

Mode-selective excitation using ultrafast chirped laser pulses

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We propose a method to control population transfer and coherence in a multimode system using a transform-limited pump and a linearly chirped Stokes pulse in stimulated Raman scattering. Simultaneously applied pump and Stokes pulse are shown to induce the ac Stark shifts that result in nonadiabatic coupling of the dressed states, through which the pulse chirp governs population distribution. The method may be applied to selectively excite Raman transitions having the frequency difference less than the bandwidth of a transform-limited pulse.

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Laser control of multimode dynamics is a topical and challenging domain in the quantum control theory and experiments. It has implementations in quantum computing, mode-selective photochemistry, light manipulation, etc. Theoretical and experimental approaches to coherent control of state excitation are numerous and have been developed in weak and strong fields. Spectroscopic experiments commonly use an adaptive learning technique [1,2], and span from control of molecular dynamics in gases and liquids [3–5], to control of the energy transfer and state population in biological systems [6,7]. Other approaches are based on the amplitude and phase modulation. A number of examples includes control of vibrational dynamics in gaseous I_2 using pulse chirp in femtosecond four-wave mixing spectroscopy [8], selective excitation of Raman modes in CCl_4 and $CHBr_3$ liquids using a pair of time-shifted, linearly chirped pulses [9], selective excitation of the chain modes of polydiacetylenes implementing four-wave mixing spectroscopy with varying the timing and phases of the femtosecond pulses [10]. High spectral resolution of coherent anti-Stokes Raman scattering (CARS) signals is achieved in [11] using chirped pump pulse and stepping the delay between ω_p and ω_s . An antisymmetric phase function is proposed in [12] to be used in CARS to probe spectrally close Raman levels in molecules. Much attention has been devoted to methods of adiabatic population transfer such as stimulated Raman adiabatic passage (STIRAP), to control population transfer between specified quantum states [13,14], and Raman chirped adiabatic passage, to climb vibrational ladders [15,16]. In [17], an approach for the pulse amplitude modulation in stimulated Raman spectroscopy is developed, that allows selective excitation of *different* normal vibrational modes in molecules, having frequencies less than the bandwidth of an exciting broadband pulse.

In this paper a general method is proposed for mode selective excitation where the magnitude of transition frequencies is not limited by the bandwidth of the exciting pulse. It may be much larger than that, while the frequency difference of normal vibrational modes may be not resolved by the pulse bandwidth. The external field intensities used, are about 10^{12} W/cm². Normal mode selective excitation is achieved by means of the two-photon Raman transition using a transform-limited pump and a linearly chirped Stokes pulse. According to the dressed state analysis, selective ex-

citation occurs due to nonadiabatic interaction of the medium with ultrafast intense laser pulses. It is caused by the ac Stark shifts generated as a nonlinear response of a system on the two-photon excitation, and can be controlled by the chirp of the Stokes pulse.

The Raman model consists of the two uncoupled two-level systems having slightly different frequencies, and interacting with the pump and Stokes pulse, Fig. 1(a). The Stokes pulse bandwidth at zero chirp is close to the difference between transition frequencies of the two-level systems, and the effective Rabi frequency is larger than that. The Raman model is compared to the one-photon model, Fig. 1(b), where the two uncoupled two-level systems interact with a single linearly chirped pulse. Obviously, in strong fields the one-photon model demonstrates adiabatic population transfer in the resonant and detuned two-level systems, giving no selective excitation of spectrally close modes. The features of the Raman and the one-photon model, resulting in such a different quantum yield, are discussed explicitly to provide understanding of the control mechanisms.

The parameters of the two-level systems are chosen to be the same in both models. Transition frequency of the 1–2 two-level system is ω_{21} , that of the 3–4 two-level system is ω_{43} , and the frequency difference is $\delta \ll \omega_{21}$. Initially only

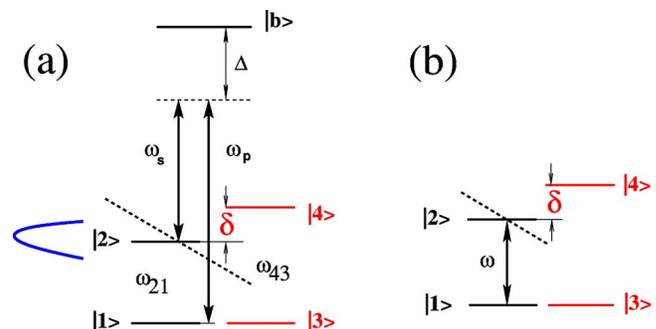


FIG. 1. (Color online) Schematic picture of two models each consisting of two, two-level systems having frequencies ω_{21} and ω_{43} and initial population of the lower levels 0.5. The uncoupled transitions are driven by an off-resonant femtosecond pulse(s), (a) a transform-limited pump and a linearly chirped Stokes pulse—the Raman model, and (b) a linearly chirped pulse—the one-photon model.

ground states $|1\rangle$ and $|3\rangle$ of the two-level systems are evenly populated.

