Linear Response in the Strong Field Domain

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We show that, while it is well-known that first-order perturbation theory leads to linear response (of, e.g., a material system to an external field), the reverse is not true: linear response does not necessarily imply the validity of first-order perturbation theory, nor does it follow from it that the external perturbation is weak. We do so by analyzing the intensity dependence in the photoexcitation followed by dissociation or isomerization of a bound molecular system by a shaped broadband laser pulse. We show that, in certain cases where strong field effects are definitely present, the observed photoexcitation yield as a function of intensity may exhibit linear dependence over a wide range of intensities. The behavior is shown to coexist with a rather extensive range of *coherent control* over the branching ratios, an effect that was shown in the past to be impossible in the single precursor state (e.g., in the first-order perturbation theory) domain. For example, we demonstrate computationally that when (flat continuum-mediated) Raman transitions are present, appropriate pulse shaping can lead to a linear yield with intensity over a wide range of intensities, while coherent control over the branching ratio is significant. Thus, it is not necessary to invoke external bath effects (as is currently being done) to explain present-day experiments where coherent control is observed in the linear response regime.

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When a pulse of coherent light excites (dissociates or photoisomerizes) a molecular system, the system can undergo dipole transitions to a number of channels, such as different electronic states or different photoproducts. By carefully designing the light pulses, the branching ratios between the various channels yields can be controlled. With strong field control, optimization in field parameters such as intensity, chirp rate, or pulse duration can be employed to control such branching ratios, even in the presence of a dissipative environment [1,2]. It is also possible to control the branching ratios by tuning only the relative phase between two frequency components of the excitation light, in a process called "phase-only" bichromatic control [3,4]. It has been shown that phase-only bichromatic control requires the interference between two "indistinguishable" paths, which means that the information as to which path is followed should be lacking. Such control cannot be realized in the weak field (i.e., the first-order perturbation) limit when one starts from a single bound state [5].

In spite of the above, a recent experiment [6] reported coherent control, including phase-only control, in the photoisomerization of bacteriorhodopsin by shaped broadband laser pulses, which exhibited a linear dependence of the yield as a function of laser intensity. In order to explain this finding, it was subsequently assumed that bath-environmental effects cause the control [7,8], although it was not easy to see how the environment could generate and preserve the coherence necessary for phase-only control. Here, we offer an alternative explanation of this finding which obviates the need to invoke environmental effects. In doing so, we correct a common, potentially misleading, concept in laser-molecule interaction physics, which is that linear intensity response implies the validity of (first-order) perturbation theory. We show that, as we shape the pulse beyond the transform-limited form, we modify the non-first-order continuum-mediated Raman transitions among bound vibrational levels (Fig. 1) and in this way modify phase control, while at the same time maintaining or even enhancing the linear nature of the overall yield. The clear conclusion is that linearity does not necessarily imply the validity of (first-order) perturbation theory, as it can occur way beyond the first-order perturbative regime.

We consider a molecule initially in a bound state undergoing a transition to a degenerate (quasi)continuum (Fig. 1) due to the action of an excitation pulse whose electric field is given as $\mathbf{E}(t) = 2\hat{\epsilon}\epsilon(t)\cos(\omega_L t)$, where $\hat{\epsilon}$ is the polarization direction, $\epsilon(t)$ is the pulse temporal envelope, and ω_L is the "center frequency." The combined light-matter Hamiltonian (in atomic units, $\hbar = 1$) is

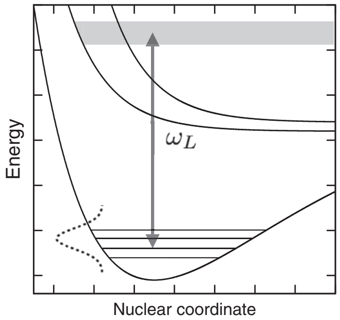

FIG. 1. A schematic illustration of a broadband photoexcitation with two excited electronic potentials. The pulse's spectrum is wide in energy, compared with ground vibrational level separation.

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$$\begin{aligned} H &= H_M + H_I, \\ H_M &= \sum_{j=1}^{N} E_j |E_j\rangle\langle E_j| + \sum_n \int E|E, n^-\rangle\langle E, n^-|dE, \\ H_I &= -\vec{\mu}\cdot\mathbf{E}(t), \end{aligned} \tag{1}$$

where $\vec{\mu}$ is the electric dipole operator; $|E, n^-\rangle$ are continuum eigenstates characterized by the energy E and by n, the asymptotic (dissociation or isomerization) channel index, which is the main quantity we wish to control. N is the number of bound states that are effectively coupled by (continuum-mediated) resonance Raman transitions as enabled by the bandwidth of the excitation pulse.

