PERSPECTIVE

New Ideas for Guiding the Evolution of a Quantum System

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In the 18th century, natural philosophers viewed the universe as an elaborate machine that followed the laws of what we now know as classical mechanics. Applied to a collection of many particles, this view implies that it should be possible to steer the temporal evolution of such a system if all of the forces acting on it can be controlled. Scientists of the 19th century, however, knew that this kind of detailed control is not possible. The recognition of that impossibility is part of the conceptual foundation of thermodynamics; it leads, for example, to the difference between mechanical work and thermodynamic work, and to the second law of thermodynamics.

The general outlook for external control of the temporal evolution of a many-particle system is not changed when the system is described by quantum mechanics instead of classical mechanics. The difficulties associated with controlling all the forces acting on such a system are common to the classical and quantum descriptions.

Yet now, at the end of the 20th century, motivated by advances in laser technology, molecular spectroscopy and in the understanding of molecular dynamics, researchers are again interested in finding ways to partially or fully control the temporal evolution of complex systems, one example of which is control of the selection of products of a chemical reaction. Typically, a polyatomic molecule will, for defined initial conditions, react to form several products in different amounts. In most instances one of these products is wanted much more than the others. What is sought is a method for controlling the molecular dynamics actively, in real time, so as to guide the molecule to form the wanted product.

The developments in laser technology that have stimulated interest in actively controlling selectivity of product formation in a chemical reaction include methods for the generation of very short pulses, of shaped pulses, of pulses with well-defined phase relationship, of light fields with extraordinarily pure frequency, and of light fields with very high intensity. Application of laser technology to molecular spectroscopy has yielded a wealth of information concerning molecular potential energy surfaces. It has also led to an increased awareness that exploitation of interference effects inherent to the quantum mechanical description of a system can be used to guide system evolution; to recognition that the dynamics of a strongly coupled light-matter system can be influenced by alteration of the temporal and spectral distributions of the light; and to the realization that a polyatomic molecule may have sufficiently few degrees of freedom that it is not impossible to control all of them. The underlying principle of the new approach to controlling product selectivity in a reaction is different from that used in earlier attempts to achieve "bond selective chemistry." The new approach is based on exploitation of quantum interference effects whereas the old approaches are, typically, based on use of a very intense laser field to generate a very high level of local bond excitation and the hope that the rate of bond breakage will then greatly exceed the rate of transfer of energy from the excited bond to the rest of the molecule. Two different ways of using quantum mechanical interference to control product selectivity have been proposed (*1–3*).

