Analytic spectrum of multifrequency Raman generation with chirped pulses

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(Received 6 March 2023; revised 27 July 2023; accepted 6 September 2023; published 22 September 2023)

Multifrequency Raman generation is a promising method of producing ultrashort laser pulses with high intensities and visible wavelength frequencies. Experimental realizations of multifrequency Raman generation have a spectrum that displays several behaviors that are not explained by theories calculating the relative Raman order amplitudes. We derive an analytic and perturbative expression for the spectra of the individual Raman orders radiated by a Raman medium excited by multiple Gaussian laser pulses. We use a method of Dawson function approximations to derive an analytic spectrum showing that the Raman order spectra are dependent on both the energy and chirp of the pumps, as observed experimentally.

DOI: 10.1103/PhysRevA.108.033516

I. INTRODUCTION

Ultrafast lasers are useful for a variety of applications such as medicine [1] and spectroscopy [2]. These applications make use of the femtosecond or subfemtosecond timescales of ultrashort pulses to image with molecular precision or access the powers required for nonlinear effects. There are currently processes that can generate ultrashort pulses at a wide range of wavelengths but they have low peak intensities due to the inefficiency of the processes [2,3]. Multifrequency Raman generation (MRG) is a promising method of generating ultrashort laser pulses with high intensities at a range of visible frequencies [4].

When light interacts with a medium, it normally exhibits spontaneous Raman scattering with a small proportion of the incoming light being scattered at a frequency offset by the Raman frequency of the medium. However, when the medium is instead excited by two lasers—a pump laser and a probe laser that is offset from the pump by the Raman frequency—there is efficient conversion of energy from the pump beam frequency to the probe beam frequency, which is called stimulated Raman scattering [3]. Energy can also be efficiently converted to higher Raman order frequencies: frequencies which are offset from the pump frequency by multiples of the Raman frequency. This effect is known as multifrequency or high-order Raman generation [5]. Due to this high efficiency, MRG can produce a spectrum of discrete Raman order peaks that have both short durations (on the order of femtoseconds) and high intensities. The efficient conversion process was first described theoretically by Hickman *et al.* [6]. This theory and others [7,8] are primarily concerned with the propagation of the different Raman orders and their relative amplitudes. They make transformations and approximations to obtain numerically solvable expressions for the amplitudes.

Experimentally, there are other optical effects that can occur and compete with the MRG process for energy. For example, a process known as self-phase modulation can compete with MRG but this can be avoided by using chirped pulses [9]. However, when exciting the Raman medium with chirped pulses, the Raman orders have a sideband shifted to a lower frequency [10]. These redshifted shoulders on the Raman orders are not predicted by the previous theories since they do not investigate the spectrum of radiation emitted at individual Raman orders. Further, the central frequency of the Raman orders depends on the energy of the pump and probe beams, redshifting as the energy increases [4].

In this paper, we derive an analytic spectrum for the individual Raman orders, which shows the dependency of the spectrum on variables such as chirp and pulse energy that cannot be seen from the amplitudes calculated in previous theory. These behaviors are also seen in experiment so the analytic spectrum can provide insight into the origins of these behaviors. The solution makes use of methods to solve Hilbert transforms of Gaussian functions, functions that commonly appear in signal processing and plasma dispersion [11–13].

This paper is organized as follows: in Sec. II we review the simplification of multiwave propagation to a two-state Schrödinger equation, in Sec. III we find expressions for the wave-function amplitudes assuming linearly chirped Gaussian pulses, in Sec. IV we derive the polarization of the Raman medium upon excitation, in Sec. V we derive the spectrum radiated by the Raman medium, and in Sec. VI we discuss the features of the spectrum and the applicability of the theoretical methods. A preliminary report of these results was given in [14,15].

II. TWO-STATE SCHRÖDINGER EQUATION

We first review the theory of a Raman medium excited by a multiwave field, which is described in Hickman *et al.* [6].

In absence of an electric field, the Raman medium has the Hamiltonian H_0 with eigenfunctions $|n\rangle$ and eigenenergies $\hbar W_n$. The electric field of the Raman orders perturbs H_0 with potential $V(z,t) = -p\epsilon(z,t)$ where p is the electric dipole moment operator and $\epsilon(z,t)$ is the electric field. Here we

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have assumed the electric field propagates spatially in the z direction. To describe the propagation of the multiple Raman order fields, we take the electric field to be a sum of the orders:

$$\epsilon(z,t) = \frac{1}{2}\sum_j \epsilon_j(z,t)e^{i\omega_j t} + \text{c.c.} \tag{1}$$

where $\epsilon_j(z,t)$ is the envelope of the electric field of the jth Raman order with frequency $\omega_j = \omega_0 + j\omega_R$. We denote the pump laser frequency as ω_0 and the Raman frequency as ω_R.

We wish to obtain the solution to the Schrödinger equation:

$$[H_0 + V(z,t)]\,|\psi(z,t)\rangle = i\hbar\frac{\partial}{\partial t}\,|\psi(z,t)\rangle\,. \tag{2}$$

To find this solution, we begin by writing the wave function in terms of the unperturbed energies:

$$|\psi(z,t)\rangle = \sum_{n=1}^{\infty} c_n(z,t)e^{-iW_n t}\,|n\rangle\,. \tag{3}$$

The amplitudes $c_n(z,t)$ can be found from our perturbed Schrödinger equation and will determine the wave function of the Raman material under excitation by the multiwave electric field.

When we evaluate Eq. (2) with $|\psi\rangle$ given by Eq. (3), we obtain the set of coupled equations

$$i\hbar\frac{\partial c_n}{\partial t} = -\frac{1}{2}\sum_{n'}\sum_j c_{n'}p_{nn'}[\epsilon_j e^{i(\omega_j + W_{nn'})t}\epsilon_j^* e^{-i(\omega_j - W_{nn'})t}] \tag{4}$$

where $W_{nn'} \equiv W_n - W_{n'}$ and $p_{nn'} \equiv \langle n|p|n'\rangle$.

