Coherent anti-Stokes Raman scattering in isolated air-guided modes of a hollow-core photonic-crystal fiber

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Hollow-core photonic-crystal fibers are shown to offer the unique possibility of coherent excitation and probing of Raman-active vibrations in molecules by isolated air-guided modes of electromagnetic radiation. A 3-cm section of a hollow photonic-crystal fiber is used to prepare isolated air-guided modes of pump and probe fields for a coherent excitation of 2331-cm^{-1} Q-branch vibrations of molecular nitrogen in the gas filling the fiber core, enhancing coherent anti-Stokes Raman scattering through these vibrations by a factor of 15 relative to the regime of tight focusing.

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Coherent Raman excitations is one of the most important pathways of laser-matter interactions. Coherent Raman processes are at the heart of many efficient spectroscopic [1,2] and microscopic [3] techniques, methods of frequency conversion [4] and time-resolved studies [5,6], as well as laser-cooling [7] and quantum-control [8] schemes. Multiple Raman sidebands produced through high-order stimulated Raman scattering allow few-field-cycle pulses to be synthesized [9]. The potential of nonlinear Raman techniques has been recently enhanced by coherent control approaches [10].

Many interesting possibilities of coherent Raman processes are associated with waveguide regimes of Raman excitation [11,12]. Hollow fibers [13,14] and Bragg planar waveguides [15] have been shown to improve the efficiency of coherent anti-Stokes Raman scattering (CARS) in the gas phase. Large nonlinear interaction lengths make hollow fibers filled with a Raman-active gas efficient generators of sub-4-fs pulses [9].

Air-guided modes in standard hollow fibers are, however, leaky, with the magnitude of losses scaling as λ^2/a^3 with the fiber inner radius a and the radiation wavelength λ [16], which dictates the choice of hollow fibers with $a \sim 50-300\ \mu$m for nonlinear-optical experiments. Such large-a fibers are essentially multimode, with many guided modes typically contributing to nonlinear-optical interactions [14,17]. This multimode nature of nonlinear-optical processes complicates a precise calibration of the coherent Raman signal as a function of the concentration of Raman-active species, leads to unwanted interference phenomena in spectroscopic and time-resolved coherant Raman measurements, and should be one of the factors limiting the duration of ultrashort pulses synthesized in hollow fibers.

The number of air-guided modes can be radically reduced by using hollow-core photonic-crystal fibers (PCFs) [18,19]. Such fibers guide light due to the high reflectivity of a two-dimensionally periodic (photonic-crystal) cladding (the inset in Fig. 1) within photonic band gaps. Low-loss guiding in a few or even a single air-guided mode can be implemented under these conditions in a hollow core with a typical diameter of $10-20\ \mu$m [18–20]. Hollow PCFs with such core diameters have been recently demonstrated to enhance nonlinear-optical processes, including stimulated Raman scattering [21], four-wave mixing (FWM) [22], and self-phase modulation [23]. Air-guided modes in hollow PCFs can support high-power optical solitons [24,25] and allow transportation of high-intensity laser pulses for technological [26,27] and biomedical [28] applications.

In this work, we will use hollow-core PCFs to prepare isolated air-guided modes of pump and probe fields to coherently excite and probe Raman-active vibrations in nitrogen molecules. To visualize coherently excited Raman vibrations in N_2 molecules in a hollow PCF, we employed a two-color CARS process, leading to the generation of a signal at the frequency $\omega_{CARS}=2\omega_1-\omega_2$, where ω_1 and ω_2 are the frequencies of the pump waves. We will show that a 3-cm section of a hollow PCF enhances CARS through 2331-cm^{-1} vibrations of molecular nitrogen by a factor of 15 with respect to the regime of tight focusing.

For a quantitative analysis of air-guided modes supported by hollow PCFs, we developed a numerical procedure solving the vectorial wave problem for the electric field [29]. The two–dimensional profile of the refractive index was approximated, as in [30,31], with a series expansion in Hermite-Gaussian polynomials and trigonometric functions.

Based on the results of our numerical simulations, we designed hollow-core PCFs intended for a coherent excitation and probing of Raman-active modes through a two-color CARS process $\omega_{CARS}=2\omega_1-\omega_2$, resulting in the generation of the CARS signal at the frequency ω_{CARS} through the FWM of the fields with the frequencies ω_1 and ω_2. Our hollow PCFs were designed to simultaneously support air-guided modes of the second harmonic of neodymium-doped yttrium aluminum garnet (Nd:YAG) laser radiation with a wavelength of 532 nm (ω_1), dye-laser radiation (ω_2) with the wavelength (607 nm) 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 molecular nitrogen with the central frequency $\Omega=2331\ cm^{-1}$ (inset 1 in Fig. 1), and the resulting CARS field with a wavelength of 473 nm (ω_{CARS}).

