Raman depolarization ratio of liquids probed by linear polarization coherent anti-Stokes Raman spectroscopy

F. Munhoz, S. Brustlein, D. Gachet†, F. Billard‡, S. Brasselet and H. Rigneault*

We present a simple analytical model to describe the linear polarization coherent anti-Stokes Raman scattering (CARS) spectroscopy. In this scheme, the pump and Stokes beams can have arbitrary linear polarization states and the CARS emitted signal is analyzed along two perpendicular directions. We concentrate on isotropic media without electronic resonances and show that only two polarization CARS measurements performed at the peak and the dip of a CARS spectrum are sufficient to deduce the Raman depolarization ratio, the resonant versus nonresonant contribution, the Raman resonance frequency and the linewidth. We demonstrate the applicability of our scheme to toluene and cyclohexane solutions. Copyright © 2009 John Wiley & Sons, Ltd.

Keywords: CARS; polarization; spectroscopy; microscopy

Introduction

Among nonlinear optical processes, the specificity of the coherent anti-Stokes Raman scattering (CARS) is its coherent and resonant nature. The interaction of the incident fields with the sample induces a third-order nonlinear polarization, whose properties depend on the vector nature and frequencies of the incident electromagnetic fields, as well as the structure of the medium. The latter is characterized by a fourth-rank susceptibility tensor \( \chi^{(3)} \) that has a resonant \( \chi_R^{(3)} \) and a nonresonant \( \chi_{NR}^{(3)} \) contribution. Probing a medium with polarized incident fields allows the activation of different components of this tensor and can be useful to determine the spatial orientation and symmetries of the probed molecular bonds. Pioneer work in polarization CARS has been performed in the late seventies as a powerful alternative tool to spontaneous Raman spectroscopy and polarization-resolved CARS has also been rapidly demonstrated as an efficient mean to modulate the nonresonant background contribution. Polarization analysis has been applied successfully in electronic resonant and nonresonant multiplex coherent Raman spectroscopy. The case of anisotropic photo-induced orientation of molecules has also been addressed when electronic resonances are present. More recently, anisotropic samples, such as water molecules in phospholipid bilayer, tissues or liquid crystals, have been investigated in polarization-resolved CARS microscopy, in order to characterize molecular orientation and director structures. In all these works, either the different linear polarization states of the CARS emitted signal were analyzed spectrally, or the incident parallel polarizations of the pump and Stokes beams were tuned at the same time.

In this work, we consider a more general CARS linear polarization scheme where the pump and Stokes beams can have arbitrary and independent linear polarization states and the emitted CARS signal is analyzed along two perpendicular directions. We restrict our analysis to isotropic media exhibiting no electronic resonances. Although we are interested in CARS micro-spectroscopy, we present here a simple approach where we neglect the spatial confinement of the pump and Stokes focused beams. This crude approximation leads to a complete analytic description of the spectral polarized CARS signal, including the ratio between the resonant and nonresonant contributions. Careful inspection of the outcomes shows that performing only two measurements at the peak and the dip of a CARS spectral band with a 45° angle between the pump and Stokes beams leads to all spectroscopic CARS parameters (Raman depolarization ration, resonant versus nonresonant contribution, Raman resonance frequency and linewidth (HWHM)). This simple scheme is applied as a proof of principle to measure the spectroscopic CARS parameters of toluene and cyclohexane solutions, where we show that this analytic approach applies well to focused beams conditions.

The paper is organized as follows: the first section presents an analytic model for the polarized emitted far field CARS signal. The second section deals with the polarized signals emitted at the peak and dip of the CARS spectrum and the subsequent determination of the spectroscopic CARS parameters. Finally, the third section
reports the experimental implementation of our technique and a
comparison with related measurements.

Analytic model of the polarized CARS signal
emitted from an isotropic medium

The CARS signal depends on the structure of the medium under
investigation, that is characterized by a third order susceptibility
tensor $\chi^{(3)}$. This tensor has 81 components but some of them
can vanish or be dependent on the others according to some
symmetry rules. For an isotropic medium where only two-photon
vibrational resonances are allowed, only two components are
independent and the whole tensor can be described by\(^{(15)}\):

$$
\chi_{ijkl}^{(3)} = \chi_{xyxy}^{(3)}(\delta_{ij} \delta_{kl} + \delta_{ik} \delta_{jl} + \chi_{xyxy}^{(3)} \delta_{il} \delta_{jk})
$$

(1)

where the subscripts $i, j, k$ and $l$ stand for the cartesian coordinates $x, y$ and $z$ and $\delta$ is the Kronecker delta function.