Since this is an off-resonance Raman process, the medium is excited from a vibrational state to a high-energy virtual state $|n'\rangle$ and then decays to another vibrational state. To do MRG, we excite the medium with two lasers separated by approximately the difference in the ground and first vibrational states. We call this difference the Raman frequency of the medium. We assume that transitions between the ground and first vibrational states do not occur directly and the only transitions are between these two states and higher vibrational states. Mathematically, we assume the only nonzero dipole moment terms are $p_{1n} = p_{n1}$ and $p_{2n} = p_{n2}$ where $n \neq 1, 2$. We can therefore simplify Eq. (4) for the higher electronic states, $n > 2$, in terms of just the amplitudes $c_1(z,t)$ and $c_2(z,t)$.

It is now important to consider the regime of the laser pulse duration compared to the frequency of electric-field oscillations. We want to compare this theory to experiments with visible range frequencies and pulses that are chirped to long-time durations (on the order of hundreds of femtoseconds or longer) while propagating through the Raman medium. We are therefore in the adiabatic regime where the pulse is effectively constant over an oscillation of the electric field.

In this regime, the amplitudes $c_n(z,t)$ and pulse shapes $\epsilon_j(z,t)$ are both slowly varying in time compared to the oscillations of the complex exponentials. With this assumption there are several ways of integrating Eq. (4), the simplest being to hold $c_{n'}$ and ϵ_j constant while integrating the exponential.

We can then write a simplified Schrödinger equation for the ground $[c_1(z,t)]$ and first $[c_2(z,t)]$ vibrational states:

$$i\hbar\frac{\partial}{\partial t}\begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = \begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix}\begin{pmatrix} c_1 \\ c_2 \end{pmatrix} \tag{5}$$

where

$$\begin{aligned} H_{11} &= -\frac{\alpha_{11}}{4}\sum_j \epsilon_j\epsilon_j^*, \\ H_{12} &= -\frac{\alpha_{12}}{4}\sum_j \epsilon_j\epsilon_{j-1}^*, \\ H_{21} &= H_{12}^*, \\ H_{22} &= -\frac{\alpha_{22}}{4}\sum_j \epsilon_j\epsilon_j^*, \end{aligned} \tag{6}$$

and

$$\alpha_{ik}(\omega_j) = \frac{1}{\hbar}\sum_{n=3}^{\infty} p_{in}p_{nk}\left(\frac{1}{W_{ni} - \omega_j} + \frac{1}{W_{nk} + \omega_j}\right). \tag{7}$$

We call α_{ik} a two-photon polarizability since it describes the effect of an electric field on a state with some intermediate state. We have assumed $W_{21} \approx \omega_R$ to write the two-photon polarizability. We will assume that α_{ik} are constant for the rest of the calculations since ω_j are far from resonance.

The two-state Schrödinger equation is the same as derived in Hickman *et al.* [6].

III. AMPLITUDES FOR STATES OF INTEREST

To find an analytic approximation for the emitted radiation, we now deviate from the previous theory and determine the amplitudes for the states of interest, $c_1(z,t)$ and $c_2(z,t)$, by solving the two-state Schrödinger equation [Eq. (5)] directly. Since the Hamiltonian is time dependent, we expand it perturbatively in a Dyson series. We can determine the order of the perturbation from the degree of the two-photon polarizability α_{ik}, which are all small parameters.

We assume the system begins in the ground state so our initial condition is

$$\begin{pmatrix} c_1(z,-\infty) \\ c_2(z,-\infty) \end{pmatrix} = \begin{pmatrix} 1 \\ 0 \end{pmatrix}. \tag{8}$$

We now need to make an assumption about the general shape of the electric-field envelopes $\epsilon_j(z,t)$. We choose a linearly chirped Gaussian pulse shape in time to resemble the experimental laser pulses:

$$\epsilon_j(z,t) = A_j(z)e^{-\beta_j t^2/4} \tag{9}$$

where we have a complex Gaussian width $\beta_j = \frac{1}{a_j^2} - ib_j$ dependent on the pulse width a_j and the linear chirp b_j [16]. We assume the coefficient $A_j(z) = E_j(z)e^{i\phi_j(z)}$ is time independent and spatially dependent. We also note that taking the complex conjugate of $\epsilon_j(z,t)$ will only change the time dependence of the field by changing the sign of the chirp $\beta_j^* = \frac{1}{a_j^2} + ib_j$.

Assuming a chirped Gaussian pulse shape, the amplitudes $c_1(z,t)$ and $c_2(z,t)$ are straightforward to calculate to first

order. For the second-order term, we must calculate double integrals of the form

$$D(a,b;t)=\int_{-\infty}^{t}\int_{-\infty}^{t'}\exp\left(-\frac{t'^2}{a^2}\right)\exp\left(-\frac{t''^2}{b^2}\right)dt''dt' \quad (10)$$

where a and b are each one of $2/\sqrt{\beta_j+\beta_{j-1}^*}$ and $\sqrt{2}a_j$. Since the pulse widths of the Raman orders are similar, we can assume $|a-b|$ is small.

Integrating over t'', we are left with the integral of a Gaussian function and the integral of a Gaussian function multiplied by an error function. Since $|a-b|$ is small, we will write $b=a+\delta$ in the error function and Taylor expand it to first order about $\delta=0$.

