

# Laser Selective Chemistry

## A New Challenge for Chemists and Physicists

by Ahmed Zewail

How can molecules be cracked selectively with lasers, and what happens to them under heavy doses of laser radiation?

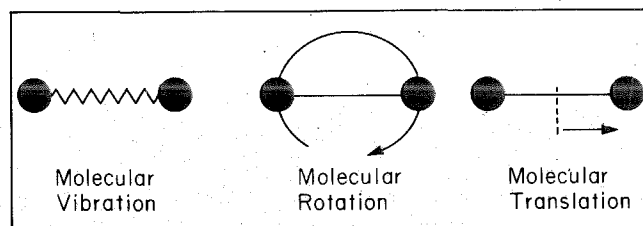
One of the main goals of chemists is to understand the "alchemy" that leads to the cracking and building of molecules. Approaches toward this goal are numerous and involve a working team of organic and inorganic chemists and chemical physicists. For centuries large molecules have been put together and taken apart using conventional organic synthesis or photochemistry.

To achieve total organic synthesis, an organic architect designs the different parts of a desired molecule and then joins these blocks, made of atoms and bonds, chemically. A photochemist, on the other hand, is interested in taking apart the blocks by adding energy in the form of light to break the bonds. This bond breakage is limited by statistical thermodynamic laws. Furthermore, a conventional light source excites all bonds indiscriminately — with no selectivity. With lasers we hope to bypass these laws and to build and crack large molecules selectively — to break molecules precisely where we want to break them. Intellectually this is a challenging problem to understand, and, if we succeed, laser selective chemistry will have application in various areas of applied chemistry and perhaps in medicine.

Laser chemistry involves two basic questions: *How* can we crack molecules selectively with lasers? And *what* happens when molecules are subjected to heavy doses of laser radiation? Before discussing these questions, perhaps it

will be useful to explain a few things about both molecules and lasers.

Molecules are made of chemical bonds holding atoms together. In large molecules (that is, those with more than two 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, by heating for example, the bonds vibrate according to well-known rules in physics. In addition to vibrations, the molecules can convert the input energy to translational motion, changing their position, and/or to rotational motion, which causes the entire molecule to rotate in well-defined steps. It takes different amounts of energy to produce these different degrees of freedom (vibrational, translational, and rotational) — the vibrational energy is greater than the rotational energy. Because the molecule accepts the energy in a

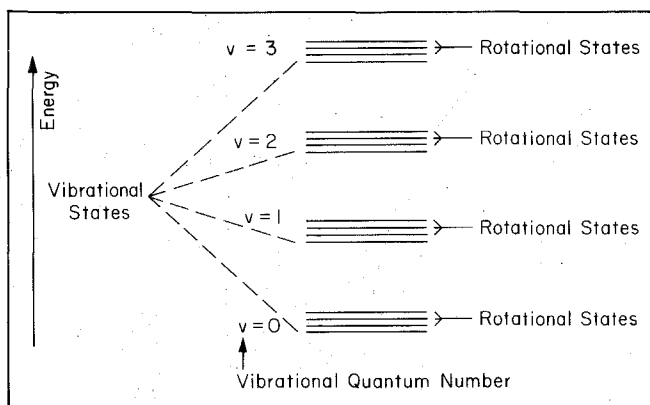


A diatomic molecule consists of two atoms connected by a bond. Energy supplied to the molecule is converted to vibrational, rotational, or translational motion.

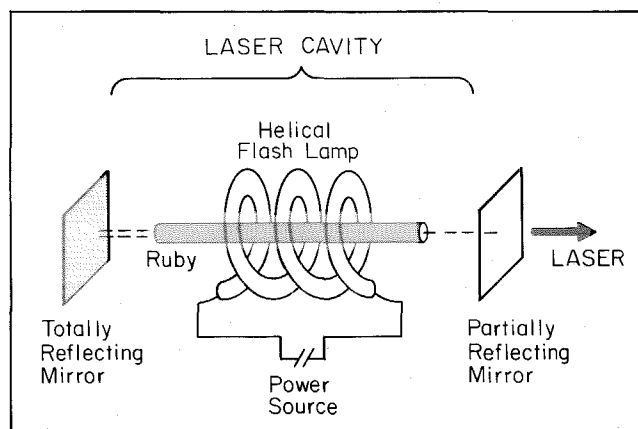
quantized or discrete way, chemists describe vibrational and rotational events using states diagrams with the vibrational and rotational energies dictated by the laws of quantum mechanics. These vibrational and rotational states can be probed by using different light sources, but it is vibrational energy we are mainly interested in here.

