Background-free coherent anti-Stokes Raman spectroscopy near transverse interfaces: a vectorial study

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A full-vectorial theoretical investigation of the recently proposed background-free coherent anti-Stokes Raman scattering (CARS) spectroscopy near transverse interfaces (Phys. Rev. A, 77, 061802(R) (2008)) is presented. In this scheme, the field symmetries of the focused excitation beams are applied to recover the pure Raman spectrum of a medium forming a transverse interface with a nonresonant medium. We show that this method is robust to spatial shift of the excitation volume relative to the interface and does not depend on the linear polarizations states of the pump and Stokes beams. Finally, we extend the applicability of this scheme to a succession of planar interfaces between resonant and nonresonant media, which is potentially interesting for fast chemical analysis in microfluidic devices. Interestingly, this method can be extended to nondegenerated resonant four-wave-mixing processes to remove the nonresonant background. © 2008 Optical Society of America

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1. INTRODUCTION

Coherent anti-Stokes Raman scattering (CARS) has proved over the past four decades to be a powerful spectroscopic tool to study rotational and vibrational structures in materials [1–4]. In brief, CARS is a nonlinear optical process in which two frequency-shifted beams interact in a medium to give rise to the so-called anti-Stokes signal. This signal is enhanced when the frequency difference of the two incoming beams coincides with a rotational or vibrational frequency of the medium. The CARS process can be described in terms of the third-order nonlinear tensor $\chi^{(3)}$ and gives access to the same kind of information that can usually be extracted from spontaneous Raman spectroscopy. CARS spectroscopy has several advantages over spontaneous Raman spectroscopy. On the one hand, due to the coherent nature of the CARS process, it is far more efficient than spontaneous Raman spectroscopy. On the other hand, as the signal is blue-shifted as compared to the excitation, it is insensitive to parasite linear fluorescence. Nonetheless, it is not a background-free technique as the vibrational signal coherently mixes with the instantaneous electronic response of the investigated material [5]. In particular, when the electronic background is strong, it can overwhelm the resonant signal. Several techniques have been proposed in the 1970’s to overcome this problem. Polarization-CARS [6–8] (P-CARS) or time-resolved-CARS [9] (T-CARS) techniques are valuable tools to remove the background. Nonetheless, a large amount of vibrational signal is usually lost. Another solution is to coherently mix the arising CARS signal with another beam at the same frequency [10]. This so-called heterodyne technique allows the recovery of the real and imaginary parts of the $\chi^{(3)}$ tensor but at the price of a somewhat complicated set-up. The introduction of femtosecond laser in CARS spectroscopy gave rise to several specific approaches to overcome the nonresonant background such as time-resolved [11,12] or phase-shaping-based techniques [13–15]. Nonetheless, all these schemes also require instrumental complexity.

More recently, the introduction of the collinear excitation scheme by Zumbusch et al. [16] has opened the way to CARS microscopy. In this configuration, the pump and Stokes beams are focused through a common microscope objective. To obtain background-free images, P-CARS [17], T-CARS [18], or heterodyne [19,20] techniques were transposed to microscopy. In the collinear excitation scheme, depending on the object size, an epi-detection scheme (E-CARS) [21] can be efficiently set up to remove the nonresonant background from the environment of the object. Nonetheless, this scheme is unable to remove the intrinsic background of the imaged object itself. Recently, the background-free CARS microscopy revival has derived benefit from the properties of focused beams as highlighted by Krishnamachari et al. in order to improve the contrast of lateral and axial interfaces between two resonant and nonresonant media [22–24]. In the reported schemes, the improvement in the contrast arises from the introduction of high-order Hermite–Gauss beams. Using conventional focused excitation, our group has recently...
reported the theoretical and experimental demonstration of background-free CARS spectroscopy near transverse interfaces [25]. Our scheme takes advantage of the inherent symmetry properties of focused fields to remove the nonresonant background of the investigated medium. To do so, the resonant medium has to make a planar transverse interface with a purely nonresonant medium.

The background-free spectra of the resonant medium is thus achieved by the subtraction of two CARS spectra near the interface where the role of the two (resonant and nonresonant) media is spatially reversed.

This paper is devoted to the detailed theoretical study of background-free CARS spectroscopy near transverse interfaces under focused beam excitation. Our goal is to make precise and to extend the concepts and methods presented in [25]. To do so, we implement a full-vectorial analysis of the far-field CARS signal generated in the vicinity of a transverse interface between resonant and nonresonant media. The nonlinearly induced dipole-based polarization. In Section 6, we introduce the symmetry of the electric field and the nonlinear induced polarization. In particular, we show how the Gouy phase anomaly that affects the focused exciting beams is transferred to the nonlinear induced polarization. In Section 5, we describe the two studied configurations for the two media that form a unique transverse interface. For each of them, we give analytical expressions of the generated anti-Stokes fields and intensities. In Section 6, we introduce the symmetries found in Section 4 on the nonlinear induced polarization into the expression of the anti-Stokes intensities generated near the interface to show how the subtraction of the two signals leads to background-free CARS spectra. The influence of different parameters, such as the excitation spatial shift or the Raman depolarization ratio of the resonant medium on the recovered spectra, is discussed. In Section 7, we extend our analysis to the case of two successive transverse interfaces. Finally, in Section 8, we discuss our results in the context of CARS spectroscopy and give a brief summary of this work.

