Experiments show how product pathways can be controlled by irradiation with one or more laser beams during individual bimolecular collisions or during unimolecular decompositions. For bimolecular collisions, control has been achieved by selective excitation of reagent vibrational modes, by control of reagent approach geometry, and by control of orbital alignment. For unimolecular reactions, control has been achieved by quantum interference between different reaction pathways connecting the same initial and final states and by adjusting the temporal shape and spectral content of ultrashort, chirped pulses of radiation. These collision-control experiments deeply enrich the understanding of how chemical reactions occur.

One of the intriguing aspects of reaction dynamics is the possibility that what we learn might allow us to control the outcome of chemical reactions (1). The practical reasons for seeking such control range from suppressing unwanted side products to synthesizing new structures and new materials. Control of chemical reactions is a well-established concept. Successful control is commonly practiced by a variety of means, such as varying the external conditions of the reaction mixture by changing, for example, the temperature or the pressure, or finding a suitable catalyst that selectively lowers the activation barrier to the desired reaction products.

Here, I explore a different approach to reaction control where we, as chemists, "guide" the reaction process during a single reactive encounter. This guidance usually takes one of two forms. First, we may select one or more internal energy states of the reagent before collision. State preparation has a long history of successful applications. Some preparations depend simply on increasing the energy available to the reagents. Others involve more subtle effects such as control by promoting internal motions that aid or hinder various reaction pathways and stereodynamic control in which the three-dimensional geometry of the activated complex is selected. Second, we may actively intervene during the course of the reaction and guide the reactants by controlling the phase of their motions. This active control may cause the reactants to follow preferentially one of many different reaction routes. This second procedure is less well established, but in some cases, very promising results have been recently obtained. In what follows, I present a few examples of collision control along with an assessment of what has been accomplished to date and what likely lies ahead.

Mode-Selective Chemistry

In 1972, Polanyi (2) proposed that vibrational excitation along the reaction coordinate would be more efficacious than translational motion in promoting endoergic (uphill) reactions with a "late" reaction barrier, that is, reactions in which the transition-state region occurs late in the passage from reactants to products. Since then, a number of atom-plus-diatom reaction studies confirmed this conjecture (3), but extension of the idea to reactions involving polyatomic molecules was rather slow in coming. In 1984, Schatz and co-workers (4) carried out quasi-classical trajectory calculations on the H + H₂O → H₂ + OH reaction, which is estimated to have a reaction barrier of 7580 cm⁻¹ (5). Schatz et al. (4) clearly demonstrated that the reaction rate should be enhanced by excitation of the H-OH stretching vibration of water, because the transition-state geometry shows a marked preference for extension of one of the O-H bonds in water.

An isotopic variant of water, HOD, has proven to be an excellent candidate system for demonstrating the power of vibrational control of polyatomic reagents to influence the outcome of a chemical reaction. The H-OD and HO-D stretching frequencies are approximately at 3800 cm⁻¹ and 2800 cm⁻¹, respectively. Consequently, these two stretches are quite distinct and represent nearly pure stretching modes. The first example of the power of reagent vibrational excitation in controlling the outcome of a bimolecular reaction with a polyatomic reagent was achieved by Crim and co-workers (6), who found that reaction of thermal H atoms with HOD prepared with four quanta in the H-OD stretch produces almost exclusively H₃ + OD, whereas reaction of thermal H atoms with HOD prepared with five quanta in the HO-D stretch produces almost exclusively HD + OH. In this experimental study, the H atoms were generated with a microwave discharge, and the HOD molecule was prepared in a selected overtone stretch by laser irradiation in the visible wavelengths. Zare and co-workers (7) showed that the product-branching ratio selectivity was reduced but still survived for reactions of fast H atoms with HOD prepared in either the H-OD or HO-D stretching fundamental. Here, fast H atoms were generated by photolysis of HI, and the HOD stretching fundamental was excited by laser irradiation in the infrared. Broniowski et al. (8) went on to examine the reaction of fast H atoms with D₂O, in which the D₂O was prepared in either the asymmetric stretching fundamental or in a combination band consisting of the asymmetric stretch and one quantum of the bend. The bending motion was found to be ineffective in promoting reaction, as expected. Other examples of vibrational-state control on polyatomic reactions are Cl + HOD (9) and Cl + HCN (10). All these studies definitively demonstrate what is called mode-selective chemistry, which means for the same internal energy content, the mode of internal excitation controls the reaction outcome.