We then have the general form for the second-order term of the amplitudes:

$$D(a,b;t)=\frac{\pi ab}{8}\left[1+\mathrm{erf}\left(\frac{t}{a}\right)\right]^2+\frac{\delta b}{4}\exp\left(-\frac{2t^2}{a^2}\right)+\mathcal{O}(\delta^2). \quad (11)$$

Thus, the amplitudes for the ground and first vibrational state are to second order

$$c_1(z,t)=1+\frac{i\alpha_{11}}{4\hbar}\sum_j|A_j|^2\sqrt{\frac{\pi}{2}}a_j\left[1+\mathrm{erf}\left(\frac{t}{\sqrt{2}a_j}\right)\right]+\frac{\alpha_{11}^2}{16\hbar^2}\sum_j\sum_k|A_j|^2|A_k|^2D(\sqrt{2}a_j,\sqrt{2}a_k;t)$$
$$+\frac{\alpha_{12}^2}{16\hbar^2}\sum_j\sum_k A_jA_{j-1}^*A_k^*A_{k-1}D\left(\frac{2}{\sqrt{\beta_j+\beta_{j-1}^*}},\frac{2}{\sqrt{\beta_k^*+\beta_{k-1}}};t\right), \quad (12a)$$

$$c_2(z,t)=\frac{i\alpha_{12}}{4\hbar}\sum_j A_j^*A_{j-1}\sqrt{\frac{\pi}{\beta_j^*+\beta_{j-1}}}\left[1+\mathrm{erf}\left(\frac{\sqrt{\beta_j^*+\beta_{j-1}}t}{2}\right)\right]$$
$$+\frac{\alpha_{11}\alpha_{12}}{16\hbar^2}\sum_j\sum_k A_j^*A_{j-1}|A_k|^2D\left(\frac{2}{\sqrt{\beta_j^*+\beta_{j-1}}},\sqrt{2}a_k;t\right)$$
$$+\frac{\alpha_{12}\alpha_{22}}{16\hbar^2}\sum_j\sum_k|A_j|^2A_k^*A_{k-1}D\left(\sqrt{2}a_j,\frac{2}{\sqrt{\beta_k^*+\beta_{k-1}}};t\right). \quad (12b)$$

IV. POLARIZATION

The polarization induced by the sum of Gaussian electric fields is given by the expectation value of the dipole moment:

$$\langle p\rangle=\langle\psi(z,t)|p|\psi(z,t)\rangle. \quad (13)$$

To determine the polarization, we substitute Eq. (3) for $|\psi(z,t)\rangle$ and then take the Fourier transform. We define the Fourier transform as

$$\hat{f}(\omega)\equiv\mathcal{F}\{f(t)\}(\omega)=\int_{-\infty}^{\infty}f(t)e^{-i\omega t}dt \quad (14)$$

and the inverse Fourier transform as

$$f(t)\equiv\mathcal{F}^{-1}\{\hat{f}(\omega)\}(t)=\frac{1}{2\pi}\int_{-\infty}^{\infty}\hat{f}(\omega)e^{i\omega t}d\omega. \quad (15)$$

If we recall our assumption that $p_{1n'}$ and p_{n2} are the only nonzero dipole matrix elements, we can rewrite the polarization as a single infinite sum over $n>2$. We can also consider Eq. (4) written in terms of just the amplitudes c_1 and c_2 for $n>2$. By taking the Fourier transform of Eq. (4) for $n>2$, substituting it into our polarization, and recalling our assumption that $W_{21}\approx\omega_R$, we can write the Fourier transform of the polarization solely in terms of convolutions of $\hat{c}_1$, $\hat{c}_2$, and $\hat{\epsilon}_j$.

The Fourier transform of the polarization is given by the sum

$$\mathcal{F}\{\langle p\rangle\}=\sum_{n=3}^{\infty}\sum_j\sum_{p=1,2}\sum_{q=1,2}p_{pn}p_{nq}\times[\hat{S}_{pq}(\omega,\omega_{j+p-q},\epsilon_j)+\hat{S}_{pq}(\omega,-\omega_{j-p+q},\epsilon_j^*)]+\mathrm{c.c.} \quad (16)$$

over terms of the following form:

$$\hat{S}_{pq}(\omega,\omega',\epsilon_j)=\frac{-1}{8\pi^2\hbar}\int_{-\infty}^{\infty}\hat{c}_p^*(\omega-u-W_{pn})\frac{1}{u}\times\int_{-\infty}^{\infty}\hat{c}_q(y)\hat{\epsilon}_j(u-y+W_{pn}-\omega')dudy. \quad (17)$$

To integrate this general term, we first determine the Fourier transform of the general amplitude c_p. This general amplitude is a sum over the different time dependencies of the amplitudes given by Eq. (12):

$$c_p = \eta_p^{(0)} + \sum_j \Bigg[\eta_{pa}^{(1)}(j)\mathrm{erf}\left(\frac{t}{\sqrt{2}a_j}\right) + \eta_{pb}^{(1)}(j)\mathrm{erf}\left(\frac{\sqrt{\beta_j+\beta_{j-1}^*}t}{2}\right) + \eta_{pa}^{(2)}(j)\mathrm{erf}\left(\frac{t}{\sqrt{2}a_j}\right)^2 + \eta_{pb}^{(2)}(j)\mathrm{erf}\left(\frac{\sqrt{\beta_j+\beta_{j-1}^*}t}{2}\right)^2 + \eta_{pa}^{(3)}(j)e^{-t^2/a_j^2} + \eta_{pb}^{(3)}(j)e^{-(\beta_j+\beta_{j-1}^*)t^2/2}\Bigg]. \tag{18}$$

The Fourier transform of the error function is $\mathcal{F}\{\mathrm{erf}(t)\} = -2ie^{-\omega^2/4}/\omega$. We can determine the Fourier transform of the square of the error function by taking a convolution of two error functions. The resulting integrals are improper but we will take the principal value since they describe a physical system.

Using partial fraction decomposition, we can separate the integrand into two terms with a single pole each. We can then identify the principle value of the Fourier transform of $\mathrm{erf}^2(t)$ as a sum of Hilbert transforms of Gaussian functions, where the Hilbert transform is defined as

$$H(y) = \frac{1}{\pi}P\int_{-\infty}^{\infty}\frac{e^{-x^2}}{y-x}dx \tag{19}$$

and it can be shown that the Hilbert transform of a Gaussian function is proportional to the Dawson function $F(x)$ (see Appendix A).

Using the oddness of the Dawson function, we find that

$$\mathcal{F}\{\mathrm{erf}^2(t)\} = \frac{-8e^{-\omega^2/8}}{\sqrt{\pi}\omega}F\left(\frac{\omega}{2\sqrt{2}}\right). \tag{20}$$

We thereby determine $\hat{c}_p$ and then can integrate Eq. (17) over y. Since $\hat{\epsilon}_j$ is a Gaussian function, we have to integrate several more terms that are Hilbert transforms of Gaussian functions. We also have to integrate Hilbert transforms of Gaussian functions that are multiplied by Dawson functions.

