Real versus virtual excitonic Stark effect in semiconductor quantum wells

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(Received 14 June 1990)

We investigate the dynamics of the ac Stark effect induced by short laser pulses (pump-probe configuration) in quantum-well structures in the limits of both real excitonic population (resonant pump pulses) and virtual excitation (off-resonant pump pulses). We use a microscopic model describing exciton-phonon interaction in the weak-coupling limit and consider the regime of small excitonic density (i.e., weak optical nonlinearity). Exciton-phonon coupling induces exciton damping and renormalizes one of the two nonlinearity parameters.

Optical nonlinearities of semiconductors excited by short laser pulses in the vicinity of excitonic resonances are attracting considerable attention.[1] The experimental investigation of optical properties of Wannier excitons in semiconductors has been made possible using femtosecond techniques, which allow creation of excitons without generating a high density of electron-hole pairs causing screening and dissociation of excitonic bound states. Particular attention has been given to the question of whether the excitonic-based optical nonlinearity can be employed for the fabrication of optical materials with large $\chi^{(3)}$ susceptibilities. The optical properties of multilayered, quasi-two-dimensional materials (quantum wells)[2,3] as well as amorphous structures such as semiconductor microcrystallites embedded in a transparent medium have been extensively studied.[4] More theoretical efforts[2,3] were devoted to the limit when the incident light is not resonant with the excitonic line (i.e., the excitons responsible for the nonlinear effects are virtual) and effects related to exciton-phonon coupling are negligible. Clearly, for resonant excitation the exciton-phonon interaction cannot be neglected since it plays an important role leading to relaxation processes, and therefore should be incorporated in a complete microscopic theory; likewise in the off-resonant regime, processes mediated by phonons were found to significantly contribute to the optical nonlinearity.[5] Therefore in general the interaction of excitons with phonons leads to both relaxation and phonon-induced nonlinearities. Zimmerman and Hartmann[6] have discussed the optical excitonic nonlinearity in the resonant regime including phonon-induced relaxation, using a phenomenological approach which did not take into account the phonon-induced nonlinearity. We have recently calculated the optical nonlinearity of excitons using a tight-binding two-band model of the semiconductor, where the exciton density was assumed to be low enough to employ approximations equivalent to an interacting boson model. In this Brief Report we apply this formalism to quantum-well structures. A similar procedure for calculating the nonlinear optical properties by decomposing the Heisenberg equations into a linear (bosonic) part and nonlinear corrections may be used for Frenkel excitonic polaritons.[7] Within the framework of the applied model, the standard description of exciton-phonon interaction through the Frohlich and short-range potentials leads to a simple effective Hamiltonian,[8] which is found to be a straightforward generalization of the weak-coupling model of exciton-phonon interaction for Frenkel excitons.[9] We investigate the Heisenberg dynamics of the excitonic polarization operator and make a semiclassical approximation leading to a simple equation for the averaged excitonic polarization driven by the electromagnetic field. Based on this equation we calculate the differential absorption spectrum for a pump-probe measurement and discuss the Stark shift of the absorption profile.

Consider the standard two-band Hamiltonian for a semiconductor coupled to the electromagnetic field:[10]

$$\hat{H}=\int d\mathbf{k}(\hat{a}_{\mathbf{k}}^{\dagger}\hat{a}_{\mathbf{k}}+\tfrac{1}{2})\hbar\omega_{k}+\int d\mathbf{r}\,\hat{\psi}^{\dagger}(\mathbf{r})[\hat{p}(\mathbf{r})-e\hat{A}(\mathbf{r})]^{2}\hat{\psi}(\mathbf{r})+\int d\mathbf{r}_{1}d\mathbf{r}_{2}\hat{\psi}^{\dagger}(\mathbf{r}_{1})\hat{\psi}^{\dagger}(\mathbf{r}_{2})V^{C}(\mathbf{r}_{1}-\mathbf{r}_{2})\hat{\psi}(\mathbf{r}_{2})\hat{\psi}(\mathbf{r}_{1})+\int d\mathbf{r}\,\hat{\psi}^{\dagger}(\mathbf{r})V^{B}(\mathbf{r})\hat{\psi}(\mathbf{r})\,, \tag{1}$$