Examples of mode-selective chemistry are not limited to bimolecular neutral reactions. For example, the NH₃⁺ + ND³ reaction shows clear distinctions among the three product branches [NH₂ + ND₂⁺ (charge transfer), NH₃ + ND₂H⁺ (proton transfer), and NH₃D⁺ + ND₂ (D-atom abstraction)], depending on whether the NH₃⁺ was selectively prepared with excitation of its umbrella inversion mode or its all-symmetric stretching mode (11). Charge transfer is enhanced with umbrella inversion motion, and this effect has been rationalized by the preference of the neutral molecule to take on a pyramidal geometry. This argument is analogous to the Franck-Condon principle (12). The more energetic all-symmetric stretch is found to be essentially inactive. Theoretical calculations are able to model this behavior well (13).

Another example of how the selection of nuclear motion of the reagent can influence reaction outcome has been provided by Anderson and co-workers (14) who studied the ion-molecule reaction C₃H₆⁺ + CH₄ in which the acetylene cation was prepared with vibrational excitation in either the C-C stretch or the cis-bend. The reaction proceeds by two mechanisms. At low collision energies, the dominant reaction is mediated by a strongly bound C₃H₆⁺...
complex that breaks apart to produce either 
C₆H₅⁺ + H or C₂H₄⁺ + H₂. This complex is 
sufficiently long-lived that the H atoms in 
an isotopically labeled experiment are 
scrambled. The complex-mediated mecha-
nism decreases in importance with increasing 
collision energy and with C-C stretch 
vibration to a similar extent, but cis-bend-
ing excitation enhances the reactivity via 
this mechanism by 50 to 100%, depending 
on collision energy. A direct H-atom ab-
straction mechanism competes with this 
mechanism, yielding C₂H₅⁺ + CH₃. This 
slightly endothermic complex is enhanced by 
nearly a factor of 30 by cis-bending excita-
ton. At low collision energies, this bending 
excitation favors the direct over the com-
plex reaction channel by a factor of 40. 
Collision energy and C-C stretching also 
enhance the direct mechanism at low col-
lision energies, but much less markedly than 
bending excitation. Recoil velocity mea-
surements reveal that direct H-atom ab-
traction proceeds through a weakly bound 
complex with a lifetime of about 1 ps. 
Anderson and co-workers proposed that 
two different bent transition-state geome-
tries control the direct and complex-medi-
at ed reaction channels. Subsequent theo-
retical studies by Klippenstein (15) are 
consistent with this model.

Just as mode-selective chemistry can be 
achieved by localizing vibrational energy in 
a bond or a motion along the reaction 
coordinate, so can selectivity also be 
achieved by localized electronic excitation. 
Examples are the selective breaking of the 
C-I or C-Br bonds in CH₃IBr and the C-S 
and S-H bonds in CH₂SH by Butler, Lee, 
and co-workers (16).

How effectively mode-selective chemistry 
can be applied to collisions between large 
polyatomic molecules remains an unsettled 
issue. It seems that three conditions must be 
met to achieve mode-selective chemistry: 
First, it must be possible to excite a state of 
the reagent (an eigenstate or a superposition 
of eigenstates) that localizes energy in some 
part of the molecule; second, this energy 
must remain relatively localized during the 
reaction; and third, this prepared state must 
progress or hinder reactivity of that portion 
of the molecule to cause a change in the 
product-branching ratio. Fast, direct reac-
tions fulfill these criteria best because it is 
necessary for the reaction to occur before the 
excitation energy becomes statistically dis-
btributed among the degrees of freedom avail-
able, in which case vibrational excitation is 
no more effective than heat.

