

Laser-induced chemical processes

Isotope separation, which continues to be an active field of laser photochemistry, is joined now by methods for producing very pure substances and by studies of biologically important molecules.

V. S. Letokhov

Proposals for controlling or inducing chemical reactions with laser light have been around almost as long as lasers themselves. Immediately after Theodore Maiman's invention of the ruby laser¹ in 1960 and Ali Javan, William Bennett and Donald Herriott's invention of the helium-neon gas laser² in 1961 suggestions for using this new type of light source in chemical processes followed. The proposals resulted essentially from adapting already well-known principles of photochemistry. Yet almost no research employing lasers in chemistry was done for ten years. Not until tunable lasers and high-powered infrared lasers arrived at the end of the 1960's and in the early 1970's did laser chemistry become experimentally feasible, and the period since then has seen intense and systematic study of atomic and molecular processes. Of particular interest are those selective processes applicable to laser isotope separation,³ such as the work on carbon isotopes carried out in the apparatus shown in figure 1 and discussed later in this article. Selective processes also appear to be useful for the production of highly pure substances and for the study of certain photobiochemical compounds. In this article I will be able to give only a brief survey of the great amount of work currently in progress, concentrating particularly on those aspects being studied at laboratories in the Soviet Union.

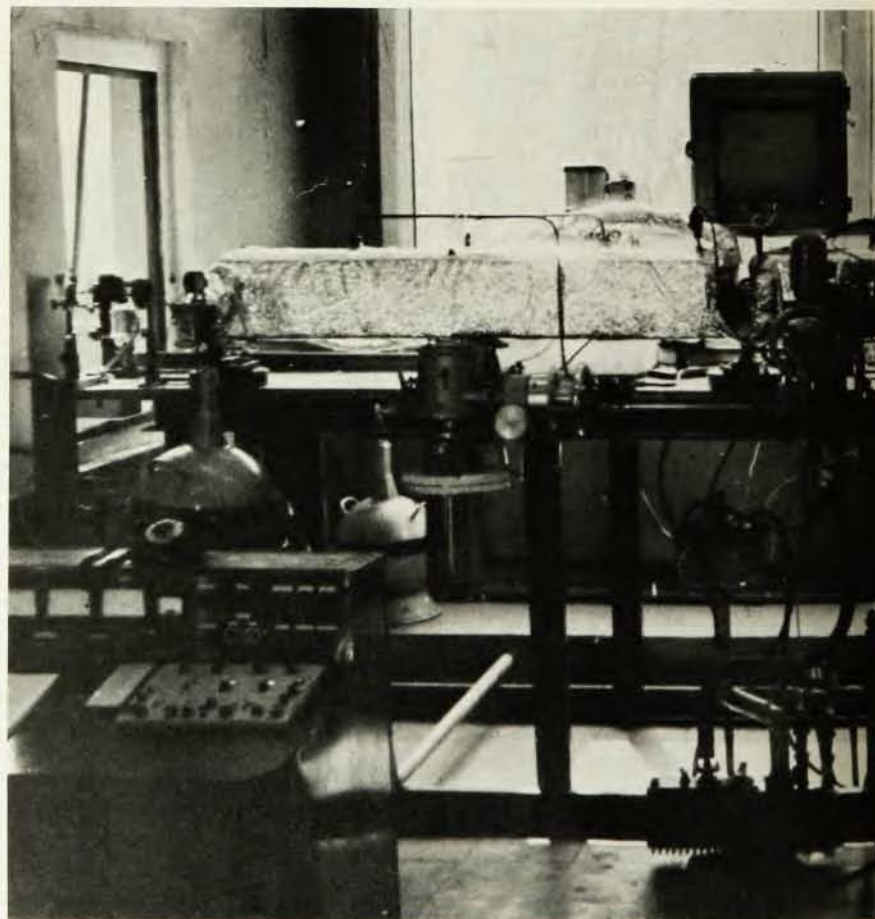
Types of molecular photoexcitation

With laser radiation new methods for molecular photoexcitation have become available that are not possible

with "classical" light sources. Figure 2 compares the old and new techniques for selective molecular photoexcitation in schematic form. The classical, or "pre-laser," photochemical method (figure 2a) is based on single-step excitation of an electronic state of an atom or molecule. It has the serious disadvantage for selective photochemistry that most molecules, particularly polyatomic ones, have broad structureless electronic absorption bands at room tem-

perature; the scheme cannot be used for, say, isotopically selective excitation. Only for a few simple molecules is the absorption line narrow enough for isotope selection. On the other hand, excitation of electronic states does give a high quantum yield for the photochemical reaction.

Single-step excitation of a molecular vibrational state (photochemistry in the ground electronic state) features rather high excitation selectivity for



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both simple and complex molecules. The main disadvantage of this method is that the fast relaxation of vibrational excitation to heat leads to a low quantum yield of the subsequent photochemical process. In any case, the method can only be used for photochemical reactions with low activation energy.

Two-step excitation of a molecular electronic state through an intermediate vibrational state by joint action of infrared and ultraviolet radiation (figure 2b, left side) combines the advantages of single-step ir and uv processes and removes their disadvantages.³ In two-step excitation by a two-frequency laser field (ir + uv) it is possible to separate the functions of selective excitation, when the molecule acquires a rather low energy from the ir photon, and the absorption of a much greater amount of energy, from the uv photon, by the selectively excited molecule. Thus this kind of two-step photoexcitation combines sufficiently high selectivity with high quantum yield for photochemistry.

Two-step excitation of molecules through an intermediate electronic state (figure 2b, right side) is not so widely used as joint ir + uv excitation. Its advantage over single-step excitation of electronic states is that it offers

the possibility of exciting states with specific properties and of reaching high-lying states (with large quantum yields for photochemical reactions) without requiring radiation in the extreme ultraviolet. The process is most important for laser excitation of biologically important molecules in solution.

