Phase coherence control and subcycle transient detection in nonlinear Raman scattering with ultrashort laser pulses

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A model of two-level weakly interacting quantum systems is used to demonstrate that the phase of molecular vibrations excited through stimulated Raman scattering can be controlled by the relative phase of time-separated laser pulses, allowing synchronization and amplitude control of coherence excitation in a medium. For transients with a phase relaxation time less than the field cycle, the field half-cycle can serve as a subfemtosecond probe of coherent vibrations. In this regime, the high-frequency field-induced modulation of molecular dipole moments gives rise to a detectable modulation of the optical response of a medium at the frequency 2ω, ω being the frequency of the laser field.

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I. INTRODUCTION

Femtosecond laser pulses have provided an access to ultrafast processes in matter, allowing the femtosecond dynamics in molecular systems to be measured with an unprecedented time resolution [1] and suggesting the way to control energy transfer and chemical transformations [2] with specially tailored field wave forms and adaptively optimized pulse sequences [3–6].

The interval within which an ultrashort burst of electromagnetic field lasts in time is the key parameter of a laser pulse, which limits the temporal resolution in most of the time-resolved methods in laser spectroscopy, microscopy, and quantum control. However, for laser pulses containing only a few field cycles under a pulse envelope, this limit can sometimes be overcome. In such pulses, the field amplitude substantially changes from cycle to cycle [7,8], making a broad class of light—matter interactions sensitive [9–11] to the absolute phase of the laser field and to the shift of the carrier wave relative to the pulse peak—the carrier-envelope phase (CEP). In particular, direct time-domain characterization of attosecond pulses can be performed by cross-correlating photoelectrons ejected by an x-ray attosecond pulse with a single cycle of a laser field [12], with the momentum distribution of photoelectrons modified depending on the absolute phase of the laser field [13]. Subfemtosecond timing of attosecond x-ray pulses and few-cycle laser pulses is the key for direct measurements of light waves [14], attosecond pump-probe spectroscopy [15], and electron wave-packet steering [16]. CEP tuning has been used, on the other hand, to control the motion of electronic wave packets with a time resolution better than 250 attoseconds, enabling an attosecond control of the temporal structure of harmonic emission produced by atomic currents in the soft-x-ray range [17].

An interesting question that arises in the context of those recent revolutionary breakthroughs in ultrafast science is whether phase-controlled ultrashort pulses can offer new solutions for all-optical pump-probe techniques of time-resolved studies and coherence control, which proved recently to be a powerful tool for on-line analysis and control of ultrafast transformations in physical, chemical, and biological objects [18,19]. The phase sensitivity has been shown to be an intrinsic property of many nonlinear-optical techniques, such as transient gratings, photon echo, and coherent anti-Stokes Raman scattering (see, e.g., [20–22]), offering interesting new approaches for time-resolved studies of ultrafast processes in matter. Here we resort to a model of two-level weakly interacting quantum systems to demonstrate the ability of phase-controlled ultrashort laser pulses to synchronize and control molecular vibrations, as well as to detect transient excitations with a phase relaxation time T_2 less than the field cycle T_0. Since nonlinear-optical time-resolved techniques typically provide an access to coherent vibrations driven by incident laser fields [23,24], we calculate the amplitude of such vibrations excited through stimulated Raman scattering and show that their phase is controlled by the relative phase of the input laser pulses, allowing synchronization and amplitude control of coherence excitation in a medium. For transients with $T_2 < T_0$, the field half-cycle can serve as a subfemtosecond probe, driving coherent oscillations at the frequency 2ω, with ω being the frequency of the laser field.

II. THE DENSITY-MATRIX FORMALISM AND THE AMPLITUDE OF COHERENT VIBRATIONS

We consider an ensemble of weakly interacting two-level systems in the presence of a laser field E. The evolution of such an ensemble is governed by the Liouville equation for density-matrix components ρ_{ij} [25]

$$\frac{\partial \rho_{ij}}{\partial t} = \frac{i}{\hbar}[\rho H]_{ij} + \sum_{kl} R_{ijkl}. \tag{1}$$

Here, the indices i, j, k, and l can take the values a and b for the initial and final states of the two-level system, $R_{ijkl} = R_{ijkl}(\rho_{kl} - \rho_{kl}^{(0)})$ is the matrix of relaxation coefficients, which depend on the difference $\rho_{kl} - \rho_{kl}^{(0)}$, $\rho_{ij}^{(0)}$ being the equilibrium, steady-state value of the density-matrix component ρ_{ij}. The square brackets in the first term on the right-hand side of Eq.

