Coherence Chemistry: Controlling Chemical Reactions with Lasers

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1. Introduction

Manipulating the yield of chemical reactions is at the heart of chemistry, and controlling reactions by using lasers has been a goal for decades. Recently, we demonstrated[1] how this goal could be achieved. An appreciation of this approach, termed coherent control of chemical reactions, opens up new avenues in chemistry by introducing a world of chemical control based upon previously unutilized quantum effects.
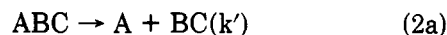
The purpose of this Account is to provide an introduction[2] to the concepts underlying coherent control of chemical reactions. It is organized as follows: Section 2 reviews some fundamental concepts in the application of quantum mechanics to chemical reactions; these may be skipped by the reader who is well versed in collision theory. Section 3 deals directly with control of chemical reactions whereas sections 4 and 5 provide overview summary remarks.

1.1. Aspects of Scattering Theory and Reaction Dynamics.
Consider a bimolecular reaction at energy E:

$$A + BC(k) \rightarrow A + BC(k') \qquad (1a)$$
$$\rightarrow AB(k'') + C \qquad (1b)$$

where A, B, and C are atomic or molecular units and k or k' denotes the vibrational, rotational, etc., state of the reactant or product pair. Both inelastic (1a) and reactive scattering (1b) are indicated. Also of interest below is the unimolecular case where decomposition into more than one product is possible, i.e.,

$$ABC \rightarrow A + BC(k') \qquad (2a)$$
$$\rightarrow AB(k'') + C \qquad (2b)$$

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(1) (a) Brumer, P.; Shapiro, M. Chem. Phys. Lett. 1986, 126, 541. (b) Brumer, P.; Shapiro, M. Faraday Discuss. Chem. Soc. 1986, No. 82, 177. (c) Shapiro, M.; Brumer, P. J. Chem. Phys. 1986, 84, 4103. (d) Asaro, C.; Brumer, P.; Shapiro, M. Phys. Rev. Lett. 1988, 60, 1634. Shapiro, M.; Hepburn, J.; Brumer, P. Chem. Phys. Lett. 1988, 149, 451. (e) Brumer, P.; Shapiro, M. J. Chem. Phys. 1989, 90, 6179. (f) Kurizki, G.; Shapiro, M.; Brumer, P. Phys. Rev. B 1989, 39, 3435. (g) Seideman, T.; Shapiro, M.; Brumer, P. J. Chem. Phys. 1989, 90, 7136. (h) Krause, J.; Shapiro, M.; Brumer, P., to be published. (i) Levy, I.; Shapiro, M.; Brumer, P., to be published. (j) Jiang, X.-P.; Brumer, P.; Shapiro, M., to be published.

(2) Space limitations necessitate that we assume an appreciation of quantum interference, time dependence, etc. (see, e.g.; Macomber, J. D. The Dynamics of Spectroscopic Transitions; Wiley: New York, 1976). However, a more introductory version of this paper, which covers these issues, is available upon request from the authors.

Treating the dynamics of a chemical reaction requires that we solve the time-dependent Schrödinger equation (eq 3) for the wavefunction $\psi(t)$ associated with specific

$$H\psi(t) = i\hbar \frac{\partial \psi(t)}{\partial t} \qquad (3)$$

initial reactant conditions, i.e., $\psi(t=0)$. The wavefunction at long times (i.e., the time when the products are well separated) then provides the probabilities of forming the products. As is well-known, we could choose to solve the problem in two steps. First we obtain the stationary eigenfunctions ψ_i as solutions to the time-independent Schrödinger equation $H\psi_i = E_i\psi_i$, and then we build in the time dependence of the collision, or dissociation, via a superposition of time-dependent eigenstates. Let us therefore first consider the nature of the solutions ψ_i and E_i.

First note, due to the possibility of unbounded translational motion, that the reacting system lies in the continuum energy regime, i.e., the E_i are continuous. Focus attention then on the system at a fixed energy E where, as we shall see, the essence of controlling reactions is manifest. Since we require, at such an energy, an independent wavefunction to describe each of the possible events that can be observed in the product regions,[3] one expects substantial degeneracy at energy E. Further, the fact that this set of degenerate wavefunctions of the separated products exists implies[4] that a related set of degenerate eigenfunctions of the total Hamiltonian exists.

This requirement, that total system eigenfunctions correlate with specific asymptotic product state eigenfunctions, may be included as a boundary condition on the total system wavefunctions and serves to simplify considerably the case of unimolecular decay, which will serve as our primary example below. Specifically, say we distinguish the different possible chemical product arrangements of the decay of ABC by the numerical value of an index q, (e.g., $q = 1$ denotes A + BC in eq 2, etc.) and m denotes all additional identifying state labels (e.g., j', v', scattering angle, etc.). Then we define the set of Hamiltonian eigenfunctions $\psi^-(E,m,q)$ via the Schrödinger equation $H\psi^-(E,m,q) = E\psi^-(E,m,q)$ and via the requirement that the wavefunction describes, at large distances, that state of the separated products, denoted $\psi^0(E,m,q)$, which is of energy E, arrangement q, and remaining quantum numbers m. The superscript, minus, serves to indicate this choice of boundary condition.