For polyatomic molecules, a powerful source of infrared radiation acting alone may suffice for isotope-selective excitation to high vibrational or even excited electronic states.⁴ Figure 2c shows how, by multiple absorption of infrared photons of the same frequency, a molecule can derive an energy comparable to the typical energy of electronic excitation. Therefore with this process we can simultaneously realize the excitation selectivity for separating isotopes and a rather high quantum yield of the subsequent photochemical process.⁴ The method is, however, limited in that it can be applied only to polyatomic molecules with a high density of excited vibrational levels in the ground electronic state.

The methods of selective photochemistry illustrated in parts b and c of figure 2 can only be carried out with laser radiation, because the intermediate quantum levels need to be highly

populated. "Conventional" (incoherent) light sources have too low a radiation temperature for all processes except the single-step one of figure 2a, and they have a higher efficiency for electronic states than for vibrational ones in this process.

Types of selectivity

In laser chemistry generally, an important feature of each different approach is the "selectivity" it offers, which of course determines the kind of work it is suitable for. As an example by which we can discuss different kinds of selectivity let us consider infrared multiphoton laser chemistry. This field provides an ideal example because of its recent rapid development (about 500 papers so far) and good prospects for further expansion.

Resonant multiphoton excitation of molecular vibrations in a strong infrared field forms the basis for several essentially different approaches to laser chemistry. They can be classified according to the relations between the various relaxation times for an excited vibrational level interacting with the infrared field:

$$\tau_{v-v'}^{\text{intra}} \ll \tau_{v-v'} \ll \tau_{v-T} \quad (1)$$

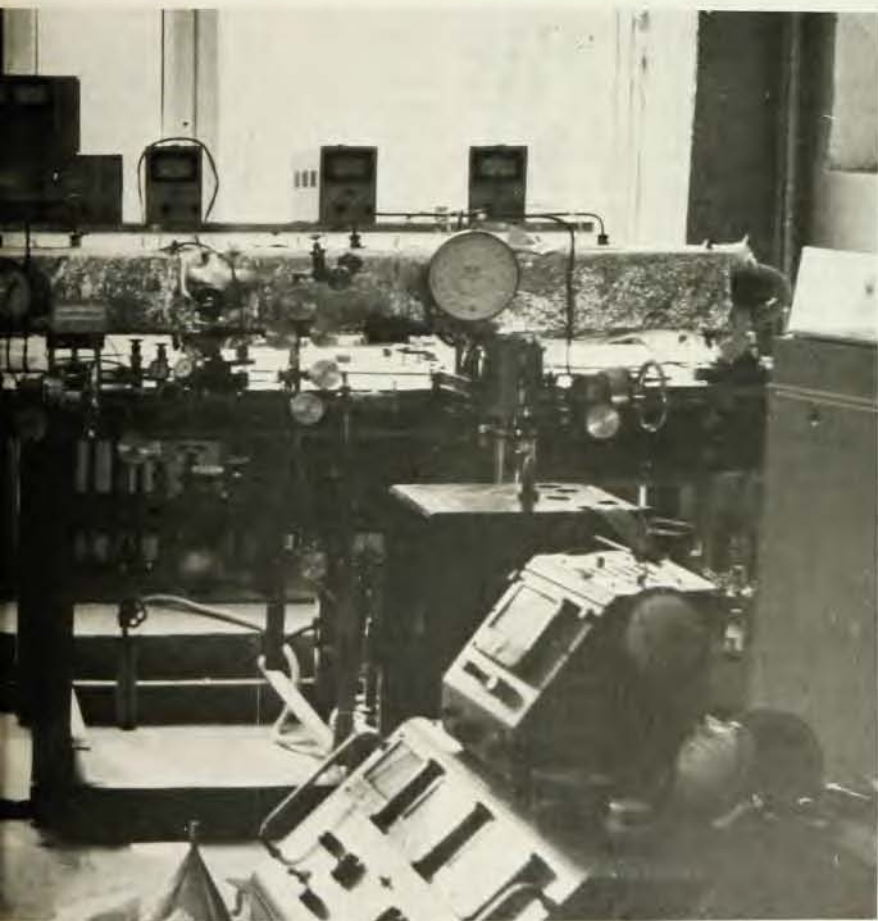
Here $\tau_{v-v'}^{\text{intra}}$ is the time for intramolecular transfer of vibrational energy between different vibrational modes of the molecule being excited;

$\tau_{v-v'}$ is the time for intermolecular transfer of vibrational energy between molecules of different kinds in a mixture (for example, molecules of different isotopic composition), and

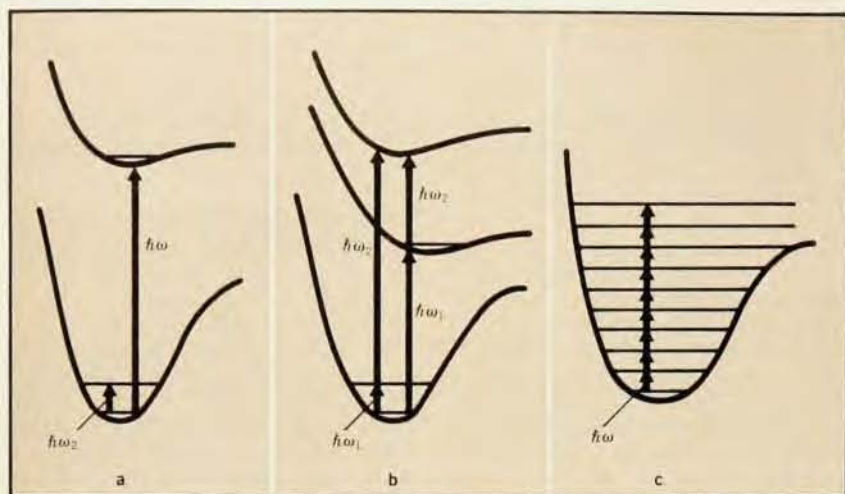
τ_{v-T} is the relaxation time for molecular vibrational energy to be transferred to translational degrees of freedom—which is the time for complete thermal equilibrium to be reached in the molecular mixture.