In the Raman model an intense, transform-limited pump pulse has central frequency ω_p and the duration τ_0 . A linearly chirped Stokes pulse has the central frequency ω_s , such that $\omega_p - \omega_s = \omega_{21}$. The pulses are defined as $E_p(t) = E_{p0}(t)\cos(\omega_p t)$, $E_s(t) = E_{s0}(t)\cos(\omega_s t - \beta t^2/2)$, where $E_{p0}(t) = E_0 \exp(-t^2/2\tau_0^2)$ and $E_{s0}(t) = E_0 \sqrt{\tau_0/\tau} \exp(-t^2/2\tau^2)$ are the time-dependent pump and Stokes field envelopes, $\tau = \tau_0 \sqrt{1 + \beta'^2/\tau_0^4}$ is the chirp-dependent Stokes pulse duration, β and β' are the linear temporal and spectral chirps related as $\beta = \beta' \tau^{-4}/(1 + \beta'^2/\tau_0^4)$. For zero chirp, the Stokes pulse duration is τ_0 . This specifies the maximum value of temporal linear chirp $\beta_{\max} = 1/(2\tau_0^2)$ and the value of related spectral linear chirp $\beta'|_{\beta_{\max}} = \tau_0^2$ [18].

In the one-photon model a linearly chirped laser pulse has the chirp-dependent pulse duration τ , the central frequency ω , and the linear temporal chirp β having spectral counterpart β' . The pulse is defined as $E(t) = E_0(t)\cos(\omega t - \beta t^2/2)$, where $E_0(t) = E_0 \sqrt{\tau_0/\tau} \exp(-t^2/2\tau^2)$ is the pulse envelope. The frequency ω is equal to ω_{21} .

To explore the dynamics of the two-level systems, we have numerically solved the time-dependent Schrödinger equation with the Hamiltonian that describes the interaction of the two, two-level systems with an external electromagnetic field(s). The Hamiltonian was derived in the field-interaction representation, by adiabatically eliminating state $|b\rangle$ and implementing the rotating wave approximation. There is an important difference in the structure of the related Hamiltonians for the Raman model and the one-photon model. The Hamiltonian that describes the 3–4 two-level system in the Raman model reads $H_{34} = \Lambda \hat{\sigma}_z/2 + \Omega_3(t) \hat{\sigma}_x$, where $\hat{\sigma}_{x,z}$ are the Pauli matrices, $\Lambda = \delta - \beta t + \Omega_S(t)$, $\Omega_S(t) = \Omega_1(t) - \Omega_2(t)$ is the ac Stark shift difference, $\Omega_1(t) = \bar{\mu}^2 E_{p0}^2(t)$ and $\Omega_2(t) = \bar{\mu}^2 E_{s0}^2(t)$ are the ac Stark shifts, $\Omega_3(t) = \bar{\mu}^2 E_{p0}(t) E_{s0}(t)$ is the effective Rabi frequency, note, that the peak effective Rabi frequency at zero chirp we define as Ω_3 , $\bar{\mu}^2 = \mu^2/4\hbar^2\Delta$, μ is the dipole moment, Δ is the detuning from the excited state [Fig. 1(a)], such that $\Delta \gg \omega_p, \omega_s$.

In the one-photon model the H_{34} differs from the expression above by $\Omega_S(t) \equiv 0$ and the coupling term, which is the Rabi frequency $\Omega_R(t) = \mu E_0(t)/\hbar$. Setting $\delta=0$ in each H_{34} gives the Hamiltonians H_{12} that describe the 1–2 two-level system. The crucial difference in the Hamiltonians for the one-photon and the Raman model is $\Omega_S(t)$. It causes nonadiabatic coupling between the dressed states, as we show in this paper.

