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A Theoretical Study on Chirped Coherent Raman Spectroscopy†

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On the basis of a second-order perturbation theory, some analytical formulas are derived for describing spontaneous and stimulated Raman scatterings of a molecular system in the presence of weak pulse-mode chirped laser field. We are concerned, in particular, with the effect of chirping of the incident laser pulse on the Raman spectroscopic profile and the molecular vibrational distribution. From the derived formulas in the small chirp rate limit, it was found that the molecular vibrational distribution by the spontaneous emission is enhanced in the chirped pulse case relative to the transform-limited pulse and that the difference caused by the sign of the chirp rate essentially does not exist. On the other hand, the overtone molecular vibrational distribution by the stimulated emission was found to change considerably, depending on the sign of the chirp rate.

I. Introduction

In recent years, with the rapid development of technology to produce powerful ultrashort pulse lasers, many useful and powerful spectroscopic techniques, e.g., absorption and emission spectroscopies, have become conveniently available for investigating static and dynamic aspects of chemical reactions. For example, Raman spectroscopy, which is a two-photon process involving incident and scattered photons, is receiving much attention as a powerful technique for extracting information about potential energy surfaces (PESs), vibrational force constants, etc. On the other hand, the absorption process is utilized as a complement to the Raman interaction for a variety of molecular vibrations. A complete vibrational spectrum can be obtained by combining these two spectroscopy methods.

In regards to the kind of laser incident on the chemical species, the chirped (phase-modulated) laser pulse is attracting more attention in recent years. At present, it is being intensively investigated and used for controlling molecular dynamics[1−8] and can be shaped experimentally.[9,10] Ultrashort optical pulses generally create nonstationary vibrational states on both the ground and excited electronic states. It is recognized that the nonstationary vibrational states created on the ground electronic state are the result of a stimulated Raman (stimulated emission due to intense pulse interaction) or second-order process. In particular, intense laser pulses with a moderate negative chirp rate are known to create nonstationary vibrational states on the ground electronic state.[8,11−14] This dynamical effect is known as the intrapulse pump−dump mechanism,[15−17] experiments on which have been quite recently analyzed by a nonperturbative analytic approach.[18] This mechanism has been found to be efficient for predissociation lifetime control of the wave packet excited to the upper electronic quasibound state from the bound ground eletronic state[8] and for quantum control of photodissociation and photodesorption dynamics.[19,20]

Currently, while continuum Raman experiments are conducted at a broad range of time scales, ranging from the continuous-wave (CW) mode to the femtosecond regime, the lasers employed are mostly fixed at the resonant or off-resonant excitation frequency. Here follows some research conducted using short laser pulses with different incident pulse wavelength. As a first example, Rousseau et al. classified Raman scatterings into three types according to the excitation frequency: off-resonance, discrete resonance, and continuum resonance Raman scatterings.[21] They found that there are many differences in scattering properties in these three excitation frequency regions. As a second example, the excitation frequency dependence of emission lines was measured for the molecules IBr[22] and CH_3I,[23] and it was found that the Raman spectrum contains more structure than the absorption spectrum.[24−26,28] From theoretical considerations, Shapiro compared the theory of Raman scattering by pulse-mode lasers with that by CW lasers,[24−26] by which the Raman amplitude α_{fi} is calculated on the basis of the Kramers−Heisenberg-Dirac (KHD) expression

$$\alpha_{\mathrm{fi}} \propto \sum_j \frac{\langle\phi_{\mathrm{f}}|\chi_j\rangle\langle\chi_j|\phi_{\mathrm{i}}\rangle}{\hbar(\omega_{\mathrm{i}}+\omega_{\mathrm{L}}-\omega_j+i\Gamma)} \tag{1.1}$$

where $|\phi_{\mathrm{i}}\rangle = \mu_{12}|\chi_{\mathrm{i}}\rangle$ and $|\phi_{\mathrm{f}}\rangle = \mu_{21}|\chi_{\mathrm{f}}\rangle$. The ket vectors $|\chi_{\mathrm{i}}\rangle$ and $|\chi_{\mathrm{f}}\rangle$ are the initial and final vibrational eigenstates of the ground electronic state, respectively. μ_{12} and μ_{21} are the transition dipole moments between the ground and excited electronic states. The ket vectors $|\chi_j\rangle$'s are the *j*th vibrational eigenstates of the excited electronic state. ω_{i}, ω_{j}, and ω_{L} are the initial and final vibrational state energies and the incident radiation frequency, respectively. Γ is the phenomenological lifetime of the excited electronic state. Shapiro also extended his study to Raman scattering by strong laser pulses.[27] Lu et al.[29] and Keller et al.[30] approached continuum Raman scattering with (monochromatic) pulses by time-dependent wave packet methodology. They also took

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stimulated Raman scattering into account. So far, only Duppen et al. have investigated chirped coherent Raman scattering in connection with chirped four-wave mixing.[31] Melinger et al. studied time-dependent resonance Raman scattering and resonance hot luminescence induced by pulse-mode laser by use of a perturbative density matrix formalism.[32] They later also considered the effect of the phase incoherence of the incident light on the resonance secondary radiation,[33,34] which bears a certain resemblance to chirped laser pulses (see eq 3 of ref 33). However, none of these studies has investigated the effect of coherent chirping of the incident laser pulse on the spontaneous and stimulated emission spectra.

In this paper, it is shown theoretically how a small chirp rate, together with the excitation center frequency, influences the spontaneous and stimulated Raman spectrum and the molecular vibrational distribution. The present paper is organized as follows. In section II, using the stationary eigenstates approach, a time-dependent theory is derived of the spontaneous and stimulated Raman scatterings for chirped laser pulses that are treated perturbatively with regard to the chirp rate. After that, our focus is directed to the Lorentzian pulse profile, which allows the transient and static behaviors to be analyzed in detail. From the derived formulas, the time-dependent spontaneous emission amplitude $b_l^{\mathrm{L}}(t)$ and the stimulated emission amplitude $c_j^{\mathrm{gr}}(t)$ are found to have three characteristic transient behaviors, common to both chirp-free and chirp-dependent terms, which are dependent on the pulse duration and spontaneous emission lifetime. In the stimulated emission amplitude, the mixed transient term was found to decay at the rate of pulse profile plus phenomenological spontaneous emission rate. In both the spontaneous and stimulated Raman scatterings, the transient behavior is similar, irrespective of the existence of the chirp. In section III, the numerical results are demonstrated by applying the derived formulas to the laser pulse excitation of the $\mathrm{O_2}$ molecule from the $\mathrm{X^3\Sigma_g^+}$ state to the $\mathrm{B^3\Sigma_u^-}$ state. In section IV, the conclusions of this paper are presented.

II. Theory

Our theoretical treatment of the spontaneous and stimulated Raman scatterings is primarily based on that of Shapiro,[24−26] which is mainly the sum-over-states approach. The main difference is that we include the influence of the stimulated emission and the chirping of the laser pulse.

Consider the single molecule ($\mathrm{O_2}$) placed in a weak radiation field. The temporal state of the total system is described by both molecular and radiation states. In the case of the $\mathrm{B^3\Sigma_u^-}$ state that accommodates some bound vibrational states and many continuum states in the same frequency range as the excitation laser pulse, we have, in the interaction representation

$$\begin{aligned}|\Psi(t)\rangle = |\{n_k\}\rangle\{a_{\mathrm{i}}(t)|\psi_{\mathrm{i}}^{\mathrm{gr}}\rangle \exp(-iE_{\mathrm{i}}^{\mathrm{gr}}t/\hbar) + \\ \sum_j b_j^{\mathrm{ex}}(t)|\psi_j^{\mathrm{ex}}\rangle \exp(-iE_j^{\mathrm{ex}}t/\hbar - \gamma_{\mathrm{ex}}t/2) + \\ \sum_n\int \mathrm{d}Eb_n^E(t)|\psi_n^-(E)\rangle \exp(-iEt/\hbar - \Gamma_{\mathrm{ex}}t/2) + \\ \sum_j c_j^{\mathrm{gr}}(t)|\psi_j^{\mathrm{gr}}\rangle \exp(-iE_j^{\mathrm{gr}}t/\hbar)\} + \\ \sum_{\mathrm{L},l}|\{n_k + 1_L\}\rangle b_l^{\mathrm{L}}(t)|\psi_l^{\mathrm{L}}\rangle \exp(-iE_l^{\mathrm{gr}}t/\hbar)\end{aligned} \quad (2.1)$$

The stationary state $|\psi_{\mathrm{i}}^{\mathrm{gr}}\rangle$ is the initial state and $|\psi_l^{\mathrm{L}}\rangle$ and $|\psi_j^{\mathrm{gr}}\rangle$ are the final states produced by spontaneous and stimulated Raman scatterings, respectively. The stationary states of the electronic state manifold $|\psi_j^{ex}\rangle$ and $|\psi_n^-(E)\rangle$ are intermediate bound and continuum scattering states, respectively. The constants γ_{ex} and Γ_{ex} are phenomenological spontaneous emission rates for the intermediate bound and continuum scattering states, respectively. It is a reasonable approximation to take γ_{ex} or Γ_{ex} to be equal for all levels since all the excited eigenstates have about the same energy and one does not expect γ_{ex} and Γ_{ex} to vary much from level to level. The ket vector $|\{n_k\}\rangle$ denotes the state of the multimode field of the incident light with respective modes $k1$, $k2$, ..., kj, 0, 0, ... and with quantum number n_{k1}, n_{k2}, ..., n_{kj}... The ket vector $|\{n_k\}\rangle$ is the product of the respective mode state

$$|\{n_k\}\rangle = |n_{k1}\rangle|n_{k2}\rangle...|n_{kj}\rangle... = |n_{k1},n_{k2},...,n_{kj},0,0,...\rangle \quad (2.2)$$

It is assumed that the quantum states of mode larger than kj are vacant. The state $|\{n_k + 1_{\mathrm{L}}\}\rangle$ represents the state $|\{n_k\}\rangle$ plus the photon with mode L emitted spontaneously by the molecule

$$|\{n_k + 1_{\mathrm{L}}\}\rangle = |n_{k1},n_{k2},...,n_{kj},0,...,1_{\mathrm{L}},0,...\rangle \quad (2.3)$$

In the following, the continuum state of the excited electronic state $|\psi_n^-(E)\rangle$ can be neglected for convenience and instead formulate only in terms of the bound states $|\psi_j^{\mathrm{ex}}\rangle$. It does not matter if the initial wave packet is nearly completely excited to the continuum state, as in the laser pulse excitation of the $\mathrm{O_2}$ molecule from the $\mathrm{X^3\Sigma_g^-}$ state to the $\mathrm{B^3\Sigma_u^-}$ state. Here, the summation over the internal state $|n\rangle$ and the integration over the translational energy E, $\sum_n\int$ dE, is only replaced by the summation $\sum_j$ in eq 2.1.