The first of these processes is intramolecular by definition, and it may therefore occur without collisions; the other two are naturally collisional, so that the times $\tau_{v-v'}$ and τ_{v-T} vary with the experimental conditions such as gas pressure.

Let us call the rate of vibrational excitation of a molecule by multiphoton absorption W_{exc} . The value of this rate W_{exc} depends on radiation intensity and vibrational transition cross sections. From a consideration of inequality 1 we can distinguish four different conditions for the relations between W_{exc} and the relaxation rates of vibra-



Carbon-isotope separation system operated jointly by the Kurchatov Institute for Atomic Energy and the Institute of Spectroscopy of the Academy of Sciences, at the Industrial Institute of Stable Isotopes in Tbilisi. Separation is by multiphoton dissociation of CF_3I with pulsed CO_2 laser radiation of average power 1 kilowatt. See also figure 4. Figure 1



Selective molecular photoexcitation. a: Single-step excitation of electronic or vibrational state; b: Two-step excitation of an electronic state through intermediate vibrational or electronic states, and c: Multiple-photon excitation by infrared radiation. Figure 2

tional energy in different circumstances. Accordingly, there are four different approaches to infrared multiphoton laser photochemistry depending on how far from equilibrium the vibrational excitation in the molecule and molecular mixture lies. Let us consider all four:

$$\text{When } W_{\text{exc}} \gg 1/\tau_{v-v'}^{\text{intra}} \quad (2)$$

mode- or bond-selective excitation of molecules is possible when there is no vibrational equilibrium even inside the molecule interacting with the strong infrared field. A certain mode or a functional group of a polyatomic molecule must have a higher vibrational temperature compared with the remaining modes or functional groups to bring about this condition, in which mode- or bond-selective photochemistry is quite feasible.

$$\text{When } 1/\tau_{v-v'}^{\text{intra}} \gg W \gg 1/\tau_{v-v'} \quad (3)$$

which is a more moderate condition on

the multiphoton vibrational excitation rate, molecular-selective excitation becomes possible; the requirements are that there is no vibrational equilibrium among the molecules in the mixture but there is intramolecular vibrational equilibrium for those that interact with the infrared field.

The molecules in resonance with the infrared field acquire a higher vibrational temperature than all the other molecules. (The translational temperature of all the molecules in the mixture remains, of course, constant.)

The field of molecular-selective infrared photochemistry that becomes possible under condition 3 has been very well explored since its origins in 1974 with experiments on laser isotope separation.⁴ Almost all the published work in this general area relates to this case, because of the important practical applications of selective excitation and dissociation of molecules in a mixture.

At the much more moderate condition:

$$1/\tau_{v-v'} \gg W_{\text{exc}} \gg 1/\tau_{v-T} \quad (4)$$

the vibrational equilibrium among all the molecules in a mixture is stronger, but there is still no relaxation to general heating. The condition is possible only if no component in the mixture has a fast $V \rightarrow T$ relaxation. Because the vibration temperature differs from the translational one in the mixture, nonselective vibrational infrared photochemistry is possible when reactions with a minimum energy barrier take place in a time no greater than about τ_{v-T} . When the fourth and final condition,

$$1/\tau_{v-T} \gg W_{\text{exc}} \quad (5)$$

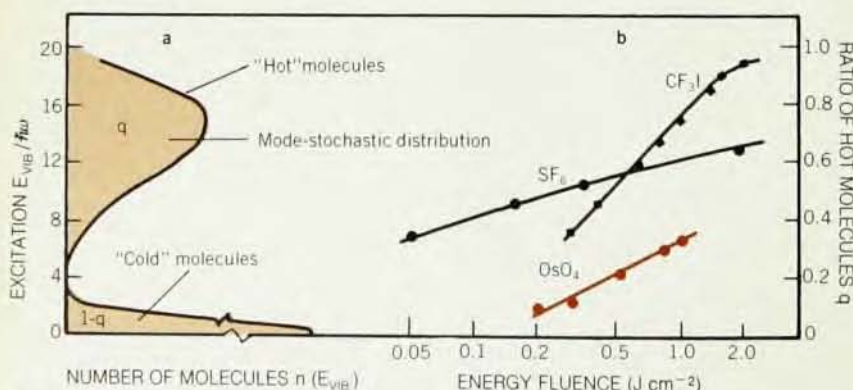
applies, equilibrium thermal excitation of all the molecules in the reaction cell is established (provided no heat is supplied to the walls). In this case the vibrational and translational temperatures of all the molecules in the mixture are equal, or almost equal, because of the vibrational excitation relaxation to heat through collisions. We will therefore be dealing with thermal heating of the molecular gas as observed⁵ as long ago as 1966 with continuous-wave CO_2 laser radiation. This field of infrared thermal chemistry is of interest only when the reaction-cell volume needs to be heated while the walls remain cool.

Having stated these different conditions, let us now review the various methods of infrared laser chemistry that follow them.

Nonselective laser photochemistry

When condition 4 and especially condition 5 apply, no selective photoprocesses are possible in molecular mixtures. Yet even in those circumstances multiphoton excitation of any component in the mixture can be of some practical interest despite the fast transfer of vibrational energy to other molecules. Suppose that certain molecules in the mixture with a high dissociation energy absorb the infrared energy and transfer it to other molecules that have a lower dissociation energy but do not interact with the infrared field. There will of course always be some vibrational-to-thermal relaxation, but if τ_{v-T} is sufficiently greater than $\tau_{v-v'}$, in condition 4 we can generate a vibrationally excited molecular mixture in which, for a limited time, photochemical reactions (particularly molecular dissociation at a minimum energy barrier) will occur.