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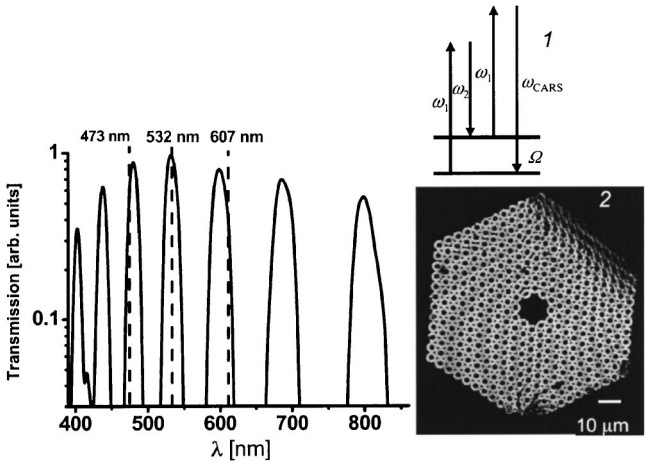

FIG. 1. (Color online) Transmission spectrum of the hollow PCF designed to simultaneously support air-guided modes of the pump, probe, and CARS signal fields in the hollow core of the fiber. The insets show (1) diagram of the CARS process $\omega_{\mathrm{CARS}}=2\omega_1-\omega_2$ and (2) an image of the PCF cross section.

The hollow-core PCFs had an inner diameter of approximately 13 μm and a period of the photonic-crystal cladding of about 4.5 μm. A typical structure of the PCF cross section is shown in inset 2 of Fig. 1. The PCFs were fabricated [20,29] with the use of a preform consisting of a set of identical glass capillaries. Seven capillaries were removed from the central part of the preform for the hollow core of PCFs. The manifold of passbands in the transmission spectra of these PCFs, mapping photonic band gaps of the PCF cladding, was adjusted, through PCF structure engineering, in such a way as to simultaneously support air-guided modes of the pump, probe, and CARS fields in the follow core of the PCF (Fig. 1).

Photonic-crystal cladding not only serves to lower propagation losses of air-guided modes, but also reduces the number of such modes relative to a standard hollow fiber. Figure 2 illustrates the properties of air-guided modes in our hollow PCFs within the region of wavelengths from 0.59 to 0.62 μm, which corresponds to a typical wavelength range of dye-laser radiation in our experiments. The fundamental mode has the maximum propagation constant β (solid curve in Fig. 2), and the electric-field intensity in this mode reaches its maximum at the center of the fiber core, monotonically decreasing off the center of the fiber (inset 1 in Fig. 2). Higher-order modes form degenerate multiplets, with their superposition supporting the full symmetry of the fiber [32]. The second-order mode is fourfold degenerate [33], displaying a two-lobe intensity profile (insets 2 and 3 in Fig. 2). Dispersion of this multiplet of higher-order air-guided modes of a hollow PCF is shown by the dashed line in Fig. 2. Hollow PCFs designed for the purposes of our experiment, as can be seen from Fig. 2, can support a few air-guided modes of electromagnetic radiation. Although these PCFs are not exactly single mode, the guided modes can be easily discriminated by tilting the fiber with respect to the axis of the incident beam. This property of hollow PCFs to support isolated air-guided modes of electromagnetic radiation was used in our experiments for single-mode waveguide excitation and probing of Raman-active vibrations in nitrogen molecules.

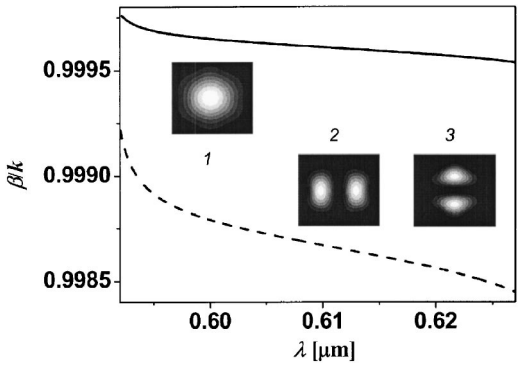

FIG. 2. (Color online) Propagation constant β normalized to the wave number k as a function of the wavelength for the fundamental (solid curve) and a doublet of higher-order (dashed curve) air-guided modes of a hollow PCF with a core diameter of approximately 13 μm and a period of the photonic-crystal cladding of about 4.5 μm. The insets show intensity profiles for the fundamental (1) and the doublet of higher-order air-guided modes (2, 3) of the hollow PCF.

