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2013 Laser Phys. 23 115403

(http://iopscience.iop.org/1555-6611/23/11/115403)

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Laser Phys. **23** (2013) 115403 (4pp) doi:10.1088/1054-660X/23/11/115403

A high-resolution two-pulse coherent anti-Stokes Raman scattering spectrum using a spectral amplitude modulation

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Received 20 June 2013
Accepted for publication 11 September 2013
Published 7 October 2013
Online at stacks.iop.org/LP/23/115403

Abstract

Femtosecond coherent anti-Stokes Raman scattering (CARS) spectra suffer from low spectral resolution because of the broadband laser spectrum. In this paper, we propose a feasible scheme to achieve a high-resolution two-pulse CARS spectrum by shaping both the pump and probe pulses using rectangular amplitude modulation. We show that a narrowband hole in the CARS spectrum can be created by the amplitude-shaped laser pulse, the position of which is correlated with the Raman resonant frequency of the molecule. Thus, by observing holes in the CARS spectrum, we are able to obtain a high-resolution CARS spectrum and the energy-level diagram of the molecule.

(Some figures may appear in colour only in the online journal)

Coherent anti-Stokes Raman scattering (CARS) is a four-wave-mixing process [1], as shown in figure 1(a), where a pump pulse of frequency ω_p, a Stokes pulse of frequency ω_s and a probe pulse of frequency ω_{pr} interact in a nonlinear medium, generating a CARS signal with a frequency $\omega_p - \omega_s + \omega_{pr}$. When the frequency difference between the pump and Stokes pulses $\omega_p - \omega_s$ is tuned to be equal to the Raman resonant frequency of the medium Ω_R, the CARS signal is resonantly enhanced. Because its high sensitivity against a fluorescence background, high collection efficiency and high spatial resolution, CARS is considered to be one of the most important nonlinear spectroscopic techniques [1], and has been successfully employed to study molecular constants [2], collisional parameters [3], local structure formation [4], molecular temperatures [5, 6], vibrational imaging [7–9], and remote sensing [10, 11].

Femtosecond CARS inevitably suffers from low spectral resolution because of the large bandwidth of the laser spectrum. Fortunately, with the advent of ultrafast pulse shaping techniques [12], a coherent control strategy making use of a shaped femtosecond laser pulse has proved to be an effective method to improve the spectral resolution of femtosecond CARS, and various pulse shaping schemes have been proposed and experimentally realized [13–17]. Spectral phase modulation is considered as the main means of control. For example, a three-pulse CARS spectrum can be greatly narrowed by shaping the probe pulse using a π phase step function [13], high spectral resolution of the Raman levels can be obtained by shaping both the pump and Stokes pulses using rectangular step phase modulation [14], and a high-resolution single-pulse CARS spectrum can be achieved by shifting a π phase gate within the input pulse spectrum [15, 16]. Recently, spectral amplitude modulation was proposed to improve the spectral resolution of femtosecond CARS—for example, a high-resolution single-pulse CARS spectrum can also be realized by spectral notch shaping [18]. In this paper,

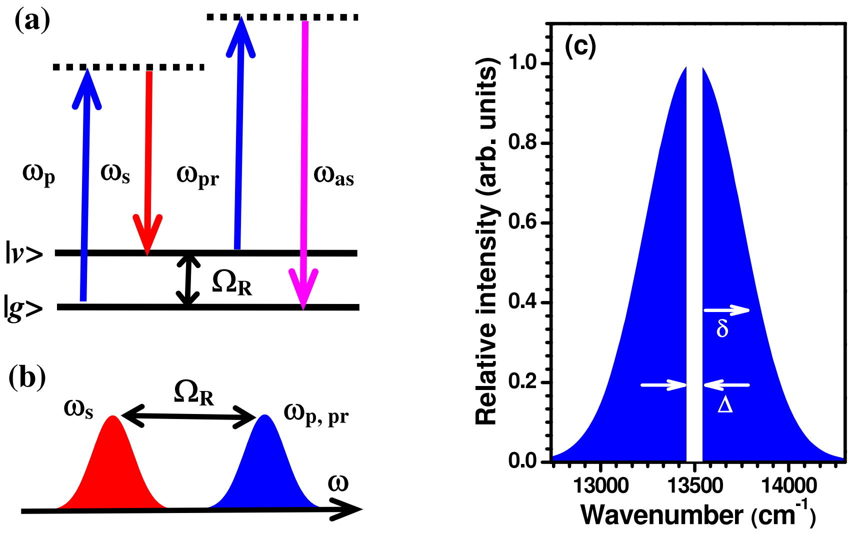

Figure 1. (a) Energy-level diagram of the CARS process. (b) Pump, Stokes and probe pulses in the frequency domain. Here the pump and probe pulses share the same laser field, and the frequency difference between the pump and Stokes pulses is equal to the Raman resonant frequency of the molecule. (c) The pump and probe laser spectra are subjected to rectangular amplitude modulation, where the frequency components in the rectangular window are cut off while those outside the rectangular window are preserved.

