Coherent Pulse Sequence Induced Control of Selectivity of Reactions

Exact Quantum-mechanical Calculations

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We present a novel approach to the control of selectivity of reaction products. The central idea is that in a two-photon or multiphoton process that is resonant with an excited electronic state, the resonant excited-state potential-energy surface can be used to assist chemistry on the ground-state potential-energy surface. By controlling the delay between a pair of ultra-short (femtosecond) laser pulses, it is possible to control the propagation time on the excited-state potential-energy surface. Different propagation times, in turn, can be used to generate different products. There are many cases for which selectivity of product formation should be possible using this scheme. Our examples show a variety of behaviour ranging from virtually 100% selectivity to poor selectivity, depending on the nature of the excited-state potential-energy surface. Branching ratios obtained using a swarm of classical trajectories are in good qualitative agreement with full quantum-mechanical calculations.

As originally conceived, flash photolysis is a pump-and-probe technique for studying chemical reactions. Although the experimenter exerts some control over the system by virtue of choice of the pump, e.g. selection of wavelength and pulse duration, the probe part of the experiment is only used to follow the natural evolution of the initially prepared system. This paper describes a conceptual extension of flash photolysis, conveniently schematized as a pulse-pulse methodology. The idea is to exploit the properties of the coupling of a molecule to the electromagnetic field so that, following preparation in some initial state and evolution for a defined period of time, a second pulse directs the evolution of the system to some desired final state. The methodology we describe achieves coherent pulse sequence induced control of selectivity of chemical reaction. This short paper, summarizing work reported in detail elsewhere,1,2 defines a theoretical paradigm, i.e. shows that, for realistic model systems, control of selectivity of chemical reaction can be achieved.

General Remarks

We consider a system for which there can be a reaction on the ground electronic state potential-energy surface and ask how that reaction can be mediated by excitation to, evolution on and stimulated de-excitation from an excited electronic state. In particular, our proposed methodology exploits the coherence properties of exciting and stimulating ultrashort pulses (femtosecond timescale), and the dynamics of wavepacket evolution between exciting and stimulating pulses. The pulse shapes, durations and separations required to achieve selectivity of product formation depend on the properties of the
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Excited-state potential-energy surface. In the relevant time domain, which is defined by the shape of the excited-state potential-energy surface, it is possible to take advantage of the localization in phase space of the time-dependent quantum-mechanical amplitude and thereby carry out selective chemistry.

Briefly, it is assumed that the ground electronic state Born-Oppenheimer potential-energy surface has two or more exit channels corresponding to the formation of two or more distinct chemical species. It is also assumed that there exists an excited-state potential-energy surface whose minimum is displaced from that of the ground-state surface and whose normal coordinates are rotated from those of the ground-state surface. This excited-state potential-energy surface is used to assist the chemistry on the ground-state potential-energy surface. The time spent on the excited-state surface is used to select the desired chemical species. To see how this works, it is instructive to begin with a classical mechanical description of the dynamics. Consider the hypothetical potential-energy surface shown in fig. 1; it has a central minimum and two inequivalent exit channels separated from the minimum by saddle points. The trajectory that begins at rest at the minimum of the ground-state surface is projected vertically up to the excited-state surface (fig. 2). It now evolves for some time on the excited-state surface, after which it projected vertically back down to the ground-state surface. The time spent on the excited-state surface is one of the controllable variables in our scheme. The trajectory is now propagated on the ground-state surface long enough to determine its ultimate fate, i.e. whether it leads to A + BC, AB + C or ABC. Fig. 3(a) shows a trajectory that exits from channel 1 (A + BC; excited-state propagation time is 600 a.u.). Fig. 3(b) shows a trajectory that exits from channel 2 (AB + C; excited state propagation time is 2100 a.u.). As may be seen in fig. 4 and 5, in the classical mechanical description there are windows of 50–100 a.u. width for exit out of a desired channel.

