The phase-controlled Raman effect

A. A. Lanin1,2, I. V. Fedotov1,2, A. B. Fedotov1,2, D. A. Sidorov-Biryukov1,2 & A. M. Zheltikov1,2,3

1International Laser Center, Physics Department M. V. Lomonosov MSU, Moscow, Russia, 2Russian Quantum Center, Novaya 100, 143025 Skolkovo, Moscow Region, Russia, 3Department of Physics and Astronomy, Texas A&M University, College Station TX, 77843-4242 USA.

Unlike spontaneous Raman effect, nonlinear Raman scattering generates fields with a well-defined phase, allowing Raman signals from individual scatterers to add up into a highly directional, high-brightness coherent beam. Here, we show that the phase of coherent Raman scattering can be accurately controlled and finely tuned by using spectrally and temporally tailored optical driver fields. In our experiments, performed with spectrally optimized phase-tunable laser pulses, such a phase control is visualized through the interference of the coherent Raman signal with the field resulting from nonresonant four-wave mixing. This interference gives rise to Fano-type profiles in the overall nonlinear response measured as a function of the delay time between the laser pulses, featuring a well-resolved destructive-interference dip on the dark side of the Raman peak. This phase-control strategy is shown to radically enhance the coherent response from weak Raman modes, thus helping confront long-standing challenges in nonlinear Raman imaging and microspectroscopy.

Results

The idea of phase-controlled coherent Raman scattering is illustrated in Figs. 1 and 2. Here, a probe field with a central frequency \( \omega_{pu} \) is inelastically scattered off a Raman vibration of frequency \( \Omega_R \), coherently driven by a spectrally and temporally tailored optical driving field, giving rise to a coherent anti-Stokes Raman scattering (CARS) signal at the frequency \( \omega_{st} = \omega_{pu} + \Omega_R \). For efficient excitation of the Raman mode, the optical driving field should include sufficiently intense spectral components with frequencies \( \omega_{pu} \) and \( \omega_{st} = \omega_{pu} - \Omega_R \). In the canonical CARS arrangement, such a resonant excitation of a Raman mode is provided by applying spectrally isolated pump and Stokes fields with frequencies \( \omega_{pu} \) and \( \omega_{st} \). In our scheme (Fig. 1a), the optical driver includes a pair of broadband laser pulses with an identical linear chirp \( \varphi(t) = 2t \) and central frequencies \( \omega_{pu}(t) = \omega_1 + 2\eta_1 t \) and \( \omega_{st}(t) = \omega_2 + 2\eta_2 t \), where \( \eta_1 \) and \( \eta_2 = \eta_1 + \tau \) stand for the time measured in the frames of reference moving with the laser pulses and \( \tau \) is the delay time between the laser pulses. The spectrum of the optical driver

...
Figure 1 | Coherent Raman scattering of tailored optical waveforms: (a) the spectral–temporal map of the optical driver and anti-Stokes fields and (b) the pump (blue) and Stokes (red) fields, the optical driver $A_{pu}A^*_{St}$ (green), and the coherent Raman response (purple). The optical driver, consisting of two linearly chirped pulses with equal chirp parameters and central frequencies $\omega_{pu}$ and $\omega_{St}$ (shown in panel (a)), is used for coherent excitation of a Raman-active mode with a frequency $\Omega_R$. Due to the chirp of the laser pulses, the modulation frequency $\Omega_m$ of the optical driver can be scanned by varying the delay time $\tau$ (as shown in panel (b)). The delay times $\tau_1$ and $\tau_2$ in panels (a) and (b) correspond to modulation frequencies $\Omega_1$ and $\Omega_2$. With the delay time between the pulses chosen in such a way (time delay $\tau_1$ in panels (a) and (b)) that the modulation frequency of the optical driver is tuned to a resonance with the frequency of the Raman mode, $\Omega_m = \Omega_R$, the Raman vibration is driven with a maximum efficiency (panel (b)). The linearly chirped pulse with the central frequency $\omega_{pu} = \omega_{pu}$ and chirp parameter $\chi$ also serves as a probe field, giving rise to a chirped anti-Stokes signal centered at $\omega_{St} = \omega_{pu} + \Omega_R = 2\omega_{pu} - \omega_{St}$ (panel (a)). (c) Experimental setup: TiS MPA, Ti: Sapphire laser consisting of a mode-locked master oscillator and a multipass amplifier; OPA, optical parametric amplifier; BS, beam splitter, LBO, lithium triborate crystal; DG, diffraction grating; DM, dichroic mirror; MO, microscope objective; S, sample, SP, short-pass filter; BP, band-pass filter; PMT, photomultiplier tube.

