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An Introduction

by

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## LASER-ENHANCED CHEMICAL REACTIONS AND THE LIQUID STATE: AN INTRODUCTION

by

C. K. Rofer-DePoorter and G. L. DePoorter

### ABSTRACT

Laser enhancement of chemical reactions has mostly been studied in the gaseous state, but cannot be ruled out for the liquid state. Laser enhancement of reactions taking place in the liquid state could have important economic consequences for many industrial chemical processes. Physical and chemical principles involved in laser enhancement of chemical reactions are reviewed, and relevant literature is discussed.

### I. INTRODUCTION

The use of lasers to influence the course of chemical reactions has been much discussed in the past few years. This application could have tremendous implications for the field of chemistry, from pure theory to the economics of chemical manufacturing. In addition, it might make possible the direct investigation of biological systems, particularly those involved in energy transfer.

Laser-enhanced chemistry could give information on energy transfer processes within and between polyatomic molecules that is not available by any other method. This information would contribute to an understanding of the bonding in molecules and would strengthen molecular orbital theory.

The use of lasers could also improve current industrial processes for manufacturing chemicals, or might make possible totally different processes that would be simpler and cheaper. Any industrial chemical process has the potential for this sort of improvement if the reactions involved can be enhanced by laser light. Isotope separation is one process being considered. Production of pharmaceuticals and other complex organic chemicals seems to be another field in which laser chemistry might provide great savings.

Most pharmaceuticals are closely related to natural products (compounds produced by living organisms). Synthesis of many pharmaceuticals proceeds

from a starting material that is isolated from a particular plant or culture of microorganisms. Total synthesis of pharmaceuticals from substances produced in great volume by chemical manufacturers is usually not efficient because of the very particular requirements of most syntheses: one functional group must react, but not another; or a group must be added on in a particular orientation. Even with a natural product starting material, these problems may be present, and the yield is usually less than 50%.

Laser-enhanced chemistry may improve these processes in several ways. Laser excitation of one particular functional group may make that functional group react more readily than a similar one elsewhere in the molecule. Laser excitation may also make one product configuration more likely than another (Berry and Pimentel, 1970). Improvements in both these areas would lead to cost reductions in current pharmaceutical syntheses by making it possible to start the synthesis with a more readily available material or by increasing the yield. Compounds not now easily synthesized might become more available. For example, insect hormones might be valuable as insect control agents, but many of them cannot economically be synthesized in the amounts needed for field tests; prostaglandins control many processes in the human body and may prove to be potent drugs with few side effects, but research is limited because they cannot be efficiently synthesized.

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Many reactions in the biosynthesis of natural products cannot be carried out economically in the laboratory because enzymes participate in the biosynthesis. The enzymes make the reaction efficient, but their isolation from the living system is difficult and their synthesis often more difficult than that of the final product. The detailed functions of most enzymes are not well known; if those functions include resonant energy transfer to aid in the reaction of the substrate molecule, then lasers, or perhaps a combination of a laser and some method of holding the molecule in a particular configuration, such as adsorption, could act as a mechanical enzyme.

Resonant energy transfer has been suggested as the mechanism by which energy is provided by adenosine triphosphate (ATP) for muscle contraction (McClare, 1971, 1972a, 1972b). Laser studies could improve the understanding of this and other biological energy transfer problems.

Many industrial chemical processes, most pharmaceutical processes, and all biological processes are carried out in the liquid state. Most laser chemistry studies have been carried out on small molecules in gases. Gases and small molecules offer a certain theoretical simplification to the process involved, but more must be known about liquids and organic compounds to allow application of lasers to industrial processes. In this report we try to extend some of the concepts of laser chemistry to the liquid state and to larger molecules, and to explain these concepts for an audience who may not be acquainted in detail with the application of lasers to chemistry. We assume that the reader is acquainted with, but not expert in, spectroscopy, chemistry, reaction kinetics, statistical mechanics, and lasers. Reviews and textbooks are referenced for those who wish to pursue a topic more thoroughly.