The time-dependent Schrödinger equation to be solved is given by

$$i\hbar\frac{\partial|\Psi(t)\rangle}{\partial t} = \{\hat{H}_0 + V(t)\}|\Psi(t)\rangle \quad (2.4)$$

where

$$V(t) = V_{\mathrm{d}}(t) + V_{\mathrm{s}}(t) \quad (2.5)$$

The zeroth-order Hamiltonian part $\hat{H}_0$ consists of two terms: field-free Born−Oppenheimer molecular Hamiltonian $\hat{H}_{\mathrm{BO}}$ and the field $\hat{H}_{\mathrm{F}}$ Hamiltonian

$$\hat{H}_0 = \hat{H}_{\mathrm{BO}} + \hat{H}_{\mathrm{F}} \quad (2.6)$$

The light-matter interaction term $V(t)$ is the sum of the radiative interaction of the molecule in the dipole approximation $V_{\mathrm{d}}(t)$ and the spontaneous emission term $V_{\mathrm{s}}(t)$

$$\mathrm{V}_d(t) = |\{n_k\}\rangle(-\hat{\mu}_E{\bullet}E_c(t))\langle\{n_k\}| \quad (2.7)$$

$$\begin{aligned}V_{\mathrm{s}}(t) = i\sum_{\mathrm{s}}\sqrt{\frac{\hbar\omega_{\mathrm{s}}}{2\epsilon_0 v}} \times \\ |\{n_k + 1_{\mathrm{s}}\}\rangle\, \hat{\mu}_{\mathrm{s}}(\exp(ik_{\mathrm{s}}r - i\omega_{\mathrm{s}}t) + \mathrm{c.c.})\langle\{n_k\}|\end{aligned} \quad (2.8)$$

where v is the cavity volume, ϵ_0 the permittivity of vacuum, and $\hat{\mu}_E$ and $\hat{\mu}_{\mathrm{s}}$ are the components of the molecular electronic dipole operators in the direction of the incoming laser field and the scattered light. Quantization of the radiation field is essential to obtain the spontaneous part of the scattering process, while the stimulated scattering can be well formulated in terms of the classical field. Because the center frequency of our laser pulse (8.7 eV) is much smaller (or the wavelength is much longer) than the typical orbit diameter of the electrons (a_0, 5 ×

10^{-11} m), the position dependence of $V_s(t)$ is ignored

$$V_s(t) \approx i\sum_s \sqrt{\frac{\hbar\omega_s}{2\epsilon_0 v}} |\{n_k + 1_s\}\rangle\, \hat{\mu}_s(\exp(-i\omega_s t) + \text{c.c.})\langle\{n_k\}| \tag{2.9}$$

Using the instantaneous frequency of the carrier wave $\omega(t)$

$$\omega(t) = \omega_0 + \alpha t \tag{2.10}$$

We define the classical external electric field $E_c(t)$ by a polarization vector $\hat{\epsilon}_c$, a pulse shape $S(t)$, and the instantaneous frequency of the carrier wave $\omega(t)$

$$\begin{aligned} E_c(t) &= \hat{\epsilon}_c S(t)[\exp(i\int_0^t \omega(t')\,\mathrm{d}t') + \exp(-i\int_0^t \omega(t')\,\mathrm{d}t')] \\ &= \hat{\epsilon}_c S(t)[\exp(it(\omega_0 + \alpha t/2)) + \exp(-it(\omega_0 + \alpha t/2))] \end{aligned} \tag{2.11}$$

In the present work, our focus is directed to the Lorentzian pulse shape and the pulse frequency modulation by the linear chirp for the classical external electric field $E_c(t)$

$$S(t) = \frac{E_0}{2}\exp(-A|t|) \tag{2.12}$$

The constant A determines the time length of the classical electric field, ω_0 the center frequency of the laser pulse, and α is the linear chirp rate. The laser pulse is called a positively chirped pulse if α is positive and a negatively chirped pulse if α is negative. The instantaneous frequency of the pulse increases over time for a positively chirped pulse, while it decreases for a negatively chirped pulse.

In the small chirp rate limit, $|\alpha t| \ll \omega_0$, the classical electric field $E_c(t)$ can be expanded to first order with regard to the chirp rate α using eq 2.10

$$E_c(t) = E_{c0}(t) + \delta E_c(t) \approx \hat{\epsilon}_c S(t)[(\exp(i\omega_0 t) + \exp(-i\omega_0 t)) + i\alpha t^2/2(\exp(i\omega_0 t) - \exp(-i\omega_0 t))] \tag{2.13}$$

The second term of eq 2.13 is the term for perturbation by the chirp rate. The frequency profile of the chirped laser pulse $E_c(\omega) = E_{c0}(\omega) + \delta E_c(\omega)$ is obtained by Fourier transform of eq 2.13

$$E_c(\omega) = \int_{-\infty}^{\infty} E_c(t)\exp(i\omega t)\,\mathrm{d}t \tag{2.14}$$

$$E_{c0}(\omega) = \int_{-\infty}^{\infty} E_{c0}(t)\exp(i\omega t)\,\mathrm{d}t \tag{2.15}$$

$$\delta E_c(\omega) = \int_{-\infty}^{\infty} \delta E_c(t)\exp(i\omega t)\,\mathrm{d}t \tag{2.16}$$

If the Lorentzian pulse shape eq 2.12 is assumed, the following are obtained

$$E_{c0}(\omega) = \frac{E_0}{2}\left(\frac{2A}{A^2 + (\omega - \omega_0)^2} + \frac{2A}{A^2 + (\omega + \omega_0)^2}\right) \tag{2.17}$$

$$\delta E_c(\omega) = \mathrm{i}\alpha\frac{E_0}{2}\left(\frac{2}{(A + i(\omega - \omega_0))^3} + \frac{2}{(A - i(\omega - \omega_0))^3} - \frac{2}{(A - i(\omega + \omega_0))^3} - \frac{2}{(A + i(\omega + \omega_0))^3}\right) \tag{2.18}$$

If we assume that the molecule is initially in the ground vibrational state of the ground electronic state ($\alpha_i(t = -\infty) = 1$) and the transition probability to the other states from the initial state is negligible, the following equalities are valid at all times

$$a_i(t) \approx 1 \tag{2.19}$$

$$b_j^{\text{ex}}(t) \approx c_j^{\text{gr}}(t) \approx b_j^{\text{L}}(t) \approx 0 \tag{2.20}$$

Under these conditions, the system total wave function $|\Psi(t)\rangle$ is substituted into the time-dependent Schrödinger equation eq 2.1 to obtain

$$b_j^{\text{ex}}(t) = \frac{i}{\hbar}\langle\psi_j^{\text{ex}}| - \hat{\mu}_E\cdot\hat{\epsilon}_c|\psi_i^{\text{gr}}\rangle \times \int_{-\infty}^{t}\mathrm{d}t'\, E_c(t')\exp(i\omega_{j,i}^{\text{ex}}t' + \gamma_{\text{ex}}t'/2) \tag{2.21}$$

where $\omega_{j,i}^{ex} = (E_j^{\text{ex}} - E_i^{\text{gr}})/\hbar$.

It can be easily shown that this expression of the light absorption stage of the photoemission process is equivalent to the representation by means of wave packet. The light absorption part of the total wave function, $|\chi(t)\rangle \equiv \sum_j b_j^{\text{ex}}(t)|\psi_j^{\text{ex}}\rangle \times \exp(-iE_j^{\text{ex}}t/\hbar - \gamma_{\text{ex}}t/2)$, can be reformulated by using eq 2.21

$$|\chi(t)\rangle = \frac{i}{\hbar}\int_{-\infty}^{t}\mathrm{d}t'\,\exp((-i\hat{H}_{\text{ex}}/\hbar - \gamma_{\text{ex}}/2)(t - t')) \times (-\hat{\mu}_E\cdot\hat{\epsilon}_c E_c(t'))\exp(-i\hat{H}_{\text{gr}}t'/\hbar)|\psi_i^{\text{gr}}\rangle \tag{2.22}$$

The same equation can be derived when the continuous orthonormal basis $\{\psi_n^-(E)\}$ is included. Equation 2.22 can be easily understood as follows. The initial wave packet of the system, $|\psi_i^{gr}\rangle$, is propagated on the electronic ground state during a time interval $[-\infty,t']$ by the time-development operator $\exp(-i\hat{H}_{\text{gr}}t'/\hbar)$. At $t = t'$, the perturbative interaction term, $-\hat{\mu}_E\cdot\hat{\epsilon}_c E_c(t')$, forces the ground-state time-evolved wave packet to be scattered onto the electronic excited state. The wave packet is then propagated on the electronic excited state for a time interval $[t',t]$ by the evolution operator $\exp(-i\hat{H}_{\text{ex}}(t - t')/\hbar)$ and attenuated by the spontaneous emission term $\exp(-\gamma_{\text{ex}}(t - t')/2)$. Final integration over all possible values of t' during the time interval $[-\infty,t]$ gives the first-order amplitude of the wave packet on the electronic excited state at time t.

The spontaneous emission amplitude of the total wave function $|\Psi(t)\rangle$ can also be derived using the time-dependent Schrödinger equation

$$i\hbar\dot{b}_l^{\text{L}}(t) = i\sqrt{\frac{\hbar\omega_{\text{L}}}{2\epsilon_0 v}}(\exp(-i\omega_{\text{L}}t) + \exp(+\,i\omega_{\text{L}}t)) \times \sum_j b_j^{\text{ex}}(t)\langle\psi_l^{\text{L}}|\hat{\mu}_{\text{L}}|\psi_j^{\text{ex}}\rangle\exp(-i\omega_{j,l}^{\text{ex}}t - \gamma_{\text{ex}}t/2) \tag{2.23}$$

On the other hand, the last term of the total wave function (eq 2.1) $\sum_{\text{L},l}|\{n_k + \text{l}_\text{L}\}\rangle b_l^{\text{L}}(t)|\psi_l^{\text{L}}\rangle\exp(-iE_l^{\text{gr}}t/\hbar)$ can be shown to express the second-order amplitude of the ground-state wave packet by using the integrated form of $\dot{b}_l^{\text{L}}(t)$: $b_l^{\text{L}}(t)$

$$\sum_{\text{L},l}|\{n_k + \text{l}_\text{L}\}\rangle b_l^{\text{L}}(t)|\psi_l^{\text{L}}\rangle\exp(-iE_l^{\text{gr}}t/\hbar) = \frac{1}{\hbar}\sum_{\text{L}}|\{n_k + \text{l}_\text{L}\}\rangle\sqrt{\frac{\hbar\omega_{\text{L}}}{2\epsilon_0 v}}\int_{-\infty}^{t}\mathrm{d}t''(\exp(-i\omega_{\text{L}}t'') + \exp(+i\omega_{\text{L}}t''))\exp(-i\hat{H}_{\text{gr}}(t - t'')/\hbar)\hat{\mu}_{\text{L}}|\chi(t'')\rangle \tag{2.24}$$

It is evident that there are two scattering processes: from the ground to the excited state at time $t = t'$, which is contained in $|\chi(t'')\rangle$, and from the excited to the ground state at time $t = t''$. Summing over all intermediate excited states $|\psi_j^{\rm ex}\rangle$ with respect to the variable j and integrating over all possible values of t' in the interval $[-\infty,t'']$ and t'' in the interval $[-\infty,t]$ gives the second-order amplitude on the ground electronic state.