The time-dependent state of the material system is thus expanded as

$$\begin{aligned} |\Psi(t)\rangle = &\sum_{j=1}^{N} b_j(t)e^{-iE_jt}|E_j\rangle \\ &+ \sum_n \int b_{E,n}(t)e^{-iEt}|E, n^-\rangle dE. \end{aligned} \tag{2}$$

The Schrödinger's equation for the time evolution of this state then translates into the following differential equations (with rotating wave approximation):

$$\begin{aligned} \underline{\dot{b}}(t) &= i\sum_n \int \underline{\Omega}_{E,n}(t) b_{E,n}(t)dE, \\ \dot{b}_{E,n}(t) &= i\underline{\Omega}^{\dagger}_{E,n}(t)\cdot\underline{b}(t), \end{aligned} \tag{3}$$

where we have organized the bound level amplitudes and Rabi frequencies as vectors $[\underline{b}(t)]_j \equiv b_j(t)$ and $[\underline{\Omega}_{E,n}(t)]_j \equiv \epsilon(t)\mu_{j,n}(E)e^{-i\Delta_{E,j}t}$. The transition dipole matrix elements are $\mu_{j,n}(E) \equiv \langle E_j|\vec{\mu}\cdot\hat{\epsilon}|E, n^-\rangle$, and the laser detuning from resonance is $\Delta_{E,j} = E - E_j - \omega_L$.

The time evolution of the bound-state amplitudes is obtained by formally integrating $b_{E,n}(t)$ and substituting the expression into the first part of Eq. (3), assuming that $b_{E,n}(-\infty) = 0$ for all E and n:

$$\dot{b}_j(t) = -\epsilon(t)e^{iE_jt}\int_{-\infty}^{t} \epsilon^*(t')\sum_{k,n} F^{(n)}_{j,k}(t - t')b_k(t')e^{-iE_kt'}dt', \tag{4}$$

where

$$F^{(n)}_{j,k}(t - t') = \int \mu_{j,n}(E)\mu_{n,k}(E)e^{-i(E-\omega_L)(t-t')}dE. \tag{5}$$

The matrix spectral correlation function $F^{(n)}_{j,k}(t - t')$ can be further simplified by applying the "slowly varying continuum approximation" [3], in which we replace each energy-dependent transition dipole matrix element by some average value $\mu_{j,n}(E) \cong \mu_{j,n}(\omega_L) \equiv \bar{\mu}_{j,n}$, and it follows that $F^{(n)}_{j,k}(t - t') \cong 2\pi\bar{\mu}_{j,n}\bar{\mu}_{n,k}\delta(t - t')$. This approximation is valid whenever the bound-continuum transition dipole matrix element changes little over the pulse's energy bandwidth. The result is a simplified set of equations for the bound amplitudes

$$\underline{\dot{b}}(t) = -\underline{\underline{\Omega}}^{I}(t)\cdot\underline{b}(t), \tag{6}$$

which can be solved as (with Dyson series exponential)

$$[\underline{\underline{\Omega}}^{I}(t)]_{j,k} = \pi|\epsilon(t)|^2\sum_n \bar{\mu}_{j,n}\bar{\mu}_{n,k}e^{i(E_j-E_k)t}, \tag{7}$$

which can be solved in a closed form as

$$\underline{b}(t) = \exp\Big[-\int_{-\infty}^{t}\underline{\underline{\Omega}}^{I}(t')dt'\Big]\underline{b}(-\infty). \tag{8}$$

