

## Coherent Control of Femtosecond Energy Localization in Nanosystems

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We predict and quantitatively evaluate the unique possibility of concentrating the energy of an ultrafast excitation of a nanosystem in a small part of the whole system by means of coherent control (phase modulation of the exciting ultrashort pulse). Such concentration is due to dynamic properties of surface plasmons and leads to local fields enhanced by orders of magnitude. This effect exists for both “engineered” and random nanosystems. We also discuss possible applications.

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There recently has been a tremendous interest in both ultrafast (femtosecond and attosecond) laser-induced kinetics and in nanoscale properties of matter. Particular attention has been attracted by phenomena that are simultaneously nanoscale and ultrafast; see, e.g., Refs. [1–10]. Fundamentally, nanosize eliminates effects of electromagnetic retardation and thus facilitates coherent ultrafast kinetics. On the applied side, nanoscale design of optoelectronic devices is justified if their operating times are ultrashort to allow for ultrafast computing and ultrawideband transmission of information.

One of the key problems of ultrafast/nanoscale physics is ultrafast excitation of a nanosystem where the transferred energy *localizes* at a given site. Because the electromagnetic wavelength is on a much larger microscale, it is impossible to employ light-wave focusing for that purpose. Also, the long-range dipole interaction will cause ultrafast transfer of excitation in nanostructures causing delocalization. *To solve this problem, we propose to use phase modulation of an exciting femtosecond pulse as a functional degree of freedom to coherently control spatial distribution of the excitation energy.* This possibility exists due to the fact that polar excitations (surface plasmons) in inhomogeneous nanosystems tend to be localized with their oscillation frequency (and, consequently, phase) correlated with position [11,12]. The pulse phase modulation will cause the exciting field to take energy away from surface plasmons localized in those parts of the system where the oscillations are out of phase with the driving pulse and move it, with time, to the surface plasmon excitations in other parts where such oscillations occur in phase with the driving pulse. We confirm below this heuristic idea by quantitative computations.

Coherent control was used recently to spectrally concentrate the energy of an ultrashort, nonlinearly generated pulse in a certain high harmonic [13]. Impressive results were obtained by using coherent control to affect spatial movement of particles and polarization using continuous-wave fields (see, e.g., [14,15] and references therein). The possibility was shown to spatially concentrate the energy

of laser-generated acoustic waves [16]. Our effect is based on a similar general idea of interference between different components of the resonant exciting radiation, governed by the phase modulation. However, it is different, because it requires ultrashort pulses in contrast to Refs. [14,15], and it is a linear effect unlike Refs. [13,15]. Also, it results in a nanoscale spatial concentration of energy, in contrast to the macroscale to microscale concentration in Ref. [16].

The local field potential  $\varphi(\mathbf{r}, t)$ , induced by the external potential  $\varphi_0(\mathbf{r}, t)$ , is determined by the retarded Green’s function  $G^r(\mathbf{r}, \mathbf{r}'; t)$  of the system

$$\varphi(\mathbf{r}, t) = \varphi_0(\mathbf{r}, t) - \int \varphi_0(\mathbf{r}', t') \frac{\partial^2}{\partial \mathbf{r}'^2} \times G^r(\mathbf{r}, \mathbf{r}'; t - t') d^3 r' dt'. \quad (1)$$

We consider the nanosystem formed by an active component (e.g., a metal or semiconductor), described by the relative dielectric function  $\varepsilon(\omega)$ , embedded in a dielectric host. This Green’s function is computed as a spectral expansion in the coordinate-frequency domain:

$$G^r(\mathbf{r}, \mathbf{r}'; \omega) = \sum_i \varphi_i(\mathbf{r}') \varphi_i(\mathbf{r}) s_i / [s(\omega) - s_i], \quad (2)$$

where  $s(\omega) = 1/[1 - \varepsilon(\omega)]$  is the spectral parameter [17]. The material-independent eigenmodes (surface plasmons)  $\varphi_i(\mathbf{r})$ , and the corresponding eigenvalues  $s_i$ , are found by numerically solving a generalized Dirichlet-Neumann eigenproblem on a grid, as described in Ref. [18]. We smooth the discontinuities of the system components’ density using Gaussian filtering with an rms width equal to the grid step size. This does not affect the properties of the system at intermediate or large scales and actually makes the small-scale structure more realistic by eliminating sharp edges. After computing Green’s function of Eq. (2) in the real-space and frequency domains, the convolution in Eq. (1) is effected using a fast Fourier transform. We use 4096 frequency or temporal points. The rank of the eigenproblem is 8192, corresponding

to space dimensions in  $x, y$ , and  $z$  of  $32 \times 8 \times 32$  (all sizes are in grid steps). We have verified, by testing, that this number of spatial and time-frequency points leads to acceptable computational precision.