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(1) stand for a commutation, $[AB]_{ij} \equiv (AB-BA)_{ij}$, with the subscripts i and j specifying the component of the matrix resulting from this operation.

The Hamiltonian appearing on the right-hand side of Eq. (1)

$$H = H_0 + V, \tag{2}$$

includes the field-free unperturbed Hamiltonian H_0 and the operator

$$V = -\frac{1}{2}\alpha(q)E^2 \approx -\frac{1}{2}(\alpha_0 + \alpha' q)E^2, \tag{3}$$

accounts for a dipole interaction between the quantum system and the laser field E, with the polarizability $\alpha = \alpha(q)$, defined as the proportionality coefficient, $p = \alpha E$, between the induced dipole moment p and the applied electric field E, with q being the vibrational coordinate operator. The second relation in Eq. (3) is derived by expanding $\alpha(q)$ as a Taylor series around the equilibrium value $q=0$ of the vibrational coordinate operator, with $\alpha_0 = \alpha$ (0) being the equilibrium electron polarizability of molecules and $\alpha' = (\partial\alpha/\partial q)_{q=0}$.

We now use a standard procedure of quantum-mechanical averaging to define the amplitude of coherent molecular vibrations [26–29]

$$Q \equiv \langle q \rangle = \mathrm{Tr}(\rho q) = \sum_{ij} \rho_{ij} q_{ji}. \tag{4}$$

For a harmonic oscillator with a frequency Ω_0 and mass M, $q_{ab}^2 = \hbar(2M\Omega_0)^{-1}$, and Eq. (1) reduces to [26–29]

$$\frac{d^2Q}{dt^2} + \frac{2}{T_2}\frac{dQ}{dt} + \Omega_0^2 Q = \frac{1}{2M}\alpha' n E^2, \tag{5}$$

where $n = \rho_{aa} - \rho_{bb}$ is the population difference between the levels a and b normalized to the total population number density.

In the regime where the laser-induced changes in n are small, so that we can set $n = n_0 = \mathrm{const}$, Eq. (5) is reduced to the equation for the amplitude of molecular vibrations in Placzek's classical model of electron-phonon coupling [30]. The solution to Eq. (5) can then be written through the Duhamel integral [31]:

$$Q(t) = \int_0^\infty h(\eta) F(t-\eta) d\eta, \tag{6}$$

where

$$h(\eta) = \frac{n_0}{M\Omega} \exp\left(-\frac{\eta}{T_2}\right) \sin(\Omega\eta) \tag{7}$$

is the impulse response (Green's) function with $\Omega = (\Omega_0^2 - T_2^{-2})^{1/2}$ and

$$F(\xi) = \frac{1}{2}\alpha' [E(\xi)]^2 \tag{8}$$

is the driving force.

In the following sections, we apply Eqs. (6)–(8) to demonstrate a phase-controlled excitation of coherent vibrations in a medium and to show that, for transients with a relaxation time T_2 less than the period of light field oscillation, the field cycle can serve as a subfemtosecond probe, resolving ultrafast features in the dynamics of a quantum system.

III. THE RELATIVE PHASE OF A PULSE DYAD MAPPED ON THE PHASE OF COHERENT RAMAN VIBRATIONS

We first consider the case when an incident laser field includes a dyad of pulses with well-resolved carrier frequencies ω_1 and ω_2 ($\omega_1 > \omega_2$):

$$E = E_1(t)\cos(\omega_1 t - \mathbf{k}_1\mathbf{r}) + E_2(t)\cos(\omega_2 t - \mathbf{k}_2\mathbf{r} + \varphi), \tag{9}$$

where E_1 and E_2 are the field envelopes, $\mathbf{k}_1$ and $\mathbf{k}_2$ are the wave vectors, and φ is the relative phase of the second field.