**Stereodynamic Control**

Another type of state preparation is control 
of the reagent approach geometry, which 
also may be called stereodynamic control (17). 
The orientation of one reagent with respect 
to the other is usually achieved by 
colliding two beams of reagents in which 
one reagent is oriented or aligned by the 
application of an external electric field, 
such as a strong homogeneous electric field 
(18) or an inhomogeneous field created by a 
hexapole. Alternatively, the rotational 
angular momentum direction of one re-
agent is controlled by the absorption of 
linearly polarized light (19). For example, 
Brooks and co-workers (20) and Bernstein 
and co-workers (21, 22) reacted alkali at-
oms M with CH₃I molecules oriented by a 
hexapole field to give MI + CH₃ and 
showed that reaction preferentially oc-
curred when M collided with the I end of 
the molecule (Fig. 1). Loesch and co-
workers (23) reacted Sr and K atoms with vibra-
tionally excited HF molecules aligned with 
linearly polarized light to give SrF + H and 
KF + H₂, respectively. At low collision en-
ergy, reactivity of Sr with HF is favored by 
the HF bond being perpendicular to the Sr 
approach direction, whereas reactivity of K 
with HF is favored by the HF bond being 
parallel to the K approach direction. In 
contrast, at higher collision energies, reac-
tivity of Sr with HF reverses so that the HF 
product being parallel to the Sr approach 
direction, whereas reactivity of K 
with HF is favored by the HF bond being 
parallel to the K approach direction. In 
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data as involving fast neutralization of the ion on the surface followed by collision-induced dissociation and electron capture, the order of these two latter events being undetermined. This mechanism suggests that the end-on approach geometry is favored for O\textsuperscript{-} production because it leads to the lengthening of the N-O bond upon surface impact (Fig. 2). Classical trajectory calculations (32) support this explanation and suggest that vibrational excitation of the NO\textsuperscript{+} would enhance O\textsuperscript{-} production. Indeed, in subsequent studies of NO\textsuperscript{+} on the (110) face of gallium arsenide, it was shown that that NO\textsuperscript{+} (ν = 6) is 2.4 times more effective than NO\textsuperscript{+} (ν = 0) in production of O\textsuperscript{-}, whereas if the same energy of vibrational excitation is placed into NO\textsuperscript{+} (ν = 0) translation, the O\textsuperscript{-} yield increases only by a factor of 1.14 (33). Thus, both stereochemical and vibrational control should be expected to be applicable for such processes.

**Quantum Control**

I turn next to phase control, which is most easily understood by reference to Young’s celebrated two-slit experiment in optics. Here, a monochromatic plane wave is incident on two small circular apertures (slits). At each aperture, a new spherical wave emerges and travels to an observation screen at a distance large compared to the wavelength of the light. Each spherical wave has a fixed phase relation to the incident light wave and, hence, to each other. The observation screen shows an alternating pattern of bright and dark fringes. This interference pattern depends on whether the two waves are in or out of phase at any point on the observation screen, that is, whether they interfere constructively or destructively. Mathematically, the intensity of the screen spot is proportional to the square of the total electric field |E| at that spot, that is, |E\textsubscript{1} + E\textsubscript{2}|\textsuperscript{2} = |E\textsubscript{1}|\textsuperscript{2} + |E\textsubscript{2}|\textsuperscript{2} + 2 |E\textsubscript{1}||E\textsubscript{2}| cosθ, where θ is the phase difference. The generalization to more than two slits is straightforward. Control of the phase difference θ governs the intensity at any point.

The molecular scattering equivalent to Young’s two-slit experiment arises when an initial molecular state can follow two different paths, characterized by wave functions Ψ\textsubscript{1} and Ψ\textsubscript{2}, that lead to the same final scattering state. The probability of being in that final state is then proportional to the square of the total wave function. Once again, the two wave function amplitudes must be summed together before squaring, and the probability of the process contains a cross term involving the phase of the two wave functions. It follows that by altering the relative phases of a set of competing paths, it is possible to control the transition probability. This idea for phase control of a molecular scattering event was first put forward by Brumer and Shapiro (34) and was successfully demonstrated by Chen et al. (35) for atoms and by Park et al. (36) for molecules. The basic idea they use is to excite an atom or a molecule by two different optical pathways that lead to the same upper state from which various processes such as ionization or dissociation can occur by the absorption of a subsequent photon (37). In this manner, the upper state is created in a coherent superposition of (at least) two different product channels. The particular superposition depends on the optical pathway, that is, on how many photons are used to produce the excitation. It is to be expected that different optical pathways have different relative phases.

