [5.189]. The master oscillator, pumped with a fiber ytterbium laser, generated 30–60 fs light pulses of radiation with a wavelength of 1.23–1.25 μm at a repetition rate of 120 MHz. These pulses were then transmitted through a stretcher and an isolator, to be amplified in a Nd:YLF-laser-pumped amplifier and recompressed to the 200 fs pulse duration with the maximum laser pulse energy up to 20 μJ at 1 kHz. The energy of laser pulses used in experiments presented in this paper ranged from 0.5 up to 200 nJ.

![Fig. 5.29](image)

**Fig. 5.29** (a) An SEM image of soft-glass photonic-crystal fibers. (b) Intensity spectra of the dispersion-managed blue-shifted output of soft-glass PCFs. The wavelength offset δ is 50 nm (1), 110 nm (2), 150 nm (3), 190 nm (4), 220 nm (5), and 300 nm (6).

For the PCFs used in experiments, the central wavelength of Cr:forsterite laser pulses falls within the range of anomalous dispersion. Such pulses can therefore form solitons in the fiber. High-order dispersion induces wave-matching resonances between solitons and dispersive waves [5.21, 22], giving rise to intense blue-shifted emission, observed as prominent features in the PCF output spectra (Fig. 5.29b). The central wavelength of this blue-shifted emission correlates well with the wavelength where dispersive waves guided in the fundamental mode of the PCF are phase-matched with the soliton produced by Cr:forsterite laser pulses. The phase matching between the soliton produced by the input laser pulse and the dispersive laser pulses, which defines the frequency of the dominant peaks in output
spectra of PCFs, is controlled by the dispersion of the fiber. The central frequency of the blue-shifted signal in the output of PCFs can thus be tuned by modifying the dispersion profile of the fiber. The GVD profiles of waveguide modes were modified in our experiments by scaling the geometric sizes of the fiber without changing the type of the structure shown in Fig. 5.29a. The core diameter of PCFs fabricated for these experiments was varied from 0.9 to 3.8 μm. Figure 5.29b shows the spectra of the blue-shifted output of the fiber, tuned by changing the offset $\delta = \lambda_0 - \lambda_z$ between the central wavelength of the input laser field, $\lambda_0$, and the zero-GVD wavelength $\lambda_z$. With the PCF length remaining unchanged (10 cm), larger blue shifts are achieved by increasing the offset $\delta$ (cf. curves 1–6 in Fig. 5.29b). The power of the input laser field needs to be increased for larger $\delta$ in these experiments to keep the amplitude of the blue-shifted signal constant. In these experiments, dispersion-managed soft-glass PCFs are shown to serve as frequency shifters of femtosecond Cr:forsterite laser pulses, providing an anti-Stokes output tunable across the range of wavelengths from 400 to 900 nm.

Experiments presented in this section show that the structural dispersion and nonlinearity management of multicomponent-glass photonic-crystal fibers allows a wavelength-tunable frequency shifting and white-light spectral transformation of femtosecond Cr:forsterite laser pulses. We have explored the ways toward optimizing non-silica PCFs for frequency shifting and white-light spectral super-broadening of femtosecond Cr:forsterite laser pulses and identified important advantages of multicomponent-glass PCFs over silica microstructure fibers for the spectral transformation of laser pulses in the 1.2–1.3 μm spectral range. By coupling 200 fs pulses of 1.24 μm Cr:forsterite laser radiation into different types of multicomponent-glass PCFs, where the zero-GVD wavelength is tuned by scaling the sizes of the fiber structure, we have demonstrated spectrally tailored supercontinuum generation and frequency up-shifting providing a blue-shifted output tunable across the range of wavelengths from 400 to 900 nm.

### 5.9.3 Coherent Anti-Stokes Raman Scattering Spectroscopy with PCF Sources

In this section, we show that PCF frequency shifters can serve as convenient sources of chirped wavelength-tunable pulses for CARS spectroscopy. In CARS experiments, sub-microjoule Cr:forsterite-laser pulses with an initial duration of about 90 fs are launched into the central core of the PCF (Fig. 5.30), resulting in the efficient generation of a blue-shifted signal (Fig. 5.31), with a central wavelength dictated by phase matching for dispersive-wave emission and controlled by fiber dispersion. The wavelength of the blue-shifted signal can be finely tuned by changing the intensity of the pump pulse (Fig. 5.31) due to the nonlinear change in the refractive index of the fiber core and the spectral broadening of the pump pulse.

Cross-correlation frequency-resolved optical gating (XFROG) [5.190, 191] was used to characterize the blue-shifted output of the PCF. An XFROG signal was generated by mixing the blue-shifted signal from the fiber $E_a$ with the 620 nm 90 fs second-harmonic output of the Cr:forsterite laser $E_{SH}$ in a BBO crystal. A two-dimensional XFROG spectrogram, $S(t, \tau) \propto \left| \int_{-\infty}^{\infty} E_a(t) E_{SH}(t-\tau) \exp(-i\omega t) dt \right|^2$, was then plotted by measuring the XFROG signal as a function of the delay time $\tau$ between the second-harmonic pulses and the blue-shifted output of the PCF and spectrally dispersing the XFROG signal. The XFROG spectrum shown in inset 1 to Fig. 5.31 visualizes
Fig. 5.31 The spectrum of the blue-shifted output of a photonic-crystal fiber pumped by 1.24 μm 90 fs Cr:forsterite-laser pulses with an input energy of (solid line) 170 nJ, (dashed line) 220 nJ, and (dash–dotted line) 270 nJ. The insets show: (1) the intensity of the sum-frequency signal generated in a BBO crystal by the second-harmonic pulse from the Cr:forsterite laser and the blue-shifted PCF output as a function of the wavelength and the delay time τ between the second-harmonic and anti-Stokes pulses, (2) theoretical fit of the XFROG trace, and (3) the pulse envelope and the phase of the anti-Stokes pulse providing the best fit.

