Laser selective chemistry —is it possible?

With sufficiently brief and intense radiation, properly tuned to specific resonances, we may be able to fulfill a chemist's dream, to break particular selected bonds in large molecules.

Ahmed H. Zewail

One of the main goals of chemists is to understand the "alchemy" that leads to the building and breaking of molecules. There are many different ways of approaching this goal. One of these is photochemistry, the cracking of molecules by adding energy in the form of light to break bonds in the molecules. The resulting bond breakage is in most cases limited by statistical thermodynamic laws. With sufficiently brief and intense laser radiation properly tuned to specific resonances, we hope to bypass the statistical laws and break molecules precisely where we want to break them. Intellectually this is a challenging problem; if we succeed, laser selective chemistry may also have application in various areas of pure and applied chemistry and, perhaps, in medicine.

Laser chemistry involves two basic questions: How can we break molecules selectively with lasers, and what happens when molecules are subjected to heavy doses of laser radiation? These questions on selectivity open the door to many other fundamental questions pertaining to absorption and emission light by molecules, intramolecular vibrational relaxation, dephasing and coherent pumping by nonlinear optical processes. This article and the article by Vladimir Letokhov will explore what happens during and after the interaction between molecules and the laser field, covering single-photon and multiphoton absorption events. The other two articles in this issue by Richard N. Zare and Richard B. Bernstein, and by Yuan T. Lee and Ron Y. Shen are more concerned with state-to-state chemistry using lasers as effectors or detectors.

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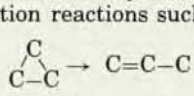
In large molecules (that is, those with more than several atoms) the bonds are weak or strong depending on the atomic constituents and on the shape of the molecule. When the atoms take on energy, the bonds vibrate according to well-known rules of physics. In addition to vibrations, the molecules can convert the input energy to translational or rotational motion. It takes different amounts of energy to excite these different degrees of freedom; for example, the quanta of vibrational energy are larger than those for rotation.

When molecules are heated indiscriminately, the energy will be distributed statistically among all degrees of freedom; as the internal energy increases the weakest bonds will break, so that one can induce only a limited set of reactions in this way. However, because lasers can produce much more power in very short times and over much narrower spectral ranges than conventional light sources, they can, in principle, supply energy only to certain bonds in a molecule, leaving the other bonds cold. Thus, chemists could direct chemical reactions by breaking specific bonds that are not necessarily the weakest ones. But how do we go about such selective heating? To answer this question we must first know what goes on inside these large molecules—how the bonds "communicate" with each other, how fast the heat (or energy) spreads among the bonds or the different vibrational states. We must also understand why certain lasers can do the job while others cannot. In other words, we must still resolve some problems standing in the way of a happy marriage between lasers and molecules—laser chemistry.

Chemical selectivity

When the degrees of freedom of a large molecule are efficiently coupled, energy supplied to one of the bond vibrations is soon distributed among them. Even a light source well tuned to one vibrational mode heats the molecule uniformly, and all vibrations reach equilibrium in accordance with the laws of statistical thermodynamics. The reactivity of the molecule under these conditions has been described by a well-known theory advanced by Oscar K. Rice, Herman C. Ramsberger, Louis S. Kassel, and Rudolph A. Marcus (the RRKM theory), in which the intramolecular vibrational relaxation is very rapid.[1] In some sense, by using selective bond chemistry we hope to deviate from the RRKM scheme. There are several situations in which this statistical theory may not apply. For example, the reaction may depend on the energy present in *each* vibrational mode. Noel B. Slater has used a nonstatistical harmonic-oscillator theory to describe some isomerization reactions such as



that ought to follow such a scheme.

Another way in which the statistical theory can break down is that energy is supplied to one degree of freedom much faster than the energy can be distributed to the others— because the intramolecular vibrational relaxation is slow on the time scale of the experiment, the incoming power is so large and mode-specific that one bond breaks before the vibrational modes can communicate.

Intramolecular dephasing

A large molecule containing N atoms has $3N-6$ vibrational modes. The potential energy of these vibrations becomes anharmonic for large oscillations, as the graph in figure 1 shows, reflecting the finite energy needed to break the molecular bonds. As a result of the anharmonicity, the spacing between vibrational levels decreases with