By analogy to the spontaneous Raman spectroscopy theory, we
can define a depolarization ratio $\rho_{\text{CARS}}$ that links two components
of the susceptibility tensor as\(^{(2)}\):

$$
\rho_{\text{CARS}} = \frac{\chi_{xyxy}^{(3)}}{\chi_{xxxx}^{(3)}} = \frac{\chi_{xyxy}^{(3)}}{2\chi_{xyxy}^{(3)} + \chi_{yyyy}^{(3)}}
$$

(2)

Equations (1) and (2) together show that any component of $\chi^{(3)}$ is a
function of $\chi_{xyxy}^{(3)}$ and $\rho_{\text{CARS}}$.

In Eqn (1), the spectral behavior of $\chi^{(3)}$ is not taken into
account. To do so, one must consider the two contributions
to the susceptibility tensor in CARS spectroscopy, namely the
vibrational resonant term $\chi^{(3)}_{\text{NR}}$ and the electronic nonresonant
term $\chi^{(3)}_{\text{R}}$. The $\chi^{(3)}_{\text{NR}}$ tensor can then be written as the sum of these
two contributions $\chi^{(3)}_{\text{NR}} = \chi_{\text{R}}^{(3)} + \chi_{\text{NR}}^{(3)}$. We can insert this relation in
Eqn (1) and use Eqn (2) to obtain the complete description of $\chi^{(3)}_{\text{NR}}$, following

$$
\chi_{ijkl}^{(3)} = \chi_{\text{NR}}^{(3)}(\delta_{ij} \delta_{kl} + \delta_{ik} \delta_{jl} + \chi_{xyxy}^{(3)} \delta_{il} \delta_{jk})
$$

(3)

where $\chi_{\text{NR}}^{(3)}$ (respectively $\chi_{\text{R}}^{(3)}$) stands for $\chi_{xyxy}^{(3)}$
(respectively $\chi_{xyxy}^{(3)}$) and $\rho_{\text{R}}$ is the Raman depolarization
ratio. For the resonant contribution, the latter term is equal to the
CARS depolarization ratio and its value lays between 0 and 3/4.\(^{(10)}\)

For the nonresonant contribution, according to the Kleinman’s
symmetry rule,\(^{(16)}\) $\chi_{xyxy}^{(3)} = \chi_{xyxy}^{(3)}$ and consequently $\rho_{\text{CARS}} = 1/3$, which has been already inserted in the equation above. The
nonresonant term $\chi_{\text{NR}}^{(3)}$ is a real constant whereas the resonant
term $\chi_{\text{R}}^{(3)}$ holds the lorentzian spectral dependency given by

$$
\chi_{\text{R}}^{(3)} = \frac{a}{(\delta \omega - \Omega_{\text{R}}) + \Gamma}
$$

(4)

where $a$, $\Omega_{\text{R}}$ and $\Gamma$ are respectively the oscillator strength,
the resonance angular frequency and the HWHM of the probed Raman
line and $\delta \omega = \omega_p - \omega_S$ is the angular frequency difference between
the pump and Stokes fields.

The susceptibility tensor $\chi^{(3)}$ couples the induced third order
nonlinear polarization with the excitation electromagnetic fields
and can be written as

$$
\rho_{ijkl}^{(3)} = 3 \sum_{jkl} \chi_{ijkl}^{(3)}(-\omega_3; \omega_1, \omega_2, \omega_3) E_{ij}(\omega_1) E_{jk}(\omega_2) E_{kl}(\omega_3)
$$

(5)

where $E_{ij}$ and $E_{jk}$ are the pump and Stokes incident fields at angular
frequencies $\omega_1$ and $\omega_3$ respectively and $\omega_3 = 2\omega_1 - \omega_2$ is the
angular frequency of the emitted anti-Stokes field.