2. DESCRIPTION OF THE NONLINEAR MEDIUM

CARS is a third-order nonlinear process and is thus governed by the medium, $\chi^{(3)}$ tensor, which is the superposition of a vibrational resonant term $\chi^{(3)}_{R}$ and an electronic nonresonant term $\chi^{(3)}_{NR}$ [28] following

$$
\chi^{(3)} = \chi^{(3)}_{R} + \chi^{(3)}_{NR}.
$$

In a homogeneous isotropic medium in which only two-photon vibrational transitions are allowed, the components of the $\chi^{(3)}$ tensor resonant and nonresonant parts write [26]

$$
\chi^{(3)R}_{ijkl} = \chi^{(3)R}_{xxyy} \left( \delta_{i} \delta_{k} + \delta_{j} \delta_{l} \right),
$$

$$
\chi^{(3)NR}_{ijkl} = \chi^{(3)NR}_{xxyy} \left( \delta_{i} \delta_{k} + \delta_{j} \delta_{l} \right),
$$

where $\rho_{R}$ is the Raman depolarization ratio of the probed Raman line and $\delta_{i}$ is the Kronecker delta function. Because the nonresonant part of the tensor follows the Kleinman symmetry rule [29], an equivalent Raman depolarization ratio equaling 1/3 has been introduced in Eq. (3). According to the two former equations, only the $\chi^{(3)}_{ijkl}$ components that possess two pairs of identical indices do not vanish. At the point r of the medium, the two pump and Stokes incident fields (at respective angular frequencies $\omega_{p}$ and $\omega_{s}$) induce an oscillating nonlinear polarization (at angular frequency $\omega_{as}$) given by

$$
P^{(3)}(r, -\omega_{as}) = \chi^{(3)}(r; -\omega_{as}, \omega_{p}, \omega_{p}, -\omega_{as})
\times E_{p}(r, \omega_{as}) E_{p}(r, \omega_{as}) E_{s}^{*}(r, -\omega_{as}).
$$

Taking into account the pump field frequency-degeneracy and omitting angular frequency arguments $\omega_{p}$, $\omega_{s}$, and $\omega_{as}$, the ith component ($i=x, y, z$) $P^{(3)}_{i}(r)$ of the nonlinear polarization induced at point r can be expressed as

$$
P^{(3)}_{i}(r) = 3 \sum_{j,k,l} \chi^{(3)E}_{ijkl} E_{p}^{*}(r) E_{p}(r) E_{s}^{*}(r),
$$

where the subscripts $j, k, l$ run over $x, y, z$. The tensorial component $\chi^{(3)}_{ij}$(3) is the superposition of the resonant and nonresonant tensorial components $\chi^{(3)R}_{ij}$ and $\chi^{(3)NR}_{ij}$ expressed in Eqs. (2) and (3). In the same way, we can split the induced nonlinear polarization into two resonant and nonresonant parts following

$$
P^{(3)}_{R}(r) = P^{(3)}_{R}(r) + P^{(3)}_{NR}(r).
$$

The combination of Eqs. (2), (3), and (5) leads to

$$
P^{(3)}_{R}(r) = \rho_{R} \chi^{(3)R}_{xxyy} S(r, \rho_{R}),
$$

$$
P^{(3)}_{NR}(r) = \chi^{(3)NR}_{xxyy} S(r, 1/3),
$$

where the $S$ parameter, which depends on the pump and Stokes fields and the Raman depolarization ratio, is defined by

$$
S(r, \rho_{R}) = [E_{p}(r) \cdot E_{s}^{*}(r)] E_{p}(r)
+ \frac{\rho_{R}}{1 - \rho_{R}} [E_{p}^{2}(r) + E_{s}^{2}(r) + E_{p}^{2}(r)] E_{s}^{*}(r),
$$

$$
S(r, 1/3) = [E_{p}(r) \cdot E_{s}^{*}(r)] E_{p}(r)
+ \frac{1}{2} [E_{p}^{2}(r) + E_{p}^{2}(r) + E_{p}^{2}(r)] E_{s}^{*}(r).
$$

The notations $\cdot$ and $*$ stand respectively for the scalar product and the complex conjugation. Thus, the induced nonlinear polarization writes
3. FOCUSED FIELD EXPRESSIONS

Most CARS microscopes are now operated under a collinear excitation scheme [16], in which pump and Stokes exciting beams are focused through a common microscope objective. In order to study the spatial properties of the induced nonlinear polarization [given by Eq. (11)], the expressions of the pump and the Stokes fields near the objective focus have to be established. For weakly focused beams, a paraxial approximation based model can be acceptable. However, for tightly focused beams, as often met in microscopy, this approximation breaks and a rigorous vectorial analysis becomes necessary [30].

In order to establish the vectorial excitation field expression, let us start just before the focusing objective according to Fig. 1(a). We consider an incident monochromatic collimated beam that propagates in air along the optical axis (Oz). It is defined by its wave vector amplitude \( k_0 \). A Gaussian profile, characterized by its half-width (at 1/e) \( \sigma \), is assumed. The incident field \( E \) is supposed linearly polarized in a direction of the (xy) plane that makes an angle \( \alpha \) with the \( x \) axis [Fig. 1(b)]. This beam is focused through a microscope objective (aberration free) in a medium of refractive index \( n \). The microscope objective is defined by its focal length \( f' \), its numerical aperture \( NA \) and its back focal plane radius \( r_0 \).

In order to establish the vectorial excitation field expression [30], we write an expression for the complex amplitude \( E_0 \) of the incident Gaussian beam [32], which is focused at point \( M(r) \) [Fig. 1(c)].

\[
E_0 = k_0 \frac{1}{2\pi} \exp \left( -ik_0 \rho M \right)
\]

where \( k_0 \) is the wave number of the incident beam and \( \rho M \) is the distance between \( r \) and \( M(r) \).