The influence of laser light on chemical reactions is the primary concern of this report. Studies of fluorescence and other molecular excitation phenomena are considered only insofar as they have been shown to influence chemical reactions. Since vibrational excitation seems to promise greater selectivity of reaction, we will primarily consider initial vibrational excitation, rather than electronic excitation, although the latter may lead to vibrationally excited states. We shall further restrict the discussion to situations in which the amount of laser

energy is insufficient to cause initial dissociation of the reactants. In short, we intend to discuss how bonds between atoms can be made more reactive by the input of laser light.

We shall proceed from general principles, as they apply to laser chemistry, to specific examples of laser-aided reactions. Energy transfer from the laser to the reactants and the distribution of energy, with time, within and among the reactants will be discussed first. Then reaction rate theory and its implications for laser chemistry will be covered. Finally, a discussion of specific examples from the literature will bring the general principles together.

## II. ENERGY TRANSFER PROCESSES

### Gas Phase

The amount of laser energy that can be deposited per unit time in a gas and the subsequent redistribution of this laser energy within the gas are strongly dependent on the collision frequency in the gas. Energy redistribution takes place as a result of collisions in the gas phase, and this energy redistribution both allows more laser energy to be input into the system and restricts what can be done with the excited molecules. To illustrate this, we will consider separately the effects of the laser energy on the rotational and vibrational energy distributions in the gas, remembering, however, that these processes are occurring simultaneously. To best illustrate the processes we assume that the laser pulse duration is less than the mean time between collisions and consider a pure gas only.

A schematic representation of the rotational distribution for the ground vibrational state is given in the left side of Fig. 1. Also indicated is the available rotational distribution for a vibrationally excited state. The large arrow represents the energy of the laser photons available. Again, it must be emphasized that we are discussing one vibration-rotation transition in the gas; about sixty transitions are available at room temperature for a triatomic molecule.

The effect of the laser radiation is indicated in the area of the graph in Fig. 1 to the left of one collision. Under the most ideal conditions, the laser radiation will cause the number of molecules in the energy states at each end of the indicated