The weaker bonds of a molecule are more vulnerable to breakage when vibrating; when they do break, the chemical reaction proceeds. Unlike conventional light sources, lasers can, in principle, heat certain bonds in the molecule and leave all others cold, enabling chemists to direct a chemical reaction by causing certain bonds — not necessarily the weakest ones — to break. 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.

The word “laser” is an acronym for light amplification by stimulated emission of radiation. A basic laser apparatus consists of a lasing medium and two mirrors, one of them totally reflecting and the other partially reflecting and partially transmitting. The lasing medium or material can be the atoms, molecules or ions in a gas (for example, argon ion laser) or a solid (for example, ruby in a solid state laser). When these molecules or atoms are pumped into an excited state by a flash of intense light, or sometimes by another laser, the process begins: One excited



According to the laws of quantum mechanics, energy is given to a molecule in discrete steps or vibrational states. The quantum number,  $v$ , equals 1, 2, 3 . . . as the deposited energy is increased. Since rotational energy is less than vibrational (less energy is needed to turn a molecule than to stretch its bonds), each vibrational state contains many rotational states.

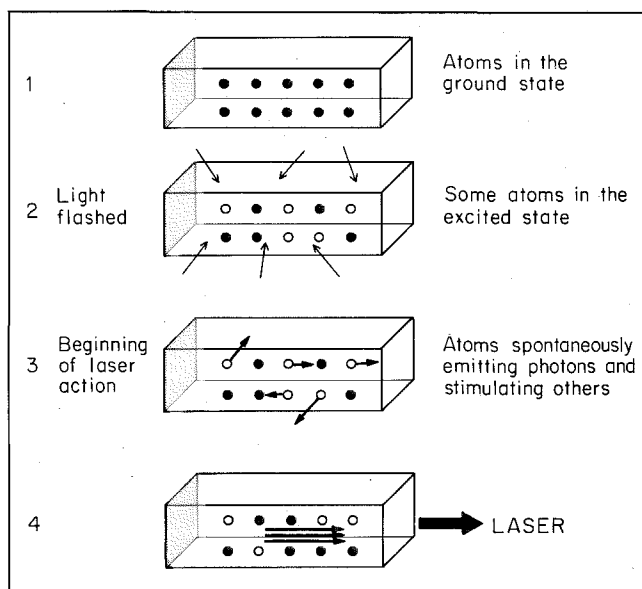


In this typical laser device, the lasing medium (ruby) is encircled by an intense light flash that excites the atoms so that they emit photons. The photons emitted in a path horizontal to the axis of the lasing medium bounce between the mirrors on either end of the laser cavity and are released as a laser beam through the partial mirror at right.

atom spontaneously emits a photon, which hits another excited atom, causing it to emit another photon of the same frequency and direction. While photons emitted in wrong directions will leave the lasing medium, those perpendicular to the mirrors will be “trapped,” bouncing back and forth between the mirrors until all the waves of emitted radiation are aligned in “sync” with each other (with the same frequency and direction). Thus an intense, coherent beam of light — the laser — is born and released through the partially transmitting mirror at one end.