Substitution of the bound-state coefficients of Eq. (8) into the expression for the continuum coefficients of Eq. (3), while imposing $b_{E,n}(-\infty) = 0$, results in

$$b_{E,n}(t) = i\int_{-\infty}^{t}\underline{\Omega}^{\dagger}_{E,n}(t')e^{-\int_{-\infty}^{t'}\underline{\underline{\Omega}}^{I}(t'')dt''}\underline{b}(-\infty)dt', \tag{9}$$

from which we obtain the probability amplitude for photodissociation (or photoisomerization) to channel n as

$$P_{E,n} = |b_{E,n}(t\to\infty)|^2. \tag{10}$$

We now apply the above to the case of two bound vibrational states $|E_1\rangle$ and $|E_2\rangle$, coupled to two continuum channels $n = \alpha, \beta$, where we calculate the energy-averaged branching ratio, which is $\rho_{\alpha,\beta} = \int_{-\infty}^{\infty} P_{E,\alpha}dE/\int_{-\infty}^{\infty} P_{E,\beta}dE$. It is convenient to investigate the bound-state coefficients using three dimensionless parameters, $q_n \equiv \bar{\mu}^{(n)}_2/\bar{\mu}^{(n)}_1$, $n = \alpha, \beta$, and $Q = \bar{\mu}^{(\beta)}_1/\bar{\mu}^{(\alpha)}_1$, and, with shorthand notation, $\mu^2 \equiv |\bar{\mu}_{1,\alpha}|^2$,

$$\begin{aligned} \underline{b}(t) &= e^{-\underline{\underline{M}}(t)}\underline{b}(-\infty), \\ \underline{\underline{M}}(t) &= \pi\begin{pmatrix} (1 + Q^2)S(t) & (q_\alpha + Q^2q_\beta)R(t) \\ (q_\alpha + Q^2q_\beta)R^*(t) & (q^2_\alpha + Q^2q^2_\beta)S(t) \end{pmatrix}, \\ S(t) &= \mu^2\int_{-\infty}^{t}|\epsilon(t')|^2dt', \\ R(t) &= \mu^2\int_{-\infty}^{t}|\epsilon(t')|^2e^{i(E_1-E_2)t'}dt'. \end{aligned} \tag{11}$$

Although q_α, q_β, and Q are complex in general, we simplify the analysis by choosing them to be real. We note that, when $q_\alpha = q_\beta$, the branching ratio becomes $\rho_{\alpha,\beta} = 1/Q^2$ and no optical control is possible.

In a typical experimental setup, one employs a "pulse shaper" [9] which allows one to specify the amplitudes and phases of each frequency component. Here, we simplify this process by considering a subclass of pulses consisting of two equally wide, linearly chirped subpulses. The interaction Hamiltonian now assumes the form

$$\begin{aligned} H_I &= -2\mu\{\epsilon(t + t_0)\cos[\omega(t)t] + \epsilon(t - t_0)\cos[\omega(t)t - \phi]\} \\ &\cong -\mu\epsilon_s(t)e^{-i\omega_Lt}, \quad \omega(t) = \omega_L + a_0t, \\ \epsilon_s(t) &\equiv [\epsilon(t + t_0) + e^{i\phi}\epsilon(t - t_0)]e^{-ia_0t^2}. \end{aligned} \tag{12}$$

Choosing

$$\epsilon_s(t) = I^{1/2}[2(1+2iA)(1+\cos\phi e^{-t_0^2/\tau^2})]^{-1/2} \cdot \left\{\exp\left[\frac{-(t+t_0)^2}{2\tau^2(1+2iA)}\right] + \exp\left[\frac{-(t-t_0)^2}{2\tau^2(1+2iA)} + i\phi\right]\right\}, \tag{13}$$

whose spectrum is

$$\tilde{\epsilon}_s(\omega) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty}\epsilon_s(t)e^{-i\omega t}dt = \cos(\omega t_0 - \phi/2)\cdot\frac{(2I)^{1/2}\tau\exp[i\phi/2 - iA\tau^2\omega^2 - \omega^2\tau^2/2]}{[1+\cos\phi\exp(-t_0^2/\tau^2)]^{1/2}}, \tag{14}$$

guarantees that the total pulse energy is preserved for all t_0, ϕ, and A pulse parameters.

The results below are displayed using the dimensionless shaping parameters, $T_0 \equiv t_0/\tau$ for subpulse delay, yielding the number of "teeth" in the spectral "comb," where τ is further parametrized by the W parameter via the relation $\tau = W/|E_1 - E_2|$; the phase angle ϕ, which shifts the spectral comb in frequency space; and A, which determines the linear chirp rate $a_0 = A/[\tau^2(1+4A^2)]$. This type of parametrization allows for the separate control of the amplitude via T_0 and ϕ and the control of the phase via A. Note that the choice $(T_0, \phi, A) = (0, 0, 0)$ corresponds to a transform-limited pulse with temporal profile $\epsilon_s(t) = I^{1/2}\exp[-t^2/(2\tau^2)]$.