We study two planar systems, an “engineered” V shape and a random planar composite (RPC). An RPC can be made, in practice, by partially covering a smooth dielectric surface by a metal (or semiconductor), forming what is often called a semicontinuous metal-dielectric film. The geometry of these systems after smoothing is shown in Fig. 1. We have computer generated them by positioning cubes of size  $2 \times 2 \times 2$  on the central  $xz$  plane. The material dielectric function is set as that of silver [19] in a host whose dielectric constant is  $\epsilon_h = 2.0$ . The exciting field  $\varphi_0(\mathbf{r}, t)$  is a  $z$ -polarized chirped pulse with Gaussian envelope and duration  $T$ :

$$\varphi_0(\mathbf{r}, t) = -z \exp\{-i\omega_0(t - T/2)[1 + \alpha(t - T/2)/T] - (3/2)[(t - T/2)/T]^2\} + \text{c.c.}, \quad (3)$$

where  $\alpha$  is a dimensionless phase-modulation parameter.

Starting with the V shape, we show in Figs. 2(a) and 2(d) two excitation pulses, with *identical spectral composition and envelopes*, but with *different phase modulation* ( $\alpha = \pm 0.3$ ): these pulses are *time reversed* (phase conjugated) with respect to each other. Another excitation pulse (not shown) had the identical envelope and the same mean (carrier) frequency  $\omega_0$ , but no phase modulation ( $\alpha = 0$ ). Comparing the responses to these pulses allows one to distinguish the effects of the *phase control proper* (i.e., the time dependence of pulse phases) from those of the *spectral composition* that is also changed by the phase modulation.

In Fig. 2, panels (b),(e) and (c),(f) show the temporal dynamics of the local fields at two characteristic sites of the system: the opening and the apex of the V shape. It is evident that even with identical power spectra and envelopes, the phase modulation dramatically affects the temporal behavior: For the negative chirp, oscillations at the opening of the V shape [panel (b)] first grow and then decay rapidly due to an unfavorable phase relation with the driving pulse.

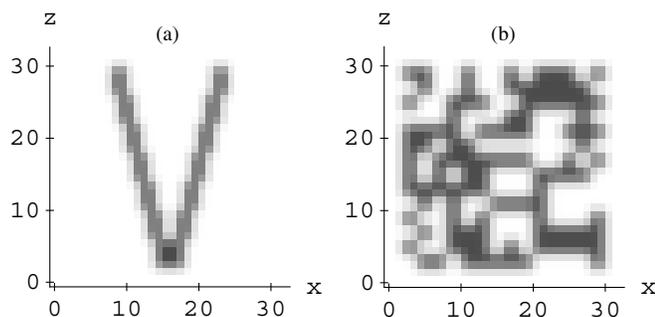


FIG. 1. Spatial distribution of smoothed density of two nanostructures: V shape (a) and random planar composite (b). Each unit on the coordinate axes represents 2 to 10 nm.

This is analogous to the phenomenon of adiabatic passage through a resonance. By contrast, oscillations at the apex [panel (c)] evolve later and last longer. Consequently, the field oscillations in different parts of the system do not overlap in time, which suggests that a localized wave of the oscillating polarization is compelled to propagate from the opening to the apex of the nanostructure. In marked contrast to this behavior, for the positively chirped pulse, the oscillations at the opening [Fig. 2(e)] and apex [Fig. 2(f)] of the V shape essentially overlap in time, indicating that there is no spatial localization of the excitation energy. In the absence of phase modulation (data not shown), the temporal dynamics is radically different from both of these cases: The local fields then closely reproduce the shape of the excitation pulse, except for a tail of free-induction decay, a behavior similar to the response of noble-metal nanospheres [5].

The spatial distributions of the local fields at different instants for the case of negative chirp are shown in Fig. 3. The distribution in panel (a) for  $t = 57.3$  fs (near the time of the excitation pulse maximum) is peaked at the V-shape “opening.” At the end of the driving pulse [ $t = 80.3$  fs, panel (b)], the excitation energy has sharply concentrated at the apex of this nanosystem, where the maximum field enhanced almost by 2 orders of magnitude (with respect to the driving field) develops [with the normal ( $x$ ) polarization]. Within two oscillations [ $t = 89.7$  fs, panel (c)], the maximum field is equally enhanced and concentrated at the apex, but in the parallel ( $z$ ) polarization. This energy concentration persists long after the excitation pulse