Such a field can resonantly induce a running wave of Raman-active coherent molecular vibrations with a frequency $\Omega = \omega_1 - \omega_2$ and a wave vector $\mathbf{q} = \mathbf{k}_1 - \mathbf{k}_2$. A standard way to read out this wave from the medium with no interference from other coherence and population laser-induced gratings is to apply a probe field with a central frequency ω_3 [in two-color coherent anti-Stokes Raman scattering (CARS) [19–21], $\omega_3 = \omega_1$] and a wave vector $\mathbf{k}_3$ and to detect an anti-Stokes signal in the direction of phase matching $\mathbf{k}_a = \mathbf{k}_3 + q = \mathbf{k}_3 + \mathbf{k}_1 - \mathbf{k}_2$.

Calculation of the integral in Eq. (6) for the running wave of coherent molecular vibrations with $\Omega = \omega_1 - \omega_2$ and the wave vector $\mathbf{q}$ yields

$$|Q_1(t)|^2 \propto \sin^2[(\omega_1 - \omega_2)t - (\mathbf{k}_1 - \mathbf{k}_2)\mathbf{r} - \varphi][Y_1(t)]^2, \tag{10}$$

where

$$Y_1(t) = \int_0^\infty \exp\left(-\frac{\eta}{T_2}\right) E_1(t-\eta) E_2(t-\eta) d\eta. \tag{11}$$

The integral (11) defines the temporal envelope of the coherence wave Q, with its rising time controlled by the durations of the laser pulses and its tail determined by the coherence relaxation time. In an idealized case of infinitely short laser pulses, $E_i(t) = E_{0i}\delta(t-t_0)$, integration in Eq. (11) recovers the exponential dephasing of molecular vibrations

$$Y_1(t) = E_{01}E_{02}\theta(t-t_0)\exp[-(t-t_0)/T_2], \tag{12}$$

where $\theta(\xi)$ is the Heaviside step function.

For the field (9) consisting of two Gaussian pulses, $E_i(t) = E_{0i}\exp(-t^2/\tau^2)$, with equal pulse widths τ, integration in Eq. (11) gives

$$Y_1(t) = E_{01}E_{02}\frac{\tau}{2}\left(\frac{\pi}{2}\right)^{1/2} \exp\left(\frac{\tau^2}{8T_2^2}\right)\exp\left(-\frac{t}{T_2}\right) \times \mathrm{erfc}\left(\frac{\tau}{2\sqrt{2}T_2} - \frac{\sqrt{2}t}{\tau}\right), \tag{13}$$

where $\mathrm{erfc}(\xi) = 2(\pi)^{-1/2}\int_\xi^\infty \exp(-t^2)dt$ is the complementary error function.

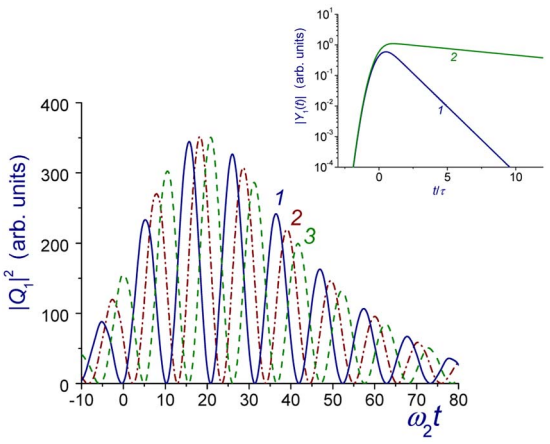

FIG. 1. (Color online) The amplitude of coherent vibrations with a frequency $\mathbf{\Omega}$ in the Q wave with a wave vector $\mathbf{q}=\mathbf{k}_1-\mathbf{k}_2$ induced through a Raman process by the field (9) with $\omega_1-\omega_2=\Omega, \omega_1/\omega_2=1.3$, and $\omega_2\tau=30$ as a function of time. The phase relaxation time of molecular vibrations is $T_2=50/\omega_2$. The carrier–envelope phase is $\varphi=0(1)$, $\pi/4(2)$, and $\pi/2(3)$. The inset shows the temporal envelope of the Q wave, controlled by the $Y_1(t)$ integral, for Gaussian laser pulses with equal pulse widths τ set to coherently excite molecular vibrations with $T_2=\tau(1)$ and $10\tau(2)$.