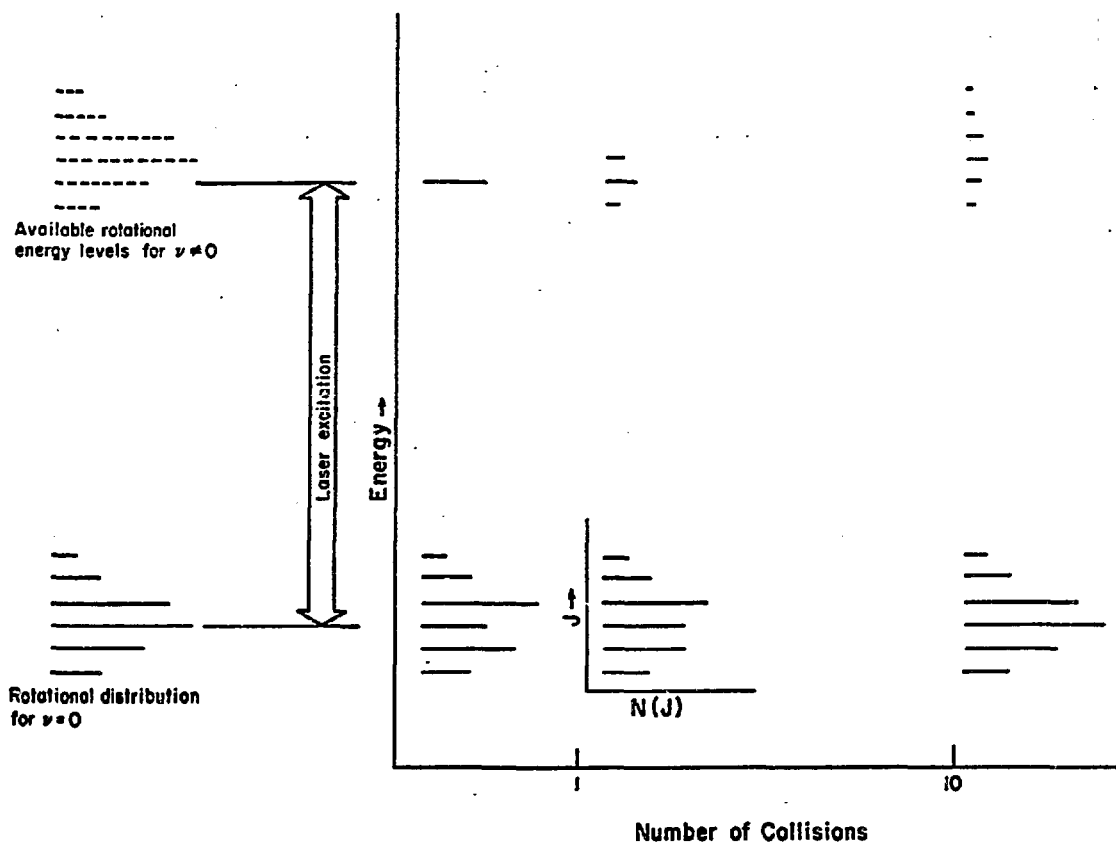


Fig. 1. Effect of laser irradiation and subsequent collisions on rotational distribution.

transition to be equal. After one collision, sufficient rotational relaxation will have occurred to begin to redistribute the rotational energy as indicated in Fig. 1. By the time each molecule has undergone ten collisions, rotational equilibrium will again be established.

To illustrate the effect of laser energy on the vibrational energy distribution we will use as an example a small polyatomic gas. Its vibrational energy levels are shown schematically at the left side of Fig. 2. The large arrow again represents the energy of the laser photons available. The effect of the laser radiation is indicated in Fig. 2 to the left of one collision. As for rotation, under the most ideal conditions, the laser radiation will again cause the number of molecules in the energy states at each end of the indicated transition to be equal.

The redistribution of this vibrational energy controls the selectivity of subsequent processes. After a few collisions, the energy initially put into one mode by the laser excitation is redistributed among all the available modes. By this time in an isotope separation experiment, if one isotopic species were initially vibrationally excited by the laser, all isotopic species present would be vibrationally excited. This redistribution is schematically depicted in Fig. 2 at 10 collisions, which is a typical number for many systems. At this time very little bulk heating of the gas has occurred. Simultaneously, rotational energy redistribution is taking place.

Several experimental studies have shown that vibration to translation (V-T) energy transfer occurs from the lowest energy vibrational mode of the molecule. Also, the probability per collision for V-T processes is such that very little V-T energy