we propose rectangular spectral amplitude modulation to improve the spectral resolution of two-pulse CARS. In the two-pulse CARS process [19, 20], the pump and probe pulses share the same laser field, as shown in figure 1(b). Compared with single-pulse or three-pulse CARS [13–18], two-pulse CARS uses simpler experimental apparatus and has wider practical applications. Our results show that a narrowband hole in the CARS spectrum can be created by shaping both the pump and probe pulses using rectangular amplitude modulation, where the position of the hole is correlated with the Raman resonant frequency of the molecule. Therefore, a high-resolution CARS spectrum and the energy-level diagram of the molecule can be obtained by observing the holes in the CARS spectrum.

As shown in figure 1(a), the third-order nonlinear polarization producing the CARS signal by the three-beam configuration can be approximated based on time-dependent perturbation theory as [13–15, 17]

$$P^{(3)}(t) \propto -\frac{1}{\hbar^3}\sum_{mnk}\mu_{gk}\mu_{kn}\mu_{nm}\mu_{mg}\mathrm{e}^{[-(\mathrm{i}\omega_{kg}+\Gamma_{kg})t]} \times \int_{-\infty}^{t}\mathrm{d}t_1\int_{-\infty}^{t_1}\mathrm{d}t_2\int_{-\infty}^{t_2}\mathrm{d}t_3\, E_{\mathrm{p}}(t_3)E_{\mathrm{s}}^*(t_2)E_{\mathrm{pr}}(t_1) \times \mathrm{e}^{[(\mathrm{i}\omega_{kn}+\Gamma_{kn})t_1]}\mathrm{e}^{[-(\mathrm{i}\omega_{mn}+\Gamma_{mn})t_2]}\mathrm{e}^{[(\mathrm{i}\omega_{mg}+\Gamma_{mg})t_3]}, \qquad (1)$$

where $|m\rangle$, $|n\rangle$ and $|k\rangle$ are the intermediate levels, μ_{ij} $(i, j = g, m, n, k)$ are the dipole moments and ω_{ij} are the transition frequencies from the states $|i\rangle \to |j\rangle$. In the frequency domain, the nonlinear polarization can be separately calculated by non-resonant and resonant components, where the non-resonant contribution is attributed to the instantaneous electronic responses and the resonant contribution is correlated with the molecular vibrational motion. Thus, the nonlinear polarization can be further written as [13–15, 17]

$$P^{(3)}(\omega_{\mathrm{as}}) = P_{\mathrm{nr}}^{(3)}(\omega_{\mathrm{as}}) + P_{\mathrm{r}}^{(3)}(\omega_{\mathrm{as}}), \qquad (2)$$

with

$$P_{\mathrm{nr}}^{(3)}(\omega_{\mathrm{as}}) \propto \int_0^{+\infty}\mathrm{d}\Omega\int_0^{+\infty}E_{\mathrm{pr}}(\omega_{\mathrm{as}}-\Omega)\,\mathrm{d}\omega_{\mathrm{p}} \times E_{\mathrm{p}}(\omega_{\mathrm{p}})E_{\mathrm{s}}^*(\omega_{\mathrm{p}}-\Omega), \qquad (3)$$

and

$$P_{\mathrm{r}}^{(3)}(\omega_{\mathrm{as}}) \propto \int_0^{+\infty}\mathrm{d}\Omega\int_0^{+\infty}E_{\mathrm{s}}^*(\omega_{\mathrm{p}}-\Omega)\,\mathrm{d}\omega_{\mathrm{p}} \times \frac{E_{\mathrm{pr}}(\omega_{\mathrm{as}}-\Omega)E_{\mathrm{p}}(\omega_{\mathrm{p}})}{\Omega_{\mathrm{R}}-\Omega+\mathrm{i}\Gamma}, \qquad (4)$$

where $E(\omega) = A(\omega)\exp[\mathrm{i}\Phi(\omega)]$ is the Fourier transform of $E(t)$, and $A(\omega)$ and $\Phi(\omega)$ are the spectral amplitude and phase in the frequency domain, respectively. Ω_{R} is the Raman resonant frequency and Γ is the bandwidth of the Raman level.