Lasers have many nice properties that are useful in numerous areas of research. They are monochromatic, that is, all the photons have very nearly the same frequency. In contrast to “white” radiation, such as a flash of ordinary light, which contains all colors at wide frequency ranges (for example, blue to red), laser radiation is selective and has a narrow band width. For example, a tunable dye laser, in which the lasing medium is a dye solution instead of the ruby in the diagram above, can produce radiation at  $6000\text{\AA}$  with a resolution (or band width) of better than  $10^{-4}$  reciprocal centimeters ( $\text{cm}^{-1}$ ). This is equivalent to an energy of approximately  $10^{-8}$  electron volts or to a temperature of approximately  $10^{-4}$  Kelvin. For contrast, a tungsten bulb has a “resolution” of about  $10^4$  Kelvin. In the United States, primarily at the National Bureau of Standards and the Massachusetts Institute of Technology, and in the Soviet Union, extremely small laser band widths of less than 50 kilohertz have been achieved. This property enables scientists to conduct optical spectroscopy and laser chemistry with very high resolution — the resolution of radio frequency or microwave spectroscopy. Thus rotational and vibrational states of molecules *can* be excited

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With dots in a box representing the atoms of the lasing medium, figure 1 shows unexcited atoms. When light is flashed, some atoms become excited (open dots — 2), emit photons (arrows — 3), and stimulate others to emit more photons. Some of these leave the system, while those in a horizontal direction trapped by the mirrors bounce back and forth to form a laser radiation.

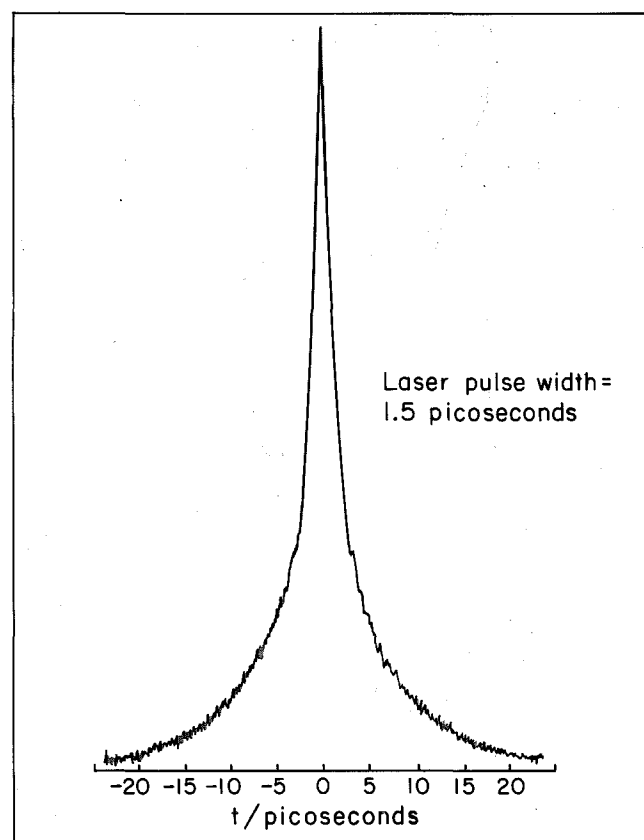
selectively, and indeed many laboratories around the world are involved with laser spectroscopy of rotational and vibrational states in molecules.

Other advantages of the laser are its high intensity, its capacity to propagate over long distances, and its variable time duration. In laboratories today a burst of radiation carrying  $10^9$  watts per square centimeter at, say,  $6000\text{\AA}$  can be generated routinely. The burst, which travels with the speed of light, has a time resolution of better than a trillionth of a second ( $10^{-12}$  or picosecond). These ultrafast light sources (although perhaps in five to ten years picosecond pulses will be considered comparatively long in duration) open the door for the study of the ultrafast processes in molecules. Selective bond cracking may require ultrafast lasers for reasons I will cover later. Such picosecond pulses have been generated at Caltech to study molecular and chemical processes and reactions.

Lasers may induce the chemical reaction selectively or non-selectively. When a large molecule is excited in a non-selective way, the different bond vibrations "communicate" with each other so that the energy is distributed statistically among them. In effect, the molecule is heated uniformly, and equilibrium is reached among all vibrations 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 Rice,

Ramsperger, Kassel, and Marcus (RRKM). In some sense, by using selective laser chemistry, we hope to deviate from the RRKM limit and achieve a highly non-statistical bond cracking. This objective may be gained in either or both of two ways: by slowing down the communications among certain vibrations, or by breaking one bond so fast that there is no time for communication among the different vibration bonds of the large molecule.

