Theory of coherent anti-Stokes Raman scattering for mesoscopic particle with complex molecules: angular-dependent spectrum

C. H. Raymond Ooi\textsuperscript{a,b,*}

We present a microscopic theory of nonlinear scattering of mesoscopic particle that may be composed of complex molecules. We predict that the spectrum of the scattered field depends on the angle of observation. Transform theory is used to compute the third-order susceptibility for coherent anti-Stokes Raman scattering (CARS) of molecules with known absorption spectrum and vibrational modes. By incorporating the theory into an integral scattering formula, we develop a rigorous theory which leads to powerful numerical experimentation of nonlinear optical process in mesoscopic systems composed of complex molecules and driven by laser pulses with arbitrary shape and spectral content. We obtain an expression for spectral dependent CARS field which includes multiple internal reflection and refraction of the incident fields via Mie theory. The theory is used to study the variations of the CARS spectra and intensity on laser parameters and direction of detection. High-resolution spectra computed for hybrid CARS scheme shows that the relative intensities of the characteristic peaks in the CARS spectrum depend on the direction of detection. This effect can be explained by the interference between the linear response (absorption and dispersion) and the four-wave mixing process in the mesoscopic medium. The theory is useful for nonlinear spectroscopy, microscopy and nanophotonics involving small particles. Copyright © 2009 John Wiley & Sons, Ltd.

Keywords: CARS spectrum; mesoscopic particle; transform theory; angular dependence; Mie scattering

Introduction

Coherent anti-Stokes Raman spectroscopy (CARS) is a nonlinear spectroscopic technique that has been significantly advanced in the fields of nonlinear optical microscopy through high-resolution imaging and excellent chemical selectivity of biological tissues and cells\cite{1,2,3}, measurements of gaseous properties in combustive environment\cite{4}, surface enhanced Raman spectroscopy\cite{5}, and a promising tool for spectroscopic identification of molecular species\cite{6} in remote location.\cite{7}

Spectroscopic resolution in CARS has been demonstrated with nanosecond laser pulses.\cite{8} The use of ultrashort laser pulses in CARS leads to a significant progress in laser spectroscopy. The many successful applications of CARS microscopy and spectroscopy are attributed to: (1) the effective methods for circumventing nonresonant (NR) background, (2) collective excitations of multi-vibrational modes via engineered laser pulses and (3) noninvasive and labeled-free probing. The usefulness of ultrashort laser pulses has gone a long way through the control of chemical reactions in femtochemistry,\cite{9} for example, via prepared superposition of initial states\cite{10} and pump-probe delay technique.\cite{11} CARS spectroscopy has been performed via single-beam\cite{12,13} coherently engineered by spatial light modulation, optimal control\cite{14} and tunable supercontinuum source from photonic-crystal fibers.\cite{15,16} Recently, CARS is also used to study molecules in background plasmas\cite{17} and terahertz regime,\cite{18} simultaneous detection of multi-species gas\cite{19} and determination of temperature\cite{20} and collision induced dephasing and rotational energy transfer.\cite{21}

Good reviews on the fundamentals, developments and applications of CARS technique were given by Kiefer\cite{22} and Zheltikov.\cite{23} However, the theoretical aspect is equally important and challenging. \textit{Ab initio} calculation of CARS spectra\cite{24} and density matrix approach\cite{25} are possible theoretical techniques for molecules. However, these techniques are not practical for complex molecules of biological origin. It would be useful to have a rigorous but practical theoretical scheme that can compute the CARS spectra conveniently from accessible data. Such theory is available, called transform theory.\cite{26} The theory relates\cite{27} absorption spectra to the CARS susceptibility $\tilde{\chi}^{(3)}$ and has been shown to give good agreement with the sum-over states method\cite{28,29} and experimental data.\cite{30} Recently, the theory has been used to compute the time dependent polarization\cite{31} under pulsed laser excitations.

In this paper, we use the transform theory to obtain the CARS signal in spectral domain from a mesoscopic particle composed of a collection of complex molecules driven by arbitrarily shaped laser pulses with intensity within the perturbative nonlinear regime. The theory provides a powerful...
access to numerical experimentation for studying the variations of the CARS signal (spectra, intensity) on laser parameters and the direction of detection. It is the first (to our knowledge) to incorporate a rigorous theory capable of describing nonlinear spectroscopy of complex molecules to mesoscopic systems.

The aim is to study the effect of finite-size particle composed of complex molecules on the angular dependence of the scattered CARS spectra. For a spherical microparticle, optical refraction and reflection give lensing effect that leads to dramatic enhancement of backscattered light.[7] How does the mesoscopic size of the particle affect the CARS spectra when the four-wave mixing signal overlaps with the absorption spectra? It is a common belief that the spectra from the microparticle should be independent of the angle of observation. On the basis of analytical and numerical results, we will show how the CARS spectra from mesoscopic particle vary significantly with the observation angle. The finding would be relevant to works in nonlinear microscopy and spectroscopy involving mesoscopic particles like aerosols, colloidal particles, nanoparticles and bacteria spores, particularly for standoff real-time identification of airborne particles using CARS.[7,33] We predict that the angle of observation can be a new variable for multidimensional spectroscopy, just like the time-resolved CARS spectroscopy[34] yields valuable multidimensional information of the internal dynamics of molecular systems in time-frequency frame.

Below, we review the techniques for suppression of the NR background and identify the conditions where it can be neglected in subsequent formulation. Then we present a practical relation for the third-order susceptibility $\tilde{\chi}^{(3)}_{\text{pqr}}$ expressed in terms of a response function $\Phi$ that is related to the absorption spectrum. A pedagogically unified and self-contained transform theory is given in the Appendices to show the derivation of the expression. Following, we elaborate on the physics behind an integral formula that is used for describing the far field scattered by a dielectric microsphere. Then, the origin of the angular-dependent CARS spectrum is discussed and we incorporate the transform theory into the integral formula and obtain the main expression for the electric field of the CARS signal from a microparticle composed of real molecules driven by arbitrary laser pulses. In the following section, we study the spatial distribution and polarization of the fields inside the particle through the Lorenz-Mie theory. Then, we use realistic models for absorption spectrum and vibrational modes to compute the CARS spectra and study the dependency of the spectra on the angle of observation for various laser parameters. Finally, the last section provides the summary and outlook on the potential applications of the theory in connection with existing works.

