Probe Beam Dichroism and Birefringence in Stimulated Raman Scattering of Biologically Relevant Polyatomic Molecules

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Abstract

The dichroism and birefringence effects in stimulated raman scattering (SRS) in polyatomic molecules were studied theoretically. General expressions have been derived describing the change of the intensity and polarization of the probe pulse after transmission through a solution of arbitrary polyatomic molecules for any initial polarization of each of the laser pulses. The expressions were written in terms of spherical tensor operators that allowed for separation of the both beams polarization matrices and the material part containing three scalar values of nonlinear optical susceptibility $\chi^{(3)}_K$ where that rank $K$ is limited to the values $K = 0, 1, 2$. The expressions are valid for arbitrary directions of propagation of both pump and Stokes light beams and arbitrary polarizations of both beams. The expressions contain contributions from linear dichroism and birefringence in the molecular excited states. It was shown that, under certain conditions, both effects can be observed simultaneously. The geometry of almost collinear propagation of the pump and Stokes pulse beams through the molecular sample was considered, and it was shown that the contributions from linear dichroism and birefringence to the signal can be completely separated in the experiment by means of an appropriate choice of a probe beam polarization analyzer placed in front of the photodetector. The expressions obtained were used to describe the signals obtained using the polarization-modulation technique developed recently by the authors (Gorbunova et al, Phys. Chem. Chem. Phys. 2020, Vol. 22, 18155–18168). It was shown that the modulated dichroism and birefringence signals could be observed in quadrature to the second harmonic of the modulated reference signal.

I. INTRODUCTION

Stimulated Raman scattering (SRS) spectroscopy in particular SRS microscopy has nowadays found wide applications for analysis and label-free imaging of functional endogenous biomolecules in living systems as it offers critical information to understand the fundamentals in biology and to assist clinical diagnostics [1–4]. An advantage of SRS microscopy in comparison with spontaneous Raman microscopy is the dramatic increase of experimental signals and improvement in imaging speed, which gives rise to real-time hyperspectral vibrational imaging of live biological samples. Another popular coherent Raman scattering technique is anti-Stokes Raman scattering (CARS) that is also widely used in life science
applications [2] is usually accompanied by a nonresonant background, resulting from non-
linear optical responses mediated through molecular virtual or electronic states, or both [5] 
while in SRS the nonresonant background is usually sufficiently reduced allowing for rapid 
hyperspectral imaging at low analyte concentrations [6].

Both techniques are based on the interaction of laser beams at pump frequency $\omega_p$ and 
Stokes frequency $\omega_s$ when the frequency difference $\Delta \omega = \omega_p - \omega_s$ is equal to the resonant 
frequency of a molecular vibrational transition within the sample. The SRS signal is gener-
ated at the frequency of an incident beam and is based on the energy transfer between 
the pump and the Stokes beams where the measured signal may either be a power gain in 
the Stokes beam (Stimulated Raman Gain (SRG)) or a loss in the pump beam (Stimulated 
Raman Loss (SRL)).

According to the theory [7, 8], all information on the dynamics of third-order nonlinear 
optical phenomena is contained in the fourth-order tensor of nonlinear optical susceptibility 
$\chi^{(3)}_{ijkl}(\omega_m, \omega_n, \omega_q)$, where the subscript indices $i, j, k, l$ are Cartesian directions of light 
polarizations and $\omega_m, \omega_n, \omega_p$ are light frequencies involved in the nonlinear scattering process. 
The nonlinear susceptibility performs the relationship between the components of nonlinear 
polarization $P_i(\omega)$ generated in the sample and the Fourier components of the light electric 
vectors [8]:

$$P_i(\omega) = \varepsilon_0 \sum_{jkl} \sum_{(mnq)} \chi^{(3)}_{ijkl}(\omega_m, \omega_n, \omega_q)E_j(\omega_m)E_k(\omega_n)E_l(\omega_q),$$

(1)

where $\omega$ is the frequency of the outgoing detected light beam.

