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On the Origin of Pulse Shaping Control of Molecular Dynamics[†]

Moshe Shapiro

Department of Chemical Physics, The Weizmann Institute of Science, Rehovot, 76100 Israel and ITAMP, Center for Astrophysics, Harvard University, 60 Garden Street, Cambridge, Massachusetts 02138

Paul Brumer*

Chemical Physics Theory Group, Department of Chemistry, University of Toronto, Toronto, Ontario, M5S3H6, Canada

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Pulsed laser control of photodissociation in the strong and the weak coupling regimes is analyzed. Simple pulse shaping conditions are derived and are given explicitly in the weak coupling regime. Implicit equations in the strong coupling regime are also derived. Short, shaped pulses, yielding optimal control, are shown to work due to quantum interference among routes to the same final energy. This is contrary to the prevailing view that the role of a short pulse is to be fast enough so as to "beat the process of intramolecular vibrational redistribution (IVR)".

I. Introduction

Coherent control constitutes a method in which quantum interference effects are used to control molecular processes.[1] There are, at present, two distinct paradigms for the coherent control of chemical reactions. One, due to Brumer and Shapiro,[2] approaches control in energy space. This is done by expanding the molecular states in terms of the eigenstates of the molecular Hamiltonian. Control is shown to be attainable by populating each continuum state using multiple interfering pathways. Ideally, this interference is made to be destructive for all states but one, the ("target" or "objective") state of interest.

The alternative paradigm, originally due to Tannor and Rice[3] and central to the optimal control approach,[4] attempts to achieve the same goal by considering the explicit time dependence of states that evolve to a desired target. Although not as manifestly evident, this approach also relies upon the existence of multiple interfering pathways to bring about control.

Both of these paradigms bring their own correct insights to coherent control. In addition, they each motivate appropriate experiments in different technological domains. Thus, the energy-resolved viewpoint has been used mainly to motivate ns pulsed laser experiments, whereas the time-dependent perspective was used mainly to devise and interpret ultrafast experiments.[5]

Consider now control of the dynamics of isolated systems (e.g., photodissociation processes). Adopting the time-dependent approach to this case has a conceptual drawback that has led to some misunderstanding. Specifically, despite efforts to counter this incorrect viewpoint,[6] there is still talk about the need for faster laser pulses, or more complex laser pulse shapes, to "beat out the effects of intramolecular vibrational redistribution (IVR)". That is, there remains the incorrect perception that control over chemical reactions in isolated molecules is achieved by creating molecular states whose controlled time scale of evolution is faster than IVR rates.[7]

It is the purpose of this paper to show that the energy resolved perspective both corrects this perception and adds considerably to our understanding of pulse-shaped control. Specifically, we show that even for strong laser fields, the shape of the exciting laser pulse, and hence certainly the time scale of the subsequent molecular evolution, is irrelevant to the control over unimolecular processes in the case where a *single* bound state is photodissociated. Second, we explicitly consider pulsed laser excitation when *many* bound states are coupled to a continuum, and show that in this case control is possible. We also derive the pulse shaping conditions that allow for control in this case and show the origin of control in quantum interference.

II. Multichannel Dissociation/Ionization of a Single Precursor State

Consider first the case of a single bound state excited to dissociation using a pulsed laser. Naive thinking would suggest that shaping the pulse, either to enhance particular frequencies or to shorten the pulse in time, might prove useful in order to increase the yield of a desired product state. Here we show that this is not the case. In particular, we show that, contrary to common wisdom, as long as only a single bound state is effectively involved, the situation is uncontrollable, irrespective of the pulse shape used.

Consider the action of a pulse of light, described by a classical time-evolving electric field of polarization $\hat{\epsilon}$,

$$\vec{\epsilon} = 2\hat{\epsilon} R_{\mathrm{e}}\{\epsilon(t) e^{i w_L t}\} \qquad (1)$$

on an initially bound molecular system. Given the total radiation−matter Hamiltonian in the "electric-dipole" approximation,

$$H_{\mathrm{tot}} = H - \vec{\mu}\cdot\vec{\epsilon}(t) \qquad (2)$$

where H is the molecular Hamiltonian and $\vec{\mu}$ is the dipole operator, the outcome of the action of the pulse is obtained by

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solving the time-dependent Schrödinger equation,

$$i\hbar\frac{\partial}{\partial t}|\Psi\rangle = H_{\text{tot}}|\Psi\rangle \tag{3}$$