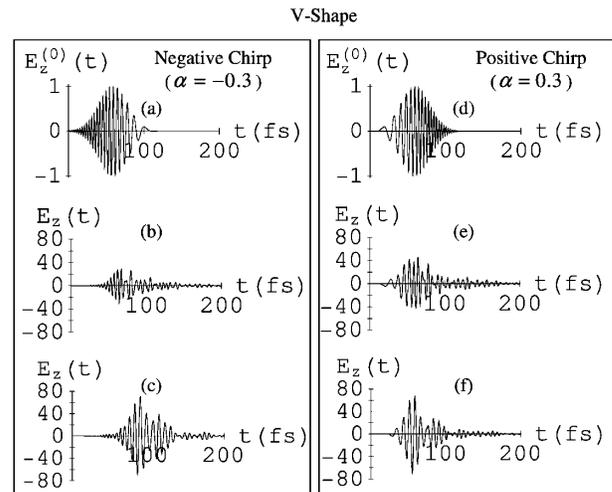


FIG. 2. Time dependence of fields in a V-shaped nanostructure, excited by pulses of duration  $T = 50$  fs, carrier frequency  $\hbar\omega_0 = 0.8$  eV, and amplitude 1, with negative chirp ( $\alpha = -0.3$ ) (left panel) and positive chirp ( $\alpha = 0.3$ ) (right panel). Panels (a) and (d) show the exciting pulses; (b) and (e) show the field at the “opening” of the V shape ( $x = 23$ ,  $z = 32$ ); (c) and (f) show the field at the apex of this nanosystem ( $x = 17$ ,  $z = 2$ ). All fields are plotted using the same units, where the maximum value of the exciting field is set as 1.

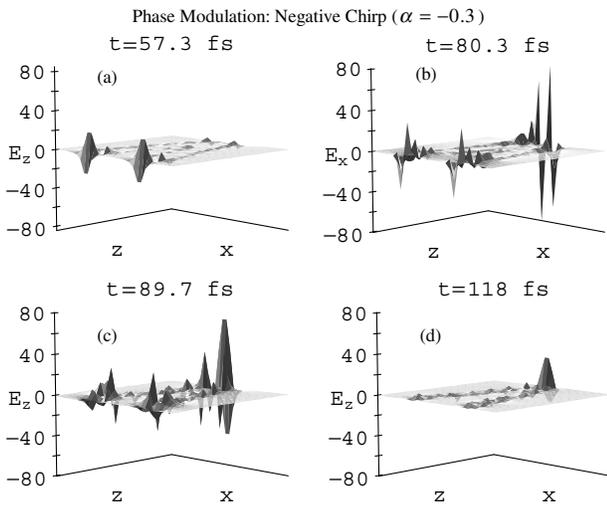


FIG. 3. Spatial distributions of local electric fields for V shape and negative chirp ( $\alpha = -0.3$ ) at various instants of time. The largest field component is displayed for each instant. Panel (a) corresponds to the instant of maximum field exhibited in Fig. 2(b), and panel (c) corresponds similarly to Fig. 2(c).

is over [see panel (d) at  $t = 118$  fs]. To summarize, for a comparatively long period ( $t \approx 80-120$  fs), almost the entire excitation energy is concentrated at one point, at the apex of the V-shaped nanostructure, where the local fields are greatly enhanced and the oscillations persist in the form of free induction long after the driving pulse is over. This energy concentration is very similar to the “ninth wave” effect [10] with one principal distinction: Here it is due to the phase modulation of the exciting pulse, while in Ref. [10] it is a result of the randomness of the system.

The local fields at the V shape for the case of positive chirp, shown in Fig. 4, behave quite differently.

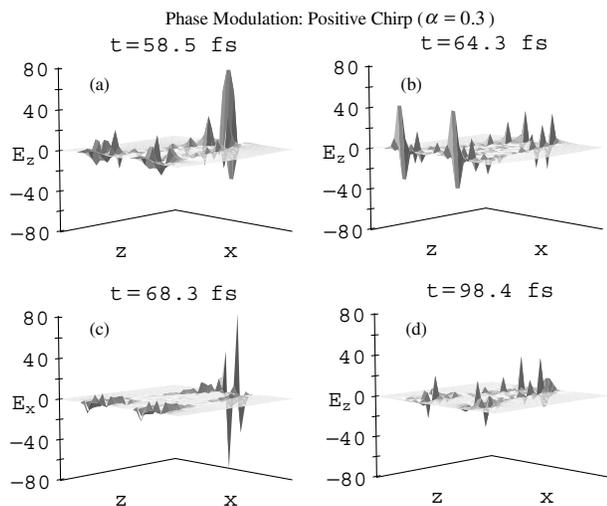


FIG. 4. Spatial distributions of local electric fields for V shape and positive chirp ( $\alpha = 0.3$ ) at various instants of time. The largest field component is displayed for each instant.

