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Dmitri G. Abrashkevich, Moshe Shapiro, and Paul Brumer

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Dmitri G. Abrashkevich, Moshe Shapiro,[a] and Paul Brumer
Chemical Physics Theory Group, Department of Chemistry, University of Toronto, Toronto M5S 3H6, Canada

Control over the product branching ratio in the photodissociation of Li_2 into $Li(2s) + Li(2p)$ and $Li(2s) + Li(3p)$ channels is explored computationally using the pump–pump coherent control scenario. Extensive control over the $Li(3p)/Li(2p)$ branching ratio is demonstrated as the delay time between the two pulses is varied. The pulse width dependence is examined and better control is found to result from a narrow pump pulse which excites a superposition of only two levels, followed by a broad dissociation pulse. © *1998 American Institute of Physics.* [S0021-9606(98)01707-3]

I. INTRODUCTION

Considerable theoretical[1–4] and experimental[5–14] effort is being devoted to the study of coherent control, where control over the motion of molecules is achieved by manipulating quantum interferences.[1–4] In this paper we describe a theoretical application of the pump–pump coherent control scenario to the two-photon dissociation of Li_2. In particular, control over the product yields of $Li(2s) + Li(2p)$ and $Li(2s) + Li(3p)$ is demonstrated as one varies the time delay between the two pulses and the excitation energy of the pulses. Various versions of this scenario have been developed[3] but we continue to emphasize the extent of control possible with smooth Gaussian pulses. We have successfully applied this method to model systems (e.g., the control of bimolecular $D + H_2$ reaction[15] and to the selective bond breaking in DH_2[3b]) and to the study of electronic branching in the photodissociation of IBr.[16] In all cases, an extensive range of control over product ratios has resulted from varying the detuning of the excitation pulse and the delay between two pulses.

This extension of the pump–pump control scenario to Li_2 is significant in light of recent experiments by Leone and co-workers[17] in which they prepared wave packets in the E electronic state by laser excitation from a single well-defined rovibronic intermediate state. We show below that this initial step can be successfully used in the pump–pump control scenario and hence that Li_2 is well poised for control studies in the laboratory. In addition, Li_2 provides a convenient system for theoretical study insofar as both the potential energy surfaces and the electric dipole moments, necessary for photodissociation studies, are well characterized.[18] For example, control of isotope effects and angular distributions in Li_2 using high intensity lasers has been previously discussed.[19]

The paper is organized as follows. In Sec. II we briefly describe the coherent radiative control methodology via pulse sequencing with narrow-band pump pulses. In Sec. III

we apply the method to control of branching ratios in the Li_2 photodissociation. We summarize our results in Sec. IV.

II. COHERENT RADIATIVE CONTROL VIA PULSE SEQUENCING

Consider a molecule, initially (at time $t = 0$) in the bound state $|E_s\rangle$, which is subjected to two laser pulses.[20] The time dependence of each laser field can be written as

$$\epsilon_i(t) = \frac{\epsilon_i}{2} \exp\{-i(\omega_i t + \delta_i) - \alpha(t - t_i)^2/\Delta_{it}^2\}; \quad i = 1,2, \tag{1}$$

where $\alpha = 4 \ln 2$, ϵ_i is the electric field amplitude of the i-th pulse, t_i is its temporal center position, and ω_i is the carrier frequency of the pulse which is assumed to be Gaussian in shape with FWHM Δ_{it} and overall phase δ_i. The corresponding frequency distribution is given by the Fourier transform of Eq. (1):

$$\epsilon_i(\omega) = (\alpha/2)^{1/2} \frac{\epsilon_i}{\hbar \Delta_{i\omega}} \exp[-\alpha(\omega_i - \omega)^2/\Delta_{i\omega}^2]$$
$$\times \exp\{-i[(\omega_i - \omega)t_i + \delta_i]\}, \tag{2}$$

where $\Delta_{i\omega} = 2\alpha/\Delta_{it}$. The first laser pulse prepares the nonstationary superposition state in the excited electronic state consisting of eigenstates $|E_j\rangle$ with energies E_j of the radiation-free Hamiltonian. At times $t > t_1 + 2\Delta_{1t}$, the wave function of the system can be expanded as,

$$|\psi_b(t)\rangle = c_s|E_s\rangle \exp\left(-i \frac{E_s}{\hbar} t\right) + \sum_j c_j|E_j\rangle$$
$$\times \exp\left(-i \frac{E_j}{\hbar} t\right), \tag{3}$$

where the c_j coefficients are obtained (assuming that the laser field is weak) as[21]

$$c_j = \frac{\sqrt{2\pi}}{i\hbar} \langle E_j|\mu|E_s\rangle \epsilon_1(\omega_{js}), \tag{4}$$