Imposition of such boundary conditions and choosing to describe the system in terms of $\psi^-(E,m,q)$ has a number of important simplifying consequences. For example, if one sets up (either experimentally or conceptually) a state at $t = 0$, at energy E, consisting of $\psi^-(E,m,q=1)$, then the probability of observing the product (at long times) in the $q = 1$ arrangement, and with quantum numbers m, is unity since $\psi^-(E,m,q=1)$

uniquely correlates with that particular product state. Similarly, if we set up the system, for example, as

$$\psi(t=0) = c_1\psi^-(E,m,1) + c_2\psi^-(E,m,2) \qquad (4a)$$

then the probability of observing the arrangement 1 or 2, at long time, is $|c_1|^2$ or $|c_2|^2$, respectively. The most general case (for the situation where there are two product arrangements) is one in which the initial preparation includes a number of m states, such as

$$\psi(0) = \sum_m [c_{1m}\psi^-(E,m,1) + c_{2m}\psi^-(E,m,2)] \qquad (4b)$$

Then the probability of observing one of the arrangements, say $q = 1$, is $\sum_m |c_{1m}|^2$. This apparently simple discussion allows us to make a few crucial statements:

(1) *The product yield, i.e., the probability of obtaining a particular chemical product at long time, is solely determined by the state created at $t = 0$.* Further, our choice of "minus states" $\psi^-(E,m,q)$ allows expression of this fact in a relatively simple way, i.e., the coefficients in the $t = 0$ superposition state are directly related to the coefficients at long time, which, in turn, yield the product probabilities. The fact that the long-time state is predetermined by the initially created state is, admittedly, intuitively obvious. However, consequences of this feature are often misunderstood. For example, it makes clear that arguments such as "intramolecular energy scrambling makes reaction control difficult" are misleading.[5]

(2) Since product probabilities are predetermined by the composition of the prepared ($t = 0$) superposition state, the route to controlling a chemical reaction is to control the content of the initially prepared superposition state.

(3) The branching of the reaction probabilities into various product channels occurs at a fixed energy E. As such, a range of energies, and its associated time dependence, need not be introduced in order to consider control over reaction yields.

Below we demonstrate that the key to laser control of chemical reactions is to use the lasers to alter the nature of the prepared superposition state and hence to alter the product probabilities. That this strategy is the essence of controlling chemical reactions should be clear from the above discussion. First, however, we review preparation of states from the viewpoint of perturbation theory.

1.2. Perturbation Theory, System Preparation, and Coherence. In preparation for a discussion of laser-induced unimolecular dissociation, consider the effect of an electric field on a molecule. As a specific example, consider an isolated molecule with Hamiltonian H_M in an eigenstate ϕ_g, of energy E_g, which is subjected to a perturbing incident radiation field. The overall Hamiltonian is then given by

$$H = H_M - \mu[\bar{\epsilon}(t) + \bar{\epsilon}^*(t)] \qquad (5)$$

where μ is the component of the dipole moment along the electric field $[\bar{\epsilon}(t) + \bar{\epsilon}^*(t)]$.

To ascertain the effect of the field on the molecule requires that we solve eq 3 for the given Hamiltonian, including the perturbation. To do so we invoke time dependent perturbation theory and expand the solution

(3) To see this requirement, note that it should be possible to set up initial reactant conditions (i.e., relative velocities, internal rotation and vibration states, etc.) so as to produce a wide variety of possible reaction outcomes (e.g., probabilities of observing products with different relative velocities, internal rotational and vibrational states, scattering angles, etc.). To properly describe these product states requires, then, a host of wavefunctions, *all at energy E*, which can be added arbitrarily together so as to yield this wide variety of allowed final states.

(4) Rigorously, this is the asymptotic condition in scattering theory (see: Taylor, J. R. *Scattering Theory*; J. Wiley: New York, 1972).