While infinitely short laser pulses give rise to an infinitely sharp step function in the temporal envelope of the Q wave, the build up of the coherence wave induced by laser pulses with a finite duration τ is described by the complementary error function. A typical rise time of the Q wave in this case (see the inset in Fig. 1), as can be seen from the argument of $\mathrm{erfc}(\xi)$ in Eq. (13), is $\tau/\sqrt{2}$. The tail of the Q wave is controlled by the exponential phase relaxation of molecular vibrations (cf. curves 1 and 2 in the inset to Fig. 1), represented by the $\exp(-t/T_2)$ factor in Eq. (13).

The phase φ appearing in the argument of the sine function in Eq. (10) shows that the coherent excitation of Raman-active vibrations by a pair of phase- and frequency-shifted laser pulses maps the phase shift between these pulses onto the phase of coherent vibrations in the Q wave. A pair of phase-shifted laser pulses can thus be used to control the phase of molecular vibrations. This option is illustrated in Fig. 1, showing how the phase of Q oscillations is shifted by changing the phase φ of the second pulse with respect to the phase of the first pulse.

IV. AMPLITUDE CONTROL OF COHERENT RAMAN VIBRATIONS BY A PHASE-SHIFTED PULSE DYAD

For ultrashort laser pulses, the spectral bandwidth of radiation field can be broad enough to access Raman-active vibrations in a medium even when the spectrum is centered around a single carrier frequency. To examine the influence of the relative phase of a pulse dyad on coherence excitation in this case, we represent the laser field as

$$E = E_1(t)\cos(\omega t - \mathbf{k}\cdot\mathbf{r}) + E_2(t)\cos(\omega t - \mathbf{k}'\cdot\mathbf{r} + \varphi). \tag{14}$$

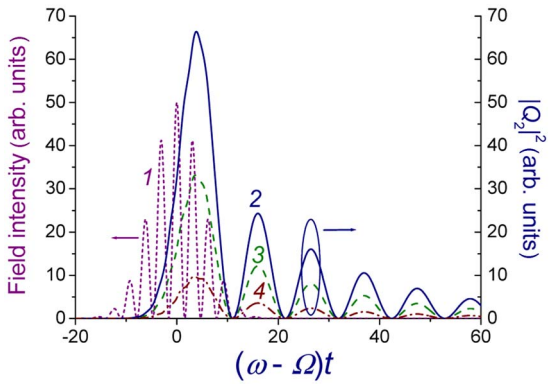

FIG. 2. (Color online) The amplitude of coherent vibrations with a frequency $\mathbf{\Omega}$ in the Q grating induced by the field (14) consisting of two Gaussian pulses with equal pulse widths τ (the field intensity is shown by curve *1*) with $\omega=4.33\Omega$ and $\omega\tau=13$ as a function of time. The phase relaxation time of molecular vibrations is $T_2=65/\omega$. The total phase of Q_2, $\mathbf{\Phi}=(\mathbf{k}-\mathbf{k}')\mathbf{r}_0+\varphi$, is varied for a fixed $\mathbf{r}_0$ by varying the carrier–envelope phase: $\mathbf{\Phi}=0(2)$, $\pi/4(3)$, and $3\pi/8(3)$.

We thus consider two laser beams with the same central frequency ω_1 and noncollinear wave vectors $\mathbf{k}$ and $\mathbf{k}'$. A pair of phase-shifted ultrashort pulses with the same carrier frequency can be produced, for example, as a part of a pulse train generated by a femtosecond mode-locked laser. A tunable delay line can then be employed to provide a temporal overlap of the pulses in the interaction region.