[a]Permanent address: Chemical Physics Department, The Weizmann Institute of Science, Rehovot, 76100, Israel.

where $\omega_{js} = (E_j - E_s)/\hbar$ is the excitation frequency from $|E_s\rangle$ to $|E_j\rangle$ and μ is the electronic transition dipole moment.

Subsequently, the system, in the superposition state [Eq. (3)], is subjected to a second (dissociation) pulse $\epsilon_2(t)$ [see Eq. (1)] which induces transitions to the continuum eigenstates of the excited electronic states. The resultant system wave function can be expanded in the following form:

$$|\psi(t)\rangle = |\psi_b(t)\rangle + \sum_{n,q} \int dE B(E,n,q|t)|E,n,q^-\rangle e^{-iEt/\hbar}.$$

(5)

Here $|E,n,q^-\rangle$ are continuum eigenstates with energy E leading, as $t \to \infty$, to the desired $\{q,n\}$ product of a given electronic state q and a set of rovibrational quantum numbers n, and $B(E,n,q|t)$ are coefficients which are to be determined. The probability of forming product in channel q at energy E is given by[3b]

$$P(E,q) = \sum_n |B(E,n,q|t=\infty)|^2.$$

(6)

Substituting Eq. (5) into the time-dependent Schrödinger equation, using first-order perturbation theory and the rotating wave approximation gives

$$B(E,n,q|t) = (i/\hbar) \int_0^t dt' \langle E,n,q^-|\mu|\psi_b(t')\rangle \epsilon_2(t') e^{iEt'/\hbar}.$$

(7)

Inserting $|\psi_b(t)\rangle$ from Eq. (3) and the form of $\epsilon_2(t')$ in Eq. (6), we obtain

$$P(E,q) = (2\pi/\hbar^2) \sum_n \left| \sum_j c_j \langle E,n,q^-|\mu|E_j\rangle \epsilon_2(\omega_{EE_j}) \right|^2,$$

(8)

where $\omega_{EE_j} = (E-E_j)/\hbar$ and c_j is given by Eq. (4). To obtain the *total* probability to populate arrangement q, it is necessary to integrate $P(E,q)$ from Eq. (8) over the width of the pulse:

$$P(q) = \int_0^\infty dE P(E,q).$$

(9)

In the simplest case, when the width of the first (pump) pulse is wide enough to encompass only two excited levels, the wave function of the superposition state takes the following form:

$$|\psi_b(t)\rangle = |E_s\rangle e^{-iE_s t/\hbar} + c_1|E_1\rangle e^{-iE_1 t/\hbar} + c_2|E_2\rangle e^{-iE_2 t/\hbar}.$$

(10)

Inserting the explicit form of c_j into Eq. (8) and expanding the square gives

$$P(E,q) = (2\pi/\hbar^2)[|c_1|^2 \mu_{1,1}^{(q)} \epsilon_1^2 + |c_2|^2 \mu_{2,2}^{(q)} \epsilon_2^2$$
$$+ 2|c_1 c_2 \epsilon_1 \epsilon_2||\mu_{1,2}^{(q)}|\cos(\omega_{2,1}\tau + \alpha_{1,2}^{(q)}(E) + \phi)],$$

(11)

where $\tau = t_2 - t_1$, $\epsilon_i = |\epsilon_2(\omega_{EE_i})|$, $\omega_{2,1} = (E_2 - E_1)/\hbar$, and ϕ and $\alpha_{1,2}^{(q)}(E)$ are phases defined from the following expressions