(5) For an introductory discussion of intramolecular energy transfer, see: Brumer, P. *Encyclopedia of Physical Sciences and Technology*, Academic Press: New York, 1987; Vol. 5, p 119 ff.
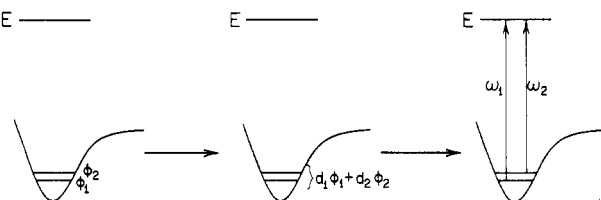
Figure 1. A general two-step scheme for inducing controllable quantum interference effects into the continuum state at energy E. The two bound states ϕ_1 and ϕ_2 belong to a lower electronic state whereas the level at energy E is that of an excited electronic state. Coherence introduced in the first step is carried into the continuum.
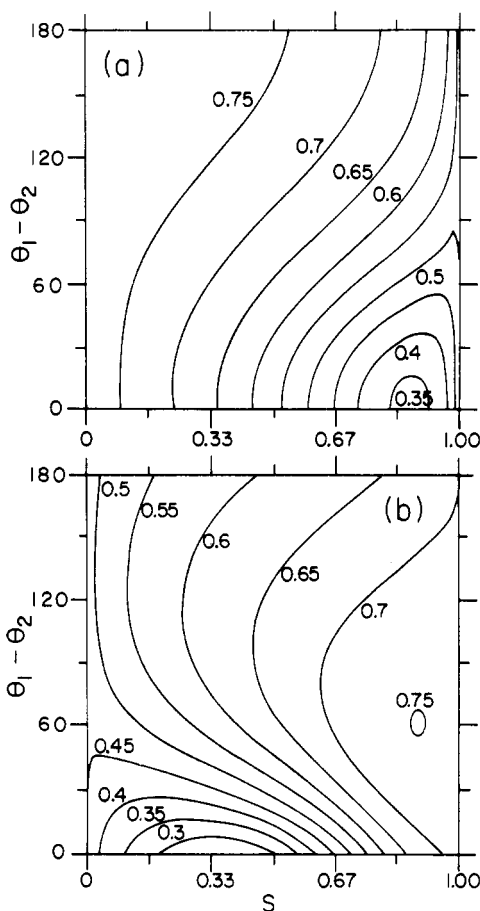

Figure 2. Contour plot of the yield of I^* (i.e., fraction of I^* as product) in the photodissociation of CH_3I from a superposition state comprising $(v_1, J_1, M_1) = (0, 1, 1)$ with $(v_2, J_2, M_2) = (0, 2, 1)$. Here v_i, J_i, and M_i are the vibrational, rotational, and rotational projection quantum numbers of the ith bound state. The two cases shown correspond to frequencies (a) $\omega_{E,E_1} = 39\,638$ cm^{-1} and (b) $\omega_{E,E_1} = 42\,367$ cm^{-1}.

$\Psi(t)$ in solutions to the problem in the absence of the perturbation, i.e., the solutions to

$$H_M\phi_i = E_i\phi_i \qquad (6)$$

Specifically, we write $\Psi(t)$ as

$$\Psi(t) = \sum_i c_i(t)\phi_i e^{-iE_it/\hbar} \qquad (7)$$

with the $c_i(t)$ as yet to be determined. Note that eq 7 expresses the solution precisely in terms we want physically, i.e., the $|c_i(t)|^2$ gives the probability of being in the molecular state ϕ_i at time t.

Inserting eq 7 into eq 3 yields a set of ordinary differential equations for $c_i(t)$ which may be solved nu-

merically.[6] For weak fields this is not necessary, and a simple perturbation theory solution for the long-time (i.e., when the electric field is off) behavior can be obtained as

$$c_i(t\to\infty) = \left(\sqrt{2\pi}/i\hbar\right)\epsilon(\omega_{E_i,E_g})\int \phi_i\mu\phi_g \, dx \qquad (8)$$

with

$$\epsilon(\lambda) = (1/\sqrt{2\pi})\int_{-\infty}^{\infty} e^{i\lambda t}\bar{\epsilon}(t) \, dt \qquad (9)$$

In this case $\lambda = \omega_{E_i,E_g} = (E_i - E_g)/\hbar$. Note specifically that the object that is created by the incident electric field is a *pure state*, i.e., describable by a wavefunction $\Psi(t)$ with well-defined phases. The fact that a well-defined electric field produces a pure state (and hence a state that is phase-coherent) is crucial to the discussion below.

Consider now laser-induced unimolecular dissociation, where we excite a molecule in an eigenstate ϕ_g by using an electric field whose frequency provides enough energy to dissociate the molecule. Our interest is in ascertaining the probability of forming particular products. With the electric field assumed weak enough to allow the use of first order perturbation theory, we proceed in the standard fashion[7] and expand the wavefunction in eigenstates of the molecular Hamiltonian. Since the photon lifts the system into the continuum, our expansion is in terms of the eigenstates $\psi^-(E,m,q)$, i.e.,

$$\Psi(t) = \sum_{m,q}\int dE \, c_{E,m,q}(t)\psi^-(E,m,q)e^{-iEt/\hbar} \qquad (10)$$

where the continuous nature of the energy yields an integral as well as a sum. Following through with standard perturbation theory gives, for the long-time coefficients, and hence for the probability $P(E,q)$ of forming product in arrangement q,