Diagonalization of the H_{34} gives energy separation between the dressed states in the 3–4 two-level system, which for the Raman model is $\Omega(t) = \sqrt{(\delta - \beta t + \Omega_S(t))^2 + 4\Omega_3^2(t)}$, and for the one-photon model is $\Omega(t) = \sqrt{(\delta - \beta t)^2 + 4\Omega_R^2(t)}$. Dressed states dynamics is governed by the Hamiltonian $H_d = -\Omega(t) \hat{\sigma}_z/2 + i\dot{\Theta}(t) \hat{\sigma}_x$, where $\dot{\Theta}(t)$ is the nonadiabatic coupling parameter. It is found that $\dot{\Theta}(t) = [\Lambda \dot{\bar{\Omega}}(t) - \dot{\Lambda} \bar{\Omega}(t)]/\Omega(t)^2$, where $\bar{\Omega}(t) = \Omega_3(t)$ for the Raman model and $\bar{\Omega}(t) = \Omega_R(t)$ for the one-photon model.

Note, that the measure of the adiabaticity of a process

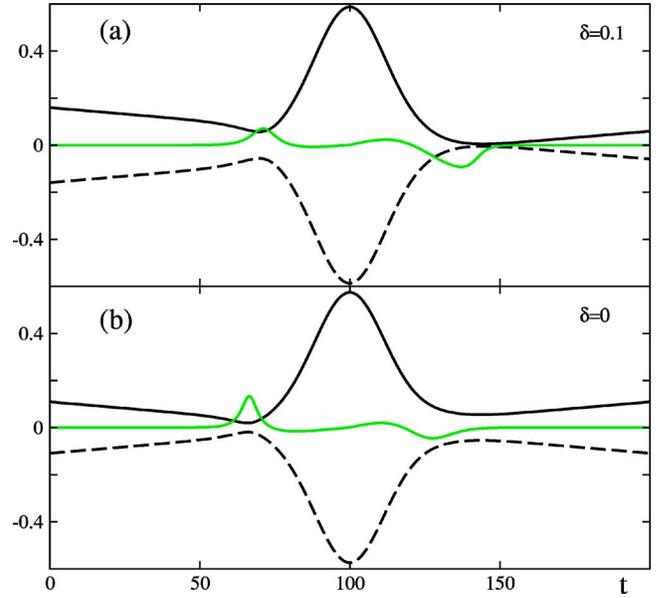


FIG. 2. (Color online) The energy of the dressed states (black solid and dashed), and the coupling parameter as a function of time for the Raman model at $\Omega_3=0.7$, $\tau_0=15$, $\beta'=270$, (a) $\delta=0.1$, and (b) $\delta=0$.

may be provided by the Massey parameter $M(t)$ defined as a ratio of the energy splitting of the dressed states $\Omega(t)$ to the coupling parameter $\dot{\Theta}(t)$ [19]. If $M(t) \gg 1$, the field-matter interaction is essentially adiabatic, if $M(t) \leq 1$, strong nonadiabatic effects take place.

Let us discuss the parameters of the fields and the systems. They correlate with experimental conditions in [20]. These parameters result in nonadiabatic effects in the Raman model and adiabatic population transfer in the one-photon model. Transition frequency ω_{21} is equal to one frequency unit. All the frequency parameters are given in $[\omega_{21}]$ units, the temporal parameters are in $[\omega_{21}^{-1}]$ units, the β' is in $[\omega_{21}^{-2}]$ units, and the β is in $[\omega_{21}^2]$ units. Then ω_{43} is equal to 1.1, giving $\delta=0.1$. These values are related to frequencies of symmetric 2837 cm^{-1} and asymmetric 2942 cm^{-1} stretch modes in liquid methanol [20]. The initial population of states $|1\rangle$ and $|3\rangle$ is 0.5. In the Raman model the peak effective Rabi frequency and the ac Stark shifts at zero chirp are equal to 0.7, indicating the strong field regime. Nonzero chirp reduces $\Omega_2(t)$ and $\Omega_3(t)$ by the factor of τ_0/τ and $\sqrt{\tau_0/\tau}$, respectively. This reduction is in accordance with the total pulse energy conservation. Parameter τ_0 is equal to 15, it gives the spectral bandwidth about the frequency difference δ . The respective linear chirps are $\beta_{\max}=0.002$, and $\beta'|_{\beta_{\max}}=225$.