The electric field seen by the point \( M \) in the object space, \( \theta \) is the angle between the optical axis and the refracted ray that originates from the elementary ray considered in the object space [see Fig. 1(a)]. Following the analysis made by Novotny and Hecht [32], the electric field seen by the point \( M(p \rho M, \varphi M, z) \) [see Fig. 1(c)] in the vicinity of the focus is expressed in cylindrical coordinates (where the origin is defined by the point \( F' \)) by

\[
E_x(p \rho M, \varphi M, z) = \cos(\varphi M)I_0(p \rho M, z) + \cos(2\varphi M)I_2(p \rho M, z)
+ \sin(\varphi M)\sin(2\varphi M)\frac{\rho M}{z}
\]

\[
E_y(p \rho M, \varphi M, z) = \cos(\varphi M)\sin(2\varphi M)\frac{\rho M}{z}
\]

\[
E_z(p \rho M, \varphi M, z) = \cos(\varphi M)I_1(p \rho M, z)
\]

In these equations, the integral factors \( I_0, I_1, \) and \( I_2 \) are defined by

\[
I_0(p \rho M, z) = \int_0^{\theta_{\text{max}}} A(\theta)\sin(\theta)[1 + \cos(\theta)]J_0([k \rho M \sin(\theta)]\frac{\rho M}{z})d\theta
\]

\[
I_1(p \rho M, z) = \int_0^{\theta_{\text{max}}} A(\theta)\sin^2(\theta)J_1([k \rho M \sin(\theta)]\frac{\rho M}{z})d\theta
\]

\[
I_2(p \rho M, z) = \int_0^{\theta_{\text{max}}} A(\theta)\sin(\theta)[1 - \cos(\theta)]J_2([k \rho M \sin(\theta)]\frac{\rho M}{z})d\theta
\]

where \( \theta_{\text{max}} = \arcsin(\text{NA}/n) \) and \( J_0, J_1, \) and \( J_2 \) are respectively the zero-th, first- and second-order Bessel functions. Compared to the analysis of Novotny and Hecht, we have introduced the angle \( \alpha \) between the polarization of the incident beam and the \( x \) axis.

Fig. 1. Gaussian beam focusing through a microscope objective. (a) \( f \), objective focal length; \( F' \), objective focus; \( r_0 \), microscope objective's back aperture; \( \theta_{\text{max}} \), focusing maximal angle; \( \theta \), focusing angle of an elementary ray; \( \sigma \), Gaussian profile half-width (at 1/e); \( E_0 \), amplitude of the incoming beam. (b) \( \alpha \), field polarization direction in the object space. (c) Cylindrical coordinates system adopted to define the position of a point \( M(r)=M(p \rho M, \varphi M, z) \) near the microscope objective focus \( F' \).
4. SYMMETRY RELATIONS ON THE FOCUSED FIELDS AND THE NONLINEAR INDUCED POLARIZATION

The examination of Eqs. (13)–(18) leads to interesting conclusions regarding the focused field. The field’s \( x, y \) and \( z \) components exhibit symmetries that are summarized in Table 1. The \( E_x \) and \( E_y \) components are unchanged by a \( \pi \)-rotation around the \( z \) axis. This rotation can be also seen as successive variable changes \((x \rightarrow -x, y \rightarrow -y)\). Nonetheless, they experience a phase anomaly as \( E_x(x,y,z)=E_y(x,y,z) \) and \( E_y(x,y,z)=-E_x(x,y,z) \) by symmetry around the \((z=0)\) plane [33]. This so-called Gouy phase anomaly [34,35], is well known in coherent nonlinear microscopy. It explains, for instance, why no third-harmonic generation (THG) signal is generated when the exciting laser is focused in a bulk medium [36,37]. In the case of the \( E_z \) component, the \( \pi \)-rotation around the \( z \) axis leads to sign inversion, but it experiences no phase anomaly by symmetry around the \((z=0)\) plane as \( E_z(x,y,z)=E_z(x,y,z) \). All these symmetry relations lead to the vectorial relation

\[
E(-\mathbf{r}) = -E'\mathbf{(r)} \tag{19}
\]

that can be seen as a vectorial writing of the Gouy phase anomaly. In a collinear geometry, the pump and Stokes fields are focused so that they verify Eq. (19) [38]. The resonant and nonresonant parts of the induced nonlinear polarization are given by Eqs. (9) and (10). Reporting Eq. (19) in this set of equations leads to the relations

\[
S(-\mathbf{r}, \rho_\|) = -S'\mathbf{(r, \rho_\|)}, \tag{20}
\]

\[
S(-\mathbf{r}, 1/3) = -S'\mathbf{(r, 1/3)}. \tag{21}
\]

Therefore, the induced nonlinear polarization also experiences the Gouy phase anomaly. This relation is independent of the pump and Stokes incident polarization. In particular, an angle can be introduced between them.

5. ANTI-STOKES FAR-FIELD GENERATED NEAR TRANSVERSE INTERFACES

A. Description of the Two Transverse Interfaces

We are interested in CARS emission near a transverse interface that separates two resonant and nonresonant media (media 1 and 2). Their respective tensors, \( \chi^{(3)}_{1R} \) and \( \chi^{(3)}_{2NR} \), write as a function of their resonant and nonresonant components.