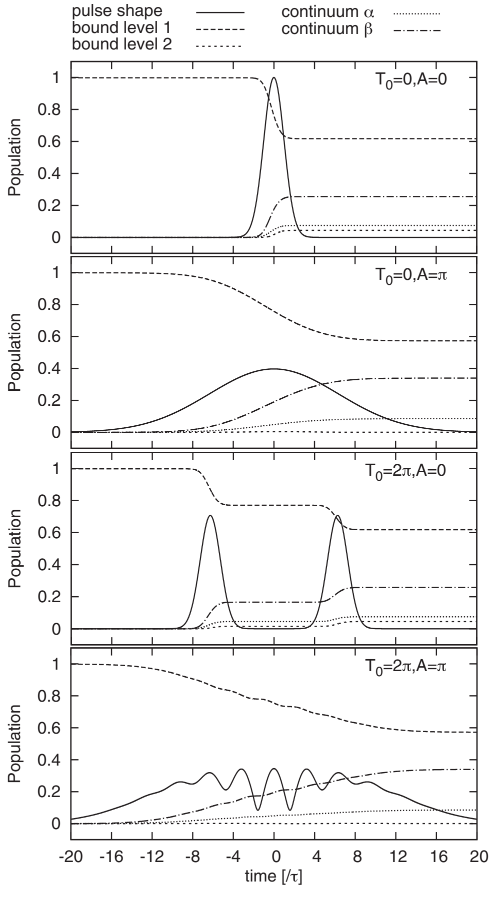

FIG. 2. Sample photoproduct population dynamics for different time delays and chirping parameters. The intensity value is $\mu^2\tau I = 0.01$.

Given the pulse shape, the probabilities of photodissociation (photoisomerization) into the $n = \alpha, \beta$ channels are calculated using Eq. (11). For the $Q = 2$, $q_\alpha = 0.6$,

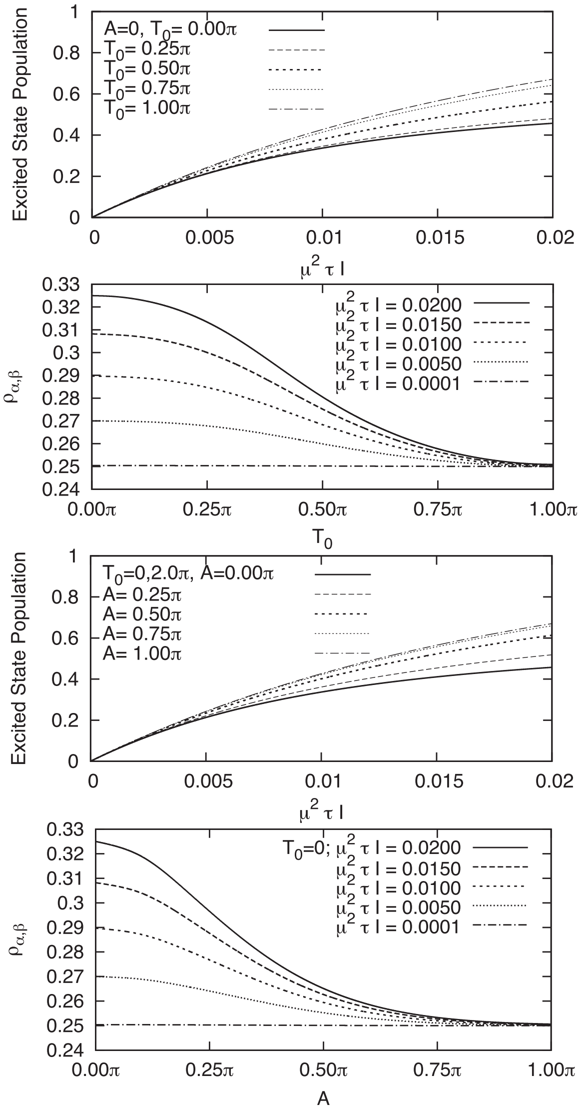

FIG. 3. The photoexcitation yields and branching ratios vs the field intensity. At $\mu^2\tau I \leq 0.03$, the photoexcitation yield becomes more linear due to shaping.