For most mixtures of complex molecules there will be a channel of rapid $V \rightarrow T$ relaxation via which total heating of the mixture will inevitably occur. Each mixture needs to be studied in detail, comparing rather complicated



Generation of two molecular ensembles ("hot" and "cold") at multiphoton excitation by intense infrared laser pulses (part a); part b of the figure shows the relative fraction of highly excited ("hot") molecules as a function of energy fluence in the CO_2 laser pulse. (Data taken from publications in reference 8.) Figure 3

ed $V \rightarrow V$ and $V \rightarrow T$ relaxation pathways. In the literature one therefore often meets discussions about the difference between vibrational and translational molecular temperatures in experiments at high pressure, when the degree to which condition 5 is fulfilled is unknown.

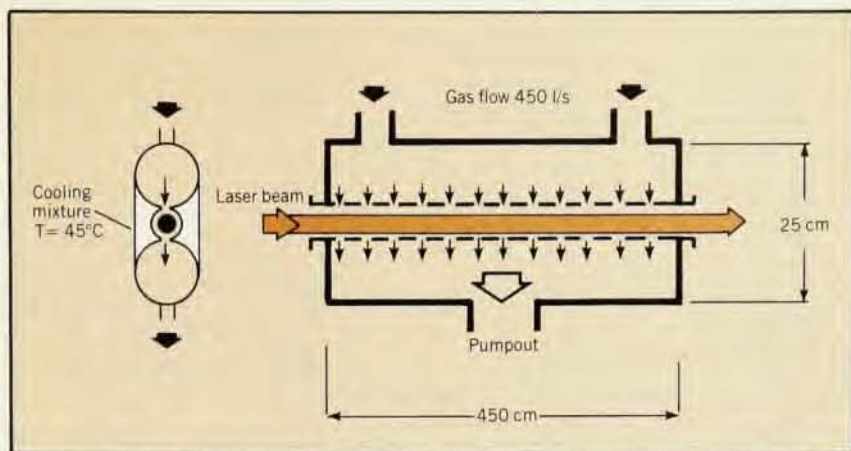
At first sight it seems unprofitable to use expensive laser systems to realize the processes of nonselective thermal chemistry. But in applications where remote or localized heating of matter is essential the laser may provide the best solution. Examples are thermal chemical surface treatment by infrared laser radiation, and highly localized thermal destruction by a focused laser beam in medical applications.

Intermolecular selective processes

Molecular-selective laser chemistry is the best developed and most promising field. In a wide range of problems we are tempted to use laser light for selective action on molecules of a particular type in gaseous mixtures, in solutions, on surfaces, and so on. Three major applications are laser isotope separation, laser production of very pure substances, and laser-induced photo-biochemical processes. Let us consider these three briefly.

Laser isotope separation. Many methods have been proposed and studied⁶ for using lasers to separate isotopes. The best developed processes involve multistep selective photoionization of atoms, and photodissociation of molecules. These are both monomolecular processes, which are very amenable to control by laser radiation, so their prominence is not altogether surprising. In this article we are considering only molecular processes, and in any case the atomic process is relatively well understood from the physics standpoint and currently offers mainly technical problems. For isotope selection by multi-step or multiphoton dissociation of molecules, on the other hand, we still have physics problems to solve. Let us consider some of them.

Our qualitative understanding⁷ of multistep photodissociation of molecules by infrared radiation is clear, and the work of the last two or three years has concentrated on obtaining experimental data for true (that is, nonaveraged) characteristics of the process and their correlation with theoretical models. Detailed checks of various theoretical models would be possible if we could measure the vibrational distribution produced in molecules by multistep infrared excitation; however, until very recently, we could only measure the average energy absorbed per molecule in the interaction region of the infrared field and the gas. Such measurements are rather uncertain, because the radiation pulse excites only a



Fast transverse flowing separation cell for carbon isotope separation by high-power, high-repetition-rate CO_2 TEA lasers. (See also the photograph, figure 1.) A productivity of about 1 gram per minute of highly enriched carbon-13 is expected. Figure 4

fraction q of the molecules, leaving a fraction $(1 - q)$ unexcited. (See figure 3a.) To measure the true characteristics of the process, not averaged over these two ensembles ("hot" and "cold") we need to know the value of q and its dependence on the intensity or energy flux and the laser frequency. In some recent work⁸ various methods have been used to measure q and its dependence on energy fluence for the molecules OsO_4 , SF_6 and CF_3I . Figure 3b shows some of the results—the variation of q with energy fluence for a 100 nanosecond laser pulse in these three molecules.

Last year⁹ we took an important step forward when we elaborated some theoretical models to make a determination of q by comparing theoretical data with experiment for the CF_3I molecule. The next step is to calculate q directly, starting from spectroscopic information about vibrational-rotational molecular transitions between the low lying vibrational levels responsible for molecular "leakage" into the vibrational quasicontinuum.

This type of isotope separation is very promising for light and moderate-mass isotopes in polyatomic molecules. For example, our experiments⁹ in CF_3I (for carbon-isotope selection) show that theoretically limiting parameters for the multiphoton selective-dissociation process can be reached. Specifically:

- The minimum energy consumption is equal to the dissociation energy of the weakest molecular bond, C-I (2 eV);
- The dissociation yield for molecules in the irradiated volume reaches almost 100% for only moderate energy flux;
- The dissociation has high selectivity (> 30) at comparatively high gas pressure (5–10 torr);
- Significant extraction of the desired rare isotope carbon-13 is possible (about

