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Active Control of Molecular Dynamics: Coherence versus Chaos

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The status of theoretical and experimental studies of the active control of molecular dynamics is surveyed, with attention focused on the control of product formation in a branching unimolecular reaction.

KEY WORDS: Control of molecular dynamics.

1. INTRODUCTION

The contributions to this meeting in honor of Gregoire Nicolis are devoted, almost exclusively, to the influence of nonlinearity and dynamical chaos on the properties of a system described by classical mechanics. These analyses focus attention on the evolution of the statistical properties of a dynamical system. Since the generic system described by classical mechanics will display dynamical chaos, it is then implied that control of the evolution of the system to a precisely defined final state is not possible. This paper challenges that implication for systems that are described by quantum mechanics. In particular, I will discuss the active control of molecular dynamics, with specific reference to control of product selection in a branching unimolecular chemical reaction. By active control I mean the exploitation of the temporal distributions of frequency, amplitude and phase in a pulsed electromagnetic field coupled to a molecule for the purpose of forcing the molecule to a specified final state. I shall show that control of the dynamical evolution of a molecule is possible because of the

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fundamental role played by interference effects in quantum mechanics. Indeed, all of the control methods I discuss below depend, in one way or another, on the exploitation of quantum interference effects. Since my purpose is to acquaint this audience with the possibilities for dynamical control in quantum systems I will give only a broad stroke description of several different strategies for using quantum mechanical interference to control product selectivity in a chemical reaction, focusing attention on those strategies that have been verified experimentally.

2. WHEN IS CONTROL OF MOLECULAR DYNAMICS ATTAINABLE?

As mentioned in the Introduction, it is not immediately obvious that a control field that will generate a specified molecular state exists for arbitrary choices of the initial and final states of a many-body system such as a polyatomic molecule. Certainly, intuitive notions concerning the internal motions of molecules derived from classical mechanics suggest that, in general, control of the molecular dynamics is not possible. The classical dynamics of a polyatomic molecule exhibits, in different and sometimes interleaved energy regimes, both quasiperiodic and chaotic(1–3) motion. In the chaotic regime the trajectory representing the evolution of the state of the molecule in phase space is extremely sensitive to the initial conditions. Specifically, in the chaotic regime two trajectories started with infinitesimally different initial conditions will diverge such that the distance between them grows exponentially with increasing time. When this is the case, and there is any small uncertainty in the parameters defining the initial state of the molecule, after a short time it is impossible to accurately predict the state to which the molecule has evolved.

The exponential rate of divergence of pairs of initially adjacent trajectories is measured by the Liapanov characteristic number $\chi(\Gamma)$, where Γ is a point in the phase space $\mathbf{\Gamma}$. When $\chi(\Gamma) > 0$ the trajectories diverge from the point Γ, and conversely. The quantitative measure of chaotic motion in a system described by classical mechanics is the Kolomogorov–Sinai entropy, h_{KS}, which can be shown to be equal to the average over phase space of the characteristic e-folding time for exponential growth of the distance between initially close trajectories (Pesin's theorem(4)):

$$h_{\mathrm{KS}} = \sum_i \int \chi_i(\Gamma)\, d\Gamma \tag{1}$$

Clearly, if the motion of the system is chaotic $\chi(\Gamma) > 0$ hence $h_{\mathrm{KS}} > 0$, in which case a small region of phase space of volume W will become uniformly distributed over the entire accessible phase space with e-folding time $-\ln W/h_{\mathrm{KS}}$. On the other hand, if the motion of the system is quasiperiodic two trajectories started with infinitesimally different initial conditions will diverge such that the distance between them grows only linearly with increasing time, hence $\chi(\Gamma) = 0$ and $h_{\mathrm{KS}} = 0$. Because the Kolmogorov–Sinai entropy associated with this motion is zero, the uncertainty in the initial state of the molecule does not prevent accurate prediction of the state to which the molecule has evolved.

At this point a qualitative observation is pertinent. Although the existing theory of control does not directly address whether or not dynamical chaos influences the extent of controllability, it is known that it is possible to find external fields which control the evolution of the broad category of systems whose time dependence is describable by an equation of motion of the form

$$\dot{z}(t) = \left[\hat{H}_0 + \sum u_l(t)\, \hat{H}_l \right] z(t) \tag{2}$$

where $z(t)$ represents the state of the system, $\hat{H}_0$ is the generator of the uncontrolled system dynamics, the $\hat{H}_l$ are operators in the system phase space and the $u_l(t)$ are time dependent scalar functions. The practical demonstration (by direct calculation) that control fields exist for this category of equations of motion implies that for any such system the controlled system dynamics is regular even if the uncontrolled "bare" system dynamics is chaotic. Furthermore, Ott(5) has demonstrated, for a particular example, that it is possible to find a field that controls the dynamics of a system that exhibits chaotic dynamics in the absence of the field. This analysis has been extended by Ott(6) and others(7, 8) with the result that some of the general conditions under which it is possible to find such fields have been delineated.

I wish to focus attention on active control of product selectivity in a chemical reaction, which requires the use of quantum mechanics to describe the dynamics of molecular motion. A characteristic feature of quantum mechanics is that the spectrum of a bounded system is necessarily discrete, hence its dynamics is necessarily quasiperiodic. Kosloff and Rice(9, 10) extended the definition of the Kolmogorov–Sinai entropy to quantum mechanics and showed that the dynamics of a bounded quantum system is always characterized by $h_{\mathrm{KS}} = 0$; other investigators have reached the same conclusion using different considerations.(11) In this class of systems there is no reason to doubt the existence of a field which can control the evolution of the state of the system, even when the motion in the corresponding classical system is chaotic.

Less is certain about the existence of chaotic motion when the quantum system has a spectrum with both discrete and continuum states. It is plausible that motion associated with those states that can be represented as narrow resonances embedded in the continuum is similar to that associated with discrete states, since under a complex rotation transformation of the system Hamiltonian the narrow resonances can be transformed into bound states (in the sense that wave packet states are transformed to surrogate localized states whose wave functions are L^2 integrable).(12–17) Consequently, it is plausible that reactions that are initiated in resonant states can be controlled to some degree; the experimental evidence to be described in the next Section implies that this assertion is valid.