The bound and continuum eigenstates of the molecular Hamiltonian H satisfy the time-independent Schrödinger equation,

$$[E_i - H]|E_i\rangle = [E - H]|E, \mathbf{n}^-\rangle = 0 \tag{4}$$

where $|E_i\rangle$ denote the bound eigenstates and $|E, \mathbf{n}^-\rangle$ the continuum eigenstates, labeled by the indices $\mathbf{n}$ and E, with $\mathbf{n}$ comprising a set of quantum numbers that specify the final ($t \to \infty$) internal (vibrational, rotational, etc.) states of the dissociated polyatomic fragments as well as the product arrangement. These indices label the eigenstates $|E, \mathbf{n}; 0\rangle$ of the separated fragments Hamiltonian, $H_0 = H - V$. That is,

$$[E - H_0]|E, \mathbf{n}; 0\rangle = 0 \tag{5}$$

Here V is the interaction between the fragments, which naturally decays as R, the distance between the fragments, becomes sufficiently large,

$$\lim_{R\to\infty} V(R) = 0 \tag{6}$$

We denote the "incoming" eigenstates of H by $|E, \mathbf{n}^-\rangle$. These states satisfy the incoming Lippmann Schwinger equation,

$$|E, \mathbf{n}^-\rangle = |E, \mathbf{n}; 0\rangle + \lim_{\zeta\to 0}[E - i\zeta - H_0]^{-1}V|E, \mathbf{n}^-\rangle \tag{7}$$

which guarantees[8] that the incoming states correlate in the $t \to \infty$ limit with a single $|E, \mathbf{n}; 0\rangle$ eigenstate of H_0. That is, we say that

$$\lim_{t\to\infty}|E, \mathbf{n}^-\rangle e^{-iEt/\hbar} = |E, \mathbf{n}; 0\rangle e^{-iEt/\hbar} \tag{8}$$

meaning more precisely that an arbitrarily narrow wave packet of scattering states $|E, \mathbf{n}^-\rangle$ correlates with an equally narrow wave packet of product states $|E, \mathbf{n}; 0\rangle$ in the long time limit:

$$\lim_{\Delta\to 0}\lim_{t\to\infty}\int_\Delta c_E|E, \mathbf{n}^-\rangle e^{-iEt/\hbar}\, dE = \int_\Delta c_E|E, \mathbf{n}; 0\rangle e^{-iEt/\hbar}\, dE \tag{9}$$

The above radiation-free basis set enables us to explicitly include the $t \to \infty$ limit in the full time dependent wave function. Considering now the case where only a *single* bound state $|E_1\rangle$ is coupled to the continuum, we can expand $|\Psi(t)\rangle$ as[9-11]

$$|\Psi(t)\rangle = b_1(t)|E_1\rangle e^{-iE_1t/\hbar} + \sum_{\mathbf{n}}\int dE\, b^{(1)}_{E,\mathbf{n}}(t)|E, \mathbf{n}^-\rangle e^{-iEt/\hbar} \tag{10}$$

Substituting this expansion into the time-dependent Schrödinger equation and using the orthogonality of the basis functions yields a set of first-order differential equations for the expansion coefficients,

$$\frac{d}{dt}b_1 = i\int dE\sum_{\mathbf{n}}\Omega_{1,E,\mathbf{n}}(t)b^{(1)}_{E,\mathbf{n}}(t)\, e^{-i\Delta_{E,1}t} \tag{11a}$$

$$\frac{d}{dt}b^{(1)}_{E,\mathbf{n}} = \Omega^*_{1,E,\mathbf{n}}(t)e^{i\Delta_{E,1}t}b_1(t), \text{ for each } E \text{ and } \mathbf{n} \tag{11b}$$

where we have retained only the rotating waves terms. $\Delta_{E,i}$, the detuning, is defined as

$$\Delta_{E,i} \equiv \omega_{E,i} - \omega_L \text{ with } \omega_{E,i} \equiv (E - E_i)/\hbar,\ i = 1, ..., \tag{12}$$

and $\Omega_{1,E,\mathbf{n}}(t)$, the (time-varying) Rabi-frequency, is defined as

$$\Omega_{1,E,\mathbf{n}}(t) \equiv \langle E_1|\mu|E, \mathbf{n}^-\rangle\epsilon(t)/\hbar \tag{13}$$

where μ is the projection of the dipole operator along the polarization vector of the field.