The field (14) can coherently excite Raman-active vibrations with a frequency Ω if the spectrum of the field is broad enough to provide a sufficient number of pump (ω) and Stokes $(\omega-\Omega)$ photons. The principal part of the grating of Raman-active coherent vibrations with a grating vector $\mathbf{q}=\mathbf{k}-\mathbf{k}'$ can be then represented as

$$|Q_2(t)|^2 \propto \cos^2[(\mathbf{k}-\mathbf{k}')\mathbf{r}+\varphi][Y_2(t)]^2, \tag{15}$$

where

$$Y_2(t) = \int_0^\infty \exp\left(-\frac{\eta}{T_2}\right)\sin(\Omega\eta)E_1(t-\eta)E_2(t-\eta)d\eta. \tag{16}$$

With infinitely short laser pulses, $E_i(t)=E_{0i}\delta(t-t_0)$, the integral in Eq. (16) recovers harmonic oscillations of the Raman-active mode with the frequency Ω damped with the phase relaxation time T_2

$$Y_2(t) = E_{01}E_{02}\theta(t-t_0)\sin[\Omega(t-t_0)]\exp[-(t-t_0)/T_2]. \tag{17}$$

When the field (14) consists of two Gaussian pulses, $E_i(t)=E_{0i}\exp(-t^2/\tau^2)$, with equal pulse widths τ (curve *1* in Fig. 2), integration in Eq. (16) yields

$$Y_2(t) = \frac{i\tau}{4}\sqrt{\frac{\pi}{2}}E_{01}E_{02}\exp\left(\frac{\tau^2}{8T_2^2}\right)\exp\left(-\frac{t}{T_2}\right)\exp\left(-\frac{\Omega^2\tau^2}{8}\right)$$
$$\times\left\{\exp\left[i\Omega\left(\frac{\tau^2}{4T_2}-t\right)\right]\mathrm{erfc}\left[\frac{\tau}{2\sqrt{2}}\left(\frac{1}{T_2}-\frac{4t}{\tau^2}+i\Omega\right)\right]\right.$$
$$\left.-\exp\left[-i\Omega\left(\frac{\tau^2}{4T_2}-t\right)\right]\mathrm{erfc}\left[\frac{\tau}{2\sqrt{2}}\left(\frac{1}{T_2}-\frac{4t}{\tau^2}-i\Omega\right)\right]\right\}. \quad (18)$$

Similar to the case of two-color excitation, the build-up of coherent vibrations in the Q grating is controlled by durations of laser pulses. When finite pulse widths are taken into consideration, an infinitely sharp step function, appearing in Eq. (17) is replaced by a complementary error function, describing a finite rise time of coherence in the Q grating (curve *2* in Fig. 2). The relaxation time, as is seen from Eq. (18), can be extracted from the exponential factor $\exp(-t/T_2)$, appearing in the expression for the amplitude of the Q grating.

The effect of the relative phase of the laser pulses is included through the parameter φ, which appears in the argument of the cosine function in Eq. (15). As can be seen from this expression, with the laser field of the form (14), the amplitude of coherent vibrations at a certain point $\mathbf{r}=\mathbf{r}_0$ of a Raman-active medium can be efficiently controlled by varying the relative phase of a pulse dyad. This effect is illustrated in Fig. 2, where the total phase of Q_2, $\Phi=(\mathbf{k}-\mathbf{k}')\mathbf{r}_0+\varphi$, is varied for a fixed $\mathbf{r}_0$ from 0 to $\pi/2$. The amplitude of coherent vibrations under these conditions changes from its maximum at $\Phi=0$ (curve *2*) through an intermediate value at $\Phi=\pi/4$ (curve *3*) to zero, corresponding to a complete suppression of coherent vibrations, at $\Phi=\pi/2$.