The analytic model of the polarization-resolved CARS emission
for an isotropic medium is developed from the elements
introduced above and under some simplificative assumptions.
First, the pump and Stokes fields are linearly polarized with
polarizations angles $\alpha_p$ and $\alpha_S$ with respect to the $x$ direction.
Second, the incident fields are plane waves propagating in the z
direction. As a consequence, $E_{ij}$ and $E_{jk}$ are zero and $\rho_{ijkl}^{(3)}$ vanishes.
This is a crude approximation for an implementation in microscopy,
where strongly focused beams are used. Nevertheless, we will see
further that the main features for the polarization CARS signal
are surprisingly well described. Under these assumptions the $x$ and $y$
components of the CARS signal polarization can be then
determined by introducing Eqn (3) in Eqn (5), following

$$
\begin{align*}
\rho_{x}^{(3)} &= 3 \chi_{x}^{(3)} E_{x}^{*} E_{y}^{*} \\
\rho_{y}^{(3)} &= 3 \chi_{y}^{(3)} E_{x}^{*} E_{y}^{*}
\end{align*}
$$

(6)

where the effective susceptibilities $\chi_{x}^{(3)}$ and $\chi_{y}^{(3)}$ are defined as

$$
\begin{align*}
\chi_{x}^{(3)} &= \chi_{\text{NR}}^{(3)} [2 \cos \alpha_p \sin \alpha_p \sin \alpha_S + \sin^2 \alpha_p \cos \alpha_S + 3 \cos^2 \alpha_p \cos \alpha_S] \\
&+ 2 \chi_{\text{R}}^{(3)} \left[ \cos \alpha_p \sin \alpha_p \sin \alpha_S + \frac{\rho_{\text{R}}}{1 - \rho_{\text{R}}} \sin^2 \alpha_p \cos \alpha_S \right] \\
&+ \frac{1}{1 - \rho_{\text{R}}} \cos^2 \alpha_p \cos \alpha_S
\end{align*}
$$

(7)

$$
\begin{align*}
\chi_{y}^{(3)} &= \chi_{\text{NR}}^{(3)} [2 \cos \alpha_p \sin \alpha_p \cos \alpha_S + \cos^2 \alpha_p \sin \alpha_S + 3 \sin^2 \alpha_p \sin \alpha_S] \\
&+ 2 \chi_{\text{R}}^{(3)} \left[ \cos \alpha_p \sin \alpha_p \cos \alpha_S + \frac{\rho_{\text{R}}}{1 - \rho_{\text{R}}} \cos^2 \alpha_p \sin \alpha_S \right] \\
&+ \frac{1}{1 - \rho_{\text{R}}} \sin^2 \alpha_p \sin \alpha_S
\end{align*}
$$

After some algebraic manipulations, Eqn (7) can be recast under

$$
\begin{align*}
\chi_{x}^{(3)} &= \chi_{\text{NR}}^{(3)} [2 \cos \alpha_S + \cos(2\alpha_P - \alpha_S)] \\
&+ \frac{a}{(\delta \omega - \Omega_{\text{R}}) + \Gamma} \left[ 1 + \rho_{\text{R}} \cos \alpha_S + \cos(2\alpha_P - \alpha_S) \right] \\
\chi_{y}^{(3)} &= \chi_{\text{NR}}^{(3)} [2 \sin \alpha_S + \sin(2\alpha_P - \alpha_S)] \\
&+ \frac{a}{(\delta \omega - \Omega_{\text{R}}) + \Gamma} \left[ 1 + \rho_{\text{R}} \sin \alpha_S + \sin(2\alpha_P - \alpha_S) \right]
\end{align*}
$$

(8)

where $\chi_{\text{R}}^{(3)}$ was replaced by its expression given by Eqn (4). From
Eqn (8), both expressions of $\chi_{x}^{(3)}$ and $\chi_{y}^{(3)}$ have a nonresonant
term that only depends on the incident polarization direction and
a resonant contribution that depends also on the spectral shift
and the Raman depolarization ratio.

