

The Use of Pulse Shaping To Control the Photodissociation of a Diatomic Molecule: Preventing the Best from Being the Enemy of the Good

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Previous work has shown that selectivity of product formation in the dissociation of a polyatomic molecule can be enhanced through the application of a pair of ultrashort laser pulses separated by a controlled delay. For the practical application of this Tannor-Rice scheme for selective photochemistry, the effects of changes in the laser temporal pulse shapes must be understood. To this end, we treat here the effects of pulse shaping for the Tannor-Rice scheme as applied to simple diatomic molecules. Since the molecular dynamics of diatomic systems are considerably simpler than those for polyatomics, the detailed effects of the laser pulses can be easily examined. Two systems of practical interest have been studied: (1) molecular I_2 , and (2) a van der Waals complex of Hg and Ar. Optimal control theory is used to generate a pulse shape which provides enhanced reaction yield. Results of constrained optimizations which limit the laser pulses to experimentally achievable shapes are also reported. These results demonstrate the importance of pulse shaping in the enhancement of selectivity of product formation in a chemical reaction. They also show that achievable approximations to the optimum pulse shape provide valuable enhancement of the product yield.

I. Introduction

Recent theoretical work has shown that it is, in principle, possible to influence the selectivity of product formation in a chemical reaction by use of external resonant electric fields which modify the molecular dynamics. The approaches proposed fall into two categories emphasizing, respectively, the use of time-independent and time-dependent control fields.

Brumer and Shapiro¹⁻⁴ have shown that control of product selectivity can be achieved if two degenerate exit channel wave functions can be made to interfere constructively or destructively, as a result of two or more simultaneous coherent excitation routes, to the degenerate final states. This control scheme focuses attention on the properties of eigenstates of the system and its implementation requires controlling the phase difference between two continuous-wave laser sources driving the different excitation routes.

Tannor and Rice,⁵ and Tannor, Kosloff, and Rice⁶ have shown that controlling the duration of propagation of a wavepacket on an excited-state electronic potential energy surface, by controlling the time delay between pump and dump pulses, can be used to selectively influence product formation on the ground-state potential energy surface. This two-pulse experiment will be referred to as the Tannor-Rice scheme for selective photodissociation. Rabitz and co-workers⁷⁻⁹ have shown that it is possible to design optimally shaped pulses that will guide the evolution of a system from a chosen initial state to a selected final state in a specified time interval. Their work, which has been applied only to reactions on one potential energy surface, has been extended by Kosloff, Rice, Gaspard, Tersigni, and Tannor¹⁰ to the design of optimally shaped pulses that utilize modulation of wavepacket evolution on an excited-state potential energy surface to influence the selectivity of product formation on the ground-state potential energy surface. This control scheme focuses attention on the temporal and spatial

evolution of wavepackets on one or more potential energy surfaces. In the simplest situation, in which the shaping of the control field pulses is forsaken, implementation of this scheme requires the development of techniques to control both the temporal separation and the relative phases of the pump and dump pulses. The achievement of optimal control of the selectivity of product formation, which will typically involve generation of a pulse with complicated spectral content and time signature, requires further development of femtosecond pulse shaping technology, as exemplified by the work of Heritage et al.¹¹⁻¹⁴ and Warren and co-workers.¹⁵⁻¹⁷

With present day technology, the most convenient way to excite multiple molecular transitions, simultaneously and coherently, is to use ultrashort, transform limited, optical pulses. The wavepackets so generated have a particularly simple form in the limit that the excitation is of infinitesimal duration; in that limiting case the spectral content of the wavepacket spans all states of the system connected to the initial state with nonvanishing transition moments, and the amplitudes of the states contributing to the wavepacket do not depend on the nuclear dynamics. However, infinitesimally short laser pulses cannot be generated, and pulses shorter than 50 fs are difficult to generate reliably. A 50-fs Gaussian pulse has a spectral bandwidth of only 300 cm^{-1} , which is not large enough to excite a great number of the states of most molecules. Moreover, the amplitudes of the components of the typical wavepacket generated by a 50-fs pulse are influenced by coupling to nuclear motions with comparable periods, and hence so is the evolution of the wavepacket. We must then expect that with fixed shape 50-fs pump and dump pulses we will achieve only a lower limit to the control of selectivity of product formation.

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In this paper we address three problems:

(i) What are the requirements for an experimental demonstration of the two-pulse Tannor–Rice scheme when applied to a real reaction?

(ii) What improvement in product formation is generated when optimally shaped pulses replace the fixed shape pump and dump pulses used in (i)?

(iii) Is there a simple approximation to the optimal pulse shape found in (ii), one which can be generated with present day technology?

Our approach to problem (i) is to examine the modulation of the product yield in the photodissociation of a diatomic molecule as a function of the delay between pump and dump pulses. Although controlling the amount of product formed in the photodissociation of a diatomic molecule does not demonstrate the enhancement of the formation of a particular reaction product selected from a set of possible reaction products, it does depend on the same features of the wavepacket dynamics and wavepacket interference. The real reactions we have studied are the photodissociation of the van der Waals molecule HgAr and the photodissociation of I₂. HgAr is very nearly an ideal vehicle with which to study the simplest version of the Tannor–Rice scheme in that the level spacings are small, so that even 80-fs pump and dump pulses can generate marked modulation of the photofragment population as a function of pump–dump delay. In contrast, I₂ has a large enough vibrational frequency that the wavepacket generated by a 50-fs pulse has only a few components. In this case the use of pump–dump pulse separation to modulate the yield of the photofragment reaction leads to small but measurable effects.

Our approach to problem (ii) is to carry out an optimization of the pulse shape using the method of Kosloff et al.¹⁰ It is found that the use of optimally shaped pulses in place of fixed shape pump and dump pulses increases the photofragmentation yield per pulse by many orders of magnitude. The calculated pulses shapes are not overwhelmingly complicated, but they are also not simple. Were attention to be focused solely on using the optimally shaped pulse to control the photofragmentation yield, we would generate the classical conundrum of the best being the enemy of the good. Aside from verifying our theoretical analysis, it serves little purpose to predict that a photofragmentation reaction can be efficiently driven by a specially shaped pulse if that shaped pulse is too complicated to produce in the laboratory. Accordingly, we argue that the use to which we put the calculated optimal pulse shape is as important as its calculation.

Our approach to problem (iii) is to use the optimally shaped pulses found in (ii) to identify the spectral content and durations of the principal components of the optimal field. We then construct simple approximations to the optimally shaped pulses by superposing a few Gaussian pulses selected to have spectral content and temporal widths which are close to those of the major Fourier components of the optimally shaped field. We find that these approximations to the optimally shaped pulses suffice to generate photofragmentation yields within a factor of 2 of those generated by the optimally shaped pulses. Furthermore, we show that those enhanced yields are not appreciably degraded by rotational dephasing.

The calculations described in this paper are for real systems. Moreover, these systems have been chosen keeping in mind the limitations of current femtosecond laser technology. We have, in fact, designed experiments which will test the predictions of the calculations reported.

II. Qualitative Considerations

As already mentioned, we shall analyze the effectiveness of controlling the photofragmentation of HgAr and I₂ by altering the time delay between pump and dump pulses with fixed (Gaussian) shape, and by shaping the pulses. The relevant potential energy curves for the several electronic states of interest in these molecules are shown in Figure 1.