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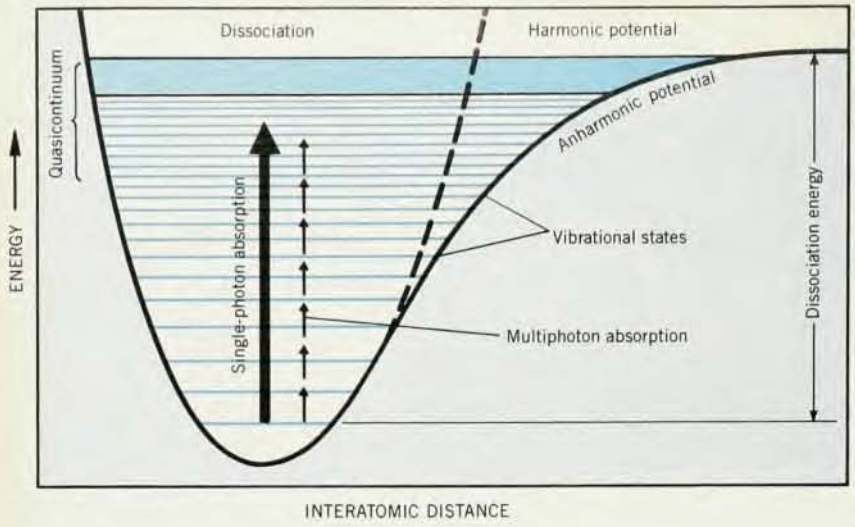
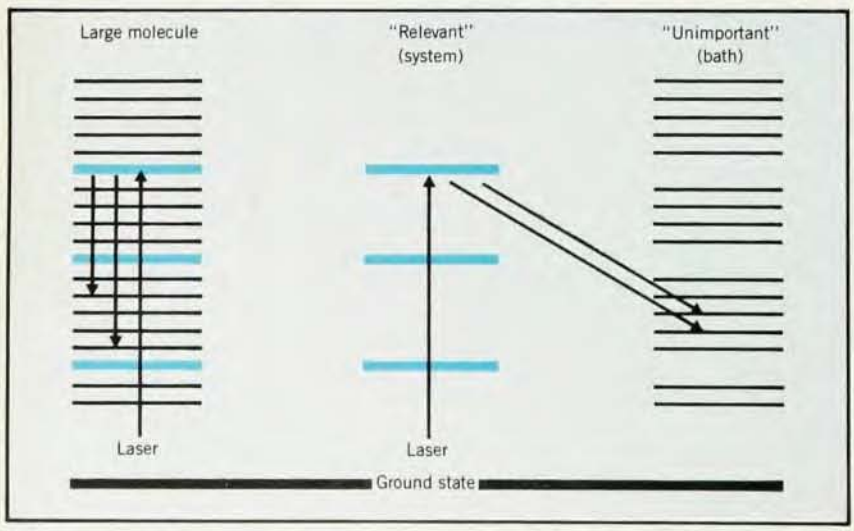


Vibration of a polyatomic molecule. The graph shows a plot of the potential energy of large molecule as a function of intratomic distances. At low energies the potential is nearly harmonic, so the vibrational quantum states are evenly spaced. For large bond-stretches the vibrations become anharmonic and the levels are more closely spaced, producing a quasicontinuum below the true continuum of dissociated states. The arrows show two possible modes of excitation, with single or multiple photons. Figure 1

increasing energy, producing a "quasicontinuum" of levels below the dissociation energy. For example, in benzene at about two electron volts of excitation energy there are about 10^8 states per reciprocal cm (about 10^{-4} eV—see the table on page 26). The variation of energy-level spacing caused by the anharmonic potential also permits different vibrational modes to exchange energy at excitations where the spacings in different modes match up. This happens, of course, particularly at high energies, so that many modes are coupled in the quasicontinuum.

In molecules with many degrees of freedom it is useful, for many purposes, to divide modes into two groups, a "relevant" part and an "unimportant" part. In other words, we may say that the molecule has some modes that we excite ("R-type" modes) and many others ("U-type" modes) that are not excited directly but interact with the excited R-modes (see figure 2). Accordingly, the "relevant" R-modes form a subsystem in the molecule while the remaining modes, the unimportant U-modes, make a large system that functions as a "heat bath" or energy sink for the R-modes. Unlike the heat baths encountered in other fields, such as magnetic resonance spectroscopy, the bath here is entirely intramolecular:



Energy levels in a large molecule. Only some of the levels interact directly with the laser field; the remaining levels form a heat bath for this "relevant" part of the molecule. Figure 2

here we are dealing only with interactions within isolated molecules. In other words, the large number of vibrational degrees of freedom in a large molecule is sufficient for the molecule to be its own energy sink. A similar formalism describes another type of transition, "electronic radiationless" transitions, in large molecules.[2] The vibrational problem we are considering is similar in many ways to the electronic radiationless transition problem.

Consider, for example, benzene (figure 3). With 12 atoms it has thirty vibrational modes; there are oscillations of the carbon–hydrogen bonds, out-of-plane vibrations and many others. The carbon–hydrogen bond resonates at a wave number of approximately 3000 cm^{-1}; all other modes have lower resonant frequencies. We may consider the C–H stretch to be the relevant part and all the other normal modes to form the bath. The interaction between them is due to the off-diagonal anharmonicity terms of the Hamiltonian.

The theoretical formalism for this system-bath picture of a molecule may be borrowed from the literature. We can partition the Hamiltonian for the molecule into parts dealing with system, the bath, and their interaction:

$$H_{\text{tot}} = H_{\text{sys}} + H_{\text{bath}} + H_{\text{int}}(\text{sys–rad}) + H_{\text{int}}(\text{sys–bath}) \quad (1)$$

Equation 1 includes a term describing the interaction of the system with an external radiation field; for dipole transitions it is of the form $\mu\mathcal{E}$, where μ is the dipole-moment operator for the system and $\mathcal{E}$ is the laser-field amplitude. (We may regard $\mathcal{E}$ as a given parameter rather than a dynamical variable, so we need not include a term H_{rad} in the Hamiltonian. Only if we consider spontaneous emission do we need H_{rad}.)