The words "to some degree" in the preceding paragraph are important. For both bounded and unbounded systems we do not presently know whether or not there is a fundamental limit to the extent of control of the quantum many-body dynamics that is attainable. Put another way, we do not know if control of the evolution of a quantum many-body system is subject to a limit analogous to the limit imposed by the Second Law of Thermodynamics on the extent of transformation of heat into work by an engine.

There are a few extant investigations of the potential for control of the quantum dynamics of a many-body system, and the character of that control. The goal of this class of investigations is the establishment of existence theorems, for which purpose it is necessary to distinguish between complete controllability and optimal control of a system. A system is said to be completely controllable if there exists a time interval $[0, T]$ and a set of admissable control fields such that an arbitrary initial state can be transformed, without loss to other states, into an arbitrary final state at *some time* T. A system is said to be strongly completely controllable if there exists a time interval $[0, T]$ and a set of admissable control fields such that an arbitrary initial state can be transformed, without loss to other states, into an arbitrary final state at a *specified time* T. In contrast, optimal control theory designs a field, subject to specified constraints, that guides the evolution of an initial state of the system to be as close as possible to the desired final state at time T.

The work of Huang, Tarn and Clark(18–22) deals with a general formulation of the complete controllability problem for quantum many-body dynamics and includes an existence proof that establishes sufficient (but not necessary) conditions for complete control. They consider a system which can be described by the Hamiltonian $\hat{H}_0$ in the absence of control fields; the system is assumed to have a discrete, but not necessarily bounded, spectrum (e.g., a harmonic oscillator). To control the dynamical evolution of the system external fields are applied and the Schrödinger equation has the form

$$i\hbar \frac{d}{dt}\psi(t) = \left[\hat{H}_0 + \sum_l u_l(t)\, \hat{H}_l \right] \psi(t) \tag{3}$$

where the u_l are real functions of the time and the $\hat{H}_l$ are linear Hermitian operators. Note that the u_l needed to control the evolution of the state of the system depend on the state of the system, so Eq. (3) is, in fact, strongly nonlinear.

The Huang–Tarn–Clark theorem is developed for the case that the $\hat{H}_l$ are independent of the time and the control amplitudes u_l are piecewise constant functions of the time. They show that, for a system with a discrete spectrum, under the conditions stated for the control field amplitudes and the corresponding operators, one can always find a set of field amplitudes that will guide the evolution of an initial state to come arbitrarily close to a chosen final state at some time. If the Lie algebra generated by the set of operators has finite dimension it can be shown that a system with a discrete non-degenerate spectrum is completely controllable in the sense that an arbitrary initial state can be transformed into an arbitrary final state at some later time. The scope of the Huang–Tarn–Clark theorem is not strictly restricted to systems with a discrete spectrum, although only one very simple example of control of a system with a continuous spectrum has been discussed.

Ramakrishna *et al.*(23) have studied the controllability of quantum many body dynamics of systems with a finite number of levels from a point of view which is somewhat different from that used by Huang, Tarn and Clark. For the purpose of investigating controllability, Huang, Tarn and Clark interpret Eq. (3) as an infinite dimensional bilinear system. Ramakrishna and coworkers instead express the Schrödinger equation with included control field in terms of the eigenstates of an operator of interest. This approach yields, for a finite set of states, a finite dimensional bilinear control representation. A loose paraphrasing of the results of Ramakrishna *et al.* is that in a system with a finite number of nondegenerate discrete levels it is always possible to completely control the evolution of an arbitrary initial state to a selected final state. This result confirms the inference drawn by Tersigni, Gaspard and Rice(24) from a study of the optimal control fields which transform various initial states to selected final states in a model five level system.

Despite the results just mentioned, it is not always possible to completely control the evolution of an arbitrary initial state to a selected final state in a system with a discrete spectrum of states. The situations in which there is a loss of complete controllability are associated with one or more restrictions on the paths in state space along which the system may evolve, e.g., cases in which the spectrum of states is partitioned and one wishes to generate an evolution which does not pass through some particular subset of these states. Shapiro and Brumer(25) have examined a system in which the eigenstates of the Hamiltonian are subdivided into three sets, with dimensions M_0, M_1 and M_2. The question they pose is: Is it possible to transform a specified initial state of the system which lies in the subset of states with dimension M_0 into a specified final state of the system which lies in the subspace of states with dimension M_1 without passage through the states of the system which lie in the subspace with dimension M_2? It is shown that if $M_2 \geqslant M_0$ stringent restrictions are required to prevent involvement of the states in M_2 in the specified transformation. This inability to direct the evolution of the state of the system away from a specified set of substates does not contradict the Huang–Tarn–Clark theorem, since that theorem does not admit constraints on the evolution pathway of the state of the system.

Establishing the complete controllability of the quantum dynamics of a many body system is an important backdrop to the development of practical algorithms for generating that control. However, the extant existence theorems give no hint as to how such algorithms can be formulated or how the controllability is influenced by constraints on the applied fields and/or on the evolution pathways which can be used. It is just the latter issues which play a central role in the optimal control theory analysis of the guided evolution of quantum many body dynamics. We note that setting up a calculation of the optimal control field for the transformation of an initial state of a system into a particular final state of that system does not guarantee that such a field exists. And, it must be remembered that even when the optimal control field can be found it does not, in general, provide complete control, since the latter implies that the norm of the difference between the final state reached with the optimal field and the target final state can be made arbitrarily small with respect to variation across admissable controls, not merely a minimum.

Because of the prominent role played by the optimal control theory analysis of the evolution of quantum many body dynamics in recent developments, we will mention some of the results of studies of the existence of optimal control fields. Briefly, for the case that the control field is bounded and can be expressed as an integral operator of the Hilbert–Schmidt type:

(i) Peirce, Dahleh and Rabitz$^{(26)}$ proved that for a spatially bounded quantum system, which necessarily has spatially localized states and a discrete spectrum, optimal control of the evolution of a state is possible.

(ii) Zhao and Rice$^{(27)}$ adapted the analysis of Pierce, Dahleh and Rabitz to show that in a system with both discrete and continuous states optimal control of evolution in the subspace of discrete states is possible.

(iii) Zhao and Rice also showed that evolution can be optimally controlled in the subset of continuum states that can be transformed to be L^2 integrable by a complex rotation (wavepacket states which can be transformed to surrogate localized states).