The quantum-mechanical description of the dynamics follows a very similar pattern. At the instant that the first photon is incident the ground-state wavefunction makes a vertical (Franck-Condon) transition to the excited-state surface. The ground-state...
wavefunction is not a stationary state on the excited-state potential-energy surface, so it must evolve as $t$ increases. There are some interesting analytical properties of this time evolution if the excited-state surface is harmonic. In that case a Gaussian wavepacket remains Gaussian for all time, the centre of the Gaussian wavepacket follows the classical trajectory for harmonic oscillation, both in coordinate and momentum space, and the Gaussian wavepacket develops a phase equal to the classical-action integral for the same motion, namely $\phi = \int_0^t (p\dot{q} - E) \, dt$. These properties are retained to a good approximation for smooth anharmonic potential-energy surfaces. Moreover, Ehrenfest’s theorem ensures that the centre of the wavepacket will obey the classical equations of motion for any potential surface, provided the wavepacket remains sufficiently localized. The duration of the propagation on the excited-state surface can be regulated by the delay of a second pulse relative to the initial pulse of light. The second pulse leads to a vertical (Franck-Condon) transition down to the ground-state surface. Note that the wavefunction amplitude is unchanged in the Franck-Condon transition. If the delay and width of the second pulse is chosen on the basis of the position and width of the windows in fig. 2 it is plausible to expect the wavepacket amplitude on the ground-state surface to select one channel over the other. The results of quantum-mechanical calculations of wavepacket propagation on the excited-state and ground-state potential-energy surfaces for a variety of different excited-state potential-energy surfaces and a range of pulse delays show that this expectation is fulfilled.
Fig. 3. Classical trajectories on the ground-state surface that arise from a vertical transition down (coordinates and momentum unchanged) after propagation time $t_2 - t_1$ on the excited-state potential-energy surface. (a) $t_2 - t_1 = 600$ a.u., (b) $t_2 - t_1 = 2100$ a.u.

Fig. 4. Probability (0 or 1) of exit from channel 1 as a function of excited-state potential-energy surface propagation time.
Results

The reader is referred elsewhere for details of the theoretical calculations. We show below results for four different model systems. All the systems use the same ground-state potential-energy surface (fig. 1), but different excited-state potential-energy surfaces. All the surfaces are models for the coupled symmetric and asymmetric stretch vibrations in a collinear molecule. The masses for the system are 1823, 1823 and 3646 a.u., corresponding to HHD. Although the ground-state potential-energy surface of true HHD is not bound there are excited electronic states which are bound. Our primary reason for choosing hydrogenic masses was to facilitate the quantum-mechanical calculations, which are substantially more difficult for larger masses. In general, one expects the classical–quantum correspondence, upon which our selectivity scheme is based, to improve for larger masses.

Excited-state surface I is harmonic and rotated relative to the ground-state surface. In this case, because the potential-energy surface is harmonic, the wavepacket on the excited state will not break up. Indeed, we observe excellent selectivity for this model: for one choice of delay time between pulses we generate an exit from channel 1, while with a second delay time we generate an exit from channel 2.

The second to fourth examples include a variety of anharmonic excited-state potential-energy surfaces.

Model II has a very broad and shallow excited-state potential-energy surface. It was initially believed that use of this surface as an intermediary would favour slow alternation (as a function of pulse delay) in the flux out of channel 1 or channel 2 because of the low antisymmetric stretch frequency. We find, instead, that wavepacket spreading is particularly dramatic in this example because of the flatness of the surface.

Model III has a ‘typical’ anharmonic potential-energy surface, with frequencies approximately commensurate with those on the ground-state surface. This model was
intended to represent the case in which the wavepacket stays close to the harmonic region of the excited-state potential-energy surface, and thus reasonably well localized. In fact, as will be seen, the wavepacket spreading is pronounced. In model IV the excited-state potential-energy surface is taken to have shorter bond lengths than the ground-state surface. The difference in bond lengths leads to a variety of effects not seen with the other potential-energy surfaces since the initial transition is to the soft part of Morse potential, while the second transition (depending on the instant) is to the strongly repulsive part of the Morse potential. This model was designed to explore the possibility of the wavepacket returning to the original potential-energy surface with a great deal of potential energy, which could be converted to the kinetic energy required for dissociation. A related feature is that there is a dramatic wavepacket contraction, or focussing, as the wavepacket evolves on the excited state surface from the soft to the hard part of the potential.