$$\langle E_1|\mu|E_s\rangle\langle E_s|\mu|E_2\rangle \equiv |\langle E_1|\mu|E_s\rangle\langle E_s|\mu|E_2\rangle|e^{i\phi},$$
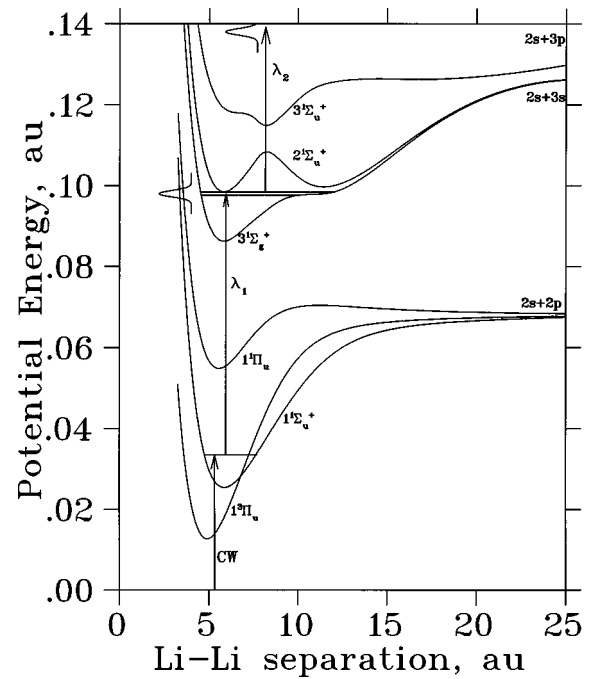
(12)

FIG. 1. Schematic of the pulse sequencing control scheme used in this work. The realistic Li$_2$ potentials used in this work are shown.

$$\mu_{i,j}^{(q)}(E) \equiv |\mu_{i,j}^{(q)}(E)|e^{i\alpha_{i,j}^{(q)}(E)}$$
$$= \sum_n \langle E,n,q^-|\mu|E_i\rangle\langle E_j|\mu|E,n,q^-\rangle.$$

(13)

The essential result is then that the probability $P(q)$ [Eqs. (9), (11)] and therefore the yield of the desired product [i.e., the ratio $P(q)/[\Sigma_{q'}P(q')]$, can be changed by varying the values of the c_j coefficients or by changing the time delay τ between the two pulses. Note in addition that although expressions for both pulses contain absolute phases and absolute times, the phase of the total probability in Eq. (11) depends only on the delay time τ and on molecular phases defined in Eqs. (12) and (13). Results of the $P(q)$ calculations are discussed below.

III. COHERENT CONTROL OF Li$_2$ PHOTODISSOCIATION

Consider then the application of this approach to control branching in the photodissociation of Li$_2$. The computations have been carried out using the realistic potential curves of Schmidt-Mink *et al.*[18] and are shown in Fig. 1. The schematic description of the suggested experiment is also given in Fig. 1. In particular, a cw laser prepares a single rovibrational state of the $A(^1\Sigma_u^+)$ electronic state, which serves as the starting point for the subsequent pump–pump control. In accord with Leone[17] we choose this as A ($v=14$, $J=22$). The pump then lifts the system to the $3\,^1\Sigma_g^+$ state, forming a coherent superposition of states. The subsequent pulse lifts the system above the dissociation energy for the Li($2s$) +Li($3p$), Li($2s$)+Li($3s$), and Li($2s$)+Li($2p$) pairs.[22]