(iv) Demiralp and Rabitz$^{(28)}$ have shown that, in general, there is a denumerable infinity of solutions to a well posed problem of control of quantum dynamics; the solutions can be ordered in quality according to the magnitude of the minimum of the objective functional which is achieved.

3. REALIZATIONS OF CONTROL OF MOLECULAR DYNAMICS

Consider the case that branching to form different reaction products can occur on the ground state potential energy surface of a molecule. Tannor and Rice$^{(29)}$ suggested that transfer of amplitude from the ground state to an excited state and then, after a specified time delay, back to the ground state, can be used to control the selection of products in the branching reaction. In the simplest realization of the Tannor–Rice control method,$^{(29, 30)}$ attention is focused on amplitude control by altering the separation in time of pump and dump pulses. In this simplest scheme an incident (first) pulse of light transfers probability amplitude from the electronic ground state to the excited state, creating a wave packet on the excited state potential energy surface. In general, the ground and excited states of the molecule have somewhat different bond lengths and bond angles, so the wave packet created on the excited state potential energy surface cannot be stationary with respect to the excited state Hamiltonian. Necessarily, then, the wave packet on the excited state potential energy surface evolves by translation and by dephasing of its components. A second pulse of light, incident after an interval t, will, depending on the position and momentum of the wave packet, dump some of the amplitude from the excited state potential energy surface into a selected reaction channel on the ground state potential energy surface. The idea is to dump the amplitude beyond any barrier obstructing the exit channel on the ground state potential energy surface. To second order in perturbation theory the transfer of amplitude from the excited state to the ground state is not sensitive to whether that amplitude is in phase or out of phase with the preexisting amplitude.

An experimental confirmation of the simplest version of the Tannor–Rice control method has been provided by Gerber and coworkers.(31–34) They studied the competition between ionization and dissociative ionization of Na_2, namely

$$\mathrm{Na_2 \rightarrow Na_2^+ + e^-}$$

versus

$$\mathrm{Na_2 \rightarrow Na^+ + Na + e^-}$$

by varying the time delay between the first and second pulses. Figure 1a displays the relevant molecular potential energy curves, the preparation of the wave packet in the $2^1\prod_g$ state and the one-photon product generating process. The pump laser prepares a wave packet at the inner turning point of the potential curve, which then propagates to the outer turning point. The time delayed second pulse can generate either Na_2^+ by direct excitation to the ${}^2\sum_g^+$ ionic ground state (if it is applied when the wave packet is at the inner turning point of the potential curve) or the doubly excited neutral species Na_2^{**} with a large internuclear separation (if it is applied when the wave packet is at the outer turning point of the potential curve). In the latter case the excited molecule then undergoes autoionization and autoionization induced fragmentation to yield $Na^+ + Na(3s)$. The results of such experiments are shown in Fig. 1b, which displays the ratio of molecular to atomic ion products as a function of delay between the laser pulses. The Na_2^+ signal has a maximum each time the second pulse is applied when the wave packet is at the inner turning point of the $A^1\sum_u^+$ state potential energy curve. Since, for the pulse frequency used, the doubly excited state Na^{**} can only be accessed when the wave packet on the $2^1\prod_g$ state potential curve is in the region of large internuclear separation, the formation of Na^+ is out of phase with the formation of Na_2^+ and the former is modulated at the vibrational frequency in the $2^1\prod_g$ state.

A more sophisticated version of the Tannor–Rice method exploits both amplitude and phase control by pump-dump pulse separation.(35) In this case the second pulse of the sequence, whose phase is locked to that of the first pulse, creates amplitude in the excited electronic state which is in superposition with the initial, propagated, amplitude. The intramolecular superposition of amplitudes is subject to interference; whether the interference is constructive or destructive, giving rise to larger or smaller excited state population for a given delay between pulses,

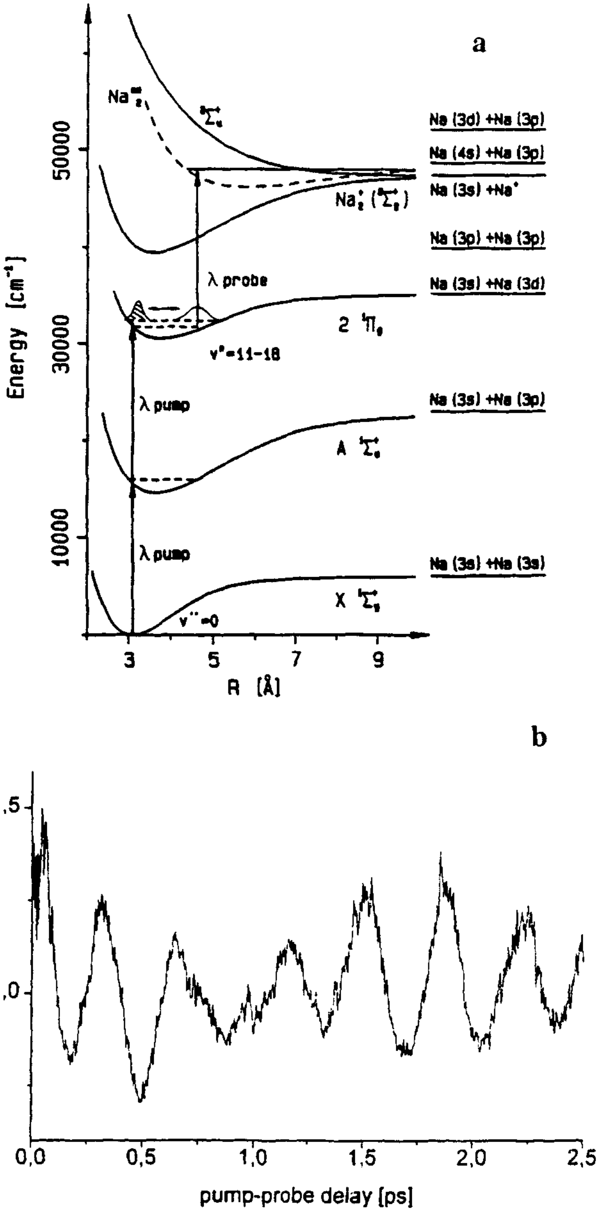

Fig. 1. (a) Potential energy curves for Na$^+$ and Na$_2^+$ ionization, illustrating the preparation of the wave packet in the $2^1\prod_g$ state and the second photon excitation process. (b) Ratio of the Na$^+$ and Na$_2^+$ signals as a function of the control parameter, namely the time delay between the preparation and product forming pulses. From ref. 31.

depends on the optical phase difference between the two pulses and on the detailed nature of the evolution of the initial amplitude. The situation described is analogous to a two-slit experiment. This more sophisticated Tannor–Rice method has been used by Scherer *et al.*(35) to control the population of a level of I_2. The success of this experiment confirms that it is possible to control population flow with interference that is local in time.