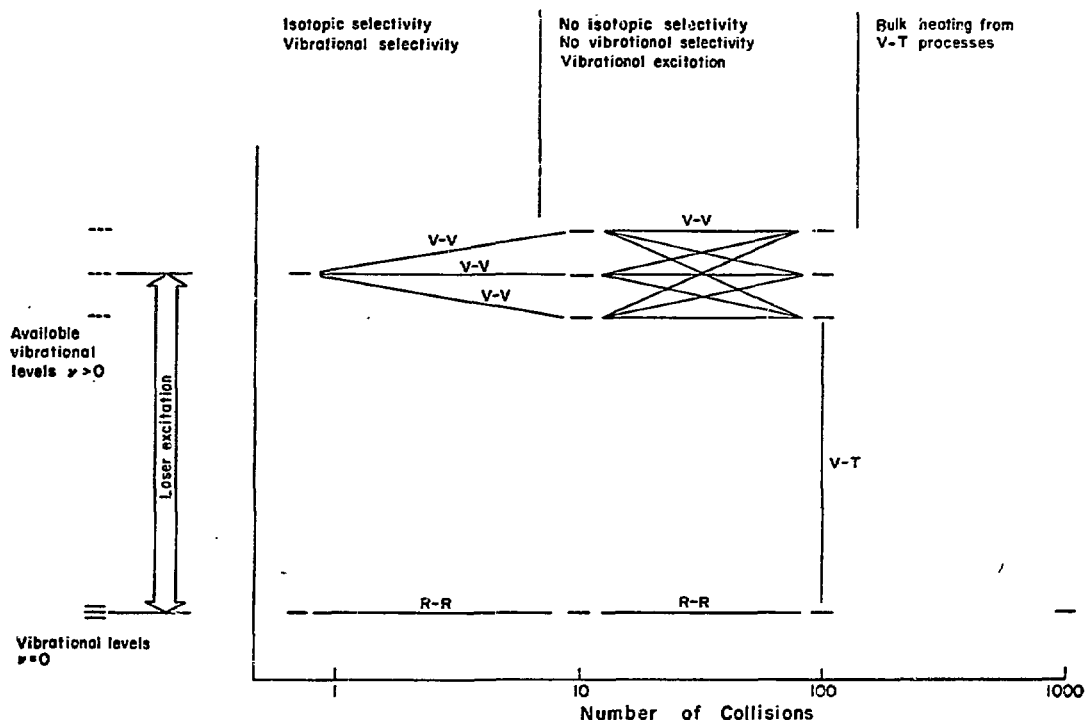


Fig. 2. Effect of laser irradiation and subsequent collisions on vibrational distribution.

transfer and therefore very little bulk heating will have occurred after about 100 collisions. Therefore, during the time between about 10 and 100 collisions, a fraction of the gas will be vibrationally excited and at a different vibrational temperature than the remainder of the gas.

In the time between 100 and 1000 collisions the picture becomes mixed up. Sufficient V-T exchanges are occurring that bulk heating of the gas is beginning. The vibrational temperature is coming back to the equilibrium value. After about 1000 collisions, the initial vibrational excitation has completely relaxed and a bulk heating of the gas is the final result.

We must emphasize that this discussion has been very general. For different gases the collision numbers may vary, but the qualitative description is still valid. We will discuss the numbers of molecules involved in the various processes in the section on numerical examples.

From the above discussion several facts about laser chemistry due to vibrational excitation become

clear. First, if isotopic selectivity or selective vibrational excitation of a portion of a molecule is required, any operation subsequent to the vibrational excitation must be complete before very many gas phase collisions can occur. For example, if a chemical reaction of only one isotopic species were desired, the rate of reaction of the vibrationally excited species would have to be comparable to the collision rate at the equilibrium temperature and pressure of the system. In short, isotopic or vibrational selectivity will last for only a few collisions of the excited molecule.

For processes involving only vibrational excitation and where neither isotopic nor vibrational selectivity is required, the restrictions are not as rigid. This is the region in which laser chemistry due to vibrational excitation can be carried out without bulk heating effects. The vibrationally excited gas molecules can suffer from 100 to about 500 collisions before bulk heating becomes significant. For research studies the collision limit is probably inflexible, but for industrial processing more bulk heating effects may be tolerable.

In the above discussion we have considered only a pure gas and have assumed that the laser pulse is short compared to the mean time between collisions. For gas mixtures some of the problems discussed above are not so severe. Longer laser pulse durations can affect a larger number of gas molecules, but at the expense of selectivity. These topics will be more thoroughly discussed in the section on numerical examples.

For a complete discussion of energy transfer processes the books by Herzfeld and Litovitz (1959) and Matheson (1971) and the reviews and work of Moore (1973) are recommended. The absorption of laser radiation and a description of experimental results on the redistribution of the laser energy are discussed in the papers by Burak et al. (1969), Steinfeld et al. (1970), and Houston et al. (1973).

#### Liquid Phase

The liquid phase is the most difficult of the three states of matter to consider mathematically. Solids are ordered, gases are random, but liquids are somewhere in between. As a result, our present knowledge of the structure of liquids does not give as detailed a picture as we have of gases and solids.

For liquids, as was the case for gases, the redistribution of the laser energy occurs during collisional encounters. At first thought, it appears that the situation with respect to vibrational energy transfer is hopeless because of the high collision rates in liquids. However, a closer examination shows that liquids may have advantages over gases for laser chemistry experiments. We will first discuss molecular motions in liquids and then show how the energy redistribution is affected by these motions.