The notation $(m, n, q)$ in eq. (1) indicates that, in performing the summation over $m$, 
$n$, and $q$ the sum $\omega_m + \omega_n + \omega_q$ is to be held fixed to $\omega$, although the $m$, $n$, and $q$ are 
each allowed to vary. In case of SRS-SRG and narrow spectral widths of both laser beams: 
$\omega = \omega_s$, $\omega_m = -\omega_n = \omega_p$, and $\omega_q = \omega_s$.

The nonlinear optical susceptibility $\chi^{(3)}_{ijkl}(\omega_m, \omega_n, \omega_q)$ contains summations over the 
products of transition matrix elements between real and virtual quantum states, and the energy 
differences between molecular quantum states [7, 8]. The number of independent matrix 
elements depends on the sample symmetry, in particular in isotropic media in solutions and 
in certain biological samples the number of third-order nonlinear susceptibility independent 
matrix elements is limited to three [7, 8].

Although the general quantum mechanical theory of SRS and other third-order nonlinear
optical phenomena in any media is well developed [7, 8] and particular experimental geometries were considered [9] the detailed theory of possible polarization effects under SRS in biologically relevant polyatomic molecules was not exist till now.

This paper aims to address this problem. The general expression for the change of the polarization matrix of the Stokes laser pulse transmitted through the ensemble of polyatomic molecules excited by a pump laser pulse for arbitrary polarizations and arbitrary propagation directions of the pump and Stokes pulses were obtained and analyzed. The expression is presented also in the terms of Stockes parameters of the incoming and outgoing laser beams for arbitrary polarizations that elucidate the contributions of linear dichroism and birefringence to the change in the polarization of Stockes beam transmitted through a molecular sample. The spherical tensor approach were used throughout the paper for description of the molecular and light density metrices [10, 11]. Similar approach was used to describe SRS before [12] where however no specification for excitation of polyatomic molecules and no general expression and its analysis were presented. The paper extends the approach used in our recent papers [13–16] to describe the SRS of polyatomic asymmetric top molecules in the condensed phase.

The main results obtained are as follows. As shown, the spherical tensor approach allowed for complete separation of an anisotropic tensor part containing all light polarizations from the isotropic part containing three scalar nonlinear optical susceptibility terms \( \chi_0 \), \( \chi_1 \), and \( \chi_2 \) having each clear physical meanings. The tensor part can be completely controlled by experimentalist that allows for analysis of an arbitrary experimental SRS geometry including all possible light beams propagation directions and polarizations. The particular geometries allowing for convenient determination of the nonlinear optical susceptibility terms from experiment were discussed.

The general expressions derived was applied for elucidation of the results of our recent experiments on NADH anisotropic excited state relaxation in the sub-picosecond time domain using a novel polarization-modulation transient method [15, 17]. The method demonstrated an extremely high sensitivity, it allows for the study of excited state dynamics at a less than nJ level of pump pulse energy and therefore may be suitable for analysis of molecular excited state energy transfer in living cells.

The paper is organised as follows. Section II describes the derivation and analysis of general quantum mechanics-based expressions for SRS signals at arbitrary light beams po-
Section III describes the particular SRS geometries allowing for convenient determination of the nonlinear optical susceptibility terms from experiment and the application of the derived expressions for elucidation of the results of recent experiments on NADH anisotropic excited state relaxation. The conclusions are given in Sec. IV. The calculation details are collected in Appendix.