Consider, first, model I. We exploit the dissociation windows in fig. 4 and 5 to choose a suitable pulse sequence for quantum-mechanical calculations. We choose

$$\mu E(t) = A(t) \cos(\omega_d t) + B(t) \cos(\omega_d t)$$

where \(A(t)\) and \(B(t)\) are Gaussian pulses with a delay between them chosen on the basis of the classical windows. The parameters of the pulse sequence are given elsewhere.\(^2\) The pulse delay \(t_a - t_c = 600\) a.u. was chosen to correspond to the broad window in fig. 4 of \(t_2 - t_1 = 600\) a.u. The first pulse was deliberately chosen to be very narrow in time so the wavefunction on the excited state closely approximates the time-evolved initial state. The values for \(A\) and \(B\) were chosen such that

$$\int_{-\infty}^{\infty} A(t) \, dt = \pi$$

and

$$\int_{-\infty}^{\infty} B(t) \, dt = \pi.$$
Fig. 6. Magnitude of the excited-state wavefunction for the pulse sequence described in the text (pulse delay = 600 a.u., $A = B = 0.125$). (a) $t = 200$ a.u., (b) $t = 400$ a.u., (c) $t = 600$ a.u. Note the agreement with the results obtained for the classical trajectory (fig. 2).
Fig. 7. Magnitude of the ground-state wavefunction for the pulse sequence in fig. 4. (a) \( t = 0 \), (b) \( t = 800 \) a.u., (c) \( t = 1000 \) a.u. Note the agreement with the results obtained for the classical trajectory [fig. 3(a)]. Although some of the amplitude remains in the bound region, that which does exit does so exclusively from channel 1.
Fig. 8. Magnitude of the ground-state wavefunction for the pulse sequence in Fig. 5. (a) $t=0$, (b) $t=1000$ a.u., (c) $t=1200$ a.u. That amplitude which does exit does so exclusively from channel 2.
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Fig. 9. (a) Anharmonic excited-state potential-energy surface (I) in the text). The classical trajectory that originates from rest from the ground-state equilibrium geometry is shown superposed. (b) Probability (0 or 1) of exit from channel 1 as a function of excited state propagation time. (c) Same as (b) only for exit channel 2.

Equipotential contours for the excited-state surface are shown in fig. 9. As before, we show the initial vibrational wavefunction as well as the classical trajectory on the excited-state surface which originates from rest on the ground-state surface.

The parameters for the pulse sequence chosen are given elsewhere. Fig. 10(a)–(c) show the excited-state wavefunction at $t = 200$, 600 and 800 a.u., respectively, before the second pulse. Clearly, the quantum-mechanical amplitude is spreading severely. Fig. 10(d) shows the amplitude on the ground-state surface at $t = 1200$ a.u., after the second pulse. The poor selectivity is apparent from the figure.

The failure to achieve selectivity in this model system can be traced to the dynamics on the anharmonic excited-state surface and in particular the wavepacket bifurcation. This observation motivated us to explore systematically the features of the excited potential-energy state surface and excited-state wavepacket dynamics that are compatible with the proposed selectivity scheme. The next several examples explore the behaviour induced by a variety of anharmonic excited-state potential-energy surfaces.

Model III has a 'typical' excited-state potential-energy surface. Specifically, the excited-state minimum is displaced to larger distance relative to the ground-state
Fig. 10. Magnitude of the excited-state wavefunction before the second pulse. (a) \( t = 200 \) a.u., (b) \( t = 600 \) a.u., (c) \( t = 800 \) a.u. Note the extensive wavepacket spreading because the surface is so flat. This spreading will undermine the selectivity of products. (d) Ground-state wavefunction at \( t = 1200 \) a.u., after the second pulse. The poor selectivity of products is apparent.

minimum, the frequencies in the symmetric and asymmetric stretch coordinates are roughly equal and the force constants are in the same range as their ground-state values. The parameters defining this surface are given elsewhere.²

Equipotential contours for the excited-state surface are shown in fig. 11(a). Fig. 12(a)-(c) show the excited-state wavefunction at \( t = 200, 400 \) and \( 600 \) a.u., respectively, before the second pulse. Again, the quantum-mechanical amplitude is spreading severely as the wavepacket migrates toward the soft part of the Morse potential. Fig. 12(d) shows the amplitude on the ground-state surface at \( t = 1000 \) a.u., after the second pulse. The selectivity out of channel 2 is virtually complete (no amplitude exits from channel 1). This result was unexpected: the classical window predicts an exit from channel 1.