Nonresonant Background

The success of femtosecond CARS as a versatile spectroscopic and imaging technique is due to the ability to overcome the NR background against the spectroscopic signal. Delayed probing of free induction decay[35] gives the CARS signal without NR background. The so-called hybrid CARS excites the Raman coherence with broadband pulses followed by a delayed narrowband probe pulse, producing a strong resonant CARS[36] Other successful techniques of NR suppression are multiplex CARS,[37] combined time-domain and frequency-domain CARS with supercontinuum pulses,[38] and FTCARS, a technique based on Fourier transform of CARS signal in time domain with interferometric setup.[39] Pulse shaping method[40] and polarization excitation technique[41] have also been successfully implemented to suppress the NR signal. When the NR signal is unavoidable, there are clever signal detection/processing techniques to remove the NR signal, such as heterodyne detection[42] and epi-detection scheme.[43] The symmetry property of Gouy phase shift in focused laser field can also be used to cancel the NR signal when a resonant medium is forming a planar interface with an NR medium.[43]

Many of the above CARS schemes incorporated the following condition(s) to some extent for NR suppression. First, the electronic resonant enhancement (ERE)[44,45] enhances the resonant CARS signal when a narrowband probe laser is tuned close to a few electronic transition frequency) and $\Gamma^{-1}$, i.e. $10^{-15} - 10^{-13}$. Hence, in the presence of quasi-resonant, narrowband and delayed probe pulse, the NR contribution to the susceptibility may be neglected. The quasi-resonant CARS described by complex susceptibility is sufficient to provide well-defined spectroscopic features for the purpose of showing the angular dependence of CARS signal.

CARS Susceptibility and Polarization via Transform Theory

There are various processes that contribute to the expression of the third-order susceptibility tensor $\tilde{\chi}^{(3)}_{\text{pqr}}$. In order to study the spectral dependence, we need a microscopic expression of $\tilde{\chi}^{(3)}_{\text{pqr}}$ that can describe real molecules. The previously used few-level atomic model[7] is no longer valid, and the density matrix approach[25,47] is no longer practical. The multilevel perturbation theory[44] serves as a standard starting point. We focus on the third-order process that describes quasi-resonant CARS as depicted in Fig. 1 with the corresponding third-order susceptibility tensor in frequency domain,[48]

$$\tilde{\chi}^{(3)}_{\text{pqr},\alpha_1\alpha_2\alpha_3\alpha_4} = \sum_{g,t} \frac{N\delta(\omega - \omega_t)}{V_h^3} \left( \langle g | \hat{d}_g | h \rangle \langle h | \hat{d}_t | i \rangle \langle i | \hat{d}_r | g \rangle \right) + \sum_{h'} W_{gh} \left( \langle h' | \hat{d}_h | g' \rangle \langle g' | \hat{d}_t | h' \rangle \langle h' | \hat{d}_r | g' \rangle \right) - W_{ht} \left( \langle h' | \hat{d}_h | g' \rangle \langle g' | \hat{d}_t | h' \rangle \langle h' | \hat{d}_r | g' \rangle \right)$$

where $W_{gh}$ is the vibrational statistical weight in ground electronic state.
are shown in Fig. 2.

The nonlinearly generated/scattered signal in the far field from the pump pulses backscattered from the exciting pulses is shown in Fig. 2. The relationship between the susceptibility tensor can be expressed as

\[ \tilde{\chi}^{(3)}_{pqrs}(\omega) = -\frac{N}{\hbar^3} C_{pqrs} \left( \frac{\Phi(\omega)}{\omega_p - \omega_s - \omega_t} \right) + \sum_j \frac{\lambda_j^2}{\hbar} \left\{ \tilde{\tau}_j + 1 \right\} A_j^{(s)}(\omega_p, \omega_t) + \tilde{\tau}_j A_j^{(i)}(\omega_p, \omega_t) \right\} 
\]

where \( \alpha_j^{(s)}(\omega_p) = \Phi(\omega_p) - \Phi(\omega_p \pm \omega_t) \) with the complex linear response function \( \Phi(\omega) \) defined by Eqsns (A31) and (A33), \( \omega_T = \omega_p + \omega_s - \omega_t, \tilde{\tau}_j = \{ \delta_h / k_B T - 1 \}^{-1} \) the thermal occupation number, \( C(\omega) = \frac{N(\omega - \omega_T)}{\hbar k_B T} \) and \( C_{pqrs} = \epsilon^{s_p} \epsilon^{s_q} \epsilon^{r_p} \epsilon^{r_q} \) is the product of electronic transition dipole moments. The populations in the ground vibronic levels depend on the temperature \( T \).

The zeroth order and first-order Raman processes correspond to the first and second lines of Eqn 1, respectively. Expression for second-order Raman processes is given by Eqn (A37) in Appendix A5. schematic representations for the Raman processes are shown in Fig. 2.

\[ \tilde{\chi}_{pqrs}^{(3)}(\omega) = -\frac{N}{\hbar^3} C_{pqrs} \left( \frac{\Phi(\omega)}{\omega_p - \omega_s - \omega_t} \right) + \sum_j \frac{\lambda_j^2}{\hbar} \left\{ \tilde{\tau}_j + 1 \right\} A_j^{(s)}(\omega_p, \omega_t) + \tilde{\tau}_j A_j^{(i)}(\omega_p, \omega_t) \right\} 
\]

where \( \alpha_j^{(s)}(\omega_p) = \Phi(\omega_p) - \Phi(\omega_p \pm \omega_t) \) with the complex linear response function \( \Phi(\omega) \) defined by Eqsns (A31) and (A33), \( \omega_T = \omega_p + \omega_s - \omega_t, \tilde{\tau}_j = \{ \delta_h / k_B T - 1 \}^{-1} \) the thermal occupation number, \( C(\omega) = \frac{N(\omega - \omega_T)}{\hbar k_B T} \) and \( C_{pqrs} = \epsilon^{s_p} \epsilon^{s_q} \epsilon^{r_p} \epsilon^{r_q} \) is the product of electronic transition dipole moments. The populations in the ground vibronic levels depend on the temperature \( T \).

The zeroth order and first-order Raman processes correspond to the first and second lines of Eqn 1, respectively. Expression for second-order Raman processes is given by Eqn (A37) in Appendix A5. Schematic representations for the Raman processes are shown in Fig. 2.