Consider, for example,

$$\int_{-\infty}^{\infty} e^{-(u-y+W_{pn}-\omega')^2/\beta_j}\frac{e^{-a_l^2y^2/4}}{y}F\left(\frac{a_l y}{2}\right)dy = \exp\left(\frac{-a_l^2}{a_l^2\beta_j+4}(u+W_{pn}-\omega')^2\right)\int_{-\infty}^{\infty}\frac{1}{y}F\left(\frac{a_l y}{2}\right) \times \exp\left[-\frac{a_l^2\beta_j+4}{4\beta_j}\left(y-\frac{4(u+W_{pn}-\omega')}{a_l^2\beta_j+4}\right)^2\right]dy. \tag{21}$$

The center of the Gaussian function in the integral is far from the center of the Dawson function. Since the Gaussian function decays quickly, it will pick out the value of the Dawson function near the center of the Gaussian, $y = 4(u+W_{pn}-\omega')/(a_l^2\beta_j+4)$. Therefore, we can approximate this integral as the product of the Dawson function evaluated at the center of the Gaussian and a Hilbert transform of the Gaussian. Thus, the terms of this form in the integral over y result in the product of a Gaussian function with two Dawson functions.

$\hat{S}_{pq}(\omega,\omega',\epsilon_j)$ is then a single integral over 49 terms that depend on u. However, we are only considering up to second-order effects, which means we can neglect any terms of third order or higher in the polarizability. This leaves 17 terms to consider.

Seven of the terms are integrals of a Dirac delta function multiplied by the result of the integral over y. Two of the terms are Hilbert transforms of Gaussian functions, which integrate to Dawson functions as discussed previously. The other eight terms can be integrated and simplified in the following way.

(1) Use partial fraction decomposition to separate the term into two terms with poles at $u = 0$ and $\omega - W_{pn}$.

(2) Both terms take the form of a Gaussian function centered at ω' multiplied by one or two Dawson functions and divided by $W_{pn} - \omega$.

(3) Since the width of the Gaussian function is much narrower than the difference between W_{pn} and ω', we can approximate the denominators as $W_{pn} - \omega'$.

(4) The terms integrated over a pole at $u = 0$ have a Dawson function with an input on the order of the pulse width times the laser frequency. Since we are in the adiabatic regime, this is very large and the Dawson function $F(x)$ can be approximated as $1/(2x)$.

(5) The terms integrated over a pole at $u = \omega - W_{pn}$ have only Dawson functions that depend on ω as $\omega - \omega'$. Since these are multiplied by a Gaussian function centered at ω', the input to these Dawson functions is therefore small and we can approximate the Dawson function $F(x)$ as x.

After making these approximations, we can take the inverse Fourier transform of $\hat{S}_{pq}(\omega,\omega',\epsilon_j)$ and return to the time domain. The only dependence on W_{pn} remaining in $S_{pq}(t,\omega',\epsilon_j)$ is in the denominator of the terms. The denominators are either $W_{pn}^2 - \omega'^2$ from the terms with the pole at $u = 0$ or $W_{pn} - \omega'$ from all the others.

We can now consider the entire equation for $\langle p\rangle$:

$$\langle p\rangle = \sum_{n=3}^{\infty}\sum_j\sum_{p=1,2}\sum_{q=1,2} p_{pn}p_{nq}[S_{pq}(t,\omega_{j+p-q},\epsilon_j) + S_{pq}(t,-\omega_{j-p+q},\epsilon_j^*)] + \mathrm{c.c.} \tag{22}$$

We eliminate the terms where $p = q$ and consider the sum over n of $S_{pq}(t,\omega_{j+p-q},\epsilon_j)$ and $S_{qp}^*(t,-\omega_{j-p+q},\epsilon_j^*)$. The terms with $W_{pn}^2 - \omega'^2$ in the denominator are multiplied by i and sum to zero while the terms with $W_{pn} - \omega'$ in the denominator sum to the polarizability α_{12}.

Thus we obtain the polarization to second order as the following simplified equation:

$$\langle p\rangle = \frac{\alpha_{12}}{2}\sum_j[E_j e^{i\phi_j}e^{i\omega_{j-1}t}R_{12}(t,\beta_j) + E_j^* e^{-i\phi_j}e^{-i\omega_{j+1}t}R_{12}(t,\beta_j^*) + \mathrm{c.c.}] \tag{23}$$

where R_{12} are given in Appendix B.

To better understand this equation, we will assume that the Raman orders maintain approximately the same width

and chirp, which we will denote a and b respectively. We define also the sum of electric-field amplitudes $\mathcal{I} \equiv \sum_j |E_j|^2$. We then have the polarization to second order as

$$\langle p \rangle = \frac{\alpha_{12}}{2} \sum_j \left[E_j e^{i\phi_j} e^{i\omega_{j-1}t} e^{ibt^2/4} R_{12}(t,b) + E_j^* e^{-i\phi_j} e^{-i\omega_{j+1}t} e^{-ibt^2/4} R_{12}(t,-b) + \text{c.c.} \right] \tag{24}$$

where

$$\begin{aligned} R_{12}(t,b) = \sum_j E_j^* E_{j-1} e^{-i(\phi_j - \phi_{j-1})} \Bigg\{ & \left[\frac{\pi a^2 \alpha_{12}}{64\hbar^2} (3\alpha_{11} + \alpha_{22}) \mathcal{I} + \frac{ia\alpha_{12}}{4\hbar} \sqrt{\frac{\pi}{2}} \right] e^{-t^2/(4a^2)} \\ & + \sqrt{\frac{2}{\pi}} \frac{3 - ia^2 b}{1 - ia^2 b} \left[\frac{\pi a^2 \alpha_{12}}{32\hbar^2} (3\alpha_{11} + \alpha_{22}) \mathcal{I} + \frac{ia\alpha_{12}}{4\hbar} \sqrt{\frac{\pi}{2}} \right] \frac{t}{a} e^{-3t^2/(4a^2)} \\ & + \frac{1}{1 - ia^2 b} \frac{a^2 \alpha_{12}}{16\hbar^2} (3\alpha_{11} + 2\alpha_{22}) \mathcal{I} \left(\frac{t^2}{a^2} (5 - ia^2 b) - 2 \right) e^{-5t^2/(4a^2)} \Bigg\}. \end{aligned} \tag{25}$$

At zeroth order, the time dependence of the polarization is the same as the perturbing electric field as expected. However, the higher-order terms introduce a more complex time dependence that is narrower in time and depends on higher powers of time. We expect this trend to continue if we consider higher-order effects, which would introduce for example a term proportional to $t^3/a^3 e^{-7t^2/(4a^2)}$ at third order.