$$P(E,q) = (2\pi/\hbar^2)\sum_m |\epsilon(\omega_{E,E_g})\int \phi^*_g\mu\psi^-(E,m,q) \, dx|^2 \qquad (11)$$

or the ratio $R(1,2;E)$ of products in channel $q = 1$ to $q = 2$ at energy E is

$$R(1,2;E) = \frac{\sum_m|\epsilon(\omega_{E,E_g})\int \phi^*_g\mu\psi^-(E,m,q=1) \, dx|^2}{\sum_m|\epsilon(\omega_{E,E_g})\int \phi^*_g\mu\psi^-(E,m,q=2) \, dx|^2} = \frac{\sum_m|\langle\phi_g|\mu|\psi^-(E,m,q=1)\rangle|^2}{\sum_m|\langle\phi_g|\mu|\psi^-(E,m,q=2)\rangle|^2} \qquad (12)$$

where we now utilize the convenient Dirac notation for integrals, $[\int f^*_1(x)\mu f_2(x) \, dx = \langle f_1|\mu|f_2\rangle$, etc.]. An understanding of the qualitative structure of this yield ratio, provided below, is crucial to recognizing the difficulties associated with attempts to alter experimentally the yield in a traditional unimolecular decay experiment. It also motivates the specific control approach which we advocate below.

(6) See, e.g.: Taylor, R. D.; Brumer, P. *Faraday Discuss. Chem. Soc.* **1983**, *No. 75*, 17.
(7) Bersohn, R.; Shapiro, M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 409. Shapiro, M. *J. Chem. Phys.* **1972**, *56*, 2582.

$$R(1,2;E) = \frac{\sum_m |\langle (\epsilon(\omega_{E,E_1})e^{i\chi_1}d_1\phi_1 + \epsilon(\omega_{E,E_2})e^{i\chi_2}d_2\phi_2)|\mu|\psi^-(E,m,q=1)\rangle|^2}{\sum_m |\langle (\epsilon(\omega_{E,E_1})e^{i\chi_1}d_1\phi_1 + \epsilon(\omega_{E,E_2})e^{i\chi_2}d_2\phi_2)|\mu|\psi^-(E,m,q=2)\rangle|^2}$$

$$= \frac{\sum_m |\langle \epsilon(\omega_{E,E_1})e^{i\chi_1}d_1\phi_1|\mu|\psi^-(E,m,q=1)\rangle + \langle \epsilon(\omega_{E,E_2})e^{i\chi_2}d_2\phi_2|\mu|\psi^-(E,m,q=1)\rangle|^2}{\sum_m |\langle \epsilon(\omega_{E,E_1})e^{i\chi_1}d_1\phi_1|\mu|\psi^-(E,m,q=2)\rangle + \langle \epsilon(\omega_{E,E_2})e^{i\chi_2}d_2\phi_2|\mu|\psi^-(E,m,q=2)\rangle|^2} \qquad (13)$$
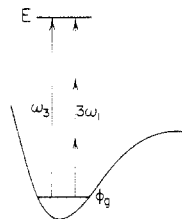

Figure 3. A multiple optical route scheme to inducing controllable quantum interference effects into the continuum state at energy E. Here the level ϕ_g is a bound state of a lower electronic state, and that at E is a continuum state of the excited electronic state. Simultaneous application of frequencies ω_1 and $\omega_3 = 3\omega_1$ leads to interference in the continuum state.

2. Coherent Radiative Control of Chemical Reactions

Consider then our primary goal, i.e., to alter experimentally the yield ratio R so as to control the product distribution. Equation 12 makes clear that this cannot be achieved, for example, by moderately altering the laser power. That is, the field cancels out in forming the ratio R. Hence this, and any quantity that appears in a similar form in both the numerator and denominator, cannot serve as a handle on yield control. An alternate possibility to control the reaction yield is to alter the frequency of excitation $[(E - E_g)/\hbar]$ and see the effect on the ratio. However, such a procedure is not systematic, and its success, if any, is based solely upon a change occurrence of a desirable result with variations in the laser frequency.

The discussion above does, however, suggest an alternate possibility. Specifically, note the form of eq 12, which has the square of an amplitude in both the numerator and the denominator. If we could manage to alter experimentally the quantity *within* the square, then the effect on the numerator and the denominator might differ, and we would have experimental control over the ratio. Our approach reflects this philosophy and is coupled with the recognition that quantum interference phenomena alter the amplitude within the square in a particularly useful fashion.