V. TRANSIENT DETECTION WITH A SUBCYCLE RESOLUTION

In this section, we demonstrate the ability of ultrashort laser pulses to detect transients with a phase relaxation time T_2 less than the field cycle T_0. To this end, we fix the coordinates of the interaction region and represent the input laser field as

$$E = E_0(t)\cos(\omega t). \quad (19)$$

Expression for the amplitude of coherent vibrations [Eq. (6)] then includes two parts

$$Q_3(t) = Q_{dc}(t) + Q_{2\omega}(t), \quad (20)$$

where

$$Q_{dc}(t) \propto \frac{\alpha'}{2}\int_0^\infty h(\eta)E_0^2(t-\eta)d\eta \quad (21)$$

and

$$Q_{2\omega}(t) \propto \frac{\alpha'}{2}\int_0^\infty h(\eta)\cos[2\omega(t-\eta)]E_0^2(t-\eta)d\eta. \quad (22)$$

The first term in Eq. (20) involves the integral (16) and plays a dominant role in the impulsive excitation of Raman vibrations. The temporal profile of Q_{dc} is defined by a convolution of the impulse response function $h(\eta)$ and the pulse intensity envelope. This term can provide a probe for ultrafast transients with a characteristic relaxation time exceeding the duration of the laser pulse.

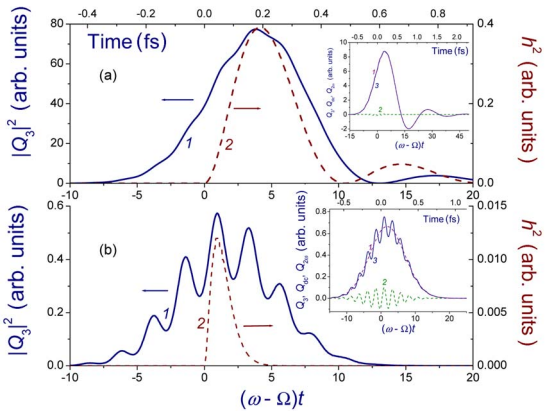

FIG. 3. (Color online) The amplitude of coherent vibrations with a frequency $\mathbf{\Omega}$ driven by the field (19) with $\omega=4.33\Omega$ and $\omega\tau=13$ as a function of time. The phase relaxation time of molecular vibrations is $T_2=13/\omega$ (a) and $1.3/\omega$ (b). Also shown is the impulse response function $h(t)$ for a harmonic oscillator with a frequency $\mathbf{\Omega}$ and relaxation time $T_2=1.3/\omega$. The insets show $Q_{dc}(1)$, $Q_{2\omega}(2)$, and $Q_3(3)$ as functions of time for $T_2=13/\omega$ (a) and $1.3/\omega$ (b). Dimensionless time, shown along the lower abscissa axis, is converted into the physical time with a 970-attosecond oscillation period, corresponding to a bending vibrational motion of correlated electrons in $2s^2\ {}^1S^e$–$2p^2\ {}^1S^e$-excited helium.

The second term in Eq. (20) involves the high-frequency part of the laser pulse spectrum. This term describes a high-frequency modulation of the dipole moment of the medium at twice the laser frequency. As long as the relaxation time T_2 is larger than half the field cycle $T_0=2\pi/\omega$, the second term in Eq. (20) is negligible compared with the first term. The inset in Fig. 3(a) displays Q_3, Q_{dc}, and $Q_{2\omega}$ as functions of time for the case when $T_2=13/\omega=2.1T_0$ and $\tau=T_2$. The term $Q_{2\omega}$ (curve *2*) is small compared to Q_{dc} (curve *1*) in this case, and the overall amplitude Q_3 (curve 3) is determined by the first term in Eq. (20). The impulse response function $h(t)$ corresponding to $T_2=2.1T_0$ is shown by the dashed line in Fig. 3(a). The temporal profile of the Q wave in this case [solid line in Fig. 3(a)] is noticeably broader than the profile of $h(t)$ because of the finite pulse width, $\tau=T_2$.

The situation changes in the case of very fast transients with $T_2<T_0$. The $Q_{2\omega}$ term starts to play a nonnegligible role in this regime [see the inset in Fig. 3(b), where $T_2=1.3/\omega=0.21T_0$]. Physically, this implies that the 2ω modulation of the dipole moment [curve *2* in the inset to Fig. 3(b)] becomes noticeable against the stimulated Raman response (curve *1* in the same plot), giving rise to detectable modulation of the Q wave at 2ω. It is intuitively clear from this physical argument that a high-frequency modulation of the dipole moment at the frequency 2ω can serve as a probe to detect ultrafast transients with a temporal resolution of $(2\omega)^{-1}$. To provide a mathematical explanation to this ability of the field half-cycle to serve as an ultrafast probe, we calculate the integrals in Eqs. (21) and (22) with an impulse response function $h(\eta)$ given by Eq. (7).