By identifying \( \omega_p, -\omega_q, \omega_s \) as \( \omega_1, \omega_2, \omega_3 \) and defining \( \Omega = \omega_1 + \omega_2 \) the susceptibility tensor can be expressed as

\[ \tilde{\chi}_{pqrs}^{(3)}(\omega) = \sum_j \frac{\lambda_j^2}{\hbar} \left\{ \tilde{\tau}_j + 1 \right\} A_j^{(s)}(\omega_p, \omega_t) + \tilde{\tau}_j A_j^{(i)}(\omega_p, \omega_t) \right\} 
\]

where \( \alpha_j^{(s)}(\omega_p) = \Phi(\omega_p) - \Phi(\omega_p \pm \omega_t) \) with the complex linear response function \( \Phi(\omega) \) defined by Eqsns (A31) and (A33), \( \omega_T = \omega_p + \omega_s - \omega_t, \tilde{\tau}_j = \{ \delta_h / k_B T - 1 \}^{-1} \) the thermal occupation number, \( C(\omega) = \frac{N(\omega - \omega_T)}{\hbar k_B T} \) and \( C_{pqrs} = \epsilon^{s_p} \epsilon^{s_q} \epsilon^{r_p} \epsilon^{r_q} \) is the product of electronic transition dipole moments. The populations in the ground vibronic levels depend on the temperature \( T \).

The zeroth order and first-order Raman processes correspond to the first and second lines of Eqn 1, respectively. Expression for second-order Raman processes is given by Eqn (A37) in Appendix A5. Schematic representations for the Raman processes are shown in Fig. 2.

By identifying \( \omega_p, -\omega_q, \omega_s \) as \( \omega_1, \omega_2, \omega_3 \) and defining \( \Omega = \omega_1 + \omega_2 \) the susceptibility tensor can be expressed as

\[ \tilde{\chi}_{pqrs}^{(3)}(\omega) = \sum_j \frac{\lambda_j^2}{\hbar} \left\{ \tilde{\tau}_j + 1 \right\} A_j^{(s)}(\omega_p, \omega_t) + \tilde{\tau}_j A_j^{(i)}(\omega_p, \omega_t) \right\} 
\]

where \( \alpha_j^{(s)}(\omega_p) = \Phi(\omega_p) - \Phi(\omega_p \pm \omega_t) \) with the complex linear response function \( \Phi(\omega) \) defined by Eqsns (A31) and (A33), \( \omega_T = \omega_p + \omega_s - \omega_t, \tilde{\tau}_j = \{ \delta_h / k_B T - 1 \}^{-1} \) the thermal occupation number, \( C(\omega) = \frac{N(\omega - \omega_T)}{\hbar k_B T} \) and \( C_{pqrs} = \epsilon^{s_p} \epsilon^{s_q} \epsilon^{r_p} \epsilon^{r_q} \) is the product of electronic transition dipole moments. The populations in the ground vibronic levels depend on the temperature \( T \).

The zeroth order and first-order Raman processes correspond to the first and second lines of Eqn 1, respectively. Expression for second-order Raman processes is given by Eqn (A37) in Appendix A5. Schematic representations for the Raman processes are shown in Fig. 2.

\[ \tilde{\chi}_{pqrs}^{(3)}(\omega) = \sum_j \frac{\lambda_j^2}{\hbar} \left\{ \tilde{\tau}_j + 1 \right\} A_j^{(s)}(\omega_p, \omega_t) + \tilde{\tau}_j A_j^{(i)}(\omega_p, \omega_t) \right\} 
\]
The angular dependence enters through the amplitude $J_0$ and the phase $e^{-i\kappa(k_0)}$ in Eqn (13). For $\Theta = 90^\circ$, the linear response has no effect on the phase but has maximum effect on the amplitude. Here, the field is amplitude modulated by $J_0(k_0)\sin \theta$ with generally decreasing signal at higher frequencies. For $\Theta = 0$ and $180^\circ$ we have $J_0(0) = 1$ and the field is phase modulated by $e^{-i\kappa(k_0)}\cos \theta$.

In general, the angular dependence of the spectra stems from the linear response of $n(\omega)$ and not from the CARS polarization $\tilde{P}_p^{(3)}(\omega)$ or the Lorenz-Mie theory. It is due to the interference between the four-wave mixing process and linear response (dispersion and absorption). The CARS spectrum would still depend on the observation angle even if $\tilde{P}_p^{(3)}$ is independent of $\omega$, as in the case of truly off-resonant CARS. Thus, the angular dependence is always present unless $n(\omega)$ becomes independent of $\omega$.

### CARS Field for Mesoscopic Particle

Now, we proceed to obtain the main expression upon combining the transform theory in spectral domain (Eqns (6)) and the integral formula (Eqn (11)), giving

$$\tilde{E}(\omega, r) = -K(\omega) \sum_{l,p,q,r,s} \tilde{W}_{p-q} \Phi(\omega) \int \Phi(\omega_1) \Psi^{(0)}(\omega, \omega_1) d\omega_1$$

with the geometrical and field dependent factor

$$\Psi^{( \pm)}(\omega, \omega_1, \omega_2) = \frac{1}{V} \int \frac{dV e^{-i\kappa(k_0)/(\Theta, \Phi, \phi, \rho)}}{V}$$

where $\kappa_{\pm} = \pm \frac{m_j}{\xi}$ with the finite values of $m_j$ taken into account the first non-Condon effect due to Jahn-Teller interaction.

The $\Psi^{(0)}(\omega, \omega_1, \omega_2)$ is obtained by setting $\nu_j = 0$ in $\Gamma^{(\pm)}_{r_0}$. The coefficient $K(\omega) = \frac{N \omega^{2}}{2\pi e_R^2} \frac{\alpha^{2}}{Z^2}$ is frequency dependent with $k(\omega) = n(\omega)/c$ and the refractive index $n(\omega) = [1 + \chi(\omega)]^{1/2}$ is obtained from the relationship between complex susceptibility and $\Phi$.

$$B(\omega) = \chi(\nu_2) \frac{\text{Re} \Phi(\nu_2)}{\Phi(\nu_2)}$$

The $B$ can be determined from refractive index, for example, $n'(\nu_2) \sim 1.52$ taken from Ref. [52].