An example of the power of this type of phase control is the study by Gordon and co-workers (38) who excited a beam of DI molecules with one photon at 118 nm and three photons at 354 nm. The experiment was begun with some phase relation between the two laser beams, and this phase relation was varied by passing both beams through a transparent gas medium. Because the refractive indices at the two different wavelengths vary, the phase can be controlled by changing the pressure inside the gas cell. The excited DI decays either by autoionization to produce DI\textsuperscript{+} + e\textsuperscript{-} or by predissociation to produce a ground-state D atom and an excited I(2P\textsubscript{1/2}) atom, which absorbs an additional photon to yield I\textsuperscript{+}. As the phase between the two laser beams is varied, the I\textsuperscript{+} and DI\textsuperscript{+} ion signals vary sinusoidally in and out of phase, and the depth of modulation typically reaches 15%. The relative yields are predicted to be a sinusoidal function of this phase difference and a function of the relative intensities of the fundamental and third harmonic of the light. Recently, Bersonh and co-workers (39, 40) studied the interference between the 1\textsuperscript{+} + 2 and 3 + 2 multiphoton ionization of methyl iodide (Fig. 3), ammonia,

![Fig. 2](image_url)

**Fig. 2.** Schematic drawing illustrating the effect of stereodynamic control in the production of O\textsuperscript{-} in collisions of aligned NO\textsuperscript{+} with a single-crystal silver surface: (A) NO\textsuperscript{+} approaches the Ag(111) surface either end-on or side-on, and in either case, the ion is rapidly neutralized; (B) the end-on collision causes a compression of the N-O bond, whereas the side-on collision does not compress the bond; (C) the compressed N-O bond is more likely to break, causing the formation and escape of O\textsuperscript{-}; whereas the uncompressed molecule is less likely to rupture. The time ordering between N-O bond rupture and electron transfer from the surface is not known. This figure is based on the work of Jacobs and co-workers (32).

![Fig. 3](image_url)

**Fig. 3.** Illustration of quantum control in the multiphoton ionization of CH\textsubscript{3}I. (A) Three-photon and one-photon transitions from the ground state of methyl iodide to the same intermediate Rydberg state interfere in the (3 + 2) and (1 + 2) photon-ionization of methyl iodide. As the argon pressure is increased in a gas cell through which both the (one-photon) red and (three-photon) ultraviolet beams pass (red and blue arrows, respectively), the phase varies between them, which causes the observed modulation in the CH\textsubscript{3}I ionization signal (B). This figure is adapted from Bersonh and co-workers (39).
trimethylamine, triethylamine, cyclooctatetraene, and 1,1-dimethylhydrazine. [Here, the notation (n + m) indicates that n photons are absorbed in the transition from the ground state to the intermediate state and m photons are absorbed in the transition from the intermediate state to the ionization continuum. A prime is added to a number to indicate a different frequency from the unprimed number.] In all experiments, interference was observed, which suggests that molecular size may be little obstacle to this type of phase control, provided that the molecule has sufficiently strong absorptions at the fundamental and at the frequency-tripled output of the laser beam to a bound intermediate state. One intriguing possibility for placement of the laser beam to a bound intermediate state is sufficiently strong absorptions at the fundamental transition from the intermediate state to the ground state and the corresponding wave packet may be little obstacle to this type of phase control. Moreover, in many cases the effects of the molecular system in such a manner is the medium in which most chemistry is controlled acousto-optic pulse shaper to excite fluorescence and a dump pulse of radiation that transmits amplitude in the opposite direction.

Concluding Remarks

Collision control is presently a topic of intense research activity. The increasing versatility of laser sources and laser techniques underpins almost all advances. Until the cost of performing photon-induced chemical reactions is greatly reduced, however, no practical applications can be anticipated for this type of chemical reaction control. Moreover, in many cases the effects are too small to be useful. Nevertheless, the real gain in pursuing laser-based collision control is likely to be the increased understanding of how chemical reactions occur, which in time will no doubt lead to important applications.

REFERENCES AND NOTES

33. J. S. Martin et al., ibid. 100, 6791 (1994).
Quantum Theory of Chemical Reaction Dynamics

David C. Clary

It is now possible to use rigorous quantum scattering theory to perform accurate calculations on the detailed state-to-state dynamics of chemical reactions in the gas phase. Calculations on simple reactions, such as $\text{H} + \text{D}_2 \rightarrow \text{HD} + \text{D}$ and $\text{F} + \text{H}_2 \rightarrow \text{HF} + \text{H}$, compete with experiment in their accuracy. Recent advances in theory promise to extend this capability to more complicated reactions, such as $\text{OH}$ and $\text{H}_2\text{O}$, and even to reactions of molecules on solid surfaces. New experimental techniques for probing reaction transition states, such as negative-ion photodetachment spectroscopy and pump-probe femtosecond spectroscopy, are stimulating the development of new theories.