<table>
<thead>
<tr>
<th>Table 1. Symmetry Relations on the Focused Field Components 𝑎</th>
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<tbody>
<tr>
<td>( \phi_{\text{off}} \rightarrow \phi_{\text{off}} + \pi )</td>
</tr>
<tr>
<td>( E_x(-x,-y,z)=E_x(x,y,z) )</td>
</tr>
<tr>
<td>( E_y(-x,-y,z)=E_y(x,y,z) )</td>
</tr>
<tr>
<td>( E_z(-x,-y,z)=-E_z'(x,y,z) )</td>
</tr>
</tbody>
</table>

\( \psi_{\text{off}} \) is the rotation of a \( \psi \)-angle in the \((xy)\) plane corresponds to the changes on variables \((x \rightarrow -x, y \rightarrow -y)\).

In these two relations, \( \chi^{(3)}_{1R} \) is a complex tensor, and \( \chi^{(3)}_{1NR} \) and \( \chi^{(3)}_{2NR} \) are real. The excitation volume defines the \((z=0)\) plane as shown in Fig. 2(a). We are interested in the two symmetrical configurations shown in Figs. 2(b) and 2(c). Following the configuration, the media 1 lie in the upper (b) or lower (c) half-space, and the interface between the two media is found at \((z=z_0)\) or \((z=-z_0)\). These two configurations are respectively related to \( \alpha \) and \( \beta \)-problems. They are symmetrical by the \((z=0)\) plane. Through this paper, we will make two important assumptions. First, the refractive index of each medium is constant for pump, Stokes, and anti-Stokes frequencies. Second, the two media have the same refractive index.

According to Cheng et al. [39], the anti-Stokes far-field emitted in the \( \mathbf{k} \) direction by the induced nonlinear polarization \( \mathbf{P}^{(3)} \) located at position \( \mathbf{r} \) can be related to a real matrix \( \mathbf{M} \) that only depends on the \( \mathbf{k} \) direction. The vector \( \mathbf{k} \) can be indifferently orientated in the forward or epi direction. The anti-Stokes far-field emitted in the \( \mathbf{k} \) direction near a transverse interface is given by

\[
E_{\text{off}}^m(\mathbf{k}) = \int \int \int M(\mathbf{k})P^{(3),m}(\mathbf{r}) \exp(i\mathbf{k} \cdot \mathbf{r}) \, d\mathbf{r}, \tag{23}
\]

where the superscript \( m \) refers to \( \alpha \) or \( \beta \) following the problem we deal with. The far-field anti-Stokes intensity generated in the \( \mathbf{k} \) direction thus writes

\[
I_{\text{off}}^m(\mathbf{k}) = |E_{\text{off}}^m(\mathbf{k})|^2 = E_{\text{off}}^m(\mathbf{k}) \cdot E_{\text{off}}^m(\mathbf{k}). \tag{24}
\]

B. Application to the \( \alpha \)-Problem

In the case of the \( \alpha \)-problem, Eq. (23) becomes

Fig. 2. Scheme of the studied configuration. (a) Excitation volume. The focal plane defines the \((z=0)\) plane. (b) \( \alpha \)-problem: the resonant medium 1 lies above the nonresonant medium 2, and the position of their common interface is \( z_0 \). (c) \( \beta \)-problem: the resonant medium 1 lies below the nonresonant medium 2, and the position of their common interface is \( -z_0 \).
The anti-Stokes intensity generated in the \( \mathbf{k} \) direction is the summation over pure contributions from the resonant and nonresonant parts of media 1 and 2, and cross terms between these contributions.

### C. Application to the \( \beta \)-Problem

In the same way, we express the anti-Stokes field generated in the \( \mathbf{k} \) direction for the \( \beta \)-problem following

\[
E_{\text{as}}^\beta(\mathbf{k}) = \int_{z=-\infty}^{z=+\infty} \int_{x=-\infty}^{x=+\infty} \int_{y=-\infty}^{y=+\infty} M(\mathbf{k}) \mathbf{P}_{1}^{(3),\beta}(\mathbf{r}) \exp(i \mathbf{k} \cdot \mathbf{r}) \, d\mathbf{r}.
\]

The relative position of media 1 and 2 is now reversed relative to the \( \alpha \)-problem, and Eq. (30) writes

\[
E_{\text{as}}^\beta(\mathbf{k}) = \int_{z=-\infty}^{z=+\infty} \int_{x=-\infty}^{x=+\infty} \int_{y=-\infty}^{y=+\infty} M(\mathbf{k}) \mathbf{P}_{2}^{(3)}(\mathbf{r}) \exp(i \mathbf{k} \cdot \mathbf{r}) \, d\mathbf{r}.
\]

and similarly to Eq. (27), we can write

\[
E_{\text{as}}^\beta(\mathbf{k}) = 6 \left[ \chi^{(3)NR}_{xyy} I_{e_2}^{(z_0)}(p_R) + \chi^{(3)NR}_{xyy} I_{e_2}^{(1/3)} + \chi^{(3)NR}_{xxxy} I_{e_2}^{(1/3)} \right].
\]

Using condensed notations on integrals, we can express the anti-Stokes far-field intensity generated in the \( \mathbf{k} \) direction following

\[
I_{\text{as}}^\beta(\mathbf{k}) = 36 \left[ \chi^{(3)NR}_{xyy} | I_{e_2}^{(z_0)}(p_R) |^2 + 2 \chi^{(3)NR}_{xyy} \text{Re}[\chi^{(3)NR}_{xyy} I_{e_2}^{(z_0)}(p_R) \cdot I_{e_2}^{(z_0)}(1/3)] + \chi^{(3)NR}_{xxxy} | I_{e_2}^{(z_0)}(1/3) |^2 + 2 \chi^{(3)NR}_{xxxy} \text{Re}[\chi^{(3)NR}_{xyy} I_{e_2}^{(z_0)}(p_R) \cdot I_{e_2}^{(z_0)}(1/3)] \right].
\]
6. SUBTRACTION OF SIGNALS GENERATED NEAR THE INTERFACE