We can now rewrite Eqn (7) as

$$\Gamma^{(\pm)}_{r_0}(\nu_2)$$

$$= \frac{\tilde{E}(\omega_1, \omega_2) \tilde{E}(\nu_2, \omega_1, \omega_2)}{\Omega \pm \nu_j \pm i\nu^{\prime}}$$

$$\int d\Omega$$

with geometrical function

$$F(\Theta, \omega) = \sum_{l,p,q,r,s} \tilde{W}_{p-q} \Phi(\omega)$$

and $\Theta$-dependent wavevector $k(\omega) = \omega n(\omega)/c$ and $k = k_p - k_{\pm} + k_c$. The $\omega$ and $\Theta$-variables in $G(\rho, \theta)$ are still not separable.
\[ \psi_{q_1}(\omega_1, \omega) = \sum_{\nu} \int \frac{E^P_{q_1} (\omega_1 - \nu) E^C_{\nu} (\omega - \nu) F_{q_1} (\Omega, \omega_1, \omega; \Theta, \Phi)}{\Omega \pm \nu + i \Gamma} d\Omega \]

\[ F_{q_1} (\Omega, \omega_1, \omega) = \frac{1}{V} \int \sum_j \int e^{-i \nu \Omega (\nu, \phi, \theta)} u^*_j (\nu, \omega_1) u_j (\nu, \omega - \nu - \Omega) dV \]

The integration in \( \psi_{q_1}(\omega_1, \omega) \) can be performed, giving the final expressions

\[ \psi_{q_1}(\omega_1, \omega) = 2 \pi i \sum_{\nu} \int \left[ \phi (\omega) \tilde{E}_{q_1}^P (\omega) \right] d\omega_1 \]

\[ + \sum_{j} | \xi |^2 \left( \tilde{\gamma}_j + 1 \alpha_j \right)^{-1} (\omega) E^C_{\nu} (\omega - \nu + i \Gamma) \]

\[ \times \int \left[ \tilde{\gamma}_j^{-1} (\omega) \tilde{E}_{q_1}^P (\omega - \nu + i \Gamma) \right] F_{q_1} (\Omega, \omega_1, \omega) d\omega_1 \]

\[ + \tilde{\gamma}_j^{-1} (\omega) \tilde{E}_{q_1}^P (\omega + \nu + i \Gamma) \int \tilde{\gamma}_j (\omega) \tilde{E}_{q_1}^P (\omega + \nu + i \Gamma) d\omega_1 \]

\[ \tilde{E}_{q_1}^P (\omega) F_{q_1} (\Omega, \omega_1, \omega) d\omega_1 \]

(24)

**Focused Internal Fields**

The internal fields depend on position and can be obtained from the incident fields by using the Lorenz-Mie theory.** The incident laser fields can be written as \( \tilde{E}_{\nu} (z, t) = \tilde{E}_{\nu} (r) e^{-i \nu \tau} \) for \( z \)-polarized where \( \tau = t - z/c \). In particular, we assume Gaussian pulse-shape \( \tilde{E}_p (z, t) = \tilde{E}_p e^{-i \nu \tau} e^{-i (t - \tau)^2 / \sigma^2} e^{-i \nu \tau} \) with the spectral profile

\[ \tilde{E}_p (z, \omega) = \frac{k \sigma}{\sqrt{\pi}} \tilde{E}_p e^{-i \nu \tau} e^{i (t - \tau)^2 / \sigma^2} \]

(25)

which may be rewritten as \( \tilde{E}_{\nu} (z, \omega) = \tilde{E}_p (\omega) e^{i k z} \) where \( k = \omega / c \) and \( \tilde{E}_p (\omega) = \frac{k \sigma}{\sqrt{\pi}} \tilde{E}_p e^{-i \nu \tau} e^{i (t - \tau)^2 / \sigma^2} \). Note that \( z \) and \( \omega \) variables in \( e^{i k z} \) cannot be separated. The spectral intensities \( \tilde{I} (\omega) = | \tilde{E}_p (\omega) |^2 \) are plotted in Fig. 4(c). The fields inside the microparticle can be written as \( \tilde{E}_p (r, \omega) = \tilde{E}_p (r) u_\nu (r, \omega) \), with \( \alpha \) being the polarization index. The \( u_\nu \) functions are computed from the Lorenz-Mie theory as was done in our previous work.** The \( u_\nu \) depend \( \omega \) through the wavevector \( k(\omega) = n(\omega) c / \omega \), where the refractive index \( n(\omega) \) depends on the Fourier frequency \( \omega \) and not the carrier frequency \( \nu \) of a laser. Therefore, the spatial

**Results and Discussion**

We compute the CARS spectra using Eqn (24) which based on the susceptibility up to the first order, modeled absorption profile and vibrational modes. We use the absorption profile for ZnPC(53) as a model (Fig. 4(a)). The vibrational lines in Fig. 4(b) are modeled by Lorenzian profile across the Raman shift \( \nu_R \) by the expression

\[ g(\nu_R) = \sum_j \frac{| \xi_j |^2 \Gamma_j}{(\nu - \nu_j)^2 + \Gamma_j^2} \]

(26)
Figure 4. (a) Real and imaginary parts of the complex refractive index \( n(\omega) \) corresponding to three absorption peaks at wavenumbers 14 700, 15 400 and 16 350 cm\(^{-1}\) with width 250 cm\(^{-1}\). (b) Shifted Raman (vibrational) wavenumber based on Eqn (26) where each line peaks at \( \nu_c + \nu_j \) (with parameters \( \nu_j, \Gamma_j \) given below in e). (c) Spectral intensities \( I_f^{\nu_2} / V^2 m^{-2} s^2 \) of the three incident laser pulses from Eqn (25), (d) Intensities of CARS spectra in the forward \( I_{xx}^{\nu_2} / V^2 m^{-2} s^2 \), orthogonal \( I_{xy}^{\nu_2} / V^2 m^{-2} s^2 \) and backward \( I_{yy}^{\nu_2} / V^2 m^{-2} s^2 \) directions. (e) 3D plots of the CARS intensities \( I_{\alpha} = |\tilde{E}_{\alpha}(\omega, \Theta)|^2 \) (\( \alpha = x, y, z \) components) clearly show the spectra depend on the angle of observation/detection \( \Theta \). Parameters for non-Condon parameters \( \xi_j \) are given below in e). Laser carrier wavenumbers (in cm\(^{-1}\)) are \( \nu_p = 14 387 \text{ cm}^{-1} = \nu_c, \nu_s = \nu_p - \text{mean } \{\nu_j\} \); thermal temperature 0.2 K; duration of pulses \( \sigma_p = \sigma_s = 10, \sigma_c = 7 \sigma_p \); delay of control pulse \( \tau_c - \tau_p = \Gamma_1^{-1} \); particle properties \( \rho_o = 0.5 \mu m, N = 5 \times 10^8 \text{ m}^{-3} \); refractive indices \( n(\nu_j) = 1.52 + i0.129, n(\nu_p) = 1.53 + i0.229, n(\nu_s) = 1.525 + i0.329 \) and detection distance \( R = 1 \text{ km} \). Peak electric field \( E_0 = 2.2 \times 10^9 \text{ V m}^{-1} \) is taken to be the same for all pulses. This figure is available in colour online at www.interscience.wiley.com/journal/jrs.
Six wavenumbers are used to represent the main vibrational frequencies of typical bacterial spores. Note that the linewidths of the absorption spectra and the vibrational spectra are determined by \( \gamma \) and \( \Gamma \), respectively.