In keeping with the notion that we are designing real experiments, we propose initiating each of the photofragmentation re-

TABLE I: Morse Potential Parameters^a

	ω_e , cm ⁻¹	D_e , cm ⁻¹	r_e , Å	electronic energy, cm ⁻¹	ref
HgAr A state	39.6	369.0	3.38	39183	18
HgAr C state	112.0	1560.0	2.81	60930	19
I ₂ X state	214.5	12439.4	2.6663	0	20, 21
I ₂ B state	125.69	5168.14	3.0247	15769	22

^aHgAr reduced mass: 33.4 u. I₂ reduced mass: 63.5 u.

actions from an electronically excited state. This choice of initial state generates a minor experimental complication in that the initial state must be prepared by laser excitation. Both HgAr and I₂ have transitions in convenient spectral regions which are strong enough to saturate with quite modest laser power, so the initial (excited) state can have a very large concentration. Our choice of initial state also generates a major experimental simplification in that it makes possible the monitoring of the reaction yield by spontaneous emission, since the products formed are electronically excited Hg or I atoms. In the case of photofragmentation of HgAr, such a detection scheme is advantageous because of the expected large background of ground-state Hg and Ar atoms in the supersonic jet in which the van der Waals molecule is formed. In the case of photofragmentation of I₂, the major gain is that it is much easier to detect electronically excited I atoms than ground-state I atoms.

Note that for the I₂ system we have selected as the initial state a vibrationally excited level. This selection was made so that the largest Franck–Condon factors to the X state levels correspond to the strongly anharmonic portion of the potential energy curve, with the consequence that the vibrational motion is slow enough (~400-fs period of motion) to be resolved with typical laser technology. The wavelength needed to excite the (B, $v' = 34$) ← (X, $v'' = 0$) transition is also fortuitously near the maximum of the B ← X electronic absorption spectrum.

To obtain a qualitative picture of the results to be expected from these experiments, we have carried out Wigner swarm calculations for the Tannor–Rice pump–dump pulse photodissociation scheme for each of the systems mentioned above. The results are shown in Figure 2. Morse potential energy surfaces were used for all states involved and the parameters used are displayed in Table I. The calculations were carried out by approximating the initial wave function as a swarm of classical points with distributions of initial positions and momenta given by the Wigner distribution. The pump pulse is assumed to instantaneously transfer that initial distribution of points to the second potential energy surface, where they propagate according to classical mechanics. For any given delay, the dump pulse transfers these points back to the initial surface. In general, only a fraction of the points will have acquired enough kinetic energy on the second potential energy surface to dissociate when projected back to the initial potential energy surface. The weighted fraction of Wigner swarm particles that do in fact dissociate is plotted as a function of pulse delay in Figure 2.

The most significant feature of the calculations displayed in Figure 2 is the modulation of the probability of dissociation as a function of delay. We note that there is a high probability for dissociation (a dissociation window) at roughly 400-fs intervals in both systems. The pattern for I₂ has a smaller amplitude of modulation than for HgAr due to the extended initial wave function used in that system. The results illustrated in Figure 2 will be used in the following analysis to select parameters for the initial laser field in the calculation of the optimal pulse shape. That is, from this figure, one can select the appropriate delay between short laser pulses so as to enhance the probability of dissociation. In addition, transition frequencies can also be predicted, since in this model the kinetic energy of the Wigner swarm particles is conserved upon transfer between potential energy surfaces.

III. General Theory

We now briefly outline the optimal control theory approach to optical pulse shaping. The details are given in Appendix A.

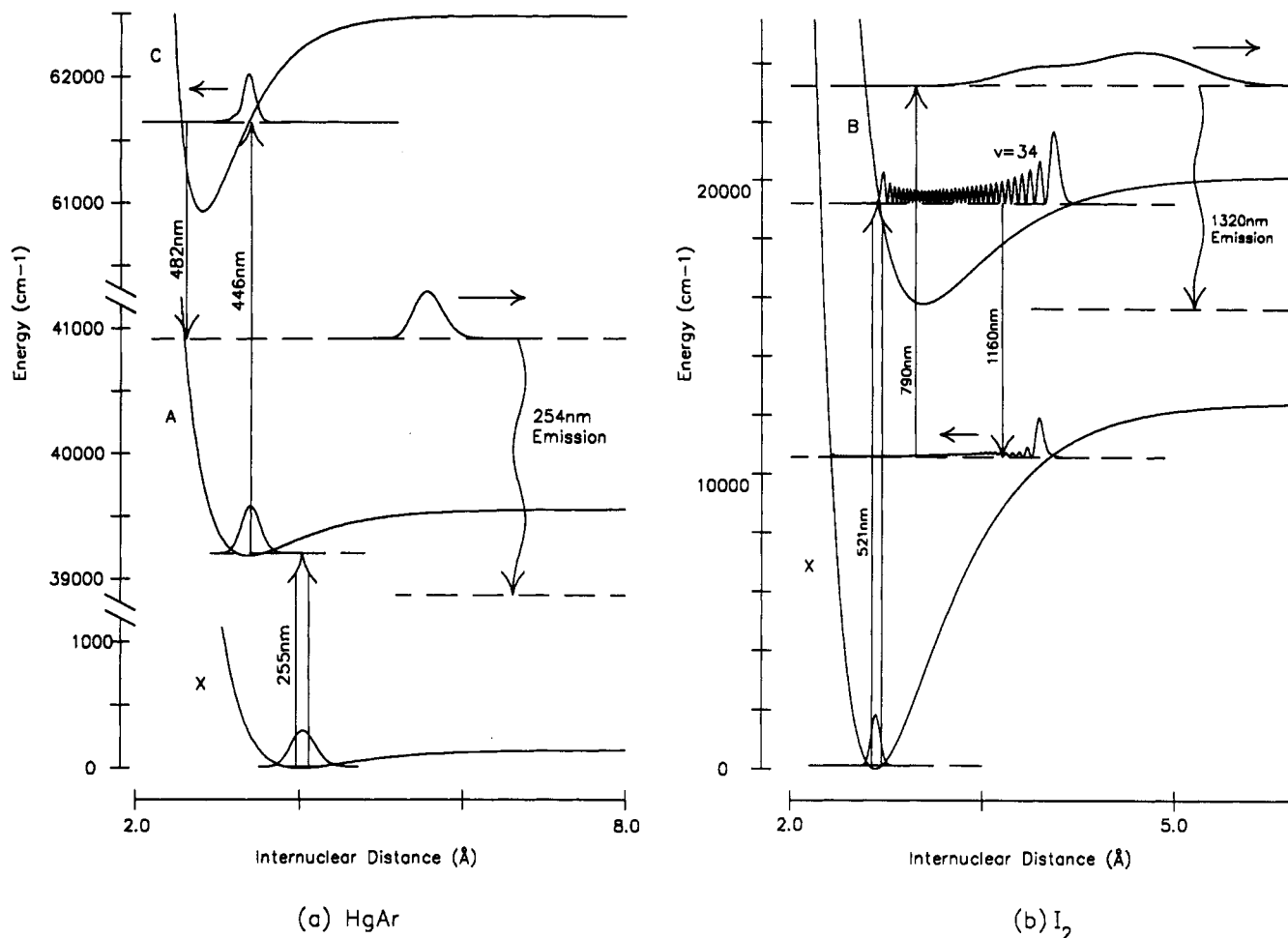


Figure 1. Potential energy surfaces for (a) HgAr and (b) molecular iodine. The double arrows correspond to resonant continuous-wave excitation.