We proceed[12] by integrating the $b^{(1)}_{E,\mathbf{n}}$ continuum coefficients of eq 11 over time, while imposing the boundary condition that only the $|E_1\rangle$ state is initially populated, i.e., that $b^{(1)}_{E,\mathbf{n}}(t \to -\infty) = 0$. With this boundary condition, we have that

$$b^{(1)}_{E,\mathbf{n}}(t) = i\int_{-\infty}^{t} dt'\,\Omega^*_{1,E,\mathbf{n}}(t')b_1(t')e^{i\Delta_{E,1}t} \tag{14}$$

Of interest is the state-specific probability, $P_{\mathbf{n}}(E)$, which is the long-time probability, at fixed energy E, of observing a particular internal state $|\mathbf{n}\rangle$ of the dissociated fragments. It is given using eq 14 as

$$P_{\mathbf{n}}(E) = P_{\mathbf{n}}(E, t \to \infty) = |b^{(1)}_{E,\mathbf{n}}(t \to \infty)|^2 = \left|\frac{1}{\hbar}\langle E_1|\mu|E, \mathbf{n}^-\rangle\int_{-\infty}^{\infty} dt'\,\epsilon^*(t')b_1(t')e^{i\Delta_{E,1}t'}\right|^2 \tag{15}$$

It follows from eqs 14 and 15 that the long-time ratio of probabilities (which is the key quantity to control in chemical reactions) to observe two internal fragment states is given by

$$\frac{P_{\mathbf{n}}(E)}{P_{\mathbf{m}}(E)} = \frac{P_{\mathbf{n}}(E, t)}{P_{\mathbf{m}}(E, t)} = \left|\frac{b^{(1)}_{E,\mathbf{n}}(t)}{b^{(1)}_{E,\mathbf{m}}(t)}\right|^2 = \left|\frac{\langle E_1|\mu|E, \mathbf{n}^-\rangle}{\langle E_1|\mu|E, \mathbf{m}^-\rangle}\right|^2 \tag{16}$$

We see that the relative probabilities of populating different asymptotic states at a fixed energy E are independent of the laser pulse attributes (save for the polarization direction). Moreover, the branching ratio does not change during the pulse. This result, which coincides with that of perturbation theory, holds true irrespective of the laser power, provided that only one bound state $|E_1\rangle$ is coupled to the continuum.

The above result holds true even when the rotating waves approximation, adopted above, breaks down, because even in this case the probability can be written as

$$P_{\mathbf{n}}(E) = |b^{(1)}_{E,\mathbf{n}}(t \to \infty)|^2 = \left|\frac{1}{\hbar}\langle E_1|\mu|E, \mathbf{n}^-\rangle\int_{-\infty}^{\infty} dt'\{\epsilon^*(t')e^{i\Delta_{E,1}t'} + \epsilon(t')e^{i(\omega_{E,1}+\omega_L)t'}\}b_1(t')\right|^2 \tag{17}$$

and the pulse attributes still cancel out when the $P_{\mathbf{n}}(E)/P_{\mathbf{m}}(E)$ branching ratio is evaluated.

We conclude that pulse shaping does not provide a means of controlling the ratio of products formed in the excitation of a single bound state. Hence, the common phrase that it is advantageous to shorten the laser pulse "in order to beat IVR" is totally misleading: the fate of the system merely follows the nature of the radiation-free $|E, \mathbf{n}^-\rangle$ molecular eigenstates.

III. Quantum Interference Control

The lack of pulse-shaping control demonstrated above can be overcome by photodissociating not just one $|E_1\rangle$ bound state, but a superposition of several bound states $|E_i\rangle$. Such a superposition state can be created separately by a preparation pulse. This is in essence the pump–dump control scenario.[3,13] Alternatively, the superposition state can be created by the photolysis pulse itself (by, e.g., a stimulated Raman process), provided that the bandwidth of the pulse is comparable to the energy spacings between the $|E_i\rangle$ levels.