The communication process can be illustrated by using zigzag lines resembling springs (which stretch with vibra-



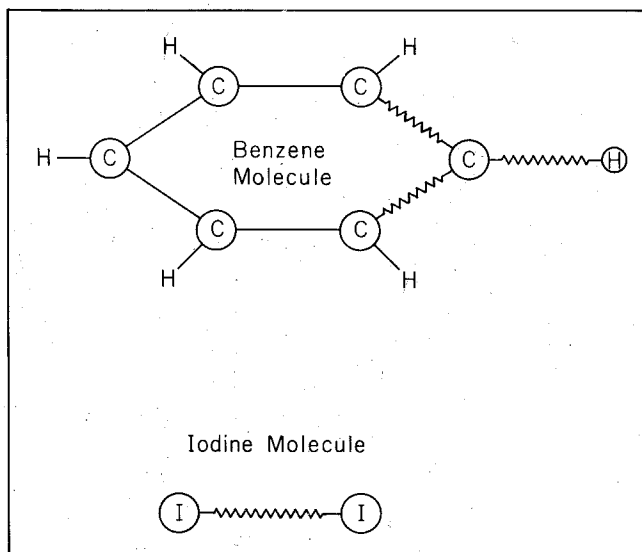
This optical radiation of picosecond laser pulse with a pulse width of 1.5 picoseconds and wavelength of about  $6000\text{\AA}$  was obtained at Caltech. Even smaller pulses may be necessary to break molecules selectively.

tion) to indicate the bond vibrations between the atoms. The "springs" of a polyatomic molecule such as benzene are the bonds connecting two carbon atoms or carbon and hydrogen atoms, etc. According to simple laws, there are  $3N-6$  vibrations (where  $N$  is the number of atoms); since the benzene molecule has 12 atoms, 6 carbons and 6 hydrogens, there are 30 different vibrations.

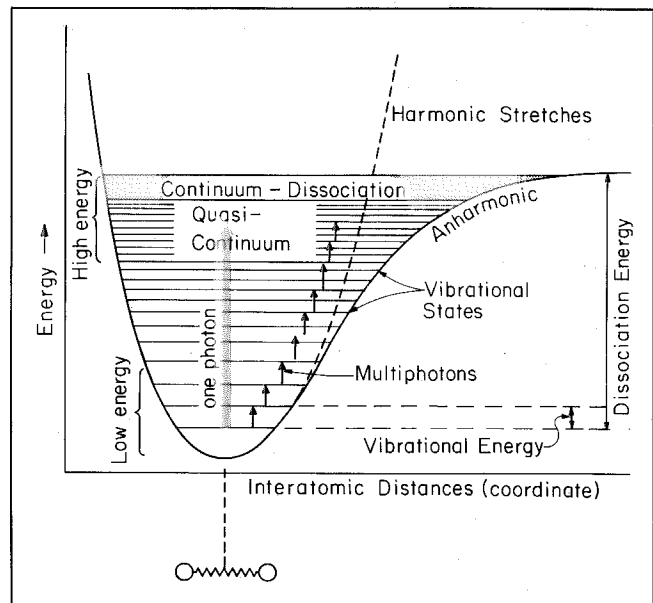
In a diatomic molecule, on the other hand, there is only one vibration (or one spring). If the diatomic molecule is

given a relatively low energy, the bond vibrates in a harmonic way (like a harmonic oscillator or regular pendulum motion). As the energy increases, the vibration becomes anharmonic, or irregular. The motion in the low- and high-energy limits can be visualized in terms of a potential energy surface — energy versus vibrational displacement — or in terms of the vibrational states discussed earlier. The more energy is added, the farther the bonds stretch in either direction; the wider the stretch expands, the more possibility of irregular motion or anharmonicity. Because of anharmonicity, in a polyatomic molecule vibrations that are close together can couple to each other (communicate their energy). This happens particularly at high energies, where there are numerous vibrational states, or *combinations* of many vibrations. For example, for about two electron volts of energy in the benzene molecule there will be about one hundred million states per reciprocal centimeter ( $\text{cm}^{-1}$ ). At these very high energies the vibrational levels are so close in energy that they form what is called a *quasi-continuum* of levels. The quasi-continuum, which represents a density of vibrational levels — or energy states — that are so close together they are practically indistinguishable, may or may not help us achieve selectivity. It will depend on how fast the deposited energy in a given bond spreads or randomizes to all other bonds.

