

# Stimulated coherent anti-Stokes Raman spectroscopy (CARS) resonances originate from double-slit interference of two-photon Stokes pathways

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**Coherent anti-Stokes Raman spectroscopy (CARS) uses vibrational resonances to study nuclear wavepacket motions and is widely used in cell imaging and other applications. The resonances usually lie on top of a parametric component that involves no change in the molecular state and creates an undesirable background which reduces the sensitivity of the technique. Here, by examining the process from the perspective of the molecule, rather than the field, we are able to separate the two components and recast each resonance as a modulus square of a transition amplitude which contains an interference between two Stokes pathways, each involving a different pair of field modes. We further propose that dissipative signals obtained by measuring the total absorption of all field modes in a convenient collinear pulse geometry can eliminate the parametric component and retain the purely resonant contributions. Specific vibrational resonances may then be readily detected using pulse shapers through derivatives with respect to pulse parameters.**

CARS microscopy | pulse shaping | ultrafast spectroscopy

Coherent Raman spectroscopy is a powerful nonlinear optical tool widely used in the study of molecular vibrational wavepacket motions and their relaxation and dephasing (1, 2). Broadband femtosecond lasers have been used to stimulate gain and loss signals (3, 4). Common applications include imaging (5–8), single molecule spectroscopy (7), and remote sensing (9, 10). The desired molecular resonances are usually accompanied by large parametric, off-resonant, solvent contributions which limit the sensitivity and selectivity of CARS spectroscopy and microscopy (11, 12). Several approaches have been employed to suppress the parametric signal. Detection of the signal at long delays, when the fast background signal has decayed (13) was found to be effective, as was the use of chirped (5, 6, 14) or coherently shaped pulses in a collinear geometry (10, 15–18). Developing new approaches, which may be advantageous for specific applications, is of great interest.

In this paper we examine what happens to the matter, rather than to the radiation field, in a stimulated (i.e. heterodyne-detected) CARS set up. The probabilities of transitions between molecular states are described naturally in terms of modulus squares of *transition amplitudes*, as is commonly done in photon counting (19) and in the Kramers Heisenberg description of spontaneous and stimulated Raman scattering (2). In contrast, coherent wave-mixing optical signals such as CARS are commonly expressed in terms of nonlinear susceptibilities (2, 20) which connect the induced polarization in matter to the driving fields. We show that CARS resonances may be expressed in terms of transition amplitudes. We then demonstrate that the parametric processes are eliminated by measuring the total energy exchanged between *all* modes of the field and the molecule, resulting in a purely dissipative signal which clearly reveals the desired resonances. Since it requires subtracting the energy contained in the incoming fields from the transmitted energy, the dissipative signal is not “background-free.” Nevertheless,

specific vibrational resonances can be readily detected by varying the pulse envelope parameters.

## Discussion

**Material Perspective of Wave-Mixing Processes** We consider a material system coupled to an optical field  $E(\tau)$  and described by the Hamiltonian

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}'(\tau) = \mathcal{H}_0 - E(\tau)\hat{V}, \quad [1]$$

where  $\mathcal{H}_0 = \sum_b \epsilon_b |b\rangle\langle b|$  represents the pure matter, while  $\hat{V} = \sum_{a,b} \mu_{ab} |a\rangle\langle b|$  is the dipole operator which couples the field and matter.

In a time-domain nonlinear wave-mixing measurement such as CARS, the optical field interacts with the molecule for a finite time [ $E(\tau)$  is finite only for  $t > \tau > t_0$ ]. Optical signals ultimately measure the absorption and emission of photons. Many material processes generally contribute to a given optical signal and it is not obvious how to tell them apart. From the material perspective, the quantity of interest is the probability to find the system at a final state  $c$  given that it was initially in state  $a$

$$P_{a \rightarrow c} = |\langle c(t) | \hat{\mathcal{U}}(t, t_0) | a(t_0) \rangle|^2, \quad [2]$$