The linear chirp defines a simple linear mapping between the instantaneous frequency of the blue-shifted PCF output and the delay time τ, allowing spectral measurements to be performed by varying the delay time between the pump pulses. Experiments were performed with 90 fs second-harmonic pulses of the Cr:forsterite laser (at the frequency ω₁) and the linearly chirped pulses from the PCF (at the frequency ω₂) as a biharmonic pump for the CARS spectroscopy of toluene solution. The frequency difference ω₁ – ω₂ was scanned.
through the frequencies of Raman-active modes of toluene molecules by tuning the delay time between the pump pulses (Fig. 5.32a). The second-harmonic pulse also served as a probe in our CARS scheme, generating the CARS signal at the frequency \( \omega_{CARS} = 2\omega_1 - \omega_2 \) through the scattering from Raman-active vibrations coherently excited by the pump fields. The light beams with frequencies \( \omega_1 \) and \( \omega_2 \) were focused into a cell with toluene solution at a small angle with respect to each other (Fig. 5.30). The CARS signal generated in the area of beam interaction in this non-coplanar boxcars geometry had a form of a sharply directed light beam with a low, phase-matching-controlled angular divergence spatially separated (Fig. 5.30) from the pump beams. Figure 5.32b presents the map of CARS spectra from the toluene solution measured for different delay times \( \tau \) between the biharmonic pump pulses. This procedure of measurements, in fact, implements the XFROG technique [5.190, 191]. However, while FROG-based techniques [5.192] are usually employed to characterize ultrashort pulses, our goal here is to probe Raman-active modes of toluene molecules, used as a test object, by means of CARS spectroscopy.

In the case of a positively chirped pulse from the PCF (insets 2 and 3 in Fig. 5.31), small delay times \( \tau \) correspond to the excitation of low-frequency Raman-active modes (\( \tau \approx -200 \text{ fs} \) in Fig. 5.32b). In particular, the 1004 cm\(^{-1}\) Raman mode of toluene is well resolved in the presented XFROG CARS spectrogram. This mode is excited with the second harmonic of Cr:forsterite-laser radiation and the spectral slice around the wavelength of \( \lambda_2 \approx 661 \text{ nm} \) picked with an appropriate \( \tau \) (Fig. 5.32a) from the positively chirped blue-shifted PCF output, giving rise to a CARS signal with the wavelength \( \lambda_{CARS} \approx 584 \text{ nm} \). Raman modes with higher frequencies are probed at larger delay times (\( \tau \approx 100–200 \text{ fs} \) in Fig. 5.32b).

As a simple model of the Raman spectrum of toluene molecules in the studied spectral range, we employ a doublet of Lorentzian lines interfering with the coherent nonresonant background (Fig. 5.32c). The frequencies of the peaks in these spectra are used as fitting parameters. The ratio of the peak value of the resonant part of the CARS susceptibility, \( \chi^{(3)} \), to the nonresonant susceptibility, \( \chi^{(3)_{nr}} \), was estimated by measuring the intensities of the CARS signal on and off the Raman resonances, yielding \( |\chi^{(3)_{nr}}|/|\chi^{(3)}| \approx 0.05 \). The best fit (Fig. 5.32d) is achieved with the Raman peaks centered at 1004 and 1102 cm\(^{-1}\), which agrees well with earlier CARS studies of toluene [5.99].

Although the slope of the XFROG CARS trace and positions of Raman peaks can be adequately described with the use of this simple model, some of the spectroscopic features of the experimental XFROG CARS trace deviate from the theoretical fit. These deviations may originate from variations in the coherent background as a function of the frequency. For a quantitative spectroscopic analysis, these inhomogeneities in the frequency dependence of the coherent background should be carefully measured and included in the fit. On the other hand, the nonresonant contribution to CARS spectral profiles can be efficiently suppressed [5.99, 106] by using three input pulses in the CARS arrangement instead of two and by introducing the delay time between the third pulse (probe) and the two-color pump, tuned to a Raman resonance under study.

### 5.9.4 Pump–Probe Nonlinear Absorption Spectroscopy using Chirped Frequency–Shifted Light Pulses from a Photonic–Crystal–Fiber Source

Time-resolved nonlinear-optical spectroscopy of molecular dynamics and fast excitation transfer processes typically involves specifically designed sequences of pump and probe pulses with a variable delay time and a smoothly tunable frequency of the probe field. In a laboratory experiment, such pulse sequences can be generated by femtosecond optical parametric amplifiers (OPAs). Femtosecond OPAs, however, inevitably increase the cost of laser experiments and make the laser system more complicated, unwieldy, and difficult to align. An interesting alternative strategy of pump–probe spectroscopy employs a pump field in the form of a broadband radiation (supercontinuum) with a precisely characterized chirp. A time–frequency map, defined by the chirp of such a supercontinuum pulse, allows time- and frequency-resolved measurements to be performed by tuning the delay time between the transform-limited pump pulse and chirped supercontinuum pulse [5.176, 193]. The supercontinuum probe pulse for pump–probe experiments is most often generated by focusing amplified femtosecond pulses into a silica or sapphire plate. The chirp of the probe pulse in such an arrangement is dictated by the regime of nonlinear-optical spectral transformation and dispersion of the nonlinear material, leaving little space for the phase tailoring of the probe field.

In this section, we demonstrate the potential of PCFs as compact and cost-efficient fiber-optic sources
of probe pulses with a tunable frequency and tailored phase for a time-resolved nonlinear spectroscopy of molecular aggregates. We will show that PCFs can provide efficient nonlinear-optical transformations of femtosecond Cr:forsterite laser pulses, delivering linearly chirped frequency-shifted broadband light pulses, optimized for pump–probe nonlinear absorption spectroscopy of molecular aggregates. The blue-shifted output of a photonic-crystal fiber with a spectrum stretching from 530 to 680 nm will be used to probe one- and two-exciton bands of thiacarbocyanine J aggregates in a polymer film excited by femtosecond second-harmonic pulses of the Cr:forsterite laser.