V. SPECTRUM

The polarization given in the previous section is the response of the potential in time. The frequencies emitted by the Raman medium are therefore given by the magnitude of the Fourier transform of the polarization. By taking the Fourier transform of Eq. (24), we obtain the MRG spectrum, $W(\omega) = |\mathcal{F}\{\langle p \rangle\}|^2$:

$$\begin{aligned} W(\omega) = \Bigg| \frac{\alpha_{12}}{2} \sum_j [& E_j e^{i\phi_j} \hat{R}_{12}(\omega - \omega_{j-1}, b) + E_j^* e^{-i\phi_j} \hat{R}_{12}(\omega + \omega_{j+1}, -b) + E_j^* e^{-i\phi_j} \hat{R}_{12}^*(\omega + \omega_{j-1}, b) \\ & + E_j e^{i\phi_j} \hat{R}_{12}^*(\omega - \omega_{j+1}, -b)] \Bigg|^2 \end{aligned} \tag{26}$$

where

$$\begin{aligned} R_{12}(\nu,b) = \sum_j E_j^* E_{j-1} e^{-i(\phi_j - \phi_{j-1})} \Bigg\{ & \frac{a\sqrt{\pi}}{\sqrt{1 - ia^2 b}} \left[\frac{\pi a^2 \alpha_{12}}{32\hbar^2} (3\alpha_{11} + \alpha_{22}) \mathcal{I} + \frac{ia\alpha_{12}}{2\hbar} \sqrt{\frac{\pi}{2}} \right] \exp\left(-\frac{a^2 \nu^2}{1 - ia^2 b} \right) \\ & - \frac{ia^2 \sqrt{2}}{(1 - ia^2 b)\sqrt{3 - ia^2 b}} \left[\frac{\pi a^2 \alpha_{12}}{8\hbar^2} (3\alpha_{11} + \alpha_{22}) \mathcal{I} + \frac{ia\alpha_{12}}{\hbar} \sqrt{\frac{\pi}{2}} \right] \nu \exp\left(-\frac{a^2 \nu^2}{3 - ia^2 b} \right) \\ & - \frac{a^3 \sqrt{\pi}}{(1 - ia^2 b)(5 - ia^2 b)^{3/2}} \frac{a^2 \alpha_{12}}{2\hbar^2} (3\alpha_{11} + 2\alpha_{22}) \mathcal{I} \nu^2 \exp\left(-\frac{a^2 \nu^2}{5 - ia^2 b} \right) \Bigg\}. \end{aligned} \tag{27}$$

We can specifically find the spectrum radiated by the Raman medium due to the initial excitation. Initially, the only electric fields are the pump and the probe beams with frequency ω_0 and ω_{-1} and amplitudes E_0 and E_{-1} respectively. We will assume the electric-field amplitudes are the same since we will compare to experiments where this is approximately the case.

As expected, the spectrum has four peaks corresponding to the pump, probe, first Stokes, and first anti-Stokes frequencies.

For the rest of this paper, we will be inspecting the behavior of the first anti-Stokes peak (near $\omega_1 = \omega_0 + \omega_R$). The dependence of the first anti-Stokes peak on varying electric-field amplitudes and chirps is shown below.

VI. DISCUSSION

The energies in Fig. 1 correspond to the electric-field amplitude expected from laser pulses with mJ order energy that lose several orders of magnitude to processes besides Raman.

At low energies and no chirp ($b = 0$), the spectrum $W(\omega)$ [Eq. (26)] near the anti-Stokes frequency is a singular peak centered at the anti-Stokes frequency. As we increase