By the time integration, we obtain from eq 2.23

$$b_l^{\rm L}(t) = \frac{i}{\hbar^2}\sqrt{\frac{\hbar\omega_{\rm L}}{2\epsilon_0 v}}\sum_j \langle\psi_l^{\rm L}|\hat{\mu}_{\rm L}|\psi_j^{\rm ex}\rangle\langle\psi_j^{\rm ex}|\hat{\mu}_E|\psi_{\rm i}^{\rm gr}\rangle J({\rm L},l,j,t) \tag{2.25}$$

where

$$\begin{aligned} J({\rm L},l,j,t) = \int_{-\infty}^{t} {\rm d}t''(&\exp(-i\omega_{\rm L}t'') + \\ &\exp(+i\omega_{\rm L}t''))\exp(-i\omega_{j,l}^{\rm ex}t'' - \gamma_{\rm ex}t''/2) \times \\ &\int_{-\infty}^{t''} {\rm d}t'\ E_{\rm c}(t')\exp(i\omega_{j,l}^{\rm ex}t' + \gamma_{\rm ex}t'/2) \end{aligned} \tag{2.26}$$

If the field frequency of the mode L is nearly resonant on the emission light frequency $\omega_{j,l}^{\rm ex}$, the rotating wave approximation (RWA) can be applied, and the highly rotating term exp$(-i\omega_{\rm L}t'' - i\omega_{j,l}^{\rm ex}t'')$ in the integral of eq 2.26 can be omitted. Thus, $J({\rm L},l,j,t)$ can be simplified as

$$\begin{aligned} J({\rm L},l,j,t) = \int_{-\infty}^{t} {\rm d}t''\ &(\exp(i(\omega_{\rm L} - \omega_{j,l}^{\rm ex} + i\gamma_{\rm ex}/2)t'')) \times \\ &\int_{-\infty}^{t''} {\rm d}t'\ E_{\rm c}(t')\ \exp(i\omega_{j,l}^{\rm ex}t' + \gamma_{\rm ex}t'/2) \end{aligned} \tag{2.27}$$

For calculating the time integral in eq 2.27, the following inverse Fourier transform is used for the classical laser pulse $E_{\rm c}(t)$

$$E_{\rm c}(t) = \frac{1}{2\pi}\int_{-\infty}^{\infty} E_{\rm c}(\omega)\ \exp(-i\omega t)\ {\rm d}\omega \tag{2.28}$$

Substituting the time profile $E_{\rm c}(t)$ to frequency profile $E_{\rm c}(\omega)$ in eq 2.26, we can first perform the time integration and the integration with regard to the frequency ω for the next step. Finally, the spontaneous emission amplitude $b_l^{\rm L}(t)$ is found to be composed of the zeroth-order term $b_{l0}^{\rm L}(t)$ and the first-order perturbation term $\delta b_l^{\rm L}(t)$ regarding the linear chirp rate α

$$b_l^{\rm L}(t) = b_{l0}^{\rm L}(t) + \delta b_l^{\rm L}(t) \tag{2.29}$$

It may be observed that $\delta b_l^{\rm L}(t)$ is proportional to the linear chirp rate α. We divide $J({\rm L},l,j,t)$ into the zero-order term $J_0({\rm L},l,j,t)$ and the first-order perturbation term $\delta J({\rm L},l,j,t)$

$$J({\rm L},l,j,t) = J_0({\rm L},l,j,t) + \delta J({\rm L},l,j,t) \tag{2.30}$$

By contour integration, we get for $t > 0$

$$\begin{aligned} J_0({\rm L},l,j,t)/E_0 = \Bigg[\Bigg\{&\frac{A}{A^2 + (\omega_{j,{\rm i}}^{\rm ex} + \omega_0 - i\gamma_{\rm ex}/2)^2} + \\ &\frac{A}{A^2 + (-\omega_{j,{\rm i}}^{\rm ex} + \omega_0 + i\gamma_{\rm ex}/2)^2}\Bigg\} \times \\ &\frac{\exp(i(\omega_{\rm L} - \omega_{j,l}^{\rm ex} + i\gamma_{\rm ex}/2)t)}{i(\omega_{\rm L} - \omega_{j,l}^{\rm ex} + i\gamma_{\rm ex}/2)}\Bigg] + \\ &\frac{1}{2}\Bigg[\frac{1}{i(\omega_{j,{\rm i}}^{\rm ex} + \omega_0 + i(A - \gamma_{\rm ex}/2))} \times \\ &\frac{\exp(i(\omega_{l,{\rm i}} + \omega_{\rm L} + \omega_0 + iA)t)}{i(\omega_{l,{\rm i}} + \omega_{\rm L} + \omega_0 + iA)} + \\ &\frac{1}{i(\omega_{j,{\rm i}}^{\rm ex} - \omega_0 + i(A - \gamma_{ex}/2))}\ \frac{\exp(i(\omega_{l,{\rm i}} + \omega_{\rm L} - \omega_0 + iA)t)}{i(\omega_{l,{\rm i}} + \omega_{\rm L} - \omega_0 + iA)}\Bigg] + \\ &\Bigg[\Bigg\{\frac{A}{A^2 + (\omega_{l,{\rm i}} + \omega_{\rm L} + \omega_0)^2} + \frac{A}{A^2 + (\omega_{l,{\rm i}} + \omega_{\rm L} - \omega_0)^2}\Bigg\} \times \\ &\frac{1}{i(\omega_{j,l}^{\rm ex} - \omega_L - i\gamma_{\rm ex}/2)}\Bigg] \end{aligned} \tag{2.31}$$

$$\begin{aligned} \delta J({\rm L},l,j,t)/(\alpha\ E_0) = \Bigg[&\frac{1}{\{\omega_{j,{\rm i}}^{\rm ex} + \omega_0 + i(A - \gamma_{\rm ex}/2)\}^3} + \\ &\frac{1}{\{\omega_{j,{\rm i}}^{\rm ex} - \omega_0 - i(A + \gamma_{\rm ex}/2)\}^3} - \\ &\frac{1}{\{\omega_{j,{\rm i}}^{\rm ex} + \omega_0 - i(A + \gamma_{\rm ex}/2)\}^3} + \\ &\frac{1}{\{\omega_{j,{\rm i}}^{\rm ex} - \omega_0 + i(A - \gamma_{\rm ex}/2)\}^3}\Bigg]\frac{\exp(i(\omega_{\rm L} - \omega_{j,l}^{\rm ex} + i\gamma_{\rm ex}/2)t)}{i(\omega_{\rm L} - \omega_{j,l}^{\rm ex} + i\gamma_{\rm ex}/2)} + \\ &\frac{i}{2}\{B(\omega_{j,{\rm i}}^{\rm ex} - i\gamma_{\rm ex}/2,\omega_{l,{\rm i}} + \omega_{\rm L},-\omega_0 + iA,t) - \\ &B(\omega_{j,{\rm i}}^{\rm ex} - i\gamma_{\rm ex}/2,\omega_{l,{\rm i}} + \omega_{\rm L},\omega_0 + iA,t)\} + \\ &\Bigg\{\frac{1}{(\omega_{\rm L} + \omega_{l,{\rm i}} + \omega_0 + iA)^3} + \frac{1}{(\omega_{\rm L} + \omega_{l,{\rm i}} - \omega_0 - iA)^3} - \\ &\frac{1}{(\omega_{\rm L} + \omega_{l,{\rm i}} + \omega_0 - iA)^3} - \frac{1}{(\omega_{\rm L} + \omega_{l,{\rm i}} - \omega_0 + iA)^3}\Bigg\} \times \\ &\frac{1}{i(\omega_{j,l}^{\rm ex} - \omega_{\rm L} - i\gamma_{\rm ex}/2)} \end{aligned} \tag{2.32}$$

and for $t < 0$

$$\begin{aligned} J({\rm L},l,j,t)/E_0 = \frac{1}{2} \times& \\ \Bigg[&\frac{1}{i(\omega_{j,{\rm i}}^{\rm ex} + \omega_0 - i(A + \gamma_{\rm ex}/2))}\ \frac{\exp(i(\omega_{l,{\rm i}} + \omega_{\rm L} + \omega_0 - iA)t)}{i(\omega_{l,{\rm i}} + \omega_{\rm L} + \omega_0 - iA)} + \\ &\frac{1}{i(\omega_{j,{\rm i}}^{\rm ex} - \omega_0 - i(A + \gamma_{\rm ex}/2))}\ \frac{\exp(i(\omega_{l,{\rm i}} + \omega_{\rm L} - \omega_0 - iA)t)}{i(\omega_{l,{\rm i}} + \omega_{\rm L} - \omega_0 - iA)}\Bigg] \end{aligned} \tag{2.33}$$

$$\begin{aligned} \delta J({\rm L},l,j,t)/(\alpha E_0) = \frac{i}{2}\{&B(\omega_{j,{\rm i}}^{\rm ex} - i\gamma_{\rm ex}/2,\omega_{l,{\rm i}} + \omega_{\rm L},\omega_0 - iA,t) - \\ &B(\omega_{j,{\rm i}}^{\rm ex} - i\gamma_{\rm ex}/2,\omega_{l,{\rm i}} + \omega_{\rm L},-\omega_0 - iA,t)\} \end{aligned} \tag{2.34}$$

where the function $B(a,b,c,t)$ is defined as

$$B(a,b,c,t) = \frac{\exp(i(c+b)t)}{(c+a)^3(c+b)^3} \times [\{(2c+a+b) - it(c+a)(c+b)\}^2 + (c+a)^2 + (c+b)^2] \tag{2.35}$$

Observe that the total spontaneous emission amplitude $b_l^{\mathrm{L}}(t)$ is proportional to the chirp rate α. Furthermore, it may be noticed that the spontaneous emission amplitude entirely follows the profile of the pulse ($\exp(At)$) for $t < 0$, indicating that the spontaneous Raman process dominates during the initial period of the laser pulse and that there is no contribution of the resonance fluorescence component. In the transient region $t > 0$, the spontaneous emission amplitude has a complicated structure, consisting of time-dependent terms indicative of decay and oscillation caused by the laser and excited-state lifetime parameters. The first term of eq 2.31 represents the resonance fluorescence part of the spontaneous emission amplitude, decaying at the radiative decay rate γ_{ex} associated with the excited vibronic state lifetime. The second term is the spontaneous Raman process component. After the pulse finishes, the contribution of the resonance fluorescence and the spontaneous Raman process to the spectrum depends on the relative value of γ_{ex} versus A. In our case ($\gamma_{\mathrm{ex}} = 0.0413$ fs^{-1} and $A = 0.620$ fs^{-1}), the resonance fluorescence part contributes more to the stationary Raman spectra. The third term of eq 2.31 is time-independent and expresses the KHD formula with damping factors.

From eq 2.32, it is evident that the influence of the chirping on the spontaneous emission amplitude is also composed of two distinct time-dependent terms—resonance fluorescence and spontaneous Raman—as well as time-independent KHD terms.

The time-dependent stimulated emission amplitude $c_j^{\mathrm{gr}}(t)$ can be obtained by inserting the total system wave function $|\Psi(t)\rangle$ into the time-dependent Schrödinger eq 2.1 and multiplying both sides by $\langle\psi_j^{\mathrm{gr}}|\langle\{n_k\}|$

$$\dot{c}_j^{\mathrm{gr}}(t) = -\frac{i}{\hbar}\sum_{j_{\mathrm{ex}}}\langle\psi_j^{\mathrm{gr}}| - \hat{\mu}_E\cdot E_{\mathrm{c}}(t)|\psi_{j_{\mathrm{ex}}}^{\mathrm{ex}}\rangle b_{j_{\mathrm{ex}}}^{\mathrm{ex}}(t) \times \exp(-i\omega_{j_{\mathrm{ex}},j}t - \gamma_{\mathrm{ex}}t/2) \tag{2.36}$$

where $\omega_{j_{\mathrm{ex}},j} + (E_{j_{\mathrm{ex}}}^{\mathrm{ex}} - E_j^{\mathrm{gr}})/\hbar$.