Now, we want to write the effective susceptibilities in polar
coordinates\(^{(17)}\) in order to simplify the previous expressions
and to obtain analytic equations of the CARS amplitudes
at different spectral positions. In the first step, we define

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the functions \( G_s(\alpha_p, \alpha_S) = \chi^{(3)}_{NR}[2 \cos \alpha_S + \cos(2\alpha_P - \alpha_S)] \) and \( G_s(\alpha_p, \alpha_S) = \chi^{(3)}_{NR}[2 \sin \alpha_S + \sin(2\alpha_P - \alpha_S)] \), that correspond to the respective nonresonant terms in the expressions of \( \chi^{(3)}_{eff} \) and \( \chi^{(3)}_{eff} \) in Eqn (8). Defining a normalized spatial spectral as \( \zeta = (\delta \omega - \Omega_R)/\Gamma \), the effective susceptibilities become

\[
\chi^{(3)}_{x(\zeta, \rho)} = G_x(\zeta, \rho_R) \left[ 1 + \frac{a}{\chi^{(3)}_{NR} \Gamma(\zeta + \eta_R \alpha^2 + \beta x(\zeta))} \frac{1 + \rho_R}{1 - \rho_R} \beta x(\zeta) \right] \tag{9}
\]

where \( \beta_x = \cos(2\alpha_P - \alpha_S)/\cos(\alpha_S) \) and \( \beta_y = \sin(2\alpha_P - \alpha_S)/\sin(\alpha_S) \). In order to shorten the notation, the angular dependency in the functions \( G \) and \( \beta \) are omitted in Eqn (9).

By analogy with \( [17] \) we define a function \( \eta_{x(\zeta)} = -2\Gamma \chi^{(3)}_{NR}/(aF_x(\zeta)) \) that characterizes the strength of the resonant over the nonresonant CARS signal. Here, the function \( F_x(\zeta) \) expresses the angular-dependent term of the resonant contribution, as follows

\[
F_x(\zeta) = \frac{1}{2} + \beta_x \left( \frac{1 + \rho_R}{1 - \rho_R} + \beta x(\zeta) \right) \tag{10}
\]

After some algebraic manipulations, Eqn (9) can be recast under a polar form following

\[
\chi^{(3)}_{x(\zeta, \rho)} = \frac{G_x(\zeta)}{\eta_{x(\zeta)}(\zeta^2 + 1)} \frac{\eta_{x(\zeta)}(\zeta^2 + 1) - 2\zeta + 2i}{\sqrt{\eta_{x(\zeta)}(\zeta^2 + 1)}} \tag{11}
\]

where \( l \) corresponds to a CARS intensity analyzed in the \( x(y) \) directions. The last equality of Eqn (11) is a crude simplification that does not take into consideration the far field structure and its relation to the spatial dependent susceptibility \( \chi^{(3)} \). Nevertheless we know that the total emitted CARS intensity is proportional to the modulus square of the susceptibility, which is expressed here on a simple plane wave basis. From Eqn (11), the CARS intensity \( I \) and the phase of the effective susceptibility \( \phi \) write

\[
I_x(\zeta, \rho_R) \propto G_x^2(\zeta) \left( 1 + 4 \frac{\eta_{x(\zeta)}(\zeta^2 + 1)}{\eta_{x(\zeta)}(\zeta^2 + 1) - 2\zeta + 2i} \right) \tag{12a}
\]

\[
\tan \phi_x(\zeta, \rho_R) = \frac{2}{\eta_{x(\zeta)}(\zeta^2 + 1) - 2\zeta} \tag{12b}
\]

When the pump and Stokes fields are fixed, the term \( 3E_p^2E_S^2 \) in Eqn (6) contributes only as a multiplicative constant and does not come into account in Eqns (12a) and (12b). Eqn (12a) includes any linear polarization states of the pump and Stokes beams together with the spectral dispersion associated with the Raman line.

**Determination of the spectroscopic CARS parameters**

In this section, we propose a simple method to determine the Raman depolarization ratio and the strength of the resonant over the nonresonant amplitudes \( a/\chi^{(3)}_{NR} \) of an anisotropic medium, together with its spectral parameters \( \Omega_R \) and \( \Gamma \). In this purpose, we derive the expressions of the polarized CARS intensities at two specific spectral positions, corresponding to the maximum and minimum of the CARS signal. These intensities are named respectively peak and dip.\(^{[18]}\) The peak and dip spectral positions are chosen here as singular positions that are convenient to determine experimentally. The first step is to calculate the spectral shifts \( \zeta_{P(\Phi)} \) and \( \zeta_{D(\Phi)} \) (P and D stand for peak and dip values respectively) that respectively maximize and minimize Eqn (12a), by cancelling the first derivative of the CARS intensities with respect to \( \zeta \). One finds

\[
\zeta_{P(\Phi)} = \left[ 1 - \frac{1 + \eta_{P(\Phi)}^2}{\eta_{x(\zeta)}} \right] \quad \text{and} \quad \zeta_{D(\Phi)} = \left[ 1 + \frac{1 + \eta_{D(\Phi)}^2}{\eta_{x(\zeta)}} \right] \tag{13}
\]