The equation of motion for the density matrix of the system is

$$i\hbar\frac{d\rho}{dt} = [H, \rho] \quad (2)$$
$$= [H_{\text{sys}}, \rho] + [\mu\mathcal{E}, \rho] + (\text{relaxation})_1 + (\text{relaxation})_2$$

The two relaxation terms arise from the interaction of the system with the bath:

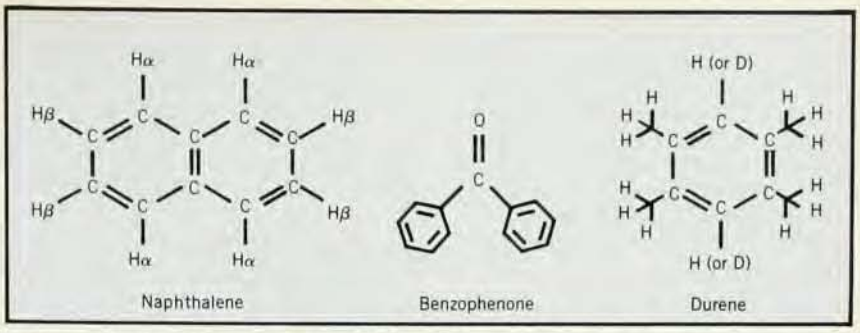
- The first describes the loss of energy from the system to the bath; this is an irreversible process. We shall denote the characteristic time with which it takes place as T_1.
- The second describes the "elastic" part of the interaction which leads only to phase changes in the system; it also contributes to the broadening of the system transitions. The time constant for the phase relaxation is T_2.

To make the separation in equation 2 of the energy-relaxation and phase-relaxation terms one must assume that both these processes are slow compared to the rate at which the bath reaches

internal equilibrium. That is, one assumes

$$T_1, T_2 \gg \tau_c \qquad (3)$$

where τ_c is the correlation time of the bath; it reflects the random fluctuations in the bath and is typically on the order of the vibrational period of the bath. If this criterion is satisfied, the resonance of the system will be homogeneous. On the other hand, in cases where τ_c is long, we expect complete or partial inhomogeneous broadening, depending on the strength of nonradiative coupling and relaxation in isolated systems. To understand non-RRKM chemistry we must understand the origin of T_1 and T_2. We shall come to this point later.



Naphthalene, benzophenone and durene. The "relevant" parts of these molecules are the virational modes of the C–H bonds in naphthalene, the C=O bond in benzophenone, and the C–H bonds of the methyl groups in durene. Figure 3

Bond localization

To break a specific bond we must be able to supply energy to that bond rather than to some broadly spread-out, nonlocal vibrational mode. In large molecules what are the criteria for bond locality? How does locality relate to T_1 and T_2? By "locality" here we mean spatial or temporal localization of vibrational excitation energy. Let us turn to some relevant experimental results.

Classical chemical activation experiments have provided vibrational relaxation times for some molecules. Seymour Rabinovitch's group at the University of Washington has measured[3] product distributions from reactants activated by different chemical means; they concluded that the vibrational relaxation time is of the order of 10^{-12} sec. This is a rather short time, and implies, unfortunately, that ultrashort laser pulses may be required for laser-induced selective chemistry. The theoretical group at the University of Southern California[4] have argued, however, that the measured quantity for chemical activation and also for beam experiments is not very sensitive to departures from RRKM behavior.

Unlike chemical activation methods, lasers can, in principle, produce monochromatic excitation of certain vibrations. One can excite the molecule with single a photon or with multiple photons. In the former case the molecule is provided with the required energy in a single shot. In multiphoton excitation the photon energy is much smaller than the necessary dissociation energy, but the molecule successively absorbs many of the low-energy photons among its many vibrational levels until it has accumulated sufficient energy to dissociate. The quasicontinuum helps the "climbing up" process because it contains many states whose separation can match the energy of the infrared photons. Nicolaas Bloembergen and Eli Yablonovitch discussed this mechanism earlier in PHYSICS TODAY.[5]

With single photons one may, in principle, excite either normal or local vibrational modes of the molecule. Vibrational spectroscopists, a long time ago, told us that when the molecule is excited to the fundamental region (that is, a first excited vibrational state) the excited states are normal modes whose wavefunctions have a symmetry determined by the full point group of the molecule. Recently, however, some experimental and theoretical results have given support for the "local-mode" picture. This picture, is, of course, what we want for laser selective chemistry.

In molecule such as benzene one expects the C–H-stretch modes to be different in character from the rest of the modes simply because of the frequency mismatch: the C–H modes have the highest vibrational frequency. Thus, in a very simple picture, one would expect the C–H modes to be local and to have a large diagonal anharmonicity and small off-diagonal anharmonic couplings to other modes.

Several research groups have examined the local-mode character of large molecules, both experimentally and theoretically. Here we shall discuss our own work,[6] which is concerned with large molecules at low temperatures, (around 1.7 Kelvin); as we shall see, this is important for obtaining high-resolution information on intramolecular dynamics. The other groups have focussed their attention on liquid and gas spectra.[7,8] The experimental work of Andy Albrecht and Robert Swofford in the US and of Brian Henry in Canada has provided the foundations for understanding the energetics of local modes. The gas-phase experiments of Robert Bray, Michael Berry, and Don Heller have raised important questions regarding the broadening of overtones as a function of energy.

We have investigated bond locality in naphthalene and benzophenone (figure 3). We excited the molecules to C–H or C=O vibrational states with single photons, over a range which covers the low- and high-energy limits. The low temperatures allowed us to avoid rotational congestion and also kept the quasicontinuum out of the picture, because no molecules could be in those states at the start of the experiment—at 1.7 K all molecules are essentially in the ground state.

Cooling of large molecules is very important and may be done by:

- isolating the molecules in a cold host matrix
- cooling a crystal of these molecules, for example, to liquid helium temperatures
- expanding the molecules with an inert gas through a pinhole nozzle.