Inserting eq 2.21 into eq 2.36 and integrating both sides of the equation gives

$$c_j^{\mathrm{gr}}(t) = -\frac{1}{\hbar^2}\sum_{j_{\mathrm{ex}}}\langle\psi_j^{\mathrm{gr}}|\hat{\mu}_E|\psi_{j_{\mathrm{ex}}}^{\mathrm{ex}}\rangle\langle\psi_{j_{\mathrm{ex}}}^{\mathrm{ex}}|\hat{\mu}_E|\psi_{\mathrm{i}}^{\mathrm{gr}}\rangle \times \int_{-\infty}^{t} \mathrm{d}t_2\, E_{\mathrm{c}}(t_2)\exp(-i\omega_{j_{\mathrm{ex}},j}t_2 - \gamma_{\mathrm{ex}}t_2/2) \times \int_{-\infty}^{t_2} \mathrm{d}t_1\, E_{\mathrm{c}}(t_1)\exp(i\omega_{j_{\mathrm{ex}},\mathrm{i}}t_1 + \gamma_{\mathrm{ex}}t_1/2) \tag{2.37}$$

We divide $c_j^{\mathrm{gr}}(t)$ into zero-order term $c_{j,0}^{\mathrm{gr}}(t)$ and first-order term $\delta c_j^{\mathrm{gr}}(t)$ with regard to the chirp rate α

$$c_j^{\mathrm{gr}}(t) = c_{j,0}^{\mathrm{gr}}(t) + \delta c_j^{\mathrm{gr}}(t) \tag{2.38}$$

If we substitute $E_{\mathrm{c0}}(t) + \delta E_{\mathrm{c}}(t)$ for $E_{\mathrm{c}}(t)$ as indicated in eq 2.37 and we neglect the second-order terms, which contain such factors as $\delta E_{\mathrm{c}}(t_1)\ \delta E_{\mathrm{c}}(t_2)$, we get in the zeroth order $c_{j,0}^{\mathrm{gr}}(t)$

$$c_{j,0}^{\mathrm{gr}}(t) = -\frac{1}{\hbar^2}\sum_{j_{\mathrm{ex}}}\langle\psi_j^{\mathrm{gr}}|\hat{\mu}_E|\psi_{j_{\mathrm{ex}}}^{\mathrm{ex}}\rangle\langle\psi_{j_{\mathrm{ex}}}^{\mathrm{ex}}|\hat{\mu}_E|\psi_{\mathrm{i}}^{\mathrm{gr}}\rangle\int_{-\infty}^{t} \mathrm{d}t_2\, E_{\mathrm{c0}}(t_2) \times \exp(-i\omega_{j_{\mathrm{ex}},j}t_2 - \gamma_{\mathrm{ex}}t_2/2)\int_{-\infty}^{t_2} \mathrm{d}t_1\, E_{\mathrm{c0}}(t_1) \times \exp(i\omega_{j_{\mathrm{ex}},i}t_1 + \gamma_{\mathrm{ex}}t_1/2) \tag{2.39}$$

In the first order, we get

$$\delta c_j^{\mathrm{gr}}(t) = -\frac{1}{\hbar^2}\sum_{j_{\mathrm{ex}}}\langle\psi_j^{\mathrm{gr}}|\hat{\mu}_E|\psi_{j_{\mathrm{ex}}}^{\mathrm{ex}}\rangle\langle\psi_{j_{\mathrm{ex}}}^{\mathrm{ex}}|\hat{\mu}_E|\psi_{\mathrm{i}}^{\mathrm{gr}}\rangle \times \int_{-\infty}^{t} \mathrm{d}t_2\, \delta E_{\mathrm{c}}(t_2)\exp(-i\omega_{j_{\mathrm{ex}},j}t_2 - \gamma_{\mathrm{ex}}t_2/2) \times \int_{-\infty}^{t_2} \mathrm{d}t_1\, E_{\mathrm{c0}}(t_1)\exp(i\omega_{j_{\mathrm{ex}},i}t_1 + \gamma_{\mathrm{ex}}t_1/2) - \frac{1}{\hbar^2}\sum_{j_{\mathrm{ex}}}\langle\psi_j^{\mathrm{gr}}|\hat{\mu}_E|\psi_{j_{\mathrm{ex}}}^{\mathrm{ex}}\rangle\langle\psi_{j_{\mathrm{ex}}}^{\mathrm{ex}}|\hat{\mu}_E|\psi_{\mathrm{i}}^{\mathrm{gr}}\rangle \times \int_{-\infty}^{t} \mathrm{d}t_2\, E_{\mathrm{c0}}(t_2)\exp(-i\omega_{j_{\mathrm{ex}},j}t_2 - \gamma_{\mathrm{ex}}t_2/2) \times \int_{-\infty}^{t_2} \mathrm{d}t_1\, \delta E_{\mathrm{c}}(t_1)\exp(i\omega_{j_{\mathrm{ex}},i}t_1 + \gamma_{\mathrm{ex}}t_1/2) \tag{2.40}$$

We put

$$c_j^{\mathrm{gr}}(t) = c_{j,0}^{\mathrm{gr}}(t) + \delta c_j^{\mathrm{gr}}(t) = -\frac{1}{\hbar^2}\sum_{j_{\mathrm{ex}}}\langle\psi_j^{\mathrm{gr}}|\hat{\mu}_E|\psi_{j_{\mathrm{ex}}}^{\mathrm{ex}}\rangle\langle\psi_{j_{\mathrm{ex}}}^{\mathrm{ex}}|\hat{\mu}_E|\psi_{\mathrm{i}}^{\mathrm{gr}}\rangle M(j,j_{\mathrm{ex}},t) = -\frac{1}{\hbar^2}\sum_{j_{\mathrm{ex}}}\langle\psi_j^{\mathrm{gr}}|\hat{\mu}_E|\psi_{j_{\mathrm{ex}}}^{\mathrm{ex}}\rangle\langle\psi_{j_{\mathrm{ex}}}^{\mathrm{ex}}|\hat{\mu}_E|\psi_{\mathrm{i}}^{\mathrm{gr}}\rangle\{M_0(j,j_{\mathrm{ex}},t) + \delta M(j,j_{\mathrm{ex}},t)\} \tag{2.41}$$

where

$$M_0(j,j_{\mathrm{ex}},t) = \int_{-\infty}^{t} \mathrm{d}t_2\, E_{\mathrm{c0}}(t_2)\exp(-i\omega_{j_{\mathrm{ex}},j}t_2 - \gamma_{\mathrm{ex}}t_2/2) \times \int_{-\infty}^{t_2} \mathrm{d}t_1\, E_{\mathrm{c0}}(t_1)\exp(i\omega_{j_{\mathrm{ex}},i}t_1 + \gamma_{\mathrm{ex}}t_1/2) \tag{2.42}$$

and

$$\delta M(j,j_{\mathrm{ex}},t) = \int_{-\infty}^{t} \mathrm{d}t_2\, E_{\mathrm{c}}(t_2)\exp(-i\omega_{j_{\mathrm{ex}},j}t_2 - \gamma_{\mathrm{ex}}t_2/2) \times \int_{-\infty}^{t_2} \mathrm{d}t_1\, E_{\mathrm{c0}}(t_1)\exp(i\omega_{j_{\mathrm{ex}},i}t_1 + \gamma_{\mathrm{ex}}t_1/2) + \int_{-\infty}^{t} \mathrm{d}t_2\, E_{\mathrm{c0}}(t_2)\exp(-i\omega_{j_{\mathrm{ex}},j}t_2 - \gamma_{\mathrm{ex}}t_2/2) \times \int_{-\infty}^{t_2} \mathrm{d}t_1\, \delta E_{\mathrm{c}}(t_1)\exp(i\omega_{j_{\mathrm{ex}},i}t_1 + \gamma_{\mathrm{ex}}t_1/2) \tag{2.43}$$

In eq 2.41, we divided $M(j,j_{\mathrm{ex}},t)$ into the zero-order term $M_0(j,j_{\mathrm{ex}},t)$ and the first-order perturbation term $\delta M(j,j_{\mathrm{ex}},t)$

$$M(j,j_{\mathrm{ex}},t) = M_0(j,j_{\mathrm{ex}},t) + \delta M(j,j_{\mathrm{ex}},t) \tag{2.44}$$

Now, to concentrate on the term $c_{j,0}^{\mathrm{gr}}(t)$. By substituting the inverse Fourier transform eq 2.28 for the classical laser pulse $E_{\mathrm{c}}(t)$, and by time integration followed by contour integration with regard to the frequency, we obtain for $t > 0$

$$
\begin{gathered}
M_0(j,j_{\mathrm{ex}},t) = \left(\frac{E_0}{2}\right)^2 \times \\
\Bigg[\frac{1}{i(\omega_{j_{\mathrm{ex}},i} + \omega_0 + i(A - \gamma_{\mathrm{ex}}/2))}\,\frac{\exp(i(\omega_{j,i} + 2\omega_0 + 2iA)t)}{i(\omega_{j,i} + 2\omega_0 + 2iA)} + \\
\frac{1}{i(\omega_{j_{\mathrm{ex}},i} - \omega_0 + i(A - \gamma_{\mathrm{ex}}/2))}\,\frac{\exp(i(\omega_{j,i} - 2\omega_0 + 2iA)t)}{i(\omega_{j,i} - 2\omega_0 + 2iA)} + \\
\bigg\{\frac{1}{i(\omega_{j_{\mathrm{ex}},\mathrm{i}} - \omega_0 + i(A - \gamma_{\mathrm{ex}}/2))} + \\
\frac{1}{i(\omega_{j_{\mathrm{ex}},\mathrm{i}} + \omega_0 + i(A - \gamma_{\mathrm{ex}}/2))}\bigg\}\frac{\exp(i(\omega_{j,\mathrm{i}} + 2iA)t)}{i(\omega_{j,\mathrm{i}} + 2iA)}\Bigg] + \\
\frac{AE_0{}^2}{2}\bigg\{\frac{1}{A^2 + (\omega_{j_{\mathrm{ex}},\mathrm{i}} + \omega_0 - i\gamma_{\mathrm{ex}}/2)^2} + \\
\frac{1}{A^2 + (\omega_{j_{\mathrm{ex}},\mathrm{i}} - \omega_0 - i\gamma_{\mathrm{ex}}/2)^2}\bigg\} \times \\
\bigg\{\frac{\exp(i(-\omega_{j_{\mathrm{ex}},\mathrm{j}} + \omega_0 + i(A + \gamma_{\mathrm{ex}}/2))t)}{i(-\omega_{j_{\mathrm{ex}},\mathrm{j}} + \omega_0 + i(A + \gamma_{\mathrm{ex}}/2))} + \\
\frac{\exp(i(-\omega_{j_{\mathrm{ex}},\mathrm{j}} - \omega_0 + i(A + \gamma_{\mathrm{ex}}/2))t)}{i(-\omega_{j_{\mathrm{ex}},\mathrm{j}} - \omega_0 + i(A + \gamma_{\mathrm{ex}}/2))}\bigg\} + \frac{AE_0{}^2}{2} \times \\
\Bigg[\frac{1}{i(\omega_{j_{\mathrm{ex}},\mathrm{i}} + \omega_0 - i(A + \gamma_{\mathrm{ex}}/2))}\,\frac{1}{A^2 + (\omega_{j,\mathrm{i}} + 2\omega_0 - iA)^2} + \\
\frac{1}{i(\omega_{j_{\mathrm{ex}},\mathrm{i}} - \omega_0 - i(A + \gamma_{\mathrm{ex}}/2))}\,\frac{1}{A^2 + (\omega_{j,\mathrm{i}} - 2\omega_0 - iA)^2} + \\
\frac{1}{i(\omega_{j_{\mathrm{ex}},j} - \omega_0 - i(A + \gamma_{\mathrm{ex}}/2))}\,\frac{1}{A^2 + (\omega_{j,\mathrm{i}} + 2\omega_0 + iA)^2} + \\
\frac{1}{i(\omega_{j_{\mathrm{ex}},\mathrm{j}} + \omega_0 - i(A + \gamma_{\mathrm{ex}}/2))}\,\frac{1}{A^2 + (\omega_{j,\mathrm{i}} - 2\omega_0 + iA)^2} + \\
\bigg\{\frac{1}{i(\omega_{j_{\mathrm{ex}},\mathrm{i}} - \omega_0 - i(A + \gamma_{\mathrm{ex}}/2))} + \\
\frac{1}{i(\omega_{j_{\mathrm{ex}},\mathrm{i}} + \omega_0 - i(A + \gamma_{\mathrm{ex}}/2))}\bigg\}\frac{1}{A^2 + (\omega_{j,\mathrm{i}} - iA)^2} + \\
\bigg\{\frac{1}{i(\omega_{j_{\mathrm{ex}},j} + \omega_0 - i(A + \gamma_{\mathrm{ex}}/2))} + \\
\frac{1}{i(\omega_{j_{\mathrm{ex}},j} - \omega_0 - i(A + \gamma_{\mathrm{ex}}/2))}\bigg\}\frac{1}{A^2 + (\omega_{j,\mathrm{i}} + iA)^2}\Bigg]
\end{gathered}
\tag{2.45}
$$