This operation requires some caution because Eqn (13) is not valid when \( G_x(\zeta) = 0 \) or \( \eta_{x(\zeta)} \) tends to infinity (in both situations the derivative of the intensity with respect to \( \zeta \) is always zero). The polarization configuration that verifies \( G_x(\zeta) = 0 \) correspond to \( \alpha_P = 0^\circ \) and \( \alpha_S = 90^\circ \) modulo 180°. Two polarization’s arrangements satisfy \( G_x(\zeta) = 0 \): either \( \alpha_S = 0^\circ \) and \( \alpha_P = 0^\circ \) modulo 90°, or \( \alpha_P = 0^\circ \) and \( \alpha_S = 90^\circ \) modulo 180°. \( \eta_{x(\zeta)} \) can tend to infinity only when \( \rho_R = 0 \) and \( \beta_x(\zeta) = -1 \).

Replacing Eqn (13) into Eqn (12a) leads to the final expressions for the CARS peak and dip intensities:

\[
I_{P(\Phi)} \propto G_x^2(\zeta) \frac{1 + \eta_{P(\Phi)}^2 + 1}{\sqrt{1 + \eta_{P(\Phi)}^2}} \quad \text{and} \quad I_{D(\Phi)} \propto G_x^2(\zeta) \frac{1 + \eta_{D(\Phi)}^2 - 1}{\sqrt{1 + \eta_{D(\Phi)}^2}} \tag{14}
\]

Both expressions are very similar except for the fact that they interchange \((-\) and \(+)\) signals. Consequently, if we sum them up, we obtain a simple quadratic function of \( \eta_{x(\zeta)} \) and therefore of \( \rho_R \) and \( a/\chi^{(3)}_{NR} \). Besides, multiplying \( I_{P(\Phi)} \) by \( I_{D(\Phi)} \) results in the nonresonant contribution \( G_{NR}^2 \).\(^{[17]}\) We can define the related quantity \( S_{PD} \) as

\[
S_{PD(\Phi)}(\alpha_p, \alpha_S, \rho_R) = \frac{I_{P(\Phi)} + I_{D(\Phi)}}{\sqrt{I_{P(\Phi)}I_{D(\Phi)}}} = 2 + \left( \frac{a}{\chi^{(3)}_{NR} \Gamma} \right)^2 F_x^2(\zeta) \tag{15}
\]

where \( F_x(\zeta) \) is given by Eqn (10) and the normalization factor \( \sqrt{I_{P(\Phi)}I_{D(\Phi)}} \) was chosen to eliminate the contribution of \( G_x(\zeta) \). When \( \alpha_S = 0^\circ \), \( \beta_x \) tends to infinity for any value of \( \alpha_P \) and as a consequence \( F_x \) tends to 1 (cf Eqn (10)) and \( S_{PD} \) does not depend on the Raman depolarization ratio. As a result, measuring the y component of the peak and dip CARS intensities leads to the ratio \( a/\chi^{(3)}_{NR} \) following

\[
\frac{a}{\chi^{(3)}_{NR} \Gamma} = - \sqrt{S_{PD}(\alpha_S = 0^\circ) - 2} \tag{16}
\]

When \( \alpha_S = 0^\circ \), this expression is valid for any value of \( \alpha_P \), excepted when they cancel \( G_y \). In particular, Eqn (16) is verified when \( \alpha_P = 45^\circ \), the pump polarization direction that maximizes the CARS intensity in the y direction (as shown in Figs. 1 and 2). By setting the incident polarizations \( \alpha_S = 0^\circ \) and \( \alpha_P = 45^\circ \) and inserting Eqn (16) in the expression of \( S_{PD} \) given by Eqn (15), the
Raman depolarization ratio can be calculated following

\[
\rho_R = \frac{2}{\sqrt{2 \sqrt{\frac{S_{PD}(\alpha_p = 45^\circ, \alpha_S = 0^\circ) - 2}{S_{PD}(\alpha_p = 45^\circ, \alpha_S = 0^\circ) - 2} + 1}} - 1}
\]