The difference between molecular motion in gases and liquids is best illustrated by considering the difference between the mean free paths in the two states. In gases the mean free path is much greater than the molecular diameters, while in liquids the mean free path is of the order of a molecular diameter. In addition, in a liquid the free volume is less than the molecular volume. In a gas, then, a molecule can travel one molecular diameter with a very small probability of striking another gas molecule as it travels this distance. In a liquid, a molecule cannot travel one molecular diameter without

a very high probability of striking another molecule (Fig. 3).

Molecular motion in liquids can be considered as follows. The motion of the molecule is a vibration about a particular point in the liquid, that is, the molecule bounces around inside the cage made up of its nearest neighbors (molecules S in Fig. 3). Occasionally, the molecule A squeezes between two of its nearest neighbors and moves to another place, A', in the liquid. Thus, diffusion in liquids is slower than in gases. When two molecules that are potential reaction partners diffuse into contact, their repeated collisions are called an encounter within a solvent cage.

At this point the terminology can get confused. We will try to be especially careful to distinguish between the movement inside the solvent cage, which we called vibration of the molecule about a particular point in the liquid, and vibration within the molecule itself.

To describe vibrational energy transfer in liquids we shall use the theory of "isolated binary encounters" (IBC theory) proposed by Litovitz (1957) and Herzfeld and Litovitz (1959). According to the IBC theory, the rate of vibrational relaxation in some liquids is a product of two factors, the probability of energy transfer per collision and the number of collisions per second. The probability of

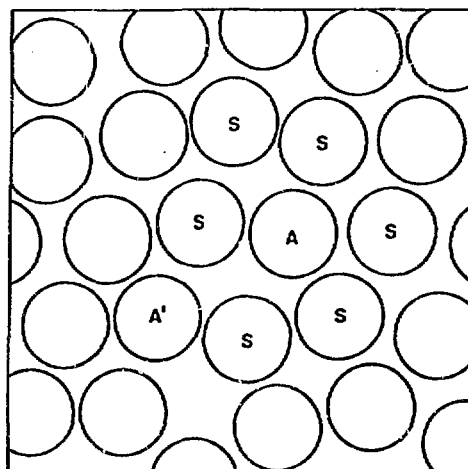


Fig. 3. Molecules in a liquid.

energy transfer per collision is taken to be the same as in the gas phase.

Some authors, namely Fixman (1961) and Zwanzig (1961), have questioned the assumptions behind the IBC theory. In another paper, Herzfeld (1962) has discussed some of the objections and stated that he did not believe that they were correct. We point out these facts so that the reader is aware that the theory of vibrational relaxation in liquids is not a closed subject. For our purposes, the IBC theory provides a tool for comparing and contrasting vibrational relaxation in gases and liquids.

Since the energy transfer probability per collision is taken to be the same in both the gas and the liquid, the difference between the vibrational relaxation rates will be due to the differences in collision rates, which are several orders of magnitude greater in the liquid than in the gas. Some numerical examples will now be useful. The duration of an encounter (as defined above) in a liquid is from  $10^{-10}$  to  $10^{-8}$  seconds. The vibration of the whole molecule around its equilibrium position has a period from  $10^{-13}$  to  $10^{-12}$  seconds. Therefore, during an encounter,  $10^3$  to  $10^4$  collisions occur. This means that before a molecule can get out of its solvent cage, it has lost its internal vibrational energy to the solvent. This also means, that in a dilute solution, the chance for internal vibrational energy exchange between different isotopic species of the same compound is very slight. For example, in Fig. 3, if A is one isotopic species and A' is another, vibrational energy input by laser will be lost from A to one of the members of the cage before it is picked up by A'. Because of the high rate in liquids, rotational equilibrium can be assumed.

The book by North (1964) contains a good description of molecular motion and chemical reactions in liquids. Matheson (1971) discusses energy transfer in liquids.

### III. REACTION RATE THEORY

There are currently two approaches to the theory of chemical reaction rates: transition-state theory and collision theory. The main feature of transition-state theory is the idea that the reactants form a transition state (or activated complex) of higher energy than either reactants or products, from which they can proceed to products or back to their initial

state. Collision theory relies on statistical mechanics and considerations of energy distributions and reaction probabilities. Both approaches give similar results in cases where they can both be applied. We will use both approaches where they are most useful in our discussion of laser chemistry. Laidler (1969) and Johnston (1966) treat the theories of reaction rates in some detail.