We analyze the energy of the dressed states $\pm \frac{1}{2}\Omega(t)$ and the coupling parameter $\dot{\Theta}(t)$ as a function of time. In Fig. 2 the dressed state energies (black solid and dashed) and the coupling parameter (green) are shown for the Raman model and parameters $\beta'=270$, $\delta=0.1$ (a), and $\delta=0$ (b). For particular times the energy separation of the dressed states $\Omega(t)$ decreases with a significant increase of the $\dot{\Theta}(t)$ in both cases, (a) and (b). As the result the Massey parameter de-

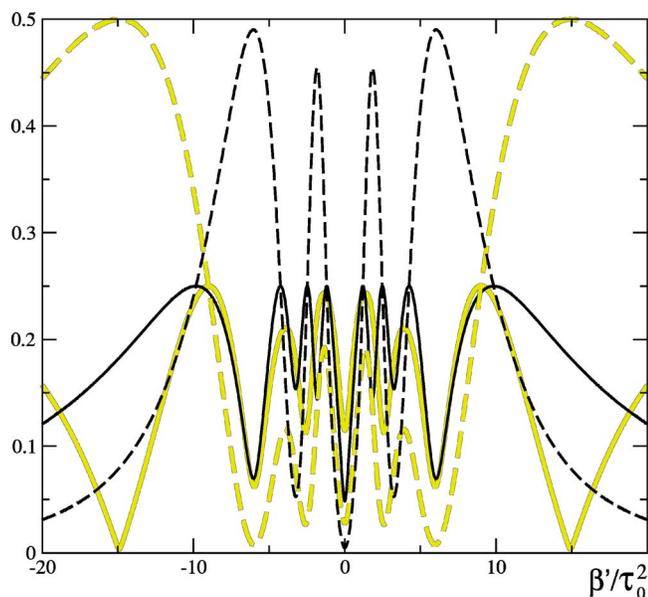


FIG. 3. (Color online) The coherence $|\rho_{12}|$ and $|\rho_{34}|$ (solid) and upper state population ρ_{22} and ρ_{44} (dashed) as a function of linear spectral chirp β'/τ_0^2 for the Raman model at $\omega_{21}=1.$, $\omega_{43}=1.1.$, $\Omega_3=0.7.$, $\tau_0=15.$

increases to much less than unit, implying nonadiabatic nature of field-matter interaction. The nonadiabatic coupling between the dressed states takes place owing to the ac Stark shifts. In the vicinity of small energy separation of the dressed states, the ac Stark shifts provide large values of the $\dot{\Theta}(t)$, giving rise to nonadiabatic coupling between the dressed states. It is known that the dressed states are a linear symmetric and antisymmetric combination of the bare states $|1\rangle$ and $|2\rangle$ (or $|3\rangle$ and $|4\rangle$). Nonadiabatic coupling between the dressed states leads to population transfer from the lower to upper dressed state resulting in the final population of both bare states. It may be only partial depending on the coupling strength. Nonadiabatic coupling and, consequently, the quantum yield are determined by the value of the pulse chirp, the effective Rabi frequency and the ac Stark shifts.

Nonadiabatic coupling gives rise to a spectacular dependence of final population distribution and the coherence in the two-level systems as a function of the spectral linear chirp, shown in Fig. 3. Solid yellow and black curves show the $|\rho_{12}|$ and $|\rho_{34}|$ respectively, dashed yellow and black curves show upper state populations ρ_{22} and ρ_{44} . For $\beta'/\tau_0^2 = \pm 15$, the coherence $|\rho_{12}|$ drops to zero, because the ρ_{22} is maximum, and the coherence $|\rho_{34}|$ increases to 0.18, since the ρ_{44} is equal to 0.08. Determined by this value of the β' , the duration of the pulse τ is equal to 225. Variation of the field amplitude leads to variation of the ac Stark shifts and the effective Rabi frequency, resulting in different β'/τ_0^2 that gives the desired small $|\rho_{12}|$ and large $|\rho_{34}|$. In Fig. 4(a) a contour plot of $|\rho_{12}|=0.05$ (yellow) and $|\rho_{34}|=0.24$ (black) is shown as a function of the peak effective Rabi frequency Ω_3 in the range from 0.1 to 4.1, corresponding to the field amplitudes $5.6 \times 10^7 - 3.5 \times 10^8$ V/cm, and β'/τ_0^2 for $\tau_0=15$. Oscillations of the coherence are observed for the whole range of chosen parameters, indicating non-adiabatic nature