where $V^{C}(\mathbf{r})$ is the Coulomb potential and $V^{B}(\mathbf{r})$ is the potential describing the interaction of carriers with nuclei, $\hat{a}_{k}^{\dagger}$ are bosonic operators describing the electromagnetic field, $\hat{A}(r)$ is the electromagnetic vector potential operator, and $\hat{p}$ is the electronic momentum operator. The electronic field operator is

$$\hat{\psi}(\mathbf{r})=\sum_{n}[\hat{c}_{\mathbf{n}}\Phi^{b}(\mathbf{r}-\mathbf{r}_{\mathbf{n}})+\hat{d}_{\mathbf{n}}^{\dagger}\Phi^{a}(\mathbf{r}-\mathbf{r}_{\mathbf{n}})]\,,$$

where $\Phi^{a}(\mathbf{r}-\mathbf{r}_{n})$ and $\Phi^{b}(\mathbf{r}-\mathbf{r}_{n})$ denote Wannier functions for the valence and conduction bands, localized near the nth site. $\hat{c}_{n},\hat{c}_{n}^{\dagger}$ ($\hat{d}_{n},\hat{d}_{n}^{\dagger}$) are the annihilation and creation operators of electrons and holes. These operators obey the Pauli commutation rules $[\hat{c}_{n},\hat{c}_{\mathrm{m}}^{\dagger}]=\hat{I}-2\delta_{\mathrm{nm}}\hat{c}_{\mathrm{n}}^{\dagger}\hat{c}_{\mathrm{n}}$, $[\hat{d}_{\mathrm{n}},\hat{d}_{\mathrm{m}}^{\dagger}]=\hat{I}-2\delta_{\mathrm{nm}}\hat{d}_{\mathrm{n}}^{\dagger}\hat{d}_{\mathrm{n}}$. We model the quantum well as an infinite layer with thickness L much smaller than the optical wavelength. We introduce the two-body operator $\hat{Y}_{\mathrm{nm}}(t)\equiv\hat{c}_{\mathrm{n}}(t)\hat{d}_{\mathrm{m}}(t)$ corresponding to the annihilation of an electron-hole pair.[8,11] For small exciton density $\langle[\hat{Y}_{\mathrm{nm}},\hat{Y}_{\mathrm{n'm'}}^{\dagger}]\rangle\cong\delta_{\mathrm{nn'}}\delta_{\mathrm{mm'}}$, and the excitons can be treated as bosons. The Heisenberg equation for $\hat{Y}_{\mathrm{nm}}(t)$ is derived and the right-hand side of this equation is next partitioned into the part linear in $\hat{Y}_{\mathrm{n'm'}}(t)$ and a part consisting of other operators. The linear component of this equation is partially rediagonalized employing a linear transformation (this corresponds to solving the single interacting electron-hole pair problem). When L is larger than the radius of the 1s bulk exciton (no confinement) the transformation diagonalizing the linearized two-body (electron and hole) problem has the form

$$\hat{Y}_{\alpha kj}(t)=\sum_{nm} e^{i\mathbf{k}\cdot\mathbf{R}_{nm}}\sin(\pi j\hat{\mathbf{z}}\cdot\mathbf{R}_{nm}/L)\phi_\alpha(\mathbf{r}_n-\mathbf{r}_m)\hat{Y}_{nm}(t)\ ,$$

where $\hat{\mathbf{z}}$ is the unit vector in the direction perpendicular to the well and $\phi_\alpha(\mathbf{r}_n-\mathbf{r}_m)$ is the solution of the two-body three-dimensional hydrogen-atom problem, i.e., α is the hydrogenlike quantum number denoting bound and unbound eigenstates, $\mathbf{k}$ is a two-dimensional momentum describing the center-of-mass motion parallel to the layer surface, and j describes the motion perpendicular to the layer. In the opposite limit (strong confinement) the electron-hole motion perpendicular to the layer surface is not modified by the Coulomb interaction and the diagonalizing transformation has the form

$$\hat{Y}_{\alpha kjj'}(t)=\sum_{nm} e^{-i\mathbf{k}\cdot\mathbf{R}_{nm}}\sin(\pi j\hat{\mathbf{z}}\cdot\mathbf{r}_n/L)\sin(\pi j'\hat{\mathbf{z}}\cdot\mathbf{r}_m/L)\phi_\alpha(\mathbf{r}_n-\mathbf{r}_m)\hat{Y}_{nm}(t)\ ,$$