The overall nonlinear signal measured in experiments, $E = E_r + E_{nr}$, is a mixture of the coherent Raman signal $E_r$ and a coherent background $E_{nr}$, originating from nonresonant FWM processes due to the electronic part of optical nonlinearity and off-resonance molecular vibrations. In CARS microscopy and imaging, this nonlinear background has long been viewed as a fundamental limitation on the sensitivity of coherent Raman techniques, strongly motivating the search for effective means for its suppression through carefully optimized polarization arrangements\textsuperscript{3-4}, schemes with time-delayed probe pulses\textsuperscript{14}, and pulse-shaping approaches\textsuperscript{5}. On the other hand, nonresonant coherent Raman scattering is known to provide a constant-phase component of the overall coherent Raman signal, which helps retrieve the phases of Raman-active modes\textsuperscript{3,4,21} and resolve overlapping Raman responses from complex molecules\textsuperscript{22,23}, offering elegant solutions for phase-contrast microscopy\textsuperscript{24} and multimodal Raman imaging\textsuperscript{25-27}.

Our experimental approach employs an optical driver consisting of a pair of chirped pulses, which has been used earlier for coherent Raman spectroscopy\textsuperscript{17-19,26-28}, to demonstrate a smooth phase tunability of coherent Raman scattering. Unlike the earlier work where pulse shaping was used to efficiently suppress the nonresonant background in CARS, in our scheme, the dispersive coherent background resulting from nonresonant FWM is used to visualize the tunable phase of the coherent Raman response from molecular vibrations driven by a pair of chirped laser pulses. To explain this approach, we use standard approximations to represent the overall nonlinear signal as $E(\tau) \simeq \int dt \int dt' d\xi A_{pu}(t, \xi) \int dt'' h(t-\theta) A_{pu}(\theta, \xi) A^*_{St}(\theta-\tau, \xi)d\theta$, where $A_{pu}$, $A_{St}$, and $A_{pr}$ are the complex amplitudes of the pump, probe, and Stokes fields, $\gamma$ is the nonlinear coefficient, and the nonlinear response $h(\theta) = R(\theta) + S(\theta)$ includes the resonant, inertial term, $R(\theta)$, related to Raman modes, along with...
the off-resonance, instantaneous part, \( S(\theta) = \int \delta(\theta) \, d\theta \), \( \delta(\theta) \) being the delta function. When the phase mismatch is negligible within the beam-interaction length \( L \), the resonant and nonresonant parts of the nonlinear signal are given by

\[
E_n(\tau) \propto \int_{-\infty}^{\infty} dt A_{pr}(t) \int_{-\infty}^{\infty} dt A_{nr}(t) \exp(-\tau^2) \delta(t) \quad \text{and} \quad E_m(\tau) \propto \int_{-\infty}^{\infty} dt A_{pr}(t) A_{nr}(t) \exp(-\tau^2) \delta(t) dt.
\]

It is straightforward to see now that the product \( A_{pr} A_{nr} \) serves as an optical driver, providing a coherent excitation of the Raman modes. The Raman response \( E_n(\tau) \) is measured against a coherent background \( E_m(\tau) \) (Fig. 2a), which recovers, as can be seen from the expressions above, the cross-correlation trace of the pump, Stokes, and probe pulses.

**Discussion**

In our experiments performed within a broad class of liquid-phase and solid-film samples featuring the Raman response of a variable complexity, the overall nonlinear signal measured as a function of the delay time \( \tau \) displays a well-resolved Fano-type profile (Fig. 3), as a universal indication (Fig. 2a) of the interference of a signal with a slowly varying signal originating from nonresonant FWM. For large \( |\tau| \), the waveform of the overall nonlinear signal (the filled circles in Figs. 3a, 3c) asymptotically tends to the cross-correlation trace of the laser pulses (the open circles in Figs. 3a, 3c), in agreement with our theoretical analysis (solid and dashed lines in Figs. 2a, 3a, 3c).

The waveforms of the time-resolved nonlinear signals in all our experiments are adequately explained in terms of a damped-oscillator model of Raman vibrations (cf. filled circles and solid lines in Figs. 3a, 3c), translating into Lorentzian spectral profiles for the Raman line shapes, giving \( R(\theta) = \sum_{j}^{N} f_{j} \left( \frac{\omega_{ij}}{\omega_{ij}^2 + \gamma_j^2} \right) \sin(\theta) \left/ \eta_{ij} \right| \), and \( \sum_{j} f_{j} = 1 \) for a manifold of \( N \) Raman modes with frequencies \( \Omega_j = 2\hbar \omega_{ij} / \gamma_j \) and decay times \( \tau_j = 2 / \gamma_j \) (\( \gamma_j \) is the relevant Raman linewidth), and weighing factors \( f_{j} \). In the case of acetonitrile, an accurate fit is achieved (filled circles and solid line in Fig. 3a) with a Raman function including \( N = 2 \) Raman modes with \( \Omega_1 / 2\pi c = 2284 \, \text{cm}^{-1}, \Gamma_1 / 2\pi c = 15 \, \text{cm}^{-1}, f_1 = 0.124 \) and \( \Omega_2 / 2\pi c = 2289 \, \text{cm}^{-1}, \Gamma_2 / 2\pi c = 12 \, \text{cm}^{-1}, f_2 = 0.02 \). For polystyrene, \( N = 4 \).
To summarize, we have shown that spectrally and temporally tailored optical driver fields enable a phase control of coherent Raman scattering. In experiments with an optical driver consisting of a pair of chirped laser pulses, such a phase control has been visualized through the interference of the coherent Raman signal with the field resulting from nonresonant FWM. This interference gives rise to Fano-type profiles in the overall nonlinear response measured as a function of the delay time between the chirped laser pulses forming an optical drive. Phase-controlled Raman scattering can dramatically modify the nonlinear dynamics of ultrashort pulses and help confront long-standing challenges in nonlinear Raman imaging and microspectroscopy.