Mathematically speaking, the object of control is the preparation of a single $|E, \mathbf{n}^-\rangle$ state. If this is achieved, we are guaranteed, by eq 8, complete control insofar as only one fragment target state $|E, \mathbf{n}; 0\rangle$ is populated as $t \to \infty$. With this in mind, we rewrite eq 10 in matrix notation as

$$|\Psi^{(1)}(t)\rangle = \int \mathrm{d}E\mathrm{e}^{-iEt/\hbar}\,(b^{(1)}_{E,\mathbf{n}_1}(t), b^{(1)}_{E,\mathbf{n}_2}(t), b^{(1)}_{E,\mathbf{n}_3}(t)\ ,...,)\begin{pmatrix}|E, \mathbf{n}_1{}^-\rangle\\ |E, \mathbf{n}_2{}^-\rangle\\ |E, \mathbf{n}_3{}^-\rangle\\ .\\ .\\ .\end{pmatrix} \tag{18}$$

where $|\Psi^{(1)}(t)\rangle$ is the excited portion of the wave packet that originated from state $|E_1\rangle$, namely,

$$|\Psi^{(1)}(t)\rangle \equiv |\Psi(t)\rangle - b_1|E_1\rangle\mathrm{e}^{-iE_1t/\hbar} \tag{19}$$

To achieve the control target we consider preparing a whole array of wave packets, by, for example, starting with other initial states composed of the system bound states $|E_i\rangle$. That is,

$$\underline{\Psi}(t) = \int \mathrm{d}E\mathrm{e}^{-iEt/\hbar}\underline{\underline{\mathrm{b}}}(E)\cdot\underline{\psi}(E) \tag{20}$$

where

$$\underline{\psi}(t) \equiv \begin{pmatrix}|\Psi^{(1)}(t)\rangle\\ |\Psi^{(2)}(t)\rangle\\ |\Psi^{(3)}(t)\rangle\\ .\\ .\\ .\end{pmatrix} \tag{21}$$

$$\underline{\underline{\mathrm{b}}}(E) \equiv \begin{pmatrix}b^{(1)}_{E,\mathbf{n}_1}, b^{(1)}_{E,\mathbf{n}_2}, b^{(1)}_{E,\mathbf{n}_3}, ...\\ b^{(2)}_{E,\mathbf{n}_1}, b^{(2)}_{E,\mathbf{n}_2}, b^{(3)}_{E,\mathbf{n}_3}, ...\\ b^{(3)}_{E,\mathbf{n}_1}, b^{(3)}_{E,\mathbf{n}_2}, b^{(3)}_{E,\mathbf{n}_3}, ...\\ .\\ .\\ .\end{pmatrix} \tag{22}$$

and

$$\underline{\psi}(E) \equiv \begin{pmatrix}|E, \mathbf{n}_1{}^-\rangle\\ |E, \mathbf{n}_2{}^-\rangle\\ |E, \mathbf{n}_3{}^-\rangle\\ .\\ .\\ .\end{pmatrix} \tag{23}$$

It is easy to see that the $\underline{\underline{\mathrm{b}}}(E)$ matrix factorizes as

$$\underline{\underline{\mathrm{b}}}(E) = \underline{\underline{\widehat{\mathsf{E}}}}(E)\cdot\underline{\underline{\mathrm{M}}}(E) \tag{24}$$

where

$$\underline{\underline{\mathrm{M}}}(E) = \begin{pmatrix}\langle E_1|\mu|E, \mathbf{n}_1{}^-\rangle, \langle E_1|\mu|E, \mathbf{n}_2{}^-\rangle, ...\\ \langle E_2|\mu|E, \mathbf{n}_1{}^-\rangle, \langle E_2|\mu|E, \mathbf{n}_2{}^-\rangle, ...\\ .\\ .\\ .\end{pmatrix} \tag{25}$$

and where $\underline{\underline{\widehat{\mathsf{E}}}}(E)$ is a diagonal matrix of the Fourier transform of the pulse amplitude times the bound states coefficients, at the transition frequencies $\omega_{E,i}$,

$$\underline{\underline{\widehat{\mathsf{E}}}}(E) = \begin{pmatrix}\mathsf{E}_1(E), 0, 0, 0, ...\\ 0, \mathsf{E}_2(E), 0, 0, ...\\ 0, 0, \mathsf{E}_3(E), 0, ...\\ .\\ .\\ .\end{pmatrix} \tag{26}$$

with

$$\mathsf{E}_i(E) = \int_{-\infty}^{\infty} \mathrm{d}t\epsilon^*(t)\mathrm{e}^{i\Delta_{E,i}t}\, b_i(t) \tag{27}$$

Writing the array of possible wave function produced as,

$$\underline{\Psi}(t) = \int \mathrm{d}E\mathrm{e}^{-iEt/\hbar}\,\underline{\underline{\widehat{\mathsf{E}}}}(E)\cdot\underline{\underline{\mathrm{M}}}(E)\cdot\underline{\psi}(E) \tag{28}$$

allows us to examine the possibility of taking different linear combinations of the components of the $\underline{\Psi}(t)$ vector so as to satisfy the control objectives of producing a single $|E, \mathbf{n}_i{}^-\rangle$ state. In this way different pathways starting with different precursor states leading to the same $|E, \mathbf{n}_i{}^-\rangle$ state will be seen to interfere to achieve the desired goal.