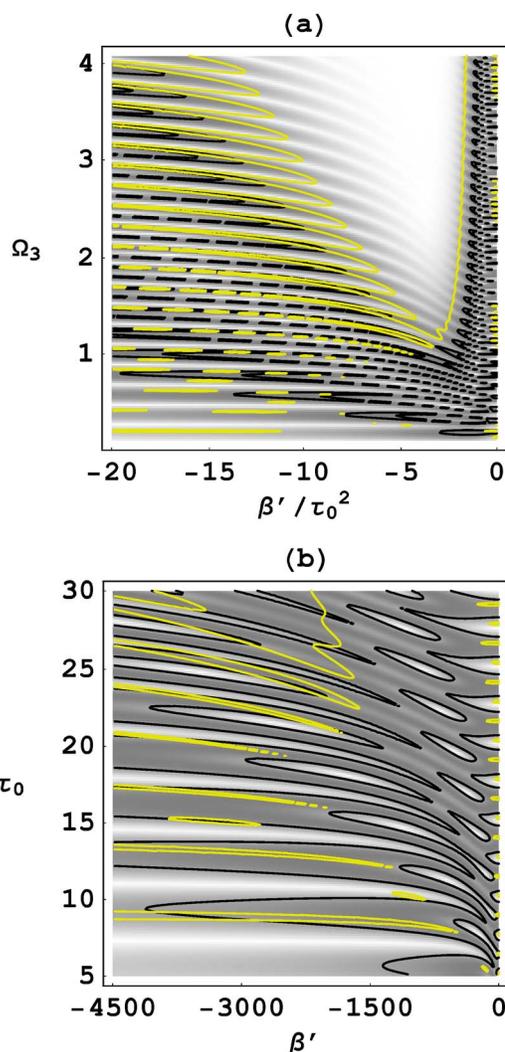


FIG. 4. (Color online) (a) $|\rho_{12}|=0.05$ and $|\rho_{34}|=0.24$ (black) as a function of the peak effective Rabi frequency Ω_3 and linear spectral chirp β'/τ_0^2 for $\tau_0=15$. (b) $|\rho_{12}|=0.05$ and $|\rho_{34}|=0.18$ (black) as a function of duration of a transform-limited pulse τ_0 and β' for $\Omega_3=0.7$.

of the dynamics of the system. We explored the dependence of the coherence of the two-level systems as a function of τ_0 in the range from 5 to 30 and the linear chirp β' , see Fig. 4(b), where $|\rho_{12}|=0.05$ (yellow), $|\rho_{34}|=0.18$ (black), and $\Omega_3=0.7$. It shows that mode selective excitation can be achieved when the bandwidth of the nonchirped Stokes pulse is broader than δ . An opposite goal of the population and coherence distribution can be reached by tuning the Stokes pulse to provide $\omega_p - \omega_s = \omega_{43}$ and keeping the same value of β' . These results suggest a method for achieving a desired state coherence in a set of modes by applying simultaneously a transform-limited pump and a linearly chirped Stokes pulse with a specific chirp value. The method may be applied for selective excitation of Raman active vibrational modes in, e.g., molecular gas CO_2 , (Raman modes have transition frequencies at 1227 and 1400 cm^{-1}), or in liquid methanol, (modes are given above).

The laser-matter interaction picture is qualitatively differ-

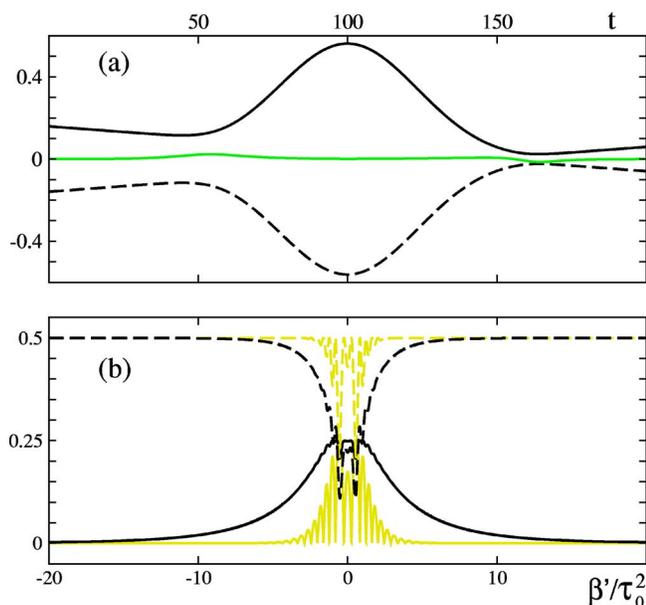


FIG. 5. (Color online) The one-photon model with parameters $\omega_{21}=1.$, $\omega_{43}=1.1.$, $\delta=0.1.$, $\Omega_R(t=0, \beta'=0)=0.7.$, $\tau_0=15.$, and $\beta'=270.$ (a) The energy of the dressed states (black solid and dashed), and the coupling parameter as a function of time. (b) The coherence $|\rho_{12}|$ and $|\rho_{34}|$ and upper state population ρ_{22} and ρ_{44} as a function of linear spectral chirp.