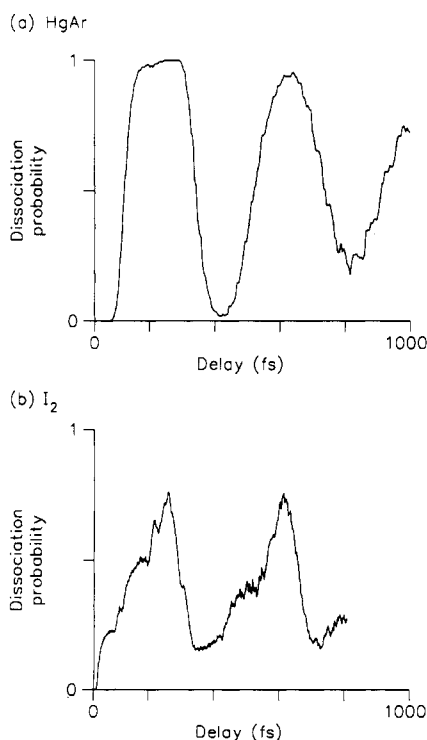


Figure 2. Probability of dissociation for (a) HgAr and (b) molecular iodine as calculated by a Wigner swarm simulation.

We will consider the simple chemical model defined by two potential energy surfaces. One of the surfaces is used to mediate the reaction on the other surface. The equation of motion in our

system is the time-dependent Schrödinger equation ($\hbar = 1$ throughout)

$$i\partial_t \Psi(\vec{x}, t) = \hat{H} \Psi(\vec{x}, t) \quad (\partial_t \equiv \partial/\partial t) \quad (3.1)$$

In the semiclassical and adiabatic approximation

$$\hat{H} = \hat{H}(t) = \begin{pmatrix} \hat{H}_u & V_{gu} \\ V_{ug} & \hat{H}_g \end{pmatrix} = \begin{pmatrix} \hat{H}_u & \mu(\vec{x}) \mathcal{E}(t) \\ \mu(\vec{x}) \mathcal{E}(t) & \hat{H}_g \end{pmatrix} \quad (3.2)$$

and

$$\Psi = \begin{pmatrix} \psi_u \\ \psi_g \end{pmatrix} \quad (3.3)$$

The subscript g refers to the "ground"-state potential energy surface and u, correspondingly, to the "upper"-state potential energy surface. Of course, $\hat{H}_i = \hat{T}_i + V_i$ where $\hat{T}_i = \hat{p}^2/2m$ is the kinetic energy operator and V_i is the corresponding potential energy. μ is the negative of the transition dipole operator and $\mathcal{E}(t)$ represents the amplitude of the classical electric field.

The first step in our optimal control theory approach is to specify the desired physical objectives. As we are interested in the ground-state wave function at some final time t_f , we first define the objective functional as a projection of the final state of the system

$$I = \langle \Psi_f | \hat{P} | \Psi_f \rangle \quad (3.4)$$

where $\hat{P}$ is a projection operator for the selected product and Ψ_f is the wave function at the time t_f .

One of our (chosen) constraints is that the energy of the electric field is to be conserved in the optimization process:

$$\int_{t_0}^{t_f} \mathcal{E}^2(t) dt = E \quad (3.5)$$

A second necessary constraint is that the system always satisfy the equation of motion in (3.1). These two constraints introduce two Lagrange multipliers λ and Φ , respectively. In analogy with Ψ , Φ is a two-component function defined by

$$\Phi = \begin{pmatrix} \phi_u \\ \phi_g \end{pmatrix} \quad (3.6)$$

and the objective functional may be written as

$$I = \langle \Psi_f | \hat{P} | \Psi_i \rangle + i \int_{t_0}^{t_f} (\langle \Phi | i\partial_t - \hat{H} | \Psi \rangle - \text{c.c.}) dt + \lambda \left[\int_{t_0}^{t_f} \mathcal{E}^2(t) dt - E \right] \quad (3.7)$$

where c.c. stands for complex conjugate. In Appendix A we show how (3.7) leads to the following coupled sets of equations to be solved:

$$i\partial_t \Psi(x, t) = \hat{H} \Psi(x, t) \quad (3.8)$$

$$i\partial_t \Phi = \hat{H} \Phi \quad (3.9)$$

$$|\Psi(t_0)\rangle = \begin{pmatrix} 0 \\ \psi_g(t_0) \end{pmatrix} \quad (3.10)$$

$$|\Phi(t_f)\rangle = \hat{P} |\Phi(t_f)\rangle \quad (3.11)$$

which are further linked by the equation for the optimal field $\mathcal{E}$

$$\mathcal{E}(t) = O(t)/\lambda \quad (3.12)$$

where

$$O(t) = \text{Im} (\langle \psi_u | \mu | \phi_g \rangle + \langle \psi_g | \mu | \phi_u \rangle) \quad (3.13)$$

The Lagrange multiplier λ is determined by substituting (3.12) into (3.5), giving

$$\lambda = \pm \left((1/E) \int_{t_0}^{t_f} O^2(t) dt \right)^{1/2} \quad (3.14)$$

In Appendix B we show how the formalism described must be modified if we restrict the electric field to a given form, specified by a set of parameters to be determined. In particular, we consider constraining the form of the electric field to a pair of laser pulses. Generalization of the formalism to allow more complex constraints is straightforward.

IV. Numerical Methods

We now describe an iterative algorithm for the self-consistent determination of the optimal $\mathcal{E}(t)$, as given by (3.12), subject to satisfying the equations of motion for Ψ and Φ ; and also the similar algorithm corresponding to the restricted two-pulse electric field. The full set of equations to be solved is given in (3.8)–(3.14) and also (B.3) for the restricted two-pulse electric field.

The iterative numerical procedure for calculating the self-consistent solution to (3.12) has the following steps:

- Make an initial guess for the electric field.
- Integrate the Schrödinger equation

$$i(\partial \Psi / \partial t) = \hat{H}(t) \Psi(t) \quad (4.1)$$

forward to final time t_f , starting from the appropriate initial state of the system.

(c) As specified by eq 3.11, apply the projection operator that selects the wanted product to $\Psi(t_f)$, and obtain the value of $\Phi(t_f)$. This $\Phi(t_f)$ is then regarded as an initial value for the backward propagation.

(d) Propagate Φ , as well as Ψ , backwards in time using the Schrödinger equation for both wave functions (3.8)–(3.9).

(e) During this propagation calculate the overlap function $O(t)$ according to (3.13).

(f1) *For the fully optimized electric field:* An improved field is generated by using the previous field and the overlap function,

$O(t)$. In some (every 5–10) steps a totally new field is generated from $O(t)$ as in (3.12), but in most steps the conjugate gradient method given by Tersigni et al.²³ is used for accelerated convergence. A negative value of λ is calculated from (3.14). Apply the new field to the system and start the next iteration from (b).