$$
\begin{gathered}
2\delta M(j,j_{\mathrm{ex}},t)/\alpha AE_0{}^2 = \frac{1}{2A}\Bigg[\frac{1}{i(\omega_{j_{\mathrm{ex}},\mathrm{i}} + \omega_0 + i(A - \gamma_{\mathrm{ex}}/2))} \times \\
\{C(\omega_{j_{\mathrm{ex}},\mathrm{i}} + 2iA,t) - C(\omega_{j_{\mathrm{ex}},\mathrm{i}} + 2\omega_0 + 2iA,t)\} + \\
\frac{1}{i(\omega_{j_{\mathrm{ex}},\mathrm{i}} - \omega_0 + i(A - \gamma_{\mathrm{ex}}/2))} \times \\
\{C(\omega_{j_{\mathrm{ex}},i} - 2\omega_0 + 2iA,t) - C(\omega_{j_{\mathrm{ex}},\mathrm{i}} + 2iA,t)\} + \\
i\{B(\omega_{j_{\mathrm{ex}},\mathrm{i}} - i\gamma_{\mathrm{ex}}/2,\omega_{j,\mathrm{i}} + \omega_0 + iA,\omega_0 + iA,t) - \\
B(\omega_{j_{\mathrm{ex}},\mathrm{i}} - i\gamma_{\mathrm{ex}}/2,\omega_{j,\mathrm{i}} + \omega_0 + iA,-\omega_0 + iA,t) + \\
B(\omega_{j_{\mathrm{ex}},\mathrm{i}} - i\gamma_{\mathrm{ex}}/2,\omega_{j,\mathrm{i}} - \omega_0 + iA,\omega_0 + iA,t) - \\
B(\omega_{j_{\mathrm{ex}},\mathrm{i}} - i\gamma_{\mathrm{ex}}/2,\omega_{j,\mathrm{i}} - \omega_0 + iA,-\omega_0 + iA,t)\}\Bigg] + \\
\bigg[\bigg\{\frac{1}{A^2 + (\omega_{j_{\mathrm{ex}},\mathrm{i}} + \omega_0 - i\gamma_{\mathrm{ex}}/2)^2} + \\
\frac{1}{A^2 + (-\omega_{j_{\mathrm{ex}},\mathrm{i}} + \omega_0 + i\gamma_{\mathrm{ex}}/2)^2}\bigg\}\{C(-\omega_{j_{\mathrm{ex}},j} - \omega_0 + \\
i(A + \gamma_{\mathrm{ex}}/2),t) - C(-\omega_{j_{\mathrm{ex}},j} + \omega_0 + i(A + \gamma_{\mathrm{ex}}/2),t)\} + \\
\frac{1}{A}\bigg\{\frac{1}{(\omega_{j_{\mathrm{ex}},\mathrm{i}} - \omega_0 - i(A + \gamma_{\mathrm{ex}}/2))^3} - \\
\frac{1}{(\omega_{j_{\mathrm{ex}},\mathrm{i}} + \omega_0 - i(A + \gamma_{\mathrm{ex}}/2))^3} + \frac{1}{(\omega_{j_{\mathrm{ex}},\mathrm{i}} + \omega_0 + i(A - \gamma_{\mathrm{ex}}/2))^3} - \\
\frac{1}{(\omega_{j_{\mathrm{ex}},\mathrm{i}} - \omega_0 + i(A - \gamma_{\mathrm{ex}}/2))^3}\bigg\} \times \\
\bigg\{\frac{\exp(i(-\omega_{j_{\mathrm{ex}},j} + \omega_0 + i(A + \gamma_{\mathrm{ex}}/2))t)}{i(-\omega_{j_{\mathrm{ex}},j} + \omega_0 + i(A + \gamma_{\mathrm{ex}}/2))} + \\
\frac{\exp(i(-\omega_{j_{\mathrm{ex}},j} - \omega_0 + i(A + \gamma_{\mathrm{ex}}/2))t)}{i(-\omega_{j_{\mathrm{ex}},j} - \omega_0 + i(A + \gamma_{\mathrm{ex}}/2))}\bigg\}\bigg] + \\
\frac{1}{A}\bigg[\bigg\{\frac{1}{(\omega_{j,\mathrm{i}} - 2iA)^3} - \frac{1}{(\omega_{j,\mathrm{i}} + 2\omega_0 - 2iA)^3}\bigg\} \times \\
\bigg\{\frac{1}{i(\omega_{j_{\mathrm{ex}},\mathrm{i}} + \omega_0 - i(A + \gamma_{\mathrm{ex}}/2))} + \frac{1}{i(\omega_{j_{\mathrm{ex}},j} - \omega_0 + i(A - \gamma_{\mathrm{ex}}/2))}\bigg\} + \\
\bigg\{\frac{1}{(\omega_{j,\mathrm{i}} + 2\omega_0 + iA)^3} - \frac{1}{(\omega_{j,\mathrm{i}} + 2iA)^3}\bigg\} \times \\
\bigg\{\frac{1}{i(\omega_{j_{\mathrm{ex}},\mathrm{i}} + \omega_0 + i(A - \gamma_{\mathrm{ex}}/2))} + \frac{1}{i(\omega_{j_{\mathrm{ex}},j} - \omega_0 - i(A + \gamma_{\mathrm{ex}}/2))}\bigg\} + \\
\bigg\{\frac{1}{(\omega_{j,\mathrm{i}} - 2\omega_0 - 2iA)^3} - \frac{1}{(\omega_{j,\mathrm{i}} - 2iA)^3}\bigg\} \times \\
\bigg\{\frac{1}{i(\omega_{j_{\mathrm{ex}},\mathrm{i}} - \omega_0 - i(A + \gamma_{\mathrm{ex}}/2))} + \frac{1}{i(\omega_{j_{\mathrm{ex}},j} + \omega_0 + i(A - \gamma_{\mathrm{ex}}/2))}\bigg\} + \\
\bigg\{\frac{1}{(\omega_{j,\mathrm{i}} + 2iA)^3} - \frac{1}{(\omega_{j,\mathrm{i}} - 2\omega_0 + 2iA)^3}\bigg\} \times \\
\bigg\{\frac{1}{i(\omega_{j_{\mathrm{ex}},\mathrm{i}} - \omega_0 + i(A - \gamma_{\mathrm{ex}}/2))} + \frac{1}{i(\omega_{j_{\mathrm{ex}},j} + \omega_0 - i(A + \gamma_{\mathrm{ex}}/2))}\bigg\}\bigg] + \\
2\bigg[\bigg\{\frac{1}{(\omega_{j_{\mathrm{ex}},j} + \omega_0 - i(A + \gamma_{\mathrm{ex}}/2))^3} - \frac{1}{(\omega_{j_{\mathrm{ex}},j} - \omega_0 - i(A + \gamma_{\mathrm{ex}}/2))^3}\bigg\} \times \\
\bigg\{\frac{1}{A^2 + (\omega_{j_{\mathrm{ex}},\mathrm{i}} + \omega_0 - i\gamma_{\mathrm{ex}}/2)^2} + \frac{1}{A^2 + (\omega_{j_{\mathrm{ex}},\mathrm{i}} - \omega_0 - i\gamma_{\mathrm{ex}}/2)^2} - \\
\frac{1}{A^2 + (\omega_{j_{\mathrm{ex}},j} - \omega_0 - i\gamma_{\mathrm{ex}}/2)^2} - \frac{1}{A^2 + (\omega_{j_{\mathrm{ex}},j} + \omega_0 - i\gamma_{\mathrm{ex}}/2)^2}\bigg\}\bigg]
\end{gathered}
\tag{2.46}
$$

If $t < 0$, then

$$M_0(j,j_{\mathrm{ex}},t) = \left(\frac{E_0}{2}\right)^2 \times \left[\frac{1}{i(\omega_{j_{\mathrm{ex}},\mathrm{i}} + \omega_0 - i(A + \gamma_{\mathrm{ex}}/2))} \frac{\exp(i(\omega_{j,\mathrm{i}} + 2\omega_0 - 2iA)t)}{i(\omega_{j,\mathrm{i}} + 2\omega_0 - 2iA)} + \frac{1}{i(\omega_{j_{\mathrm{ex}},\mathrm{i}} - \omega_0 - i(A + \gamma_{\mathrm{ex}}/2))} \frac{\exp(i(\omega_{j,\mathrm{i}} - 2\omega_0 - 2iA)t)}{i(\omega_{j,\mathrm{i}} - 2\omega_0 - 2iA)} + \left\{\frac{1}{i(\omega_{j_{\mathrm{ex}},\mathrm{i}} - \omega_0 - i(A + \gamma_{\mathrm{ex}}/2))} + \frac{1}{i(\omega_{j_{\mathrm{ex}},\mathrm{i}} + \omega_0 - i(A + \gamma_{\mathrm{ex}}/2))}\right\} \frac{\exp(i(\omega_{j,\mathrm{i}} - 2iA)t)}{i(\omega_{j,\mathrm{i}} - 2iA)}\right] \quad (2.47)$$

$$2\delta M(j,j_{\mathrm{ex}},t)/\alpha A{E_0}^2 = \frac{1}{2A}\left[\frac{1}{i(\omega_{j_{\mathrm{ex}},\mathrm{i}} + \omega_0 - i(A + \gamma_{\mathrm{ex}}/2))} \times \{C(\omega_{j_{\mathrm{ex}},\mathrm{i}} - 2iA,t) - C(\omega_{j_{\mathrm{ex}},\mathrm{i}} + 2\omega_0 - 2iA,t)\} + \frac{1}{i(\omega_{j_{\mathrm{ex}},\mathrm{i}} - \omega_0 - i(A + \gamma_{\mathrm{ex}}/2))} \times \{C(\omega_{j_{\mathrm{ex}},\mathrm{i}} - 2\omega_0 - 2iA,t) - C(\omega_{j_{\mathrm{ex}},\mathrm{i}} - 2iA,t)\} + i\{B(\omega_{j_{\mathrm{ex}},\mathrm{i}} - i\gamma_{\mathrm{ex}}/2,\omega_{j,\mathrm{i}} + \omega_0 - iA,\omega_0 - iA,t) - B(\omega_{j_{\mathrm{ex}},\mathrm{i}} - i\gamma_{ex}/2,\omega_{j,i} + \omega_0 - iA,-\omega_0 - iA,t) + B(\omega_{j_{\mathrm{ex}},\mathrm{i}} - i\gamma_{\mathrm{ex}}/2,\omega_{j,\mathrm{i}} - \omega_0 - iA,\omega_0 - iA,t) - B(\omega_{j_{\mathrm{ex}},\mathrm{i}} - i\gamma_{\mathrm{ex}}/2,\omega_{j,\mathrm{i}} - \omega_0 - iA,-\omega_0 - iA,t)\}\right] \quad (2.48)$$

The function $C(a,t)$ is defined as follows:

$$C(a,t) = \frac{\exp(iat)}{a^3}(-a^2t^2 - 2iat + 2) \quad (2.49)$$

As can be easily recognized from the formulas derived above, at $t > 0$, the stimulated emission amplitude $c_j^{\mathrm{gr}}(t)$ is found to have three characteristic transient behaviors common to both the chirp-free $M_0(j,j_{\mathrm{ex}},t)$ and the chirp-dependent terms $\delta M(j,j_{\mathrm{ex}},t)$, as in the time-dependent spontaneous emission amplitude $b_l^{\mathrm{L}}(t)$: $\exp(-2\,At)$, $\exp(-(A + \gamma_{\mathrm{ex}}/2)t)$, and the time-independent term. In $c_j^{\mathrm{gr}}(t)$, the mixed transient term $\exp(-(A + \gamma_{\mathrm{ex}}/2)t)$ is a characteristic that is not found in $b_l^{\mathrm{L}}(t)$. This term decays at the rate of the pulse profile plus the phenomenological spontaneous emission rate. At $t < 0$, we find that both the chirp-free $M_0(j,j_{\mathrm{ex}},t)$ and the chirp-dependent terms $\delta M(j,j_{\mathrm{ex}},t)$ entirely follow the profile of the pulse ($\exp(2At)$).