As a pedagogical example, consider starting with an initial molecular eigenstate ϕ_1 at energy E_1 and proceeding in two steps (see Figure 1). First, we excite this level to another bound state ϕ_2 (energy E_2). The state resulting from this initial preparatory step is a linear combination of ϕ_1 and ϕ_2, say $d_1\phi_1 + d_2\phi_2$. The nature of the coefficients d_1 and d_2 will be similar to that in eq 8, the essential point being that the phase and magnitude of the d_i coefficients are functions of the *experimentally controllable* parameters of the electric field used to create the bound superposition state. As a second step we subject this bound superposition state to an electric field that contains frequency components which can independently lift both of these states to an energy E. That is, $\bar{\epsilon}(t) = \varepsilon_1 e^{-i\omega_1 t + i\chi_1} + \varepsilon_2 e^{-i\omega_2 t + i\chi_2}$ where

$\hbar\omega_i = E - E_i$. We then ask for the yield ratio R under these circumstances. A straightforward computation[1a] gives the result (eq 13). That is, the superposition state $d_1\phi_1 + d_2\phi_2$ replaces the initial state ϕ_g of eq 12, and the electric fields, *which now remain in this expression*, are those that raise each of the individual levels to the excited state.

Equation 13 comprises two types of terms, those associated with the two different independent excitations of levels at energies E_1 and E_2 and those corresponding to the interference between these two processes. The interference term can either constructively enhance or destructively cancel out contributions to either product channel. What makes eq 13 so important *in practice* is that the interference terms have coefficients whose magnitude and sign depend upon *experimentally controllable* parameters. Thus the experimentalist can manipulate laboratory parameters and, in doing so, directly alter the reaction product yield by varying the magnitude of the interference term. In the case of eq 13, the experimental parameters that alter the yield are particular combinations of the magnitudes ε_i of the electric fields and the magnitudes of the coefficients d_i, and combinations of the relative phases of the d_i and/or the relative phases χ_i of the lasers. What makes eq 13 so important *conceptually* is that this control over the reaction yield is a direct consequence of quantum interference effects induced by using several independent optical routes to the same energy E.

Results of a specific computational example based upon eq 13 are shown in Figure 3. Here we consider control over the relative probability of forming $^2P_{3/2}$ vs $^2P_{1/2}$ atomic iodine, denoted I and I*, in the dissociation of methyl iodide:

$$CH_3I \rightarrow CH_3 + I$$

$$\rightarrow CH_3 + I^* \qquad (14)$$
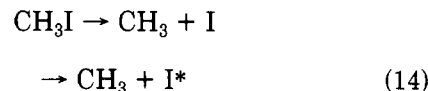
Although this reaction is an example of electronic branching of products and is chosen for computational convenience, the same principles of control as described above apply. Specifically, an examination of eq 13 shows that the relevant experimental parameters that occur are $|A|$ and $\arg(A)$, where

$$A = (\epsilon(\omega_{E,E_2}) \exp(-i\chi_2)d_2)/(\epsilon(\omega_{E,E_1}) \exp(-i\chi_1)d_1)$$

Figure 2 shows a typical plot of the yield of I* as a function of these parameters, collected as $S = A^2/(1 + A^2)$ and $\theta_1 - \theta_2 = \arg(A)$. Note the enormous range of control possible with variations in S and $\theta_1 - \theta_2$, i.e., from an I* yield ratio of 35% to 75%. Higher and lower ratios can also be achieved[8] with different choices of the initial pair of states ϕ_1 and ϕ_2.

The two-step approach demonstrated in Figures 1 and 2 and described above is but one particular implementation of the general philosophy of coherent control. That is, as discussed in this section, the essence
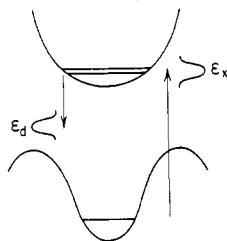
Figure 4. Coherent radiative control via a picosecond pulse scheme. In this case a single level is excited with a laser pulse to produce a superposition of two bound states in an excited electronic state. Subsequent deexcitation of this state to the continuum of the ground state allows control over the reaction on the ground-state surface.

of controlling chemical reactions is to control the content of the superposition state at energy E where dissociation into various products is possible. What we have demonstrated above is one way to use independent coherent optical excitation routes to alter the content of that superposition state in an experimentally controllable way.

As a second example of a possible experimental implementation of coherent control, consider eq 12 once again. Above, we introduced quantum interference by modifying the initial state prior to excitation into the continuum. An alternative method, suggested by the general idea of using different optical routes to energy E, suggests itself. Specifically, note that eq 12 involves the operator μ, which results from the coupling of the molecule to the electric field via the dipole coupling. Imagine now that we had an additional route for achieving excitation to energy E, but via a different coupling of the external field to the molecule. An example is excitation to energy E via multiphoton excitation. In this case the effective molecule–field coupling is due to successive applications of the dipole operator[1d] leading to a different function, which we term T, in place of μ. If *both* the multiphoton route and the single-photon route are active (i.e., we apply an electric field of frequency ω and one of frequency 3ω at the same time), as shown in Figure 3, then eq 12 becomes

$$R(1,2;E) = \frac{\sum_m |\langle \phi_g|(\epsilon_3\mu + \epsilon_1{}^3T)|\psi^-(E,m,q=1)\rangle|^2}{\sum_m |\langle \phi_g|(\epsilon_3\mu + \epsilon_1{}^3T)|\psi^-(E,m,q=2)\rangle|^2} \quad (15)$$

where ϵ_3 and ϵ_1 are the field strengths associated with the one-photon and three-photon absorptions, respectively. Upon expanding the squares in eq 15, one sees the now-characteristic interference term, this time between the single-photon and multiphoton optical excitation routes. Once again, the control parameters are the relative magnitudes of the electric fields associated with the two optical routes and the phases between them. Thus, the principle is the same as in the example above, but the interference is introduced in an entirely different way.