where now $\phi_\alpha(\mathbf{r}_n-\mathbf{r}_m)$ is the two-dimensional hydrogen-atom wave function and jj' are the quantum numbers for the perpendicular motion of electrons and holes, respectively. $\hat{Y}_{\alpha kjj'}(t)$ is the annihilation operator of a Wannier exciton with α quantum number of internal (relative) electron-hole motion. In the following we assume that the incident-light wave vector exciting the semiconductor is perpendicular to its surface and consider only the $j=j'=1$ state. We have used an effective potential

$$V^{\text{eff}}_{e(h)}(\mathbf{r},t)=-(+)\left[\frac{1}{\epsilon_0}\int d\mathbf{r}'\frac{\nabla[\mathbf{Q}\hat{\xi}(\mathbf{r}',t)]}{|\mathbf{r}-\mathbf{r}'|}+d_{e(h)}\hat{\xi}(\mathbf{r},t)\right]\ ,$$

acting on electrons and holes and describing the interaction with the phonon bath, $\xi(\mathbf{r},t)$ is the quantized phonon displacement, and $V^{\text{eff}}_{e(h)}(\mathbf{r},t)$ is a sum of the Frohlich (long-range) interaction and the short-range potential ("contact") interaction. The exciton-phonon coupling can be rewritten as[7]

$$\hat{H}_{\text{ex-ph}}=\sum_{\alpha,\beta,j_1,j_2}\int d\mathbf{q}\int d\mathbf{k}\,F_{\alpha\beta j_1 j_2 j_3 j_4}(\mathbf{k}+\mathbf{q},\mathbf{k},\mathbf{q})\times\hat{Y}^{\dagger}_{\alpha\mathbf{k}+\mathbf{q}j_1 j_2}\hat{Y}_{\beta,\mathbf{k}j_3 j_4}(\hat{b}_{\mathbf{q}}+\hat{b}^{\dagger}_{-\mathbf{q}})\ , \tag{2}$$

where $\hat{b}_{\mathbf{q}}$ is the phonon annihilation operator. In the following we consider the Heisenberg equation for the operators $\hat{Y}_{\alpha\mathbf{k}j_1,j_2}(t)$ and $\hat{b}_{\mathbf{q}}$ describing the interacting exciton-phonon system governed by Eq. (2), and treat the exciton-phonon interaction using the Fermi golden rule.[8] For low enough exciton density the density matrix of the excitonic system can be approximated by a superposition of coherent states, so that the right-hand side of the averaged Heisenberg equation for the excitonic polarization has the form of a product of the expectation values $\langle\hat{Y}_{\alpha kj_1,j_2}(t)\rangle$. This approximation leads to the identification of a system of interacting semiclassical bosons, and is valid provided the relative strength of the nonlinearity is small in comparison with the broadening induced by the interaction with the phonon bath. We believe that even the zero-point phonon vibration is sufficient to justify such semiclassical treatment. Since the incoming radiation is assumed to be perpendicular to the layer, only the $k=0$ mode is excited. We next assume that the radiation field is tuned near the $1s$ exciton line so that only the $\alpha=1$ exciton should be considered. Invoking the rotating-wave approximation for the exciton-phonon interaction, we obtain a simple equation for the averaged amplitude,

$$y(t)\equiv\langle\hat{Y}_{\alpha kjj'}(t)\rangle\exp(i\Omega_0 t)\ ,$$

with $\alpha=1$, $k=0$, and $j=j'=1$, where $\hbar\Omega_0$ is the energy of the $1s$ excitonic state:

$$\dot{y}(t)=-\gamma y(t)+\mu E(t)+i\lambda_1 y(t)y^*(t)y(t)+\lambda_2\mu E(t)y^*(t)y(t)\ , \tag{3}$$