In this paper, our interest is focused on the calculations of physical quantities such as (1) the Raman spectrum, in other words, the probability to observe a spontaneously emitted photon in the L mode at the time t

$$P_{\mathrm{L}}(t) = \sum_l |b_l^{\mathrm{L}}(t)|^2 \quad (2.50)$$

and (2) the molecular vibrational distribution of the vibrational state $v = l$ of the ground electronic state due to spontaneous emission $Q_l^{\mathrm{sp}}(t)$ and stimulated emission $Q_l^{\mathrm{st}}(t)$

$$Q_l^{\mathrm{sp}}(t) = \frac{v}{\pi^2 c^3}\int \mathrm{d}\omega_{\mathrm{L}}\, \omega_{\mathrm{L}}^2 |b_l^{\mathrm{L}}(t)|^2 \quad (2.51)$$

$$Q_l^{\mathrm{st}}(t) = |c_l^{\mathrm{gr}}(t)|^2 \quad (2.52)$$

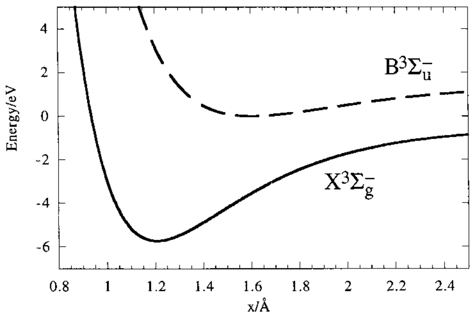

Figure 1. Schematic depiction of PECs of the states $X^3\Sigma_g^-$ and $B^3\Sigma_u^-$ of the O_2 molecule.

TABLE 1: Potential Parameters

$D_1 = 5.21$ eV	$a_1 = 2.6547$ Å^{-1}	$x_1 = 1.207$ Å
$D_2 = 1.46$ eV	$a_2 = 2.2477$ Å^{-1}	$x_2 = 1.604$ Å
$D_3 = -5.75$ eV		

TABLE 2: Laser Pulse Parameters[a]

$E_0 = 1.0 \times 10^{-5}$ au	$I = 3.54 \times 10^6$ W/cm^2	$\omega_0 = 8.73$ eV
	L1	
$A = 2.27$ fs^{-1}	$\alpha = -74.4, 0.0, 74.4$ eV fs^{-2}	
	L2	
$A = 1.16$ fs^{-1}	$\alpha = -31.6, 0.0, 31.6$ eVfs^{-2}	
	L3	
$A = 0.620$ fs^{-1}	$\alpha = -0.930, 0.0, 0.930$ eV fs^{-2}	
detuning $= -2.43$ eV		

[a] The quantity I denotes the laser pulse intensity.

III. Results and Discussion

In this section, the analytical formulas derived in the preceding section are applied to the O_2 molecule that has previously been studied experimentally and theoretically, but with CW laser and by the time-dependent wave packet method.[35,36] In Figure 1, the potential energy curves (PECs) of the O_2 molecule relevant to the present paper are shown: the $X^3\Sigma_g^-$ and $B^3\Sigma_u^-$ states. Both of the PECs, $V_1(x)$ for the $X^3\Sigma_g^-$ state and $V_2(x)$ for the $B^3\Sigma_u^-$ state, are expressed as Morse functions

$$V_1(x) = D_1[1 - \exp\{-a_1(x - x_1)\}]^2 + D_3 \quad (3.1)$$

$$V_2(x) = D_2[1 - \exp\{-a_2(x - x_2)\}]^2 \quad (3.2)$$

Their parameters are listed in Table 1, which is reproduced from ref 37. The vibrational eigenfunctions and eigenenergies of the two electronic states were calculated by the Fourier grid Hamiltonian method.[38] It was found that the ground electronic state supports 53 vibrational eigenstates and the excited electronic state 34, although the continuum states are dominant at the resonant frequency. The laser pulse parameters appearing in eq 2.11 are shown in Table 2. Three kinds of the laser pulses are derived according to duration: the shortest L1, the medium L2, and the longest L3. At $t = 0$, the laser pulses are resonant in the resonant Raman scattering (see Figure 2). The detuning (−2.43 eV) is for the nonresonance Raman scattering at $t = 0$ (see Figure 5). Throughout the present paper, the simple hypothesis is adopted that the bond length is independent of the transition dipole moment: $\hat{\mu}_E = \hat{\mu}_{\mathrm{L}} = 1D$.

In Figure 2 the transient resonant Raman spectra calculated by eq 2.50 are shown. For pulses of the shortest duration (L1) (Figure 2a−c), only simple bell-shaped spectra are detected, whereas some structure appears in the longer pulse case (L2) (Figure 2d−f). The latter case indicates that resonance fluorescence sets in at the terminal period of the pulse. Some chirp

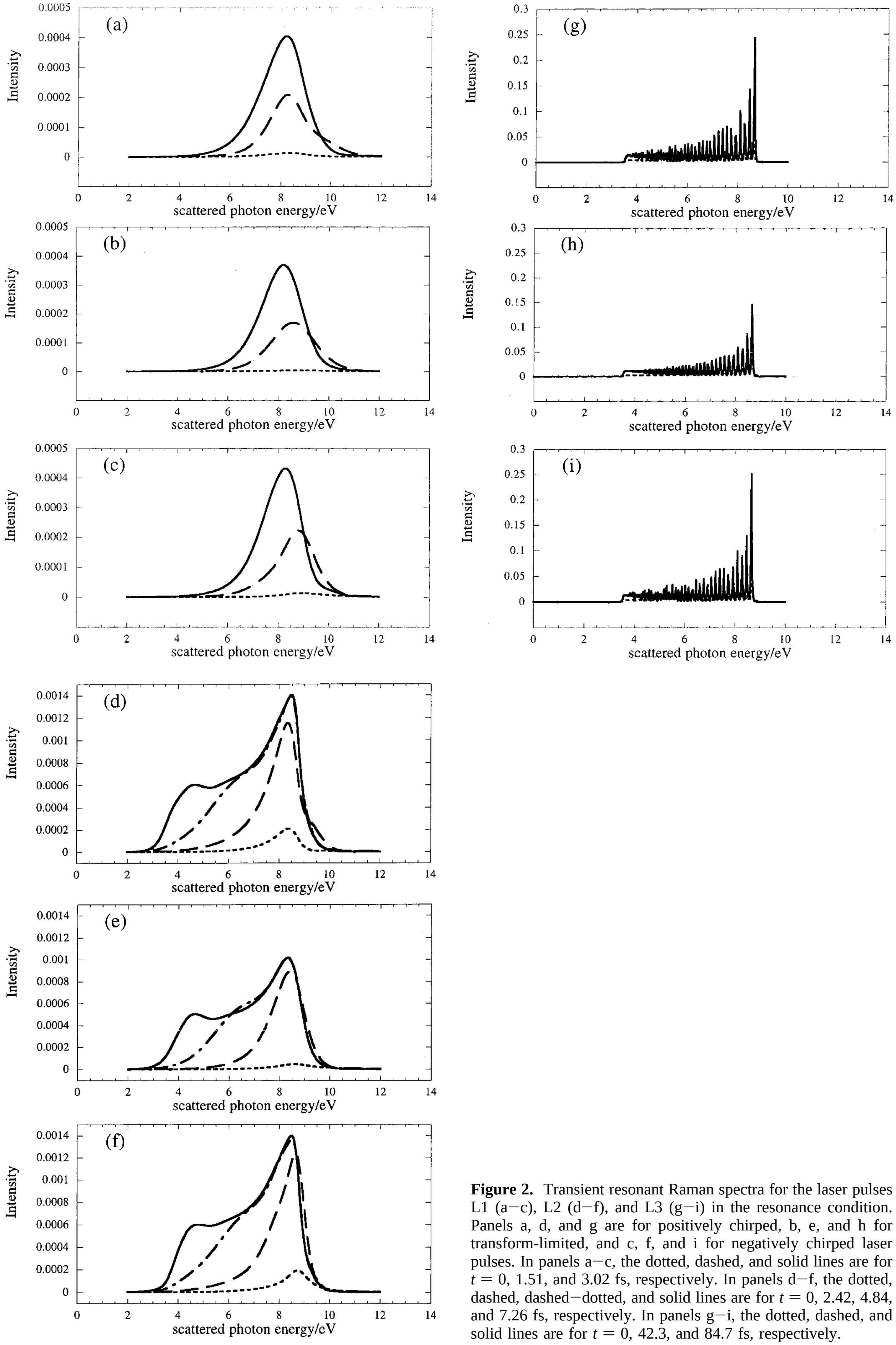

Figure 2. Transient resonant Raman spectra for the laser pulses L1 (a–c), L2 (d–f), and L3 (g–i) in the resonance condition. Panels a, d, and g are for positively chirped, b, e, and h for transform-limited, and c, f, and i for negatively chirped laser pulses. In panels a–c, the dotted, dashed, and solid lines are for $t = 0$, 1.51, and 3.02 fs, respectively. In panels d–f, the dotted, dashed, dashed–dotted, and solid lines are for $t = 0$, 2.42, 4.84, and 7.26 fs, respectively. In panels g–i, the dotted, dashed, and solid lines are for $t = 0$, 42.3, and 84.7 fs, respectively.

dependence of the transient Raman spectra is noticed, although differences due to chirp rate are quite small.

The situation changes when the longest pulse L3 is used (Figure 2g−i). Initially, the Raman spectra are completely structureless and are well described by the KHD formula. At the end of the pulse, however, the Raman spectra show many well-resolved peaks.

In each of the cases (L1, L2, or L3), the real wave packet created on the excited-state PEC persists in the Franck−Condon region as long as the resonance fluorescence has an overall dominant effect. This can be understood later in Figure 3 by the exponential decay of the excited-state population long after the irradiation of the molecule.