The description above should make clear that there are a variety of ways to achieve the desired controllable superposition state. A word of caution is in order to avoid leaving the reader with the impression that designing coherent control schemes requires little care. First, selection rules place considerable restriction on the nature of the interfering excitation paths. Specifically, the independent paths to energy E both must
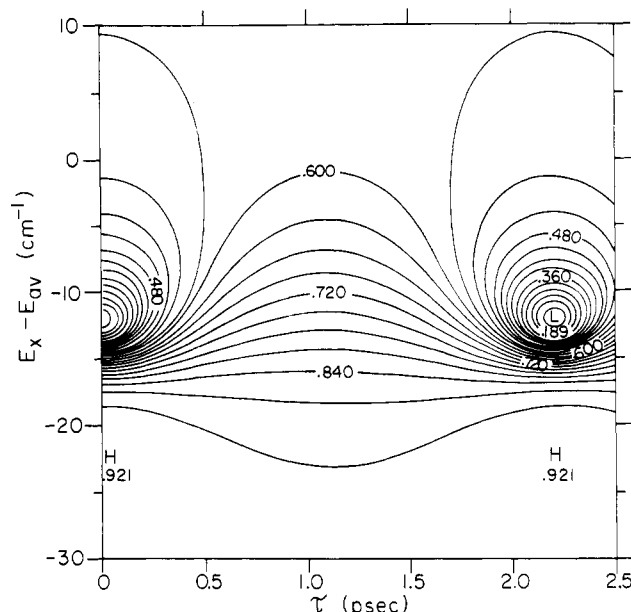

Figure 5. Contour plot of the DH yield in the reaction D + H$_2$ → DH + H. The control parameters are the difference in energy between the excitation pulse center E_x and the average of the energy of the two excited levels E_{av}, and the time between the pulses τ. Although the abscissa begins at 0 and spans approximately one period, the results are periodic in the delay time, and the experimentalist must wait sufficiently long between the two pulses to insure that they do not overlap.

excite the system so as to yield the same set of *all* conserved quantities. Thus, for example, a scheme similar to that of eq 13, but using ω and 2ω, can be ruled out because the selection rules for excitation by ω and by 2ω are different. Second, all implementations of control require that there be at least some degree of phase coherence in the finally created state since it is through the phases of the created state that the desired interference manifests itself. Finally, note that care must be taken to insure that the experimental implementation leads to the cancellation of all spatial phase factors (not discussed above) which are associated with the individual electric fields.

With the basic principle firmly established, theoretical work continues on innovative routes to implement coherent control. Successes thus far include (1) a demonstration that yield at a fixed angle can be controlled by varying the polarization of light,[1d] (2) an implementation in which the created continuum state is within the continuum band of a semiconductor, allowing for laser control of current directionality without a bias voltage,[1f] (3) an approach that utilizes pulses of light to create the level coherences,[1g] and (4) an extension of the latter procedure to controlling bimolecular reactions.[1h] We briefly describe the time-dependent approach (number 3), which will allow us to demonstrate graphically the way information regarding the preferred reaction products is carried in the phase of the wavefunction.

Consider then the approach shown schematically in Figure 4. In this case we are attempting to control the relative yield of a hypothetical reaction with masses of DH$_2$, that is, the model reaction
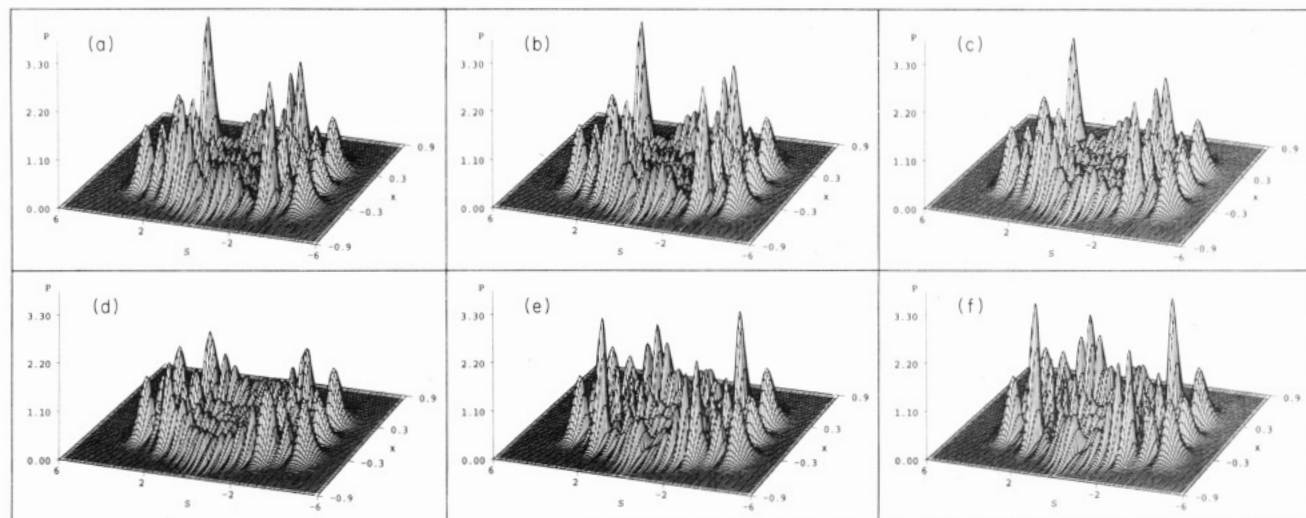
$$DH_2 \rightarrow D + H_2$$