As an example to illustrate the theory, we use the laser parameters of fs/ps CARS or hybrid CARS. In this scheme, broadband pump and Stokes pulses excite a wide range of vibrational modes and establish the coherences. Then a narrowband control pulse scatters off the coherences to generate the CARS signal. The scheme provides good spectral and temporal resolution and can give an overall enhancement of the CARS signal. For simplicity, the carrier frequency of the control pulse is taken to be the same as the pump pulse \( \nu_p = 2.71 \times 10^{15} \text{ s}^{-1} \) (or wavenumber 14,387 cm\(^{-1}\)), which falls in the mean value of the absorption lines. The pump and Stokes pulses overlap in time. The spectral profiles of the laser pulses are shown in Fig. 4(c).

The control pulse has a width of \( \sigma_c = 7\sigma_p \) and delayed by one vibrational period from the pump pulse. In practice, this serves to suppress the NR signal.

**Spatial components:** Figure 4(d) shows that the backward (\( \Theta = 180^\circ \)) signal is only about 100 times weaker than the forward (\( \Theta = 0^\circ \)) signal, i.e. \( f_{\text{for}}/f_{\text{back}} \approx 100 \). The CARS spectra and intensities for \( x \) and \( y \) polarizations are identical only in the forward and backward directions,

\[
I_x(\omega, \Theta = 0) = I_x(\omega, \Theta = 0) \quad (27)
\]
\[
I_y(\omega, \Theta = 180^\circ) = I_y(\omega, \Theta = 180^\circ) \quad (28)
\]

This is due to the radial symmetry around the laser axis, which is along the \( z \)-axis. There is no \( z \)-component in these two directions. Although the internal field has no \( y \)-component (Fig. 3), there is a \( y \)-component in the far field, generated via four-wave mixing. The signal detected at \( \Theta = 90^\circ \) (orthogonal to the axis of incident lasers) is \( y \)-polarized and \( z \)-polarized, with

\[
I_y(\omega, 90^\circ) = I_z(\omega, 90^\circ) \quad (29)
\]

but there is no \( x \)-component signal. Thus, the signal is orthogonal to the polarization of the incident laser fields, which remind us of the Brewster effect. For other directions, the spectra for both polarizations are quite different, as seen in Fig. 4(e). By comparing these CARS spectra with reference to the absorption spectrum of Fig. 4(a), it might be possible to separate the effects due to linear process and nonlinear process. The peaks in the CARS spectra of Fig. 4(d) contain essential information on the vibrational modes and the excited levels. The spectra for forward and backward directions appear quite different although the main peaks are present in both cases. Some peaks are shifted due to the interference with the linear absorption profile.

**Angular dependence:** The angular dependence of the CARS spectra becomes more evident in the 3D plots of Fig. 4(e) for \( x \), \( y \) and \( z \) polarizations. This finding might be a surprise or in contrast to usual expectation, but it has been justified analytically above and numerically in Fig. 4. As explained, the physics can be understood as due to the strong frequency dependence in the linear response of the mesoscopic matter. Unlike in the gas phase, the wavenumber \( k(\omega) = \omega(n(\omega))/c \) in optically dense medium like microparticle depends strongly on the frequencies around optical absorption resonances. The linear response characterized by the complex function \( n(\omega) \) can interfere with the purely (microscopic) process of CARS at molecular level through (P3). We emphasize that the effect of angular-dependent CARS spectra occurs when the linear resonances overlap with the CARS peaks. We have verified by numerical simulations that when the control laser frequency \( \nu_c \) is tuned away from the absorption lines, the angular-dependent effect vanishes.

**High-resolution CARS spectra:** The characteristic lines of the vibrational modes of Fig. 4(b) are not well resolved in the CARS spectra of Fig. 4(d) and (e). All the peaks are spectrally broadened by the finite bandwidth of the pulses. By using a longer control pulse \( \sigma_c = 38\sigma_p \) (narrower bandwidth), we obtain high-resolution CARS spectra. Figure 5 shows all the Raman mode lines modeled in Fig. 4 are well resolved. In addition, the relative intensities of the modes in Fig. 5 are different for forward and backward directions. For backward case, the line at carrier wavenumber of the control laser, \( \nu_c = 14,387 \text{ cm}^{-1} \) is suppressed while the lines corresponding to the Raman modes 850 and 1000 cm\(^{-1}\) are enhanced. This is a clear signature of the angular dependence of the CARS spectrum. The presence of the zeroth order laser line at \( \nu_c = 14,387 \text{ cm}^{-1} \) (pump laser line) is due to the first terms in Eqsns (3), (6) or (15). Physically, the line appears because of the short pump and Stokes pulses which provide sufficiently large spectral widths (about \( 3 \times 10^{14} \text{ s}^{-1} \)) such that they contain the same frequency components (spectrum of pulse pump overlaps with the spectrum of Stokes pulse − Fig. 4(c)) to produce the line at \( \nu_c \) via degenerate CARS process. For smaller particle size we find that the spectra remain the same but with much reduced intensities due to the stronger diffraction for a smaller particle.