A. Symmetries on the Integral Expressions

It is interesting to note that the symmetries on the S vector expressed by Eqs. (20) and (21) lead to the following properties on the I integrals:

\[ \Gamma_{\text{up}}^{\text{low}}(\rho_R) = -\Gamma_{\text{up}}^{\text{low}}(\rho_R), \]  
(34)

\[ \Gamma_{\text{up}}(1/3) = -\Gamma_{\text{up}}^{\text{low}}(1/3). \]  
(35)

To obtain these properties, it is necessary to (i) make the change of variable \( r \rightarrow -r \), (ii) permute the lower and upper limits on integration domains over \( x, y, \) and \( z \), (iii) introduce Eqs. (20) and (21), and (iv) use properties of conjugation regarding product and integration. The introduction of Eqs. (34) and (35) into Eq. (33) leads to

\[ I_{\beta}^0(k) = 36[(31NR)_{\chi_{\text{xyxy}}} \cdot \Gamma_{\text{xyxy}}^{\text{up}}(\rho_R)]^2 \]

\[ + 2(31NR)_{\chi_{\text{xyxy}}} \cdot \Re(\chi_{\text{xyxy}}^{\text{up}}(\rho_R) \cdot \Gamma_{\text{xyxy}}^{\text{low}}(1/3)) \]

\[ + (31NR)_{\chi_{\text{xyxy}}} \cdot \Gamma_{\text{xyxy}}^{\text{up}}(1/3)) \]

\[ + 2(32NR)_{\chi_{\text{xyxy}}} \cdot \Re(\chi_{\text{xyxy}}^{\text{up}}(\rho_R) \cdot \Gamma_{\text{xyxy}}^{\text{low}}(1/3)) \]

\[ + (32NR)_{\chi_{\text{xyxy}}} \cdot \Gamma_{\text{xyxy}}^{\text{up}}(1/3)) \]

\[ + 2(31NR)_{\chi_{\text{xyxy}}} \cdot \Re(\chi_{\text{xyxy}}^{\text{up}}(1/3) \cdot \Gamma_{\text{xyxy}}^{\text{low}}(1/3))]. \]  
(36)

In this way, the anti-Stokes far-field intensity generated in the \( k \) direction for the \( \beta \)-problem explicitly depends on the same vectorial integrals as for the \( \alpha \)-problem.

B. Expression of the Intensity Difference

We can now subtract Eq. (29) from Eq. (36) to obtain the difference between the anti-Stokes far-field intensities generated in the \( k \) direction for the \( \beta \) and \( \alpha \) problems as follows

\[ \Delta I_{\beta}(k) = I_{\beta}^0(k) - I_{\alpha}^0(k), \]

\[ \Delta I_{\alpha}(k) = 72[(31NR)_{\chi_{\text{xyxy}}} \cdot \Re(\chi_{\text{xyxy}}^{\text{up}}(\rho_R) \cdot \Gamma_{\text{xyxy}}^{\text{low}}(1/3) - \Gamma_{\text{xyxy}}^{\text{low}}(\rho_R)) \]

\[ \cdot \Gamma_{\text{xyxy}}^{\text{up}}(1/3))] + (32NR)_{\chi_{\text{xyxy}}} \Re(\chi_{\text{xyxy}}^{\text{up}}(\rho_R) \cdot \Gamma_{\text{xyxy}}^{\text{low}}(1/3)) \]

\[ - \Gamma_{\text{xyxy}}^{\text{up}}(\rho_R) \cdot \Gamma_{\text{xyxy}}^{\text{low}}(1/3)) \]

\[ + (31NR)_{\chi_{\text{xyxy}}} \cdot \chi_{\text{xyxy}}^{\text{up}} \cdot \Re(\chi_{\text{xyxy}}^{\text{up}}(1/3) \cdot \Gamma_{\text{xyxy}}^{\text{low}}(1/3)) \]

\[ - \Gamma_{\text{xyxy}}^{\text{up}}(1/3) \cdot \Gamma_{\text{xyxy}}^{\text{low}}(1/3)]. \]  
(37)

This difference is the sum over three terms \( T_1, T_2, \) and \( T_3 \) to which we refer following their order of appearance. Some basic operations on these three terms lead to

\[ T_1 = -2(31NR)_{\chi_{\text{xyxy}}} \cdot \Im(\chi_{\text{xyxy}}^{\text{up}}(1/3) \cdot \Gamma_{\text{xyxy}}^{\text{low}}(\rho_R)) \]  
(38)

\[ T_2 = -2(32NR)_{\chi_{\text{xyxy}}} \cdot \Im(\chi_{\text{xyxy}}^{\text{up}}(1/3) \cdot \Gamma_{\text{xyxy}}^{\text{low}}(\rho_R)) \]  
(39)

\[ T_3 = 0. \]  
(40)

The intensity difference can be thus rewritten under the expression

\[ \Delta I_{\beta}(k) = -144(F_1(k,z_0,\rho_R)\chi_{\text{xyxy}}^{(3)NR}) \]

\[ + F_2(k,z_0,\rho_R)\chi_{\text{xyxy}}^{(3)2NR}) \cdot \Im(\chi_{\text{xyxy}}^{(3)})], \]  
(41)

with

\[ F_1(k,z_0,\rho_R) = \Im(\Gamma_{\text{xyxy}}^{\text{up}}(1/3) \cdot \Gamma_{\text{xyxy}}^{\text{low}}(\rho_R)), \]  
(42)

\[ F_2(k,z_0,\rho_R) = \Im(\Gamma_{\text{xyxy}}^{\text{up}}(1/3) \cdot \Gamma_{\text{xyxy}}^{\text{low}}(\rho_R)). \]  
(43)