Experimentally, selective laser stimulation of vibrational states in molecules can be accomplished by exciting the bonds with a single photon or with multiphotons. In the former we provide the molecule with the required energy for dissociation in a single shot. In multiphoton excitation,



The six carbon atoms and six hydrogen atoms of the polyatomic benzene molecule are connected together by "springs" or bond vibrations. The diatomic iodine molecule has only one vibration.



If you consider the horizontal axis in this diagram of polyatomic molecular states as the length of a "spring" or vibrating bond between atoms, you can see the spring stretch to the breaking point (dissociation) as the energy is increased. Higher energy also creates anharmonicity, or irregular vibration, shown by the curve veering to the right. Anharmonicity also causes coupling of vibrations, especially when there are many vibrational states close together in a quasi-continuum; this makes dissociation of the molecule possible through many low-energy photons (small arrows), which can "climb up" through the numerous vibrational states of the molecule to the dissociation level. The molecule can also be broken by a single photon (arrow) of the dissociation energy. In that case the photon is typically in the ultraviolet rather than in the infrared.

however, the laser energy (frequency times Planck's constant) is much smaller than the necessary dissociation energy. But the many low-energy photons will be successively absorbed among the many vibrational levels until sufficient energy has been accumulated to dissociate the molecule. The quasi-continuum helps the "climbing up" process (through successive energy levels) because it contains many states that can match the energy of the low-energy or infrared photons. So even though the photon energy is much less than the dissociation energy, this mechanism does not violate the energy conservation laws of quantum mechanics simply because the molecule is immersed in a sea of infrared photons.

Visible and infrared single-photon excitation can be achieved through conventional sources of light and heat, such as flame, electric arc, etc., after passing the radiation through a frequency selector, or monochromator, to achieve high resolution. But the energy left after passing through the frequency selector is very small compared to laser energy with the same resolution, which is millions or

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even trillions of times greater. This makes lasers much more efficient than conventional light sources in the multiphoton process.

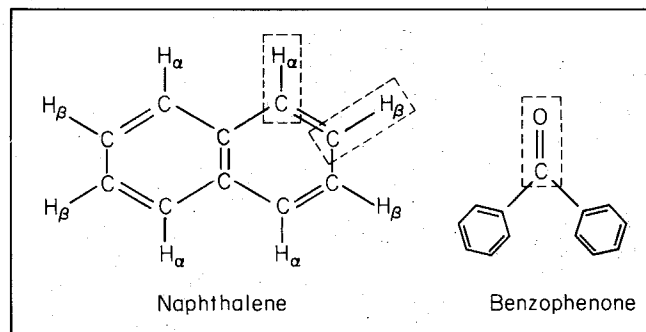
Here at Caltech our work has been particularly involved with the role of energy relaxation — the rate at which energy is distributed to other modes, or bonds, after being locally, or selectively, excited in one mode. In our laser group Joe Perry and Duane Smith, graduate students in chemistry, have investigated bond locality in the molecules naphthalene and benzophenone. Using single photons, we vibrationally excited the molecules to their C–H and C=O bonds as a function of energy, covering the low- and high-energy limits. The experiments were done on molecules frozen to 1.3 Kelvin, so that rotational and translational motions of the molecule were absent. Cooling also kept the quasi-continuum “out of the picture,” since no molecules could be in that state before turning on the light source — at 1.3 Kelvin all molecules are in  $v=0$ .