Finally, by using Stokes and control pulses with longer duration; for example, 0.5 ps, we find that the laser line around \( \nu_c \) disappears in both forward and backward spectra. Here, the first-order resonance depicted in Fig. 2 is no longer satisfied, i.e. there is no components from Stokes and pump with the same frequency, or \( \omega_p \neq \omega_n \). If we use \( \nu_c = \nu_p = 2.51 \times 10^{15} \text{ s}^{-1} \) (or wavenumber 13,325 cm\(^{-1}\)) such that the lines \( \nu_c + \nu_p \) overlap partially with the absorption spectrum we see several effects. First, resonant enhancement of a line near the absorption maxima. Second, the zeroth order line becomes vanishingly weak and disappears. The backscattered CARS technique should also be developed beyond terrestrial applications, i.e. for detection of extraterrestrial biological entities in astrobiological research under space exploration.

**Impact and Outlook**

To summarize, the theory presented above provides a powerful access to study complex molecules with CARS via numerical experimentation. Optimum laser pulse parameters can be found by simulation to obtain high-resolution CARS microspectroscopy. The theory is the first kind to incorporate rigorous molecular physical aspects. The theory could be useful in spectroscopic studies involving nanophotonic materials, such as colloidal systems and nanoparticles. Surface enhancement of CARS by silver nanoparticles was found long time ago. Recently, the effect is being used to detect a single biomolecule in the presence of colloidal silver particles. Exciting developments are underway...
thank to Prof. M. O. Scully for stimulating discussions and support to the summer molecular meeting in 2007.

References

[38] H. Kano, H. Hamaguchi, J. Raman Spectrosc. 2006, 37, 411.

Figure 5. CARS spectra with resolved lines using much longer control pulse, $\sigma_x = 38r_0$. Signals for forward $I^\text{forward} = |\tilde{E}_{x y}(\omega, 0')|^2$, orthogonal $I^\text{orthogonal} = |\tilde{E}_{x y}(\omega, 90')|^2$ and backward $I^\text{backward} = |\tilde{E}_{x y}(\omega, 180')|^2$ directions. Other parameters are the same as in Fig. 4. Identical spectra are obtained for a particle ten times smaller, $\rho = 0.05$ μm but with much reduced intensity (in far field) mainly due to diffraction. This figure is available in colour online at www.interscience.wiley.com/journal/jrs.

in using CARS to study nano-materials like carbon nanotubes, metallic nanoparticles and colloidal quantum dots. Substantial enhancement of CARS signal in hollowed photonic-crystal fiber leads to possibilities of studying microparticles in confined environments. The angular dependence of CARS found in this work is a new nonlinear optical effect which would add more possibilities and applications, for example in remote sensing of biochemical constituents and detection of single molecules in artificially engineered materials.

Acknowledgements

The author would like to thank Prof. W. Kiefer for helpful comments and Prof. I. Tehver for helpful discussions some years ago. Special
APPENDIX: Derivation on transform theory for CARS

In integral representation, Eqn (2) can be rewritten as

\[
\mathcal{X}_{\text{pqrs}}^{(3)}(\omega; \omega_p - \omega_s, \omega_c) = C(\omega) \sum_g W_g \int_0^{\infty} dt' e^{i\omega t'} \left\langle \hat{T}(\hat{h}'; \hat{t}') \right| \left. \hat{T}(\hat{h}; \hat{t}) \right\rangle
\]

\[
\times \left( \frac{1}{\omega_g - \omega_T - i\gamma} \right) \int dt \left( \frac{1}{\omega_h - \omega_T + i\gamma} \right) \int dt' \left( \frac{1}{\omega_s - \omega_T - i\gamma} \right)
\]

\[
= C(\omega) \sum_g W_g \int_0^{\infty} dt' e^{i\omega t'} \left\langle \hat{h}' \right| \hat{d}_p \left| \hat{h} \right\rangle \sum_h e^{-i\omega h t} \int_0^{\infty} dt e^{i\omega t} \left\langle \hat{h} \right| \hat{d}_s \left| \hat{h} \right\rangle
\]

\[
\times \int_0^{\infty} dt' \sum_{\gamma} e^{-i\gamma t'} \int_0^{\infty} dt \sum_{\gamma'} e^{-i\gamma' t} \left( \frac{1}{\omega_r - \omega_T - i\gamma} \right) 
\]

\[
= C(\omega) \sum_g W_g \int_0^{\infty} dt' e^{i\omega t'} \left\langle \hat{h}' \right| \hat{d}_p \left| \hat{h} \right\rangle \sum_h e^{-i\omega h t} \int_0^{\infty} dt e^{i\omega t} \left\langle \hat{h} \right| \hat{d}_s \left| \hat{h} \right\rangle
\]

\[
\times \int_0^{\infty} dt' \sum_{\gamma} e^{-i\gamma t'} \int_0^{\infty} dt \sum_{\gamma'} e^{-i\gamma' t} \left( \frac{1}{\omega_r - \omega_T - i\gamma} \right) 
\]

\[
\times \int_0^{\infty} dt \sum_{\gamma} e^{-i\gamma t} \int_0^{\infty} dt' \sum_{\gamma'} e^{-i\gamma' t'} \left( \frac{1}{\omega_r - \omega_T - i\gamma} \right)
\]

where \( C(\omega) = \frac{N\delta(\omega - \omega_T)}{\hbar^3} \).

By using the free Hamiltonians of the vibrational states in the ground and excited electronic surfaces, respectively. After some rearrange-
where $\hat{r}_\omega = e^{-\beta \tfrac{1}{2} b + \tfrac{1}{2} b^\dagger} \hat{Z} = (1 - e^{-\beta \omega}) e^{-\tfrac{1}{2} \beta \omega b} b$ and $\hat{r}^{\text{eq}} = (g | \hat{d} \cdot \hat{\epsilon}, e) = \hat{d}_p \hat{g} \hat{e} (| g \rangle + \hat{D}^\dagger (| g \rangle) \langle e |)$ and $\hat{D}^\dagger = \sum | p \rangle m_p \hat{r}_p$.