This expression exhibits two important features. First, it is proportional to the imaginary part of \( \chi_{\text{xyxy}}^{(3)1R} \), which is known to be the pure Raman spectrum of medium 1 [40]. Second, it is also proportional to a linear combination of nonresonant terms \( \chi_{\text{xyxy}}^{(3)NR} \) and \( \chi_{\text{xyxy}}^{(3)2NR} \). In an experimental configuration, the total signal arises from the integration of the signal generated in all the \( k \) directions contained in the cone of detection. As a consequence, this signal subtraction recovers the pure Raman spectrum of medium 1. Furthermore, this spectrum is heterodyned with the nonresonant backgrounds arising from media 1 and 2 [41]. This is of fundamental interest when trying to recover weak Raman lines. In principle, the signal subtraction can be implemented in both forward and epi detection schemes. In practice, the epi-detected signal near a transverse interface is mostly a forward-reflected CARS signal [42,43]. It is thus most convenient to operate with a forward detection scheme.

C. Signal Difference With a Centered Excitation

We simply illustrate this property of transverse interfaces in Fig. 3. We plot in Fig. 3(a) the CARS signals generated on an interface for a single Raman line when the excitation is centered on the interface (\( z_0 = 0 \)) and the incident pump and Stokes beams are linearly polarized in the same direction (as will always be the case throughout this paper). For reference, we add the bulk CARS spectrum of the resonant medium (dashed curves). Off-resonance, the signals generated for the \( \alpha \) - and \( \beta \)-problems (black and gray circles) are similar. When the resonance is approached, a splitting between signals occurs. The signal difference (black dots) and the imaginary part of medium 1 (black curve) can be perfectly superimposed. To illustrate the influence of the nonresonant parts of the tensor associated with media 1 and 2 on the recovered spectrum, we plot in Fig. 3(b) the CARS signal difference for several values of the nonresonant medium tensor element \( \chi_{\text{xyxy}}^{(3)2NR} \). For easy meaning, the computation was carried out for the particular case where the Raman depolarization ratio \( \rho_R \) equals 1/3 so that the \( F_1 \) term vanishes. In this configuration the curves scale simply with the \( \chi_{\text{xyxy}}^{(3)2NR} \) value as predicted by Eq. (41).

For any different value of \( \rho_R \), the influence of the \( F_1 \) term must be discussed. In Fig. 4, the recovered Raman spectrum peak is plotted as a function of \( \chi_{\text{xyxy}}^{(3)2NR}/\chi_{\text{xyxy}}^{(3)1R} \) for three different values of \( \rho_R \) (0, 1/3, and 0.75). These values are respectively associated with totally polarized,
mildly polarized, and depolarized Raman lines [44]. For the totally polarized (black circles) and depolarized (gray dots) Raman lines, the recovered Raman spectrum peaks can be fitted as linear functions of $\chi_{\text{xyxy}}^{(3)\text{NR}}/\chi_{\text{xyxy}}^{(3)\text{R}}$. In the considered configuration (pump and Stokes incident beams linearly polarized and parallel), this study proves the weakness of the $F_1$ term (as compared to the $F_2$ term). It is not so surprising as in this case the Raman depolarization ratio only modifies the relatively small $z$ component of the nonlinear induced polarization [26]. If this $z$ component is neglected, the induced nonlinear polarization no longer depends on this ratio and the $F_1$ term systematically vanishes. In the more general case where an angle is introduced between the incident pump and Stokes beams (as in a P-CARS scheme [17] for instance), it must be rediscussed carefully as the Raman depolarization ratio discriminates the resonant and nonresonant induced nonlinear polarizations behaviors.

D. Influence of the Excitation Spatial Shift

We now turn to the influence of the excitation spatial shift $z_0$ on the recovered Raman spectrum. We plot in Fig. 5 the signals obtained for the $\alpha$ and $\beta$ problems when the lasers are focused in (a) the resonant or (b) nonresonant medium. Regarding the medium into which the lasers are focused, the signals mostly exhibit (a) the vibrational resonance or (b) a strong nonresonant background. In every case, the signal difference $\Delta I_{\text{as}}$ recovers the pure Raman spectrum of medium 1. Nonetheless, the $\Delta I_{\text{as}}$ amplitude depends strongly on the excitation volume shift $z_0$. As shown on the Fig. 5(c), the recovered spectrum is maximal when the excitation is centered on the interface. Moreover, for a shift of $z_0$ or $-z_0$, we find the same amplitude for the recovered spectrum. Once again, these curves are plotted assuming a Raman depolarization ratio that equals 1/3. In this particular case, the $F_1$ term vanishes as seen previously, and invoking Eqs. (34) and (35), it is very easy to verify that

$$F_2(k, z_0, 1/3) = F_2(k, -z_0, 1/3).$$

It is interesting to see whether, for any value of $\rho_R$, the recovered spectra have the same amplitude for opposite shifts $z_0$ and $-z_0$. In this purpose, we plot in Fig. 6 the recovered Raman spectra when the excitation is shifted of $-500 \text{ nm}$ and $500 \text{ nm}$ from the interface for the values of $\rho_R$ considered in Fig. 4. As a notable feature, the difference between spectra for opposite shifts is very low when $\rho_R$ is different from 1/3. This is the evidence that $F_1(k, z_0, \rho_R) \approx 0$ and $F_2(k, z_0, \rho_R) \approx F_2(k, -z_0, \rho_R)$.