where  $\hat{\mathcal{U}}(t, t_0) = \exp_+[-\frac{i}{\hbar} \int_{t_0}^t d\tau \mathcal{H}'(\tau)]$  is the time evolution operator in the interaction picture with respect to  $\mathcal{H}_0$ ,  $\mathcal{H}'(\tau) = U_0^\dagger(\tau, t_0) \mathcal{H}'(\tau) U_0(\tau, t_0)$ .  $U_0$  is the evolution operator of the non-interacting field and matter, while  $|a(t)\rangle \equiv U_0^\dagger(t, t_0) |a\rangle$ . The time ordered exponential is defined in the usual way, see e.g. ref. 2.  $\hat{\mathcal{U}}$  satisfies an integral equation

$$\hat{\mathcal{U}}(t, t_0) = 1 - \frac{i}{\hbar} \int_{t_0}^t d\tau \mathcal{H}'(\tau) \hat{\mathcal{U}}(\tau, t_0), \quad [3]$$

which allows recasting the matrix elements in the form

$$\langle c(t) | \hat{\mathcal{U}}(t, t_0) | a(t_0) \rangle = \delta_{ca} e^{-\frac{i}{\hbar} \epsilon_a (t-t_0)} - \frac{i}{\hbar} e^{-\frac{i}{\hbar} (\epsilon_c t - \epsilon_a t_0)} T_{ca}(\omega_{ca}), \quad [4]$$

where  $\hbar\omega_{ca} = \epsilon_c - \epsilon_a$ , and

$$T_{ca}(\omega) = \int dt e^{i\omega t} T_{ca}(\tau), \quad [5]$$

where

$$T_{ca}(\tau) \equiv \langle c(\tau) | \mathcal{H}'(\tau) \exp_+ \left[ -\frac{i}{\hbar} \int_{t_0}^{\tau} d\tau' \mathcal{H}'(\tau') \right] | a(t_0) \rangle e^{\frac{i}{\hbar} \epsilon_a (\tau-t_0)} \quad [6]$$

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is the *transition amplitude*. Note that since  $T_{ca}(\tau) = 0$  for  $\tau < t_0$  and  $\tau > t$  the integration limits can be extended to infinity. The frequency argument  $\omega_{ca}$  comes from a combination of the explicit phase in **6** and a phase coming from the difference between  $|c(t)\rangle$  in Eq. **4** and  $|c(\tau)\rangle$  in **6**. The first term in Eq. **4** represents the amplitude that no interaction between the field and matter has occurred. Note that transitions of any order in the interaction are lumped into  $T$ .

Conservation of probability implies

$$\sum_c |\langle c(t) | \hat{\mathcal{U}}(t, t_0) | a(t_0) \rangle|^2 = 1. \quad [7]$$

By substituting Eq. **4** in **7** and making use of the unitarity of  $\hat{\mathcal{U}}$ , we find that  $T_{ca}(\omega_{ca})$  satisfies an *optical theorem*

$$\Im T_{aa}(\omega_{aa}=0) = -\frac{1}{2\hbar} \sum_c |T_{ca}(\omega_{ca})|^2. \quad [8]$$

[ $\Im$  ( $\Re$ ) denotes the imaginary (real) part]. This is a natural extension of the standard stationary optical theorem of scattering theory to driven systems. Note that the sum over  $c$  in Eqs. **7** and **8** is unrestricted (i.e. includes  $c = a$ ).