We show why the stationary resonant Raman spectra after the pulse have almost the same structure irrespective of the chirp rate, as was observed by Duppen et al.[31] After the pulse, we have only to concentrate on the third terms of eqs 2.31 and 2.32. The terms containing the counter-rotating term can be omitted, $\omega_{l,\mathrm{i}} + \omega_\mathrm{L} + \omega_0$, the resonance condition used, $\omega_{l,\mathrm{i}} + \omega_\mathrm{L} - \omega_0 \approx 0$, and finally

$$J_0(\mathrm{L},l,j,t \rightarrow \infty) = \frac{E_0}{A}\frac{1}{i(\omega_{j,l}^{\mathrm{ex}} - \omega_\mathrm{L} - i\gamma_{\mathrm{ex}}/2)} \tag{3.3}$$

and

$$J(\mathrm{L},l,j,t \rightarrow \infty) = E_0\left(\frac{1}{A} - \frac{2i\alpha}{A^3}\right)\frac{1}{i(\omega_{j,l}^{\mathrm{ex}} - \omega_L - i\gamma_{\mathrm{ex}}/2)} \tag{3.4}$$

are obtained.

These render

$$b_{l0}^{\mathrm{L}}(t \rightarrow \infty) = \frac{E_0}{A}\frac{1}{\hbar^2}\sqrt{\frac{\hbar\omega_L}{2\epsilon_0 v}}\sum_j \langle\psi_l^{\mathrm{L}}|\hat{\mu}_\mathrm{L}|\psi_j^{\mathrm{ex}}\rangle\langle\psi_j^{\mathrm{ex}}|\hat{\mu}_E|\psi_\mathrm{i}^{\mathrm{gr}}\rangle \times \frac{1}{(\omega_{j,l}^{\mathrm{ex}} - \omega_\mathrm{L} - i\gamma_{\mathrm{ex}}/2)} \tag{3.5}$$

and

$$b_l^{\mathrm{L}}(t \rightarrow \infty) = E_0\left(\frac{1}{A} - \frac{2i\alpha}{A^3}\right)\frac{1}{\hbar^2}\sqrt{\frac{\hbar\omega_\mathrm{L}}{2\epsilon_0 v}}\sum_j \langle\psi_l^{\mathrm{L}}|\hat{\mu}_\mathrm{L}|\psi_j^{\mathrm{ex}}\rangle\langle\psi_j^{\mathrm{ex}}|\hat{\mu}_E|\psi_\mathrm{i}^{\mathrm{gr}}\rangle \times \frac{1}{(\omega_{j,l}^{\mathrm{ex}} - \omega_\mathrm{L} - i\gamma_{\mathrm{ex}}/2)} \tag{3.6}$$

The Raman spectral intensity ratio $P_{\mathrm{rel}}(t \rightarrow \infty) = P_\mathrm{L}(t \rightarrow \infty)/P_{\mathrm{L0}}(t \rightarrow \infty)$, with $P_\mathrm{L}(t \rightarrow \infty)$ including chirp and $P_{\mathrm{L0}}(t \rightarrow \infty)$ without chirp, reads

$$P_{\mathrm{rel}}(t \rightarrow \infty) = 1 + \frac{4\alpha^2}{A^4} \tag{3.7}$$

It can easily be recognized that the Raman spectral intensity does not depend on the sign of the chirp rate and that the intensity in the presence of the chirp increases relative to that of the transform-limited pulse, irrespective of the details of the molecular characteristics, e.g., PES. Equation 3.7 is a formula derived from the time-independent KHD terms in eqs 2.31 and 2.32 when the time-dependent Raman and fluorescence terms ($t \rightarrow \infty$) vanish. Therefore, the time-independent Raman and fluorescence processes contribute to eq 3.7. Under resonance conditions, when the temporal duration of the pulse is long (A is small), the excited-state wave packet gradually builds up and decays with the pulse, and the Raman process is dominant in eq 3.7. When the temporal duration of the pulse is short (A is large), the excited-state wave packet lingers in the Franck−Condon region and survives the laser pulse. In this case, the resonance fluorescence is dominant. Here it should be noted that this is the case only when the laser pulse is low-power and the chirp rate is small.

This intensity increase is intimately connected with the increase of the population to be excited and de-excited in succession (virtual state). Our task is to find the time dependence of the excited-state amplitude $b'_j(t) \equiv b_j^{\mathrm{ex}}(t)\exp(-iE_j^{\mathrm{ex}}t/\hbar - \gamma_{\mathrm{ex}}t/2)$. From eqs 2.13 and 2.21, $b_j^{\mathrm{ex}}(t)$ can be divide into the chirp-independent term $b_{j0}^{\mathrm{ex}}(t)$ and the chirp-dependent term $\delta b_j^{\mathrm{ex}}(t)$

$$b_{j0}^{\mathrm{ex}}(t) = \frac{i}{\hbar}\langle\psi_j^{\mathrm{ex}}| - \hat{\mu}_E \cdot \hat{\epsilon}_\mathrm{c}|\psi_\mathrm{i}^{\mathrm{gr}}\rangle \times \int_{-\infty}^{t} \mathrm{d}t'\, E_{\mathrm{c}0}(t') \exp(i\omega_{j,\mathrm{i}}^{\mathrm{ex}}t' + \gamma_{\mathrm{ex}}t'/2) \tag{3.8}$$

and

$$\delta b_j^{\mathrm{ex}}(t) = \frac{i}{\hbar}\langle\psi_j^{\mathrm{ex}}| - \hat{\mu}_E \cdot \hat{\epsilon}_c|\psi_\mathrm{i}^{\mathrm{gr}}\rangle \times \int_{-\infty}^{t} \mathrm{d}t'\, \delta E_\mathrm{c}(t') \exp(i\omega_{j,\mathrm{i}}^{\mathrm{ex}}t' + \gamma_{\mathrm{ex}}t'/2) \tag{3.9}$$

After simple integrations and applying RWA, we get for $t > 0$

$$b_{j0}^{\mathrm{ex}}(t) = \frac{iE_0}{2\hbar}\langle\psi_j^{\mathrm{ex}}| - \hat{\mu}_E \cdot \hat{\epsilon}_\mathrm{c}|\psi_\mathrm{i}^{\mathrm{gr}}\rangle\left\{\frac{\exp(pt)}{p} + \frac{1}{q} - \frac{1}{p}\right\} \tag{3.10}$$

and

$$\delta b_j^{\mathrm{ex}}(t) = \frac{\alpha E_0}{4\hbar}\langle\psi_j^{\mathrm{ex}}| - \hat{\mu}_E \cdot \hat{\epsilon}_\mathrm{c}|\psi_\mathrm{i}^{\mathrm{gr}}\rangle \times \left\{\exp(pt)\left(\frac{t^2}{p} - \frac{2t}{p^2} + \frac{2}{p^3}\right) + 2\left(\frac{1}{q^3} - \frac{1}{p^3}\right)\right\} \tag{3.11}$$

For $t < 0$, we obtain

$$b_{j0}^{\mathrm{ex}}(t) = \frac{iE_0}{2\hbar}\langle\psi_j^{\mathrm{ex}}| - \hat{\mu}_E \cdot \hat{\epsilon}_\mathrm{c}|\psi_\mathrm{i}^{\mathrm{gr}}\rangle\frac{\exp(qt)}{q} \tag{3.12}$$

and

$$\delta b_j^{\mathrm{ex}}(t) = \frac{\alpha E_0}{4\hbar}\langle\psi_j^{\mathrm{ex}}| - \hat{\mu}_E \cdot \hat{\epsilon}_\mathrm{c}|\psi_\mathrm{i}^{\mathrm{gr}}\rangle \times \exp(qt)\left(\frac{t^2}{q} - \frac{2t}{q^2} + \frac{2}{q^3}\right) \tag{3.13}$$

Here, we define

$$p \equiv (\gamma_{\mathrm{ex}}/2 - A) + i(\omega_{j,\mathrm{i}}^{\mathrm{ex}} - \omega_0) \tag{3.14}$$

and

$$q \equiv (\gamma_{\mathrm{ex}}/2 + A) + i(\omega_{j,\mathrm{i}}^{\mathrm{ex}} - \omega_0) \tag{3.15}$$

Under the near resonance condition $\omega_{j,\mathrm{i}}^{\mathrm{ex}} \approx \omega_0$, p and q are real. Therefore, it can easily be seen that $b_{j0}^{\mathrm{ex}}(t)$ is pure imaginary and $\delta b_j^{\mathrm{ex}}(t)$ is real, which leads to the conclusion that the excited-state population $|b'_j(t)|$ with chirp is always larger than

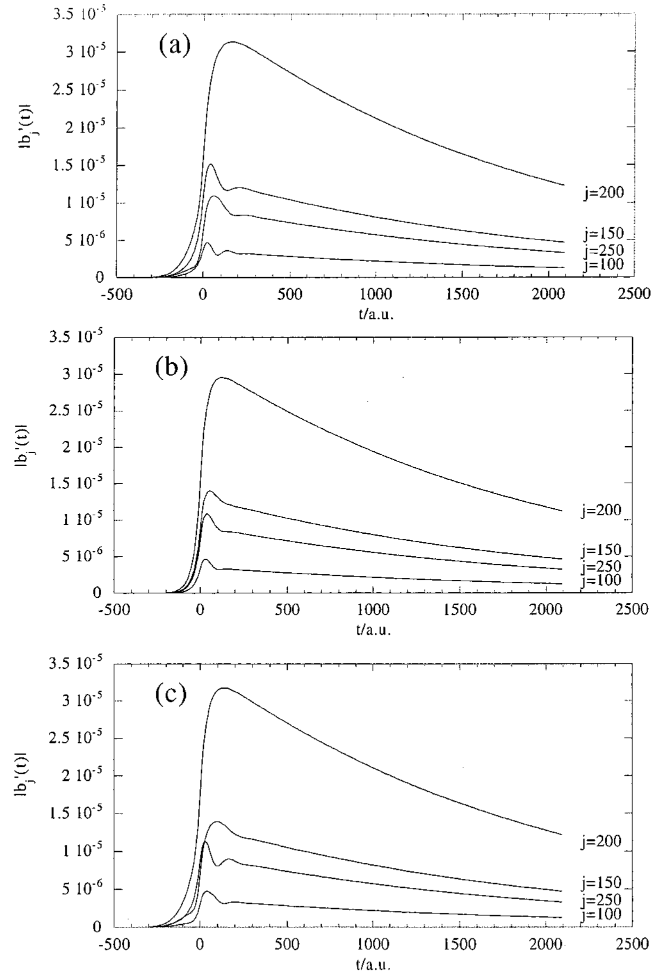

Figure 3. Time-evolution of the excited-state population $|b_j'(t)|$ for the laser pulse L2. Panels a−c are for positively chirped, transform-limited, and negatively chirped laser pulses, respectively.

that without chirp. Figure 3 clearly shows this situation. Although $|b_j'(t)|$'s of the vibrational states off-resonant with the center frequency of the incident light ($j = 100$, 150, and 250) show complex patterns, those resonant with the center frequency ($j = 200$) exhibit monotonic behavior. Nevertheless, it is easily recognized that the population in the virtual state and the emitted photon intensity increase if a chirped laser pulse is used, which leads to coherent enhancement of the Raman spectral intensity.

In general, the population transfer to the excited state is determined to be either enhanced or suppressed by the chirp, depending on the values of the relevant parameters. It is known that when a high-power incident laser pulse is of long duration, the adiabatic rapid passage (ARP) condition is satisfied, and π pulse excitation (complete population conversion) by a positively chirped laser pulse and de-excitation by a negatively chirped laser pulse are detected,[8,39] while for a high-power incident laser pulse of short time duration, the discrepancy between the two chirped laser pulses disappears. However, when the incident laser pulse is low-power, we found the excitation probability to be enhanced by chirping. The chirp rate sign independence of the intensity enhancement in the case of the low-power excitation has previously been stated from both experimental[16] and theoretical[18] points of view.