Model IV also has an anharmonic excited-state potential-energy surface; the parameters are given elsewhere.² The special feature of this excited-state surface is that
Fig. 11. (a) Anharmonic excited-state potential-energy surface (III in the text). The classical trajectory that originates from rest from the ground-state equilibrium geometry is shown superposed. (b) Probability (0 or 1) of exit from channel 1 as a function of excited-state propagation time. (c) Same as (b) only for exit channel 2.

the excited-state minimum is displaced to smaller distance than the ground-state minimum.

Equipotential contours for the excited-state surface are shown in fig. 13. As before, we show the initial vibrational wavefunction as well as the unique classical trajectory on the excited-state surface which originates from rest on the ground-state surface. The first pulse sequence examined was at $t = 30,610$ a.u. Fig. 14(a)-(c) show the excited-state wavefunction at $t = 200, 400$ and 600 a.u., respectively, before the second pulse. The wavepacket begins on the soft part of the Morse potential and initially begins to spread. However, as the wavepacket migrates to the hard part of the Morse it contracts very dramatically. Fig. 14(d)-(f) show the amplitude on the ground-state surface at $t = 800, 1000$ and 1200 a.u., respectively, after the second pulse. It is apparent that a substantial fraction of wavepacket amplitude exits from channel 2, while virtually no amplitude exits from channel 1.

The next pulse sequence examined was at $t = 30,1010$ a.u. Fig. 15(a) and (b) show the excited-state wavefunction at $t = 800$ and 1000 a.u., respectively, before the second pulse. Fig. 15(c)-(e) show the amplitudes on the ground-state surface at $t = 1200, 1400$ and 1600, respectively, after the second pulse. The wavepacket breaks up on the
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Fig. 12. Magnitude of the excited-state wavefunction before the second pulse. (a) $t = 200$ a.u., (b) $t = 400$ a.u., (c) $t = 600$ a.u. Note the wavepacket spreading is still significant, as the wavepacket approaches the soft part of the Morse potential. (d) Ground-state wavefunction at $t = 1000$ a.u., after the second pulse. There is complete selectivity out of channel 2, while the classical mechanics predicts selectivity for exit out of channel 1.

ground-state surface with roughly equal amplitudes escaping from channel 1 and channel 2.

Fig. 16 shows the quantum branching ratio as a function of stimulation time, for stimulation pulses centred 200 a.u. apart, from 210 a.u. up to 1010 a.u. Note the dramatic differences between the branching ratios at different times relative to each other as well as relative to the amplitude that remains bound.

An initial classical study of this system using the unique classical trajectory on the excited-state surface failed to reproduce many of the qualitative features of fig. 16.
A single classical trajectory cannot exhibit the tendency of the quantum wavepacket to bifurcate. Moreover, the single trajectory we used had no zero-point energy. We therefore examined a swarm of trajectories with an initial Gaussian distribution in $p$ and $x$, which corresponds to the Wigner transform of the ground vibrational state of the ground-state potential-energy surface,$^5$ where the ground-state surface is expanded up to quadratic terms about the equilibrium geometry. This distribution was discretized with 81 sets of $p, x$ initial conditions. The initial distribution in coordinate space is shown in fig. 17. There are nine initial values for $p$, corresponding to each initial values for $x$. We point out that since the initial conditions for $p$ and $x$ are independent, there is a range of zero-point energies in the swarm.