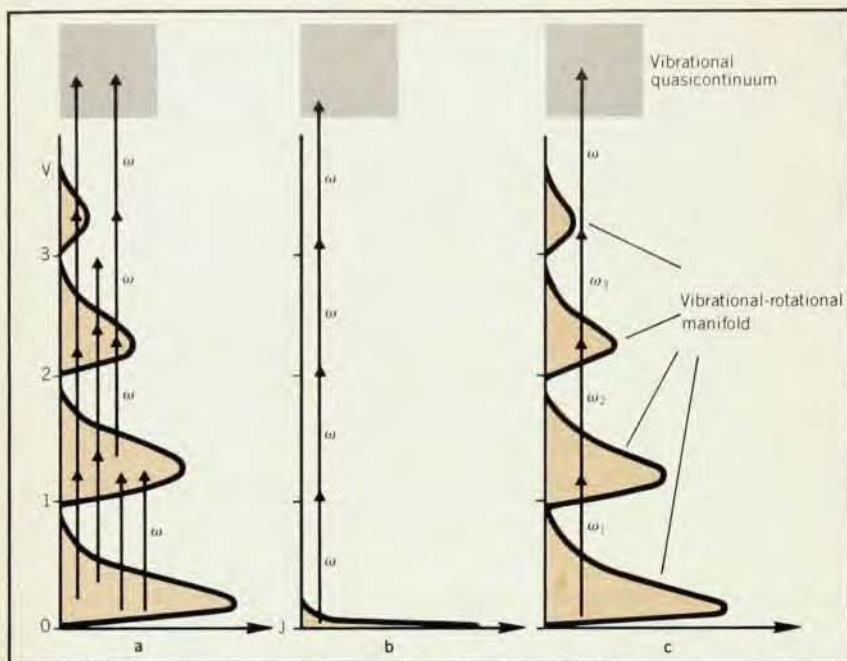
50%) without substantial decomposition ($< 2\%$) of the remaining molecules containing carbon-12, and

► Secondary photochemical processes that could destroy the high selectivity of the primary dissociation are completely eliminated.

Our group, together with the Kurchatov Institute for Atomic Energy, therefore proceeded with a scaled-up version of the original system to investigate carbon-isotope separation in macroscopic quantities. We use a CO_2 TEA laser with a high pulse repetition rate (up to 200 Hz) and average power 1 kW. This is the system shown in figure 1. The rate of enrichment in CF_3I or CF_3Br irradiated in the laser-separation cell (figure 4) was so high that it required fast transverse pumping of the gas. We expect to attain a productivity of about 1 gram/minute of highly enriched carbon-13. The simplicity and technological advantages of this method should ensure its early industrial application.

Separating light and moderate-mass isotopes with abundances of about 1% or more is relatively easy, compared with the problem of extracting rare isotopes (for example, deuterium, with an abundance of about 1/5000) and isotopes of heavy elements from molecular compounds with a small isotopic shift (for example, the uranium-235 isotope in UF_6). To separate hydrogen and deuterium we should have a high separation selectivity—at least above 1000. Recent successful experiments¹⁰ on multiphoton dissociation of some deuterium-containing molecules by CO_2 -laser radiation encourage us to expect progress in this area.

Multiphoton molecular dissociation by a single-frequency high-power infrared pulse is a "brute-force" method of exciting a multilevel system with regularly spaced levels. High excitation levels and dissociation yields are



Multistep selective excitation of vibrational-rotational levels of polyatomic molecules, shown in three schemes. Part a: Low selective excitation at room temperature by single-frequency intense infrared pulses; b: Highly selective excitation at low temperature by single-frequency intense infrared pulses, and c: Highly selective excitation at room temperature by multifrequency infrared pulses of moderate intensity

Figure 5

achievable, but with the inevitable reduction in isotopic selectivity—especially for heavy isotopes. This is because, although the frequency dependence of the rate of multistep molecular excitation by intense single-frequency radiation is resonant by its very nature, the resonance width is usually hundreds of times larger than the width of individual vibrational-rotational absorption lines. Indeed, a polyatomic molecule usually has very many vibrational-rotational levels (figure 5a). Also, at room temperature the molecules are originally distributed over many vibrational-rotational states. Because the anharmonicity of vibrations and isotopic shifts for heavy isotopes are usually less than the width of a vibrational-rotational band, several vibrational-rotational transitions turn out to be in resonance with fairly intense monochromatic infrared radiation. Cooling the molecules reduces the extent of the original distribution and so increases the sharpness of the resonance; this is particularly important for separating heavy isotopes and is illustrated in figure 5b. Yet the need to use an intense field makes the maximum selectivity impossible to realize, even in this single-frequency case. So we have to abandon multiphoton excitation and turn instead to two-step $ir + uv$ photodissociation (figure 2b). To get some increase in selectivity we can photodissociate in a two-frequency infrared field.¹¹

These techniques lead us naturally to the possibility of separating the functions of isotopically selective excitation and subsequent dissociation. Selective excitation needs radiation of finely tuned frequency ω_1 and intensity; for dissociation of the excited molecules a much less well-controlled frequency ω_2 suffices. Isotopic selectivity in such a system is enhanced because strong non-resonant radiation at frequency ω_2 does not perturb the resonant transition at frequency ω_1 .

However, only by using multifrequency infrared radiation with its individual frequencies tuned in precise resonance with successive allowed vibrational-rotational transitions (figure 5c) can we achieve a high selectivity of excitation for molecular gases at room temperature with moderate requirements on laser radiation intensity. In my opinion, multistep excitation of high-lying vibrational levels by multifrequency infrared laser pulses of moderate intensity (10^2 – 10^5 watts cm^{-2}) is one of the most interesting approaches in fundamental and applied infrared laser photochemistry.

Purification of substances. Selective molecular photodissociation can be used to clear molecular impurities from a substance in the gas phase when standard chemical or physical methods are not suitable. The method depends on the presence of differences between the physical or chemical properties (or both) of the substance to be purified

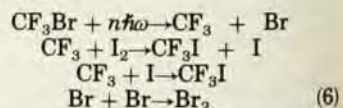
and those of the impurity products after dissociation, so that standard separation techniques apply after irradiation. In this way purification of $AsCl_3$ (with infrared radiation) has been studied at the Institute of Spectroscopy in Moscow¹² and purification of SiH_4 (with vacuum ultraviolet radiation) has been studied at Los Alamos.¹³

Such techniques for purification by laser may have important industrial applications in the future; among the most interesting of these would be a method for removing toxic impurities from nuclear-reactor waste. But I should stress that the appropriate laser engineering today is, of course, in an embryonic state as far as such large-scale applications are concerned.