Molecular aggregates are interesting and practically significant objects encountered in many physical, chemical and biological systems [5.194]. Interactions between the molecules forming aggregates give rise to collective electronic states, which can be delocalized over large chains of molecules, modifying the optical response of the system [5.195]. Specific types of molecular aggregation, known as J and H aggregation, give rise to a pronounced spectral shift and dramatic narrowing of absorption bands, indicating the cooperative nature of the optical response of molecular aggregates [5.196]. In natural systems, molecular aggregates are involved in the processes and functions of vital importance as they play the key role in light harvesting and primary charge separation in photosynthesis [5.197]. On optical resonances, the nonlinear susceptibility of molecular aggregates displays a collective enhancement [5.195], scaling as $N^2$ with the number of particles $N$ forming an aggregate. Dramatic enhancement of optical nonlinearity and the available pathways for ultrafast relaxation of excited states [5.194] suggest a variety of interesting applications of molecular aggregates, such as terahertz demultiplexing of optical signals [5.198], spectral sensitization in optical data storage and photography [5.199], energy transfer from light-harvesting antennas and complexes in artificial photosynthesis [5.197], mode locking in laser cavities, and creation of novel devices for ultrafast photonics.

Collective electronic eigenstates in aggregates of strongly coupled molecules are grouped into excitonic bands [5.194–196]. In the ground state of this band structure, all $N$ molecules of the aggregate reside in the ground state. In the lowest excited band, the molecules coupled into an aggregate share one excitation. The eigenstates of this first excited band (one-excitions, or Frenkel excitons) are represented by linear combinations of basis states corresponding to one excited and $N - 1$ ground-state molecules. Eigenstates that can be reached from the ground state via two optical transitions, making the molecules of an aggregate share two excitations, form a two-exciton band. The third-order susceptibility $\chi^{(3)}$, responsible for four-wave mixing (FWM) processes, can involve only one- and two-excitions. Although three-exciton states can be reached
by three transitions, they do not contribute to the third-order polarization as they do not have a transition dipole that would couple them to the ground state. Time-resolved nonlinear spectroscopic methods based on $\chi^{(3)}$ processes, such as spectroscopy of nonlinear absorption, degenerate four-wave mixing, and third-harmonic generation, have proven to be convenient and informative techniques for the characterization of one- and two-exciton states of aggregates, providing the data on the strength of dipole–dipole interaction between molecules in aggregates, as well as on the disorder and typical relaxation and exciton annihilation times in aggregates [5.194].

Experiments [5.200] were performed with thin-film samples of $J$ aggregates of thiacarbocyanine dye. Film samples of $J$ aggregates were prepared by spin-coating the solution of thiacarbocyanine dye on a thin substrate. The concentration of thiacarbocyanine dye was $5 \times 10^{-3}$ mol/l. The spinning speeds ranged from 1000 up to 3000 revolutions per minute. A mixture of acetonitrile, dichloroethane, and chloroform with a volume ratio of 2:2:1 was used as a solvent. The thickness of the dye layer applied to a substrate was estimated as 30 nm, and the total thickness of the sample was about 1 μm.

Absorption spectra of $J$-aggregate films (curve 1 in Fig. 5.33a) display two pronounced peaks. The broader peak centered at 595 nm corresponds to thiacarbocyanine monomers, while the narrower peak at 660 nm represents the excitonic absorption of $J$ aggregates. To provide a rough estimate of the delocalization length $N_d$ of excitons in aggregates, we apply the formula [5.201] $N_d \approx \left(\frac{3\pi^2}{2}J|J|3\pi^2|J|W\right)^{1/2} - 1$, which expresses $N_d$ through the half-width at half-maximum $W$ of the aggregate peak in the absorption spectrum and the energy $J$ of dipole–dipole interaction between nearest-neighbor molecules in the aggregate ($J < 0$ for $J$ aggregates). With the $J$ parameter estimated as $J \approx 900$ cm$^{-1}$ from the aggregation-induced red shift of the absorption peak in Fig. 5.33a, we find $N_d \approx 6$. Experimental results presented below in this paper show that, with such a delocalization length of excitons in molecular aggregates, spectra of nonlinear absorption display well-pronounced nonoverlapping features indicating [5.194–196] bleaching through transitions between the ground and one-exciton states and induced absorption via transitions between one- and two-exciton states of molecular aggregates.

The laser system used in experiments [5.200] was based on the Cr$^{4+}$:forsterite laser source with regenerative amplification, as described in Sect. 5.9.2. A 1 mm-thick BBO crystal was used to generate the second harmonic of amplified Cr:forsterite laser radi-
5.10 Surface Nonlinear Optics, Spectroscopy, and Imaging

In this section, we will dwell upon the potential of nonlinear-optical methods for the investigation of surfaces and interfaces. The ability of second-order nonlinear-optical processes, such as SHG and SFG (Sect. 5.3), to probe surfaces and interfaces is most clearly seen in the case of a centrosymmetric material. In this situation, the electric-dipole SHG and SFG response from the bulk of the material vanishes. At a surface or an interface, the bulk symmetry is broken, and electric-dipole second-order nonlinear-optical
effects are allowed. Such surface-specific SHG and SFG processes enable a highly sensitive nondestructive local optical diagnostics of surfaces and interfaces (Fig. 5.35a–b). Illuminating and physically insightful discussion of this technique can be found in the classical texts on nonlinear optics [5.9, 203].

The $\chi^{(2)}$ signal from a surface or an interface is, however, not entirely background-free, as the second-order nonlinear optical processes are not strictly forbidden even in a centrosymmetric medium. Beyond the electric-dipole approximation, the second-order nonlinear signal, as can be seen from (5.6–5.8) and (5.14), can be generated through the electric-quadrupole and magnetic-dipole effects. It is generally very difficult, often impossible, to completely distinguish between the surface and bulk contributions to the nonlinear signal. Luckily enough, the electric-quadrupole and magnetic-dipole components in the nonlinear-optical response are typically $k\alpha$ times less significant than the dipole-allowed part [5.9], with $k = 2\pi/\lambda$ and $\alpha$ being a typical size of an atom or a unit cell in a crystal. The ratio of the surface dipole-allowed susceptibility $\chi^{(2)}_{s}$ to the bulk susceptibility $\chi^{(2)}_{b}$ can be then estimated as $|\chi^{(2)}_{s}|/|\chi^{(2)}_{b}| \sim d/(k\alpha)$, where $d$ is the thickness of the surface layer. In reflection SHG (Fig. 5.35a), the bulk contribution is typically generated in a subsurface layer with a thickness of $d \sim \lambda/(2\pi)$. The ratio of the surface part of the total reflected SHG signal to the bulk contributions in this case is on the order of $d^2/\alpha^2$, which can be easily made much larger than unity. This ratio can be substantially enhanced on frequency resonances or with an appropriate choice of polarization arrangement.