As Eqn (15) is quadratic on \( \rho_R \), another solution is also possible and is given by the same expression as Eqn (17) but with the (−) and (+) signs interchanged. This results in a solution where \( \rho_R > 1 \) which is not acceptable since \( 0 \leq \rho_R \leq 3/4 \) for non electronically resonant excitation and linear incident polarizations. The scheme described above permits therefore to measure \( \rho_R \) and \( a/(\chi^{(3)}_{NR}) \) for any pump polarization angle different from \( 0^\circ \) modulo \( 90^\circ \), but one specific polarization configuration, namely \( \alpha_S = 0^\circ \) and \( \alpha_p = 45^\circ \), is chosen in order to maximize the signal to noise ratio in the \( y \) direction.

Another possible method to determine \( \rho_R \) and \( a/(\chi^{(3)}_{NR}) \) is to set \( \alpha_S = 0^\circ \) and to rotate \( \alpha_p \) from 0\(^\circ\) to 360\(^\circ\), recording the \( x \) component of the peak and dip CARS intensities for several pump polarization angles. We can then search for the parameters \( a/(\chi^{(3)}_{NR}) \), \( \rho_R \) that fit best the experimental data to the analytic expression of \( S_{PD} \), given by Eqn (15), using the least squares method. Here, we observe that the behavior of \( S_{PD} \) changes dramatically for different values of the Raman depolarization ratio. This can be explained by the fact that, according to Eqn (15), \( S_{PD} \) depends quadratically on \( F_x \), whose behavior with respect to \( \beta_x \) varies for different values of \( \rho_R \). According to Eqn (10), \( F_x \) is an increasing function of \( \beta_x \) for \( \rho_R < 1/3 \) and a decreasing function of \( \beta_x \) for \( \rho_R > 1/3 \). Unlike the first method that uses only one pump angle \( \alpha_p = 45^\circ \), this fitting method gives values for \( \rho_R \) and \( a/(\chi^{(3)}_{NR}) \) that can be determined from all the pump polarizations angles, that is more precise for a medium where the signal to noise ratio is too low.

The Raman frequency \( \Omega_R \) and its half width at half-maximum \( \Gamma \) can be determined by solving the two-equation system

\[
\left\{
\begin{array}{l}
\xi_{PD} = \delta(\omega_{PD} - \Omega_D)/\Gamma \\
\rho_R = \frac{\xi_{PD} \delta(\omega_{PD} - \Omega_D) - \xi_{D} \delta(\omega_{PD})}{\xi_{D} - \rho} \rho
\end{array}
\right.
\]

where the values of the normalized spectral shift \( \xi_P \) and \( \xi_D \) are calculated from Eqn (13).

### Experimental results

The experimental setup is described elsewhere.\(^{[19]}\) Briefly, pump and Stokes pulse trains are delivered by 2-ps tunable mode-locked lasers (Coherent Mira 900, 76 MHz, 3 ps), pumped by a Nd:Vanadate laser (Coherent Verdi). The lasers are electronically synchronized (Coherent SyncroLock System) and are externally pulse-picked (APE pulse Picker) to reduce their rate to 3.8 MHz. Achromatic half-waveplates mounted in a step rotation motor, allow to rotate the incident linear polarizations separately for the pump and Stokes beams. The beams are expanded, spatially recombined, injected into a commercial inverted microscope (Zeiss Axiovert 200 M) and focused on the sample through a microscope objective (Olympus LUCPLFLN 40X, NA = 0.6). The generated CARS signal is forwardly collected by another microscope objective (Olympus LMPFLFN 50X, NA = 0.5) and is split by a broadband polarizing cube beamsplitter (Newport). The two resulting perpendicularly polarized anti-Stokes beams are finally detected by two avalanche photodiodes (Perkin Elmer SPCM-AQR-14) used in photon counting mode.

We first present the CARS polarization response of a pure nonresonant medium, here water, when the Stokes linear polarization is set parallel to the \( x \) axis and the pump linear polarization rotates from \( 0^\circ \) to 360\(^\circ\). Pump and Stokes wavelengths are fixed to 724.5 nm and 797.0 nm and their average powers are 2 mW and 1 mW, respectively. The result is shown in Fig. 1. The shapes and ratio of these polar plots fit the expected \( G_y \) and \( G_x \), that are the nonresonant terms in the effective susceptibilities (Eqn (9)).