Although in all cases the spectra will be sharpened considerably because of the removal of thermal congestion, in the matrix-isolation and the cold-crystal methods there is some perturbation due to guest–host interactions and the crystal field. However, if these interactions are small compared to the intramolecular interactions, then these two methods are ideal for studying vibrational and electronic dynamics. Our group at Caltech has used the second method of cooling to study the spectroscopy of high-energy vibrational states and the third method of cooling, supersonic expansion of a molecular beam, to examine intramolecular relaxation processes. In the latter case, the molecules are rotationally very cool (0.3 K) and vibrationally cool (around 40 K) after they leave the nozzle of the apparatus; they are then excited by a laser beam, and one can then obtain high-resolution spectra of isolated, cooled molecules. Richard Smalley (now at Rice), Len Wharton and Don Levy successfully demonstrated[9] this method at the University of Chicago.

Figure 4 shows the vibrational overtone spectra for a cooled naphthalene crystal. Napthalene has 48 vibrational modes and benzophenone has 66. The C–H and C=O stretches are at about 3,000 cm^{-1} and 1,700 cm^{-1}, respectively. Because the dissociation energy of the C–H bond in the naphthalene molecule is about 44 000 cm^{-1}, it requires about 15 photons with the energies of the C–H mode to dissociate. To examine the C–H and C=O bond locality we measured the spectra of the modes and

the relaxation time of the excited mode by all other modes in the molecule.

From our naphthalene and benzophenone experiments[6] we found that:

▶ The overtone spectrum (that is, the spectrum of states with vibrational quantum number $v = 2, 3, \ldots$) is a simple progression of C–H or C=O bands (especially at high energies) with energies obeying a simple anharmonic rule:

$$E_v / v = A + Bv \qquad (4)$$

For naphthalene $A = 3086\ \text{cm}^{-1}$ and the diagonal anharmonicity, B, is $-55.8\ \text{cm}^{-1}$; the fit of the data to equation 4 is excellent, as figure 5 shows.

▶ At about 15 000 cm^{-1} 9about 1.9 electron volts) in the molecule, the stretches of the $C-H_\alpha$ and $C-H_\beta$ bonds (figure 3) in naphthalene are distinguishable.

▶ The vibrations of the $C-H_\alpha$ and $C-H_\beta$ bonds in naphthalene have different apparent relaxation times (.075 and .11 picosec) even when the other modes (the "bath") are cooled to 1.3 K.

▶ The relaxation time (from the spectra) gets shorter as the energy increases in the C=O stretching mode of the benzophenone molecule.

What do these findings mean? If we think of naphthalene's C–H bonds as not communicating with each other, we could represent (rather naively) the molecule as simply the sum of the different bond deformations:

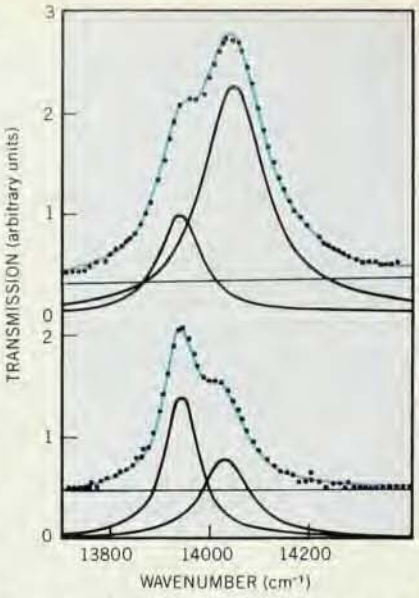
$$\text{naphthalene} = 4C{-}H_\alpha + 4C{-}H_\beta + \ldots$$

And in fact, experimentally, in both the napthalene C–H stretches and the benzophenone C=O stretch, a simple relationship, like that in a diatomic molecule between the vibrational energy and the vibrational quantum number v, holds up very nicely and accurately.

Can we conclude from this that the energy is localized in the C–H or C=O bond? In my opinion, the answer is no. All it means is that our results are consistent with a local excitation in the C–H or C=O sub-systems. But to prove the locality we need further evidence.

From the experiments we do know that the energy stays in the carbon-hydrogen system for fractions of picoseconds or longer. Now we are faced with a dilemna. On one hand the spectra are consistent with a local-bond picture, but on the other hand the relaxation time of these excited modes is extremely short. Eventually lasers may be developed that can break a bond at this speed, but for the moment it might seem that we would have to give up.

However, the other channel of relaxation, dephasing, and inhomogeneous broadening could affect our previous measurement of the energy-relaxation time. (As we mentioned, dephasing describes the loss of phase coherence; for illustration we can think of the modes are dancers in a *corps de ballet*—if one dancer misses a step and gets out of phase with the others, there will be a disturbance in the routine but this will not immediately affect the *number* of dancers on stage. Similarly, the C–H oscillations can dephase without any net loss of energy.) Simple spectroscopic experiments will not measure dephasing rates directly;[6] the line width, for example, has contributions from both relaxation rates and from inhomogeneous spreading.