Chemical reactions and synthesis. With a beam of intense infrared radiation from a laser we can deposit energy—up to several electron volts—in molecules of a single type in a mixture without affecting the other molecules. This is in strong contrast to thermal excitation, in which all the molecules in the mixture store approximately the same amount of vibrational energy. We therefore have the prospect of activating chemical reactions in new ways, with highly excited molecules or their dissociation products.

Excitation of molecules under transient reaction conditions, and the formation of dissociation products before excitation thermalization, can make these unusual ways of chemical reactions studied under equilibrium more competitive. Indeed, under stationary conditions the composition of initial and final reactants is of course governed only by thermodynamics. For pulsed excitation under transient conditions, temporal factors become as essential as thermodynamic ones; for example, the ratio between the reaction rate along a particular pathway and the relaxation time for the nonequilibrium state of the molecular mixture.

An example of infrared photochemical synthesis is the work¹⁴ on selective dissociation of CF_3I and CF_3Br in the presence of acceptors. This is part of a large study of a possible closed chemical cycle of laser separation of carbon isotopes on a practical scale. It has shown that photochemical conversion of CF_3Br molecules mixed with I_2 to CF_3I is highly effective (almost 100%) at pressures above 10 torr. The photochemical reaction in this example proceeds as follows:



An analogous set of reactions occurs in multiphoton dissociation of CF_3I in the presence of Br_2 . Analysis of the dissociation products of the $CF_3I + Br_2$

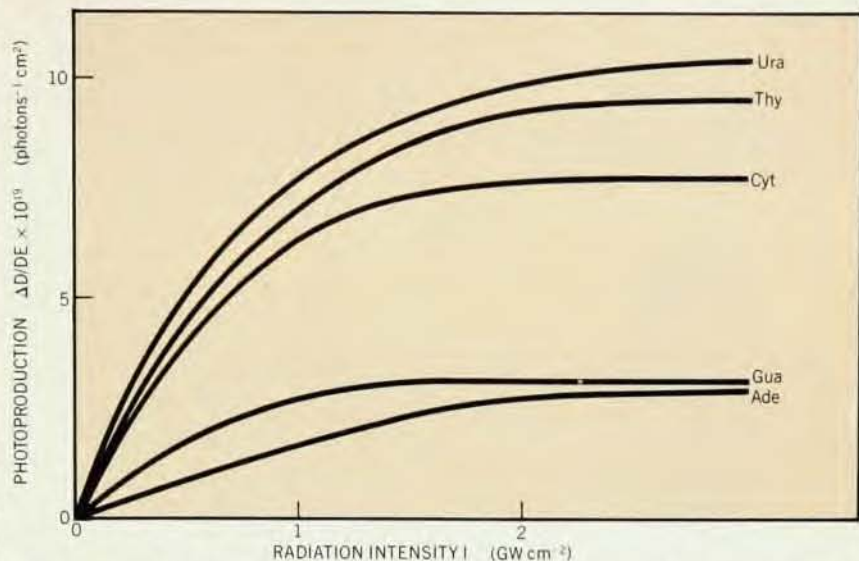
mixture shows that by changing the acceptor concentration and the temperature of the (cooled) walls it is possible to attain any ratio between the end dissociation products. When the bromine pressure is zero the only final product is the C_2F_6 molecule formed by recombination of CF_3 radicals. When CF_3I pressure is 0.2 torr and bromine pressure is greater than 3 torr, almost 100% of the dissociated CF_3I molecules are converted to CF_3Br by reactions analogous to those in 6 above.

The conclusion from this work, and other published studies, is that laser photochemical synthesis based on radical reactions will make possible the production (for short times) of any concentration of various radicals. The synthesis reaction can therefore be directed along the shortest pathway to provide the maximum yield of the desired product for the smallest quantity of initial materials. In the case of infrared multiphoton dissociation it should be remembered that the decay of the excited molecules occurs by the breaking of the weakest bond. Nevertheless, in practice this does not restrict the possibilities of laser chemical synthesis.

Photobiochemistry and photomedicine. In my opinion the prospects for laser-molecular interactions and their applications are far wider than the isotope-separation and gas molecular mixture work we have discussed so far in this article. I think the most promising possibilities lie in photobiochemistry and photomedicine. In my previous PHYSICS TODAY article⁷ I briefly discussed several problems in this area, particularly photochemistry of nucleic acid bases, where the selective abilities of laser light may prove very useful for selective mutagenesis and physical sequencing of bases in DNA.

For high selectivity it is natural to use selective excitation of vibration followed by transfer of the vibrationally excited molecules to those excited electronic states that have a high quantum yield for photoreaction (figures 2a, 2b). But absorption by solvents in the infrared region, the abundance of vibrational levels in biomolecules, the low energy limit for the vibrational quasicontinuum and the very fast intramolecular and intermolecular vibrational relaxation make this approach hard to realize with present-day tunable infrared lasers.

The first successful data¹⁵ on selective excitation of nucleic acid fragments have been obtained in a less obvious way—by two-step excitation through an intermediate electronic state. Despite the almost complete overlap of the ultraviolet spectra of electronic absorption—so that there is no selectivity at all at the first excitation stage—the total photoreaction



Photoproduct yield versus irradiation intensity for all five-nucleic-acid bases (from top: uracil, thymine, cytosine, guanine and adenine) in neutral aqueous solution. These data were obtained by two-step excitation. (From reference 15.) Figure 6

yield differs substantially for various nucleic-acid bases. For example, figure 6 shows normalized dependences of photoreaction yield on picosecond pulse intensity (the pulse duration is 20 picosec) at a wavelength of 265 nm for the five nucleic-acid bases. The photoreaction yield is here measured from the relative value of irreversible decrease in the ultraviolet absorption bands for these bases, with the total decrease over many pulses normalized to the total energy fluence of irradiating pulses (in photons cm^{-2}), that is, to the value of the ultraviolet radiation dose.

