Theory of selective excitation in
Stimulated Raman Scattering

S. A. Malinovskaya, P. H. Bucksbaum, and P. R. Berman

University of Michigan,
FOCUS Center and Department of Physics,
Ann Arbor, MI 48109
(Dated: November 11, 2018)

Abstract

A semiclassical model is used to investigate the possibility of selectively exciting one of two closely spaced, uncoupled Raman transitions. The duration of the intense pump pulse that creates the Raman coherence is shorter than the vibrational period of a molecule (impulsive regime of interaction). Pulse shapes are found that provide either enhancement or suppression of particular vibrational excitations.

PACS numbers: 42.65.Dr 42.50.Hz 33.20.Fb 82.53.Kp
I. INTRODUCTION

Studies of molecular dynamics accompanying excitation, ionization, or dissociation give rise to questions concerning the control of specific motion in molecules. Control using ultrafast lasers and adaptive learning algorithms, e.g., genetic-type algorithms [1, 2], allows one to optimize feedback and achieve predetermined goals. Series of successful experiments implementing this technique offer proof that it is possible to exercise quantum coherent control over a range of processes. Two such experiments employ stimulated Raman scattering in liquid methanol [2] and gas phase carbon dioxide [3]. In the former case a liquid medium is excited with a 100 fs pulse, which is equivalent to non-impulsive Raman excitation and, therefore, makes propagation effects important. In the latter case the selective Raman excitation of vibrational modes is achieved with a pulse of duration within a typical molecular vibrational period. In this case the seed for the Stokes transition is within the pump pulse. In the experiment with methanol the problem of intra-molecular couplings of vibrational modes is discussed using a comparative analysis with experiments on benzene and deuterated benzene molecules. The controlling optical field may be constructed using coherent quantum control theory, see, e.g., [4, 5]. An alternative approach involves a search for an analytical pulse function. In [6, 7] an antisymmetric phase function is proposed, which inverts the sign of the electric field at a given energy, inducing constructive interference of the off-resonant components of the spectrum and therefore maximizing the transition amplitude. Selectivity of the two Raman levels of pyridine, both of which lie within the bandwidth of the excitation pulses is achieved in CARS signals by positioning the phase step at each of the two peaks [8]. In [9] the use of adaptive techniques in FAST CARS is explored for an identification of related biological objects such as bacterial spores.

The Raman excitation of a single vibrational mode having frequency $\omega$ normally requires a pulse with $\omega \tau \leq 1$, where $\tau$ is the pulse duration. Optimal excitation may occur if the intensity is modulated at a frequency that corresponds to the transition frequency. For any two vibrational modes $\omega_1$, $\omega_2$ within the pulse bandwidth, $(\omega_1 - \omega_2)\tau \ll 1$, the spectral width is too large to resolve the lines. In the present paper we propose a method for achieving selective excitation using broadband pulses. In the frequency domain we introduce an intensity envelope that vanishes for a modulation frequency of the pulse equal to the frequency of vibration that we would like to suppress. The Fourier transformed field, when
applied to a molecular system, provides negligible excitation of that particular frequency
together with significant excitation of another frequency. This picture is valid for weak
fields. In strong fields the effect is not obvious and numerical analysis reveals that, for some
intensities and the designed pulse shape, it is still possible to optimize one transition versus
another.

The paper is organized as follows. In the second section the problem is formulated based
on a model of two, two level systems. An analytical function for the intensity envelope is
proposed and the equations of motion for the state amplitudes are obtained. The third
section contains results of numerical calculations that determine the field parameters that
lead to selective excitation. The paper is ended with a short summary.

II. BASIC FORMALISM

In our model a molecule is described by two, two-level quantum systems, each representing
a normal Raman-active vibrational mode. The molecular medium is represented by an
ensemble of such systems with no relaxation processes taken into account. Each two-level
system interacts with an intense off-resonant femtosecond pulse that initiates stimulated
Raman scattering via an off-resonant interaction with a virtual state. The duration of this
pump pulse is shorter than a typical vibrational period of a molecule. In this case the
frequencies of both two-level systems are within the bandwidth of the pulse and the Stokes
component of the field is supplied by the same pulse. The coherently excited ensemble is
analyzed by a weak probe pulse, not considered in this work, applied after a time delay
shorter than the coherence time. The goal of the present work is to determine a pulse shape
that provides selectivity for the excitation of one of the two-level systems.