By expanding  $T_{ca}(\omega)$  in the field-matter interaction we obtain

$$\begin{aligned} T_{ca}(\omega_{ca}) &= T_{ca}^{(1)}(\omega_{ca}) + T_{ca}^{(2)}(\omega_{ca}) + T_{ca}^{(3)}(\omega_{ca}) + \dots \\ &= -\mu_{ca} E(\omega_{ca}) + \frac{1}{2\pi\hbar} \int d\omega_1 d\omega_2 \sum_{\nu} \frac{\mu_{c\nu} \mu_{\nu a}}{\omega_1 - \omega_{\nu a} + i\eta} \\ &\quad \times E(\omega_1) E(\omega_2) \delta(\omega_{ca} - \omega_1 - \omega_2) - \frac{1}{4\pi^2 \hbar^2} \int d\omega_1 d\omega_2 d\omega_3 \\ &\quad \times \sum_{\nu_1, \nu_2} \frac{\mu_{c\nu_2} \mu_{\nu_2 \nu_1} \mu_{\nu_1 a} E(\omega_1) E(\omega_2) E(\omega_3)}{(\omega_1 + \omega_2 - \omega_{\nu_2 a} + i\eta)(\omega_1 - \omega_{\nu_1 a} + i\eta)} \\ &\quad \times \delta(\omega_{ca} - \omega_1 - \omega_2 - \omega_3) + \dots, \end{aligned} \quad [9]$$

where  $\eta$  is a small positive infinitesimal and  $E(\omega)$  denotes the Fourier transform of  $E(t)$ . The probability to make a transition is given by  $P_{a \rightarrow c} = \hbar^{-2} |T_{ca}(\omega_{ca})|^2$  for  $c \neq a$ . Eq. **9** reveals that this transition probability includes interferences of contributions of different order in the matter-field interaction (19), with all possible combinations of field modes.

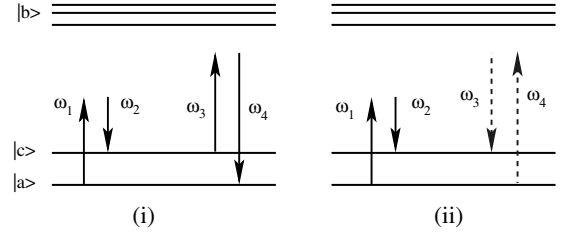
We consider the three-level model system shown in Fig. 1(i). In stimulated CARS the field is made of four narrow band pulses, centered around frequencies  $\omega_i$ ,  $i = 1, 2, 3, 4$ ,

$$E(\omega) = 2\pi \sum_{i=1}^4 [\mathcal{E}_i \delta_{\Delta}(\omega - \omega_i) + \mathcal{E}_i^* \delta_{\Delta}(\omega + \omega_i)]. \quad [10]$$

$\delta_{\Delta}$  is a slightly broadened delta function, of width  $\Delta$ , describing the (normalized) narrow band shape of the pulses. We assume that all frequencies are tuned off resonance from the electronic excited state  $b$  so that the only possible resonances are of the Raman type  $\omega_4 - \omega_3 \simeq \omega_{ca}$  and  $\omega_1 - \omega_2 \simeq \omega_{ca}$ , as depicted in Fig. 1. The transition probability  $P_{a \rightarrow c}$  is given, to leading order, by the square of the second order term in Eq. **9**

$$P_{a \rightarrow c} = \frac{1}{4\pi^2 \hbar^4} |\mu_{cb}|^2 |\mu_{ba}|^2 \left| \int d\omega \frac{E(\omega) E(\omega_{ca} - \omega)}{\omega - \omega_{ba} + i\eta} \right|^2. \quad [11]$$

By substituting Eq. **10** and using the dipole transitions of Fig. 1 we find that the integral has only two contributions from  $\omega \simeq \omega_1, \omega_4$ ,



**Fig. 1.** The stimulated CARS measurement in a three-level system interacting with four field modes.  $a$  and  $c$  are vibronic states belonging to the ground electronic state, whereas  $b$  are electronically excited states. Modes 1, 4 drive transitions between states  $a$  and  $b$  while modes 2, 3 drive transitions between states  $c$  and  $b$ . Modes 1 and 2 are spectrally well separated from 3 and 4 so that only the shown resonances are possible. The signal can be interpreted in two ways: (i) In terms of a single amplitude which suggests that this is an anti-Stokes process. This process is described by  $\Im T_{aa}^{(4)}$ , a fourth order process starting and ending state  $a$ . (ii) The resonant part of the signal is an interference between two Stokes processes, one involving the modes 1 and 2, while the other involves modes 3 and 4. The dashed lines denote the complex conjugate of the transition amplitude of the Stokes process, leading to the product  $\Re T_{ca}^{(2)}(-\omega_2, \omega_1) T_{ca}^{(2)*}(-\omega_3, \omega_4)$ .

