Selective control of vibrational modes with sequential femtosecond-scale laser pulses

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For nonresonant femtosecond-scale laser pulses, we showed earlier that the optimum FWHM pulse duration is 0.42 T if one wishes to achieve maximum relative excitation of a specific vibrational mode with period T. Here we show that much greater enhancement of a specific mode can be achieved with a sequence of laser pulses which have both this optimized duration and optimized delays between pulses. One can thus enhance a selected set of modes that are particularly useful in identifying or characterizing a chemical system, to lift them out of the background of less informative modes.

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There is widespread interest in vibrational control using ultrafast laser pulses with a variety of techniques [1–8]. Here, as in an earlier paper [9], we consider the specific case of nonresonant femtosecond-scale laser pulses, with fluences of ~ 0.1 kJ/m² (or intensities of ~ 10¹¹ W/cm²), applied to an arbitrary chemical system. Similar pulses are used in impulsive stimulated Raman scattering and related techniques [10–24]. In Ref. [9] we found that the optimum FWHM pulse duration is 0.42 T (for an approximately Gaussian profile) if one wishes to achieve maximum relative excitation of a specific vibrational mode with period T. In the present paper we now consider a sequence of pulses with this optimized duration. We employ both the simple model defined by Eqs. (3) and (11) of Ref. [9] and our density-functional-based SERID technique, which is defined in the present context by Eqs. (8)-(11) of Ref. [9].

In the SERID simulations for CH₂O, we again find that seven of the ten Raman-active modes are appreciably excited: modes \( H_g(1), A_g(2), H_g(1), H_g(4), H_g(5), H_g(6) \) and \( H_g(8) \), with periods of 61.5, 20.6, 125, 39.6, 27.0, 23.0, and 19.0 femtoseconds respectively. The relative magnitudes for the vibrational excitations depend on the pulse parameters, of course, and Fig. 1 shows results for a simulation with a 26 fs pulse at 1500 nm. As in Ref. [9], we characterize the strength of the vibrational response of a specific mode by its maximum kinetic energy \( K_{\text{max}} \). In the figures we show the numerical Fourier transform of the total kinetic energy, which has a peak at \( 2\omega_k \) with a strength proportional to the response of a normal mode with angular frequency \( \omega_k \). For this reason, the horizontal scale in Fig. 1 and subsequent figures shows \( 1/2 \) the frequency actually used in performing the Fourier transform.

For the pulse of Fig. 1, three modes are appreciably excited in the range of frequencies shown (up to 1000 cm⁻¹): \( H_g(1), A_g(1), \) and \( H_g(4) \). In the remainder of the paper we will focus on these modes, and the criteria for achieving relative enhancement of either one mode or a set of modes. It will be seen below that the principal results are so simple and robust that they should be valid for other modes and more general chemical systems.

We can start by again confirming the prediction of Ref. [9] that the optimum pulse duration \( \tau \) is 0.42 T. Fig. 2 shows the results of a SERID simulation in which \( \tau \) is chosen to be 52.5 fs, which is predicted to yield maximum relative enhancement of the \( H_g(1) \) mode. It can be seen that this mode, which is already naturally dominant for pulse durations in this general range, is now totally dominant, with almost no contribution from the other modes.

Now let us consider the effect of a sequence of pulses. First, using the simple model, we performed numerical calculations for the three modes visible in Fig. 1, with a sequence of two laser pulses having the same duration and wavelength as in Fig. 2, and separated by a delay \( t_1 \) between their onset times, as depicted in Fig. 3. Then we performed the much more complex SERID simulations, whose results are displayed in Figs. 5-7 and discussed below.

One can characterize the energy deposited in a mode by the ratio of the maximum kinetic energy after the pulse sequence is completed to the value it has after a single pulse. When each set of points is plotted as a function of the variable delay \( t_1 \), called \( \Delta t \) in Fig. 4, one finds that it is perfectly fitted by a single cosine function:

\[
K_{\text{two}}^{\text{max}} / K_{\text{one}}^{\text{max}} = 2 \cos(2\pi t_1/T_k) + 2 = 4 \cos^2(\pi t_1/T_k)
\]  

(1)

where \( T_k \) is the period of the mode labeled by \( k \).

The simple model thus implies that the optimum delay time is simply equal to the period of the mode being selected. This is not an immediately obvious result, since the numerical simulations of the present paper use the full vector potential \( \mathbf{A}(t) \) in Eq. (11) of Ref. [9], rather than the approximate form for the electric field in Eq. (2) of that
paper, and a simple analytical solution does not appear to exist. In addition, the simple model predicts that a given mode can be completely quenched if the delay time is chosen to be e.g. $3/2$ the vibrational period. In other words, this model implies that one can use the simplest imaginable picture for constructive or destructive interference of successive laser pulses.

An important question, of course, is the validity of the model, which totally neglects many important effects (and simply parameterizes others). To address this issue, as mentioned above, we performed independent SERID simulations for sequences of pulses applied to C$_{60}$. As in Ref. [9], and our earlier studies of photoinduced processes in molecules [25, 26] and materials [27], these simulations employ, in a nonorthogonal basis, (i) the time-dependent Schrödinger equation for the electron dynamics, (ii) Ehrenfest’s theorem for the nuclear dynamics, (iii) the time-dependent Peierls substitution for the coupling of the laser pulse to the electrons, and (iv) the density-functional-based approach of Frauenheim and co-workers [28, 29]. A complete description of the computational details can be found in Refs. [25–27].