In the computations reported below the rovibrational eigenenergies and the corresponding eigenfunctions in the $A\,^1\Sigma_u^+$ and $E\,^3\Sigma_g^+$ potentials were obtained by the Renor-
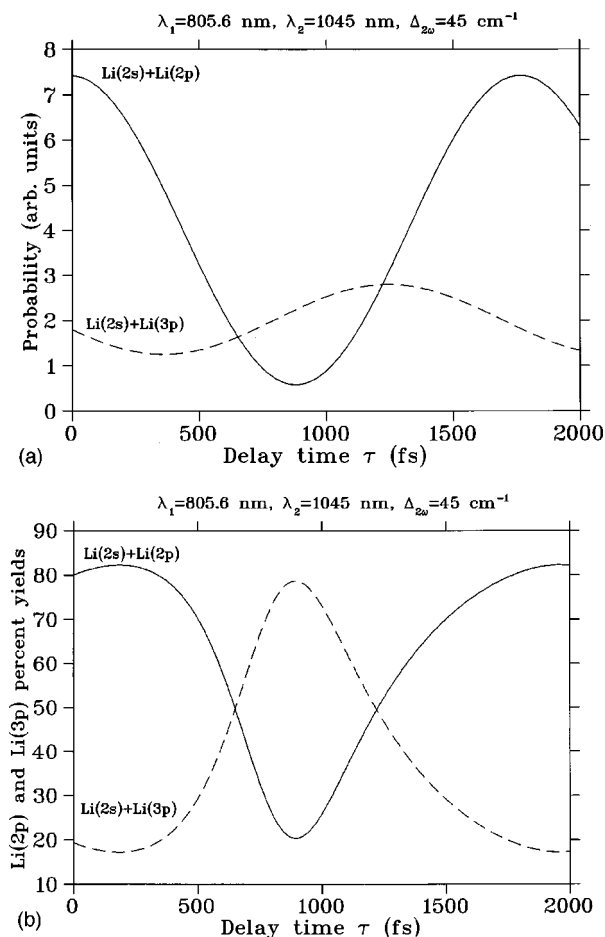
FIG. 2. (a) $P(2p)$ (solid curve) and $P(3p)$ (dashed curve) as a function of the delay time τ as calculated using Eq. (9) with $\lambda_1=805.6$ nm, $\lambda_2=1045$ nm, and pulse widths $\Delta_{1\omega}=36$ cm^{-1} and $\Delta_{2\omega}=45$ cm^{-1}. (b) the Li(2p) and Li(3p) yield ratios in percents as functions of τ. Here the initially created superposition state is between levels $v=14$, $J=21$, and $v=14$, $j=23$ of the E electronic state.

malized Numerov method.[23] The wave functions so obtained were used for the calculation of the Franck–Condon integrals $\langle E_j|\mu|E_s\rangle$ using a Simpson-type integrating quadrature. The bound-free dipole matrix elements $\langle E,n,q^-|\mu|E_i\rangle$ were calculated exactly using the artificial channel method[24] which provides the matrix elements directly in a single calculation involving both the bound and continuum potentials. The relevant electric dipole transition moments and spin-orbit coupling matrix elements between $1\,^1\Sigma_u^+$ and $1\,^3\Pi_u$ electronic states have been taken from Ref. 25.

Consider first the degree of control obtained with the pump laser sufficiently narrow to excite an initial superposition state consisting of the two rovibrational states: ($v=14$, $J=21$) and ($v=14$, $J=23$). Figures 2 and 3 show results for the case where the center of the pump pulse lies in the middle of the $v=14$, $J=21$, and $J=23$ rovibrational levels in the E electronic state and where the laser parameters were chosen as: $\lambda_1=805.6$ nm, $\lambda_2=1045$ nm, $\Delta_{1\omega}=36$ cm^{-1}, and $\Delta_{2\omega}=45$ cm^{-1}. Figure 3 shows the yield in the Li(2s) +Li(3s) channel, which is seen to vary from 0.46% to 1.03%. In all the studies reported below, the yield in this channel was found to never exceed 2% and to be relatively

invariant to changes in τ. For this reason it is ignored in the remainder of the paper.

Figure 2(a) shows the probability of forming Li(2s)+Li(2p) (solid curve) and Li(2s)+Li(3p) (dashed curve) as a function of delay time τ [Eq. (9)] and Fig. 2(b) shows the same results as a percent yield in each channel. The results clearly show an extensive variation of the relative yield of the different products as a function of τ. That is, the Li(2s)+Li(2p) yield varies from 82.2% to 20.4%, and the Li(2s)+Li(3p) yield varies from 17.2% to 78.7%. This corresponds to the change in the yield ratio $R=P(q=2p)/P(q=3p)$ from 4.8 to 0.26. The yield of the Li(2p) product is seen to change more dramatically with τ, a consequence of the fact that the μ_{12}^q associated with the Li(2p) product is approximately three times larger than that associated with the Li(3p) product.

In accord with Eq. (11), the product probability is seen to be periodic, with an approximate period of $T=2\pi/\omega_{2,1}=1773$ fs, which corresponds to the rotational spacing (between $J=21$, 23) $\omega_{2,1}$ of 18.8 cm^{-1}. However, a careful examination of Fig. 2 shows that the yields deviate from a pure cosinelike dependence on τ. This is due to the integration of probability $P(E,q)$ over the dissociation energy E to produce $P(q)$. That is, although each $P(E,q)$ [Eq. (11)] shows a cosine dependence on τ, the presence of $\alpha_{1,2}^q(E)$ makes the integrated probability $P(q)$ [Eq. (9)] deviate slightly from a pure cosine.