A semiclassical model of laser-molecule interactions is used. The model is represented
schematically in Fig.1 where \( \omega_{21} \) is the frequency of the first two-level system and \( \omega_{43} \) that
of the second system. Initially only lower levels \(|1>\) and \(|3>\) of both two-level systems
are populated, and the populations of these levels are equal. The time evolution of two,
two-level systems is described in terms of probability amplitudes, which are written in the
interaction representation

\[
\dot{a}_j = \frac{i}{4\Delta} \sum_{j'=1}^{4} \Omega_{j'}^* e^{-(\alpha_j - \alpha_{j'})\omega t} a_{j'}, \quad \Omega_j = -\frac{\mu_{jb} E_{p0}(t)}{\hbar}.
\]  

\(1\)
Here $\alpha_j \omega$ is the frequency of a single level, such that, e.g., $(\alpha_2 - \alpha_1) \omega = \omega_{21}$, $\Omega_j$ is a Rabi frequency, $\mu_{jb}$ is a dipole moment matrix element, $E_{p0}(t)$ is the pulse envelop, $\Delta$ is the detuning of the frequency of the pulse from the frequency of the virtual state $|b >$. Note, that the pulse envelope $E_{p0}(t)$ is the same for all transitions. The Rabi frequencies may differ owing to different dipole moment matrix elements.

The system of coupled differential equations (1) is derived from the time-dependent Schrödinger equation with Hamiltonian:

$$H = \frac{\hbar}{2} \begin{pmatrix}
\alpha_1 \omega & 0 & 0 & 0 & 2\Omega_1 \cos(\omega_p t) \\
0 & \alpha_2 \omega & 0 & 0 & 2\Omega_2 \cos(\omega_p t) \\
0 & 0 & \alpha_3 \omega & 0 & 2\Omega_3 \cos(\omega_p t) \\
0 & 0 & 0 & \alpha_4 \omega & 2\Omega_4 \cos(\omega_p t) \\
2\Omega_1^* \cos(\omega_p t) & 2\Omega_2^* \cos(\omega_p t) & 2\Omega_3^* \cos(\omega_p t) & 2\Omega_4^* \cos(\omega_p t) & E_b
\end{pmatrix}, \quad (2)$$

where $\omega_p$ is the laser field carrier frequency. By adiabatically eliminating state $|b >$ within the rotating wave approximation, we arrive at Eqs (1). In this work we discuss the case of uncoupled two-level systems such that the probability for the population flow from one system to another via the external field is zero. Then Eqs. (1) are represented by two independent systems of coupled differential equations with two variables.

Coherent excitation of a molecular medium induces a vibrational coherence $|\rho_{12}|$ or $|\rho_{34}|$. When a probe field is applied on the 1-b transition, the coherence $|\rho_{12}|$ serves as a source for the generation of a field on the 2-b transition. Thus it is of prime interest to calculate $|\rho_{12}|$ and $|\rho_{34}|$. The goal of this paper is to choose a pump pulse such that $|\rho_{12}|$ is suppressed while $|\rho_{34}|$ is enhanced.

We propose an analytical function for the intensity envelope which is included in the dynamical equations (1) for the probability amplitudes. It is easiest to choose this function in the frequency domain. To suppress excitation at frequency $\omega_{21}$ and enhance excitation at frequency $\omega_{43}$, we choose

$$\tilde{I}(\omega) = I_0 e^{-(\omega - \omega_{43})^2 T^2} \left(1 - e^{-(\omega - \omega_{21})^2 T_1^2}\right), \quad (3)$$

where $T$ and $T_1$ are free parameters. When the modulation frequency of the pulse $\omega$ is equal to $\omega_{43}$ the intensity approaches its maximum $I_0$ for a sufficiently large parameter $T_1$. 


\[
I(\omega_{43}) = I_0(1 - e^{-\Delta \omega^2 T_1^2}), \quad \Delta \omega = \omega_{43} - \omega_{21}.
\] (4)

For \(\omega\) equal to \(\omega_{21}\) the intensity is zero, \(I(\omega_{21}) = 0\). The intensity envelope as a function of frequency is drawn in Fig.2. The frequencies of the two-level systems are \(\omega_{21} = 1\) and \(\omega_{43} = 1.1\) in frequency units of \(\omega_{21}\). The intensity of the field at \(\omega_{43}\) and frequency region near \(\omega_{21}\) over which \(\tilde{I}(\omega)\) is approximately zero depend on \(T_1\). The larger \(T_1\), the greater is the selectivity for suppressing the \(\omega_{21}\) frequency.

The inverse Fourier transform of the spectral density (3) is a complex function. To arrive at a physically acceptable temporal pulse function, we take the real part of the inverse Fourier transform, given by

\[
I(t) = I_0 \left( \left(\sqrt{2}T\right)^{-1} e^{-\frac{t^2}{4T^2}} \cos(\omega_{43} t) - \left(\sqrt{2}\tau\right)^{-1} e^{-\Delta \omega^2 T^2 (1 - \frac{T_2^2}{T^2})} e^{-\frac{\tau^2}{4T^2}} \cos((\omega_{21} - \Delta \omega \frac{T^2}{T_2}) t) \right),
\] (5)

where \(\tau^2 = T^2 + T_1^2\). The expression for the field (5) is inserted in Eqs.(1) for the calculation of the probability amplitudes.