where μ is the dipole effective moment of the Wannier exciton.[8] Expressions for the parameters λ_1 and λ_2, which determine the optical nonlinearity, were derived in Ref. 8. λ_1 is a sum of terms representing an effective exciton-exciton interaction mediated by the dipole-dipole and Pauli exclusion interactions, plus a phonon-induced term. λ_2 has the form of a geometrical factor governed by the $1s$ excitonic wave function $\phi_\alpha(\mathbf{r}_n-\mathbf{r}_m)$. When the exciton-phonon interaction is neglected, an equation of the same form can be derived starting with Eq. (4) of Ref. 2, provided the weak excitation approximation is applied, and consequently only third-order terms in excitonic polarization are retained. The exciton-phonon interaction renormalizes the λ_1 nonlinearity parameter and introduces the relaxation term γ. The equation of motion presented in Ref. 2 is highly nonlinear with respect to the excitonic density. However, approximations regarding the exciton-exciton collision rate were made in its derivation, which restrict its validity to low excitonic densities. As pointed out in Ref. 8, for higher excitonic densities, higher-order terms in exciton polarization with other nonlinearities parameters should be included in the dynamics given by Eq. (7) [e.g., $\chi^{(5)}$ processes are in general not fully described by Eq. (7)]. Finally we point out also that the Maxwell-Bloch theory, with phenomenologically added damping constants considered in Ref. 11, is equivalent in the limit of low excitation to Eq. (7) with $\lambda_1=0$, provided we set $\Gamma=2\gamma$, which is in agreement with the fact that this approach was used to consider only the off-resonant limit.[3,12] As shown in Ref. 8, the λ_1 term can be neglected sufficiently far off-resonance.

The λ_1 and the λ_2 contributions have different effects on the optical properties of the system since the λ_1 term has the form of a cubic anharmonicity, whereas the λ_2 term is a quadratic anharmonicity proportional to the amplitude of the electric field.[8] When the phonon-mediated nonlinearity is neglected the relative strength of both nonlinearity parameters is $\lambda_1/\lambda_2\mu\sim\log(L/R_B)$ where R_B is the excitonic Bohr radius. However, λ_1 has an additional phonon-induced contribution which could be either positive or negative. We will evaluate the material response separately for each type of nonlinearity.

We have calculated the differential absorption spectrum of a weak probe pulse using Eq. (3). The electric field consists of two pulses, i.e., $E(t)=E_1(t+\tau)+E_2(t)$, where $E_1(t)$ denotes the pump pulse, $E_2(t)$ denotes the probe pulse, and τ is their relative delay. The slowly varying pulse envelopes were assumed to be Gaussian, i.e., $E_1(t)=E_1^0 e^{-t^2/\sigma_1^2} e^{-i\Delta_1 t}$ and similarly for $E_2(t)$. Here $\Delta_1=\omega_1-\Omega_0$ is the detuning of the pump field from the exciton transition frequency. We have decomposed the time-dependent polarization as $y(t)\equiv y_1(t)+y_2(t)$, where $y_1(t)$ is the solution of Eq. (3) with $E_1(t)$ only. This solution was calculated numerically using a Bulirsh-Stoer numerical integration scheme. We next calculated the polarization $y_2(t)$ induced by the weak probe pulse employing a linearization of Eq. (3) with respect to $y_2(t)$, resulting in

$$y_2(t)=\int_{-\infty}^{t} dt' \mu E_2(t') \exp\left[-\gamma(t-t')+\int_{t'}^{t} dt''[2i\lambda_1|y_1(t'')|^2+\lambda_2 E_1(t'')y_1^*(t'')]\right] . \tag{4}$$

The absorption spectrum is $\mathcal{S}(\omega;E_1)=\mathrm{Re}[\tilde{y}_2(\omega)/\tilde{E}_2(\omega)]$ $[\tilde{f}(\omega)\equiv\int_{-\infty}^{\infty} dt\, f(t)\exp(-i\omega t)]$ and the differential absorption spectrum is $D(\omega)\equiv\mathcal{S}(\omega;E_1)-\mathcal{S}(\omega;0)$.

The differential absorption spectrum for various delays of the probe for the λ_1 nonlinearity and $\lambda_2=0$ is displayed in Fig. 1(a) for the resonant pump, and for the off-resonant pump in Figs. 1(b) and 1(c). Similar calculations for the λ_2 nonlinearity with $\lambda_1=0$ are presented in Fig. 2. As indicated earlier, the λ_2 nonlinearity should be dominant for sufficiently far off-resonant excitation. The absorption for the off-resonant pump presented in Fig. 2(b) is in qualitative agreement with the calculation for the off-resonant limit presented in Refs. 12 and 13 (in our calculation the effect of heavy and light holes is not included so that multiresonance structures are absent). If the exciton-phonon coupling is neglected, the sign of λ_1 is always positive and the off-resonant absorption spectrum is very different for λ_1 and λ_2 nonlinearities. However, the phonon-induced contribution to the nonlinearity may change the sign of λ_1. For negative λ_1 the differential absorption spectrum for the off-resonant pump becomes similar for both nonlinearities as demonstrated in Figs. 1(b) and 1(c). We stress that the dependence of the averaged Stark shift on the pump detuning is distinctly different for both types of nonlinearity, since for λ_1 the shift does not change its sign when the pump is tuned across the resonance, whereas for λ_2 the dependence on the pump-exciton detuning is asymmetric.[8] We further note that in the resonant limit the differential spectrum related to the λ_1 nonlinearity has a highly oscillatory character. A simple intuitive argument for that can be made, since in this case the nonlinear effect enters the dynamics of the probe-induced polarization as a time-dependent shift, and we expect that the absorption spectrum will be a superposition of shifted Lorentzians. The oscillatory character of the absorption spectrum may therefore be viewed as an interference effect. We have also calculated the first moment of the differential absorption spectrum