A combination of the high spatial and temporal resolution with a spectral selectivity makes $\chi^{(2)}$ techniques a powerful tool for time-resolved species-selective studies of surfaces and buried interfaces (see, e.g., [5.204] for a comprehensive review of recent results), detection and size and shape analysis of adsorbed species, nanoparticles, and clusters on surfaces [5.205, 206], as well as imaging and microscopy of biological species [5.207]. The sensitivity and selectivity of the $\chi^{(2)}$ technique are enhanced when the frequency of one of the laser fields ($\omega_1$ in the inset to Fig. 5.35b) is tuned to a resonance with a frequency of one of the vibrations typical of species on a surface or an interface (Fig. 5.35b). This method of surface analysis is referred to as sum-frequency surface vibrational spectroscopy. The capabilities of this technique have been impressively

Fig. 5.35 Nonlinear optics, spectroscopy, and imaging of surfaces and buried structures. (a) Nonlinear-optical probing of surfaces and interfaces using second-harmonic generation. (b) Surface vibrational spectroscopy using sum-frequency generation. Diagram of vibrational transitions probed by SFG is shown on the right. (c) Nonlinear microscopy based on coherent anti-Stokes Raman scattering. Diagram of Raman-active transitions selectively addressed through CARS is shown on the left.
demonstrated for vapor–liquid and liquid–solid interfaces [5.205].

In sum-frequency surface vibrational spectroscopy [5.207] an infrared laser pulse \( E_1 \) with a frequency \( \omega_1 \) overlaps on the surface of a sample with the second laser pulse \( E_2 \), which typically has a frequency \( \omega_2 \) in the visible, to induce a second-order polarization at the sum frequency \( \omega_{\text{SF}} = \omega_1 + \omega_2 \):

\[
P_{\text{SF}}^{(2)}(\omega_{\text{SF}}) = \chi^{(2)}(\omega_{\text{SF}}; \omega_1, \omega_2) : E_1 E_2 .
\]

(5.226)

The intensity of the optical signal at the sum frequency is given by

\[
I_{\text{SF}} \propto |\chi^{(2)}_{\text{eff}}|^2 I_1 I_2 .
\]

(5.227)

Here, \( I_1 \) and \( I_2 \) are the intensities of the laser beams and \( \chi^{(2)}_{\text{eff}} = (\hat{L}_{\text{SF}} \cdot \hat{e}_{\text{SF}}) \cdot \chi^{(2)}_s : (\hat{L}_2 \cdot \hat{e}_2) (\hat{L}_1 \cdot \hat{e}_1) \).

(5.228)

where \( \hat{L}_1, \hat{L}_2 \) and \( \hat{L}_3 \) are the Fresnel factors at the frequencies \( \omega_1, \omega_2, \) and \( \omega_{\text{SF}} \), respectively, \( \hat{e}_1, \hat{e}_2, \) and \( \hat{e}_{\text{SF}} \) are the unit polarization vectors of the laser and sum-frequency fields, and the surface quadratic susceptibility \( \chi^{(2)}_s \) is written as

\[
\chi^{(2)}_s = \chi^{(2)\text{nr}} + \sum_q \frac{\delta_q}{\omega_1 - \omega_q + i \Gamma_q} .
\]

(5.229)

where \( \chi^{(2)\text{nr}} \) being the nonresonant quadrature susceptibility and \( \delta_q, \omega_q, \) and \( \Gamma_q \) being the strength, the frequency, and the damping constant for the \( q \)-th vibrational mode, respectively.

When the infrared field is scanned over the frequency of the \( q \)-th vibrational mode, the SFG signal is resonantly enhanced, and its spectrum gives the spectrum of the vibrational mode. Tunable dye lasers [5.204], optical parametric oscillators and amplifiers [5.205], or PCF frequency shifters [5.185, 208] are employed as sources of frequency tunable radiation, allowing selective probing of vibrational (as well as electronic and excitonic) transitions in molecules and molecular aggregates.

Through the past few years, nonlinear-optical methods of surface spectroscopy have been extensively involved in the rapid growth of nonlinear microscopic techniques based on \( \chi^{(3)} \) and \( \chi^{(5)} \) processes. In particular, SHG and THG processes have proven to be convenient techniques for high-resolution three-dimensional microscopy of biological objects [5.207, 209], as well as laser-produced plasmas and micro-explosions [5.210]. In early experimental demonstrations of SHG microscopy, grain structures and defects on the surface of thin films were visualized using SHG in transmission [5.211] and surface monolayers were imaged by reflection-geometry SHG microscopy [5.212]. In recent years, progress in laser technologies and the advent of new-generation imaging and scanning systems made it possible to extend nonlinear microscopy techniques to three-dimensional structures, buried objects, and biological tissues [5.207, 209]. In this modification of nonlinear microscopy, the nonlinear signal is generated in the focal region of the laser beam in the bulk of a sample, originating from optical micro-inhomogeneities, which break the point-group symmetry of the medium or change phase-matching conditions. In two transverse dimensions, the high spatial resolution of nonlinear microscopy techniques is controlled by the nonlinear nature of the process, tightly confining the area where the signal is generated to the focal region. Resolution in the direction of probing is achieved either due to symmetry breaking, similar to nonlinear-optical surface-imaging techniques, or through phase-matching modification.