(f2) *For the optimized restricted electric field:* Calculate the integrals in (B.3) and (B.4) using a negative value of λ , calculated from (3.14). Apply (B.9) to get a new set of parameters, apply the new field to the system, and start the next iteration from (b). However, if the change in parameters is “too big”, the change is scaled down.

The problem is assumed to be solved when the specified convergence criterion is met or when the amount of dissociating wavepacket reaches a given value.

The numerical solution of the time-dependent Schrödinger equation is carried out using a short iterative Lanczos propagation scheme together with the fast Fourier transform method for evaluating the kinetic energy. This scheme is fast and accurate and has no difficulty with time-dependent Hamiltonians.²⁴ The integration routine has been tested by using two harmonic surfaces and a constant electric field, that is

$$\mu \mathcal{E}(t) = k \quad (4.2)$$

In that case we have analytic expressions for the amplitude (and phase) on each surface. We have found very good agreement between numerical and analytical results for k values comparable to the parameters used in the calculations to be described below.

V. Results: Optimal Pulse Shapes

The model used in the calculations discussed below involves two electronic states. The potential energy surface for each state is a one-dimensional Morse function taken from the literature (see e.g. ref 25 for a review of Morse functions and refs 25 and 26 for efficient and accurate methods of calculation). The Morse parameters are summarized in Table I. We assume that at $t = 0$ the wave function is an eigenfunction of a specific vibrational state.

The “target” wave functions are chosen to be complex Gaussian wavepackets of the form

$$\chi(R) = \left(\frac{2}{\pi \delta_R} \right)^{1/4} \exp(-(R - R_{\text{cent}})^2 / \delta_R + ip_0(R - R_{\text{cent}})) \quad (5.1)$$

The classical coordinate R_{cent} and momentum p_0 give the central location of $\chi(R)$ in phase space. δ_R gives the spatial spread of the wavepacket and R_{cent} is chosen such that it is close to the end of the grid while not giving any “waste” of wave function passing the grid at late times in the forward time propagation. δ_R is chosen such that the width of the wavepacket is of the same order as suggested by preliminary calculations with Gaussian laser pulses. The final time is also chosen using considerations derived from preliminary calculations. p_0 is chosen such that the kinetic energy of the wavepacket is of the same order as the dissociation energy.

The initial guess for the electric field is the sum of two Gaussian pulses, each of the form

$$\mathcal{E}_j(t) = A_j \exp(-\alpha_j(t - t_j)^2) \cos(\omega_j t + \varphi_j) \quad (5.2)$$

The values of these parameters were selected by analysis of the Wigner swarm calculations of section II. The pulse durations were chosen to correspond to those readily achievable experimentally.

We take μ , the negative of the transition dipole operator, to be independent of the internuclear distance in our calculations.

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TABLE II: Parameters for HgAr and I₂

	HgAr	I ₂
time parameters		
initial time (<i>t</i> ₀)	0	0
final time (<i>t</i> _f)	36000 au (871.2 fs)	34000 au (822.8 fs)
no. of time steps	80001	80001
grid parameters ^a		
<i>R</i> _{min}	3.5 a ₀ (1.9 Å)	3.73 a ₀ (1.97 Å)
<i>R</i> _{max}	20.0 a ₀ (10.6 Å)	17.5 a ₀ (9.26 Å)
no. of points	512	512
target parameters		
<i>R</i> _{cent}	13.0 a ₀ (6.88 Å)	14.0 a ₀ (7.41 Å)
δ _R	0.5 au (0.14 Å ²)	0.8 au (0.22 Å ²)
ρ ₀	26.36 au (5.18 × 10 ⁻¹⁸ g cm/s)	50.0 au (9.98 × 10 ⁻¹⁸ g cm/s)
total energy ^b	0.001 au	0.001 au
total energy ^c	1.9 mJ/cm ²	20 mJ/cm ²
electronic trans moment	3.34 D ²⁷	1.0 D ²⁸

^a 1 a₀ = 4πε₀ħ²/(me²) = 0.529 × 10⁻¹⁰ m is the Bohr radius. ^b It is actually $\int_0^{t_f} (\mu \mathcal{E}(t))^2 dt$, that is given here. ^c Given the value above, and the electronic transition moments below.

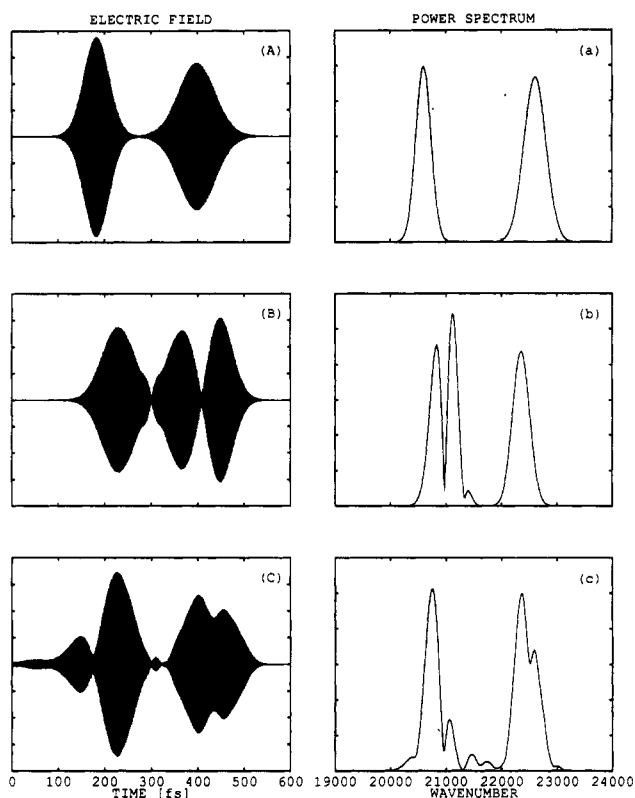


Figure 3. Electric fields for HgAr dissociation: (A) initial guess; (B) after one iteration; and (C) after 14 iterations. (a)–(c) show the corresponding power spectra (absolute values).

Parameters for the I₂ and HgAr calculations are given in Table II.

²⁰²Hg⁴⁰Ar. We examine first the dissociation of the van der Waals molecule HgAr in its excited electronic A state, using the higher excited C state as the mediating state as illustrated in Figure 1a. For this system we describe some of the results obtained when the full optimization scheme is used, and also the results when the restricted electric field, including only two Gaussian pulses, is used.

The initial guess for the electric field is shown in Figure 3A, while the field after one iteration is shown in Figure 3B and the (partially optimized) field after 14 iterations in Figure 3C. Figure 4 shows the initial and target wave functions, while Figure 5 shows the wave functions at the final time *t*_f corresponding to the electric fields in Figure 3A–C. Power spectra corresponding to the electric fields in Figure 3A–C are shown in Figure 3a–c. The power spectra are the Fourier transforms of the electric fields; note that

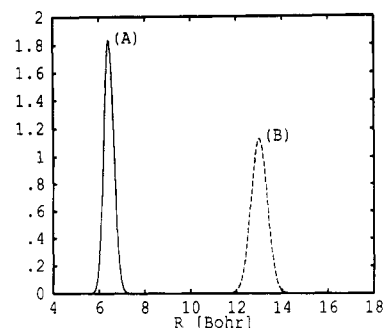


Figure 4. (A) Initial wave function (*ν* = 0), and (B) target wave function. Both are numerically squared.