Transmission spectra of naphthalene (upper graph) and naphthalene deuterated in the α positions (lower graph). The experimental curves show the low-temperature (1.3–2 K) spectra for the fifth vibrational overtone; the theoretical curves show the fixed peak due to β hydrogen and the shifting peak due to α hydrogen or deuterium. Figure 4

For successful selective chemistry we must know both T_1 and T_2: T_1 tells us how fast the deposited energy is flowing to all modes, and T_2 tells us what kind of lasers we should use. At the moment one does not know the contribution of each of these two relaxation times to the overall relaxation time of all overtones. It may be that the bond-locality time is much longer than the measured 0.1 picosecond overall relaxation time—even long enough for us to get at the bonds and break them with current laser technology. One also does not yet know how to describe theoretically the spectra of high-energy transitions. This is in contrast to our rich knowledge about the spectra of low-energy states. We shall return to this point later.

Which state do we excite?

Essential to the problem of selectivity is the question of state preparation. For any molecule, there are certain exact eigenstates that one may obtain, in principle, by using just symmetry and quantum mechanics. But, does light excite these stationary states—or does it excite a non-stationary state? If the states are non-stationary are they normal or local modes? These questions are not fully answered yet. However, we may be able to shed some light on these questions by considering the results of the following experiment.

Recently, we have studied[6,10] the high-energy vibrational overtones of the durene molecule (tetramethyl benzene) and a partially deuterium-substituted analog (see figure 3). The durene molecule has two types of C–H stretches, those in which the hydrogen atoms are in the methyl groups remote from the benzene ring, called "aliphatic-C–H" and those in which the hydrogen atoms are directly attached to the ring, called "aromatic-C–H". Figure 6 shows the spectra of durene and of deuterated durene. Two remarkable observations are noteworthy. First, when the hydrogen atoms attached to the benzene were replaced by deuterium the spectrum of region I in figure 6 (between 0 and 800 cm^{-1}) is relatively unchanged while the band of region II (above 800 cm^{-1}) is completely missing in the spectrum of deuterated compound even at high energy. Second, the bands of the "triplet" observed in region I are very sharp (as small as 20 cm^{-1} wide—the narrowest band observed in any large molecule's overtone region) in contrast with all known aromatic-C–H bands, which have a typical width of 100 cm^{-1} or larger. The bands of region I are due to the aliphatic-C–H bonds, while that of region II is from the aromatic bonds. The implications of these results are quite interesting.

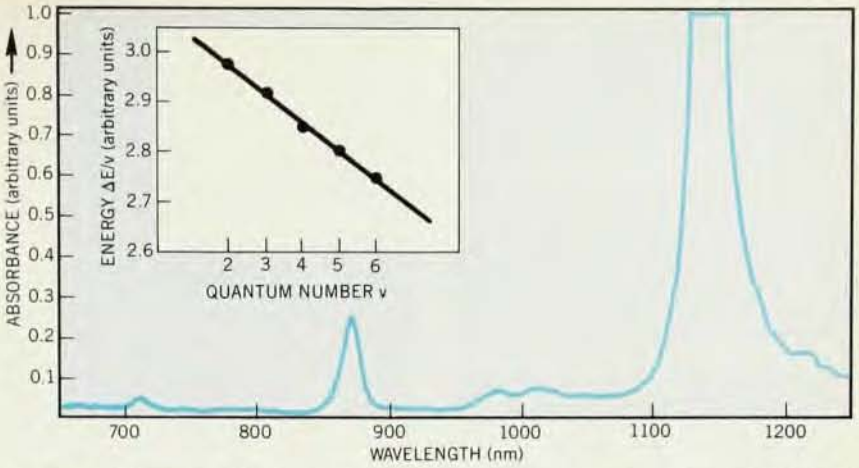
The fact that the absorption band of the aromatic-C–H bond disappears when hydrogen is replaced by deuterium indicates that the stretches of the aliphatic and aromatic bonds are not interacting with each other even in the quasicontinuum region. Furthermore the narrowness of the aliphatic bands in comparison with aromatic bands indicates that the coupling of the aliphatic-C–H vibrations to the intramolecular bath is much weaker than the coupling of the aromatic-C–H vibrations to the bath. In some sense the aliphatic-C–H bonds form a subsystem of the large molecule. This subsystem behaves like a small molecule in which the states are well separated from each other in energy. The aromatic-C–H bonds must, on the other hand, behave as if they were a part of a large molecule, where the bath is quite big and the dephasing or energy-relaxation rates are very large. This is consistent with the theoretical picture advanced by Joshua Jortner's group. An important point about the prepared states emerges from the observations.

Because aliphatic-C–H stretches in

the large molecule durene belong to the small- or intermediate-three molecule coupling limit, and because we observe three prominent lines in the overtone spectra, we conclude that the coupling among the aliphatic-carbon–hydrogen bond excitations of the methyl groups is larger than the coupling of the methyl groups to the bath. That is, the methyl groups behave as a strongly coupled system weakly coupled to a bath. We are still investigating the exact nature of the coupling, using polarized-light absorption spectroscopy.

A useful measure of the relation between the internal coupling of a subsystem of states and the coupling to the bath of other states is the ratio of the line splitting, Δ, to the line width, ϵ.

If $\Delta/\epsilon \ll 1$, we should observe only one band that in part is inhomogeneously broadened. What we excite under this condition is a statistical mixture of states (perhaps local), whose coherent character is ill-defined. On the other hand, if $\Delta/\epsilon \gg 1$, then the normal modes (or, more precisely, the anharmonic modes) can be excited. The important point here is that normal mode progressions in the quasicontinuum are possible, and that exciting a *single* bond in a molecule crucially depends on the magnitude of the intramolecular coupling and relaxation rate and on the laser source used in the experiment.