In CARS microscopy [5.207, 209, 213, 214], the nonlinear signal is resonantly enhanced when a frequency difference between two laser fields is tuned to a Raman-active mode of molecules under study, as described in Sect. 5.4.8 (see also Fig. 5.35c). This makes microscopy also species-selective as Raman resonances serve as fingerprints of a certain type of molecules or molecular aggregates. Forward CARS and backward CARS (also called epi-CARS) geometries have been developed (Fig. 5.35c). In the forward-CARS microscopy, the mismatch \( |\Delta k| \) of the wave vectors involved in wave mixing (Sect. 5.7) is typically much smaller than \( 2\pi/\lambda_{\text{CARS}} \), where \( \lambda_{\text{CARS}} \) is the wavelength of the CARS signal. For epi-CARS, \( |\Delta k| \) is larger than \( 2\pi/\lambda_{\text{CARS}} \). The intensity of the epi-CARS signal can thus be comparable with the forward-CARS signal intensity only for a thin sample with a sample thickness \( d \) meeting the inequality \( |\Delta k|d < \pi \). CARS microscopy has been one of the most successful recent developments in the field of nonlinear-optical microscopy. In addition to the high spatial resolution, this technique has a number of other important advantages over, for example, microscopy based on spontaneous Raman scattering. In particular, in CARS microscopy, laser beams with moderate intensities can be used, which reduces the risk of damaging biological tissues. The anti-Stokes signal in CARS microscopy is spectrally separated from the laser beams and from fluorescence, as the anti-Stokes wavelength is shorter than the wavelengths of the laser beams. In transparent materials, CARS microscopy can be used to image tiny buried objects inside the sample in three
dimensions. Due to the coherent nature of CARS, the
capabilities of CARS microscopy can be enhanced by
means of coherence control, as recently demonstrated
by Dudovich et al. [5.117].

5.11 High-Order Harmonic generation

5.11.1 Attosecond Metrology –
Historical Background

The invention of the laser in 1960 opened many new
fields of research. One of them is nonlinear optics trig-
gered by Franken [5.215] with the first demonstration
of frequency doubling in a crystal (1961) and pioneered
by Bloembergen and coworkers. Third-harmonic gen-
eration in gases was observed for the first time by New
and Ward in 1967 [5.216], fifth and higher-order har-
monic generation a few years later by Reintjes and others
[5.217]. The main objectives of this research were to
increase the conversion efficiency, to cover a large (con-
tinuous) spectral range with, for example, frequency
mixing processes and to reach very short wavelengths.
The most natural route for the latter goal was to use fun-
damental fields with the shortest possible wavelength, to
produce short-wavelength radiation through a low-order
nonlinear-optical process.

Another research area, which started in the late six-
ties, is the study of atoms in strong laser fields. The
objective of this fundamental research was simply to un-
derstand the behavior of atoms and molecules exposed
to intense electromagnetic fields. This field evolved in
parallel with the development of pulsed lasers towards
increasing peak powers, increasing repetition rates and
decreasing pulse durations. The character of the laser–
atom interaction also evolved from being essentially
perturbative for laser intensities below $10^{13}$ W/cm$^2$ to
strongly nonperturbative for higher intensities. for many
years, this regime of nonlinear optics was studied only by
looking at ionization processes. The number and charge
of the produced ions, as well as the energy and angular
emission of the electrons, were experimentally detected
and compared with theoretical predictions.

At the end of the 1980s, it was realized that look-
ing at the emitted photons would bring complementary
information on the physical processes taking place. In-
deed, efficient photon emission in the extreme ultraviolet
(XUV) range, in the form of high-order harmonics of the
fundamental laser field, was observed for the first time in 1987, in Saclay [5.218] (33rd harmonic of a Nd:YAG laser) and in Chicago [5.219] (17th harmonic of a KrF laser). The harmonic spectra were character-
ized by a decrease in efficiency for the first harmonics,
followed by a broad plateau of nearly constant con-
version efficiency, ending up by an abrupt cutoff. The
existence of such a plateau was clearly a nonpertur-
bative signature of the laser-atom interaction. Most of
the early work concentrated on the extension of the
plateau, i.e. the generation of harmonics of higher
frequency and shorter wavelength going progressively
from $\approx 20$ nm at the end of the 1980s to $\approx 7$ nm by
the middle of the 1990s [5.220–224]. It was soon re-
alized that, in contrast to the ideas promoted in the
nonlinear-optics community, the shortest wavelengths
were obtained with long-wavelength lasers. Today, har-
monic spectra produced with short and intense laser
pulses extend to the water window (below the carbon
K-edge at 4.4 nm) [5.225, 226].

A breakthrough in the theoretical understanding of
high-order harmonic generation processes was initi-
at by Krause and coworkers [5.227] who showed
that the cutoff position in the harmonic spectrum fol-
lows the universal law $I_p + 3U_p$, where $I_p$ is the
ionization potential, whereas $U_p = ve^2E^2/4\pi\alpha^2$, is the
ponderomotive potential, i.e. the mean kinetic en-
ergy acquired by an electron oscillating in the laser
field. Here $e$ is the electron charge, $m$ is its mass,
and $E$ and $\omega$ are the laser electric field and its fre-
cency, respectively. An explanation of this universal
fact in the framework of a simple semiclassical the-
ory was found shortly afterwards [5.228, 229], and
confirmed by quantum-mechanical calculations [5.230,
231].

Progress in experimental techniques and theoret-
ical understanding stimulated numerous studies of
harmonic generation. The influence of the laser po-
larization was investigated in great detail [5.232–239]
(see also [5.240–242] for the theory). The nonlinear
conversion process was optimized with respect to the
laser parameters [5.243, 244], and to the generating
medium [5.245–250]. Finally, the spatial [5.251–256]
and temporal [5.257–263] properties of the radiation
were characterized and optimized. The specifications
of the harmonic emission (ultrashort pulse duration,
high brightness, good coherence) make it a unique
source of XUV radiation, used in a growing number of
applications ranging from atomic [5.264, 265] and mo-
lcular [5.266–268] spectroscopy to solid-state [5.269–
271] and plasma [5.272–274] physics. Finally, it has recently been demonstrated that the low-order harmonics are intense enough to induce nonlinear optical processes in the XUV range [5.275–277].