If we assume the Condon approximation $\hat{r}^{\text{eq}} = \hat{r}^{\text{eq}}$ (dipole moment evaluated at vibrational equilibrium position and independent of vibrational state) we can write as [31]

$$A_{pnn}(\xi'_{123}) = C_{pnn} e^{-i \omega \xi'_{123}} A(\xi'_{123}) \tag{A10}$$

where

$$C_{pnn} = \frac{s_p \bar{g}^{\text{eq}}}{s_s \bar{g}^{\text{eq}}}, \quad A(\xi'_{123}) = \langle e^{-i \omega \xi_{123} / \hbar} e^{-i \beta \omega / \hbar} e^{-i \omega \xi_{123} / \hbar} e^{i \beta \omega / \hbar} \rangle$$

$$\approx \langle \hat{S}(t) \rangle = \langle e^{i \omega \xi_{123} / \hbar} e^{-i \beta \omega / \hbar} \rangle$$

$$\approx \langle \hat{S}(t) \rangle = \langle e^{i \omega \xi_{123} / \hbar} e^{-i \beta \omega / \hbar} \rangle$$

where $\xi'_{123} = \xi'_1 + \xi'_2 + \xi'_3$ with $\langle \hat{S}(t) \rangle = e^{i \omega \xi_{123} / \hbar} e^{-i \beta \omega / \hbar}$ and $\langle \hat{S}(t) \rangle = e^{i \omega \xi_{123} / \hbar} e^{-i \beta \omega / \hbar}$. Note that $e^{-i \beta \omega / \hbar}$ commutes with $\hat{r}_\omega$.

### Linear electron-phonon coupling: displacement of harmonic potential

The ground electronic vibrational Hamiltonian is assumed to be harmonic $H_g = \sum \left( b_j^a b_j^a + \tfrac{1}{2} \omega_j \right) \hat{v}_j$ where $\hat{v}_j$ is the vibrational frequency. If the excited electronic Hamiltonian is assumed to be the same shape but displaced, we can use the displacement operator $D \hat{H} = \exp \sum \left( \hat{v}_j b_j^a - \hat{v}_j^a b_j \right)$ to define the shift in the excited vibrational states relative to the ground vibrational states: $H_e = D^\dagger H_e D$. In order to estimate the magnitude of $\xi_j$ (real) the displacement parameter, we expand $\omega^2 = \omega_0^2 + \alpha \omega_0 \sqrt{n_0} / 2$, where $\xi_j = \omega_0 \sqrt{n_0} / \sqrt{2 \alpha + 1}$. From identity $D^\dagger f(b_j) D = f(b_j + \xi_j - \xi_j^a b_j)$, we get

$$H_e = \sum j \left( b_j^a b_j^a + \tfrac{1}{2} \omega_j \right) \hat{v}_j$$

$$= H_g + \sum j \left( 0 \right) b_j^a b_j^a + \tfrac{1}{2} \omega_j \hat{v}_j$$

$$= H_g + \sum j \left( 0 \right) b_j^a b_j^a + \tfrac{1}{2} \omega_j \hat{v}_j$$

where the constant factor $\sum j \xi_j^a \hat{v}_j$ can be combined with the electronic two level separation $\hbar \omega_0$ to give the zero phonon frequency $\omega_{0g} = \omega_{0g} + \sum j \xi_j^a \hat{v}_j$. So, we define the vibronic Hamiltonian,

$$V = \sum \left( 0 \right) b_j^a b_j^a + \tfrac{1}{2} \omega_j \hat{v}_j = H_e - H_g$$

If we take $\xi_j$ as real, and use $(b_j^a b_j^a) \sqrt{n_0} / \sqrt{2 \alpha + 1} = q_j$ we find

$$\sum j \left( 0 \right) b_j^a b_j^a + \tfrac{1}{2} \omega_j \hat{v}_j = \sum j q_j \hat{v}_j$$

which is the linear coupling.

If $\xi_j = 0$, the minima of the harmonic potentials coincide, which means the Franck-Condon factor is finite only for $\langle v | v \rangle$. When $\xi_j$ is finite, the linear coupling gives terms with finite $\langle v | v \rangle$ corresponding to first-order transitions. For quadratic Franck-Condon interaction, the interaction depends on higher products of the bosonic operators.

### Absorption operator

Define $S(t) = e^{i \omega t / \hbar} e^{-i \beta \omega / \hbar}$ as the FT of the absorption operator. We can write

$$\frac{d S}{dt} = -i H_e (H_e - H_g) e^{-i \beta \omega / \hbar} = -S V(t)$$

$$V(t) = e^{i \beta \omega / \hbar} e^{-i \beta \omega / \hbar} = \sum j \left( \alpha^0 \xi_j^a \xi_j + \text{adj} \right) \hat{v}_j$$

Integration gives

$$S(t) = \mathcal{T} \left[ \exp \left( -\frac{i}{\hbar} \int_0^t dt' V(t') \right) \right] \tag{A16}$$

$$= I - \int_0^t ds \int_0^t ds' \frac{V(s') V(s)}{r^2} + \cdots$$

Since the odd products of $\langle V(t) \ldots V(t') \rangle$ vanish where $\langle \ldots \rangle = \mathcal{T} \left[ \ldots \right]$, we can evaluate

$$\langle S(t) \rangle = \exp \left( -\frac{i}{\hbar^2} \int_0^t dt_1 \int_0^t dt_2 \langle V(t_2) V(t_1) \rangle \right)$$

By using $(b_j^a b_j^a) = \tilde{n}_j = (e^{i \omega_j / \hbar \tau} - 1)^{-1}$ the thermal occupation number of the $j$th vibrational mode and $(b_j^a b_j^a) = \tilde{n}_j + 1$ the two-time average becomes

$$\langle V(t_2) V(t_1) \rangle = \hbar^2 \sum_j \left( \tilde{n}_j e^{-i \omega_j \tau} + (\tilde{n}_j + 1) e^{i \omega_j \tau} \right) \xi_j^a \hat{v}_j$$

$$= \hbar^2 \int_{-\infty}^\infty J(\omega) e^{i \omega \tau} d\omega$$

where $\omega = \tau - t_2$ and the spectral correlation profile

$$J(\omega) = \sum_j \left( \tilde{n}_j \delta(\omega + \tau) + (\tilde{n}_j + 1) \delta(\omega - \tau) \right) \xi_j^a \hat{v}_j$$

$\sum_\tau \left( \tilde{n}_j \delta(\omega + \tau) + (\tilde{n}_j + 1) \delta(\omega - \tau) \right) \xi_j^a \hat{v}_j$
is the inverse Fourier transform of \( \langle V(t_2)V(t_1) \rangle \). The mean absorption operator becomes

\[
\langle S(t) \rangle \rightarrow \exp \left\{ -\int_0^t dt_1 \int_0^{t_1} dt_2 \int_{-\infty}^{\infty} J(\omega) e^{i\omega(t_1-t_2)} d\omega \right\} = \exp \left\{ \frac{t}{2} \delta(t) \right\} \left( \frac{\exp \left( \frac{t}{2} \right)}{\exp \left( \frac{t}{2} \right)} \right)^2
\]

Next, we evaluate \( \langle S(t) \rangle \) for \( \langle S(t) \rangle \rightarrow \exp \left\{ -\frac{1}{\sigma^2} \right\} \) where \( \sigma^2 = 1 + \sum_j e^{\xi_j^2} (2n_j + 1) \).