$$\begin{aligned} P_{a \rightarrow c} &\simeq \frac{4\pi^2}{\hbar^4} |\mu_{cb}|^2 |\mu_{ba}|^2 \left| \frac{\mathcal{E}_1 \mathcal{E}_2^*}{\omega_1 - \omega_{ba} + i\eta} \delta_{\Delta'}(\omega_1 - \omega_2 - \omega_{ca}) \right. \\ &\quad \left. + \frac{\mathcal{E}_4 \mathcal{E}_3^*}{\omega_4 - \omega_{ba} + i\eta} \delta_{\Delta'}(\omega_4 - \omega_3 - \omega_{ca}) \right|^2. \end{aligned} \quad [12]$$

The functions  $\delta_{\Delta'}$  in expression **12** result from an integrated product of two of the band shapes  $\delta_{\Delta}$ . While the width and shape of the  $\delta_{\Delta'}$  in expression **12** are different from those appearing in Eq. **10**, these are still narrow  $\delta$ -like shapes.

Expression **12** has a typical form of a double-slit measurement: Two interfering pathways contribute to the resonant Stokes Raman  $a \rightarrow c$  amplitude. By opening the brackets we find

$$\begin{aligned} P_{a \rightarrow c} &= P_{a \rightarrow c}^{12} + P_{a \rightarrow c}^{34} + P_{a \rightarrow c}^{1234} \\ &\simeq \frac{4\pi^2}{\hbar^4} |\mu_{cb}|^2 |\mu_{ba}|^2 \left( \left| \frac{\mathcal{E}_1 \mathcal{E}_2^*}{\omega_1 - \omega_{ba} + i\eta} \right|^2 \delta_{\Delta'}^2(\omega_1 - \omega_2 - \omega_{ca}) \right. \\ &\quad \left. + \left| \frac{\mathcal{E}_4 \mathcal{E}_3^*}{\omega_4 - \omega_{ba} + i\eta} \right|^2 \delta_{\Delta'}^2(\omega_4 - \omega_3 - \omega_{ca}) \right. \\ &\quad \left. + 2\Re \left[ \frac{\mathcal{E}_1 \mathcal{E}_2^* \mathcal{E}_3 \mathcal{E}_4^*}{(\omega_1 - \omega_{ba} + i\eta)(\omega_4 - \omega_{ba} - i\eta)} \right] \right) \\ &\quad \times \delta_{\Delta'}(\omega_1 - \omega_2 - \omega_{ca}) \delta_{\Delta'}(\omega_4 - \omega_3 - \omega_{ca}). \end{aligned} \quad [13]$$

Here  $P_{a \rightarrow c}^{12}$  ( $P_{a \rightarrow c}^{34}$ ) represents a pump-probe process involving only modes 1 and 2 (3 and 4).  $P_{a \rightarrow c}^{1234}$  describes the interference of these two pump-probe pathways. The double-slit picture has long been established for two-photon absorption and photo-electron detection (19). Eq. **13** extends it to Raman processes. In the next section we show that the resonant component of the stimulated CARS signal is given by  $P_{a \rightarrow c}^{1234}$ .

**Stimulated Cars: A Double-Slit Measurement** We shall now reexamine the setup of Fig. 1, but this time from the more traditional field perspective. Heterodyne four-wave mixing signals are usually calculated using the semiclassical approach, where a classical field interacts with a quantum material system (2). In that picture

\*One may be worried by the appearance of the factor of  $\delta_{\Delta}^2$  in those terms as the limit of narrow band shape is taken, but this is just an artifact resulting from the fact that these pump-probe processes are naturally described in terms of the *rate* of transitions while here we are studying the overall probability. Indeed,  $\delta_{\Delta}^2(x) \sim \delta_{\Delta}(x)/\Delta'$  and  $1/\Delta'$  is proportional to the overall time where the pulses are turned on.