II. OUTPUT POLARIZATION

Output electric field

\[ E_{i}^{\text{out}}(\omega) = E_{i}(\omega) + P_{i}(\omega). \] (2)

Polarization matrix

\[
\pi_{ii'}^{\text{out}}(\omega) = E_{i}^{\text{out}}(\omega)E_{i'}^{\text{out}*}(\omega) = \pi_{ii'}(\omega) + \epsilon_{0} \sum_{jkl} \sum_{(mnq)} E_{i}(\omega)\chi_{ijkl}^{(3)}(\omega_{m}, \omega_{n}, \omega_{q})E_{j}^{*}(\omega_{m})E_{k}^{*}(\omega_{n})E_{l}^{*}(\omega_{q}) \\
+ \epsilon_{0} \sum_{jkl} \sum_{(mnq)} E_{i'}^{*}(\omega)\chi_{ijkl}^{(3)}(\omega_{m}, \omega_{n}, \omega_{q})E_{j}(\omega_{m})E_{k}(\omega_{n})E_{l}(\omega_{q}). \] (3)

Firstly, we can introduce cyclic indices:

\[ E_{0}(\omega) = E_{z}(\omega), \] (4)

\[ E_{\pm 1}(\omega) = \frac{\mp E_{x}(\omega) - iE_{y}(\omega)}{\sqrt{2}}. \] (5)
Secondly, we can consider irreducible representation of the polarization matrix:

\[ IE_{KQ}(\omega) = \sum_{p,p'} (-1)^p C_{-1}^{KQ} A_{-1}^{KQ} \langle E_{-p}(\omega) E_{-p'}^{*}(\omega) \rangle, \]  

where \( I \) is the light intensity.

For isotropic medium, the susceptibility can be written as

\[ \chi_{ijkh} = \chi^0_{ijkh} - \chi^2_{ijkh} \delta_{ij} \delta_{kh} + \chi^2_{ijkh} \delta_{ih} \delta_{jk}, \]  

where \( \chi_K \) denotes the scalars for the given rang \( K = 0, 1, 2 \).

For isotropic medium we can write the irreducible representation of the output polarization as

\[ I_{out} E_{out}^{KQ}(\omega) = IE_{KQ}(\omega) - \epsilon_0 I_{pu} I_{pr} \sum_{K_{pu}, K_{pr}} A_{K_{pu}K_{pr}}^{K} \left( E_{K_{pu}}^{pu} \otimes E_{K_{pr}}^{pr} \right)_{KQ} \left( \chi_{K_{pu}} + (-1)^{K_{pu}+K_{pr}} \chi^*_{K_{pu}} \right) \]  

where the irreducible representation of the tensor product is

\[ [E_{K_{pr}}^{pr} \otimes E_{K_{pu}}^{pu}]_{KQ} = \sum_{Q_{pr}, Q_{pu}} C_{K_{pr}Q_{pr}K_{pu}Q_{pu}}^{KQ} E_{K_{pr}}^{pr} E_{K_{pu}}^{pu} Q_{pu}, \]

and the coefficients have the following form

\[ A_{K_{pu}K_{pr}}^{K} = \frac{(-1)^{K_{pr}}}{\sqrt{(2K_{pu} + 1)(2K_{pr} + 1)}} \begin{bmatrix} K & K_{pu} & K_{pr} \\ 1 & 1 & 1 \end{bmatrix}. \]  

### III. SUSCEPTIBILITY OF MOLECULES

Irreducible representation of susceptibility is

\[ \chi_{K_{pu}} = \gamma_{K_{pu}}(\omega_{pr}, \omega_{pu}, -\omega'_{pu}) + (-1)^{K_{pu}} \gamma_{K_{pu}}(\omega_{pr}, -\omega'_{pu}, \omega_{pu}) \]

\[ + \sum K_d + 1 \begin{bmatrix} K_{pu} & 1 & 1 \\ K_d & 1 & 1 \end{bmatrix} \left[ \gamma_{K_{pu}}(-\omega'_{pu}, \omega_{pu}, \omega_{pr}) + (-1)^{K_d} \gamma_{K_{pu}}(-\omega'_{pu}, \omega_{pr}, \omega_{pu}) \right] \]

\[ + (-1)^{K_{pu}} \gamma_{K_{pu}}(\omega_{pu}, -\omega'_{pu}, \omega_{pr}) + (-1)^{K_d + K_{pu}} \gamma_{K_{pu}}(\omega_{pu}, \omega_{pr}, -\omega'_{pu}) \right], \]  