We now focus on the determination of the CARS spectroscopic parameters of some liquids by the methods described in the previous section. In this purpose, we carry out polarization-resolved CARS experiments on toluene and cyclohexane. For toluene, we concentrate on the polarized Raman band at 787 cm\(^{-1}\) corresponding to the A\(_1\) vibration.\(^{[20]}\) The corresponding CARS peak arises at 776 cm\(^{-1}\) which is addressed with pump and Stokes wavelengths at 730.26 nm and 774.15 nm, respectively and average power 300 \( \mu \)W for both beams. For cyclohexane, we focus on the depolarized Raman line at 1267 cm\(^{-1}\) corresponding to the \( E_g \) CH\(_2\) twist vibration.\(^{[9]}\) In this case, the corresponding CARS peak arises at 1256 cm\(^{-1}\) and is addressed with pump and Stokes wavelengths at 724.5 nm and 797.0 nm and average powers 2 mW and 1 mW, respectively. In this section, the words ‘toluene’ and ‘cyclohexane’ will refer exclusively to these two bands.

We first acquire the CARS spectra of toluene and cyclohexane in the polarization configuration \( \alpha_p = \alpha_S = 0^\circ \), in order to determine their peak and dip wavenumbers. As we work with two picosecond lasers, the CARS spectra are obtained by fixing the wavelength of the pump field and by acquiring the CARS intensities in the \( x \) and \( y \) directions for different values of the Stokes wavelength. The peak and dip wavenumbers are determined within an experimental accuracy of \( \pm 4 \) cm\(^{-1}\).

The CARS polarization responses are shown in Fig. 2(a) for toluene and Fig. 2(b) for cyclohexane, for the same polarization configuration as the nonresonant experiment \( \alpha_S = 0^\circ \) and \( \alpha_p = 45^\circ \).
the ratio of analytic expression of spectroscopic coefficients were also deduced from fitting the ratio of the considered medium. Nevertheless, a careful observation shows that the spectral resonance plays a role in the ratio between the perpendicular polarized intensities $I_x$ and $I_y$. At the CARS peak, the ratio of $I_y$ to $I_x$ is indeed strongly dependent on the Raman line depolarization ratio. For a polarized band, as found with toluene, it is close to unity. For a depolarized band, as found with cyclohexane, it tends towards zero.

From the acquired CARS intensities, we calculate the ratio $S_{PD_{th}}$ (for $\alpha_s = 0^\circ$, $\alpha_P = 45^\circ$ — referred as method 1) and then we use Eqns (16) and (17) to obtain respectively the factor $a/(\chi^{(3)}_{NR}\Gamma)$ and the Raman depolarization ratio $\rho_R$. The results are shown in Table 1 (method 1). The uncertainties were derived from the experimental uncertainties of $I_{th}$. The same CARS spectroscopic coefficients were also deduced from fitting the analytic expression of $S_{PD}$ (Eqn (15)) to the experimental data (for $\alpha_P$ in the range $[0^\circ, 360^\circ]$ and $\alpha_s = 0^\circ$ — referred as method 2). The results are shown in Table 1 (method 2). For method 2, the retained solution is the couple $(a/(\chi^{(3)}_{NR}\Gamma), \rho_R)$ that minimizes the difference between the experimental and analytic values of $S_{PD}$ for all the pump polarization angles, that is the quantity $D = \sum_{\alpha_P} |S_{PD_{th}}(\alpha_P) - S_{PD}(\alpha_P)|^2$. Figure 3 plots $D(a/(\chi^{(3)}_{NR}\Gamma), \rho_R)$ for toluene. As this surface has only one and well defined global minimum, we demonstrate here the unicity of the solution. Figure 4 shows the experimental ratio $S_{PD}$ for toluene and cyclohexane and the best fit to Eqn (15) as a function of the pump polarization angle $\alpha_P$. We observe that $S_{PD}$ for toluene and cyclohexane exhibit very different behaviors, as expected from Eqns (15) and (10) for polarized and depolarized lines. We finally calculate $\Gamma$ and $\Omega_R$, as explained in the previous section for both methods (Table 1, methods 1 and 2).

![Figure 2](image.png)

**Figure 2.** CARS polarization responses for toluene and cyclohexane when the Stokes linear polarization is set parallel to the x axis and the pump linear polarization rotates from $0^\circ$ to $360^\circ$. The respective curves for $I_x$ and $I_y$ at peak and dip positions are shown in the graph. $I_y$ curves for cyclohexane have been magnified for clarity. This figure is available in colour online at www.interscience.wiley.com/journal/jrs.