The solution of Eqs.(1) in the limit of a weak field using perturbation theory is

\[
a_4 = i \frac{\mu_{4h} \mu_{4h}^*}{4e^2 \hbar^2} \int_{-\infty}^{\infty} I(t) e^{i\omega_{43} t} dt = i \frac{\mu_{4h} \mu_{4h}^*}{4e^2 \hbar^2} \tilde{I}(\omega_{43}) = i \frac{\mu_{4h} \mu_{4h}^*}{4e^2 \hbar^2} I_0(1 - e^{-\Delta \omega^2 T_1^2}),
\] (6)

\[
a_2 = i \frac{\mu_{2h} \mu_{2h}^*}{4e^2 \hbar^2} \int_{-\infty}^{\infty} I(t) e^{i\omega_{21} t} dt \sim e^{-T^2(\omega_{43} + \omega_{21})^2} + e^{-\Delta \omega^2 T^2} e^{-\tau^2(2\omega_{21})^2} \approx 0.
\]

The Fourier transform represented in Eq.(5) is not identical to Eq.(3), since we took the real part of the Fourier transform to arrive at (5). It now contains "counter-rotating" terms, which are small for the chosen pulse shape. Thus, by construction, we have totally suppressed the 1-2 transition in the weak field limit. On the other hand, the excitation of the 3-4 transition is still weak owing to the perturbative nature of the solution.

Polyatomic molecules often possess several or many Raman active modes with frequencies close enough to be within the bandwidth of the pulse. In order to enhance a single vibration and suppress other vibrations the function for the pulse may be constructed as a product of several terms

\[
\tilde{I}(\omega) = I_0 e^{-(\omega - \omega_{43})^2 T^2} \prod_j \left(1 - e^{-(\omega - \omega_j)^2 T_1^2}\right).
\] (7)
III. NUMERICAL RESULTS

In this section we discuss the results of numerical calculations based on the exact solution of Eqs.(1). The numerical studies reveal the influence of the field parameters on the efficiency of the excitation of the two-level systems. Parameters for the system are taken from the experimental data on impulsive excitation of vibrational modes in the molecular gas CO₂\(^2\). In CO₂ the frequencies of two selectively excited Raman modes are 36.8 and 42 THz. The FWHM of the applied intense pulse is taken equal to 18 THz. In our calculations the frequency \(\omega_{21}\) is set equal to unity; in these units the frequency \(\omega_{43}\) is equal to 1.1. From experimental data, we estimate that the parameter \(T\) is about equal to 3, in frequency units of \(\omega_{21}^{-1}\). The intensity of the field is determined by the parameter \(I_0\). The parameter \(T_1\) is related to the width of the spectral dip in \(\tilde{I}(\omega)\) centered at frequency \(\omega_{21}\). Although a value of \(T_1 \gg T\) would provide the best selectivity, the choice for the parameter \(T_1\) is strongly restricted by the requirement that the duration of the applied pulse be within a typical molecular vibrational period. It turns out that even for such values of \(T_1\), it is possible to selectively excite one transition.

We calculated the population distribution and the coherence of the excited and suppressed two-level systems as a function of \(T_1\) as shown in Fig.3. Bold solid and dotted lines depict the absolute value of the coherence \(|\rho_{34}|\) of the excited system and \(|\rho_{12}|\) of the suppressed system. Populations of the upper levels of both systems are shown by bold dashed and dot-dashed lines. The intensity of the field \(I_0\) is \(\pi/8\) which corresponds to a weak field in our calculations (but not to the perturbative regime). For the value \(T_1 = 13\) the population of levels of the 3-4 system is 0.25, and the coherence is optimal for the given intensity of the field and dipole moments, \((\mu_i = 1)\). The duration of the laser pulse corresponding to this value of the parameter \(T_1\) is about 200 fs which does not satisfy the necessary requirements on pulse duration. According to Fig.3 for smaller values of the parameter \(T_1\), corresponding to shorter pulses, the coherence of the 3-4 system is significantly reduced with a simultaneous increase of the coherence of the 1-2 system. Optimal values for the coherence of both the 1-2 and 3-4 systems were found for \(T_1 \leq T\) through a search over different intensities of the field.