Tuning ω_1 so that other nearby pairs of two rovibrational levels were excited was found to lead to equally successful control. For example, consider results (not shown) obtained for $\lambda_1=802.18$ nm (a frequency which excites the $v=15$, $J=21$, and $J=23$ states), with $\lambda_2=1050.81$ nm so that the central two-photon excitation energy is that same as in Fig. 2. In this case, the probability of forming the Li(2s)+Li(2p) channel varies from 82.6% to 25.8%, and in Li(2s)+Li(3p) from 16.8% to 73.2% with an approximate period of 1634 fs. The range of control is therefore comparable to that shown in Fig. 2.

The product ratios can also be controlled by shifting the central frequency of the pump laser, thus altering the c_j coefficients. Sample results are shown in Fig. 4 where we display a contour plot of the Li(2s)+Li(2p) product yield as a function of τ and of the detuning of ω_1 from the middle of the two rovibrational levels ($\omega_{av}=(E_2+E_1)/2\hbar-E_s$). In this case $\Delta_{1\omega}=18$ cm^{-1} and $\Delta_{2\omega}=45$ cm^{-1} with the remaining parameters of the second laser chosen as in Fig. 2(b). In Fig. 4, ω_1 is varied from 806.2 nm to 805 nm, corresponding to the centering of the first pulse on levels E_1 and E_2, respectively. The results indicate a large range of control, from 81% to 20% as one varies τ at fixed pulse detuning. Substantial control is also attained by changing ω_1 at fixed τ (e.g., at 890 fs). The results clearly show, however, that the highest level of control is attained when the wavelength of the first pulse is centered close to E_{av} ($\lambda_1=805.6$ nm). This is because, under these circumstances, the bound–bound dipole matrix elements $\langle E_j|\mu|E_s\rangle$, $j=1,2$ contributing via Eq. (4) have very similar values for the $v=14$, $J=21$, and $J=23$ levels. Tuning the first laser center frequency close to one of the bound states substantially reduces contributions from the
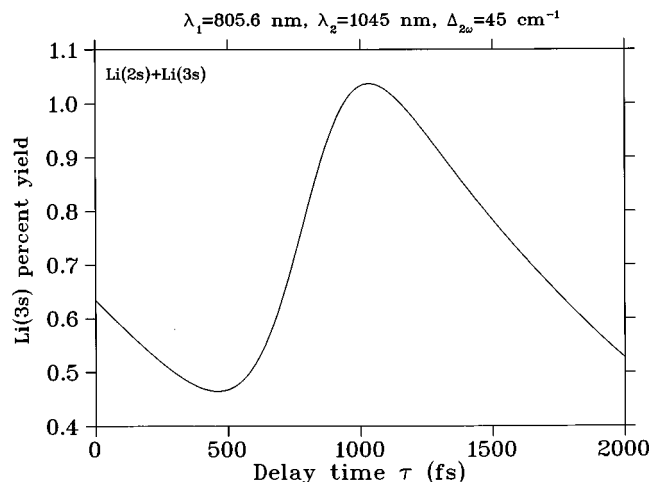
FIG. 3. Li($3s$) yield in percents as a function of the delay time τ calculated with the same laser parameters as in Fig. 2. Note the small ordinate scale.

other state in the superposition, leading to a decrease in control with changes in τ.

As a general observation we found significant changes in the range of control as the center frequency of the dissociation pulse was increased away from the Li($3p$) threshold. For example, Fig. 5 shows results for the case of $\lambda_2 = 1030$ nm where the superposition state was comprised, as above, of $v = 14$, $J = 21$, and $J = 23$ levels of the E state. A comparison with Fig. 2 shows that the range of control over the Li($3p$) product probability increases with increasing energy and that the oscillations of the two products with τ are now more in phase with one another. The net consequence is that the Li($2p$) yield is seen to vary from 52.3% to 9.0%, a substantial reduction in the range of control over that shown in Fig. 2. Hence, an interpretation of what constitutes "improved control" with changes in energy of the second pulse depends on whether one focuses on the photodissociation probability of a particular product or on relative product yield.
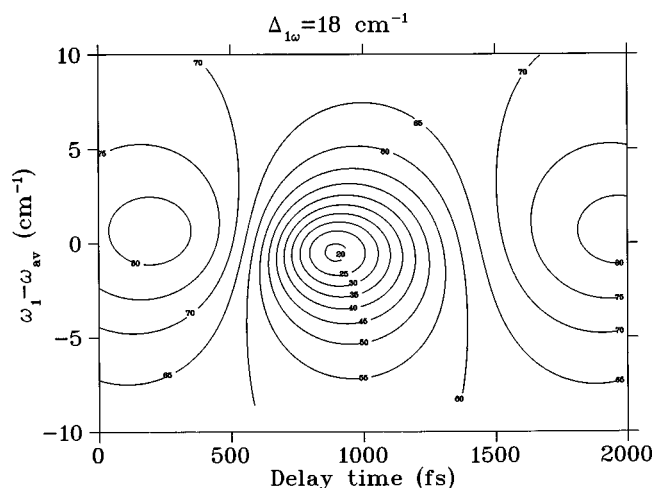