Consider, now, a branching unimolecular chemical reaction in which the excited reactant molecule can form at least two distinct product species. Brumer and Shapiro(36–38) observed that if there are two independent excitation routes between a specified state of the reactant and a specified state of the products, then two monochromatic coherent excitation sources can be used to influence the relative concentrations of the products formed. Control of the ratio of product concentrations is possible because quantum theory requires that the probability of forming a specified product is proportional to the square of the sum of the transition amplitudes for the two pathways from the initial state to that product; because the amplitudes can have different phases, the magnitude of that probability is determined by the extent of their interference. For example, when one- and three-photon transitions generate the independent pathways between the initial and final states, the extent of interference can be controlled by altering the relative phase of the two excitation sources. The situation is analogous to the formation of a diffraction pattern in a two-slit experiment in that the excited state amplitude in each molecule is the sum of the excitation amplitudes generated by two routes which are not distinguished from each other by measurement.

Gordon and coworkers(39, 40) have provided experimental verification of the Brumer–Shapiro method. They used the interference between one photon and three photon transitions between the same initial and final states to control the ratio of concentrations of the products in the branching autoionization and photodissociation reactions

$$DI \rightarrow DI^+ + e^-$$

versus

$$DI \rightarrow D + I$$

As shown in Fig. 2, both the concentration of DI^+ derived from the first reaction and the concentration of I (measured as the ion I^+) derived from the second reaction vary sinusoidally with change of the phase difference between the one photon and three photon excitation beams (noting that the hydrogen pressure is a surrogate variable for the phase difference).

Moreover, the two oscillating product concentrations are offset from one another by a constant phase lag, so the ratio of concentrations $[I]/[DI^+]$ can be controlled by varying the phase difference between the two excitation beams.

In its original formulation, the Brumer–Shapiro product control method takes advantage of the interference between two possible routes to the target states to induce control of the population of the final states of the system. Two different fields are tuned to resonance to excite the system via those pathways, and control is obtained by varying the relative phase of the two fields to modulate the interference pattern of the product wave functions. The sensitivity of this method to phase, which is the source of the selectivity, also makes it difficult to implement because of the existence of phase fluctuations in the laser sources.

A more recent version of the Brumer–Shapiro approach (denoted the "incoherent interference" method) takes a different tack:(41–43) Rather than using two pathways that lead from the same initial state to the same final states, in the new approach only a single route from the initial to the target states is used, along with an additional field that is used to couple the target states to another previously unoccupied state. Consider the case where the degenerate target states (denoted $|f_1\rangle$, $|f_2\rangle$) are dissociative, each coupling to a different asymptotic state of the system. If these states

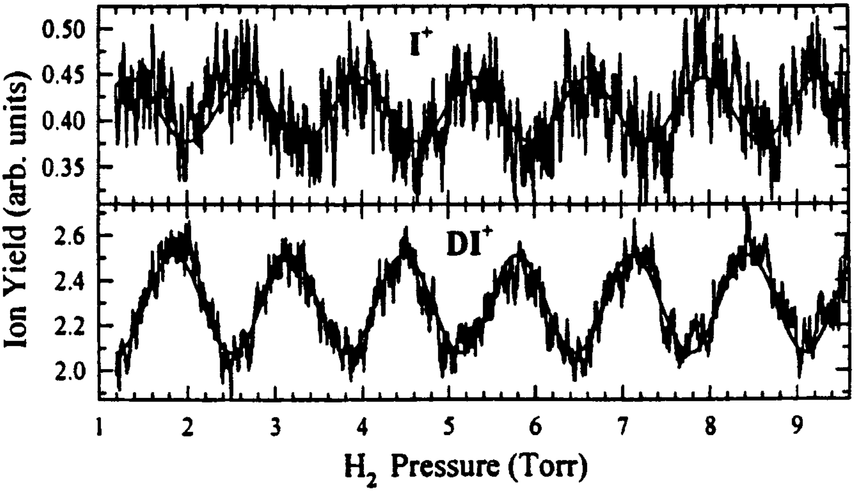

Fig. 2. Modulation of the ratio of the DI^+ and I^+ signals as a function of the phase difference between the one and three photon pathways that connect the initial and final states. From ref. 40.

are coupled to the ground state by a single field, population will be transferred to them by a single pathway $|i\rangle \to |f_j\rangle$, $j=1, 2$, which will lead to a branching ratio between $|f_1\rangle$ and $|f_2\rangle$ which is a function of their transition dipole moments with the ground state. The addition of a second field coupling the final states to another state $|m\rangle$ creates a second pathway to dissociation: $|i\rangle \to |f_j\rangle \to |m\rangle \to |f_j\rangle$. Provided both fields are sufficiently intense, the probability amplitude associated with the latter path will become significant and the two pathways will interfere with each other. This scheme has the following important advantage: When the fields are intense enough that multiple order transitions of the type $|f_j\rangle \to |m\rangle \to |f_j\rangle \to |m\rangle \to |f_j\rangle \to \cdots |f_j\rangle$ must be considered, the phase accumulated in each leg $|f_j\rangle \to |m\rangle$ is exactly cancelled by the phase accumulated on the return leg $|m\rangle \to |f_j\rangle$. Then, precise control of the phase of the field is unnecessary, and the relative yield of product states is governed by other more readily controllable features of the field, such as frequency and intensity. The validity of this scheme has been demonstrated experimentally$^{(44, 45)}$ via control of the choice of products in the branching reactions

$$\mathrm{Na}_2 \to \mathrm{Na}(3p) + \mathrm{Na}(3s)$$

versus

$$\mathrm{Na}_2 \to \mathrm{Na}(3d) + \mathrm{Na}(3s)$$

as shown in Fig. 3.