$$\rightarrow H + HD \quad (16)$$
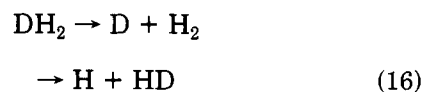
Figure 6. Time evolution of the square of the wavefunction for a superposition state comprising levels 56 and 57 of the G1 surface of H_3. The probability is shown as a function of S and x at times (a) 0, (b) 0.0825 ps, (c) 0.165 ps, (d) 0.33 ps, (e) 0.495 ps, and (f) 0.66 ps, which correspond to equal fractions of one-half the period $2\pi/\omega_{2,1}$.

occurring on the model ground-state potential shown in Figure 4. The approach is carried out in two steps. First we prepare a linear superposition of bound states of energy E_1 and E_2 on the excited surface. This can be done most readily by using a coherent pulsed laser centered about the average frequency $[(E_1 + E_2) - E_g]/\hbar$ to excite the system from the ground-state level, which has energy E_g. Then this superposition state can be subjected to a second laser pulse, which causes stimulated emission down to the ground state, but in the energy regime corresponding to the continuum of the ground electronic state. The energetics is shown as arrows in Figure 4. A detailed analysis shows that the control parameters associated with this mode of coherent control are the time between application of the two laser pulses and the relative magnitude of the intensity of the light field at the relevant frequencies. Typical results are shown in Figure 5, where the ratio of products in the above reaction is seen to be controllable over a wide yield range.

It is highly instructive to examine the nature of the superposition state that is prepared in the initial excitation from the ground to the first excited state. An example of such a state is shown in Figure 6, where we plot the wavefunction for a collinear model of reaction 16. Specifically, the coordinates are the reaction coordinate S and its orthogonal conjugate x. The wavefunction is shown evolving over $1/2$ of its total possible period. Examination of Figure 5 shows that deexciting this superposition state during frame b would yield a substantially different product yield than deexciting at the time of frame e. However, there is clearly no particular preference of the wavefunction for large positive or large negative S at these particular times, which would be the case if the reaction control were a result of some spatial characteristics of the wavefunction. Rather the essential control characteristics of the wavefunction are carried in the quantum amplitude and phase of the created superposition state. The method we advocate, which lies entirely within the regime of quantum mechanics, utilizes pulses on the relatively "long" time scale of picoseconds. An alternative pro-

cedure,[9] which takes advantage of the classical picture associated with localized wavepackets, utilizes pulses on the very short femtosecond time scale.

It should be emphasized that for picosecond and nanosecond delay times we need not worry about the effect of collisions (which tend to destroy coherence) because the probability of a collision occurring on such time scales, at ordinary pressures, is essentially 0. When a continuous source of coherent light is used, the phase-destroying effects of collisions should be taken into account. Even under these conditions, control can survive. Specifically, we have found[1e] that coherent control survives the effect of collisions provided that one continuously pumps the superposition state with a sufficiently strong light source.

3. Technical Summary

A brief technical summary is perhaps worthwhile at this point. We have shown how chemical reactions can be controlled by using weak laser fields. To appreciate control of chemical reactions requires that we understand the nature of the solutions to the Schrödinger equation in the energy regime where reactions to a number of different products are possible. The nature of these solutions is straightforward: at energy E one has a set of degenerate wavefunctions, and the reaction probability is determined by the amount of each product one has in this superposition. Further, the amount of product ultimately observed is predetermined by the preparation step. Thus, control means devising a preparation scheme that incorporates experimental parameters whose variation alters the relative amounts of each product in the superposition state. We have shown that this can be done by building quantum interference into the created state, specifically by interfering different coherent optical excitation paths to the desired energy. A number of different experimental scenarios have been discussed.