In Fig.4 the coherence is plotted as a function of the intensity of the field for parameters \(T=3\) and \(T_1 = 3\). Coherence \(|\rho_{34}|\) of the 3-4 system is represented by a bold solid line.
and coherence $|\rho_{12}|$ of the 1-2 system by a bold dashed line; thin lines show populations of the upper levels of both two-level systems. For the intense fields, coherence of the excited and suppressed systems possess somewhat chaotic structure. Several values of the intensity, e.g. $I_0 = \pi$ and $I_0 = 1.75\pi$ give rather low coherence of the 3-4 system but maximum coherence of the 1-2 system. A desired solution for maximum coherence of the excited 3-4 system is achieved for the intensity coefficient $I_0 = 2.08\pi$. This is the result of redistribution of population within that two-level system: half of population is transferred to the upper level providing maximum coherence. The corresponding coherence of the 1-2 system at this intensity is nearly zero, where most population remains in the lower level. For the intensity $I_0 = 1.4\pi$ the picture is similar, however the low coherence of the 1-2 system is due to nearly complete population transfer to the upper level.

The goal of control of the coherence of two uncoupled two-level systems is achieved with a pulse shape possessing a broad spectral dip at the suppressed frequency and a suitably chosen intensity of the field. This technique allows one to use pulses of duration $T$ to selectively excite transitions having frequency separations $\Delta \omega < 1/T$. Our results should not be taken to imply that one can spectroscopically determine frequencies to better than the inverse temporal width of the pulse. On the other hand, if the frequencies are known from previous measurements, it is possible to suppress one transition and enhance the other by the method outlined above.

Had we taken a frequency profile centered at $\omega_{43}$ with $T = 3$, the curves for the coherence and populations of the excited and suppressed systems would differ qualitatively from those show in Fig.4. The desired selectivity could not be achieved.

The time-dependence of the coherence, populations and the field is shown in Fig.5 for $T = 3, T_1 = 3, I_0 = 1.4\pi$. The pulse duration is about 50 fs (thin solid line). It induces oscillations in the population distribution (thin lines) which lead to oscillations of the coherence of the two-level systems (bold lines). At long times the coherence and populations of levels achieve stationary values.

We have carried out some preliminary calculations, including the coupling between vibrational modes via an external field used as a control mechanism. If the direct excitation of a particular vibrational mode is weak owing to a weak oscillator strength, the excitation may be enhanced through the coupling to the other Raman active vibrational modes. Details will be published in [11].
IV. SUMMARY

We have presented a semi-classical description of stimulated Raman scattering involving the selective excitation of one of two closely spaced vibrational modes. The dynamics is described in terms of probability amplitudes and depends on the shape of a femto-second laser pulse where duration is shorter than a typical molecular vibrational period. We propose an analytical function for the shape of the intensity envelop of the pulse that allows for the selective excitation of a predetermined vibrational motion with simultaneous suppression of an unfavorable one. The pulse leads to maximum coherence of a desired vibrational transition and consequently to maximum gain into Raman side bands when a probe pulse is applied. This pulse function may be used as an initial guess for the control of bond excitation in chemistry as well as a fit function within an adaptive learning algorithm.

ACKNOWLEDGMENTS

The authors acknowledge financial support from the National Science Foundation (No. PHY-9987916) through the Center for Frontiers in Optical Coherent and Ultrafast Science (FOCUS).

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FIG. 1: Schematic picture of a model system consisting of two, two-level systems having frequencies $\omega_{21}$ and $\omega_{43}$. Initially, the lower levels are populated evenly. The uncoupled transitions are driven by an off-resonant femtosecond pulse.
FIG. 2: Intensity spectral profile as a function of frequency for $T_1 = 10, 5, 3$ (dashed, dotted, and solid lines). In the insert the intensity envelop as a function of time is presented for $T_1 = 10, 3$. All frequencies are in units of $\omega_{21}$ and times in units of $\omega_{21}^{-1}$.

FIG. 3: Coherence and populations of upper levels of the 3-4 and 1-2 two-level systems as a function of $T_1$ for $\omega_{21} = 1, \omega_{43} = 1.1$, and $I_0 = \pi/8$. 
FIG. 4: Intensity dependence of the coherences $|\rho_{12}|$ and $|\rho_{34}|$ and upper states populations $\rho_{22}$ and $\rho_{44}$. Maximum coherence of the 3-4 system and negligibly small coherence of the 1-2 system are observed for $I_0 = 1.4$ and 2.08 in the intensity region shown with $T = 3, T_1 = 3$.

FIG. 5: Time evolution of $|\rho_{12}|$, $|\rho_{34}|$, $\rho_{22}$, and $\rho_{44}$ for $T=3, T_1 = 3$, and $I_0 = 1.4\pi$. The pulse intensity $I(t)$, in arbitrary units, is also shown in the figure.