Overtone progression of the carbon–hydrogen bond stretch in naphthalene. The peaks are for vibrational quantum numbers $\nu = 5,4,3$ (left to right). The inset shows the simple anharmonicity of the spectrum: $\Delta E/\nu$ is a linear function of ν. Figure 5

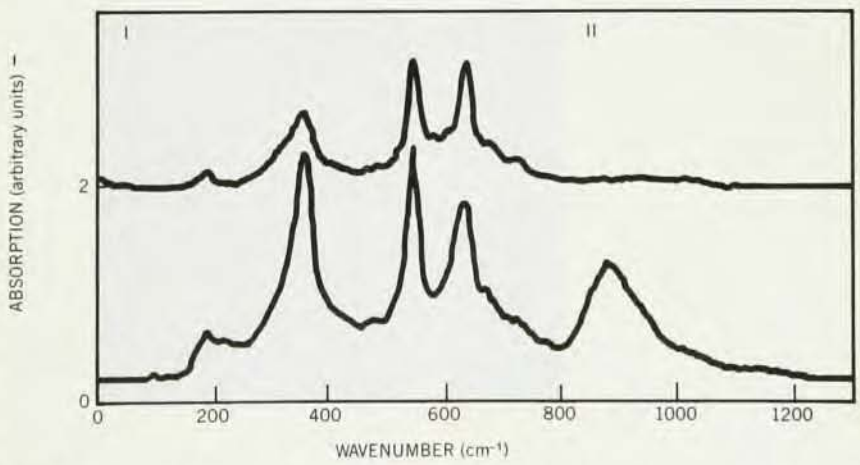
Laser-induced selective reactions.

Because of the extensive study of laser-induced chemistry in many laboratories, it is not possible to give here a full account of all the research. Rather we shall highlight the new ideas that relate to selectivity by discussing the results of three different experiments done at the University of Pennsylvania, at Allied Chemicals and at Exxon.

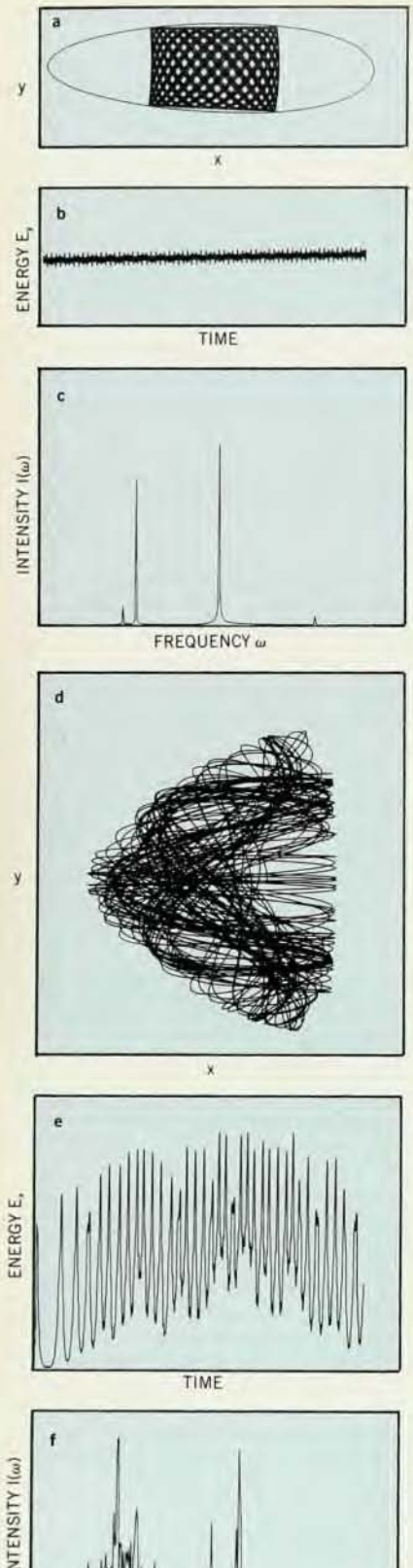
Robin Hochstrasser and David King[11] in an elegant experiment, have induced selective chemical reactions in the molecule tetrazine, $C_2N_4H_2$, which has a cyclic structure, very much like benzene. In their experiment the tetrazine molecules were dispersed in a host crystal at 1.6 K. Enrichment factors of at least 10^4 for carbon-13 and nitrogen-15 were obtained in the photodissociation products, hydrogen cyanide and nitrogen. Hochstrasser and King achieved this selectivity by tuning the laser to the absorption band of molecules with a particular isotopic composition. Such molecules will be lost because of dissociation, while molecules containing other isotopes are enriched. Even though the molecule is large and one expects the spectral levels to overlap, cooling the system to 1.6 K isolates the spectral bands of the different isotopes. In these low-temperature experiments, the reactions take place from excited electronic states and not from excited vibrational levels of the ground state. Furthermore, the selectivity is achieved because of the slow communication between different isotropically labelled molecules (molecular selectivity) and not between different vibrations in the same molecule (bond selectivity).