Almost immediately after the first observation of the harmonic plateau, it was realized that, if the harmonics were emitted in phase, i.e. phase-locked, the temporal structure of the radiation emitted from the medium would consist of a “train” of attosecond pulses separated by half the laser period [5.278, 279]. There is a clear analogy here with mode-locked lasers, where axial modes oscillating in a laser cavity are locked in phase, leading to the production of trains of short pulses. Attosecond pulses have remained, however, a theoretical prediction until recently [5.280–282]. A first possible indication of harmonic radiation containing an attosecond sub-structure was in a high-order autocorrelation of the driving laser pulse [5.283]. This was followed by a beautiful experiment showing evidence for phase-locking between five consecutive harmonics generated in argon, thus indicating that trains of 250 as pulses were formed [5.284]. In a series of experiments performed in Vienna, single pulses of duration of a few hundred attoseconds were demonstrated by using ultrashort (5 fs) laser pulses and spectrally filtering a few harmonics in the cutoff spectral region [5.285, 286]. These experimental results are the beginning of a new field of research attophysics, where processes in atoms and molecules can be studied at an unprecedented time scale.

The purpose of this section is to present to the nonexpert reader a simple description of high-order-harmonic generation, and its application to attosecond metrology. In Sect. 5.11.2, we describe the most important aspects of high-order-harmonic generation processes. We begin with a short description of the experimental set up needed to obtain high-order harmonics. Then we discuss the microscopic and macroscopic physics underlying the generation of high-order harmonics. We focus on the physics of importance for the generation of attosecond pulse trains and single attosecond pulses. We refer the reader to several review articles for a more complete overview of this research topic [5.245, 287, 288]. In Sect. 5.12, the emerging field of attosecond science is reviewed. The different measurement techniques are described and the first application of attosecond pulses is presented.

5.11.2 High-Order-Harmonic Generation in Gases

Experimental Method
Generating high-order harmonics is experimentally simple. A typical set up is shown in Fig. 5.36. A laser pulse

![Fig. 5.36 Schematic representation of a typical experimental setup for high-order-harmonic generation. An intense short pulse laser is focused into a vacuum chamber containing a gas medium. Harmonics are emitted along the laser propagation axis. A photograph of a gas target is shown at the bottom, on the left. A typical spectrum obtained in neon is shown on the right. It shows a plateau ending with a sharp cutoff.](image)
is focused into a vacuum chamber containing a rather small gas target with an atomic pressure of at least a few mbar. The harmonics (only of odd order, owing to inversion symmetry) are emitted along the laser propagation axis. Many types of lasers have been used, excimers, Nd:YAG, Nd:glass, Ti:sapphire, dye lasers, etc. [5.218,219,222,223,289,290]. In addition, the second harmonic of these lasers [5.291–293] as well as the radiation from sum- or difference-frequency mixing processes [5.294,295] for example to get into the mid-infrared range [5.296], have also been employed. Typical energies are between a fraction to a few tens of mJ, typical pulse durations are from a few femtoseconds to a few tens of picoseconds. In the last five years, the favorite tool has become the Ti:sapphire laser, providing very short pulse lengths, high laser intensities at high repetition rates. The shortest laser pulses used today to study atoms in strong laser fields are about 5 fs (two cycles) long [5.285]. The advantage of using short pulses is that atoms get exposed to higher laser intensity before they ionize, leading to higher-order harmonics. The different parameters of the laser pulses, such as the polarization, the focusing characteristics, the spatial and temporal profiles are often varied and optimized in the experiments. Recent studies do not simply vary a given parameter, but attempt to shape a laser pulse (by varying, for example, its phase [5.244], its degree of ellipticity [5.297–299], or its spatial properties [5.300,301]) to tailor the harmonics for different applications.

The gas medium is provided by a gas jet, hollow fiber [5.246–248] or a (small) gas cell [5.249,250,303]. Figure 5.36 shows a photograph of such a gas target containing argon atoms irradiated by an intense laser pulse. Rare gases are the favored species, for obvious technical reasons. In addition, some work has been done with alkali atoms [5.296], ions [5.220,304], molecules [5.305–308] and clusters [5.309–311]. Photons are separated in energy and detected by an XUV spectrometer, including a grating, sometimes a re-focusing mirror, and a detector (electron multiplier, microchannel plates, etc.). A typical experimental spectrum is shown in Fig. 5.36. This result has been obtained in a gas of neon using a 100 fs 800 nm Ti:sapphire laser [5.312]. It shows odd harmonic peaks up to the 53rd order, with a rapid decrease beyond the 49th harmonic, characteristic of the cutoff region. The spectral range of the harmonic emission as well as the conversion efficiency depends strongly on the gas medium. As schematically illustrated in Fig. 5.37 (top), the efficiency is highest in the heavy atoms Ar, Xe, Kr, but the highest photon energies are obtained in He and Ne [5.222, 245, 302]. Figure 5.37 (bottom) presents
a comparison between the generation efficiency for three
rare gases Ar, Ne, He, when ultrashort laser pulses (of
duration 5 fs) are used for the excitation [5.245, 302].

As illustrated in Fig. 5.38, two conditions are neces-
sary to observe efficient harmonic emission. First, each
individual atom must generate light at these frequencies,
requiring a highly nonlinear response to the radiation
field. Second, the harmonic field results from the co-
herent superposition of all the emitting atoms in the
medium. Harmonic generation will be efficient only if
phase matching is achieved, requiring the generated field
to be in phase with the nonlinear polarization creating it
over the medium’s length. We discuss these two aspects
in more details in the following sections.

5.11.3 Microscopic Physics

Electrons in an atom in the presence of a time-dependent
radiation field oscillate. This is described by a dipole
moment \( d(t) = \langle \Phi(t) | e r | \Phi(t) \rangle \), where \( | \Phi(t) \rangle \) is the time-
dependent electronic wavefunction, the solution of the
Schrödinger equation. When the radiation field is weak,
there is mainly one oscillation frequency, that of the
field. In a strong radiation field, the oscillatory motion
becomes distorted and the dipole moment now includes
a series of higher-order frequencies, odd harmonics of
the fundamental one. The harmonic emission from a sin-
gle atom can thus be calculated by taking the Fourier
transform of the dipole moment. Theorists often use a
single-active-electron approximation, assuming that the
interaction with the field involves essentially one active
electron, to describe the response of the atom to a strong
laser field. A number of methods have been proposed
to solve this problem and it is beyond the scope of this
paper to review all of these approaches. The most re-
alistic approach is probably the numerical solution of
the time-dependent Schrödinger equation, pioneered by
Kulander at the end of the 1980s [5.313]. Many impor-
tant results, such as the determination of the cutoff law
for high-order harmonics in 1992 [5.227] or proposals
for single attosecond pulse generation using few-cycle
laser pulses at the end of the 1990s [5.245,314,315] were
obtained directly from numerical calculations. The semi-
classical strong field approximation, originating from
a seminal paper of Keldysh in 1964 [5.316], applied by
Lewenstein in the 1990s to high-order-harmonic genera-
tion [5.230, 231] allows to explore a larger parameter
space as well as to gain intuitive insight. This model
and a related one approximating the atomic potential by
a \( \delta(r) \) potential [5.240] have been extensively used to
interpret experimental results.