Next, we evaluate \( S' = e^{i\hat{g}y/h} S(t)e^{-i\hat{g}y/h} \) through

\[
\frac{dS'}{dt} = e^{i\hat{g}y/h} \frac{dS}{dt} e^{-i\hat{g}y/h} = -\frac{1}{\hbar} e^{i\hat{g}y/h} V(t)e^{-i\hat{g}y/h} = -\frac{1}{\hbar} S' V(t) (A22)
\]

where \( V(t) = e^{i\hat{g}y/h} V(t)e^{-i\hat{g}y/h} = e^{i\hat{g}y(t+x)/h} Ve^{-i\hat{g}y(t+x)/h} = V(t+x) \). Therefore,

\[
S'(t) = T_o \exp \left\{ -\frac{1}{\hbar} \int_0^t dt' V(t' + x) \right\} (A23)
\]

which is used to write

\[
A(t', t_2, t_3) = \langle S(-t_3) \rangle < S'(t_2) < S'(t_3) \rangle = e^{-i\hat{g}y(t_3 - t_2 + t_1)/h} \left\{ e^{i\hat{g}y(t_3 - t_2 + t_1)/h} \right\} = e^{-i\hat{g}y(t_3 - t_2 + t_1)/h}
\]

\[
\times \exp \left\{ -\frac{1}{\hbar} \int_0^{t_3} dt' \left\{ e^{i\hat{g}y(t_3 - t_2 + t_1)/h} V(t') \right\} \right\} \right) (A24)
\]

**Relationship with linear response function**

We now establish the relationship with the absorption spectrum by using the definition of linear response (complex) dielectric function

\[
\Phi(\omega) = i \int_0^\infty e^{i\omega - \omega_0} \langle \hat{S}(t) \rangle dt = i \int_0^\infty e^{-i\omega_f(t)} dt (A31)
\]

which is related to the absorption spectrum \( I(\omega) \) by Kramers-Kronig relation

\[
\Phi(\omega) = i\pi \frac{I(\omega)}{\omega - \omega} (A32)
\]

and

\[
F(t) = \int_{-\infty}^{\infty} I(\omega)e^{-i\omega t} d\omega (A33)
\]

**Order of Raman process in the susceptibility**

The term with \( n = 0 \) in Eqn (A30) is the zeroth order Raman process or Rayleigh scattering,

\[
\hat{\chi}^{(1)}_{\text{Raman}} |_{n=0} = -C(\omega) C_{\text{pp}} \frac{\Phi(\omega_0) \Phi(\omega)}{\omega_0^2 - \omega^2 + i\Gamma} (A34)
\]
Now, the term for first-order Raman process, $n = 1$ is
\[
\tilde{\chi}_{pqrs}^{(1)}|_{n=1} = -i\mathcal{C}(\omega)\mathcal{C}_{pqrs} \sum_{j} |\xi_{j}|^{2} \left(\tilde{n}_{j} + 1\right)
\]
\[
\times \int_{0}^{\infty} (S(-t'))e^{-i\omega_{pq}t'}(1 - e^{-i\omega_{ij}t'})e^{i\omega_{pq}t'}e^{-i\omega_{ij}t'}dt'
\]
\[
\times \int_{0}^{\infty} e^{i\omega_{op} - \omega_{ps} - \gamma_{ij}t''}t''_{1}dt''_{1}
\]
\[
\times \int_{0}^{\infty} (S(-t''))e^{-i\omega_{pq}t''}(1 - e^{-i\omega_{ij}t''})e^{i\omega_{pq}t''}e^{-i\omega_{ij}t''}dt''
\]
\[
+ \tilde{n}_{j} \left\{ v_{j} \to - v_{j} \right\} \right) \tag{A35}
\]

The second integral can be replaced using
\[
\int_{0}^{\infty} dt'e^{i\omega_{op} - \omega_{ps} \pm \gamma_{ij}t''}t''_{1} \simeq \frac{i}{\omega_{op} - \omega_{ps} \pm v_{j} + i\Gamma}.
\]
Thus, the susceptibility due to $n = 1$ is rewritten as
\[
\tilde{\chi}_{pqrs}^{(1)}|_{n=1} = C_{pqrs} \sum_{j} |\xi_{j}|^{2}
\]
\[
\times \left\{ (\tilde{n}_{j} + 1)\alpha_{j}^{(-)}(\omega_{op})\alpha_{j}^{(-)}(\omega_{pq})\right\}
\]
\[
+ \frac{\tilde{n}_{j}\alpha_{j}^{(+)}(\omega_{op})\alpha_{j}^{(+)}(\omega_{pq})}{(\omega_{op} - \omega_{ps} - \gamma_{ij}) + i\Gamma}
\] \tag{A36}

The second-order Raman process, $n = 2$ is the lowest order hyper-Raman transition as depicted in Fig. 2. We find
\[
\tilde{\chi}_{pqrs}^{(2)}|_{n=2} = \frac{1}{2} \sum_{jk} |\xi_{j}|^{2} |\xi_{k}|^{2} \left(\tilde{n}_{j} + 1)(\tilde{n}_{k} + 1)\right)
\]
\[
\left\{ \alpha_{j}^{(-)}(\omega_{op}) - \alpha_{j}^{(-)}(\omega_{ps} - \gamma_{ij})\right\}
\]
\[
\times \left\{ \alpha_{j}^{(-)}(\omega_{pq}) - \alpha_{j}^{(-)}(\omega_{pq} + \gamma_{ij})\right\}
\]
\[
\times \left\{ \left[ \tilde{n}_{j}(\tilde{n}_{k}) + \tilde{n}_{j}(\tilde{n}_{k} + 1)\right]
\]
\[
\times \left\{ \left[ \tilde{n}_{j}(\tilde{n}_{k} + 1) + \tilde{n}_{j}(\tilde{n}_{k} + 1)\right]
\]
\] \tag{A37}

where we define the notations $\alpha_{j}^{(\pm)}(x) = \Phi(x) - \Phi(x \pm v_{j})$. 