Experiments and theory on chemical reaction dynamics aim to study the details of reactions beyond just simple rate constants at room temperature (1). Reactant and product molecules can have different translational energies, varying angles of orientation and different internal quantum states. Developing experiments and theory to study such microscopic aspects of chemical reactions, and to probe directly the structures and lifetimes of reaction transition states (2, 3), has become a major field. The results provide the most detailed insight into the mechanisms of chemical reactions and are useful also in a variety of other contexts. For example, an understanding of both atmospheric (4) and combustion processes (5) can require data on the chemical reactions of molecules in selected vibrational and rotational quantum states, and modeling of the nonequilibrium environments of interstellar clouds (6) needs information on the reaction rates of molecules in selected rotational states for low collision energies.

Theory has a special role to play in chemical reaction dynamics as it is often essential for extracting useful information from experimental results. Furthermore, reaction dynamics theory can now provide detailed predictions with an accuracy that can rival experiment on simple reactions in the gas phase (7), and the theory has been extended, albeit more approximately, to more complex problems such as reactions of polyatomic molecules (8) and reactions on solid surfaces (9) and in solution (10).

Quantum Reaction Dynamics

The best theory of chemical processes uses quantum mechanics. The Born-Oppenheimer approximation is usually invoked, allowing electronic and nuclear motion to be separated, so that a calculation reduces to two separate steps: solution of the Schrödinger equation for the electrons with fixed positions of the nuclei to obtain a potential energy surface, followed by solution of the “quantum scattering” Schrödinger equation for the nuclei moving on this potential energy surface.

Significant advances in ab initio quantum chemistry techniques are enabling potential energy surfaces to be calculated to a high accuracy for simple reactions (11). However, one problem is that reaction rate constants $k(T)$ often depend exponentially on the height $E_v$ of the barrier in a potential energy surface according to the Arrhenius expression $k(T) = A e^{E_v/(RT)}$, where $A$ is a constant, $R$ is the gas constant, and $T$ is temperature. This exponential dependence shows that $E_v$ needs to be calculated extremely accurately. This constraint presents a major problem for quantum chemistry calculations on reactions involving molecules with several electrons.

In a quantum scattering calculation on a chemical reaction $A + BC(v, j) \rightarrow AB(v', j') + C$ in the gas phase, it is necessary to use coordinates that go smoothly from reactants to products and can describe the initial $(v, j)$ and final $(v', j')$ vibration-rotation molecular states accurately. Devising the most appropriate coordinates has not been straightforward. A useful “hyperspherical coordinate” approach is to take the bonds being broken and formed in the reaction and transform them into polar coordinates $(\rho, \theta)$ (12). The “hyper-radius” $\rho$ has the advantage that it can be used as a common scattering coordinate for both the entrance and exit channels of the reaction. The time-independent Schrödinger equation $\hat{H}\Psi = E\Psi$ can then be solved, and scattering boundary conditions can be applied to calculate reaction probabilities selected in all of the vibration-rotation states of reactants and products and with well-defined collision energy. This method has been used quite widely on reactions involving three atoms (13) and has also recently been applied to four-atom reactions (8).

A different approach is to solve the time-dependent Schrödinger equation for the nuclear motion. This method has the computational advantage that reaction out of individual reactant quantum states can be computed efficiently (14). However, it has been difficult until recently to extend this “wave-packet” technique to calculate state-to-state reaction probabilities. Therefore, total reaction probabilities summed over all product states are often computed. The large number of coupled vibrational and rotational states of molecules that can be involved in chemical reactions has made the solution of the nuclear Schrödinger equation computationally expensive. Therefore, the field of theoretical reaction dynamics has had to wait for the modern generation of fast computers with large memory capabilities before reliable calculations have been possible. This is why the field of quantum reaction dynamics is now suddenly blossoming.

Simple Reactions

How well does the best theory do when compared with the best experiments? One of the simplest chemical reactions is $\text{H} + \text{D}_2(v = 0, j = 0) \rightarrow \text{HD}(v', j') + \text{D}$. This reaction has been studied in one of the most detailed experiments that can be performed, crossed-molecular beam experi-

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