FIG. 4. Contour plot of the Li($2p$) yield as a function of the detuning of the pump pulse $\omega_1 - \omega_{av}$ and the delay time τ. The initially created superposition state is between levels $v = 14$, $J = 21$, and $J = 23$. Laser parameters are given in the text.
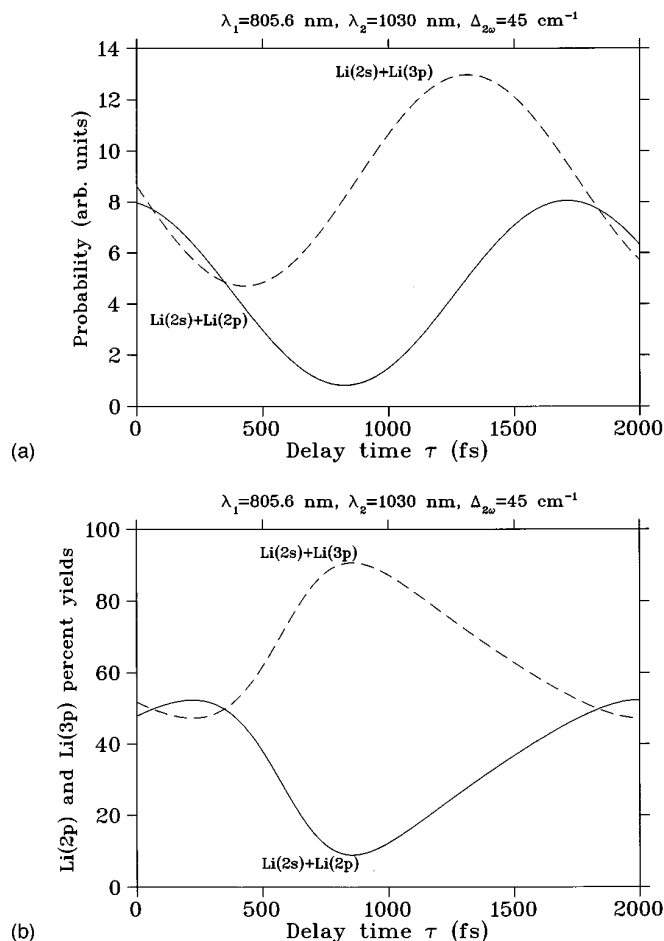

(a)

(b)

FIG. 5. As in Fig. 2, but with $\lambda_2 = 1030$ nm.