$q_\beta = 1.2$, and $W = 0.5$ case, Fig. 2 shows the probabilities as functions of time. Because of the assumed "flatness" of the continuum, the changes in the probability are rather monotonic in time. Also, having started with state $|E_1\rangle$, state $|E_2\rangle$ is populated by continuum-mediated resonance Raman transitions. Figure 3 displays $P(I)$, the photoexcitation yield given as the total population removed from the bound-state manifold after the pulse is over, with $P(I) = \sum_n P_{E,n}$, where $P_{E,n}$ are obtained from Eq. (10). The phase ϕ is found to contribute negligibly. We see that the curves start saturating after displaying a linear dependence. At moderately strong intensities, (substantial) control over the branching ratio as a function of T_0 and A is clearly in evidence. For example, at intensity values of $\mu^2\tau I = 0.01$–0.02, the yield for the ($T_0 = 0, A = 0$) pulse displays a short bout of linear I dependence followed by the onset of saturation. In contrast, the yield for the ($T_0 = \pi, A = 0$), ($T_0 = 0, A = \pi$), or ($T_0 = 2\pi, A = \pi$) pulses displays a much more protracted linear phase prior to saturation.

In spite of the nearly linear photoexcitation yield for $\mu^2\tau I = 0.01$, the branching ratios exhibit a rather extensive range of control, of about 16% for shaped pulses. This is the main result of this Letter. Even at around $\mu^2\tau I = 0.005$, where all the yield curves are essentially the same and highly linear, the range of branching ratio control is still about 8%, obviously a non-first-order behavior. Only when the intensity approaches zero (e.g., at $\mu^2\tau I = 0.0001$), where the yield approaches zero, too, does the variation in the branching ratio due to shaping disappear.

In order to quantify the visibly evident high degree of linear intensity dependence, we have also calculated $d^2P/dI^2|_{I_0} I_0/[2dP/dI|_{I_0}]$, the ratio between the second-order and the first-order terms in the Taylor series expansion about I_0. Figure 4 shows the degree of nonlinearity calculated in this manner, plotted against $\mu^2\tau I_0$. We see that, until $\mu^2\tau I_0 = 0.02$, where all the curves begin to saturate significantly, pulses whose shapes are defined by ($T_0 = \pi, A = 0$), ($T_0 = 0, A = \pi$), or ($T_0 = 2\pi, A = \pi$) exhibit a greater degree of linearity, as compared to a transform-limited pulse [i.e., ($T_0 = 0, A = 0$)]. Up to $\mu^2\tau I_0 = 0.01$, the nonlinear coefficients of the above pulses are about half their transform-limited values.

The physical reason for this enhanced linearity of the yield with pulse shaping is due to the coherent interplay between the two subpulses. Essentially, the first subpulse creates by a (continuum-mediated) Raman process a

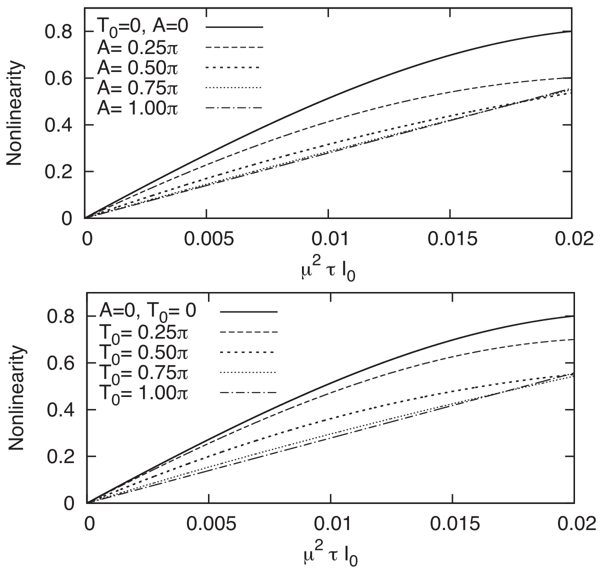

FIG. 4. The nonlinearity of the intensity response curves vs $\mu^2\tau I_0$.