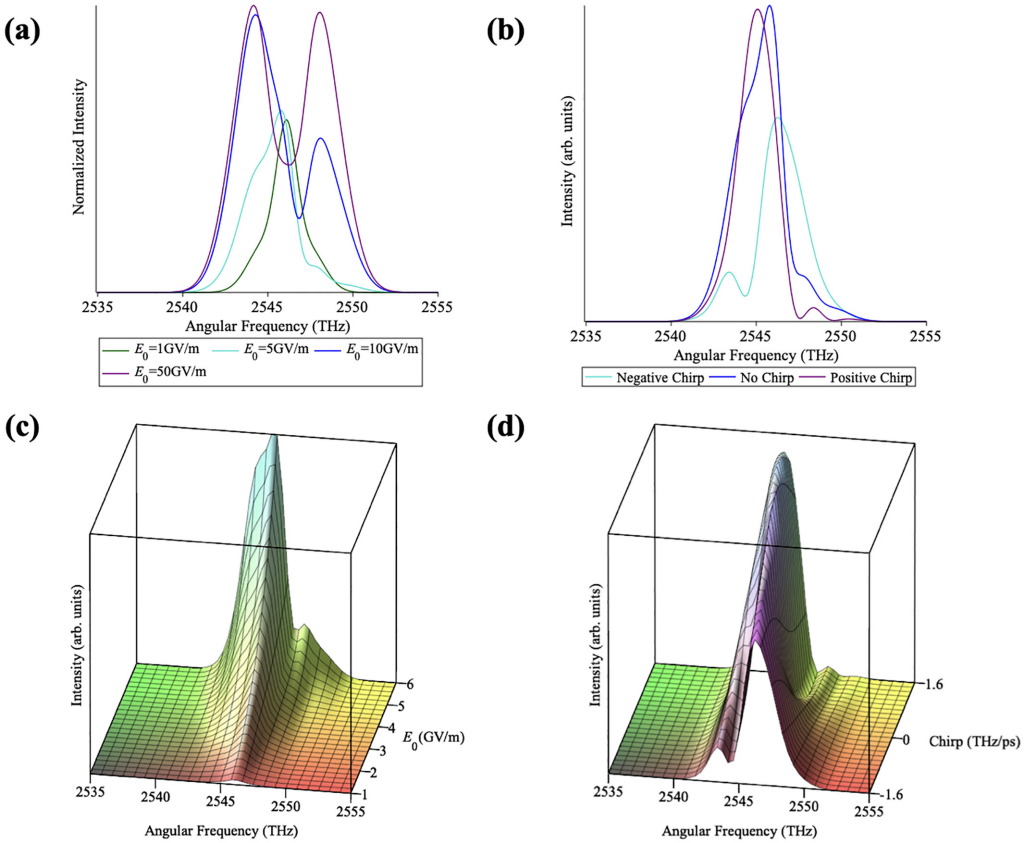

FIG. 1. Spectrum of radiation emitted by the Raman medium upon initial excitation around the anti-Stokes frequency with varying (a) electric-field amplitudes $E_0 = E_{-1}$ ($b = 0$) and (b) chirp b ($E_0 = E_{-1} = 5 \times 10^9$ V/m). (c), (d) Continuous change in spectrum with (c) electric-field amplitude and (d) chirp. We have used the example values $\omega_0 = 2\pi\,382$ THz, $\omega_R = 2\pi\,23.25$ THz, $a = 800$ fs, $\alpha_{12} = 1.465 \times 10^{-42}$ Cm^2/V, $\alpha_{11} = 1.456 \times 10^{-42}$ Cm^2/V, and $\alpha_{22} = 1.478 \times 10^{-42}$ Cm^2/V and assumed $E_0 = E_{-1}$ [17,18].

electric-field amplitude (and thereby energy), Figs. 1(a) and 1(c) show the main peak shifting to the red as the spectrum splits and the secondary peak slowly grows. The redshifting of the central peak with increasing energy agrees with experiment [4]. If we could increase the energy by an order of magnitude in a similar experiment, we would expect to clearly see the secondary peak. This provides an avenue to test our theoretical model.

When we add chirp to the pulses, we introduce another asymmetry. Negative chirps and positive chirps produce sidebands shifted to the red and blue respectively. However, we can see from Figs. 1(b) and 1(d) that the positively chirped sideband is much smaller than the negatively chirped sideband and would likely be lost in experimental noise. This occurs because the electric-field amplitude asymmetry and the positive chirp asymmetry both suppress the same side of the double peak. The spectrum for MRG with negatively chirped pulses has redshifted shoulders, as observed experimentally [10,17,19]. This theory indicates that the redshifted shoulders in MRG occur because the asymmetry from the chirp offsets the asymmetry in how the secondary peak emerges with increasing electric-field amplitude.

While the comparison between the theoretical and experimental spectral shapes is qualitative, we can already see that the method of calculating the analytic spectrum predicts the multipeaked, energy-dependent structure seen experimentally but not in previous numerical solutions. Moreover, the general form of the equation—a Schrödinger equation with a Hamiltonian of Gaussian electric fields—is common for optical systems excited by laser pulses. Solving this system results in Hilbert transforms of Gaussian functions, which are also seen both in analytic signals and the plasma dispersion function [12]. These methods can clearly be applied to find analytic spectra of other optical systems that could similarly show features not seen with other approximations or numerical methods.

VII. CONCLUSION

We have presented a theory for the analytic spectrum of radiation emitted by a Raman medium excited by a multiwave electric field. Experimental MRG has shown several spectral features that differ from the spectra of the exciting laser pulses. These features cannot be seen in numerical calculations concerned with relative amplitudes of the Raman orders.

We expand the two-state Schrödinger equation for the MRG system perturbatively in a Dyson series and assume Gaussian pulse shape for the excitations. We solve for the ground and first vibrational state amplitudes to second order in the two-state polarizability. We can then find the polarization using the amplitudes, the proportionality of Hilbert transforms of Gaussian functions with the Dawson function, and the

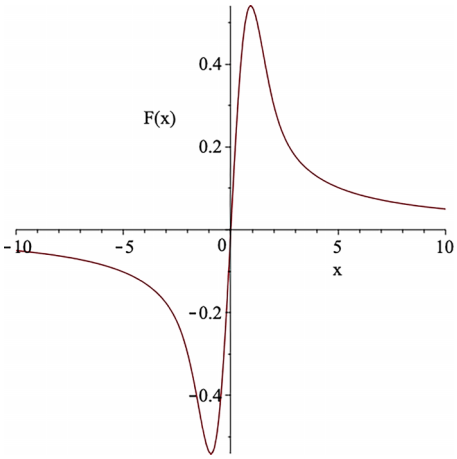

FIG. 2. Dawson function.

approximations of the Dawson function in large and small limits. The Fourier transform of the polarization yields an analytic and perturbative spectrum for the Raman orders.

This theory predicts an energy-dependent double-peaked structure and chirp asymmetry of the spectra that are not visible with numerical or approximate integration methods but that occur in experimental observations. The same theoretical methods can be applied to other systems excited by Gaussian laser pulses to find the analytic spectra and new features thereof.

ACKNOWLEDGMENTS

We wish to acknowledge Daniel James, Donna Strickland, Stephen Rand, Zujun Xu, and Kaleb Ruscitti for useful correspondence and discussion. We also acknowledge the support of the Natural Sciences and Engineering Research Council of Canada (NSERC) [Funding Reference No. 565132/2021].

APPENDIX A: DAWSON FUNCTION

The Dawson function is defined as [see Eq. (7.2.5) in [20]]

$$F(z) = e^{-z^2}\int_0^z e^{t^2}dt \tag{A1}$$

and can be graphed for real z as in Fig. 2.