Spectral phase modulation, such as rectangular step phase modulation, π phase step modulation or π phase gating, has been proved to be a tool to improve the spectral resolution of CARS [13–17], involving CARS intensity enhancement, CARS spectrum narrowing and CARS background suppression. However, here we propose a form of spectral amplitude modulation with rectangular tailoring of both the pump and probe laser spectra to improve the spectral resolution of two-pulse CARS. This simple amplitude modulation is shown in figure 1(c), where δ and Δ represent the amplitude step position and amplitude modulation width, respectively. By this rectangular amplitude modulation, the frequency components in the rectangular window are cut off while those outside the window are preserved. In our simulation, the laser central frequencies of the pump, Stokes and probe pulses are set to be $\omega_{\mathrm{p}} = 13\,500$ cm^{-1}, $\omega_{\mathrm{s}} = 12\,500$ cm^{-1} and $\omega_{\mathrm{pr}} = \omega_{\mathrm{p}} = 13\,500$ cm^{-1}, and their spectral bandwidths (full width at half maximum) are all 200 cm^{-1}.

We first demonstrate control of the CARS spectrum in benzene with a Raman level of 992 cm^{-1}. Figure 2 presents

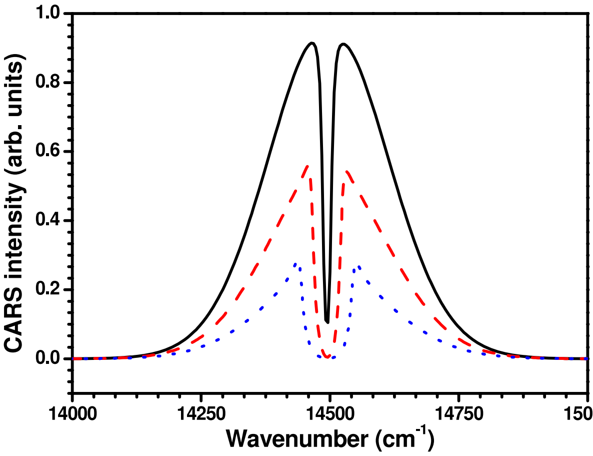

Figure 2. CARS spectra in benzene induced by a shaped laser pulse with an amplitude step position $\delta = 13\,500$ cm^{-1} for amplitude modulation widths $\Delta = 20$ (black solid line), 60 (red dashed line) and 100 cm^{-1} (blue dotted line).

the CARS spectrum in benzene induced by a shaped laser pulse with an amplitude step position $\delta = 13\,500$ cm^{-1} for amplitude modulation widths $\Delta = 20$ (black solid line), 60 (red dashed line) and 100 cm^{-1} (blue dotted line). As can be seen, in each case the CARS spectrum is strongly modulated, and a hole in the CARS spectrum is created. With increasing amplitude modulation width Δ, the CARS intensity decreases and the width of the hole increases. Thus, by applying a small amplitude modulation width Δ, a narrowband hole in the CARS spectrum can be obtained. The width of the hole (full width at half depth) is only $\sim$24 cm^{-1} for an amplitude modulation width $\Delta = 20$ cm^{-1} (see the black solid line in figure 2).

Figure 3 shows CARS spectra in benzene induced by a shaped laser pulse with an amplitude modulation width $\Delta = 20$ cm^{-1} for amplitude step positions $\delta = 13\,440$ (black solid line), 13 500 (red dashed line) and 13 560 cm^{-1} (blue dotted line). One can see that these holes in the CARS spectra for the amplitude step positions $\delta = 13\,440$, 13 500 and 13 560 cm^{-1} are obtained at frequencies of $\omega_{\mathrm{as}} = 14\,432, 14\,492$ and 14 552 cm^{-1}, respectively. It is obvious that the positions of these holes for different amplitude step positions δ occur at different frequencies ω_{as}, while the frequency difference between the position of the hole $\omega_{\text{as-hole}}$ and the amplitude step position δ is constant and equal to the Raman resonant frequency of benzene Ω_{R}, i.e., $\omega_{\text{as-hole}} = \delta + \Omega_{\mathrm{R}}$. Thus, by observing the hole in the CARS spectrum with rectangular amplitude modulation, the Raman resonant frequency Ω_{R} can be determined, providing a feasible method to study the energy-level diagram of the molecule.