the detected ( $\omega_4$ ) and the driving ( $\omega_1, \omega_2, \omega_3$ ) modes play different roles: The third order polarization due to the three driving modes is calculated first, and then interferes with a fourth local oscillator field  $\omega_4$  to generate the signal. We shall adopt instead a quantum description of the field that treats all four modes on equal footing. The resulting signal is identical to that derived from the semiclassical theory; however, by not singling out one mode as the “local oscillator” from the outset, we simplify the description of the process and can readily describe all possible stimulated and spontaneous measurements where different modes are detected. This approach will prove most natural for deriving the purely dissipative signal in the next section where all modes are detected.

Using the quantum description of all field modes, the signal is defined as (21)

$$S_4 \equiv \int dt \frac{d}{dt} \left\langle \sum_s \hat{a}_s^\dagger \hat{a}_s \right\rangle, \quad [14]$$

where  $\hat{a}_s$  ( $\hat{a}_s^\dagger$ ) is an annihilation (creation) operator for a field mode  $s$ , and the sum runs over all relevant modes of pulse 4 (which is being detected). The expectation value  $\langle \dots \rangle$  is with respect to the joint density matrix of the interacting matter and field degrees of freedom.

By assuming that all field modes are in a coherent state, we expand the signal [14] to first order in the amplitudes of the four modes and obtain the CARS signal where all frequencies within the bandwidth of mode 4 are detected (21, 22)

$$S_4 = -\frac{4\pi}{\hbar} \Im[\mathcal{E}_1 \mathcal{E}_2^* \mathcal{E}_3 \mathcal{E}_4^* \chi^{(3)}(-\omega_4; \omega_3, -\omega_2, \omega_1)] \delta(\omega_1 - \omega_2 + \omega_3 - \omega_4), \quad [15]$$

with

$$\begin{aligned} \chi^{(3)}(-\omega_4; \omega_3, -\omega_2, \omega_1) \\ = -\hbar^{-3} \frac{|\mu_{ba}|^2 |\mu_{cb}|^2}{(\omega_1 - \omega_2 + \omega_3 - \omega_{ba} + i\eta)(\omega_1 - \omega_2 - \omega_{ca} + i\eta)(\omega_1 - \omega_{ba} + i\eta)}. \end{aligned} \quad [16]$$

Since all electronic transitions are off-resonant, the denominators involving  $\omega_{ba}$  in Eq. 16 are real. Eq. 15 can be separated into two parts,

$$S_4 = -\frac{1}{2} P_{a \rightarrow c}^{1234} + S_4^{\text{par}}. \quad [17]$$

The  $P_{a \rightarrow c}^{1234}$  contribution, which is associated with  $\Im \chi^{(3)}$  in Eq. 15, is clearly related to resonant transitions between states  $a$  and  $c$ . The  $-1/2$  factor may be easily rationalized: the overall sign differs since the  $a \rightarrow c$  transition, described in Eq. 13, involves an *absorption* of a photon in mode 4, rather than *emission*. The factor of  $1/2$  arises since only one of the interfering processes in  $P_{a \rightarrow c}^{1234}$  affects the number of photons in mode 4.

The second term in Eq. 17, associated with  $\Re \chi^{(3)}$  in Eq. 15, describes an off-resonant parametric contribution where photons are exchanged between field modes, but the molecule eventually returns to its initial state,

$$\begin{aligned} S_4^{\text{par}} = \frac{4\pi}{\hbar^4} \frac{\Im[\mathcal{E}_1 \mathcal{E}_2^* \mathcal{E}_3 \mathcal{E}_4^*] |\mu_{ba}|^2 |\mu_{cb}|^2}{(\omega_1 - \omega_2 + \omega_3 - \omega_{ba})(\omega_1 - \omega_{ba})} \\ \times \Re \frac{1}{\omega_1 - \omega_2 - \omega_{ca} + i\eta} \delta(\omega_1 - \omega_2 + \omega_3 - \omega_4). \end{aligned} \quad [18]$$

Two processes of this type are possible for our model. One where  $\omega_1$  and  $\omega_3$  are absorbed while  $\omega_2$  and  $\omega_4$  are emitted, and the other where the roles of the modes, or equivalently their time

ordering, are reversed.  $S_4^{\text{par}}$ , which gives the net change in mode 4 intensity, results from the difference between the rates of these processes. A general diagrammatic approach based on transition amplitudes was used in ref. 22 to dissect electronically resonant CARS signals into its parametric and dissipative contributions. These are not generally given by simply taking the real and imaginary parts of  $\chi^{(3)}$  in Eq. 15 (23), as was done here for the off-resonant case.