#### Unimolecular Reactions

Figure 4 is a transition-state depiction of the course of an exothermic unimolecular reaction. The "reaction coordinate" in transition-state depictions is the minimum-energy path on the potential-energy surface for the reaction. The reactant molecule is represented by R, the transition state by T, and the product by P, which could be two or more molecules for a decomposition reaction, or an isomer of R.

The transition state T cannot be studied directly; it is a transient species by definition. Its form can sometimes be inferred by studies of products and from chemical principles. In some reactions, a stable intermediate may form; the graph at T would then be flattened or concave. A reaction of this type differs from the reactions we are now discussing.

The activation energy,  $\Delta E_A$ , may be introduced in many ways. In conventional chemical reactions, heat is applied; in most photochemical reactions,

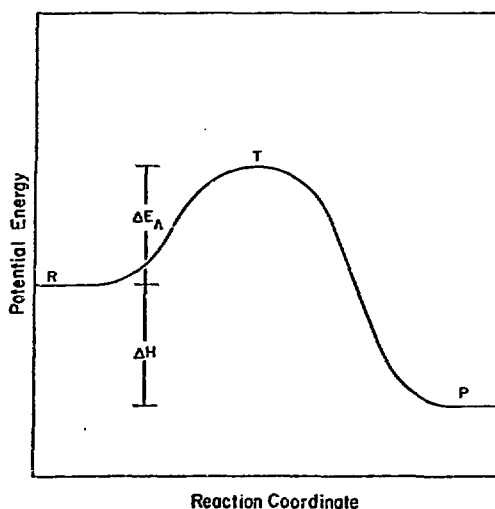


Fig. 4. Exothermic unimolecular reaction.



it is supplied by ultraviolet light. For resonant laser enhancement, it is supplied, at least partially, by coherent infrared light in resonance with one vibrational mode of the molecule.

Vibrational energy probably plays the most important part in the formation of the transition state for unimolecular decomposition. Translational energy, simply from an intuitive viewpoint, can be seen to have little to do with a molecule breaking apart, unless another body is involved, which is excluded in the consideration of unimolecular reactions. Rotational energy may play a small part, as a result of bond weakening by centrifugal distortion. Electronic energy clearly is involved in ultraviolet photochemical reactions, but there are indications that, at least in some cases, it is transformed into vibrational energy.

It is likely that in unimolecular decompositions the transition state is a vibrationally, and perhaps electronically, excited reactant molecule at the point where bonds are just starting to break.

A group of investigators in the USSR (Ambartzumian *et al.*, 1972; Ambartzumian and Letokhov, 1972a, 1972b; Letokhov, 1973a, 1973b) has developed a laser method of unimolecular decomposition; it is informative to discuss this selective two-step decomposition here in terms of transition-state theory.

Since one infrared photon may have less than the activation energy for a reaction, additional energy must be acquired by the molecule before decomposition can take place. This situation is shown schematically in Fig. 5. If this energy is small, it could be supplied by collisions. However, if extreme selectivity is desired in a reaction, collisions are undesirable. Thus, in this method, an ultraviolet photon is also supplied whose energy is less than would cause the unexcited species to react, but is enough to cause the vibrationally excited species to react. The absorption is much faster than collisions, so selectivity is maintained. By this method, rubidium vapor has been ionized and HCl and NH<sub>3</sub> have been dissociated. In the NH<sub>3</sub> dissociation, <sup>14</sup>N and <sup>15</sup>N were separated.

#### Bimolecular Reactions

Most of the discussion of unimolecular reactions can also be applied to bimolecular reactions, but certain additional factors must be considered.