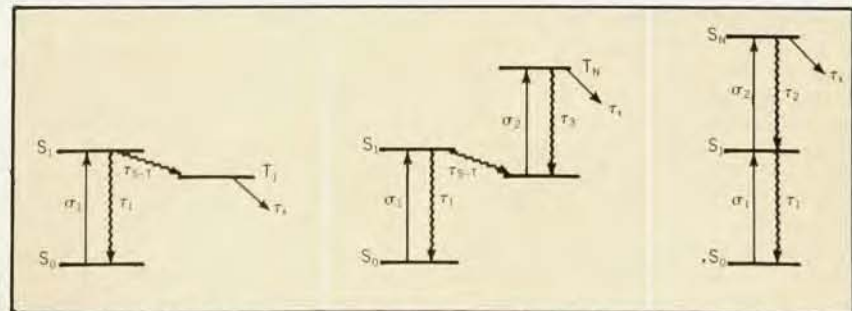
When the intensity is below saturation for the first electronic transition, the photoreaction yield scales as the square of the pulse intensity, proving that we are here dealing with two-step photoexcitation. When the electronic transition becomes saturated, the photoreaction yield becomes linearly dependent on intensity, because the second electronic transition from excited states produces a very fast photoreaction; in other words, it is an unsaturable reaction.

The mechanism of these photoreactions may be ionization, dissociation or a chemical reaction of the bases after they have absorbed two ultraviolet photons with energy totalling about 8 eV, and our studies are directed toward revealing which it is. Selectivity in such multistep reactions may arise from:

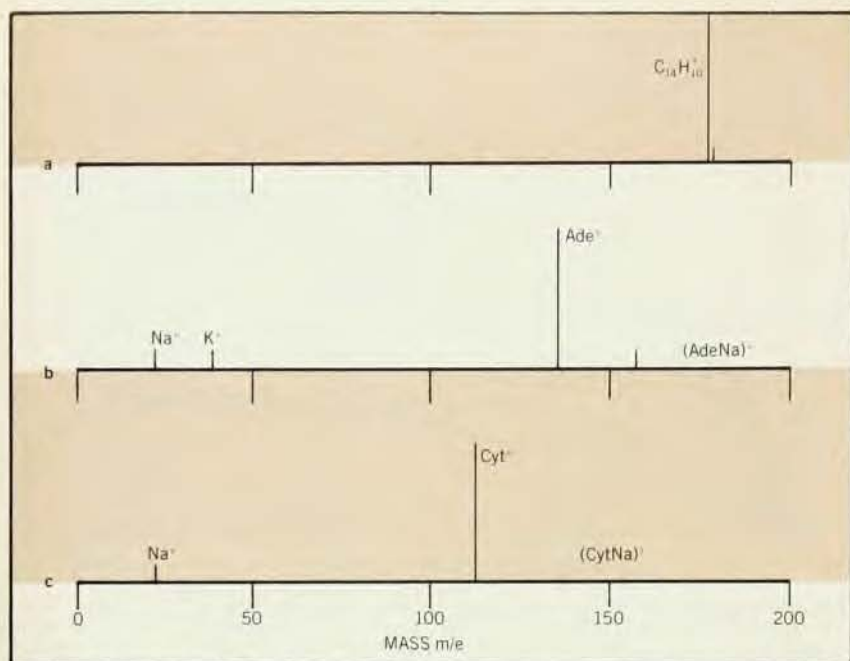
- differences in the lifetimes of intermediate states
- differences in cross sections for the subsequent (second) electron transition
- differences in the yields of the last photochemical step of the process.

When we use shorter picosecond pulses and independently tunable picosecond radiation at the second electron transition we will be able to gain insight into the mechanism that causes selectivity.

One more important feature of ultraviolet-laser induced photobiochemical reactions is the very high potential reaction yield at small irradiation doses. Figure 7 shows schematically three potential schemes for photoexciting biomolecular reactions. Under



Quantum yields of photoreactions induced by single-photon (a) and two-photon excitation through the triplet (b) and singlet (c) electron excited states of biomolecules. The yield from scheme c can reach 100% in, say, thymine. Figure 7



Mass spectra of photoions formed during irradiation of the surface of molecular crystals of anthracene (a), adenine (b) and cytosine (c) by an ultraviolet pulse from a KrF laser. (From reference 16.)

Figure 8

low-intensity radiation (no more than 10^6 – 10^7 watts per cm^2) only single quantum photoreactions from the first singlet S_1 or first triplet T_1 states are possible (figure 7a). As the intensity increases, the excitation of the molecule from the triplet state becomes possible (figure 7b). The photoreaction yield for molecules that have absorbed two ultraviolet photons may be as great as 100%. Hence the ultimate yield is limited by the probability of molecular transition to the triplet state,

$$\eta_{ST} = \left(1 + \frac{\tau_{ST}}{\tau_1}\right)^{-1}$$

The value of η_{ST} is much less than unity because the singlet-state lifetime τ_1 is usually in the range 10^{-9} – 10^{-11} sec.

If the high-power ultraviolet laser has a pulse length no longer than τ_1 , the molecule can be excited in two steps through the singlet state (figure 7c). Such processes are responsible for two-quantum photoreactions of nucleic-acid bases, such as those shown by their yields in figure 6. The yield can reach essentially 100% in this case. The photoreaction yield for thymine, for example, through the scheme of figure 7a (dimerization from the triplet state) is only 0.5×10^{-3} . The yield for intercombination conversion is 10^{-2} , thus limiting the yield of the two-step reaction in figure 7b. But at the same time the yield from the scheme in figure 7c can reach 100%.

Thus we hope for new methods of phototherapeutics in molecular photo-

medicine that will have very high efficiencies for small ultraviolet exposure.