ent in the one-photon model. The pulse intensity, used in calculations, gives the same value of the peak Rabi frequency as in the Raman model, e.g., 0.7. The τ_0 is equal to 15, and the frequency chirp β' is 270. The time dependence of the dressed state energies and the coupling parameter are

depicted in Fig. 5(a) for $\delta=0.1.$ (there is no a notable difference in the curves for $\delta=0.$). For all times the $\dot{\Theta}(t)$ is negligibly small implying perfect adiabatic population transfer between the bare states in both two-level systems. In Fig. 5(b) the final population and coherence of the two, two-level systems is depicted as a function of the $\beta'/\tau_0^2.$ Total population transfer to upper levels is observed for all values of the chirp, (except for the small ones, when $\beta'/\tau_0^2 \leq 10.$). The difference in the population transfer in two, two-level systems in the region of small values of the linear spectral chirp is due to detuning of the 3–4 two-level system off resonance with the central laser frequency $\omega.$

In summary, we have shown that selective excitation of spectrally close modes may be achieved by simultaneously applying a transform-limited pump and a linearly chirped Stokes pulse in stimulated Raman scattering. Selective excitation is a result of nonadiabatic coupling of the dressed states originated from the induced ac Stark shifts. An accurately chosen value of the spectral chirp results in a desirable final coherence in a multimode system created by the specific population distribution. This method demonstrates the possibility of coherent control over spectrally close modes with frequencies much larger than the bandwidth of the pulse. Notably, the effect takes place in strong fields implying sufficiently large Rabi frequencies with respect to $\delta.$ The method may be applied to control a wide variety of processes such as induced polarization, decoherence, quantum gates, etc.

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- [1] S. Shi and H. Rabitz, *Chem. Phys.* **139**, 185 (1989).
 [2] T. C. Weinacht *et al.*, *Chem. Phys. Lett.* **344**, 333 (2001).
 [3] C. J. Bardeen *et al.*, *Chem. Phys. Lett.* **280**, 151 (1997).
 [4] A. Assion *et al.*, *Science* **282**, 919 (1998).
 [5] T. Hornung, R. Meier, and M. Motzkus, *Chem. Phys. Lett.* **326**, 445 (2000).
 [6] J. L. Herek *et al.*, *Nature (London)* **417**, 533 (2002).
 [7] C. Ventalon *et al.*, *Proc. Natl. Acad. Sci. U.S.A.* **101**, 13216 (2004).
 [8] V. V. Lozovoy *et al.*, *J. Raman Spectrosc.* **31**, 41 (2000).
 [9] E. Gershgoren *et al.*, *Opt. Lett.* **28**, 361 (2003).
 [10] T. Chen *et al.*, *Chem. Phys. Lett.* **326**, 375 (2000).
 [11] K. P. Knutsen *et al.*, *Chem. Phys. Lett.* **387**, 436 (2004).
 [12] D. Oron, N. Dudovich, D. Yelin, and Y. Silberberg, *Phys. Rev. Lett.* **88**, 063004 (2002); *Phys. Rev. A* **65**, 043408 (2002).
 [13] K. Bergmann, H. Theuer, and B. W. Shore, *Rev. Mod. Phys.* **70**, 1003 (1998).
 [14] F. T. Hioe and J. H. Eberly, *Phys. Rev. A* **29**, 1164 (1984).
 [15] S. Chelkowski and G. N. Gibson, *Phys. Rev. A* **52**, R3417 (1995).
 [16] S. Chelkowski and A. D. Bandrauk, *J. Raman Spectrosc.* **28**, 459 (1997).
 [17] S. A. Malinovskaya, P. H. Bucksbaum, and P. R. Berman, *Phys. Rev. A* **69**, 013801 (2004).
 [18] V. S. Malinovsky and J. L. Krause, *Phys. Rev. A* **63**, 043415 (2001).
 [19] P. R. Berman, L. Yan, and K.-H. Chiam, *Phys. Rev. A* **57**, 79 (1998).
 [20] B. J. Pearson, J. L. White, T. C. Weinacht, and P. H. Bucksbaum, *Phys. Rev. A* **63**, 063412 (2001).