Varying the width of the dissociation pulse was found to have a substantial effect on product control. For example, results for $\Delta_{2\omega}$, the FWHM of the second pulse equal to 20 and 95 cm^{-1} are presented in Figs. 6 and 7, for comparison with the results for $\Delta_{2\omega} = 45$ cm^{-1} in Fig. 2(a). Clearly, the largest range of control is obtained for largest $\Delta_{2\omega}$
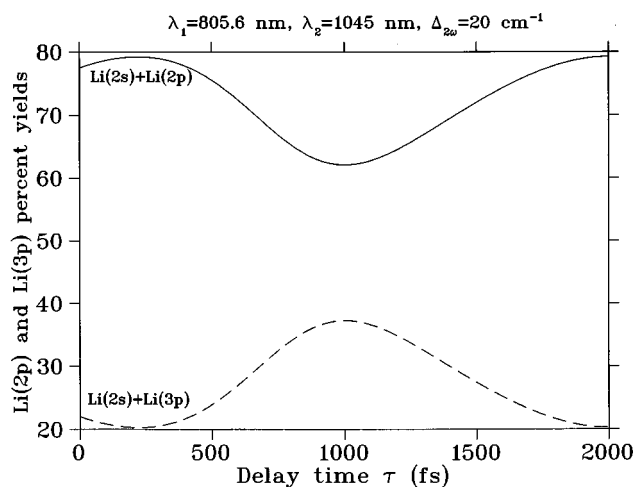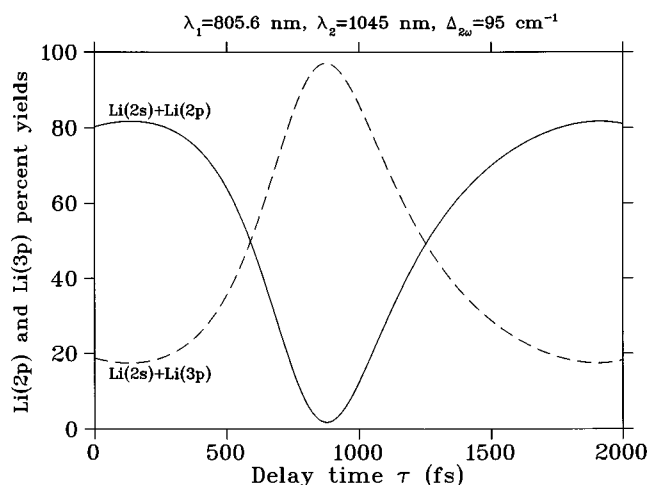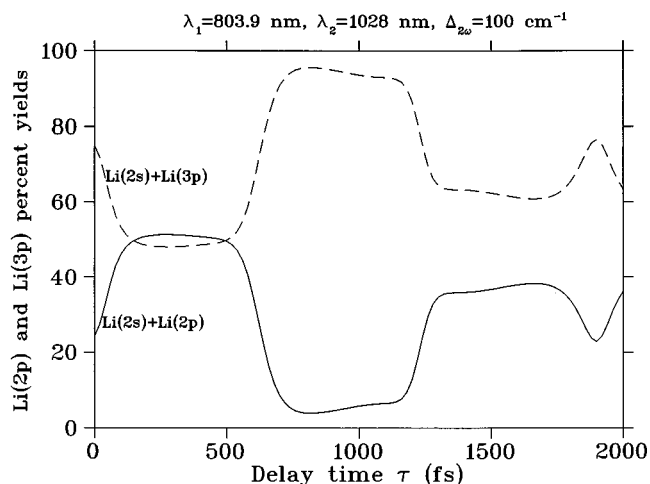

FIG. 6. As in Fig. 2(b), but with $\Delta_{2\omega} = 20$ cm^{-1}.

λ_1=805.6 nm, λ_2=1045 nm, $\Delta_{2\omega}$=95 cm^{-1}

FIG. 7. As in Fig. 2(b), but with $\Delta_{2\omega}=95$ cm^{-1}.

λ_1=803.9 nm, λ_2=1028 nm, $\Delta_{2\omega}$=100 cm^{-1}

FIG. 8. Control results with broader first pulse. The yield ratios of Li($2p$) (solid curve) and Li($3p$) (dashed curve) as a function of τ as calculated using Eq. (9) with wavelengths $\lambda_1=803.9$ nm and $\lambda_2=1028$ nm and pulse widths $\Delta_{1\omega}=60$ cm^{-1} and $\Delta_{2\omega}=100$ cm^{-1}. The superposition state consists of $v=14$, $J=21$, and $J=23$, and $v=15$, $J=21$, and $J=23$ levels.

(95 cm^{-1}). In this case the probability of forming Li($2s$)+Li($2p$) can be changed from 81.7% to 1.8% [with the Li($2s$)+Li($3p$) probability varying from 17.4% to 97.1%] as τ is varied. The dramatic increase in control for broader dissociation laser pulse is a result of the fact that increasing the width reduces contributions to the photodissociation from uncontrollable (so-called satellite) regions. These satellite energy regions are those where $\epsilon_2(\omega_{EE_1}) \ll \epsilon_2(\omega_{EE_2})$ or $(\omega_{EE_1}) \gg \epsilon_2(\omega_{EE_2})$ so that dissociation occurs due to one route only. Under these circumstances photodissociation from these energies is not controlled, diminishing the overall possible range of control.