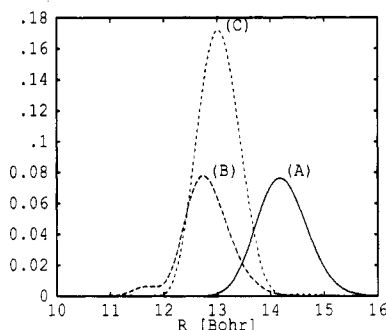


Figure 5. (A) Wave function (numerically squared and ×1000) at final time *t*_f given the initial electric field. (B) Wave function (numerically squared) at *t*_f given the electric field after first iteration. (C) Wave function (numerically squared) at *t*_f given the electric field after 14 iterations.

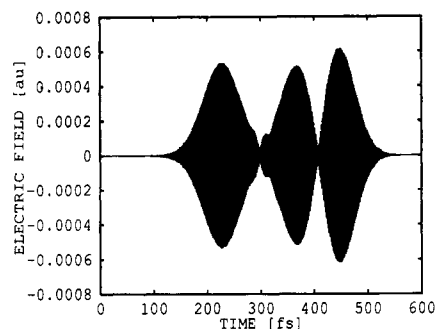


Figure 6. Simulation of the electric field from Figure 3B by use of three Gaussian pulses centered as in Figure 3B and with frequencies from Figure 3b.

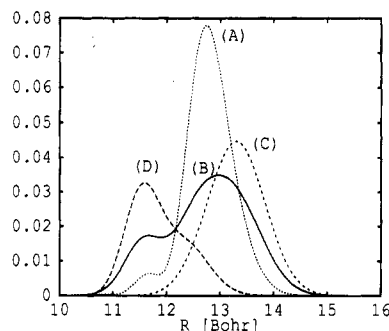


Figure 7. Wave functions (numerically squared) at final time, given the electric fields: (A) after one iteration (same wave function as in Figure 5B); (B) the simulated field with three Gaussian pulses (shown in Figure 6); (C) using only the first two Gaussian pulses from the simulated field; and (D) using only the first and last Gaussian pulse from the simulated electric field.

the units have been changed to wavenumbers.

We also consider a simple approximation to the electric field shown in Figure 3B. Three Gaussian pulses are used. The central times and widths of these pulses are taken from Figure 3B, while

TABLE III: Objective Function Values ($\langle \Psi_f | \hat{P} | \Psi_f \rangle$) and Dissociation Yield ($\int_{10}^{\infty} |\Psi_f(R)|^2 dR$) for HgAr Dissociation^a

iteration no.	$\langle \Psi_f \hat{P} \Psi_f \rangle$	dissocn yield	$\langle \Psi_f \Psi_f \rangle$
0	3.27×10^{-6}	8.96×10^{-5}	1.000
1	6.52×10^{-2}	8.18×10^{-2}	1.000
5	9.39×10^{-2}	1.63×10^{-1}	1.000
9	9.90×10^{-2}	1.19×10^{-1}	1.000
14	1.34×10^{-1}	1.68×10^{-1}	1.000
Simul1	4.06×10^{-2}	7.02×10^{-2}	1.000
Simul2	4.54×10^{-2}	6.04×10^{-2}	1.000
Simul3	4.71×10^{-3}	4.15×10^{-2}	1.000
Gaussian ^b	8.63×10^{-2}	1.51×10^{-1}	1.000

^aSimul1 is from the calculation with three Gaussian pulses; Simul2 with the first two, and Simul3 with the first and last Gaussian pulse from the simulated field. ^bFrom the 47th iteration with the electric field restricted to two Gaussian pulses.

the central frequencies are taken from Figure 3b. The resulting wave function with this electric field is shown in Figure 6 along with the results using only the first and either one of the last two of these Gaussian pulses. The total energy of the electric fields in all these calculations is the same. The values of our objective function, $\bar{I}$, and the dissociation yield are tabulated with a few other intermediate calculations in Table III. The dissociation yield is defined as the amount of the final wave function that has passed $R = 10 a_0$:

$$Y = \int_{10}^{\infty} |\Psi_f(R)|^2 dR \quad (5.3)$$

Included in the table are values of $\langle \Psi_f | \Psi_f \rangle$ to show conservation of the norm of the wave function. From this table and the figures we see that we gain a very large enhancement of our objective function as well as of dissociation yield from the first iteration, while further iterations only give modest enhancements. Some iterations even decrease the amount of dissociation, though the value of the objective function increases. We also see that the approximation to the partially optimized pulse with three Gaussian pulses, as well as the simpler approximation which includes only the first and last of these pulses, gives results that are comparable to those obtained with the partially optimized pulse. The second of the three pulses might well be some "leftover" from the initial guess since it apparently does not contribute as much to the objective function as does the last dump pulse.

We now consider the results of calculations where the electric field is generated by a sum of two Gaussian fields, as in (5.2). We have 10 parameters to optimize: the amplitudes (A_i), the frequencies (ω_i), the phases (ϕ_i), the widths (α_i), and finally the central times (t_i) of each pulse. The result after 47 iterations is given in the final line of Table III. By comparison with the other results in this table, we see that further optimization of the parameters in the two-/three-pulse Gaussian sequence introduced will further enhance the value of our objective function, indeed almost as much as for later iterations in the full optimization scheme. We note that this calculation is started with the same initial guess as in the full optimization scheme. By using the result after just one iteration there (Simul3) we could probably have achieved the present result with a much smaller number of iterations.

¹²⁷I₂. The initial electric field used is shown in Figure 8A, the field after one unconstrained iteration is shown in Figure 8B, and the field after 37 iterations is shown in Figure 8C. Figure 9 shows the initial wave function and the target wave function. The resulting numerically squared wave functions at the final time are shown in Figure 10. Power spectra of the electric fields in Figure 8A–C are shown in Figure 8a–c. In analogy with the HgAr calculations, we have approximated the electric field shown in Figure 8C by three Gaussian pulses, the result of which is shown in Figure 11. As for the HgAr dissociation, we have also made three calculations, involving either all three Gaussian pulses or the first and either one of the last two pulses. As before, the total energy of the pulses has been held constant. The amplitudes of the electric fields are, therefore, not the same. The resulting

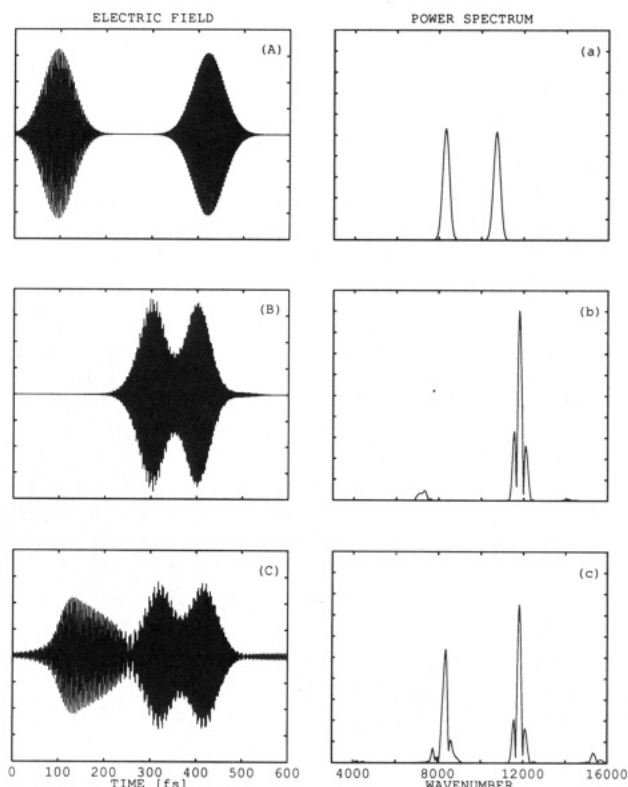


Figure 8. Electric fields for I₂ dissociation: (A) initial guess and (B) after one iteration and (C) after 14 iterations. (a)–(c) show the corresponding power spectra (absolute values).