Fig. 18(a)–(c) show the swarm on the excited-state potential-energy surface, for the same pulse sequence as fig. 14 (second pulse at 616 a.u.). The swarm mimics closely the quantum wavepacket, including the sequence of contraction and spreading. Fig. 18(d)–(f) show the swarm on the ground-state potential-energy surface, after the second pulse. Those trajectories that do exit do so from channel 2.

Fig. 19(a) and (b) show the swarm on the excited-state potential-energy surface for the same pulse sequence as fig. 15 (second pulse at $t = 1010$ a.u.). Fig. 19(c)–(e) show the swarm on the ground-state potential-energy surface after the second pulse. The swarm breaks up on the ground-state surface with a substantial number of trajectories exiting from channel 1, followed by an approximately equal number exiting from
Fig. 14. Magnitude of the excited state-wavefunction before the second pulse at $t = 610$. (a) $t = 200$ a.u., (b) $t = 400$ a.u., (c) $t = 600$ a.u. Note the dramatic wavepacket contraction as the wavepacket approaches the hard part of the Morse potential. (d) Ground-state wavefunction at $t = 800$ a.u., after the second pulse. (e) Ground-state wavefunction at $t = 1000$ a.u. (f) Ground-state wavefunction at $t = 1200$. A significant fraction of the wavepacket amplitude is exiting from channel 2 while virtually no amplitude exits from channel 1.
Fig. 15. Magnitude of the excited-state wavefunction before the second pulse at $t = 1010$. (a) $t = 800$ a.u., (b) $t = 1000$ a.u. (c) Ground-state wavefunction at $t = 1200$. (d) Ground-state wavefunction at $t = 1400$ a.u. (e) Ground-state wavefunction at $t = 1600$ a.u. Note the wavepacket breakup on the ground-state surface, with roughly equal amplitudes exiting from channel 1 and channel 2.
Fig. 16. Quantum-mechanical branching ratio as a function of stimulation time. Note the dramatic differences between the branching ratios at different times, relative to each other as well as relative to the amplitude that remains bound. ■, Channel 1; □, channel 2.

Fig. 17. Initial swarm of classical trajectories on the ground-state potential-energy surface. The swarm consists of 81 trajectories (there are nine different momentum combinations for each of the coordinate combinations).
Fig. 18. Swarm of classical trajectories on the excited-state potential-energy surface, before the second pulse at $t = 610$. (a) $t = 200$ a.u., (b) $t = 400$ a.u., (c) $t = 600$ a.u. (d) Swarm on the ground-state potential-energy surface at $t = 800$ a.u., after the second pulse. (e) Swarm on the ground state at $t = 1000$ a.u. (f) Swarm on the ground at $t = 1200$ a.u. Note the strong resemblance of the entire sequence (a)-(f) to the quantum wavefunction shown in fig. 15.
Fig. 19. Swarm of classical trajectories, on the excited-state potential-energy surface, before the second pulse at $t = 1010$. 
(a) $t = 800$ a.u., (b) $t = 1000$ a.u. (c) Swarm on the ground-state potential-energy surface at $t = 1200$. (d) Swarm on the ground state at $t = 1400$ a.u. (e) Swarm on the ground state at $t = 1600$ a.u. Note the breakup of the swarm on the ground-state surface. The entire sequence (a)-(e) is in close agreement with the quantum wavefunction, fig. 16.
channel 2. The entire sequence is in close agreement with the quantum-mechanical predictions (fig. 15).

Fig. 20 shows the classical branching ratio as a function of stimulation time for the same stimulation pulses as in fig. 16. Note the qualitative agreement with the quantum-mechanical results in both a relative and absolute sense. The classical–quantum correspondence is particularly good provided the time-evolving state has no nodes. If there are nodes, the classical propagation neglects interference terms which are likely to be significant.3

Clearly, a Wigner swarm of classical trajectories is a valuable exploratory tool for estimating quantum-mechanical branching ratios. The computer times involved are more than 100 times shorter than for the quantum-mechanical calculations. Moreover, for larger masses and more degrees of freedom the disparity between classical and quantum calculations will become even more pronounced. Finally, in most chemical systems the masses are significantly larger than the hydrogenic masses explored here. The classical–quantum correspondence should be even better than illustrated here, for larger mass systems.