Their maximum is reached earlier, between  $t = 58.5$  and  $68.3$  fs. In sharp contrast to the case of negative chirp, the energy is never concentrated for a significant period of time at one location: it transfers from the apex [ $t = 58.5$  fs, panel (a)] to the opening of the V shape [ $t = 64.3$  fs, panel (b)], and back to the apex [ $t = 68.3$  fs, panel (c)] during a period of a few oscillations of the field. This behavior is also suggested by the field oscillations overlapping in time in Figs. 2(e) and 2(f). By the end of the driving pulse [ $t = 98.4$  fs; see Fig. 4(d)], the local fields are delocalized and significantly decayed with respect to their maximum, dramatically distinct from the negative chirp case for the corresponding time interval [cf. Figs. 3(c) and 3(d)]. For an unchirped pulse ( $\alpha = 0$ ) (data not shown), there is no pronounced spatial dynamics or energy localization. We have thus demonstrated some nontrivial effects of the coherent control: (i) The phase modulation significantly affects the dynamics of the spatial distribution of local fields in nanostructures, allowing one to induce energy localization. (ii) The specific time sequence of the phases is important, and not only the spectral composition of the excitation pulse.

The other systems considered, RPC’s are random and possess chaotic eigenmodes [18]. In Fig. 5, we display two spatial distributions of the local fields for the cases of positive and zero chirp in the same RPC, at the instants when the overall maximum fields are achieved. In each case, there is a significant concentration of the excitation energy: the local fields form “hot spots” where they are enhanced by nearly 2 orders of magnitude. In the case of a positive chirp [panel (a)], the distribution differs dramatically from that of the zero chirp [panel (b)], and both are very different from the case of negative chirp (data not shown). Thus the locations of the hot spots can be coherently controlled: They are strongly dependent on the phase modulation, both the spectral composition and specific time dependence of the excitation phase. Note that the concentration of energy at hot spots, even for a nonchirped pulse [Fig. 5(b)], is exactly the “ninth wave” effect as introduced in Ref. [10], which is due to the randomness of the system causing chaos of its eigenmodes [11] and giant fluctuations of the local fields [20]. This effect is confirmed here, without relying on the dipole approximation, by solving the differential equation boundary problem.

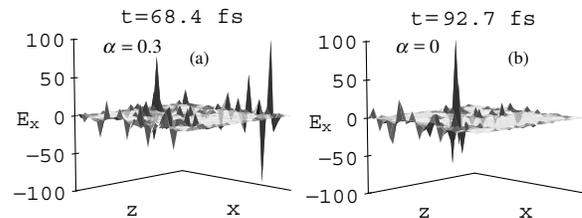


FIG. 5. Local electric fields in RPC at the indicated instants of their overall (global) maxima: (a) the case of positive chirp ( $\alpha = 0.3$ ); (b) no phase modulation ( $\alpha = 0.0$ ).

We briefly summarize the major results obtained: We predicted and quantitatively investigated the unique possibility to coherently control, on the nanoscale, the spatial concentration of energy transferred to a nanosystem by a femtosecond pulse. The phase modulation of the exciting pulse provides a degree of freedom necessary to compel the nanosystem to concentrate its excitation energy at a certain point. We showed that the excitation energy localization in nanosystems depends on the phase modulation, both on the spectral composition of the exciting pulse and, for a given spectral composition, on the specific time dependence of the pulse phase. For a V-shaped nanosystem, the negative-chirped Gaussian-envelope 50 fs pulse drives a traveling wave of surface plasmons, resulting in a concentration of the excitation energy at the tip of the V shape (Fig. 3). This energy concentration is similar to the “ninth wave” effect [10], but with the distinction that it is caused by the pulse phase modulation and not by the randomness of the system. In the case of a random planar composite, the energy concentration occurs spontaneously for the unmodulated Gaussian pulse, manifesting the “ninth wave” effect. However, when a phase modulation is introduced, the energy concentrates at a completely different location.

This effect of phase-controlled energy localization can be detected in experiments with nanometer spatial resolution, the most straightforward of which would invoke only time-integrated measurements, but no temporal resolution. In particular, the concentration of energy can be recorded by positioning a local probe (say, a dye molecule, or a cluster) at a given site of the system using the techniques of scanning probe microscopy. This effect will produce an enhanced *integral* radiation from such a probe (fluorescence, Raman scattering, etc.) that is maximized when the phase modulation of the exciting pulse concentrates the energy at the probe position. This enhancement will be most pronounced in the case of nonlinear responses, such as two-photon-excited fluorescence, or higher-order Raman effect. A phase-dependent photodamage of the probe, or even of the nanosystem itself, recorded by postradiation electron or scanning-probe microscopy, would be another indication of the effect. A time-resolved observation of radiation from the local probe would give richer information, but it is much more difficult to perform.

The coherently controlled ultrafast energy localization in nanosystems, introduced in this Letter, can have applications in different fields that require directed nanosize-selective excitation or modification. One such application

could be ultrafast computing using nanosystems, where the present effect can be used to energize and control processes on the nanoscale for femtosecond times. Ultrafast site-selective photomodification of nanosystems may be another field of application.

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