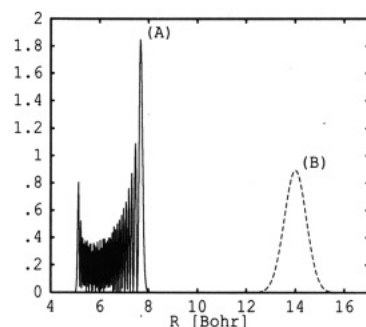


Figure 9. (A) Initial wave function ($v = 34$); and (B) target wave function. Both are numerically squared.

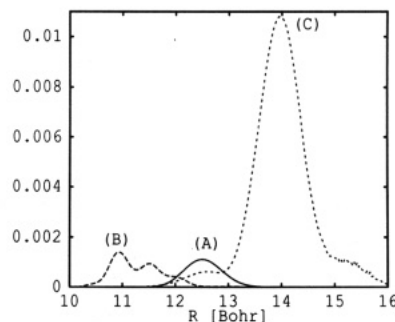


Figure 10. (A) Wave function (numerically squared) at final time t_f given the initial electric field. (B) Wave function (numerically squared and $\times 10000$) at t_f given the electric field after first iteration. (C) Wave function (numerically squared) at t_f given the electric field after 37 iterations.

wavepackets in the "dissociating part" of the grid are shown in Figure 12. The values of the objective function and dissociation yield for the I₂ dissociation are given in Table IV. In this case we find an enhancement of the objective function in the first iteration but a dramatic reduction in yield. This reduction is probably due to a bad choice of p_0 given our initial guess for the

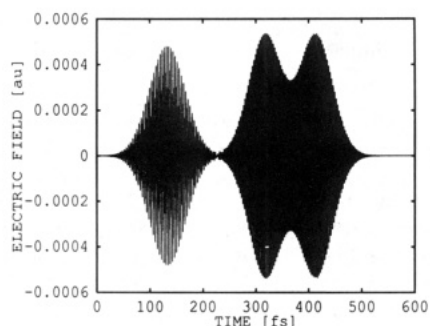


Figure 11. Simulation of the electric field from Figure 8C by use of three Gaussian pulses centered as in Figure 8C and with frequencies from Figure 8c.

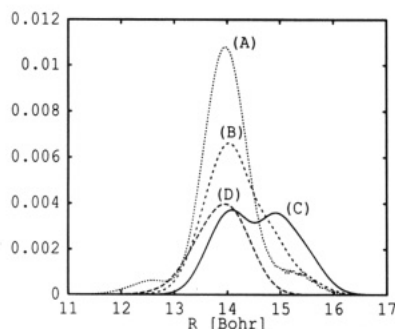


Figure 12. Wave functions (numerically squared) at final time, given the electric fields: (A) after 37 iterations (same wave function as in Figure 10C); (B) the simulated field with three Gaussian pulses (shown in Figure 11); (C) using only the first two Gaussian pulses from the simulated field; and (D) using only the first and last Gaussian pulse from the simulated electric field.

TABLE IV: Objective Function Values ($\langle \Psi_d | \hat{P} | \Psi_f \rangle$) and Dissociation Yield ($\int_{10}^{17.5} |\Psi_f(R)|^2 dR$) for I_2 Dissociation^a

iteration no.	$\langle \Psi_d \hat{P} \Psi_f \rangle$	dissocn yield	$\langle \Psi_d \Psi_f \rangle$
0	1.07×10^{-13}	9.93×10^{-4}	0.988
1	1.60×10^{-12}	1.33×10^{-7}	0.999
10	4.22×10^{-3}	6.22×10^{-3}	0.993
20	1.08×10^{-2}	1.14×10^{-2}	0.998
30	1.16×10^{-2}	1.25×10^{-2}	0.994
37	1.14×10^{-2}	1.22×10^{-2}	0.997
Simul1	8.26×10^{-3}	9.38×10^{-3}	0.989
Simul2	4.95×10^{-3}	7.39×10^{-3}	0.983
Simul3	4.72×10^{-3}	5.05×10^{-3}	0.984

^aSimul1 is from the calculation with three Gaussian pulses; Simul2 with the first two, and Simul3 with the first and last Gaussian pulse from the simulated field.

electric field. By using other parameters for the initial electric field we could have obtained much better results after the first iteration. Note that almost as much yield is obtained with the three-pulse and two-pulse Gaussian simulations as with the partially optimized electric field.

VI. Influence of Molecular Rotation on the Optimal Pulse Induced Dissociation Yield

The calculations presented in the previous sections have ignored the influence of molecular rotation on the induced dissociation yield. This approximation is intuitively plausible for the time scale over which the pump and dump pulses, or the optimally shaped pulses, act. That time scale is, for the molecules considered in this paper, about 500 fs, whereas the characteristic time associated with a rotational transition, defined by the rotational constant of the molecule, is of the order of 50 000 fs. Nevertheless, it is worthwhile examining the influence of molecular rotation on the control of selectivity of product formation. We report the results of such a calculation in this section.

We illustrate the effects of rotational motion on the modulation of yield of photofragments for the case of I_2 . Our approach is

TABLE V

initial J	10	33	66	100
reduction of yield, %	0.3	1.8	5.4	10.2

to calculate, using second-order perturbation theory, the population in the unbound region of the B state of I_2 . For our purposes it is satisfactory to use for the external field the three-pulse approximation to the optimal pulse shape which was described in section V. In view of the shape of the optimized pulse, we treat the first pulse in the three-pulse field separately from the other two pulses. For the pulse sequence described in section V, the first pulse stimulates $B \rightarrow X$ emission, generating a wavepacket on the X-state potential energy surface. By virtue of the rotational selection rule $\Delta J = \pm 1$, transitions from a particular rovibrational component of the wavepacket on the B-state potential energy surface will be connected to the two corresponding ($J + 1$, $J - 1$) rovibrational components of the wavepacket on the X-state potential energy surface, thereby creating a coherent superposition of these levels. The full wavepacket on the X-state surface is constructed by superposing the pairs of rovibrational levels generated by transitions from all of the rovibrational components of the wavepacket on the B-state surface. We now ask if the rotational "unphasing" of this wavepacket materially affects the yield of photofragments generated by the external field.