Since a laser pulse shaped with rectangular amplitude modulation can induce a narrowband hole in the CARS spectrum whose position is correlated with the Raman resonant frequency of the molecule (see figures 2 and 3), a high-resolution CARS spectrum can be obtained by observing the holes in the CARS spectrum. We consider pyridine with two Raman levels of 988 and 1028 cm^{-1}, where the frequency separation between the two Raman levels is only 40 cm^{-1}.

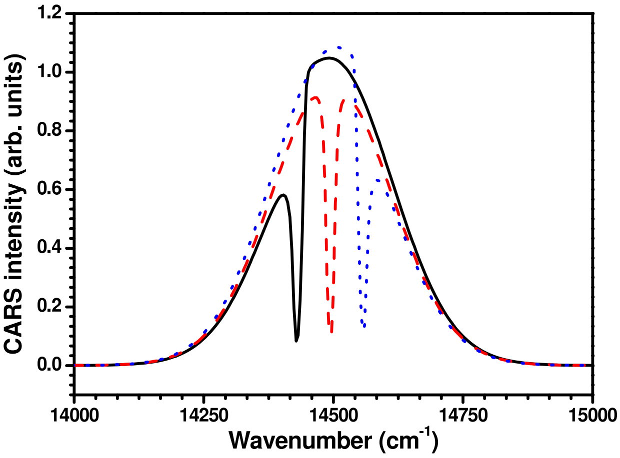

Figure 3. The CARS spectra in benzene induced by a shaped laser pulse with an amplitude modulation width $\Delta = 20$ cm^{-1} for amplitude step positions $\delta = 13\,440$ (black solid line), 13 500 (red dashed line) and 13 560 cm^{-1} (blue dotted line).

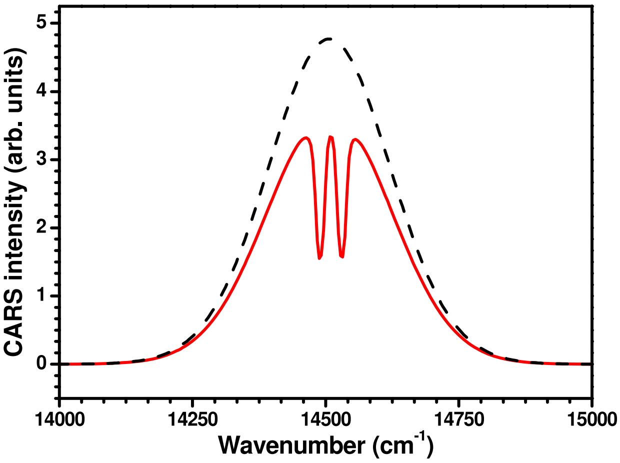

Figure 4. CARS spectra in pyridine induced by an unshaped laser pulse (black dashed line) and a shaped laser pulse with an amplitude modulation width $\Delta = 20$ cm^{-1} and an amplitude step position $\delta = 13\,500$ cm^{-1} (red solid line).

Figure 4 presents the CARS spectra in pyridine induced by an unshaped laser pulse (black dashed line) and a shaped laser pulse with an amplitude modulation width $\Delta = 20$ cm^{-1} and a amplitude step position $\delta = 13\,500$ cm^{-1} (red solid line). Only a single broadband CARS signal is observed for the unshaped laser pulse, while two distinct holes in the CARS spectrum are observed at 14 488 and 14 528 cm^{-1} for the amplitude-shaped laser pulse. Based on the relation $\omega_{\text{as-hole}} = \delta + \Omega_{\mathrm{R}}$, it is easy to verify that the two holes are related to the two Raman levels of the pyridine. Therefore, by observing the two holes in the CARS spectrum, a high-resolution CARS spectrum can be obtained—this result is similar to that obtained by spectral notch shaping in single-pulse CARS [18], whereas it is different from that obtained by π phase modulation in three-pulse CARS [13], where the CARS spectrum is greatly narrowed.

The high spectral resolution of the Raman levels can also be obtained by shifting the rectangular amplitude step position

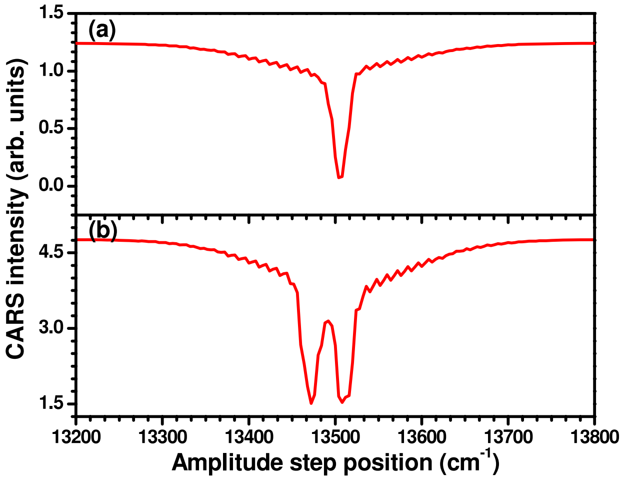

Figure 5. CARS intensity at a frequency $\omega_{as} = 14\,500$ cm^{-1} in benzene (a) and pyridine (b) as a function of the amplitude step position δ for an amplitude modulation width $\Delta = 20$ cm^{-1}.