The laser system employed in our experiments 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 and 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 5 mJ by a Nd:YAG amplifier. Fundamental radiation was then converted into the second harmonic with a potassium dihydrogen phosphate (KDP) crystal. The second harmonic produced in this crystal served as one of the pump beams in the CARS process (the frequency ω_1). Fundamental radiation that remained frequency unconverted at the output of the deuterated KDP crystal was separated from the second harmonic with a dichroic mirror and employed to generate the second harmonic in the second KDP crystal. This second-harmonic beam was then used to pump a sulforhodamine 101 dye laser. Dye-laser radiation served as the second pump beam in the CARS process (the frequency ω_2). The pump beams with the frequencies ω_1 and ω_2 were brought into a spatial coincidence with a dichroic mirror and were coupled into a 3-cm hollow PCF by a lens with a focal length of 5 cm. The energy of the second-harmonic pulse was varied in the range of 10–200 μJ in CARS experiments, while the energy of dye-laser radiation ranged from 5 up to 100 μJ. In the spectral domain, laser pulses of 532-nm radiation were substantially narrower (with their bandwidth estimated as 0.2 cm^{-1}), while dye-laser pulses were much broader (20 cm^{-1}) than the bandwidth of the N_2 Raman Q branch, probed in our experiments. The 473-nm CARS signal, related to molecular nitrogen in the atmospheric-pressure air filling the hollow PCF, was collimated with a spherical lens, separated from the pump and probe beams with a set of optical filters, dispersed with a monochromator, and detected with an optical multichannel analyzer.

Both the second-harmonic and dye-laser beams were coupled into the fundamental mode of the hollow PCF. Im-

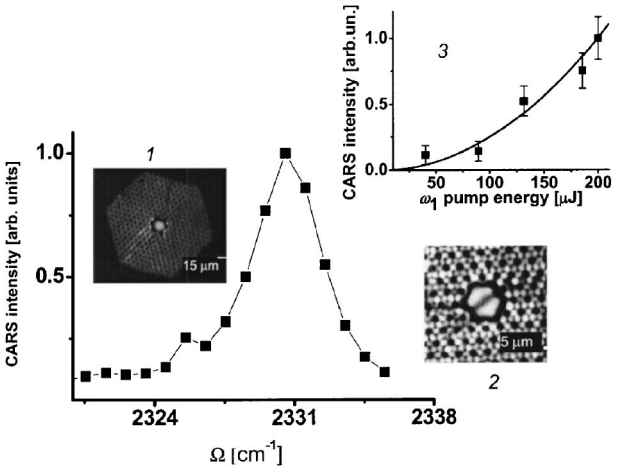

FIG. 3. (Color online) CARS spectrum of *Q*-branch Raman-active vibrations of N_2 molecules in the atmospheric-pressure air filling the hollow core of the PCF. The insets show (1, 2) output beam profiles in the fundamental (1) and higher-order (2) air-guided modes of the hollow PCF and (3) the CARS intensity as a function of the energy of the second-harmonic field.

ages of beam patterns at the output end of the PCF (insets l and 2 in Fig. 3) were used to monitor fundamental-mode guiding of the pump and probe fields. The coherence length for the CARS process involving the fundamental modes of the pump and probe fields, controlled by the mismatch of the propagation constants β_1, β_2, and β_{CARS} of the air-guided modes of the laser and CARS fields with frequencies ω_1, ω_2, and ω_{CARS}, respectively, $l_c=\pi/(2|\beta_{\mathrm{CARS}}-2\beta_1+\beta_2|)$, was estimated as $l_c\approx 5$ cm. Measurements of attenuation lengths l_α for the wavelengths of second-harmonic ($\alpha=1$), dye-laser ($\alpha=2$), and CARS-signal ($\alpha=3$) radiation yield $l_1\approx 25$ cm, $l_2\approx 18$ cm, and $l_3\approx 15$ cm. In view of this hierarchy of attenuation and coherence lengths, the PCF length was chosen equal to $L=3$ cm $<l_c<l_1,l_2,l_3$.