Mode- and bond-selective effects

When multiphoton molecular processes were first studied, around 1975 to 1977, some scientists hoped to attain mode-selective or bond-selective excitation and photoreactions. Experiments quickly showed that all vibrational modes of polyatomic molecules were involved in the multiphoton-excitation process. Typical pulse lengths of the infrared radiation would be around 10^{-6} to 10^{-8} sec. Today, with our better understanding of the processes, we can identify the experimental conditions (large molecules and ultra short pulses) where we can hope to see (and subsequently use) mode- or bond-selective effects in polyatomic molecules in a strong infrared field.

The rate of intramolecular transfer of vibrational excitation among the modes depends on many factors, including the excitation level of an individual mode and its coupling with other modes, or whether collisions are permitted, and so on. Under collisionless conditions the time for excitation transfer between weakly coupled vibrational modes (when the excitation level is sufficiently high, amounting to a substantial fraction of the dissociation energy) can be placed in the approximate range 10^{-11} to 10^{-13} sec. If the excitation rate exceeds the rate of vibrational-energy equipartition we may hope to see mode-selective effects. Current experimentation has not yet reached this stage.

The most interesting molecules for studying bond-selective infrared photochemistry are large, and they have well-separated functional groups. Clearly strong vibrational modes associated with the different functional groups will be relatively weakly coupled. So by exciting vibrations in one functional group it is possible to achieve a substantially nonequilibrium energy distribution inside a large molecule during a short time interval, and hence nonstatistical behavior in the photochemical processes.

Assume, for example, that we are conducting an experiment to observe nonstatistical behavior of a long-chain polyatomic molecule with different functional groups at its two ends. Let one of the functional groups—say CF_3 —be excited by a high-power CO_2 laser pulse. Because this group is not directly bound to the motion of the atoms at the other end of the chain, vibrational perturbation will reach that end after a characteristic time $\tau \approx n/2\pi cX_0$, where n is the number of bonds in the chain and X_0 is the characteristic anharmonicity constant responsible for the vibrational interaction (that is, for the anharmonic coupling of adjacent bonds in the chain). If the molecule is excited by a high-power infrared pulse of duration $\tau \lesssim 10^{-9}$ sec, then with $X_0 \approx 1 \text{ cm}^{-1}$ and n around 100 we can expect an essential difference between the results and the predictions of the statistical model. We could see the differences by observing hot bands in the ultraviolet or infrared spectra of another functional group at the opposite end of the molecule or (more directly) by observing the molecular photodissociation by breaking of a different bond from the one with the smallest dissociation energy.

Some experiments have shown mode-selective effects even when the laser-pulse duration is as large as 10^{-8} or 10^{-7} sec.

For example, a group at Exxon Research Laboratories has reported¹⁶ multi-photon dissociation of a rather complex gaseous compound of uranium whose simplified name is $\text{UO}_2(\text{hfac})_2\text{THF}$. They used a CO_2 laser under both continuous and pulsed operation. The photodissociation occurred in a molecular beam, free of collisions and subsequent thermal heating even under continuous irradiation. The CO_2 laser frequency was in resonance with the asymmetric O-U-O vibration of the uranium-containing part of the molecule, which is sensitive to the isotopic composition of the uranium and oxygen.

The multiphoton absorption and dissociation properties of this molecule are those of a molecule with a very low vibrational quasicontinuum limit. Excitation of the 0→1 vibrational transi-

tion of the asymmetric O-U-O vibration quickly relaxes, transferring excitation to a few tightly coupled modes, and the asymmetric mode returns to its ground state where it can continue to absorb infrared photons. Even a pulse energy density as low as 0.1 J/cm^2 yields high values of dissociation. A theoretical model reported in the same paper¹⁶ assumes that the absorbed energy is distributed among only five vibrational modes. Shorter laser pulses (about 1 nanosec or less) appear to be necessary to prove this conclusion.

Let us turn now to electronic transitions. Excitations of molecular electronic states appear to be more promising for bond-selective photochemistry than does the work with vibrational states summarized above; in fact, I believe this is the only possibility for complex biomolecules in a condensed medium. It may even be possible eventually to study, selectively, individual bases in a long chain of DNA molecules by this method. Success with that problem would allow us to develop a new method of selective mutagenesis and also give us a direct method for direct sequencing of bases in the DNA chain—that is, for reading the DNA code. This, I suspect, is the most complicated problem in selective laser photochemistry.

After the successful experiments on solutions with nucleic-acid fragments which we mentioned above (figure 6) we undertook experiments on selective action on uracil in the ApU dinucleotide (a part of a single-stranded RNA). These very preliminary experiments have already shown¹⁵ some selectivity.

Bond-selective photoionization of molecules on metal surfaces is the concept behind a possible photoion projector for direct visualization of molecular bonds. I discussed the idea of this device, which combines wave and corpuscular microscopy, in my previous PHYSICS TODAY article.⁷ To realize the device we have several problems to solve:

- ▶ Investigate molecular ion photodetachment from the surface under laser light
- ▶ Investigate the photodetachment of these molecular ions from a macromolecule
- ▶ Make these photodetachment operations photosensitive.

Although these are major and difficult tasks we have made some progress already on the first one.¹⁷ With a KrF ultraviolet laser at 249 nm, having radiation power less than 10^5 W/cm^2 (fluence less than 10^{-3} J/cm^2), we could observe molecular ions originating from various crystal surfaces—anthracene and all five nucleic acid bases. Figure 8 shows the spectra recorded with a time-of-flight mass spectrometer. We know the ions are photophy-

sical in origin because they appeared at intensities much lower than the threshold of thermal action on the surface. Assuming that the mass of the molecular ion is a clue to the type of nucleic-acid base, we can simplify the solution of the difficult third problem, above, to a simple analysis of the mass of the detached photoions.

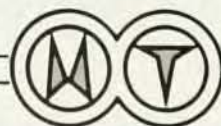
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