7. CASE OF TWO CONSECUTIVE TRANSVERSE INTERFACES

In the previous sections, we have seen that it is possible to recover the pure Raman spectrum of a resonant medium when it forms a plane transverse interface with a nonresonant medium. We will show in this section that this approach can be extended to a succession of planar transverse interfaces between resonant and nonresonant media. The nonresonant media can be chosen as desired, but only one kind of resonant medium is recommended. If not, extra terms that couple resonances from distinct media are introduced in the signal difference. We should point out that our scheme works if one is able to reverse...
the system formed by the different media. This operation is possible if one works with symmetrical stratified media. In this case, spatially shifting the excitation volume along the optical axis allows to switch between the $\alpha$- and $\beta$-problems, as we demonstrated in [25]. We focus here on the case where a resonant medium is embedded between two identical nonresonant media (Fig. 7). This situation can be, for instance, found in a microfluidic device where a liquid or a gas flows in a glass or polymer planar channel.

The resonant medium now has a finite width $\varepsilon_{0}$. Similar to the previous study, the excitation is spatially shifted of $z_{1}$ from the lower interface and $z_{2}=z_{1}+\varepsilon_{0}$ from the upper interfaces in the $\alpha$-problem, and respectively of $-z_{2}$ and $-z_{1}$ in the $\beta$-problem, as shown in Figs. 7(b) and 7(c). The anti-Stokes far-field generated in the $\alpha$-problem is expressed by

$$
E_{\text{as}}(k) = 6\chi_{xxyy}^{(3)1R}E_{z1}^{2}(\rho_{R}) + \chi_{xxyy}^{(3)NR}E_{z1}^{2}(1/3) + \chi_{xxyy}^{(3)NR}E_{z1}^{-2}(1/3) + \chi_{xxyy}^{(3)NR}E_{z2}^{-2}(1/3).$$

(45)

Due to the presence of three media, this expression now exhibits four terms, and the corresponding anti-Stokes far-field intensity is a sum of eight terms that couple the

Fig. 5. CARS generation near a unique interface. Influence of the excitation volume spatial shift $z_{0}$ to the interface on the signals generated for the $\alpha$ (black circles) and $\beta$-problems (gray circles) and their difference $\Delta l_{\text{as}}$ (black dots); (a) $z_{0}=-500$ nm and (b) $z_{0}=500$ nm. For comparison, the bulk CARS spectrum of medium 1 is plotted (dashed lines). (c) Signal difference for the previous values of the excitation spatial shift $z_{0}$: −500 nm (circles), 0 nm (dots) and 500 nm (crosses). On each graph, $\text{Im}\chi_{1}^{(3)}$ is plotted (solid curve). (d) For information, square of the nonlinear induced polarization (normalized) in a bulk medium for the same focusing parameters. The laser, the excitation and collection objective parameters, and the Raman depolarization ratio are chosen as in Fig. 3.