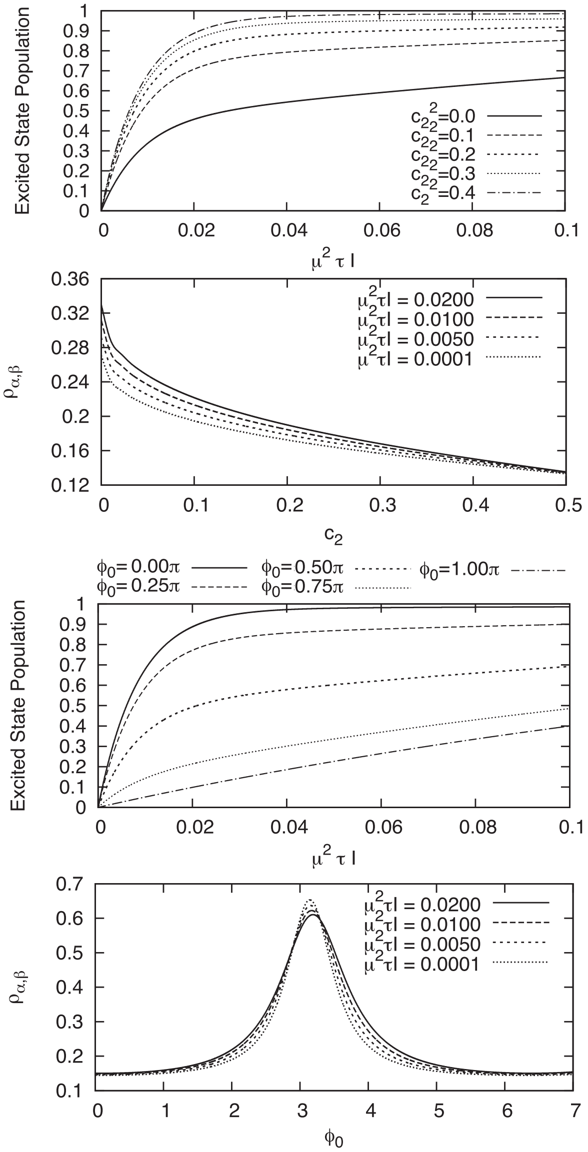

FIG. 5. The intensity response curves for an initial superposition of two bound states $\psi_i = c_1|E_1\rangle + e^{i\phi_0}c_2|E_2\rangle$. The upper two panels are the intensity response and control for $\phi_0 = 0$ and variable c_2; the lower two panels are the response and control at fixed $c_2^2 = 0.4$ and the variable ϕ_0.

superposition of the $|E_1\rangle$ and $|E_2\rangle$ bound states. The second subpulse then dissociates this superposition state in the usual bichromatic control scenario [3,4]. We verify this mechanism by looking at the intensity response (shown in the top panel of Fig. 3) as a function of T_0. As T_0 is increased, the shapes of the curves are seen to be periodically modulated. A similar periodic change of behavior is seen when the chirp parameter A is increased for a fixed value of T_0. However, when we set q_α and q_β to zero, the variations in T_0 or A no longer alter the intensity response curves, nor do such variations affect the branching ratio.

We also examine here the case in which the initial state is composed of a coherent superposition of the two bound states, $c_1|E_1\rangle + e^{i\phi_0}c_2|E_2\rangle$ with $c_1^2 + c_2^2 = 1$, subject to the action of a simple transform-limited excitation pulse, for which ($T_0 = 0, A = 0$). This time, it is the variations in c_2, or the relative phase ϕ_0, that affect the intensity response curves. In Fig. 5, we see changes to the linearity of the curves, now due to changes in the c_2 and ϕ_0 parameters. The variation in the branching ratio, due to changes in these variables, is quite significant. The branching ratios are, however, insensitive to the laser intensity because control is mainly derived from the variation in the initial superposition rather than the field.

In summary, by first developing a simple time-dependent, nonperturbative, model of coherent control of a bound molecular system interacting with a broadband pulse, we are able to probe how pulse shaping affects the intensity dependence of the photoexcitation yield. We have shown that shaped pulses may exhibit a wide range of linear response of the overall yield, even at moderately high intensities. The mechanism responsible for this behavior is bichromatic control in conjunction with continuum-mediated Raman transitions between bound states. Secondly, we have shown that extensive coherent control over the branching ratio can coexist with extended linear intensity regimes. Thus, linear intensity response, which we have shown to occur even for moderately strong pulses where nonperturbative effects are present, is not a necessary indicator for the validity of first-order perturbation theory. Third, it is not necessary to look for environmental effects in explaining the experimental results for the control of the bacteriorhodopsin isomerization channels [6].

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