The preceding scheme for product selection is found to be most efficient when the pulsed field promoting the transition $|f_j\rangle \to |m\rangle$ is applied before (but overlapping with) the pulsed field that promotes the transition $|i\rangle \to |f_j\rangle$. This anti-intuitive timing of the two pulsed fields is like that used in the stimulated Raman adiabatic passage (StiRAP) method of population transfer in a three level system.$^{(46–48)}$ Indeed, an examination of the relationship between these superficially different methods of generating population transfer is very revealing.

The StiRAP process was first defined with respect to population transfer in a three level system, which we consider to be a ground state, an intermediate state, and a final state in which we wish to maximize the population. These matter eigenstates are coupled by the effects of two electromagnetic fields; a field that is resonant with the transition from the ground to the intermediate state (the pump field) and a field that is resonant with the intermediate-to-final state transition (the Stokes field). In the limit that the Rabi frequencies ($\Omega_p = \mu_{gi}\,\varepsilon/\hbar$ and $\Omega_S = \mu_{if}\,\varepsilon/\hbar$) associated with the transfer of amplitudes between the levels are very large the exact

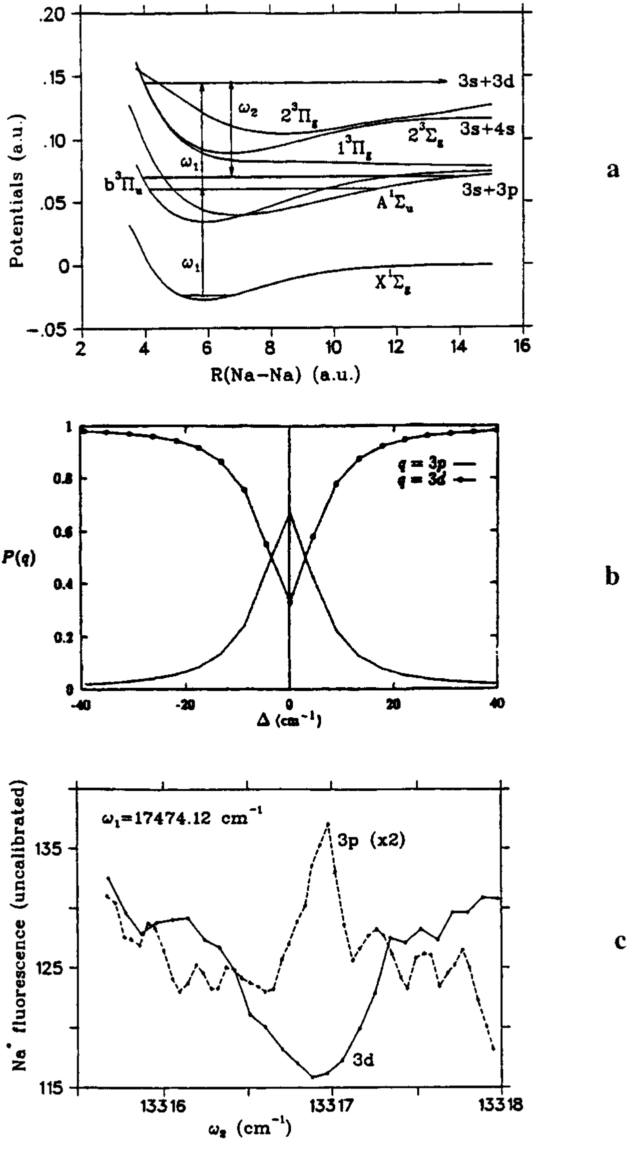

Fig. 3. (a) Potential energy curves utilized in the "incoherent interference" control of branching reactions of Na$_2$. A two phton process excites the continuum from the initial state $v=5$, $J=37$, via the $v=35$, $J=36$, 38 levels, belonging to the mixed $A^1\sum_u$ and $b^3\prod_u$ electronic states. A one photon process dresses the continuum with the (initially unpopulated) $v=93$, $J=36$ and $v=93$, $J=38$ levels of the mixed $A^1\sum_u$ and $b^3\prod_u$ electronic states. From ref. 44. (b) Probability of formation of the final states Na(3p) + Na(3s) and Na(3d) + Na(3s). $\Delta=\omega_2-\omega_1+(E_2-E_1)/h$. From ref. 41. (c) Observed yields of Na(3p) and Na(3s). From ref. 44.

eigenstates and eigenvectors of the field dressed system can be calculated. It is found that the eigenvalue of the field-dressed intermediate state is zero, corresponding to zero population in that state. Then, if the Stokes pulse precedes (but overlaps) the pump pulse all population initially in the ground state projects into the field-dressed intermediate state ($\Omega_p \ll \Omega_S$), and at the final time all of the population in the intermediate state projects onto the final state ($\Omega_p \gg \Omega_S$). The predicted nearly perfect transfer of population from the ground state to another state by the StiRAP method has been experimentally verified in atomic and diatomic systems.(46, 49–52)

Kobrak and Rice(53–55) have developed a version of StiRAP that permits control of product selectivity in a chemical reaction. They have examined the dressed field-matter states of a five level system, such as sketched in Fig. 4a, that has a pair of degenerate states representing possible reaction products. It is imagined that this system of levels is a subset abstracted from a richer spectrum of states and, in particular, that there are many possible choices for the fifth state. In this system, in addition to the pump and Stokes fields connecting $|1\rangle \to |2\rangle$ and $|2\rangle \to |3\rangle$, $|2\rangle \to |4\rangle$, respectively, a third electromagnetic field is used to connect $|3\rangle \to |5\rangle$ and $|4\rangle \to |5\rangle$; this field acts throughout the duration of both the pump and Stokes field pulses. When the frequencies of the transitions $|3\rangle \to |5\rangle$ and $|4\rangle \to |5\rangle$ are not resonant with either the pump frequency $|1\rangle \to |2\rangle$ or the Stokes frequencies $|2\rangle \to |3\rangle$ and $|2\rangle \to |4\rangle$ there is a dressed field-matter eigenstate with nodes in $|2\rangle$ and $|5\rangle$, so that the counterintuitive excitation sequence with the Stokes pulse preceding the pump pulse transfers 100% of the population to the degenerate target states. Moreover, the population branching ratio between these states is determined entirely by the coupling to $|5\rangle$, and the relative populations of the degenerate states are reversed with respect to their respective transition strengths for $|3\rangle \to |5\rangle$ and $|4\rangle \to |5\rangle$. Since $|5\rangle$ may be chosen from almost any of the available states of the system, it is implied that the branching ratio between products of the reaction can be thereby controlled.