Fig. 6. CARS generation near a unique interface. CARS signal difference $\Delta I_{\text{as}}=I_{\text{as}}^{0} - I_{\text{as}}^{z_{0}}$ for different values of the excitation volume spatial shift $z_{0}$ as a function of the Raman depolarization ratio $\rho_{R}$ associated with medium 1: (a) $\rho_{R}=0$, (b) $\rho_{R}=1/3$, and (c) $\rho_{R}=0.75$. Circles, $z_{0}=500$ nm; crosses, $z_{0}=−500$ nm. On each graph, $\text{Im}\chi_{xxyy}^{(3)1R}$ is plotted (solid curve).
resonant and nonresonant parts of media 1 and 2 following
\[
I^\alpha_{\text{sa}}(\mathbf{k}) = 36|\chi_{\text{xyy}}^{(3)} Re[\mathbf{\Gamma}_z^{(1)}(\mathbf{p}_R)]|^2 + |\chi_{\text{xyy}}^{(3)} Re[\mathbf{\Gamma}_z^{(2)}(\mathbf{p}_R)]|^2 + 2\chi_{\text{xyy}}^{(3)} Re[\chi_{\text{xyy}}^{(3)} Re[\mathbf{\Gamma}_z^{(1)}(\mathbf{p}_R)]] + |\chi_{\text{xyy}}^{(3)} Re[\mathbf{\Gamma}_z^{(2)}(\mathbf{p}_R)]|^2 + 2\chi_{\text{xyy}}^{(3)} Re[\chi_{\text{xyy}}^{(3)} Re[\mathbf{\Gamma}_z^{(1)}(\mathbf{p}_R)]] + |\chi_{\text{xyy}}^{(3)} Re[\mathbf{\Gamma}_z^{(2)}(\mathbf{p}_R)]|^2 + 2\chi_{\text{xyy}}^{(3)} Re[\chi_{\text{xyy}}^{(3)} Re[\mathbf{\Gamma}_z^{(1)}(\mathbf{p}_R)]]
\]
and the corresponding intensity is given by
\[
I^\beta_{\text{sa}}(\mathbf{k}) = 36|\chi_{\text{xyy}}^{(3)} Re[\mathbf{\Gamma}_z^{(1)}(\mathbf{p}_R)]|^2 + |\chi_{\text{xyy}}^{(3)} Re[\mathbf{\Gamma}_z^{(2)}(\mathbf{p}_R)]|^2 + 2\chi_{\text{xyy}}^{(3)} Re[\chi_{\text{xyy}}^{(3)} Re[\mathbf{\Gamma}_z^{(1)}(\mathbf{p}_R)]] + |\chi_{\text{xyy}}^{(3)} Re[\mathbf{\Gamma}_z^{(2)}(\mathbf{p}_R)]|^2 + 2\chi_{\text{xyy}}^{(3)} Re[\chi_{\text{xyy}}^{(3)} Re[\mathbf{\Gamma}_z^{(1)}(\mathbf{p}_R)]]
\]
Using the symmetry of the integral expressed in Eqs. (34) and (35), the subtraction of Eq. (48) from Eq. (46) leads to
\[
\Delta I_{\text{sa}}(\mathbf{k}) = -144[F_1(\mathbf{k},x_1,z_2,\mathbf{p}_R)\chi_{\text{xyy}}^{(3)NR} + F_2(\mathbf{k},z_1,z_2,\mathbf{p}_R)\chi_{\text{xyy}}^{(3)NR} Im[\chi_{\text{xyy}}^{(3)NR}],
\]
with
\[
F_1(\mathbf{k},x_1,z_2,\mathbf{p}_R) = \text{Im}[\mathbf{\Gamma}_z^{(1)}(\mathbf{p}_R)],
\]
\[
F_2(\mathbf{k},z_1,z_2,\mathbf{p}_R) = \text{Im}[\mathbf{\Gamma}_z^{(2)}(\mathbf{p}_R)] + \mathbf{\Gamma}_z^{(1)}(\mathbf{p}_R)]
\]
We obtain an expression that is similar in its form to Eq. (41). Note the incorporation of a new term in the \(F_2\) expression. The signal difference is proportional to \(\text{Im}[\chi_{\text{xyy}}^{(3)NR}]\) and still gives access to the pure Raman spectrum of medium 1. As previously, the recovered spectrum is heterodyned by the nonresonant signal of medium 2. In Fig. 8, the signals obtained for a 500 nm width layer are plotted. In this case, as shown in the figure, the excitation is centered on the lower interface for the \(\alpha\)-problem and on the upper interface for the \(\beta\)-problem (\(z_1=0 \text{ nm} \) and \(z_2=500 \text{ nm} \)). The signal difference perfectly matches the imaginary part of medium 1. The amplitudes of the recov-
ered Raman spectrum increases with the layer width $e_0$, as shown in Fig. 9(a). This is due only to the need for resonant oscillators to build the Raman signal. Of course, when the layer width is larger than the excitation axial dimension, a saturation of the amplitude is expected (not shown on the figure). Furthermore, the recovered spectrum amplitude is maximal when the excitation volume is centered on the two interfaces ($z_1=0\,\text{nm}$ and $z_2=e_0$), as depicted in Fig. 9(b).

Our method to recover pure Raman spectra is particularly relevant when the layer width is small compared to the axial extension of the excitation volume. Furthermore, only a small excitation spatial shift is required to switch between the $\alpha$- and $\beta$-problems. When the excitation volume is centered on the resonant layer, the obtained CARS spectrum is strongly dominated by the nonresonant background arising from medium 2. Note that in a complementary scheme, for which the nonresonant medium is embedded between two identical resonant media, it is also possible to recover the pure Raman spectrum of the resonant media.

8. CONCLUSION

Through this article, we have theoretically investigated a new background-free coherent-Raman-spectroscopy technique based on the intrinsic properties of focused optical beams. Pure spectra are recovered by subtraction of two signals acquired near the transverse interface between the investigated resonant medium and an adjacent nonresonant medium. The nonresonant medium acts as a local oscillator with which the investigated medium’s Raman spectrum is detected. Furthermore, we have demonstrated that our scheme works for any linear polarization states of the incoming pump and Stokes fields. In this purpose, for spectroscopic applications, this scheme is simpler than previous ones as the local oscillator is generated in situ. Our fully vectorial analysis is well-suited for tightly focused beams, as found in microscopy. However, Eqs. (13)–(18) hold for any focused beam (in particular for weakly focused beams). The presented scheme is thus valuable for any collinear configuration, regardless of the strength of the pump and Stokes beams focusing. Nonetheless, one should keep in mind that for a weakly focused beam, the length of interaction between the lasers and the media is longer than for tightly focused beams and thus the output signal is more sensitive to phase mismatch induced by the linear dispersion of the media.

An interesting parallel is found between this approach and the scheme proposed by Lim et al. [15]. Both rely on the differential measurement of two spectra that mix resonant and nonresonant parts. Because in the two measurements the interference patterns between these two parts are different, the signal subtraction carries useful information on the resonant part. As pointed out in the last section, this scheme is particularly relevant for fast analysis of thin layered media. They can be found in microfluidic devices for instance. In this purpose, the implementation of a multiplex CARS scheme [45,46] seems promising, as the individual CARS spectra are obtained in one shot. Interestingly, all third-order nonlinear processes obey Eqs. (20) and (21) so that our approach can be extended to recover the imaginary part of media involved in resonant third-harmonic generation or four-wave mixing processes.
REFERENCES

33. For a collimated beam with $E(r)=\exp(ikr)$ the minus sign vanishes as $E(-r)=E(r)$.
38. Interestingly, all the symmetry relations reported in Table 1 still hold if the illumination is annular. In that case, the integration over the angle $\theta$ in relations (16)-(18) is performed between a new value of $\theta_{\text{min}}$ (comprised between 0 and $\theta_{\text{max}}$) and $\theta_{\text{max}}$.
42. C. L. Evans, E. O. Potma, M. Puoriss'haag, D. Côté, C. P.