As an example, we consider a superposition state composed of the sum over the components of $\underline{\psi}(t)$,

$$\Psi'(t) = \sum_k \int \mathrm{d}E\mathrm{e}^{-iEt/\hbar}\,\mathsf{E}_k(E)\sum_j \underline{\underline{\mathrm{M}}}(E)_{k,j}|E, \mathbf{n}_j{}^-\rangle \tag{29}$$

In the weak field limit, the population and the phase of the initial levels can be assumed constant with time,

$$b_k(t) \approx b_k \equiv b_k(-\infty) \tag{30}$$

in which case all the $\mathsf{E}_k(E)$ matrix elements factor as

$$\mathsf{E}_k(E) \approx b_k\int_{-\infty}^{\infty} \mathrm{d}t\epsilon^*(t)\mathrm{e}^{i\Delta_{E,k}t} = 2\pi b_k\bar{\epsilon}(\Delta_{E,k}) \tag{31}$$

where

$$\bar{\epsilon}(\omega) \equiv (1/2\pi)\int_{-\infty}^{\infty} \mathrm{d}t\epsilon^*(t)\mathrm{e}^{i\omega t} \tag{32}$$

Our objective to populate exclusively the *i*th fragment state $|E, \boldsymbol{n}_i{}^-\rangle$ can be realized in the weak field domain by choosing the pulse shape which defines $\Psi'(t)$ [eq 29] to satisfy the condition,

$$b_k\bar{\epsilon}_i(\Delta_{E,k}) = (\underline{\underline{\mathrm{M}}}(E)^{-1})_{i,k} \tag{33}$$

This choice eliminates all but a single $|E, \boldsymbol{n}_i{}^-\rangle$ state in $\Psi'(t)$ given by eq 29.

Thus, the control objective, the *i*th product state, is seen to be realized by starting out with an initial superposition of bound states,

$$|\Phi(t)\rangle = \sum_k b_k |E_k\rangle \mathrm{e}^{-iE_k t/\hbar} \qquad (34)$$

and subjecting the system to the action of a pulse shaped according to eq 33. This allows for multiple-path interference between the various ways of generating the $|E, \boldsymbol{n}_i^-\rangle$ state. The weight of each pathway is chosen so as to cause destructive interference in the production of all the $|E, \boldsymbol{n}^-\rangle$ states but one, the $|E, \boldsymbol{n}_i^-\rangle$ state.

Thus, pulse shaping leads to control only insofar as it allows for interference between different coherently related bound states comprising Φ, or more generally, between different pathways leading to the same product. Hence, the effect of a short pulse is not to "beat IVR", but rather, due to its increased bandwidth, to allow processes originating in more bound states to interfere with each other in forming the same $|E, \boldsymbol{n}_i^-\rangle$ state.

In general, control is incomplete because the pulse shaping conditions of eq 33 cannot be satisfied simultaneously for all energies. This can be seen by noting that the $(\underline{\underline{M}}(E)^{-1})$ matrix element, which (for a single i) is a function of two variables, k and E, has to be equated to a product of a function of k, b_k, and a function of E, $\bar{\epsilon}_i(\Delta_{E,k})$. In general, this equality cannot be satisfied. There are nevertheless important cases in which eq 33 can be satisfied. These are: either when $\underline{\underline{M}}(E)$ does not vary too rapidly with E, or, conversely, when the $\langle E_1|\mu|E, \boldsymbol{n}^-\rangle$ matrix elements, which determine $\underline{\underline{M}}(E)$ (and the absorption spectrum), span a very narrow range of energies (e.g., a narrow resonance).