Kobrak and Rice then show,(55) by application of the extended StiRAP scheme to the branching reactions

$$\mathrm{Na}_2 \to \mathrm{Na}(3p) + \mathrm{Na}(3s)$$

versus

$$\mathrm{Na}_2 \to \mathrm{Na}(3d) + \mathrm{Na}(3s)$$

that it is equivalent to the high intensity limit of the Brumer–Shapiro(41–43) "incoherent interference" scheme sketched above Fig. 4b). That these methods are equivalent is hinted by the observation that strong field induced multiple order transitions of the type $|f_j\rangle \rightarrow |m\rangle \rightarrow |f_j\rangle \rightarrow |m\rangle \rightarrow |f_j\rangle \rightarrow \cdots |f_j\rangle$, which lead to cancellation of the phases accumulated the legs $|f_j\rangle \rightarrow |m\rangle$ and $|m\rangle \rightarrow |f_j\rangle$, become Rabi oscillations if enough cycles accumulate. That is, for strong enough fields, the Brumer–Shapiro coupling protocol generates the StiRAP field-matter eigenstates. The challenge in this form of control of product selectivity is therefore not in the determination

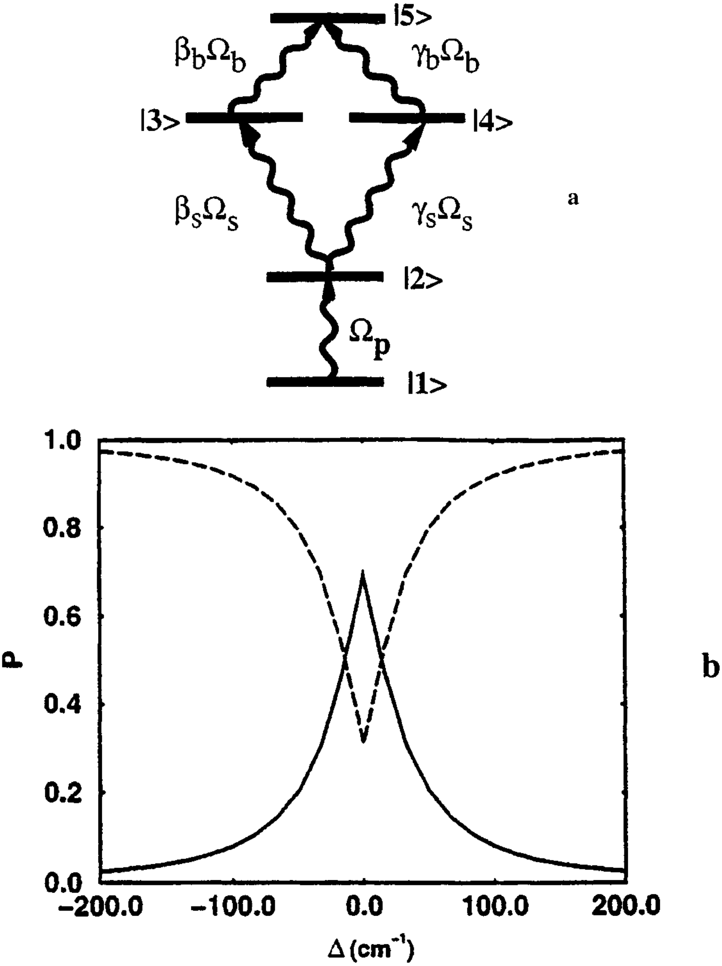

Fig. 4. (a) Five level StiRAP system with level 3 and level 4 degenerate. From ref. 53. (b) Probability of formation of the final states Na(3*p*) + Na(3*s*) (solid line) and Na(3*d*) + Na(3*s*) (dashed line). These results should be compared with those shown in Figs. 3b and 3c. From ref. 55.

of an optimal electromagnetic field *per se*, but rather in the construction of a photoselective pathway from the available states of the system.

There are yet other ways in which interference-induced control of product formation in intense electromagnetic fields can be achieved. In a very strong electromagnetic field a molecule can exhibit above-threshold dissociation (in which the molecule absorbs more photons than necessary for bond fragmentation) with both stimulated emission and multiphoton absorption in the dissociation continuum, bond softening (in which the potential energy surface of a field-dressed state has a smaller binding energy than does the field free potential energy surface), and suppression of dissociation due to temporary trapping in wells in the field-dressed potential energy surfaces of upper excited states. The competition between these processes can be modified by the use of two very strong incident coherent radiation fields, with the frequency of one a harmonic of the frequency of the other, because the adiabatic field-dressed potential energy surfaces are very sensitive to the phase difference between these fields. Calculations by Charron *et al.*(56) show that in the branching photodissociations

$$HD^+ \to H + D^+$$

versus

$$HD^+ \to H^+ + D$$

both the dissociation probability and the fragment angular distribution can be controlled by variation of the phase difference between linearly polarized incident fields with wavelengths 10.6 μm and 5.3 μm. The asymmetry of the forward/backward yield ratio that characterizes the fragment angular distribution arises from an interference between absorption from and stimulated emission to the two incident fields; this effect has been observed,(57) as illustrated in Fig. 5.