In a different type of experiment, Kammalathinna V. Reddy and Berry[12] have induced reactions in the gas phase by selectively exciting certain vibrational states. The molecule allyl isocyanide ($H_2C{=}CHCH_2NC$) undergoes photoisomerization when excited by a laser into the different C–H stretches. It was concluded that in this system, direct one-photon overtone photoactivation leads to bond-selective excitation that ultimately leads to nonstatistical photoisomerization reactions. Reddy and Berry conclude from their experiments that the time scale for complete randomization of the internal energy due to intramolecular vibrational energy redistribution must be longer than or comparable to the isomerization time scale (10^{-7}–10^{-9} sec), that is, the behavior here is not according to the RRKM theory. If this conclusion turns out to be truly general, the outlook for bond-selective chemistry is very good.

The above experiment uses single photons from a dye laser. Multiphoton absorption has also been used to search for the possibility of selective chemistry. Richard Hall and Andrew Kaldor[13] excited cyclopropane, $(CH_2)_3$, by laser either at 3.22 microns exciting the C–H asymmetric stretch, or at 9.50 microns, exciting the CH_2 wag. The excitation is in the fundamental region but the reactions are induced by multiphoton infrared absorption. The reaction induced by the absorption is isomerization to propene, $CH_2{=}CH{-}CH_3$, in addition to some products from a fragmentation



Spectra of durene and partially deuterated durene, obtained at low temperatures. The lack of absorption in region II for the deuterated molecule (upper graph) indicates that this absorption is due to hydrogen bonded to an aromatic carbon atom and that region I of the spectrum is due to the hydrogen atoms of the methyl groups. Figure 6



Two-mode systems in the quasiperiodic (upper three graphs) and ergodic regimes. We show the phase-space trajectories (**a** and **d**), the spectra (**b** and **e**) and the energy (**c** and **f**) of a computer model.[14] Figure 7

reaction. The "branching ratio" of the yield of isomerization to the yield of fragmentation depends on the frequency of the laser used; at low pressures, almost no fragmentation occurs for the 3100 cm^{-1} excitation, whereas the yields of fragmentation and isomerization are roughly equal for excitation at 1050 cm^{-1}. The fact that in each case the products are typical of those formed with thermal excitation whereas the relative yields are not, led Hall and Kaldor to conclude that their results are consistent with a non-statistical distribution of the states that lead to a reaction. More experiments of this type are obviously needed before we can generalize the conditions under which selectivity can be achieved. It is quite interesting that the above experiments indicate that selectivity may be achieved by pumping the molecule with a laser directly into the fundamental region (multiphoton experiments) or into the overtones of modes in the quasicontinuum (single photon experiments). The question now is: can we relate the experimental findings on energy localization and selectivity to a theory?

Theoretical Descriptions

We are interested here in the interaction of molecules with the radiation field and in the subsequeent intramolecular energy redistribution. The former problem is usually formulated phenomenologically in the semiclassical nonlinear optical theory: the laser field is simply described as a classical field and molecules are described as quantum systems with phenomenological energy levels. The other theoretical problem, concerning the intramolecular energy redistribution, is not at all trivial.

The theory of intramolecular energy redistribution is difficult because of the many interactions among a large number of anharmonic modes, and because accurate calculations require precise knowledge of the multi-dimensional potential-energy surface. However, several simplifications have been advanced both in classical and quantum calculations. To illustrate these, let us consider perhaps the simplest case—a system containing two anharmonically coupled modes[14,15] (such as the symmetric and antisymmetric stretches in a linear triatomic molecule). Extension to large molecules might still be a difficult, if not impossible task.

Theorists at Irvine, Chicago, Caltech, UCLA, Colorado Tel Aviv and Hebrew University and other places have considered this challenging theoretical problem. Armed with chemical intuition and the mathematical tools of nonlinear mechanics, these groups have developed some criteria for describing the energy redistribution and in some cases for the onset of chaotic, or "ergodic," behavior in "simple" molecules. One expects that as the molecule's energy increases, the vibrations will become more and more chaotic because of the large density of states at high energies. But what determines the onset for this chaotic behavior? And at what energy can classical and quantum calculations yield the same results?

Before we discuss the recent theoretical results, let us briefly review the classical theory of two coupled oscillators. For a system with two vibrational degrees of freedom, such as a triatomic molecule (neglecting bending), we can write the Hamiltonian as

$$H = T(p_1, p_2) + V(q_1, q_2)$$

where T is the kinetic energy and V is the potential energy. To describe oscillations one expands the potential around the equilibrium position

$$V = {}^1/_2k_1q_1^2 + {}^1/_2k_2q_2^2 + k_{12}q_1q_2 + \Sigma k_{ijl}q_iq_jq_l + \ldots$$

where the q_i are generalized coordinates, the p_i are the conjugate momenta and the k's are constants. The normal modes of the system are those for which the quadratic terms of T and V are diagonalized. If we denote generalized coordinates for these "normal modes" by x and y we have

$$V = {}^1/_2(K_xx^2 + K_yy^2) + \Sigma K_nx^ny^{3-n} + \ldots$$

The exact nature of the vibrational motion is given by quantum-mechanical solution of the above Hamiltonian. Even for simple anharmonic potentials that is not a simple task, so one often starts with a classical solution.