However, one must be somewhat cautious about modelling branching ratios that originate from excited vibrational states, and more important for our purposes, when the pulse duration is a significant fraction of a vibrational period. In the latter case the convolution of the pulse with the propagating wavefunction has nodes. During the free evolution stage following the pulse the classical swarm may not be faithful to the subsequent quantum interference effects.

Discussion

We have proposed a novel approach to the control of selectivity of reaction products. The central idea is that in a two-photon or multiphoton process that is resonant with an excited electronic state, the resonant excited-state potential-energy surface can be used to assist chemistry on the ground-state potential-energy surface. By controlling the delay between a pair of ultrashort (femtosecond) laser pulses, it is possible to control the propagation time on the excited-state potential-energy surface. Different propagation times, in turn, can be used to generate different products. Some selectivity of reactivity should be possible using this scheme. Our examples show a variety of behaviour ranging from virtually 100% selectivity to poor selectivity.
An excited-state potential-energy surface with shorter equilibrium bond lengths, deeper wells and/or higher barriers than those the ground-state potential-energy surface proved to be the most useful intermediary for selectivity of reactivity scheme. Although these changes in molecular parameters on excitation are not common, there are cases for which they occur. Alternatively, one may use our scheme with the roles of excited and ground state reversed. Consider starting out in the ground vibrational state of the excited electronic state. This is the initial condition for ordinary emission spectroscopy. Then one may use a two-pulse sequence to stimulate amplitude down to the ground electronic state and back up to the original electronic state. Now the steepness of the ground-state surface barriers accelerate the nuclear motion so that enough kinetic energy is acquired for dissociation on the excited-state surface; also the tighter bonds on the ground state serve to focus the wavepacket. In short, vibrational energy acquired on the steeper of the two potential-energy surfaces may be used to break a bond on the flatter of the two potential-energy surfaces.

The two choices of initial and final surface mentioned can be thought of as examples from a spectrum of possibilities inherent in a more general scheme for achieving selectivity of reactivity. That more general scheme involves use of some electronic state to assist selectivity of product formation, but allows the initial and final states to be different. Imagine a Franck-Condon transition from some initial state to an intermediate electronic state followed, after a controlled delay, by a transition to a third electronic state (which could be the initial state). If the final-state potential-energy surface and the intermediate-state potential-energy surface have the right properties, use of shaped pulses and control of pulse separation will permit selectivity of reactivity on the final-state potential-energy surface. It is also possible to imagine the use of detuning from resonance with the intermediate electronic state as a tool to augment control of the timescale for evolution in that state.

Recently, several independent theoretical studies have concluded that two-photon processes may afford some selectivity in the preparation of an initial state or the resulting product distributions. These studies differ from the present study in three major ways. (a) Those authors describe the preparation of a superposition of precisely two vibrational states. Implicitly, the wavepacket we have described consists of a superposition of a multitude of vibrational levels. (b) At least in ref. (6), the goals are more modest than in the present work. The focus there is on controlling vibrational product distributions rather than on obtaining chemically distinct species. (c) Finally, the above approaches do not exploit the classical–quantum correspondence principle. This principle plays a central role in our approach.

Clearly, there are many ways in which the ideas we have proposed must be extended. Amongst the more important extensions we cite variational optimization of the shape, duration and separation of the pulses used to generate the selectivity, and analysis of the changes induced by inclusion of all degrees of freedom of the molecule (say in the sense of a reaction path Hamiltonian, or a dynamical path Hamiltonian). For studies involving more degrees of freedom a swarm of classical trajectories should be a very useful tool.

The shortest pulses available at the present time are of the order of 10–30 fs. The classical windows shown in the examples (which refer to model systems with hydrogen masses) are on the order of a few fs. We expect the overall timescales to become longer by about a factor of five for somewhat larger masses than assumed in the model systems studied to date. Thus the experiments we are proposing are at the very edge of the existing technology. Nevertheless, as the technology improves we expect there will be many applications and variations on the ideas suggested in this paper.

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References

4 All the anharmonic potential-energy surfaces have a functional form as described in F.T. Wall and

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