As already stated, we consider the external field to be constructed of three sequential Gaussian pulses, the parameters of which were described in section V. The initial state is the full thermal distribution of rotational levels appropriate to the ground-state potential energy surface, imaged onto the $v' = 34$ vibrational level of the B-state potential energy surface. The dissociation yield generated by the pulse sequence is calculated individually for each of the rotational levels in the initial state. Since these initial rotational sublevels are not coherently related to each other, no interference between them can occur; the total yield is an incoherent summation of the yields for each initial J state. In carrying out these calculations we used the potential energy curves described in section II and in section V. We have assumed $\Delta J = \pm 1$ and that the Franck-Condon factors for transitions from J to $J - 1$ and J to $J + 1$ are equal; this is a very reasonable approximation for the levels with large J , which are the majority in the initial rotational Boltzmann distribution. The Franck-Condon factors from the intermediate bound states to the continuum were taken to be equal and then normalized to unity; this is a good approximation in the energy range of interest since the span of rovibrational level energies in the wavepacket is of the order of 300 cm^{-1} whereas, for the conditions envisioned, the kinetic energy of the photofragments is an order of magnitude larger.

The results of the calculations just sketched are to be compared with the results of the similar calculations in which the effects of molecular rotation are neglected. Table V shows the change in photofragmentation yield from the value calculated when rotational motion is neglected as a function of rotational quantum number.

The progressive degradation of the photofragment product yield as J increases is expected, since the energy difference between the levels generated by $J \rightarrow J + 1$ and $J \rightarrow J - 1$ increases as J increases. The consequence of this increase in energy is a beat frequency in the wavepacket evolution that increases as J increases, thereby also contributing to an increase in the unphasing rate. Nevertheless, as the entries in Table V show, the degradation of selectivity generated by the inclusion of molecular rotation effects is negligibly small for all practical purposes. Note that, at room temperature, the most populated rotational level is near $J = 65$, suggesting that we may expect 5% or less reduction in the predicted photodissociation yield as a result of rotational unphasing.

VII. Final Remarks

This paper has been concerned with an application of the theory of optimal control of selectivity of product formation in a chemical reaction to real, but simple, chemical reactions. We have shown that with currently achievable laser intensities and laser pulse

TABLE VI: HgAr Photodissociation Yield for Two Gaussian Pulses

pulse width fwhm, fs	yield		contrast ratio	energy density, mJ/cm ²
	at 203 fs	at 406 fs		
50	3.3×10^{-3}	1.0×10^{-6}	3300	0.54
83	1.8×10^{-3}	1.5×10^{-5}	120	0.54
120	1.7×10^{-3}	1.0×10^{-4}	17	0.54
170	8.9×10^{-4}	3.2×10^{-4}	2.8	0.54

widths it is possible to modulate the photofragmentation yield of HgAr and I₂. Although we have not discussed the matter in the text of this paper, other calculations we have made, in connection with a design for carrying out the experiments described, show that the modulation of the yield is measurable. We have also shown that it is worthwhile calculating the pulse shape which gives maximum yield of photofragments, since that field can be simply approximated with a small number of Gaussian pulses.

As an example of the practical considerations involved in these experiments, Table VI gives quantitative photodissociation yields for the HgAr system using a sequence of two Gaussian pulses. Note that, as the pulse width is increased, the contrast of the dissociation window pattern is rapidly degraded, suggesting that pulses shorter than 100 fs would be required. The absolute yield is quite large and under realistic experimental conditions is expected to give a fluorescence signal level of roughly 10 000 photons/s. The calculations of section V indicate that this yield and contrast could be increased by nearly 3 orders of magnitude by simply altering the duration, delay, intensity ratio, and frequencies of the two Gaussian pulses while maintaining the same total energy in the field! In the case of iodine, two optimized Gaussian pulses do not give an appreciable enhancement, but the simple addition of a third pulse does increase the yield by an order of magnitude. In both cases, enhanced reaction control is clearly possible with experimentally achievable laser fields.

We expect that the kind of analysis described in this paper will be widely applicable to many chemical reactions. Although the general formalism is applicable to systems with any number of degrees of freedom, visualization of the wave packet dynamics is very difficult when the system has more than two degrees of freedom. One consequence of that difficulty is inhibition of the use of physical intuition to make simple physical approximations. We believe that it is worthwhile to develop approximate dynamical descriptions of systems with many degrees of freedom (e.g., reaction path representations) which will permit, in turn, development of useful approximations to the optimal control fields that generate particular products.

Finally, it is appropriate to comment on the significance of recent experiments by Scherer et al.³⁰ on phase control as a form of pulse shaping. In brief, that work showed that it is possible to lock the optical phases of two ultrashort laser pulses, and to use the resulting quantum interference effects to enhance (or reduce, depending on the choice of phase locking angle) the excitation efficiency of those pulses. Such work demonstrates how coherent interference effects could be used to even further enhance the efficiency of product formation in experiments such as described in this paper. In practice, however, those interference effects can only occur between excitations of the same frequency, whereas the experiments reported here typically require two pulses of different frequencies. Therefore, no quantum interference effects occur. It could, however, be possible to design multiple pulse sequences in which two or more phase-locked pulses of a single color are used for the pump and dump steps. In fact, the slight increase in reaction yield we have observed for three pulse sequences compared to two pulse sequences may be due to such effects.

An additional important aspect of the phase locking concept is that most computer simulations of short pulse excitation assume phase coherent pulse sequences, whereas phase coherence is typically not achieved in the laboratory without the extensive efforts described by Scherer et al. The applicability of optimized

coherent pulse sequences as well as the use of numerical simulations of experiments must therefore be analyzed carefully in terms of phase coherence considerations!

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Appendix A: Full Optimal Control Methodology

In this Appendix the equation for the optimal field is derived, starting with the modified objective functional given in section III and setting $\delta I = 0$. The procedure is equivalent to the procedure in refs 10, 23, and 29 except that we carry out the analysis for an electric field with real values (as in ref 23) and not complex (as in refs 10 and 29). The objective functional is

$$I = \langle \Psi_f | \hat{P} | \Psi_f \rangle + i \int_{t_0}^{t_f} (\langle \Phi | i\partial_t - \hat{H} | \Psi \rangle - \text{c.c.}) dt + \lambda \left[\int_{t_0}^{t_f} \mathcal{E}^2(t) dt - E \right] \quad (\text{A.1})$$

From this one obtains

$$\begin{aligned} \delta I = & \langle \delta \Psi(t_f) | \hat{P} | \Psi(t_f) \rangle + \langle \Phi(t_f) | \hat{P} | \delta \Psi(t_f) \rangle + \\ & i \int_{t_0}^{t_f} (i \langle \Phi | \delta \Psi \rangle + i \langle \delta \Psi | \Phi \rangle - \langle \Phi | \hat{H} | \delta \Psi \rangle + \\ & \quad \langle \delta \Psi | \hat{H} | \Phi \rangle) dt + \\ & i \int_{t_0}^{t_f} \left(-\langle \Phi | \frac{\partial \hat{H}}{\partial \mathcal{E}} | \Psi \rangle + \langle \Psi | \frac{\partial \hat{H}}{\partial \mathcal{E}} | \Phi \rangle - 2i\lambda \mathcal{E}(t) \right) \delta \mathcal{E} dt \\ = & \langle \delta \Psi(t_f) | \hat{P} | \Psi(t_f) \rangle + \langle \Psi(t_f) | \hat{P} | \delta \Psi(t_f) \rangle - \\ & \langle \delta \Psi(t_f) | \Phi(t_f) \rangle - \langle \Phi(t_f) | \delta \Psi(t_f) \rangle + \langle \delta \Psi(t_0) | \Phi(t_0) \rangle + \\ & \langle \Phi(t_0) | \delta \Psi(t_0) \rangle + i \int_{t_0}^{t_f} (-i \langle \Phi | \delta \Psi \rangle - i \langle \delta \Psi | \Phi \rangle - \\ & \langle \Phi | \hat{H} | \delta \Psi \rangle + \langle \delta \Psi | \hat{H} | \Phi \rangle) dt + i \int_{t_0}^{t_f} \left(-\langle \Phi | \frac{\partial \hat{H}}{\partial \mathcal{E}} | \Psi \rangle + \right. \\ & \quad \left. \langle \Psi | \frac{\partial \hat{H}}{\partial \mathcal{E}} | \Phi \rangle - 2i\lambda \mathcal{E}(t) \right) \delta \mathcal{E} dt \quad (\text{A.2}) \end{aligned}$$