The following physical picture emerges from the above discussion. The resonant processes in  $S_4$  correspond to the  $a \rightarrow c$  transition. Because of the condition  $\omega_1 - \omega_2 + \omega_3 - \omega_4 = 0$ , this transition can take two pathways involving different combinations of field modes. For our model if  $\omega_1 - \omega_2 = \omega_{ca}$ , then  $\omega_4 - \omega_3 = \omega_{ca}$  as well. The resonant part of the signal comes from the *interference* between these pathways. CARS is, in this sense, a double-slit experiment.

The CARS acronym, historically coined for homodyne signals, originated from the field perspective: since  $\omega_4 > \omega_3$  and since  $\omega_4$  is detected this appears as an anti-Stokes process. It is ironic that the physical process underlying (the resonant part of) the stimulated *anti-Stokes* Raman scattering is in fact an interference of two *Stokes* processes.

The anti-Stokes signal (neglected here) arises from processes where the molecule is initially in state  $c$ . The sign of the resonant CARS signal, which can be controlled by varying the relative phases of the pulses, depends on whether the interference between the two pathways is constructive or destructive, thus increasing or decreasing the rate of the  $a \rightarrow c$  transition with respect to the sum of the two possible pump-probe processes, which serves as a reference.

The CARS signal where  $\omega_4$  is detected is commonly illustrated by Fig. 1(i) which suggests that this is indeed an anti-Stokes process, since  $\omega_3$  is absorbed,  $\omega_4$  is emitted, and  $\omega_4 > \omega_3$ . However, this is not actually what happens. Stimulated CARS resonances originate from the dissipative part of the process which is better described by Fig. 1(ii). *The time order of the  $\omega_3$  and  $\omega_4$  transitions is thus reversed:  $\omega_4$  is absorbed and  $\omega_3$  is emitted* making it a Stokes process. The above discussion can be generalized to include electronically resonant transitions. In that case the stimulated CARS signals from the electronic transitions can arise from interference between a one photon and three photon transitions connecting states  $a$  and  $b$  (22).

**Dissipative, Purely Resonant, Signals** The previous discussion suggests that by measuring material transitions it is possible to eliminate the parametric background. Below we show that such purely resonant signals are feasible. The following derivation is not limited to CARS and applies to arbitrary nonlinear wave-mixing optical signals. We shall consider an arbitrary multilevel molecule which interacts with many modes  $\omega_j$  of the radiation field. We now introduce the *dissipative signal* defined as the total energy absorbed by the matter from all modes of the field

$$D = \hbar^{-1} \sum_{fg} P(g) \int d\omega \omega |T_{fg}(\omega)|^2 \delta(\omega - \omega_{fg}), \quad [19]$$

where the transition amplitudes were defined in Eq. 6.

As shown earlier, conventional signals such as  $S_4$ , which only detect a single mode, may not be expressed in the dissipative form of Eq. 19 since they contain dispersive parametric contributions where photons are exchanged between field modes leaving the matter intact (it remains in state  $g$  at the end of the process). *Parametric processes affect individual modes but not the total energy of the field and thus do not contribute to the dissipative signal.* The  $D$  signal is an experimental observable obtained by measuring the total transmitted intensity in all modes, it requires no phase matching, and can be measured in a simple collinear beam

geometry, making it particularly suitable for single molecule spectroscopy, imaging, and remote sensing applications.