In order to test the validity of Eq. (1), we performed simulations with the time delay $t_1$ chosen to be equal to first the period of the $H_g(1)$ mode and then $3/2$ its period. The results, shown in Fig. 5, are in remarkably good agreement with the prediction of Eq. (1) for these two limiting cases, with a four-fold increase in the energy deposited in the $H_g(1)$ mode for the first case and nearly complete suppression in the second case. Recall again that these results are obtained in detailed simulations with many interacting electronic and nuclear degrees of freedom, and that they include anharmonic effects in the vibrations, nonlinear effects in the response to the applied field, and no simplifying assumptions about the electronic polarizability tensor.

The most interesting issue, of course, is whether one can achieve a relative enhancement of the weaker modes by optimizing both the pulse duration and the delay between pulses, and this was explored in calculations like those represented in Fig. 6, with a sequence of 2 pulses, and Fig. 7, where 4 pulses were used.

In Fig. 6(a), both the pulse duration $\tau$ and the pulse delay $t_1$ were chosen to optimize the response of the $A_g(1)$ mode, which as a result becomes totally dominant, in contrast to the results of Fig. 2.

What might appear to be a relatively modest change in the delay $t_1$, with exactly the same pulse duration $\tau$, produces the dramatic change in response that can be seen in Fig. 6(b), where the $H_g(1)$ mode reappears dominance. But with an even longer delay of 188 fs, the $H_g(1)$ mode is essentially totally suppressed, and both of the other modes make their appearance.

One expects that a longer train of pulses can yield even greater selectivity, and this is verified by the results of Fig. 7: With 4 pulses, one can select any of the three modes under consideration to be almost totally dominant with a proper choice of the pulse delays $t_1$ and $t_2$ (as defined in Fig. 3) as well as the duration.

The very strong dependence of the vibrational excitations on the pulse duration and delay times is dramatically apparent when one compares Fig. 7 with Fig. 2.

In summary, we have demonstrated that the relative response of a specific vibrational mode can be enormously enhanced by optimizing the delay times, as well as the individual pulse duration, in a sequence of nonresonant femtosecond-scale laser pulses applied to a general chemical system. Our conclusions are based on numerical calculations with a simple and general model and, more convincingly, on density-functional-based simulations for the specific example of C$_{60}$. The response in the present simulations is not as strong as it would be with resonant pulses and higher fluences, but the qualitative predictions should nevertheless be experimentally observable and potentially useful.

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FIG. 1: Fourier transform of total kinetic energy of $C_{60}$ after a 26 fs (FWHM) 1500 nm laser pulse with a fluence of 0.055 kJ/m$^2$. The 26 fs pulses represented in the following figures have this same wavelength and fluence. Here, and in the following figures, the frequency given on the horizontal scale is $1/2$ the frequency actually used in performing the numerical Fourier transform, for the reason given in the text. The results in this and the following figures, except for Fig. 4, were obtained in density-functional-based SERID simulations. Three vibrational modes are appreciably excited in the range of frequencies shown, below 1000 cm$^{-1}$. 
FIG. 2: Fourier transform of total kinetic energy of C\textsubscript{60} after a 52.5 fs (FWHM) 1500 nm laser pulse with a fluence of 0.113 kJ/m\textsuperscript{2}. The 52.5 fs pulses represented in the following figures have this same wavelength and fluence. The $H_g(1)$ mode is overwhelmingly dominant. As the inset shows, the $A_g(1)$ and $H_g(4)$ modes are observed, but only very weakly.

FIG. 3: Definition of the pulse delay times $t_1$ and $t_2$. Here $\tau$ represents the full-width-at-half-maximum (FWHM) pulse duration.
FIG. 4: Ratios of maximum kinetic energy after two laser pulses to that after one pulse, in numerical simulation with the simple model defined by Eqs. (3) and (11) of Ref. [9]. Each set of points can be fitted with a single cosine function of the time delay $\Delta t$, which is given in femtoseconds.
FIG. 5: Fourier transform of the total kinetic energy of C\textsubscript{60} after two 52.5 fs (FWHM) pulses with different time delays. (a) A delay of 125 fs enhances the H\textsubscript{g}(1) vibrational response by a factor of 4. (b) A delay of 187.5 fs almost totally suppresses this mode.
FIG. 6: Fourier transform of total kinetic energy of C<sub>60</sub> after two 26 fs (FWHM) pulses separated by various time delays. In (a), the originally small response of the \( A_g(1) \) mode is now totally dominant. In (b), the \( H_g(1) \) mode is again dominant. In (c), the \( H_g(1) \) mode is almost completely suppressed, with the combined \( A_g(1) \) and \( H_g(4) \) modes enhanced.
FIG. 7: Fourier transform of total kinetic energy of $C_{60}$ after four 26 fs (FWHM) pulses separated by various time delays (solid curves). The dashed curves are for one laser pulse, as also shown in Fig. 6. In (a), with $t_1=187.5$ fs and $t_2=277.0$ fs, the $H_g(4)$ mode is totally dominant. In (b), with $t_1=62.5$ fs and $t_2=186.0$ fs, the $A_g(1)$ mode is dominant. In (c), with $t_1=92.3$ fs and $t_2=217.8$ fs, $H_g(1)$ regains dominance.