Many insights in the physical understanding of the
interaction between atoms and strong laser fields have
been provided by a simple semiclassical model, pro-
posed first by Van der Linden, van der Heuvel, and
Muller in the context of above-threshold ionization and
extended by Corkum and others [5.228, 229] to
multiple ionization and high-order-harmonic genera-
tion. According to this model, illustrated in Fig. 5.39
(right), the electron tunnels through the Coulomb en-
ergy barrier modified by the presence of the relatively
slowly varying linearly polarized electric field of the
laser. It then undergoes (classical) oscillations in the
field, during which the influence of the Coulomb force
from the nucleus is practically negligible. If the elec-
tron comes back to the vicinity of the nucleus, it may be
rescattered one or several times by the nucleus, thus
acquiring a high kinetic energy, and in some cases,
kicking out a second or third electron. It may also
recombine back to the ground state, thus producing
a photon with energy \( I_p \), the ionization potential, plus
the kinetic energy acquired during the oscillatory mo-
tion. We also show in Fig. 5.39 (left) for comparison the
more traditional harmonic-generation process based on
multiphoton absorption in the (barely perturbed) atomic potential.

An intuitive understanding of some of the properties of harmonic generation can be gained by elementary classical calculations of the electron motion outside the binding potential. Assuming the electron to have zero velocity immediately after it has tunneled through the potential barrier at time \( t = t_0 \), and the laser field to be simply described by \( E = E_0 \sin(\omega t) \), we obtain:

\[
v = -v_0 \cos(\omega t_0) + v_0 \cos(\omega t) ,
\]

\[
x = -\frac{v_0}{\omega} \sin(\omega t_0) + \frac{v_0}{\omega} \sin(\omega t) + (t-t_0) v_0 \cos(\omega t_0) ,
\]

where \( v_0 = qE_0/m_0 \). Depending on the time at which the electron is released into the continuum \( (t_0) \), it will follow different trajectories, as illustrated in Fig. 5.40. Only those electrons released between \( T/4 \) and \( T/2 \) (where \( T \) is the laser period) are of interest for harmonic generation. When the laser field changes its sign, they come back towards the core \( (x = 0) \) with a certain kinetic energy. This energy, which determines the emitted harmonic order, is proportional to the square of the slope of the trajectory as it crosses the time axis [open circles in Fig. 5.40 (top)]. Except for the trajectory starting at approximately \( 0.3T \), giving the highest kinetic energy (cutoff), there are two (main) trajectories leading the same kinetic energy. This is illustrated in Fig. 5.40 (bottom), showing the kinetic energy when the electron returns to the core \( (\text{solid line}) \), as well as the time spent in the continuum \( (\text{dashed line}) \), as a function of release time. As shown in the figure, for each energy, and hence for each harmonic order, there are mainly two
trajectories, a short and a long one, contributing to the harmonic emission. The periodicity (for a pulse several cycles long) of the process implies that the light emission is not continuous but at discrete (odd-harmonic) frequencies.

The influence of the complex electron dynamics inherent to the harmonic-generation process is clearly visible on the intensity dependence of the harmonic components of the quantum-mechanical dipole moment. Figure 5.41 shows for example the 35-th harmonic generated in neon, calculated within the strong field approximation. The intensity and phase are represented respectively in solid and dashed line as a function of the laser intensity. The sharp intensity and phase variation at low intensity corresponds to the cutoff region. In the plateau, oscillations are clearly visible in the variation of both the intensity and the phase. They originate from interference effects between the contributions from the multiple trajectories. This fascinating conclusion stimulated the development of analysis techniques to extract the contributing electron trajectories (or rather the relevant quantum paths) from quantum-mechanical approaches [5.317, 318]. The result of such an analysis for the 35-th harmonic in neon is shown at the bottom in Fig. 5.41. The contributions to the dipole phase varying linearly with the intensity \( \phi_{dip}(I) = \alpha_j I \), corresponding to a quantum path \( \lambda_j \), are identified as vertical lines in Fig. 5.41. In this case, the dominant trajectory is the “second” one, with a coefficient \( \alpha_2 = 24 \times 10^{-14} \text{ cm}^2 \text{ W} \). At low intensity, in the cutoff region, there is only one quantum path. Note that here, the predictions of the strong field approximation differ somewhat from those of the time-dependent Schrödinger equation [5.318].

The microscopic physics (the quantum orbits) behind high-order-harmonic generation was shown in a series of experiments investigating the temporal coherence of the harmonics [5.319–321]. We present in Fig. 5.42 the principle as well as some results obtained in xenon [5.320]. Two phase-locked spatially separated harmonic sources are created by splitting the laser into two replicas in a Michelson interferometer and by slightly misaligning one of the arms. A variable time delay can be introduced between the two pulses. The generated harmonics are separated by a grating and interfere in the far field. The variation of the contrast of the fringes as a function of time delay gives the coherence time. Figure 5.42 (bottom) shows images obtained for the 13-th harmonic in xenon. (For experimental reasons, the images are not symmetrical.) These images present two spatial regions for high harmonics in xenon.