It follows from Eq. 9 that the dissipative signal  $D$  naturally groups the terms by their corresponding material transition ( $a \rightarrow c$  etc.) but mixes terms with different orders in the various fields. Nonlinear susceptibilities, in contrast, do the bookkeeping the other way around; they keep track of specific orders in the various fields but mix resonances of different type.  $D$  may be expressed in terms of a specific combination of different susceptibilities. However, this will not be necessary; the expressions given in terms of transition amplitudes are much simpler to interpret and implement numerically, since amplitudes are more intuitive and are lower order in the fields than susceptibilities.

As an example the signal  $S_1$  obtained by detecting mode  $\omega_1$  is given by Eq. 17 with the sign of  $S_4^{\text{par}}$  reversed. We then get  $S_1 + S_4 = -P_{a \rightarrow c}^{1234}$ , and the dissipative signal  $D$  is proportional to  $S_1 + S_4 - P_{a \rightarrow c}^{12} - P_{a \rightarrow c}^{34}$ .

Pulse shapers (24–26) decompose the complex field envelope into an amplitude and a phase  $\mathcal{E}(\omega) = A(\omega)e^{i\phi(\omega)}$ . Variation of  $D$  with various field parameters should allow to resolve the different molecular resonances. In the following we shall vary the field amplitude  $A(\omega)$ . We first consider the contributions due to linear absorption

$$D \simeq \hbar^{-1} \int d\omega \sum_b \omega |\mu_{ba}|^2 A^2(\omega) \delta(\omega - \omega_{ba}). \quad [20]$$

Variation of the field amplitude gives

$$\sigma(\omega) = \frac{\delta D}{\delta A^2(\omega)} = \sum_b \omega_{ba} |\mu_{ba}|^2 \delta(\omega - \omega_{ba}), \quad [21]$$

which is the linear absorption.

We now turn to electronically off-resonant pulses where  $D$  is dominated by Raman transitions. The stimulated Raman and heterodyne CARS signals are obtained from the second order transition amplitudes. The dissipative signal is then

$$D_{\text{CARS}} = \frac{1}{4\pi^2 \hbar^3} \sum_c \omega_{ca} |\mu_{cb}|^2 |\mu_{ba}|^2 \left| \int d\omega \frac{\mathcal{E}(\omega) \mathcal{E}(\omega_{ca} - \omega)}{\omega - \omega_{ba} + i\eta} \right|^2. \quad [22]$$

(The optical pulse band shape covers the frequency regime  $|\omega| \gg \omega_{ca}$ , since  $\omega_{ca}$  is a vibrational transition frequency.) Raman resonances may be obtained by taking a second order variation  $\delta^2 D / \delta A(\omega_1) \delta A(\omega_2)$ . However, these lie on the top of a smooth background resulting from the term where each of the integrals in Eq. 22 is varied once.

Instead, we shall consider a two-pulse configuration which includes one broadband and one strong narrow band pulse (Fig. 2) (3, 4, 22)

$$\mathcal{E}(\omega) \simeq 2\pi \mathcal{E}_0 \delta(\omega - \omega_0) + 2\pi \mathcal{E}_0^* \delta(\omega + \omega_0) + \tilde{\mathcal{E}}(\omega). \quad [23]$$

Specific resonances may now be resolved using variation of the signal which interacts twice with the narrow band pulse at neighboring frequencies, which are spectrally separated from the narrow  $\omega_0$  beam. The integral in Eq. 22 in the rotating wave approximation can now be approximated by

$$\int d\omega \frac{\mathcal{E}(\omega) \mathcal{E}(\omega_{ca} - \omega)}{\omega - \omega_{ba} + i\eta} \simeq 2\pi \mathcal{E}_0 \mathcal{E}(\omega_{ca} - \omega_0) \frac{1}{\omega_0 - \omega_{ba} + i\eta} + 2\pi \mathcal{E}_0^* \mathcal{E}(\omega_{ca} + \omega_0) \frac{1}{\omega_0 - \omega_{bc} + i\eta}. \quad [24]$$

Variation with respect to the amplitude of the broadband pulse,  $A(\omega)$ , gives