The following proof is a complex version of that given by [21].

The Hilbert transform of a Gaussian function is given by Eq. (19). We first make the substitution $u = y - x$:

$$H(y) = \frac{1}{\pi}P\int_{-\infty}^{\infty}\frac{e^{-(y-u)^2}}{u}(-du). \tag{A2}$$

We can then write out the principle value explicitly:

$$H(y) = \frac{-1}{\pi}\lim_{\epsilon\to 0}\left(\int_{-\infty}^{-\epsilon}\frac{e^{-(y-u)^2}}{u}du + \int_{\epsilon}^{\infty}\frac{e^{-(y-u)^2}}{u}du\right). \tag{A3}$$

We now make the substitution $z = -u$ in the first integral and reverse the order of integration to simplify $H(y)$ to

$$H(y) = \frac{2}{\pi}e^{-y^2}\lim_{\epsilon\to 0}\int_{\epsilon}^{\infty}\frac{\sinh(2yz)}{z}e^{-z^2}dz. \tag{A4}$$

We now have an integrand that is a holomorphic function of y and is continuous in z over the bounds of integration. Therefore, we can differentiate the integral in $H(y)$:

$$\frac{\partial}{\partial y}\int_{\epsilon}^{\infty}\frac{\sinh(2yz)}{z}e^{-z^2}dz = 2\int_{\epsilon}^{\infty}\cosh(2yz)e^{-z^2}dz, \tag{A5}$$

which is now just an integral of complex Gaussian functions that we can easily integrate to $\sqrt{\pi}e^{y^2}$.

Since $\sinh(0) = 0$, we can therefore write the Hilbert transform of a Gaussian in the simplified integral form that can be identified with the definition of the Dawson function above:

$$H(y) = \frac{2}{\sqrt{\pi}}e^{-y^2}\int_0^y e^{t^2}dt = \frac{2}{\sqrt{\pi}}F(y). \tag{A6}$$

APPENDIX B: POLARIZATION WITH DIFFERING PULSE SHAPES

If we do not make the approximation that all Raman order electric fields have the same width and chirp, we instead write the polarization [Eq. (13)] as a sum of unsimplified $R_{12}(t,\beta_j)$:

$$\begin{aligned}
R_{12}(t,\beta_j) &= \eta_1^{(0)*}\eta_2^{(0)}e^{-\beta_j t^2/4} \\
&+ \sum_l\left(\sqrt{\frac{2}{\pi}}\frac{a_l^2\beta_j+2}{a_l^2\beta_j}\left(\eta_{1a}^{(1)*}(l)\eta_2^{(0)}+\eta_1^{(0)*}\eta_{2a}^{(1)}(l)\right)\frac{t}{a_l}e^{-(a_l^2\beta_j+2)t^2/(4a_l^2)}\right. \\
&+ \frac{1}{\sqrt{\pi}\beta_j}\Big[(\beta_j+\beta_l^*+\beta_{l-1})\eta_{1b}^{(1)*}(l)\eta_2^{(0)}\sqrt{\beta_l^*+\beta_{l-1}}te^{-t^2(\beta_j+\beta_l^*+\beta_{l-1})/4} \\
&+(\beta_j+\beta_l+\beta_{l-1}^*)\eta_1^{(0)*}\eta_{2b}^{(1)}(l)\sqrt{\beta_l+\beta_{l-1}^*}te^{-t^2(\beta_j+\beta_l+\beta_{l-1}^*)/4}\Big] \\
&+ \frac{8}{\pi\beta_j a_l^2}\left(\eta_{1a}^{(2)*}(l)\eta_2^{(0)}+\eta_1^{(0)*}\eta_{2a}^{(2)}(l)\right)\left(\frac{t^2}{a_l^2}(a_l^2\beta_j+4)-2\right)e^{-(a_l^2\beta_j+4)t^2/(4a_l^2)} \\
&+ \frac{4}{\pi\beta_j}\Big[(\beta_l^*+\beta_{l-1})\eta_{1b}^{(2)*}(l)\eta_2^{(0)}\left[t^2(\beta_j+2\beta_l^*+2\beta_{l-1})-2\right]e^{-(\beta_j+2\beta_l^*+2\beta_{l-1})t^2/4}
\end{aligned}$$

$$
\begin{aligned}
&+(\beta_l+\beta_{l-1}^*)\eta_1^{(0)*}\eta_{2b}^{(2)}(l)\left[t^2(\beta_j+2\beta_l+2\beta_{l-1}^*)-2\right]e^{-(\beta_j+2\beta_l+2\beta_{l-1}^*)t^2/4}\Big]\\
&+\sum_k\Bigg\{\frac{2}{\pi a_k a_l\beta_j}\eta_{1a}^{(1)*}(l)\eta_{2a}^{(1)}(k)\left(t^2\frac{(a_l^2\beta_j+2)a_k^2+2a_l^2}{a_k^2a_l^2}-2\right)e^{-\frac{(a_l^2\beta_j+2)a_k^2+2a_l^2}{4a_k^2a_l^2}t^2}\\
&+\frac{\sqrt{2}}{\pi\beta_j}\Bigg[\sqrt{\frac{\beta_k+\beta_{k-1}^*}{a_l^2}}\eta_{1a}^{(1)*}(l)\eta_{2b}^{(1)}(k)\left(t^2\frac{a_l^2(\beta_j+\beta_k+\beta_{k-1}^*)+2}{a_l^2}-2\right)e^{-(a_l^2(\beta_j+\beta_k+\beta_{k-1}^*)+2)t^2/(4a_l^2)}\\
&+\sqrt{\frac{\beta_k^*+\beta_{k-1}}{a_l^2}}\eta_{1b}^{(1)*}(k)\eta_{2a}^{(1)}(l)\left(t^2\frac{a_l^2(\beta_j+\beta_k^*+\beta_{k-1})+2}{a_l^2}-2\right)e^{-(a_l^2(\beta_j+\beta_k^*+\beta_{k-1})+2)t^2/(4a_l^2)}\Bigg]\\
&+\frac{\sqrt{(\beta_k^*+\beta_{k-1})(\beta_l+\beta_{l-1}^*)}}{\pi\beta_j}\eta_{1b}^{(1)*}(k)\eta_{2b}^{(1)}(l)\left[(\beta_j+\beta_k^*+\beta_{k-1}+\beta_l+\beta_{l-1}^*)t^2-2\right]\\
&\times e^{-(\beta_j+\beta_k^*+\beta_{k-1}+\beta_l+\beta_{l-1}^*)t^2/4}\Bigg\}+\left(\eta_{1a}^{(3)*}(l)\eta_2^{(0)}+\eta_1^{(0)*}\eta_{2a}^{(3)}(l)\right)e^{-(a_l^2\beta_j+4)t^2/(4a_l^2)}\\
&+\eta_{1b}^{(3)*}(l)\eta_2^{(0)}e^{-(\beta_j+2\beta_l^*+2\beta_{l-1})t^2/4}+\eta_1^{(0)*}\eta_{2b}^{(3)}(l)e^{-(\beta_j+2\beta_l+2\beta_{l-1}^*)t^2/4}\Bigg)
\end{aligned}
\tag{B1}
$$