**Methods**

In our experiments, an optical driver consists of the second-harmonic output of a Ti:sapphire-laser-pumped optical parametric amplifier (OPA) with a wavelength $\lambda_2 = 2\lambda_1/\alpha_0$, tunable from 630 to 720 nm and a Ti:sapphire laser output with a central wavelength $\lambda_1 = 2\lambda_2/\alpha_0 \approx 808$ nm. The second-harmonic field with $\lambda_2$ also serves as a probe field, giving rise to a linearly chirped anti-Stokes signal centered at $\lambda_4 = 2\lambda_2/\alpha_0$ with $\alpha_0 = 2\alpha_1 = 2\alpha_2$. A 2-mm-thick lithium triborate (LBO) crystal was used to convert the OPA output into second harmonic radiation. A tunable chirp was imposed on the laser pulses with an adjustable pulse stretcher, consisting of a pair of 600-groove/mm diffraction gratings. Parameters of chirped pulses were retrieved from cross-correlation frequency-resolved optical gating measurements. The spectral measurements were performed with the use of fiber-optic spectrometers. A tunable delay time $\tau$ between the pulses was introduced by using a corner reflector mounted on a step-motor-driven stage. The laser pulses were brought into a spatial coincidence using a dichroic mirror and focused on a Raman sample with a microobjective with a numerical aperture NA = 0.1 and a magnification of 8. The Raman signal was collected in the forward direction with an NA = 0.1, f < 1 microobjective. This signal was separated from laser radiation by two short-pass and one band-pass filters and detected with an H9307-02 Hamamatsu photomultiplier tube. The electronic signal from PMT was amplified by an SR830 Stanford Research Systems lock-in amplifier with an integration time of 100 ms.

1. Bloembergen, N. Nonlinear Optics (Benjamin, New York, 1965).
2. Shen, Y. R. The Principles of Nonlinear Optics (John Wiley & Sons, New York, 1984).
3. Brueckner, C. L. Coherent Raman Spectroscopy (Pergamon, Oxford, 1981).
4. Zheltikov, A. M. & Koroteev, N. I. Coherent four-wave mixing in excited and ionized gas media. Phys. Usp. 42, 321–351 (1999).
5. Dudovich, N., Oron, D. & Silberberg, Y. Single-pulse coherently controlled nonlinear Raman spectroscopy and microscopy. Nature 418, 512–514 (2002).
6. Baker, S., Walmsley, I. A., Tisch, J. W. G. & Marangos, J. P. Femtosecond to attosecond light pulses from a molecular modulator. Nature Photonics 5, 664–671 (2011).
7. Pezacki, J. P. et al. Chemical contrast for imaging living systems: molecular vibrations drive CARS microscopy. Nature Chem. Biol. 7, 137–145 (2011).
8. Zumbusch, A., Holtom, G. R. & Xie, X. S. Three-dimensional vibrational imaging by coherent anti-Stokes Raman scattering. Phys. Rev. Lett. 82, 4142–4145 (1999).
9. Freudiger, C. W. et al. Label-Free Biomedical Imaging with High Sensitivity by Stimulated Raman Scattering Microscopy. Science 322, 1857–1861 (2008).
10. Pestov, D. et al. Optimizing the laser-pulse configuration for coherent Raman spectroscopy. Science 316, 260–263 (2007).
11. Malevich, P. N. et al. Ultrafast-laser-induced backward stimulated Raman scattering for tracing atmospheric gases. Opt. Express 20, 18784–18794 (2012).
12. Zheltikov, A. M., Voronin, A. A., Kitzler, M., Baltuška, A. & Ivanov, M. Optical detection of interfering pathways in subfemtosecond multielectron dynamics. Phys. Rev. Lett. 103, 033901 (2009).
13. Raman, C. V. & Krishnan, K. S. A new type of secondary radiation. Nature 121, 501–502 (1928).
14. Zheltikov, A. M. Coherent anti-Stokes Raman scattering: from proof-of-the-principle experiments to femtosecond CARS and higher order wave-mixing generalization. J. Raman Spectrosc. 31, 653–667 (2000).
15. Warren, W. S., Rabitz, H. & Dahleh, M. Coherent Control of Quantum Dynamics: The Dream is Alive. Science 259, 1581–1589 (1993).
16. Zheltikov, A. M., Voronin, A. A., Kienberger, R., Krausz, F. & Korn, G. Frequency-tunable multigigawatt sub-half-cycle light pulses from coupled-state dynamics of optical solitons and impulsively driven molecular vibrations. Phys. Rev. Lett. 105, 103901 (2010).
17. Zheltikov, A. M. & Naumov, A. N. High-resolution four-photon spectroscopy with chirped pulses. Quantum Electron. 30, 606–610 (2000).
18. Helleter, T., Enejder, A. M. & Zumbusch, A. Spectral focusing: High spectral resolution spectroscopy with broadband-width laser pulses. Appl. Phys. Lett. 85, 25–27 (2004).
19. Rocha-Mendoza, I., Langbein, W. & Borri, P. Coherent anti-Stokes Raman microspectroscopy using spectral focusing with glass dispersion. Appl. Phys. Lett. 93, 201103 (2008).
20. von Vacano, B. & Motzkus, M. Time-resolving molecular vibration for microanalytics: Single laser beam nonlinear Raman spectroscopy in simulation and experiment. Phys. Chem. Chem. Phys. 10, 681–691 (2008).