According to the formula mentioned earlier in our discussion of benzene —  $3N-6$  — naphthalene vibrates in 48 different modes, while benzophenone vibrates in 66 modes. The C–H and C=O stretches are about  $3,000\text{ cm}^{-1}$  and  $1,700\text{ cm}^{-1}$ , respectively. Since the dissociation energy of the C–H bond in naphthalene is about  $44,000\text{ cm}^{-1}$ , approximately 15 photons with the energies of the C–H mode are needed for the molecule to dissociate. To examine the C–H and C=O bond locality we measured (a) the spectra of the modes and (b) the relaxation time of the excited mode by all other modes in the molecule.

From our naphthalene and benzophenone experiments we found that:

1. The overtone spectrum (that is, the spectrum of  $v=1,2,3 \dots$  states, where  $v$  is an index for the vibrational state — the quantum number) is a simple progression of C–H or C=O spectral bands (especially at high energies) with energies obeying the *simple anharmonic rule of diatomics*.
2. At about  $15,000\text{ cm}^{-1}$  (about 1.9 electron volts) in the molecule, the stretches of C–H $_{\alpha}$  and C–H $_{\beta}$  in naphthalene are distinct.
3. The relaxation time gets shorter as the energy increases in the C=O of the benzophenone molecule.
4. The C–H $_{\alpha}$  and C–H $_{\beta}$  bonds in naphthalene have different relaxation times (.075 and .11 picoseconds) even when the other modes (sometimes called the “bath”) are cooled to 1.3 Kelvin.

What do these findings mean? If we think of naphthalene’s bonds as not communicating with each



In Caltech research on bond locality, laser energy was focused on the C–H $_{\alpha}$  and C–H $_{\beta}$  bonds of naphthalene and the C=O bond of benzophenone to determine whether these bonds could be excited selectively for a period of time before passing the excitation on to the molecules’ other bonds.

other, we could represent the molecule as simply the algebraic sum of the different diatomic bonds:

$$\text{naphthalene} = 4\text{C}-\text{H}_{\alpha} + 4\text{C}-\text{H}_{\beta} + \dots \text{ etc.}$$

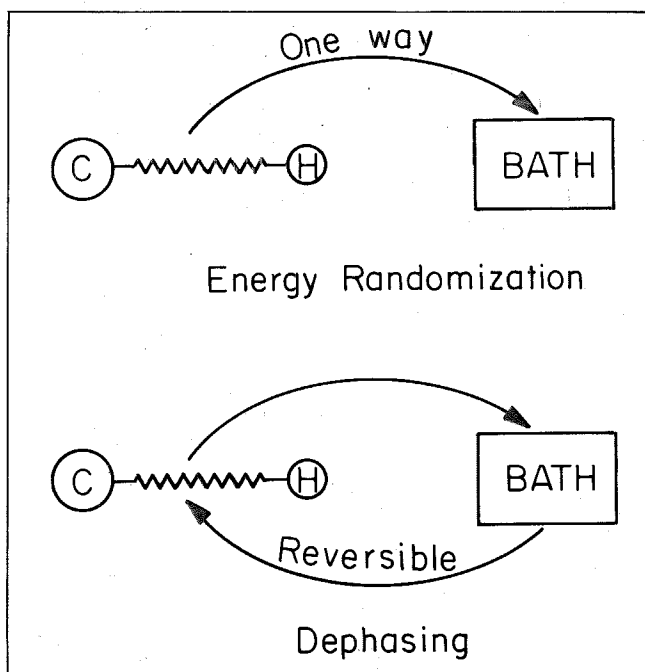
And in fact, experimentally, in both the naphthalene C–H stretches and the benzophenone C=O stretch, a simple relationship, like that in a diatomic molecule between the vibrational energy and the vibrational quantum number ( $\bar{\nu}$ ), holds up very nicely and accurately.

Can we conclude from this that the energy is localized in the C–H or C=O bond? The answer is no. All it means is that our results are consistent with a local bond. But in order to prove the locality we need further evidence.