$$S=\int d\omega(\omega-\Omega_0)D(\omega)\left[\int d\omega\, D(\omega)\right]^{-1},$$

which may be viewed as an analog of the cw Stark shift, for various delay times between the pump and probe pulses. The results for the λ_1 and the λ_2 nonlinearities are presented in Figs. 3(a) and 3(b), respectively. We see that in the first case [Fig. 3(a)] the Stark shift decreases very rapidly for negative delays and its decrease for positive delays is much slower and is governed by the relaxation time scale γ^{-1}. For λ_2, the dependence on the delay time is nearly symmetric for negative and positive delays. This is to be expected from Eq. (3), since for the λ_1 nonlinearity the impact of the pump excitation is dominated by the excitonic density and therefore the dependence of

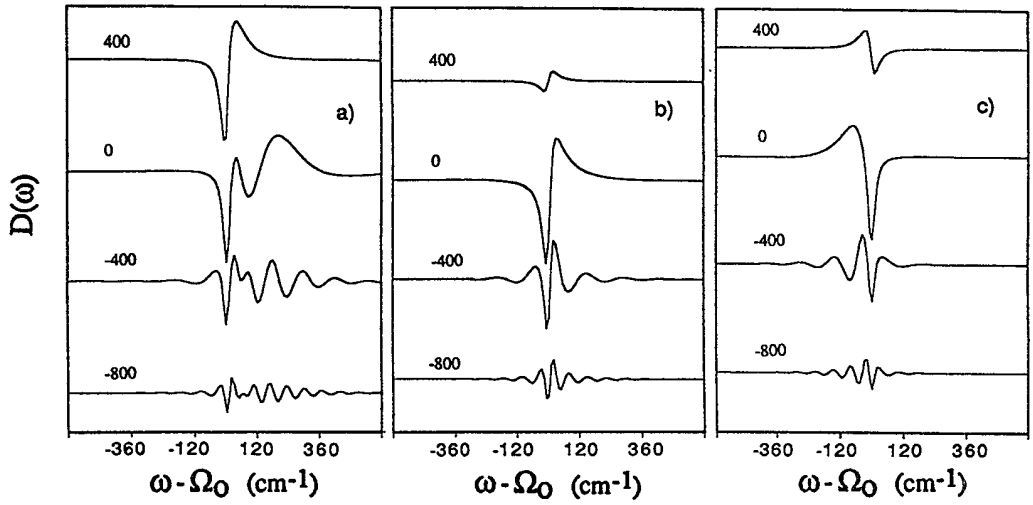

FIG. 1. The differential probe absorption $D(\omega)$ induced by λ_1 nonlinearity with $\lambda_2=0$. $\mu E_1^0\sigma_1=1$, $\gamma\sigma_1=0.2$, $\sigma_1=100$ fs, $\sigma_2=20$ fs, $\Delta_2=0$. (a) $\Delta_1\sigma_1=0$, $\lambda_1\sigma_1=1$; (b) $\Delta_1\sigma_1=-2$, $\lambda_1\sigma_1=1$; (c) $\Delta_1\sigma_1=-2$, $\lambda_1\sigma_1=-1$. The various curves in each panel correspond to different pump-probe delays τ as indicated (in fs).