where

\[ \gamma_{K_d}(\omega_m, \omega_n, \omega_q) = \frac{N_i^3}{\epsilon_0 \hbar^3} \sum_{gee'f} \sum_{\alpha=1}^4 P(g) I_{gee'f}^\alpha(\omega_m, \omega_n, \omega_q) M_{gee'f}^{K_d}. \]
\[ M_{\text{gee}'f}^{K_d} = \frac{1}{2K_d + 1} \sum_{q_0q_1q_2q_3} C^{K_dQ}_{1q_01q_1} C^{K_dQ}_{1q_21q_3} \langle g|d_{q_0}|e\rangle \langle e|d_{q_1}|f\rangle \langle f|d_{q_2}|e'\rangle \langle e'|d_{q_3}|g\rangle, \]

\[ I_1^{\text{gee}'f}(\omega_1, \omega_2, \omega_3) = -I_{\text{ge}}(\omega_3)I_{gf}(\omega_2 + \omega_3)I_{\text{ge}'f}(\omega_1 + \omega_2 + \omega_3), \]

\[ I_2^{\text{gee}'f}(\omega_1, \omega_2, \omega_3) = I_{\text{ge}}(\omega_2)I_{gf}(\omega_2 + \omega_3)I_{\text{ge}'f}(\omega_1 + \omega_2 + \omega_3) \]
\[ + [I_{\text{ge}}(\omega_2) + I_{\text{ge}'g}(\omega_1)]I_{\text{ge}'}e(\omega_2 + \omega_3)I_{\text{ge}'f}(\omega_1 + \omega_2 + \omega_3), \]

\[ I_3^{\text{gee}'f}(\omega_1, \omega_2, \omega_3) = -I_{\text{ge}e f}(\omega_1, -\omega_2, -\omega_3), \]

\[ I_4^{\text{gee}'f}(\omega_1, \omega_2, \omega_3) = -I_{\text{ge}e f}(\omega_1, -\omega_2, -\omega_3), \]

where

\[ I_{ab}(\omega) = \frac{i}{\omega - \omega_{ab} + i\Gamma_{ab}}. \]

For small damping we can simplify the expression

\[ I_2^{\text{gee}'f}(\omega_1, \omega_2, \omega_3) = I_{\text{ge}}(\omega_2)I_{gf}(\omega_2 + \omega_3)I_{\text{ge}'}g(\omega_1). \]

Here we can discuss diagrams.

Here is a discussion about \( M_{K_{pu}}^{(lmn)} \). Here and below we omit indices \( \text{gee}'f \) for brevity. One can consider the following fourth-order tensor

\[ M_{ijkl} = \langle g|d_i|e\rangle \langle e|d_j|f\rangle \langle f|d_k|e'\rangle \langle e'|d_h|f\rangle. \]

One can note that \( M_{K_{pu}}^{(123)} \) are the corresponding isotropic invariants of the tensor \( M_{ijkl} \):

\[ M_0^{(123)} = \sum_{ij} \frac{1}{3} M_{ijij}, \]

\[ M_1^{(123)} = \frac{1}{3} \sum_{ij} \left( \frac{1}{2} M_{ijij} - \frac{1}{2} M_{ijji} \right), \]

\[ M_2^{(123)} = \frac{1}{5} \sum_{ij} \left( \frac{1}{2} M_{ijij} + \frac{1}{2} M_{ijji} - \frac{1}{3} M_{ijjj} \right). \]

Other permutations \( (lmn) \) in \( M_{K_{pu}}^{(lmn)} \) correspond to the permutation of indices \( jkh \) in the tensor \( M_{ijkl} \).
IV. DISCUSSION

A. Analysis of the general expression

B. Modulation of polarization and comparison with experiment

V. CONCLUSIONS

VI. CONFLICT OF INTERESTS

There are no conflicts to declare.