We have made a partial integration in the last step. By use of

$$\frac{\partial \hat{H}}{\partial \mathcal{E}} = \mu \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad (\text{A.3})$$

$$\Psi = \begin{pmatrix} \psi_u \\ \psi_g \end{pmatrix} \quad (\text{A.4})$$

$$\Phi = \begin{pmatrix} \phi_u \\ \phi_g \end{pmatrix} \quad (\text{A.5})$$

and also the fact that the initial wave function is not varied, so that $\delta \Psi(t_0) = 0$, we get

$$\begin{aligned} \delta I = & \langle \delta \Psi(t_f) | \hat{P} | \Psi(t_f) \rangle + \langle \Psi(t_f) | \hat{P} | \delta \Psi(t_f) \rangle - \\ & \langle \delta \Psi(t_f) | \Phi(t_f) \rangle - \langle \Phi(t_f) | \delta \Psi(t_f) \rangle + \\ & i \int_{t_0}^{t_f} (\langle \delta \Psi | i\partial_t - \hat{H} | \Phi \rangle - \text{c.c.}) dt + \\ & i \int_{t_0}^{t_f} ((\langle \psi_u | \mu | \phi_g \rangle + \langle \psi_g | \mu | \phi_u \rangle - \text{c.c.}) - 2i\lambda \mathcal{E}(t)) \delta \mathcal{E} dt \quad (\text{A.6}) \end{aligned}$$

Demanding $\delta I = 0$ for all $\delta \Psi$ gives us the equation of motion for the Lagrange multiplier Φ

$$i\partial_t\Phi = \hat{H}\Phi \quad (\text{A.7})$$

which is the time-dependent Schrödinger equation subject to the final condition

$$|\Phi(t_f)\rangle = \hat{P}|\Psi(t_f)\rangle \quad (\text{A.8})$$

which relates Φ to Ψ on the boundary. From $\delta\bar{I} = 0$ for all $\delta\mathcal{E}$ we get

$$\mathcal{E}(t) = O(t)/\lambda \quad (\text{A.9})$$

where

$$O(t) = \text{Im} (\langle \psi_u | \mu | \phi_g \rangle + \langle \psi_g | \mu | \phi_u \rangle) \quad (\text{A.10})$$

is called the overlap function, and λ is determined from the energy constraint

$$\int_{t_0}^{t_f} \mathcal{E}^2(t) dt = E \quad (\text{A.11})$$

Appendix B: Restricted Optimal Control Methodology

Let us now consider the case, when there are restrictions on the form of the electric field. As an example we consider the case that the field has only two pulses of a given form, as in the Tannor-Rice pump-dump scheme. Then

$$\mathcal{E}(t) = \mathcal{E}(t, \{\xi\}) = \sum_{j=1}^2 \mathcal{E}_j(t, \{\xi_j\}) \quad (\text{B.1})$$

Since $\mathcal{E}$ is a function of the parameter set $\{\xi\} = \{\xi_1, \xi_2\} = \{\xi_1^1, \dots, \xi_1^n, \xi_2^1, \dots, \xi_2^n\}$ we have

$$\delta\mathcal{E} = \delta\mathcal{E}_1 + \delta\mathcal{E}_2 = \sum_{j=1}^n \left(\frac{\partial \mathcal{E}_1}{\partial \xi_j^1} \delta \xi_j^1 + \frac{\partial \mathcal{E}_2}{\partial \xi_j^2} \delta \xi_j^2 \right) \quad (\text{B.2})$$

Inserting (B.1) and (B.2) in (A.6) and demanding $\delta\bar{I} = 0$ for all $\delta \xi_l^i$ (that are independent of $t!$), we find the following $2n$ equations to determine $\{\xi\}$:

$$- \int_{t_0}^{t_f} (2 \text{Im} (\langle \psi_u | \mu | \phi_g \rangle + \langle \psi_g | \mu | \phi_u \rangle) - 2\lambda \mathcal{E}(t)) \frac{\partial \mathcal{E}_i}{\partial \xi_l^i}(t) dt = 0; \quad i = 1, 2; j = 1 \dots n \quad (\text{B.3})$$

This set of coupled integral equations can be solved in different ways. We have chosen an iteration procedure involving the second derivative of $\bar{I}$. Using definition (A.10) for the overlap function we find

$$\frac{\partial^2 \bar{I}}{\partial \xi_l^i \partial \xi_k^j} = -2 \int_{t_0}^{t_f} \left((O(t) - \lambda \mathcal{E}(t)) \frac{\partial^2 \mathcal{E}_i}{\partial \xi_l^i \partial \xi_k^j} - \lambda \frac{\partial \mathcal{E}_k}{\partial \xi_l^i} \frac{\partial \mathcal{E}_i}{\partial \xi_k^j} \right) dt; \quad i, k = 1, 2; j, l = 1 \dots n \quad (\text{B.4})$$

The first term in this integral can be nonzero only when $i = k$. When the pulses are given as an analytical expression (as for a Gaussian pulse) we can also find analytical expressions for the needed first and second derivatives. Let

$$F_{ij}[\xi] = \delta \bar{I} / \delta \xi_l^i \quad (\text{B.5})$$

and

$$A_{ij,kl} = \frac{\delta F_{ij}}{\delta \xi_k^j} = \frac{\delta^2 \bar{I}}{\delta \xi_l^i \delta \xi_k^j} = \frac{\delta^2 \bar{I}}{\delta \xi_k^j \delta \xi_l^i} \quad (\text{B.6})$$

Then $\bar{F}$ is a vector with elements F_{ij} and A is a matrix with elements $A_{ij,kl}$. For small changes in ξ , $\delta \xi$, we can expand $\bar{F}$ in a Taylor series

$$\bar{F}[\xi + \delta \xi] \approx \bar{F}[\xi] + A \delta \xi \quad (\text{B.7})$$

If $\bar{I}$ has an extreme value (maximum or minimum) at the extreme point ξ_0 , then $\bar{F} = \bar{0}$. If we are close to an extreme point, ξ_0 , we have

$$\bar{0} \approx \bar{F} + A \delta \xi_0 \quad (\text{B.8})$$

or

$$\delta \xi_0 \approx -A^{-1} \bar{F} \quad (\text{B.9})$$

Registry No. HgAr, 87193-95-1; I₂, 33283-93-1; Hg, 7439-97-6; Ar, 7440-37-1; I, 14362-44-8.