For a very fast transient with $T_2 \ll 2\pi/\Omega$, we approximate the $\sin(\Omega\eta)$ function in $h(\eta)$ by the first term in its power-series expansion, $\sin(\Omega\eta) \approx \Omega\eta$. Then, for a laser pulse of the form (19) with an arbitrary field envelope $E_0(t)$ being a slowly varying function on the scale of T_2, so that $E_0(t-\eta) \approx E_0(t)$, integration in Eq. (21) gives

$$Q_{dc}(t) \propto \alpha' T_2^2 E_0^2(t). \tag{23}$$

Applying the same approximations to calculate the integral in Eq. (22), we find

$$Q_{2\omega}(t) \propto \frac{\alpha' T_2^2 E_0^2(t)}{1+(2\omega T_2)^2} \sin(2\omega t + \psi), \tag{24}$$

where $\psi = \text{a tan}[(4\omega T_2)^{-1} - \omega T_2]$.

Examination of Eqs. (23) and (24) shows that the temporal profile of the Q wave in the case under consideration does indeed include a dc component and a term that oscillates at twice the frequency of the laser field. The latter component, as can be seen from the comparison of Eqs. (23) and (24), remains negligibly small compared to the dc component as long as $T_2 \gg (2\omega)^{-1}$. However, when T_2 becomes comparable to or less than $(2\omega)^{-1}$, the high-frequency component becomes noticeable against the background of the dc term, indicating the presence of a fast transient with a very short relaxation time T_2.

An optical readout of the Q wave carrying information on subcycle transients is a separate interesting issue. Here, we briefly outline one of the possible techniques to implement this operation based on a harmonic phase modulation of a probe field

$$E_p = A(t,z)[\exp(i\omega_p t - ikz) + \text{c.c.}], \tag{25}$$

propagating along the z axis through a medium with preexcited coherent vibrations with an amplitude given by Eq. (20). The nonlinear polarization probed by this field is

$$P \propto n_0 \alpha' Q_3 E_p. \tag{26}$$

The equation for the amplitude of the probe field is then written as [22]

$$\frac{\partial A}{\partial z} + \frac{1}{u_p}\frac{\partial A}{\partial t} = -i\gamma Q_3 \left(t - \frac{z}{u}\right) A, \tag{27}$$

where γ is the relevant nonlinear coefficient and u and u_p are the group velocities of the pump and probe pulses, respectively.

Neglecting the difference in the group velocities of the probe and pump fields and introducing the retarded time $\xi = t - z/u$ we write the solution to Eq. (27) as

$$B(\xi,z) = B(\xi,0)\exp\{-i[\Phi_{dc}(\xi,z) + \Phi_{2\omega}(\xi,z)]\}, \tag{28}$$

where the first term of the phase shift

$$\Phi_{dc}(\xi,z) \propto \gamma z n_0 \alpha' T_2^2 E_0^2(\xi) \tag{29}$$

is similar to a standard nonlinear phase shift induced by Kerr nonlinearity, while the second term in the phase shift is

$$\Phi_{2\omega}(\xi,z) \propto \gamma z n_0 \frac{\alpha' T_2^2 E_0^2(\xi)}{1+(2\omega T_2)^2} \sin(2\omega\xi + \psi). \tag{30}$$

The nonlinear phase shift defined by Eq. (28) scales linearly with the pump field intensity, leading to a spectral broadening of the probe field similar to conventional self-phase modulation in a Kerr medium. The second term in the nonlinear phase shift in Eq. (28) involves a harmonic dependence on time. In the frequency domain, such a phase modulation corresponds to the generation of sidebands centered at $\omega_p \pm 2m\omega$, where m is an integer, in the spectrum of the probe field. The phase shift $\Phi_{2\omega}(\xi,z)$ is noticeable against the phase shift $\Phi_{dc}(\xi,z)$ only when T_2 becomes comparable to or less than $(2\omega)^{-1}$.