In Figure 4, the molecular vibrational distributions of the vibrational state $v = l$ of the ground electronic state are represented by the spontaneous emission $Q_l^{sp}(t)$ calculated by eq 2.51. It should be noted that the final vibrational distributions are larger for the chirped pulse than for the transform-limited pulse and that the difference resulting from changing the chirp rate sign is rather trivial. The reason for this is the same as for the Raman spectral intensity mentioned above. A more distinctive feature that can be seen is that the final vibrational distributions due to the chirped pulses are larger, compared with the transform-limited pulse, for the long duration pulse than for the short duration pulse. This is determined by $P_{rel}(t \to \infty)$, given in eq 3.7. For the shortest incident pulse L1 ($\alpha = 74.4$ eV fs^{-2} and $A = 2.27$ fs^{-1}), $P_{rel}(t \to \infty) = 1.28$, and for the longest incident pulse L3 ($\alpha = 0.930$ eV fs^{-2} and $A = 0.620$ fs^{-1}), $P_{rel}(t \to \infty) = 1.79$. This tendency is the same for on- and off-resonance cases.

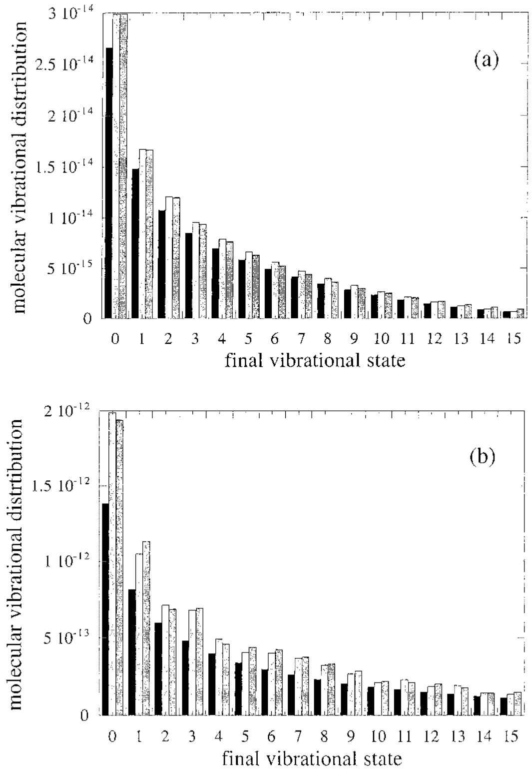

Figure 4. Final molecular vibrational distributions of the ground electronic state due to spontaneous emission $Q_l^{sp}(t \to \infty)$ in the resonance condition. Panel a is for the laser pulse L1 and b for L3. The light gray, black, and dark gray bars are for positively chirped, transform-limited, and negatively chirped laser pulses, respectively.

As can be seen in Figure 5, when the incident light is off-resonance (nonresonance Raman scattering), Rayleigh scattering is predominant, and the fundamentals or overtones are much weaker at the long time limit. This result can be readily understood by the following argument. Because the frequency $\omega_{j,l}^{ex}$ is much larger than the emission frequency ω_L and $\omega_{j,l}^{ex}$ can be supposed to be a constant with respect to the index j, the third term of eq 2.31 or (2.32) can be expressed as $B(L,l)$. Then the spontaneous emission amplitude $b_l^L(t)$ in eq 2.50 is rendered as

$$b_l^L(t) \approx \frac{i}{\hbar^2}\sqrt{\frac{\hbar\omega_L}{2\epsilon_0 v}}B(L,l)\sum_j \langle\psi_l^L|\hat{\mu}_L|\psi_j^{ex}\rangle\langle\psi_j^{ex}|\hat{\mu}_E|\psi_i^{gr}\rangle \tag{3.16}$$

As we assume the dipole moments are constant scalar quantities, we use the closure relation of $|\psi_j^{ex}\rangle$, $b_l^L(t) \propto \langle\psi_l^L|\psi_i^{gr}\rangle = \delta_{l,i}$. Therefore, $b_l^L(t)$ is significant if $l = i$ (Rayleigh scattering). The slight variation of the third term of eq 2.31 or 2.32 leads

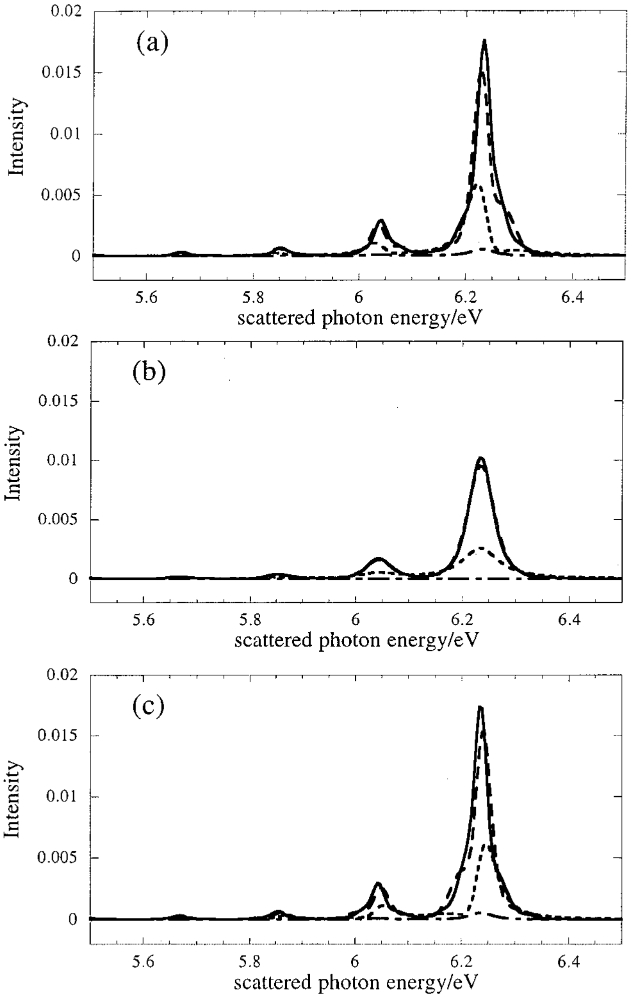

Figure 5. Transient resonant Raman spectra for the laser pulse L3 in the off-resonance condition. Panels a−c are for positively, transform-limited, and negatively chirped laser pulses. The dashed−dotted, dotted, dashed, and solid lines are for $t = -42.3$, 0, 42.3, and 84.7 fs, respectively.

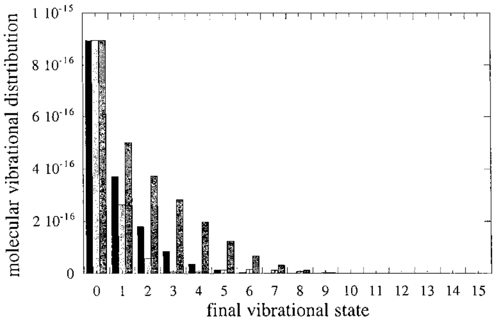

Figure 6. Final molecular vibrational distribution of the ground electronic state due to stimulated emission $Q_l^{\rm st}(t\rightarrow\infty)$ in the resonance condition. The laser pulse is L2. The light gray, black, and dark gray bars are for positively chirped, transform-limited, and negatively chirped laser pulses, respectively.

to additional small fundamentals or overtones in the Raman spectra. The same propensity was also detected in the molecular vibrational distribution due to spontaneous emission $Q_l^{\rm sp}(t \rightarrow \infty)$.

The dependence on the sign of the chirp rate appears most prominently in stimulated emission. In Figure 6, it can be seen that the molecular vibrational distributions $Q_l^{\rm st}(t \rightarrow \infty)$ are significantly different according to the chirp rate in the fundamental and the higher overtones. The distribution is the widest when the incident laser pulse is negatively chirped, while it is narrowest when a positively chirped laser pulse is used. The deduction from eq 2.45 or 2.46 is a bit cumbersome. However, it may physically be assumed that the differences observed above among the positively, negatively, and transform-limited pulses are due to the intrapulse pump-dump process. The excited-state wave packet photoinduced from the ground-state slides down along the curve because the wave packet created in the excited electronic state is not an eigenstate of the vibrational manifold. The motion along the PEC has an effect of dynamical Stokes shift: the transition energy ($V_{\rm ins}(t)$) between the excited state wave packet and the ground state PEC decreases with time. The negatively chirped pulse whose instantaneous frequency is $\omega(t)$ follows the behavior of $V_{\rm ins}(t)$, and the excited state wave packet is dumped to the ground state effectively. The existence of the pump−dump enhancement of the ground electronic state vibrations has been observed before, both theoretically[8,11−14] and experimentally.[15−17] However, positively chirped pulses do not follow the behavior of $V_{\rm ins}(t)$, and the dumping effect does not work. It should be noted that the stimulated Raman process in the presence of the chirp is quite sensitive to the molecular characteristics, in contrast to the spontaneous Raman process.

In conclusion, the spontaneous emission probability is enhanced by chirping the incident laser pulse, irrespective of the sign of the chirp rate, although the spectral profile does not change much. The stimulated Raman emission probability shows a propensity readily attributable to the intrapulse pump−dump process. The detuning renders the transient and stationary Raman spectra simple, and the chirping effect is the same as that in the on-resonance condition.

IV. Conclusions

In this paper, some analytical formulas have been derived for describing spontaneous and stimulated Raman scattering of a molecular system in the presence of a weak pulse-mode chirped laser field on the basis of a second-order perturbation theory. In particular, attention has been focused on the effect of chirping, duration, and detuning of the incident laser pulse on the Raman spectroscopic profile and the molecular vibrational distribution. Our theory was applied to laser pulse excitation of the O_2 molecule from the $X^3\Sigma_g^-$ state to the $B^3\Sigma_u^-$ state, which is mainly repulsive and accommodates some bound vibrational states. From the simulation, the transient Raman spectrum was found to be slightly dependent on the sign of the chirp rate. The stationary Raman spectra after the laser radiation look alike, irrespective of the sign of the chirp rate: they are bell-shaped in the case of the pulses of short duration and well-resolved in the long duration limit. It was revealed that the chirp has the effect of enhancing the spectral intensity, irrespective of the sign of the chirp rate. On the other hand, the overtone molecular vibrational distribution due to stimulated Raman emission was found to change considerably, depending on the sign of the chirp rate. From these results, we conclude that, for a weak field intensity and small chirp rate, the spontaneous emission probability is enhanced in the presence of chirping, while stimulated Raman emission is significantly influenced by the intrapulse pump−dump process characteristic of the (negatively) chirped laser pulse.

If a strong laser pulse is used, the perturbative approach used in this paper breaks down, and the adiabatic rapid passage (ARP) mechanism works effectively. It can then be presumed that a large part of the wave packet would be trapped in the attractive part of the excited state potential if a positively chirped pulse were used, while it would dissociate rapidly if a negatively chirped pulse was used.[8,19] Studies of Raman spectroscopy in such a strong laser pulse by Shapiro's strategy[27] may demonstrate interesting and more dramatic variations of the resonance fluorescence and spontaneous Raman spectra by changing the sign of the chirp rate and may indicate dynamic details in the two-photon transition.

Finally, we would like to point out that in order to cover this strong-field nonperturbative limit, we could also extend our theory following the concept of Raman chirped nonadiabatic passage (RCNAP).[40] Because it is often the case that enhancement of photochemical product yield with use of the stimulated Raman scattering induced by the strong laser pulse is of much interest to chemists, we could investigate the stimulated emission in more detail and eliminate the complication of spontaneous emission.

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