where we have the time-independent coefficients η from the amplitudes $c_1(t)$ and $c_2(t)$:

$$
\begin{aligned}
\eta_1^{(0)*}\eta_2^{(0)}&=\sum_l\xi_{2b}^{(1)}(l)+\sum_l\sum_k\xi_{2a}^{(2)}(l,k)\frac{\sqrt{2}\pi a_l}{4\sqrt{\beta_k^*+\beta_{k-1}}}\\
&\quad+\frac{\alpha_{11}}{\alpha_{22}}\xi_{2a}^{(2)}(k,l)\frac{\sqrt{2}\pi a_k}{4\sqrt{\beta_l^*+\beta_{l-1}}}+\xi_{1a}^{(1)*}(l)\xi_{2b}^{(1)}(k)\\
\eta_{1a}^{(1)*}(l)\eta_2^{(0)}&=\sum_k\xi_{1a}^{(1)*}\xi_{2b}^{(1)}(k)\\
\eta_{1b}^{(1)*}(l)\eta_2^{(0)}&=\eta_{1a}^{(2)*}(l)\eta_2^{(0)}=\eta_{1b}^{(2)*}(l)\eta_2^{(0)}\\
&=\eta_{1a}^{(3)*}(l)\eta_2^{(0)}=\eta_{1b}^{(3)*}(l)\eta_2^{(0)}=0\\
\eta_1^{(0)*}\eta_{2a}^{(1)}(l)&=\sum_k\xi_{2a}^{(2)}(l,k)\frac{\sqrt{2}\pi a_l}{2\sqrt{\beta_k^*+\beta_{k-1}}}\\
\eta_1^{(0)*}\eta_{2b}^{(1)}(l)&=\xi_{2b}^{(1)}(l)+\sum_k\xi_{1a}^{(1)*}(k)\xi_{2b}^{(1)}(l)\\
&\quad+\frac{\alpha_{11}}{\alpha_{22}}\xi_{2a}^{(2)}(k,l)\frac{\sqrt{2}\pi a_k}{2\sqrt{\beta_l^*+\beta_{l-1}}}\\
\eta_1^{(0)*}\eta_{2a}^{(2)}(l)&=\sum_k\xi_{2a}^{(2)}(l,k)\frac{\sqrt{2}\pi a_l}{4\sqrt{\beta_k^*+\beta_{k-1}}}\\
\eta_1^{(0)*}\eta_{2b}^{(2)}(l)&=\sum_k\frac{\alpha_{11}}{\alpha_{22}}\xi_{2a}^{(2)}(k,l)\frac{\sqrt{2}\pi a_k}{4\sqrt{\beta_l^*+\beta_{l-1}}}\\
\eta_1^{(0)*}\eta_{2a}^{(3)}(l)&=\sum_k\xi_{2a}^{(2)}(l,k)\left(\frac{1}{\beta_k^*+\beta_{k-1}}-\frac{a_l/\sqrt{2}}{\sqrt{\beta_k^*+\beta_{k-1}}}\right)\\
\eta_1^{(0)*}\eta_{2b}^{(3)}(l)&=\sum_k\frac{\alpha_{11}}{\alpha_{22}}a_k\xi_{2a}^{(2)}(k,l)\left(\frac{a_k}{2}-\frac{1}{\sqrt{2}\sqrt{\beta_l^*+\beta_{l-1}}}\right)\\
\eta_{1a}^{(1)*}(l)\eta_{2a}^{(1)}(k)&=\eta_{1b}^{(1)*}(k)\eta_{2a}^{(1)}(l)=\eta_{1b}^{(1)*}(k)\eta_{2b}^{(1)}(l)=0\\
\eta_{1a}^{(1)*}(l)\eta_{2b}^{(1)}(k)&=\xi_{1a}^{(1)*}(l)\xi_{2b}^{(1)}(k)
\end{aligned}
\tag{B2}
$$

and

$$\xi_{1a}^{(1)}(l) = \frac{i\alpha_{11}}{4\hbar}|A_l|^2\sqrt{\frac{\pi}{2}}a_l,$$
$$\xi_{1a}^{(2)}(l,k) = \frac{\alpha_{11}^2}{16\hbar^2}|A_l|^2|A_k|^2,$$
$$\xi_{1b}^{(2)}(l,k) = \frac{\alpha_{12}^2}{16\hbar^2}A_l A_{l-1}^* A_k^* A_{k-1},$$
$$\xi_{2b}^{(1)}(l) = \frac{i\alpha_{12}}{4\hbar}A_l^* A_{l-1}\sqrt{\frac{\pi}{\beta_l^* + \beta_{l-1}}},$$
$$\xi_{2a}^{(2)}(l,k) = \frac{\alpha_{12}\alpha_{22}}{16\hbar^2}|A_l|^2 A_k^* A_{k-1}. \tag{B4}$$

We have again only considered the coefficients η to second order in the polarizability.

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