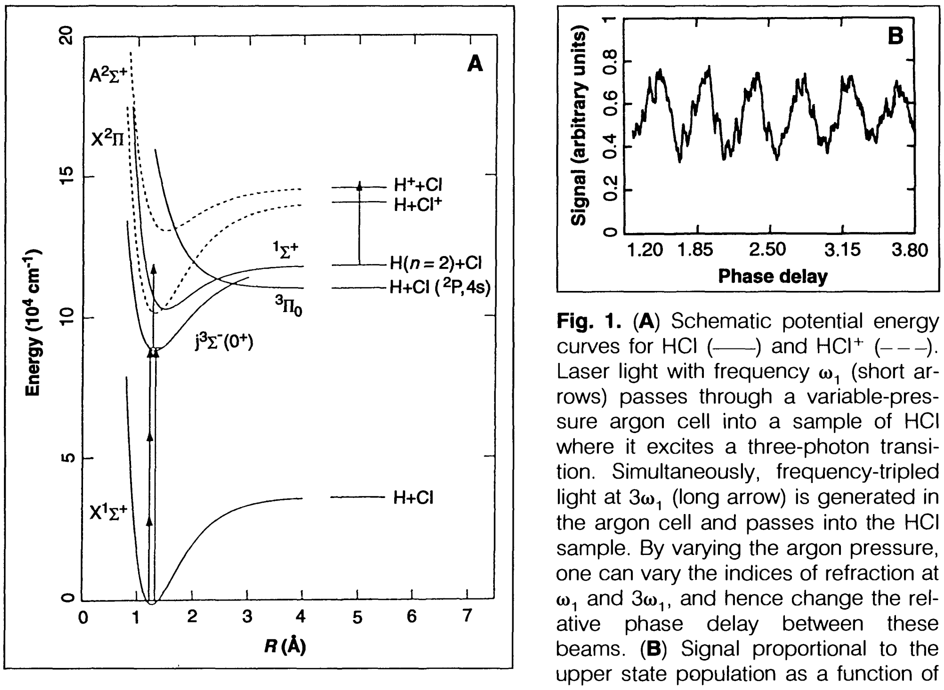

Fig. 1. (**A**) Schematic potential energy curves for HCl (——) and HCl$^+$ (– – –). Laser light with frequency ω_1 (short arrows) passes through a variable-pressure argon cell into a sample of HCl where it excites a three-photon transition. Simultaneously, frequency-tripled light at $3\omega_1$ (long arrow) is generated in the argon cell and passes into the HCl sample. By varying the argon pressure, one can vary the indices of refraction at ω_1 and $3\omega_1$, and hence change the relative phase delay between these beams. (**B**) Signal proportional to the upper state population as a function of phase delay between the one- and three-photon excitations in HCl. The data shown are for the R(2) transition in the manifold $j^3\ \Sigma^-$ ($\Omega = 0^+$, $v' = 0$) $\leftarrow$ ($^1\Sigma^+$, $v'' = 0$). [Reprinted from (*4*) with permission, copyright American Institute of Physics]

Suppose there are two independent excitation pathways between a specified initial state of a molecule and a specified final state of the products; these might be transitions involving absorption of one and three photons, respectively. Quantum mechanics tells us that the probability of forming the specified product is proportional to the square of the sum of the transition amplitudes for the two pathways; because the amplitudes can have different signs, 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. An example of control of the population of a level in HCl with this method (*4*) is shown in Fig. 1.

An alternative method of influencing the selectivity of product formation in a reaction is to modulate the product yield via interference between two excitation pulses with a variable time delay between them (*2*). In the simplest case, when only two electronic potential energy surfaces are

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involved, the first pulse transfers probability amplitude from the electronic ground state, forming a "replica" of the ground state amplitude on the excited state potential energy surface; that replica then evolves on the excited state potential energy surface during the time interval between pulses. The second pulse of the sequence, whose phase is locked to that of the first one, also creates amplitude in the excited electronic state, which is in superposition with the initial, propagated, amplitude. Such an intramolecular superposition of amplitudes can lead to interference. Whether the interference is constructive or destructive, giving rise to larger or smaller excited state population for a given interpulse delay, depends on the optical phase difference between the two pulses and on the detailed nature of the evolution of the initial amplitude. This situation is also analogous to a two-slit experiment. The method described has been used to control the population of a level of I_2 (Fig. 2) (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 that goal is an inverse problem: given the goal 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 guide fields is more easily generated than others.

The methodology used in these calculations is optimal control theory. It is usually found that the optimal guiding field has a complicated spectral and temporal structure. The underlying physical principle that determines the efficiency of the guiding field is, again, interference between the amplitudes associated with its different spectral and temporal components. In the model problems studied to date it is predicted that the use of an optimal guide field can increase the product yield by many orders of magnitude relative to the yield from a two-pulse control field.

Part of the excitement associated with learning how to guide the evolution of a quantum system comes from the realization that the methods so far devised—and there will be many more—promise to open up many new phenomena. For example, it should be possible to use interference effects in a solid-state quantum well structure to drive a photocurrent in one direction without the use of a bias voltage, which would then be an optically driven very fast switch. An improved understanding of molecular dynamics will also emerge from experimental studies of the role of pulse shape on product yield and selectivity. For example, it should be possible to invert product yield as a function of pulse shape to obtain information about the potential energy surfaces used to guide and generate the reaction. And the design of guide fields will yield new insights. For example, the design and implementation of a field which can guide the evolution of a system implies that deterministic dynamical chaos, if it exists in the absence of the guide field, is suppressed by application of the guide field.