In principle, the methods available for guiding the evolution of a quantum system by coupling it to an external field are not restricted to the use of a time-independent field or a simple pulse sequence. If the goal to be achieved is, say, maximization of the amount of a product in a reaction, the design of the external field which accomplishes the goal is an inverse problem: given the target product and the quantum mechanical equations of motion, calculate the guiding field which is required. The solution to this inverse problem is very likely not unique, which for the case under consideration is a strength since it is then plausible that one of the possible

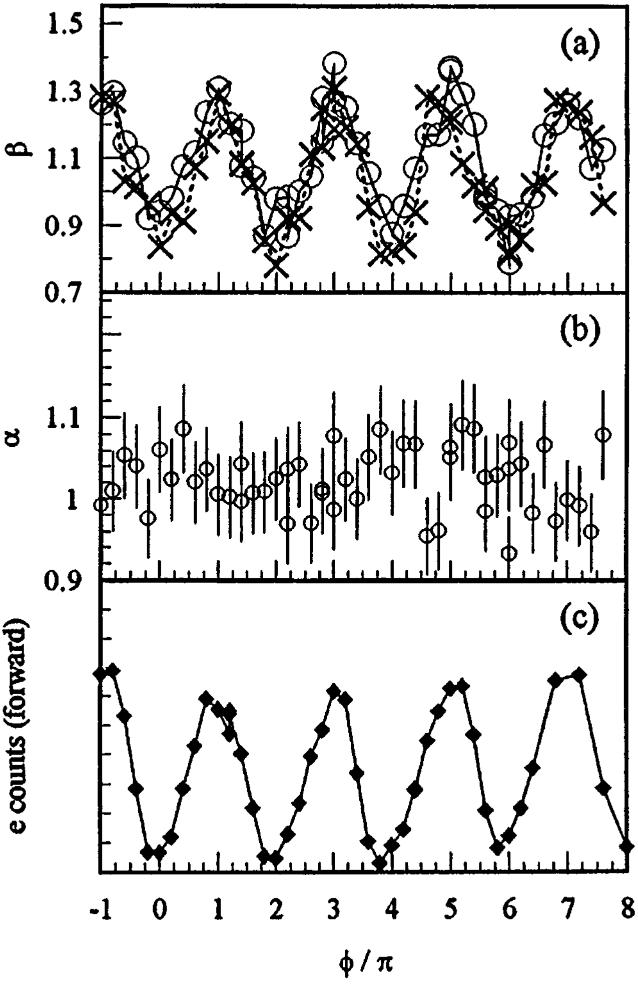

Fig. 5. (a) The forward/backward yield ratios of protons and deuterons as a function of relative phase between the electric fields used (see text). In this figure $\beta_{H^+} = H_f^+/H_b^+$ and $\beta_{D^+} = D_f^+/D_b^+$. (b) Isotope separation factor α as a function of relative phase of the two electric fields. (c) Krypton photelectric yield towards the detector as a function of the relative phase of the electric fields. From ref. 57.

guide fields is more easily generated than others. The general character of the guiding field defined by this inverse problem is easily grasped.

If one wishes to use the Tannor–Rice method to generate a large concentration of a particular reaction product, it is necessary to have most of the wave packet amplitude on the excited state potential energy surface simply and compactly distributed over that product exit channel on the ground state potential energy surface. However, in the typical case, the evolution of the wave packet on the excited state surface generates a very complicated distribution of amplitude, hence a simple dump pulse cannot efficiently transfer population to the exit channel on the ground state surface. We can, in principle, determine what initial amplitude distribution on the excited state surface will evolve to the desired amplitude distribution over the exit channel by integrating the Schrödinger equation backwards with the desired final amplitude distribution as an initial condition. The result of this calculation will be, typically, an initial distribution of amplitude so complicated that it cannot be created by a Franck–Condon transition from the ground state. Nevertheless, this calculation conveys an important message. If, instead of using separated pump and dump pulses, we use a temporally shaped field with variable amplitude, frequency and phase to continuously transfer matter amplitude back and forth between the ground state and excited state surfaces as the wavepackets move about on these surfaces it should be possible to optimize the transfer of population into the exit channel via variation of the shape of the applied field. It is this observation that led Kosloff, Rice, Gaspard, Tersigni and Tannor(58) to develop a formalism for optimal pulse shaping. Rather different considerations, derived from the general formalism of system control theory, were used by Rabitz and coworkers(57–60) in their slightly earlier development of the theory of optimal pulse shaping.

The methodology used in calculations of the field required to maximize a particular product yield is optimal control theory.(59–70) The first application of a full version of optimal control theory to the quantum dynamics of molecular systems was published by Pierce, Dahleh and Rabitz;(59) Tannor and Rice(29, 63) had earlier formulated the search for an optimal dump pulse, for fixed pump pulse shape, within the framework of perturbation theory, as a problem in the calculus of variations. Later, Kosloff, Rice, Gaspard, Tersigni and Tannor(58) also introduced optimal control theory to design the field which guides a branching reaction to generate maximum product of a particular species. In the model problems studied to date it is predicted that the use of the calculated optimal electromagnetic field can increase the desired product yield by many orders of magnitude relative to the yield from a two-pulse control field.(70) It is usually found that the optimal field has a complicated spectral and temporal structure whose efficiency is determined by the extent of interference between the amplitudes associated with its different spectral and temporal components.

It is to be expected that the typical optimal control field is sensitive to experimental perturbations and to uncertainties in molecular parameters.

To overcome these difficulties Judson and Rabitz,(71) in a seminal paper, suggested using the experimental apparatus needed to control molecular dynamics as an analog computer that solves the Schrödinger equation exactly with the true laboratory field. That experimental apparatus is viewed as an input–output device that both records a particular signal from the molecules exposed to a specified applied field and generates the applied field. In general, it will consist of a sample of the molecules under study, a laser whose pulse sequence is supplied by a computer, and a detector that feeds the signal back to the control computer. The signal from the molecules is presumed to be proportional to the extent that the objective of the experiment is achieved, e.g., the intensity of fluorescence from the reaction product desired. A learning algorithm capable of recognizing patterns in the multiple sets of applied field-signal data, is used to adjust the experimental apparatus to iteratively modify the applied field to optimize the signal from the molecules. An experimental demonstration that optimal shaping of the excitation field can be used to select between products of a branching reaction has been provided by Assion *et al.*(72) They showed that optimizing the phase distribution in a femtosecond pulse permits selection of one or the other of two different bond cleaving reactions of $CpFe(CO)_2Cl$, specifically, cleavage of one of the FeCo bonds to yield $CpFeCOCl^+$ versus cleavage of both FeCo bonds and the FeCp bond to yield $FeCl^+$ (see Fig. 6).