Pump pulses with frequencies ω_1 and ω_2 coherently excite *Q*-branch Raman-active vibrations of N_2 molecules in the atmospheric-pressure air filling the hollow core of the PCF. These coherently excited vibrations then scatter off the probe beam with the frequency ω_1, giving rise to the anti-Stokes signal (see inset 1 in Fig. 1). The spectrum of this coherently scattered signal, shown in Fig. 3, is identical to the N_2 *Q*-branch CARS spectrum of the atmospheric air measured in the tight-focusing regime. The CARS spectrum presented in Fig. 3 is slightly asymmetric (the solid line in Fig. 3 is a guide for the eye), with its blue wing being noticeably steeper than its red wing. Such a spectral shape is typical of CARS applied to the N_2 *Q* branch (a comprehensive overview of N_2 CARS studies is provided, e.g., by Akhmanov and Koroteev [1] and Dreier *et al.* [34]). The rotationally unresolved CARS spectrum of the N_2 *Q* branch, detected at the output of the PCF in our experiments, is centered around $\Omega=2331$ cm^{-1}, which is the central frequency for the Raman *Q* branch of N_2 [1]. The linewidth of this CARS spectrum is about 4 cm^{-1}, which is consistent with the analysis by Dreier *et al.* [34]. The coherent background in CARS spectra, related to the nonresonant part of the cubic susceptibility $\chi^{(3)}$ [1,2], was approximately a factor of 30 lower in our PCF experiments than the resonant part of the CARS signal. The influence of the nonresonant contribution on the shape of CARS spectra was negligible under these conditions.

Quadratic approximation provides a good fit for the dependence of the CARS signal power measured at the output of the PCF on the input power of second-harmonic radiation (inset 3 in Fig. 3), which is consistent with the perturbative regime of CARS.

The energy of the CARS signal produced in a hollow-core PCF was compared with the energy of the CARS signal generated by tightly focused second-harmonic and dye-laser beams with the same energies. This comparison allowed the waveguide CARS enhancement factor to be estimated as approximately 15 for our experimental geometry. This result qualitatively agrees with our expectations based on the $\lambda^2 l^2/a^4$ scaling law [35] of waveguide CARS enhancement in hollow PCFs (λ is the radiation wavelength, l is the nonlinear interaction length, limited by the phase mismatch and radiation losses, and a is the fiber core radius). With the validity of our expectations confirmed by experimental results, we can scale up the results of our measurements to predict waveguide CARS enhancement by two orders of magnitude in hollow-core PCFs with a dispersion profile engineered to increase the CARS coherence length up to $l_c\approx 10$ cm.

An attractive recipe to improve the signal-to-noise ratio for CARS spectra measured with air-guided modes of hollow PCFs is to substitute high-repetition-rate ultrashort laser pulses for nanosecond pulses used in this work. To illustrate this possibility, we use the quantum-limit expression for the signal-to-noise ratio of a CARS spectrometer [1,2]: $(S/N)_{\mathrm{CARS}}\propto N_r\sigma_R I_1(\eta P_2)^{1/2}(\Delta\nu)^{-1/2}$, where N_r is the density of Raman-active species, σ_R is the cross section of Raman scattering, I_1 is the pump intensity, η is the quantum efficiency of the photodetector, P_2 is the probe power, and $\Delta\nu$ is the bandwidth of the detection system. The use of laser pulses with a pulse duration $\tau_p\approx 100$ fs, repetition rate $f\approx 1$ kHz, and energy $W\approx 1$ μJ instead of pulses with $\tau_p\approx 10$ ns, $f\approx 10$ Hz, $W\approx 0.3$ mJ could thus potentially improve the CARS signal-to-noise ratio for the same photodetector and negligible contribution of the nonresonant background by more than two orders of magnitude.

Experimental results presented in this work demonstrate that hollow-core photonic-crystal fibers provide the unique possibility of coherent excitation and probing of Raman-active vibrations in molecules by isolated air-guided modes of electromagnetic radiation. A 3-cm section of a hollow PCF has been shown to enhance single-mode waveguide coherent anti-Stokes Raman scattering through 2331-cm^{-1} vibrations of molecular nitrogen by a factor of 15 relative to the regime of tight focusing. Efficient CARS observed in our experiments indicates that individual Raman vibrations can be selectively addressed with isolated air-guided modes of hollow PCFs, which suggests the possibility of using such modes for the coherent control of molecular dynamics, laser guiding and laser cooling of atoms, as well as the synthesis of ultrashort pulses in hollow PCFs. The waveguide enhancement of coherent Raman processes induced by isolated air-guided modes of hollow PCFs can be further improved

through PCF dispersion engineering aimed at increasing the coherence length of four-wave mixing for air-guided modes.

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