These results can be interpreted in a simple way by recalling that the harmonic field is a sum of the contributions from each quantum path \( j \)

\[
E_h(r, t) = \sum_j A_j(r, t) e^{-[i 2\pi \omega_j I r, t]}
\]  

(5.232)

where \( A_j \) is an envelope function, representing the strength of each path. The temporal variation of the laser
intensity $I(t)$ will produce a chirp in the emitted field, and consequently a spectral broadening (or a reduced coherence time). The radial variation of the laser intensity $I(r)$ will affect the curvature of the phase front of the harmonics, and therefore their divergence. The contribution from the quantum paths with a long excursion time in the continuum (Fig. 5.40), resulting in a large $\alpha_j$, will have a short coherence time and a pronounced curvature in the far field, whereas that from the quantum paths with a short excursion time will have a longer coherence time and be more collimated [5.322]. Similar evidence for the existence of (at least) two quantum paths has been obtained by analyzing the harmonic spectra in combination with measuring the harmonic pulse duration [5.321]. Contributions of different quantum paths can be selected macroscopically, either by spatial or spectral filtering.

### 5.11.4 Macroscopic Physics

We now turn to the second aspect of harmonic generation, namely the response of the whole medium. To achieve phase matching, i.e. to ensure efficient conversion, the wave vector difference (traditionally called the phase mismatch) between the harmonic wave and the polarization must be minimized, so that the phase difference varies as little as possible over the medium’s length. For an incident Gaussian beam, this phase difference on the propagation axis ($z$) is given by

$$\delta \phi_q = \phi_q - \phi_q^{pol} \approx k_q z - q k_1 z + q \arctan(2 z / b) - \phi_{dip} .$$  \tag{5.233}$$

In this equation, the first two terms characterize the difference in dispersion at the fundamental and $q$-th harmonic frequencies, mainly due to the effect of the free electrons in the medium. The third one is a geometrical term originating from the Gouy phase shift of a Gaussian beam with confocal parameter $b$ across the focus. The fourth term is the dipole phase described above.

According to the previous discussion, it is more physically correct to consider separately the contributions from the different quantum paths, before making a (coherent) sum. The phase difference to minimize depends on the trajectory and is given by

$$\delta \phi_{q,j} = \phi_q - \phi_q^{pol} \approx k_q z - q k_1 z + q \arctan(2 z / b) - \alpha_j I(r, z, t) .$$  \tag{5.234}$$

Figure 5.43 illustrates the variation of $\delta \phi_q$ along the propagation axis ($z$). Most contributions are monotonic. Focusing as well as the free electron dispersion (not shown in Fig. 5.43) lead to a contribution to $\delta \phi_q$ increasing with $z$, while the (normal) dispersion leads to a term decreasing with $z$, usually quite small. In contrast, the contribution of the dipole phase, here due mainly to the second trajectory, with a transition to the cutoff for $|z| \geq 7.5$ mm, first increases, then decreases with $z$. In the particular case shown in Fig. 5.43, phase matching on the propagation axis is best realized for $z \geq 7$ m, requiring the medium to be located after the focus. In general, the situation can be rather complicated. Methods have been developed to visualize where (in the nonlinear medium) and when (during the laser pulse) phase matching was best realized [5.317], using in particular three-dimensional maps representing the local coherence length, defined as

$$L_q = \pi \left( \frac{\partial \delta \phi_q}{\partial z} \right)^{-1} .$$  \tag{5.235}$$

An example of such a map for the situation corresponding to Fig. 5.43 (top) is shown at the bottom of the same page.
The white areas indicate where phase-matching is best realized. The two parts of the figure correspond to the transition between cutoff and plateau.

The brief analysis presented above can easily be generalized to include propagation in waveguides [5.246–248], which modifies somewhat the phase-matching conditions, since the geometrical and dipole phase effects are much reduced (owing to a constant intensity in the waveguide). Absorption in the nonlinear medium starts to play a role for high conversion efficiencies and long medium lengths and/or high pressures. The optimization of phase matching of high-order-harmonic generation has stimulated a great deal of efforts during the last five years. The so-called absorption limit, where the limitation on the conversion efficiency is due to absorption, and not to the coherence length, has been reached in different wavelength ranges [5.249, 250, 302]. Recently, the use of extremely long focusing geometries (which minimize both the effect of the dipole phase and that of the Gouy phase shift) has led to conversion efficiencies as high as a few times $10^{-5}$ and energies in the $\mu$J range [5.303, 323]. Phase matching of high-order-harmonic generation is by no means a solved issue, since it is a complicated three-dimensional problem, involving a number of parameters (laser focusing, pressure, medium length and geometry, laser intensity). In addition, the problem is quite different for the low-order harmonics with energy around a few tens of eV, where most of the work has been done, and for the high-order harmonics at 100 eV or more. An interesting idea, similar to quasi-phase-matching has recently been investigated [5.324]. A modulated waveguide, used for the generation of high-order harmonics, induces a periodic variation of the degree of ionization leading to enhanced conversion efficiency, especially for the high harmonics.

Finally, a conclusion of importance for the generation of attosecond pulse trains is that the different quantum paths contributing to harmonic generation discussed in the previous section are not phase matched in the same conditions (5.234). The axial variation of the laser intensity $I(z)$ leads to different phase matching conditions for the contributions from the different quantum paths. In other words, depending on the geometry, ionization, pressure conditions, phase matching will enhance one of the contributing trajectories to the detriment of the others. This conclusion is extremely important for the generation of attosecond pulse trains. As illustrated in Fig. 5.44 (left), the electron trajectories contributing to harmonic generation in the single-atom response lead to bursts of light at different times during the laser half-cycle. Phase locking between consecutive harmonics is not realized. In some conditions, however, phase matching results in efficient generation of only one of these contributions [Fig. 5.44 (right)] [5.325, 326], leading to a train of attosecond pulses. Another possibility, that makes use of the different spatial properties of the contributing trajectories, is to select the shortest trajectory by spatially filtering the harmonic beam with an aperture. Finally, a spectral filter can be used to select only the harmonics in the cutoff region, where the electron dynamics is much simpler, with only one electron trajectory in a single-atom response.
[5.330]. With this tool it should be possible to precisely control the motion of energetic electron wave packets around atoms on attosecond timescales just as the motion of nuclear wave packets in molecules can be controlled within a few femtoseconds. The single sub-femtosecond electron bunches and (XUV/X-ray) photon bursts that arise from the recently gained ability to control electron wave packets will enable the scientific community to excite and probe atomic dynamics on atomic time scales.

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