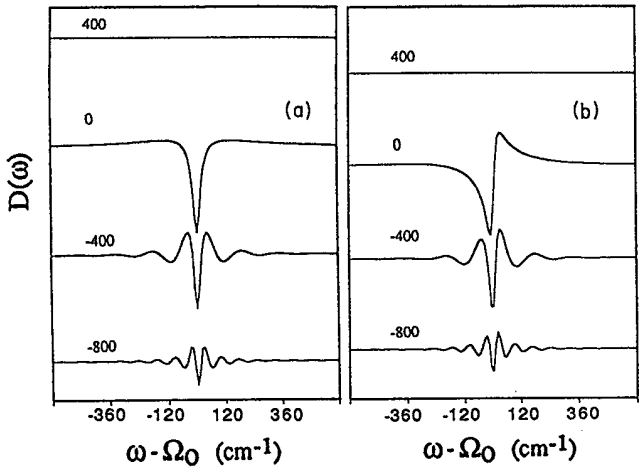

FIG. 2. The differential probe absorption $D(\omega)$ induced by λ_2 nonlinearity with $\lambda_1=0$. $\mu E_1^0\sigma_1=1$, $\gamma\sigma_1=0.2$, $\sigma_1=100$ fs, $\sigma_2=20$ fs, $\Delta_2=0$. (a) $\Delta_1\sigma_1=0$, (b) $\Delta_1\sigma_1=-2$. The various curves in each panel correspond to different pump-probe delays τ as indicated (in fs).

the Stark shift on the absorption spectrum on the pump-probe delay time reflects the time-dependent excitonic density. In contrast, the λ_2-induced shift depends on the product of the electric-field amplitude and the excitonic polarization and therefore vanishes when the probe and pump pulses do not overlap [Fig. 3(b)]. Figures 1 and 2 also show that the λ_2-induced absorption vanishes for positive delays much more rapidly than the λ_1 contribution.

In summary, we have calculated the dynamics of the Stark effect in quantum wells excited by both resonant and off-resonant ultrashort pulses, employing a microscoping model of exciton-phonon coupling. The exciton-phonon interaction contributes simultaneously to the relaxation of excitonic polarization and optical excitonic nonlinearity. We found that, depending on the relative strength of exciton-phonon coupling, the differential absorption spectrum for resonant excitation may exhibit an oscillatory behavior.

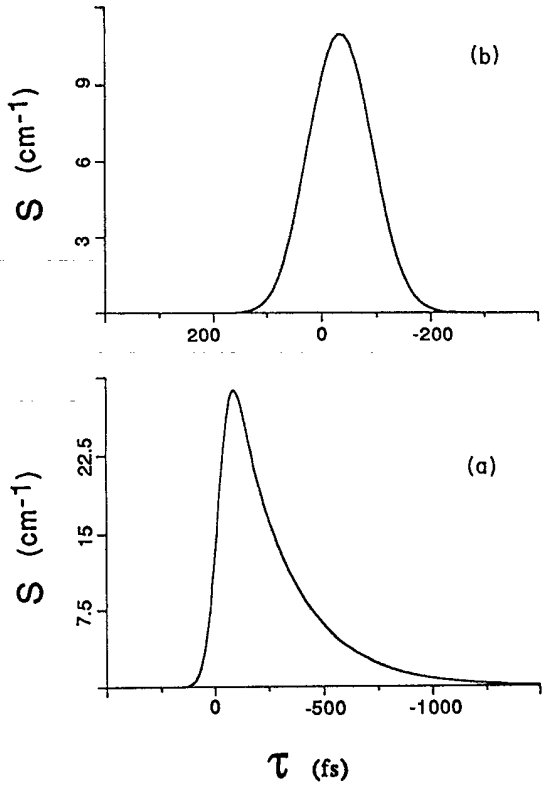

FIG. 3. The first moment of the probe absorption profile is plotted vs the pump delay τ: (a) $\lambda_1\sigma_1=1$, $\lambda_2=0$, $\Delta_1\sigma_1=0$, $\Delta_2=0$, $\mu E_1^0\sigma_1=1$, $\gamma\sigma_1=0.2$, $\sigma_1=100$ fs, $\sigma_2=20$ fs; (b) $\lambda_1=0$, $\lambda_2=1$, $\Delta_1\sigma_1=-1$, $\Delta_2=0$, $\mu E_1^0\sigma_1=1$, $\gamma\sigma_1=0.2$, $\sigma_1=100$ fs, $\sigma_2=20$ fs.

The support of the U.S. Air Force Office of Scientific Research, the National Science Foundation, and the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged. S.M. acknowledges support from the Camille and Henry Dreyfus Foundation.

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