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Appendix A: The components of the matrix $E_{KQ}(n)$ of elliptically polarized light in the beam direction frame

We consider the components of the polarization matrix $E_{KQ}(n)$ in eq. (??) in the general case of elliptically polarized (EP) light with respect to the beam direction frame (BDF) $X'Y'Z'$ shown in Fig. ??, where the vector $n \parallel Z'$ is the direction of light beam propagation, axis $Y'$ coincides with the nodal line, and the angles $\alpha$ and $\beta$ specify the direction of the vector $n$ in the laboratory frame XYZ.

The complex ort of EP light beam propagating along vector $n$ can in general be written as a linear combination of the Cartesian orts $e_{x'}$ and $e_{y'}$ in Fig. ?? both laying in the plane perpendicular to the direction $n$:

$$e(\gamma) = e_{x'} \cos \gamma + e_{y'} e^{i\delta} \sin \gamma,$$

(A1)

where $\gamma$ is the angle of rotation of the polarization ort $e$ about the direction $n$ with respect to the axis $X'$ and $\delta$ is a phase difference.
In the case of linearly polarized light the phase difference $\delta$ in eq. (A1) is equal to zero and in the case of right/left handed circularly polarized light $\delta = \pm \pi/2$ and $\gamma = \pi/4$.

Using the transformation matrices between the laboratory and body frame coordinates [10, 18] the orts $e_x', e_y'$ in eq. (A1) can be expanded over the laboratory frame orts $e_x, e_y, e_z$ in Fig. ?? as follows:

$$e_x' = e_x \cos \alpha \cos \beta + e_y \sin \alpha \cos \beta - e_z \sin \beta,$$  \hspace{1cm} (A2)

$$e_y' = -e_x \sin \alpha + e_y \cos \alpha$$  \hspace{1cm} (A3)

Combining eqs. (A2), (A3), and (A1) the spherical components of the EP light can be readily written as:

$$e_0 = -\sin \beta \cos \gamma$$  \hspace{1cm} (A4)

$$e_1 = -\frac{1}{\sqrt{2}} \left( \cos \beta \cos \gamma + i e^{i\delta} \sin \gamma \right) e^{i\alpha}$$  \hspace{1cm} (A5)

$$e_{-1} = \frac{1}{\sqrt{2}} \left( \cos \beta \cos \gamma - i e^{i\delta} \sin \gamma \right) e^{-i\alpha}.$$  \hspace{1cm} (A6)

Substituting eqs. (A4)–(A6) into eq. (??) the components of the matrix $E_{KQ}(n)$ of EP light propagating along the direction $n$ can be presented in the form:

$$E_{00}(n) = -\frac{1}{\sqrt{3}}$$ \hspace{1cm} (A7)

$$E_{10}(n) = \frac{1}{\sqrt{2}} \cos \beta \sin 2\gamma \sin \delta$$ \hspace{1cm} (A8)

$$E_{11}(n) = -E_{-1}^*(n) = -\frac{1}{2} e^{i\alpha} \sin \beta \sin 2\gamma \sin \delta$$ \hspace{1cm} (A9)

$$E_{20}(n) = \frac{1}{\sqrt{6}} \left[ \frac{3}{2} \sin^2 \beta \cos 2\gamma - \frac{1}{2} (3 \cos^2 \beta - 1) \right]$$ \hspace{1cm} (A10)

$$E_{21}(n) = -E_{-2}^*(n) = \sin \beta \cos \gamma \left[ \cos \beta \cos \gamma + i \sin \gamma \sin \delta \right] e^{i\alpha}$$ \hspace{1cm} (A11)

$$E_{22}(n) = E_{-2}^*(n) = \frac{1}{2} \left[ \cos^2 \beta \cos^2 \gamma - \sin^2 \gamma + i \cos \beta \sin 2\gamma \cos \delta \right] e^{2i\alpha}. \hspace{1cm} (A12)$$

In the case of circularly polarized light eqs. (A7)–(A12) are equivalent to the earlier tabulated expressions [10, 19, 20].

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