The classical behavior of the oscillator are the solutions to Hamilton's equations, $\dot{x} = \partial H/\partial p_x$, and so forth. One can, for example, obtain the classical trajectories—the "orbits" in the x-y plane—by integrating Hamilton's equations on a computer, starting with some representative initial conditions. Marcus and his collaborators, first at Illinois and now at Caltech, have obtained approximate energy levels for coupled anharmonic oscillations by applying the semiclassical quantum conditions

$$\oint p\mathrm{d}q = (n + {}^1/_2)h$$

(with the integrals calculated along topologically independent paths) to the classical orbits. The classical trajectories also permit one to calculate the absorption spectrum for the resonance associated with each normal mode:

$$I(\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty}\langle x(0)x(t)\rangle e^{-i\omega t}dt$$

for the x-mode, for example. (Of course, to obtain the actual infrared spectra one must use $\mu(t)$ instead of $x(t)$ in the correlation function.) Figure 7 illustrates the trajectories and spectra [assuming that $\mu(t) = x(t) + y(t)$] obtained with these methods by Marcus's group

for two important cases: the "quasiperiodic" and the "ergodic" limits.

What do we mean by quasiperiodic and ergodic motions? For a single oscillator (for example, the vibration of a single diatomic molecule) the motion is always periodic: the oscillation will be some combination of the fundamental and its overtones. For a system with two modes, the energy can go from one mode to another, but if the modes are not too highly excited, the motion will shift smoothly from one mode to the other and the motion is said to be quasiperiodic. In a phase-space diagram, such as figure 7a, the trajectory is confined to a limited region. At sufficiently high energies this quasiperiodic behavior is lost and the motion is said to be ergodic. Because of the many interfering Fermi resonances and combination bands, the behavior becomes quite chaotic and the trajectory essentially fills the entire phase space, as in figure 7c.

The next problem is to find out how accurate these classical results are by confronting them with quantum mechanical calculations on the same system. If possible, the comparison will allow us to find if quantum behavior correspond to classical behavior in the quasi-periodic and ergodic regimes.

Stuart A. Rice and his group at Chicago examined[15] quantum ergodicity of certain nonseparable, two-dimensional potential surfaces in an anharmonic oscillator basis. They pointed out that the microscopic ergodic theories of John von Neumann and Eberhard Hopf are not relevant to the problem of ergodic behavior in molecules. They then advanced their own idea, which can be summarized as follows: For a given Hamiltonian there exist a set of eigenfunctions which can, in principle, be obtained from computer diagonalization methods. The projections of these wavefunctions on the unperturbed harmonic-oscillator basis functions give an idea about the "degree of chaos": when a wavefunction has a substantial component over a number of basis functions it is termed "global", otherwise it is "local". The question is: Are the global states also ergodic (or statistical, stochastic, chaotic)? It is argued in the literature[14] that states can be global in a quantum sense without necessarily being ergodic or statistical in nature. Moreover, for certain system Hamiltonians, quantum and classical methods yield essentially the same answer in the quasiperiodic regime, but not necessarily in the ergodic limit.[14]

William Miller's group[16] at Berkeley made use of the nodal pattern of wavefunctions and concluded that many of the higher eigenstates can apparently be classified as ergodic. These particular states seem to correspond quite well to classical ergodic trajectories. Marcus's group detected the onset of chaos by searching for "overlapping avoided crossing" in the plot of eigenvalues as a function of parameters in the Hamiltonian, such as the coefficients k_{ijl}. At UCLA Eric Heller's group has found[17] a strong correlation between spectra, wavefunctions, and classical motion for certain model Hamiltonians. In more recent work Rice's group has used the Kolmogorov entropy to suggest that there is an inherent difference between classical chaos and quantum mechanical chaos. These results leave open the question of what precise relationship, if any, exists between classical chaos and quantum mechanical motion. Clearly, we still do not know the precise meaning of quantum ergodicity.

Problems for the future

Our understanding of selective bond-breaking in molecules bonds by lasers is in its infancy. There is a massive effort by chemists around the world to unravel many of the theoretical and experimental problems that stand in the way of successful laser selective chemistry. In my view we must know a lot more about intramolecular dynamics. Lasers are now available in almost laboratory, but the understanding of large-molecule dynamics is not yet fully available.

What we must expect from theory and experiments in the future can best be summarized, perhaps, by asking the following questions:

- Can we predict theoretically the yields of chemical reactions following the laser excitation into a selected quantum state?
- In large molecules, what is the precise nature of the state that we excite?
- Can we induce chemical reactions from truly local modes?
- To what extent does selective chemistry with lasers depend on the properties of the source of the excitation?
- Are the experiments on selectivity more likely to be successful in other systems than in those currently used?
- Under what conditions is the randomization of intramolecular energy slow or rapid relative to chemical reactions such as isomerization or fragmentation?
- Is our description of the statistical behavior in real isolated molecules correct?
- Can quantum calculations be done to predict intramolecular rates in real systems?
- What is the quantum origin of optical relaxation times T_1 and T_2 in large systems, such as large molecules?
- What exactly do we mean by quantum ergodicity in complicated systems?

Opportunities in this field of study are numerous. Lots of exciting questions are at hand, and if they can be answered—and if their answers are encouraging—selective chemistry, with lasers might revolutionize many fields such as photochemistry, analytical chemistry and catalysis.

With the advances made recently in lasers with ultrashort (picosecond to subpicosecond) pulses and ultrahigh resolution, the selective, and extremely fast, heating and breaking of bonds in large molecules will perhaps be no longer a chemist's dream.

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I wish to thank many of my colleagues for their critical comments and for communicating their results and ideas: S. RiceR. A. Marcus, M. Berry, R. Bernstein, A. Kaldor, M. El-Sayed, R. Hochstrasser, H. Rubalcava, E. Stechel, E. Heller and W. Miller. This work was supported in part by the National Science Foundation.

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