21. Lim, S.-H., Caster, A. G. & Leone, S. R. Single-pulse phase-control interferometric coherent anti-Stokes Raman scattering spectroscopy. Phys. Rev. A 72, 041803 (2005).

22. Koroteev, N. I., Endemann, M. & Byer, R. L. Resolved structure within the broadband vibrational line of liquid H2O from polarization coherent anti-Stokes Raman spectroscopy. Phys. Rev. Lett. 43, 398–401 (1979).

23. van Rhijn, A. C. W., Jurna, M., Jafarpour, A., Herek, J. L. & Offerhaus, H. L. Phase-shaping strategies for coherent anti-Stokes Raman scattering. J. Raman Spectrosc. 42, 1859–1863 (2011).

24. Jurna, M., Korterik, J. P., Otto, C., Herek, J. L. & Offerhaus, H. L. Vibrational phase contrast microscopy by use of coherent anti-Stokes Raman scattering. Phys. Rev. Lett. 103, 043905 (2009).

25. Pegoraro, A. F. et al. Optimally chirped multimodal CARS microscopy based on a single Ti: sapphire oscillator. Opt. Express 17, 2984–2996 (2009).

26. Konorov, S. O. et al. Cross-correlation FROG CARS with frequency-converting PCFs. Phys. Rev. E 70, 057601 (2004).

27. Ivanov, A. A. et al. Coherent Raman spectroscopy with frequency-shifted and shaped pulses from a photonic-crystal fiber. Chem. Phys. Lett. 418, 19–23 (2006).

28. Lang, T. & Motzkus, M. Single-shot femtosecond coherent anti-Stokes Raman-scattering thermometry. J. Opt. Soc. Am. B 19, 340–344 (2002).

29. Handbook of Raman Spectroscopy: From the Research Laboratory to the Process Line, ed. by Lewis, I. R. & Edwards, H. G. M. (CRC Press, 2001).

30. Druet, S. A. J. & Taran, J.-P. CARS spectroscopy. Progress Quantum Electron. 7, 1–72 (1981).

31. Jurna, M. et al. Visualizing resonances in the complex plane with vibrational phase contrast coherent anti-Stokes Raman scattering. Anal. Chem. 82, 7656–7659 (2010).

Acknowledgments

This work was supported in part by the Welch Foundation (grant no. A-1801), the Russian Foundation for Basic Research, and Skolkovo Foundation (grant no. 78).

Author contributions

A.A.L. designed and performed the experiments, analyzed the data, and prepared the graphic material. I.V.F. performed the experiments. A.B.F. and D.A.S.-B. participated in project planning and discussions of the results. A.M.Z. designed the experiments, analyzed the data, and wrote the paper.

Additional information

Competing financial interests: The authors declare no competing financial interests.

License: This work is licensed under a Creative Commons Attribution-NonCommercial-NoDerivs 3.0 Unported License. To view a copy of this license, visit http://creativecommons.org/licenses/by-nc-nd/3.0/

How to cite this article: Lanin, A.A., Fedotov, I.V., Fedotov, A.B., Sidorov-Biryukov, D.A. & Zheltikov, A.M. The phase-controlled Raman effect. Sci. Rep. 3, 1842; DOI:10.1038/srep01842 (2013).