In a particular case of a pump pulse with an envelope slowly varying within half the field cycle and $\psi = 0$, we find

$$B(\xi,z) = B(\xi,0)\exp[-i\Phi_{dc}(\xi,z)]\sum_m [J_m(\sigma) + i^m J_m(\sigma \tan\psi)]\exp(-2im\omega\xi), \tag{31}$$

where

$$\sigma = \gamma z n_0 \cos\psi \frac{\alpha' T_2^2 E_0^2(0)}{1+(2\omega T_2)^2}. \tag{32}$$

The spectrum of the probe field thus experiences an SPM-type broadening due to the $\exp[-i\Phi_{dc}(\xi,z)]$ factor in Eq. (31) and gets dressed with sidebands at $\omega_p \pm 2m\omega$ whose amplitudes are given by the Bessel functions in Eq. (31). In view of the properties of Bessel functions, the first-order sidebands at $\omega_p \pm 2\omega$ start to play a noticeable role in the spectrum when $\gamma n_0 \alpha' T_2^2 E_0^2(0)[1+(2\omega T_2)^2]^{-1} L \approx 1$, where L is the interaction length. This condition specifies the requirements on the intensity of the pump field, the interaction length L, and the parameter α', related to the cross section of Raman scattering of the probed vibrational mode.

Conceptually, the method of optical fast transient detection considered in this work has much in common with attosecond spectroscopy and pulse-characterization techniques based on the sensitivity of photoelectron momentum distribution to the absolute phase of the laser field [13,14]. By analogy with attosecond metrology, the field half-cycle in all-optical pump-probe techniques can serve as a subfemtosecond probe for molecular or atomic dynamics, detecting ultrafast transients.

While the dephasing times of molecular vibrations typically lie in the picosecond range [29], the above-described technique of subcycle transient detection can help to implement direct time-resolved measurements on correlated motions of two or more than two excited electrons in atomic systems. As shown in earlier theoretical work [32–34], such correlated motions of electrons corresponding to multiply excited states of atoms are often adequately described as rotations and vibrations, similar to those observed in polyatomic molecules, but with atoms forming a molecule replaced by a nucleus and electrons. In particular, a coherent excitation of configuration-coupled $2s^2\ ^1S^e$ and $2p^2\ ^1S^e$ states in helium, as demonstrated by Morishita *et al.* [35], can be treated as a bending vibrational motion with an oscillation period of about 970 attoseconds (in Fig. 3 and its insets, this oscillation period is used to convert the dimensionless time, shown along the lower abscissa axis, into the physical time, shown

in the upper abscissa axis). Coherence relaxation of such correlated electron motions could be then probed by the above-described subcycle transient detection technique. Another interesting example of ultrafast coherent electron dynamics in excited atomic systems potentially accessible with the considered transient detection technique involves direct time-resolved studies of the build-up of Fano resonances [36]. For super-Coster-Kronig transitions in the 4d giant resonances of lanthanides [37], the lifetime of an autoionizing resonance is estimated as approximately 400 attoseconds, suggesting a challenging object for pump-probe coherent Raman scattering, which has been already demonstrated [38,39] (on a much longer time scale, though) to be an informative method for the investigation of autoionization in atoms. Finally, the above-described formalism is also relevant to time-resolved pump--probe measurements using mid-infrared or terahertz few-cycle laser pulses applied to probe an ultrafast molecular dynamics on the subpicosecond time scale.

VI. CONCLUSION

We have thus shown in this work that the phase of molecular vibrations excited through stimulated Raman scattering can be controlled by the relative phase of time-separated laser pulses, allowing synchronization and amplitude control of coherence excitation in a medium. For transients with a phase relaxation time T_2 less than the field cycle T_0, the field half-cycle can serve as a subfemtosecond probe, driving coherent oscillations at the frequency 2ω, with ω being the frequency of the laser field. This high-frequency modulation of molecular dipole moments gives rise to a detectable 2ω component in the optical response of a medium with an amplitude comparable to the amplitude of stimulated Raman scattering, thus indicating the presence of subcycle transients in ultrafast dynamics of a quantum system.

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