and measuring the CARS intensity at a given frequency. Figure 5 presents the CARS intensity at a frequency $\omega_{as} = 14\,500$ cm^{-1} in benzene (a) and pyridine (b) as a function of the amplitude step position δ for an amplitude modulation width $\Delta = 20$ cm^{-1}. As can be seen, one hole at an amplitude step position $\Delta = 13\,508$ cm^{-1} is observed in benzene, while two distinct holes at amplitude step positions $\delta = 13\,512$ and $13\,472$ cm^{-1} are observed in pyridine. By the relation $\omega_{\text{as-hole}} = \delta + \Omega_R$, the Raman resonant frequencies can be calculated as $\Omega_R = 992$ cm^{-1} in benzene and $\Omega_R = 988$ and 1028 cm^{-1} in pyridine—in agreement with the known Raman resonant frequencies of benzene and pyridine mentioned above.

In conclusion, we have theoretically demonstrated that two-pulse CARS spectra can be modulated by shaping both the pump and probe pulses using rectangular amplitude modulation. It was shown that amplitude-shaped laser pulses can induce a narrowband hole in the CARS spectrum, the position of which is correlated with the Raman resonant frequency of the molecule. It was also shown that a high-resolution CARS spectrum and an energy-level diagram of the molecule can be obtained by observing the holes in the CARS spectrum. We believe that these theoretical results appear promising for applications in microscopic investigations into complex molecular structures and various related fields.

Acknowledgments

This work was partly supported by National Natural Science Fund (Nos 11004060, 11027403 and 51132004), and Shanghai Rising-Star Program (No. 12QA1400900).

References

[1] Schrader B 1995 *Infrared and Raman Spectroscopy* (Weinheim: VCH)
[2] Dudovich N, Oron D and Silberberg Y 2002 *Nature* **418** 512
[3] Tran H, Joubert P and Bonamy L 2005 *J. Chem. Phys.* **122** 194317
[4] Shigeto S and Hamaguchi H 2006 *Chem. Phys. Lett.* **417** 149
[5] Stampanoni-Panariello A, Hemmerling B and Hubschmid W 1998 *Appl. Phys.* B **67** 125
[6] Schenk M, Thumann A, Seeger T and Leipertz A 1998 *Appl. Opt.* **37** 5659
[7] Cheng J, Volkmer A and Xie X S 2002 *J. Opt. Soc.* B **19** 1363
[8] Evans L and Xie S X 2009 *Annu. Rev. Anal. Chem.* **1** 883
[9] Volkmer A 2005 *J. Phys. D: Appl. Phys.* **35** R59
[10] Katz O, Natan A and Silberberg Y 2008 *Appl. Phys. Lett.* **92** 171116
[11] Li H, Harris D A, Xu B, Wrzesinki P J, Lozovoy V V and Dantus M 2009 *Appl. Opt.* **48** B17
[12] Weiner A M 2000 *Rev. Sci. Instrum.* **71** 1929
[13] Oron D, Dudovich N, Yelin D and Silberberg Y 2002 *Phys. Rev. Lett.* **88** 063004
[14] Oron D, Dudovich N, Yelin D and Silberberg Y 2002 *Phys. Rev.* A **65** 043408
[15] Oron D, Dudovich N and Silberberg Y 2002 *Phys. Rev. Lett.* **89** 273001
[16] Frostig H, Katz O, Natan A and Silberberg Y 2011 *Opt. Lett.* **36** 1248
[17] Oron D, Dudovich N and Silberberg Y 2003 *Phys. Rev. Lett.* **90** 213902
[18] Katz O, Levitt J M, Grinvald E and Silberberg Y 2010 *Opt. Express* **18** 22693
[19] Zhang S, Zhang L, Zhang X, Ding L, Chen G, Sun Z and Wang Z 2007 *Chem. Phys. Lett.* **433** 416
[20] Zhang S, Zhang H, Jia T, Wang Z and Sun Z 2010 *J. Chem. Phys.* **132** 044505