From our experiments we do know that the energy stays in the C–H bond for fractions of picoseconds or longer. Now we are faced with a dilemma: On one hand the spectra are consistent with a local bond picture, but on the other hand the relaxation time out of these bonds is ultra-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, there is another channel of relaxation that affects our previous measurement of relaxation time. The calculation of a relaxation time of subpicoseconds or picoseconds was based on the assumption of no thermal excitation in the bath at absolute zero and a one-way process of the selectively excited bonds dumping their energy irreversibly into the bath in a time  $T_1$ . But it’s not quite that simple. In a distinctly different process called dephasing ( $T_2$  time constant), a network of coherence may exist by which all the modes feel each other’s existence.

For illustration we can think of the modes as dancers in a corps de ballet. If one dancer misses a step and gets out of phase with the others, she (or he) will cause a disturbance in the routine but will not affect the *number* of dan-



When assuming no initial excitation in the bonds other than the one selectively excited, energy relaxation to the bath made of other bonds is a one-way process. However, a network of coherence may connect the vibrations and allow a continually reversible exchange of energy (dephasing). Both of these situations enter into the actual time measurement of relaxation.

cers on stage. Similarly, the C-H or C=O bonds can be out of phase (dephase) with other bonds without any net loss of energy. Physically this dephasing may then be visualized as a reversible transfer of energy back from the molecules in the bath as well as to them, and this must also enter into our calculation of the total relaxation time. For successful selective chemistry both  $T_1$  and  $T_2$  must be known;  $T_1$  tells us how fast the deposited energy is flowing to all modes, and  $T_2$  tells us what kind of lasers we should use.

What we do not know at the moment is the contribution of each of the relaxation times ( $T_1$  and  $T_2$ ) to the *measured* overall relaxation time. It may be that bond locality time is much longer than the .1 picosecond we measured — even long enough for us to get at it and break it with current laser technology. We also do not yet know how to describe theoretically the spectral shapes of high-energy transitions. This is in contrast to our rich knowledge about the spectra of low-energy states.

Our laser group is currently examining this point, focusing on the following three questions:

1. In the selective excitation of molecules by lasers, can we induce picosecond or femtosecond ( $10^{-15}$  or a

thousandth of a millionth of a millionth of a second) laser chemistry?

2. If the selectively deposited energy is shared among all modes, is the distribution statistical?

3. Does the observed spectrum in the high-energy region reflect the locality of energy in bonds?

Put another way, we want to find out if there is such a thing as "permanent" bond locality. Basically, we would like to make the polyatomic molecule behave like a diatomic one, with precise mode-to-mode energy flow. Once we know the answers to these and to other remaining questions, we might be able to crack and build molecules selectively with lasers just as we can wreck a car or put it back together with the proper tools.

#### LASER SCIENCE AT CALTECH

With the interaction among its divisions, Caltech offers a particularly positive environment for probing the many aspects of laser chemistry. There are many faculty members here — in chemistry, chemical engineering, chemical physics, and applied physics — investigating, theoretically and experimentally, lasers and laser-matter interactions. In chemistry, Rudolph Marcus is interested in the behavior of molecules in the low-energy and quasi-continuum limits. Vincent McKoy is examining new theoretical implications for exciting molecules into the dissociation limit through electron-molecule scattering. And one of the leading authorities on the calculation of bond energies in molecules is William Goddard.

On the experimental side several groups are also involved. Henry Weinberg is studying molecule-surface interactions when the molecule is selectively excited into some vibrational states. Jack Beauchamp is investigating the dissociation of a number of molecules using infrared sources and ion-cyclotron-resonance spectroscopy. Vibrational excitation in diatomic molecules is being examined by Aron Kuppermann to learn about the influence of potential energy surfaces on chemical reactivity. Kenneth Janda is initiating a program to study such dynamical processes in a molecular beam, and Peter Dervan is designing the synthesis of a certain class of molecules that may localize energy better than others.

In electrical engineering and applied physics we also have some outstanding laser engineers and physicists. Among them are Amnon Yariv, William Bridges, and Fred Culick. Finally, in my own laser group we are trying to "shed some light" on the ultrafast processes that take place in molecules, using picosecond and ultra-high-resolution laser spectroscopy. □