The weak field control discussed here must be achieved in two steps. First it is necessary to create the $\Phi(t)$ superposition state of eq 34. This state is then irradiated with the pulse satisfying eq 33. This is the essence of the weak field pump–dump scenario. However, in the strong field domain these two processes cannot be separated because the factorization of eq 31 does not hold. In that case the control conditions become

$$\mathcal{E}_{i,k}(E) = (\underline{\underline{M}}(E)^{-1})_{i,k} \qquad (35)$$

In this strong field regime the $b_k(t)$ coefficients are embedded in $\mathcal{E}_k(E)$ (see eq 27) and are themselves functions of $\epsilon(t)$. Hence the problem is inherently nonlinear, necessitating an iterative solution. Nevertheless, the same interference mechanism outlined in the weak field domain applies. The only difference is that the pulse-shaping conditions are given implicitly via eq 35, rather than explicitly via eq 33, as in the weak field domain.

IV. Bichromatic Control

As an example of the general procedure described above we now examine the simple case—bichromatic control[2]—achieved by considering a two-dimensional $\underline{\Psi}(t)$ vector. Constructing a linear superposition of just two initial states

$$|\Phi(t)\rangle = b_1|E_1\rangle \mathrm{e}^{-iE_1 t/\hbar} + b_2|E_2\rangle \mathrm{e}^{-iE_2 t/\hbar} \qquad (36)$$

we have that

$$b_{E,\mathbf{n}}(t \rightarrow \infty) = \frac{i}{\hbar}\{(E, \mathbf{n}^-|\mu|E_1\rangle \int_{-\infty}^{\infty} \mathrm{d}t' \epsilon^*(t') \mathrm{e}^{i\Delta_{E,1}t'} b_1(t') + \langle E, \mathbf{n}^-|\mu|E_2\rangle \int_{-\infty}^{\infty} \mathrm{d}t' \epsilon(t') \mathrm{e}^{i\Delta_{E,2}t'} b_2(t')\} \qquad (37)$$

In first-order perturbation theory, $b_1(t)$ and $b_2(t)$ are constant. Hence in the weak field regime,

$$b_{E,\mathbf{n}}(t \rightarrow \infty) \approx \frac{2\pi i}{\hbar}\{\langle E, \mathbf{n}^-|\mu|E_1\rangle \bar{\epsilon}(\Delta_{E,1}) b_1 + \langle E, \mathbf{n}^-|\mu|E_2\rangle \bar{\epsilon}(\Delta_{E,2}) b_2\} \qquad (38)$$

where $\bar{\epsilon}(\omega)$ is defined in eq 32. Recognizing that $\bar{\epsilon}(\omega)$ has a phase, we can write

$$\bar{\epsilon}(\Delta_{E,1}) = |\bar{\epsilon}(\Delta_{E,1})| \mathrm{e}^{-i\theta(\Delta_{E,1})}, \ \bar{\epsilon}(\Delta_{E,2}) = |\bar{\epsilon}(\Delta_{E,2})| \mathrm{e}^{-i\theta(\Delta_{E,2})} \qquad (39)$$

and transform eq 38 into

$$b_{E,\mathbf{n}}(\infty) = \frac{2\pi i}{\hbar}\{\langle E, \mathbf{n}^-|\mu|E_1\rangle |\bar{\epsilon}(\Delta_{E,1})| \mathrm{e}^{-i\theta(\Delta_{E,1})} b_1 + \langle E, \mathbf{n}^-|\mu|E_2\rangle |\bar{\epsilon}(\Delta_{E,2})| \mathrm{e}^{-i\theta(\Delta_{E,2})} b_2\} \qquad (40)$$

The probability of observing the product state $\mathbf{n}$ at infinite time is therefore now given as

$$P_{\mathbf{n}}(E) = \frac{4\pi^2}{\hbar^2}|\langle E, \mathbf{n}^-|\mu|E_1\rangle |\bar{\epsilon}(\Delta_{E,1})| \mathrm{e}^{-i\theta(\Delta_{E,1})} b_1 + \langle E, \mathbf{n}^-|\mu|E_2\rangle |\bar{\epsilon}(\Delta_{E,2})| \mathrm{e}^{-i\theta(\Delta_{E,2})} b_2| \qquad (41)$$

It is clear that in this configuration the pulse attributes have been "entangled" with the material matrix elements. As a result, by shaping the pulse (e.g., by tuning the relative phase $\theta(\Delta_{E,2}) - \theta(\Delta_{E,1})$ or the relative amplitude $|\bar{\epsilon}(\Delta_{E,2})/\bar{\epsilon}(\Delta_{E,1})|$), we can change the branching ratios to different channels. The above mechanism serves as the basis for the so-called bichromatic coherent control scenario.[2]