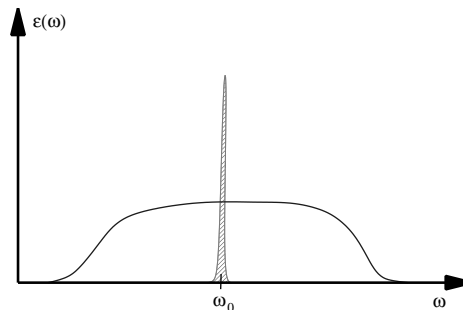


Fig. 2. The two-pulse configuration used to resolve specific resonances in  $D_{\text{CARS}}$  consists of a strong narrow band (picosecond) pulse centered at  $\omega_0$  and an overlapping (femtosecond) broadband pulse.

$$\frac{\delta D_{\text{CARS}}}{\delta A(\omega)} \simeq \frac{1}{\pi \hbar^3} \omega_{ca} |\mu_{cb}|^2 |\mu_{ba}|^2 \times \Re \left\{ \left( \frac{\mathcal{E}_0^* \mathcal{E}(\omega_0 - \omega_{ca})}{\omega_0 - \omega_{ba} - i\eta} + \frac{\mathcal{E}_0 \mathcal{E}^*(\omega_0 + \omega_{ca})}{\omega_0 - \omega_{bc} - i\eta} \right) \times \left( \frac{\mathcal{E}_0 e^{-i\phi(\omega_0 - \omega_{ca})}}{\omega_0 - \omega_{ba} + i\eta} [\delta(\omega - \omega_0 + \omega_{ca}) + \delta(\omega + \omega_0 - \omega_{ca})] + \frac{\mathcal{E}_0^* e^{i\phi(\omega_0 + \omega_{ca})}}{\omega_0 - \omega_{bc} + i\eta} [\delta(\omega - \omega_0 - \omega_{ca}) + \delta(\omega + \omega_0 + \omega_{ca})] \right) \right\}. \quad [25]$$

The right-hand side of expression 25 shows background-free Raman resonances at  $\omega = \pm\omega_0 \pm \omega_{ca}$ . (The resonances at negative and positive frequencies are mirror images of each other.) A plot of 25 at positive frequencies would show sharp positive peaks corresponding to the various vibrational modes. While the peak locations are arranged symmetrically around  $\omega_0$ , their magnitudes are not. By selecting the signal that scales as  $|\mathcal{E}_0^2|$  we eliminate the background from the outset. This demonstrates one way of separating molecular transitions contributing to  $D$  by a variation of the pulse shape. Other protocols are possible. For example, substitution of 24 in 22 shows that the signal which involves two interactions with the intense narrow band pulse has the form

$$D_{\text{CARS}} = D_1 |\mathcal{E}_0|^2 |\mathcal{E}(\omega_0 - \omega_{ca})|^2 + D_2 |\mathcal{E}_0|^2 |\mathcal{E}(\omega_0 + \omega_{ca})|^2 + D_3 \Re(\mathcal{E}_0^2 \mathcal{E}^*(\omega_0 - \omega_{ca}) \mathcal{E}^*(\omega_0 + \omega_{ca})). \quad [26]$$

The first two terms represent pump-probe processes involving  $\mathcal{E}_0$  and one mode from the broad pulse ( $\omega_0 - \omega_{ca}$  or  $\omega_0 + \omega_{ca}$ ), while the third is a CARS process involving all three modes. Variation of parameters which keep two of the field factors in Eq. 26 fixed, but vary the remaining one, should allow not only the separation of different vibrational transitions, but also the different pump-probe and CARS processes contributing to each transition.

In summary, the dissipative signal proposed here arises naturally by examining the optical process from the material perspective and connecting it to the field observables. It detects the entire transmitted field without separating it into modes and can be readily measured by a simple collinear pulse configuration (no phase matching is required). Parametric contributions which cause the background, and reduce the signal to noise ratio, are eliminated. Information about specific modes may be retrieved through the variation of the signal with field parameters.

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