These developments are in their infancy. For control of product formation in a reaction, it is not yet known how sensitive the control field is to uncertainties in our knowledge of the molecular potential energy surfaces (6), although it can be shown that a feedback mechanism eliminates the need for detailed knowledge of system properties (7). Nor is it known whether simple approximations to complicated control fields are good enough, although there is some evidence that such approximations are quite good (8). And it is not now known if there is a limit to the control of a molecular process if only the dynamics of part of a molecule is guided. But from the limited information available from model systems, it seems likely that if there is sufficiently weak dynamical coupling on the time scale needed for external field guiding of the reaction dynamics, then it will be possible to control the selectivity of product formation in a reaction of a rather complex molecule that has "interesting" chemistry.

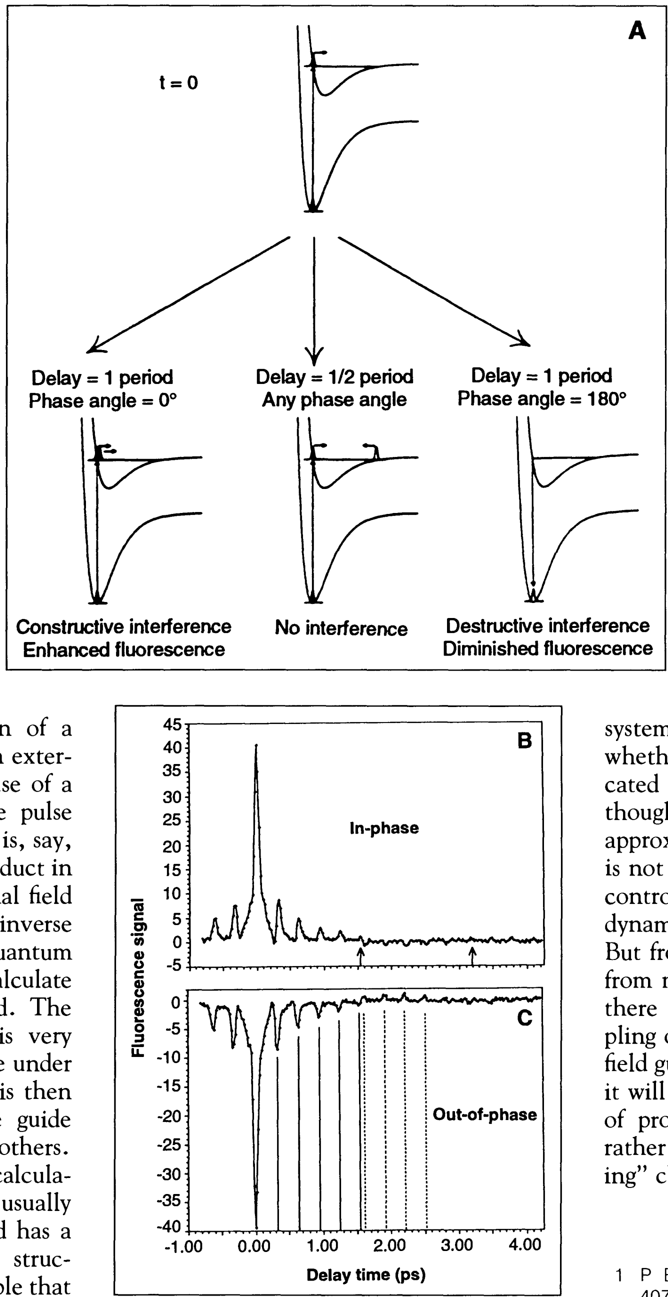

Fig. 2. (**A**) Schematic illustration of population control by interference of phase-locked time-delayed pulses. [Reprinted from (*5*) with permission, copyright American Institute of Physics] (**B**) In-phase and (**C**) out-of-phase fluorescence-detected upper state population of I_2; because short pulse excitation is used the upper state is a superposition of many rotational-vibrational states which evolves in time. The detection scheme is arranged to be proportional to the overlap of the amplitudes generated by the population due to constructive interference and a negative signal corresponds to a decrease in excited state population due to destructive interference.

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