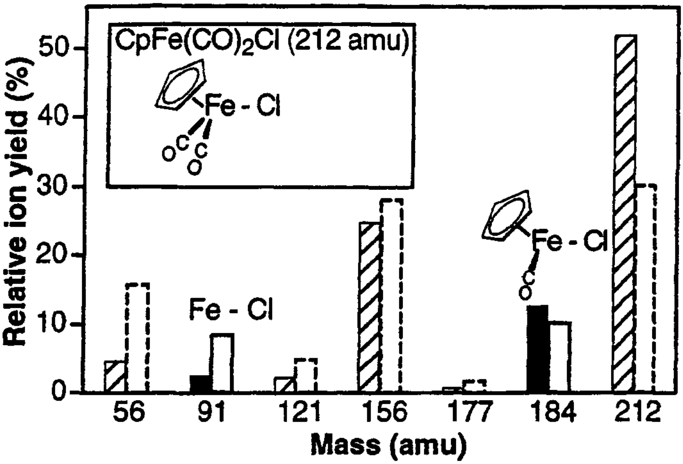

Fig. 6. The branching ratio $CpFeCOCl^+/FeCl^+$ from the feedback controlled $CpFe(CO)_2Cl$ photodissociation. The solid block is the result of maximization of the branching ratio; the open block is the result of minimization of the ratio. Other masses shown in the figure were not included in the optimization procedure. From ref. 72.

4. CONCLUDING REMARKS

Although our understanding of the requirements for active control of molecular dynamics is well founded, there remain many fundamental questions which must be addressed. Amongst these are the following:

What are the limitations to the control of quantum many body dynamical processes? Unfortunately, the two strongest results, the Huang–Tarn–Clark theorem(18) and the Shapiro–Brumer theorem,(25) apply to the case when the spectrum of the system consists of only discrete nondegenerate states. Since the vast majority of chemical reactions involve both discrete and continuum states of the molecule, these theorems provide little guidance as to the limit of controllability of the associated molecular dynamics. The demonstration of the existence of a field that optimizes the achievement of a particular objective, e.g., enhancing the yield of one product in a branching reaction, does not establish the limit to the efficiency obtainable. However, the evidence available from numerical calculations suggests that in molecules with only a few degrees of freedom one can achieve nearly complete control of a molecular process. Clearly, a better understanding of the limitations to the control of quantum many body dynamical processes will aid the design of methods that most efficiently achieve specified goals.

The utility of control processes in chemistry will depend on developing methods applicable to the reactions of large polyatomic molecules. In particular, it is important to ascertain how the efficiency of a control process depends on the number of degrees of freedom of the controlled molecule. To date, most attention has been focused on the design of control processes in reduced spaces of various sorts without consideration of the possible limit to efficiency.(68, 70) A better understanding of the influence of "bath modes" on the controllability of dynamical processes will aid the design of methods that most efficiently achieve specified goals.

How sensitive is the computed control field to fluctuations in the field source and to uncertainties in the molecular potential energy surface? The introduction of feedback in the active control process is a means of compensating for uncertainties in the molecular Hamiltonian and experimental imperfections. An associated theoretical issue is assessment of the optimality and robustness of control over quantum dynamics. Demilrap and Rabitz(73) have discussed this issue by going beyond the usual representation of the control process in terms of a functional that incorporates the physical objectives, constraints and penalties. The first order variation of such a functional yields the equations for the field that optimizes the achievement of the physical objective under the specified conditions. Demilrap and Rabitz analyze the properties of the second variation of the functional to determine whether the solution to the equations obtained from the first variation are locally optimal, and whether those solutions are robust.

To what extent is the control of molecular dynamics possible when dissipation must be accounted for, as for a reaction in the liquid phase? The effect of dissipation on the efficiency of the control process is addressed indirectly in reduced space analyses.(69) However, the development of methods to control the quantum dynamics of a molecule embedded in a dense solvent will require a more detailed accounting for the effect of dissipation than has been discussed to date. In particular, if the control field is strong enough, it generates both direct and indirect effects on the molecular dynamics. The direct effects are the same as those experienced by an isolated molecule; the indirect effects arise via the influence of the field on the coupling of the molecule to the surroundings. Schirrmeister and May(74, 75) have reported a model study which suggests that control of vibrational relaxation of a dye molecule in a solvent is possible, notwithstanding the dissipative interaction between the molecule and the solvent. And, the experimental demonstration of feedback control of the fluorescence emission from a dye molecule in solution verifies that there are situations in which dissipation does not destroy the possibility for control of molecular dynamics.(76, 77)

There are several topics associated with the control of quantum many body dynamics that I have not discussed at all, or only briefly mentioned. Amongst the more important omissions is any description of methods for the active control of the product yield in a bimolecular reaction, say

$$A + B \rightarrow C + D \tag{4}$$

which requires control of the dynamics of the three dimensional collisions of polyatomic reactants. Methods for achieving that control are in the earliest stage of development.(78–80) In the case that the mechanism of the reaction involves a long lived collision complex, the Tannor–Rice method for control of product formation in a unimolecular reaction is applicable. When a long lived collision complex is not formed the situation is more complex. Krause, Shapiro and Brumer(81) and Holmes, Shapiro and Brumer(82) have described a method, based on multiple path interference, for controlling product formation in the simple case when the collision is collinear. Abrashkevich, Shapiro and Brumer(83, 84) have generalized that method to apply to the control of three-dimensional reactive scattering.

The extant theoretical analyses and experimental demonstrations only hint at what will be possible when both theory and experimental method are further developed. Indeed, for some time to come the analyses described are likely to be most important as tools for learning more about molecular dynamics, and for testing concepts advanced to describe aspects of molecular dynamics. However, as laser technology improves and our understanding of complex molecules advances, it is likely that practical chemical applications of the control of quantum many body dynamics will be developed. Since the underlying principles of control theory as applied to quantum dynamics are very broadly applicable, it is likely that applications in a variety of other fields will also be developed in the near future. One such field is optoelectronics. For example, Bonedo and coworkers(85) have demonstrated optical field induced control of the microscopic state of a single quantum dot, and Kurizki, Shapiro and Brumer(86) have shown how interference effects can be used to generate a fast semiconductor optical switch (with experimental demonstration by Dupont, Corkum, Liu, Buchanan and Wasilewski(87)).

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