4. Coherence Chemistry

Our discussion makes clear that the characteristic features that we invoke in order to control chemical

(8) Shapiro, M.; Brumer, P. In *Methods of Laser Spectroscopy*; Prior, A, Ben-Reuven, A., Rosenbluh, M., Eds.; Plenum: New York, 1986.

(9) Tannor, D. J.; Rice, S. A. *J. Chem. Phys.* **1985**, *83*, 5013. Tannor, D. J.; Kosloff, R.; Rice, S. A. *J. Chem. Phys.* **1986**, *85*, 5805.

reactions are purely quantum in nature. There is, for example, little classical about the time-dependent picture where the ultimate outcome of the deexcitation, i.e., product H + HD or H_2 + D, depends entirely upon the phase and amplitude characteristics of the wavefunction. Indeed, as repeatedly emphasized above, if, e.g., collisional effects are sufficiently strong so as to wipe out the phases, then reaction control is lost. Hence reaction dynamics is intimately linked to the wavefunction phases which are controllable through coherent optical phase excitation.

These results must be viewed in light of the history of molecular reaction dynamics over the past two decades. Possibly the most useful result of the reaction dynamics research effort has been the recognition that the vast majority of qualitatively important phenomena in reaction dynamics are well described by classical mechanics.[10]   Quantum and semiclassical mechanics

were viewed as necessary only insofar as they correct quantitative failures of classical mechanics for unusual circumstances and/or for the dynamics of very light particles. Considering reaction dynamics in traditional chemistry to be essentially classical in character, therefore, appeared to be essentially correct for the vast majority of naturally occurring molecular processes. Coherence played no role. The approach that we have introduced above makes clear, however, that coherence phenomena have great potential for application. By calling attention to the extreme importance of coherence phenomena to controlled chemistry, we herald the introduction of a new focus in atomic and molecular science, i.e., introducing coherence in controlled environments to modify reactions, a kind of coherence chemistry.

(10) See, for example: Bernstein, R. B.; Levine, R. D. *Molecular Reaction Dynamics*; Oxford Univ. Press: New York, 1987.

Photoionization Mass Spectrometric Studies of Free Radicals

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Free radicals have been fascinating to chemists for decades, partly because of their important but ephemeral nature as intermediates in chemical reactions, e.g., combustion and atmospheric processes. For example, the reaction OH + CO → H + CO_2 is the dominant source of CO_2 in the oxidation of hydrocarbons and is important in the chemistry of the upper atmosphere and in the formation of chemical smog. This reaction is believed to proceed through a COOH intermediate, but until very recently, this species had not been detected in the gas phase. The depletion of ozone in the stratosphere is attributed to the reaction of the free radical ClO with O_3. The chemical vapor deposition method of producing solid-state devices based on Si or Ge employs a plasma containing free-radical hydrides of Si and Ge.

Some early studies demonstrating the existence of free radicals in the gas phase were performed by electron-impact mass spectrometry.[1]   However, neither structural information nor precise thermochemical data were forthcoming. Lossing and collaborators[2] improved

and developed this technique, particularly for the determination of ionization potentials of free radicals. With the advent of vacuum ultraviolet photoionization methods, it became clear that electron impact suffered two disadvantages relative to photon impact: (a) lower energy resolution, even with the use of electron monochromators, and (b) the fundamental nature of the electron-impact ionization process, which blurs details (such as autoionization). According to theory,[3] the energy dependence of photoionization at or just beyond threshold for a particular ionic state is a step function, while with electron impact the probability for ionization increases linearly from 0 at threshold. Since the energy derivative of a line of constant slope is constant, the energy derivative of an idealized electron-impact curve near threshold appears as a step in the corresponding photoionization curve. Hence, the onset in photoionization is more abrupt and can be determined more precisely.

Two complementary methods of vacuum ultraviolet (vacuum UV) photoionization have evolved: photoelectron spectroscopy (PES) and photoionization mass spectrometry (PIMS). Typically, PES employs a monochromatic light source incident upon a gaseous target, and an electron energy analyzer to measure the

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(1) Eltenton, G. C. *J. Chem. Phys.* 1942, *10*, 403; 1947, *15*, 455.
(2) Lossing, F. P. *Ann. N.Y. Acad. Sci.* 1957, *67*, 499. Lossing, F. P.; Maeda, K.; Semeluk, G. P. *Recent Dev. Mass Spectrosc. Proc. Int. Conf. Mass Spectrosc., 1969* 1970, 791–6. Also many individual papers published between the early 1950s and 1980s. See also: Holmes, J. L.; Lossing, F. P.; Maccoll, A. *J. Am. Chem. Soc.* 1988, *110*, 7339. Holmes, J. L.; Lossing, F. P. *Ibid.* 1988, *110*, 7343.
(3) Wigner, E. P. *Phys. Rev.* 1948, *73*, 1002.