It is possible to deviate from the weak field regime and incorporate some of the effects of strong fields in a simple manner by assuming that state $|E_1\rangle$ is decoupled from state $|E_2\rangle$. In that case it is possible to solve explicitly for the $b_1(t)$ coefficient by substituting eq 14 in eq 11a to obtain a first-order integro-differential equation for b_1,

$$\frac{\mathrm{d}b_1}{\mathrm{d}t} = \frac{-1}{\hbar^2}\int \mathrm{d}E \sum_{\mathbf{n}} |\langle E, \mathbf{n}^-|\mu|E_1\rangle|^2 \epsilon(t) \int_{-\infty}^{t} \mathrm{d}t' \epsilon^*(t') \mathrm{e}^{-i\Delta_{E,1}(t-t')} b_1(t') \qquad (42)$$

Equation 42 can be solved numerically in a straightforward fashion. Nevertheless, it is instructive to analyze it in terms of $F_1(t - t')$, the "spectral autocorrelation function",[12,14,11,15] defined as the Fourier transform of the absorption spectrum,

$$F_1(t - t') = \int_0^{\infty} \mathrm{d}E A_1(E) \mathrm{e}^{-i\omega_{E,1}i(t-t')} \qquad (43)$$

where $E = 0$ is taken to be the lowest (threshold) energy in the continuum, and $A_i(E)$, the absorption spectrum from the ith state, is given as

$$A_i(E) \equiv \sum_{\mathbf{n}} |\langle E, \mathbf{n}^-|\mu|\psi_i\rangle|^2 \qquad (44)$$

With the above definition of $F_1(t - t')$, we can rewrite eq 42 as

$$\frac{\mathrm{d}b_1}{\mathrm{d}t} = \frac{-\epsilon(t)}{\hbar^2}\int_{-\infty}^{t} \mathrm{d}t' \epsilon^*(t') F_1(t - t') b_1(t') \qquad (45)$$

We see that the value of the ground-state coefficient at time t

is determined by its past history at $t' < t$ through the "memory kernel" $\epsilon(t)\epsilon(t')F_1(t - t')$.

The simplest (though approximate) solution of eq 45 is obtained if one can assume that all the continua are "flat", i.e., that the bound continuum matrix elements vary slowly with energy and can be replaced by their value at some average energy, say $E_L = E_1 + \hbar\omega_L$

$$\sum_{\mathbf{n}} |\langle E, \mathbf{n}^-|\mu|E_1\rangle|^2 \approx \sum_{\mathbf{n}} |\langle E_L, \mathbf{n}^-|\mu|E_1\rangle|^2 \qquad (46)$$

If in addition one assumes that $\langle E = 0, \mathbf{n}^-|\mu|E_1\rangle \approx 0$ (i.e., the photoabsorption spectrum starts at post-threshold energies), the above approximation, called the "slowly varying continuum approximation" (SVCA),[12,16,17] localizes the autocorrelation function in time. To see this, we note that under the SVCA assumptions it follows from eq 43 that

$$F_1(t - t') \approx \int_{-\infty}^{\infty} \mathrm{d}E A_1(E) \mathrm{e}^{-i\omega_{E,1}(t-t')} \approx A_1(E_L) \int_{-\infty}^{\infty} \mathrm{d}E \mathrm{e}^{-i\omega_{E,1}(t-t')} = 2\pi\hbar A_1(E_L)\delta(t - t') \qquad (47)$$

Substituting eq 47 in eq 45 and performing the integration over E and t', we obtain that

$$\frac{\mathrm{d}b_1}{\mathrm{d}t} = -\Omega(t) b_1(t) \qquad (48)$$

hence,

$$b_1(t) = b_1(-\infty)\mathrm{e}^{-\int_{-\infty}^{t} \Omega(t')\mathrm{d}t'} \qquad (49)$$

where $\Omega(t)$—the "imaginary Rabi frequency"—is defined as

$$\Omega(t) \equiv \pi A_1(E_L)|\epsilon(t)|^2/\hbar = \pi \sum_{\mathbf{n}} |\langle E_L, \mathbf{n}^-|\mu|E_1\rangle\epsilon(t)|^2/\hbar \qquad (50)$$

The factor of 1/2 relative to eq 47 arises because the integration over $t' - t$ in eq 45 is performed over the $[-\infty, 0]$ range rather than the usual $[-\infty, +\infty]$ range.