Note that to increase Δ_2 beyond 95 cm^{-1} requires that the center frequency of the pulse be increased correspondingly to ensure that the dissociation energy is above the Li($2s$)+Li($3p$) threshold [e.g., the center of the 1045-nm pulse is 109 cm^{-1} above the ($2s+3p$) threshold]. Studies of such cases show no improvement over the range of control achieved in the $\Delta_{2\omega}=95$ cm^{-1} case above.

Finally, we examine the effect of exciting more rovibrational levels in the E electronic state by using a broader pump pulse. Results of calculations for pulses with $\Delta_{1\omega}=60$ cm^{-1} and $\Delta_{2\omega}=100$ cm^{-1} are shown in Fig. 8. The superposition state prepared by the first pulse consists of the $v=14$, 15, and $J=21$, 23 levels, where the pulse is centered half-way between the $v=14$, $J=21$, and $v=15$, $J=23$ ($\lambda_1=803.88$ nm) levels. The resultant behavior of $P(q)$ is more complicated than the previous cases since more than two terms are included in sum over j in Eq. (8). Interestingly, we find that overall control is reduced with increasing $\Delta_{1\omega}$. That is, in this case the yield in the Li($2s$)+Li($2p$) channel only changes from 51.4% to 2.6%, a much smaller control range than in the comparable (narrower pump pulse) case in Fig. 7. Shifting ω_1 from ω_{av} does not increase the range of control substantially as seen in the contour plot of the Li($2p$) yield as a function of $\omega_1-\omega_{av}$ (ω_{av}=803.88 nm) and τ (Fig. 9). Adding additional levels to the initial superposition state by pumping with a $\Delta_{1\omega}=100$ cm^{-1} resulted in slightly more

complicated behavior of $P(q)$ as a function of τ, and an even further small reduction in the extent of control.

IV. SUMMARY

In this paper we have applied the pump–pump coherent control scenario to alter the the relative yield of products in the photodissociation of Li$_2$ into Li($2s$)+Li($2p$) and Li($2s$)+Li($3p$). The dependence of control on various parameters such as pulse width and central frequency tuning has been studied. Results show that considerable control is possible using very simple pulses which prepare an initial superposition of two rotational levels. Broadening the initial pump pulse so that it excites more levels results in a reduction in control. We have deliberately chosen smooth Gaussian pulses to avoid extensive pulse shaping. However, computations with more complex pulses as well as with weak field optimal control theories can be readily performed, and
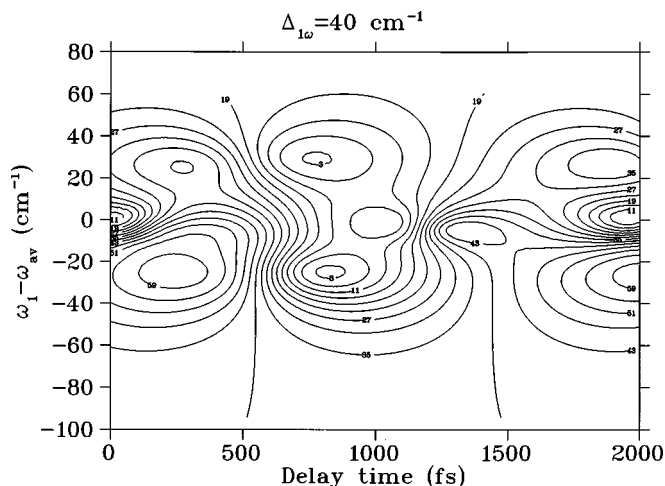
$\Delta_{1\omega}$=40 cm^{-1}

FIG. 9. Computed control over the Li($2p$) yield as a function of the detuning of the first pulse $\omega_1-\omega_{av}$ and the delay time τ with $\Delta_{1\omega}=40$ cm^{-1} and other laser parameters as in Fig. 8. The initially created superposition state is between levels $v=14$, $J=21$, and $J=23$ and $v=15$, $J=21$ and $J=23$.

effects of partial coherence can be included[26] in order to compare or to motivate experimental studies. To this end we note that recent experimental developments by Papanikolas *et al.*[17] in preparing coherent states in Li$_2$, and by Shnitman *et al.*[11] in product detection in the photodissociation of alkali dimers, suggest that the control experiments are possible by the direct extension of current technologies.

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