![Table 1](table.png)

**Table 1.** Raman depolarization ratios and spectral parameters calculated for toluene and cyclohexane

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\frac{a}{\chi^{(3)}_{NR}\Gamma}$</th>
<th>$\rho_R$</th>
<th>$\Gamma$ (cm$^{-1}$)</th>
<th>$\Omega_R$ (cm$^{-1}$)</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>$-1.301 \pm 0.003$</td>
<td>$0.037 \pm 0.002$</td>
<td>$6.5 \pm 1.5$</td>
<td>$779 \pm 3$</td>
<td>1</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>$-0.154 \pm 0.009$</td>
<td>$0.78 \pm 0.01$</td>
<td>$10.9 \pm 2.0$</td>
<td>$1266 \pm 3$</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>$-0.12 \pm 0.02$</td>
<td>$0.82 \pm 0.03$</td>
<td>$10.9 \pm 2.0$</td>
<td>$1267 \pm 3$</td>
<td>2</td>
</tr>
</tbody>
</table>

![Figure 3](image.png)

**Figure 3.** Cartography of $D = \sum |S_{PD_{th}}(\alpha_P) - S_{PD}(\alpha_P)|^2$ for toluene. The retained solution is the couple $(a/(\chi^{(3)}_{NR}\Gamma), \rho_R)$ that minimizes $D$. This figure is available in colour online at www.interscience.wiley.com/journal/jrs.
From Table 1, both methods allow recovering the degree of polarization of the toluene and cyclohexane bands ($\rho_R \approx 0$ and $\rho_R \approx 3/4$ respectively). Furthermore, the ratio of the resonant to the nonresonant contribution ($a_R/\chi_{NR}^{(3)}$), the spectral line position and its HWHM are obtained within an acceptable agreement between methods 1 and 2. The advantage of method 1 lies in its increased simplicity in an experimental setup: only one polarization configuration at two specific spectral positions (peak and dip) is required to obtain the CARS spectroscopic parameters. Results are also comparable with Raman measurements reported elsewhere for toluene$^{[20]}$ and cyclohexane.$^{[21]}$ The Raman depolarization ratio bigger than 3/4 for the depolarized band of the cyclohexane can be attributed to the dichroic filter that recombines the pump and Stokes fields in the experimental setup. The dichroic filter can introduce some ellipticity to the incident pump polarization, when $\alpha_P \neq 0^\circ$ or $90^\circ$, and this effect is not taken into account in this model. Despite its simplified assumptions, our analytic model can estimate satisfactorily the CARS spectroscopic parameters for isotropic media.

**Conclusion**

We have reported here an analytic model for the linear polarization CARS spectroscopy applied to isotropic media without electronic resonances. This model gives simple expressions for the shapes of the polar plots for the perpendicularly polarized CARS intensities $I_x$ and $I_y$ as a function of the incident pump and Stokes polarization angles. We have shown that the influence of the depolarization ratio, and thus of the resonant response, can be observed in the ratio of $I_x$ to $I_y$, although the general shape of these plots are dominated by the nonresonant response. This model allowed us to calculate analytic expressions of the CARS signal at the spectral peak and dip. Two different methods were then proposed to determine the CARS spectroscopic parameters (depolarization ratio, ratio of the resonant to the nonresonant components $a_R/\chi_{NR}^{(3)}$, spectral position of the Raman band and its half width at half-maximum). The first method uses only one polarization configuration, where the Stokes beam is polarized parallel to the $x$ axis and the pump polarization angle is $45^\circ$ with respect to the same axis. The second method keeps the Stokes field polarized parallel to the $x$ axis whereas the pump polarization angle rotates from $0^\circ$ to $360^\circ$. Satisfying results using both methods were found for toluene and cyclohexane. So far we have considered species with well separated spectral lines; in the case of congested spectra it can be difficult to identify spectral peaks and dips. However, a polarization study is always possible and the spectroscopic CARS parameters could be in principle fitted from the experimental data. The study reported into this paper shows the potential of CARS spectroscopy resolved in polarization to probe isotropic media and could be extended to some more complex systems, such as crystalline media.

**References**