It follows from eq 49 that a "slowly varying" continuum acts as an irreversible "perfect absorber", since in this approximation $b_1(t)$ decreases monotonically (though not necessarily purely exponentially) with time. In many cases the continuum may have structures that are narrower than the effective bandwidth of the pulse (which depends on its frequency profile and its intensity). Such structures may be due to either the natural spectrum of the nonradiative Hamiltonian[18,19] or to the interaction with the strong external field.[20,21] Under such circumstances we expect the SVCA approximation to break down, yielding nonmonotonic decay dynamics.

Using the SVCA we can now write an analytic formula for bichromatic control that goes beyond perturbation theory. Allowing the initial coefficients to decay according to eq 49, we obtain from eq 37 that

$$b_{E,\mathbf{n}}(t \to \infty) = \frac{i}{\hbar}\{\langle E, \mathbf{n}^-|\mu|E_1\rangle b_1 \int_{-\infty}^{\infty} \mathrm{d}t' \epsilon_1^*(t') \mathrm{e}^{i\Delta_{E,1}t' - \pi/\hbar A_1(E_L)\int_{-\infty}^{t'} |\epsilon_1(t'')|^2 \mathrm{d}t''} + \langle E, \mathbf{n}^-|\mu|E_2\rangle b_2 \int_{-\infty}^{\infty} \mathrm{d}t' \epsilon_2^*(t') \mathrm{e}^{i\Delta_{E,2}t' - \pi/\hbar A_2(E_L)\int_{-\infty}^{t'} |\epsilon_2(t'')|^2 \mathrm{d}t''}\} \qquad (51)$$

where $b_i \equiv b_i(-\infty)$, $i = 1, 2$. Therefore, the probability of observing a particular channel $\mathbf{n}$ is given as

$$P_{\mathbf{n}}(E) = \frac{4\pi^2}{\hbar^2}|\langle E, \mathbf{n}^-|\mu|E_1\rangle|\bar{\eta}(\Delta_{E,1})|\mathrm{e}^{-i\theta(\Delta_{E,1})} b_1 + \langle E, \mathbf{n}^-|\mu|E_2\rangle|\bar{\eta}(\Delta_{E,2})|\mathrm{e}^{-i\theta(\Delta_{E,2})} b_2 \qquad (52)$$

where

$$\bar{\eta}(\omega) \equiv (1/2\pi) \int_{-\infty}^{\infty} \mathrm{d}t \epsilon^*(t) \mathrm{e}^{-\pi/\hbar A_1(E_L)\int_{-\infty}^{t} |\epsilon(t')|^2 \mathrm{d}t'} \, \mathrm{e}^{i\omega t} \qquad (53)$$

This formulation therefore gives a result that is correct (within the range of validity of the SVCA) to all field strengths and that resembles the weak field bichromatic control result (eq 41). The only difference is that instead of the Fourier transform of the pulse electric field, eq 52 depends on the Fourier transform of the product of the pulse electric field and the $\mathrm{e}^{-\pi/\hbar A_1(E_L)\int_{-\infty}^{t} |\epsilon(t')|^2 \mathrm{d}t'}$ decaying factor, describing the depletion of the initial state(s) due to the action of the pulse.

Given this result, the optimal control pulse shaping conditions (eq 33) now become

$$b_k \bar{\eta}_i(\Delta_{E,k}) = (\underline{\underline{M}}(E)^{-1})_{i,k} \qquad (54)$$

This result resembles the weak field condition of eq 33, but due to the replacement of $\bar{\epsilon}_i(\Delta_{E,k})$ by $\bar{\eta}_i(\Delta_{E,k})$, it applies (within the range of validity of the SVCA) to strong fields as well.

V. Summary

We have elucidated the nature of pulsed-shaping control of photodissociation from the viewpoint of energy resolved coherent control theory. The result is a clear-cut demonstration that control is not dependent on time dependent aspects of the pulse in cases where excitation is from a single initial bound state. When excitation is from a superposition of states, the pulse shaping is seen to enhance or reduce the role of multiple interfering pathways that are responsible for control. This discussion should, therefore, lay to rest any attempt to attribute control to effective competition with internal relaxation processes in the molecule which, by their very nature, are coherent and phase preserving.

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