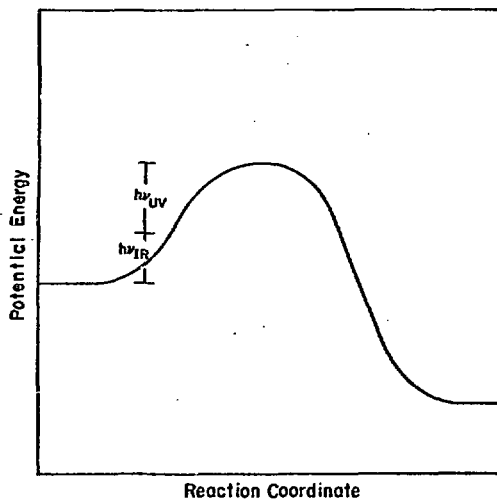


Fig. 5. Two-step decomposition.

In unimolecular reactions, collisions transfer energy, but need not be otherwise considered in the formation of the transition state. In bimolecular reactions, fewer types of collision lead to reaction than transfer energy. A unimolecular reaction can be carried out in less than the collision time, simply by absorption of radiation; a bimolecular reaction requires a particular type of collision. It is therefore slower and less likely to provide the extreme selectivity needed for isotope separation. However, bimolecular reactions enhanced by laser light may provide improved yields of a desired product of other types.

A further complication is the question of the relative importance of vibrational, translational, rotational, and electronic energies. For bimolecular reactions, since the selectivity inherently will be less than that of unimolecular reactions, inputs of energy sufficient to cause electronic excitation are less important than inputs of energy that are less than the activation energy. Some forms of electronic excitation may be less than the activation energy, but vibrational excitation more often fits this specification. Rotational energy may affect the reaction probability in that it affects the relative orientation of the two reactants, but this should be a trivial effect. Rotational energy may also make a small contribution to reactivity

through centrifugal distortion, as for unimolecular reactions.

Recently there has been some controversy over the relative importance of vibrational and translational energies in bimolecular reactions. Qualitatively, the argument is whether the molecules must be vibrationally ready to react or the force of collision produces the reaction. Molecular beam experiments (Odierne *et al.*, 1971) seem to indicate that translational energy contributes little to the probability of reaction, but an increase in vibrational energy increases the rate of reaction significantly.

Thus, even though the circumstances of reaction are significantly different, vibrational energy seems to be the most important for bimolecular reactions, as it is for unimolecular reactions.

As was previously mentioned, selectivity can be expected to be less for bimolecular reactions than for unimolecular reactions. This has several implications for the experimental conditions. Energy inputs of less than the activation energy will probably give the most significant results in this case. Larger energy inputs might enhance bimolecular reaction rates if a buffer gas is added to help dissipate the energy, but this will probably decrease the selectivity still further. To increase the probability of useful reaction, an excess of the unexcited reactant should be present, so that most of the collisions of the excited molecules will take place with molecules with which they are to react. Large molecules may also present some advantages with respect to energy transfer. Since they have more vibrational modes, they may tend to equilibrate the energy intramolecularly as well as intermolecularly, thus becoming completely deactivated less easily than diatomic molecules.

#### Liquid Phase Reactions

Although energy transfer will be faster in liquids than in gases, liquids offer some advantages for laser chemistry. Whether the rapidity of energy transfer will cancel out these apparent advantages can only be decided by experiment. Goodman *et al.* (1970) conclude from Slater's model for a unimolecular rate constant that optimum experimental conditions for detecting laser enhancement of reaction rates should involve the use of liquids at a

temperature where thermal rates are just beneath the level of detection.

Because of the great differences in properties of solvents and solutes, it will help to keep in mind in the following discussion that "solvent" means "a properly chosen solvent," one that will dissolve the solute in appropriate quantities and provide other properties needed for the reaction, such as transparency to the laser wavelength, and, in some cases, reactivity toward certain molecular fragments.

For a unimolecular reaction in which the solute is the reactant, a solvent can promote the reaction in several ways. The solvent could provide a convenient third body to react or complex with a fragment resulting from a unimolecular decomposition. If an excess of energy is put into the solute molecule by means of laser light, the reaction could be controlled by the conduction of energy into the solvent before the solute decomposes indiscriminately. In cases where the solvent forms a loosely bound complex with the solute, some catalysis may take place; the energy requirements for the transition state would be decreased (Fig. 6). Thus, a smaller input of energy would be required for the reaction of the complex than of the individual molecule.

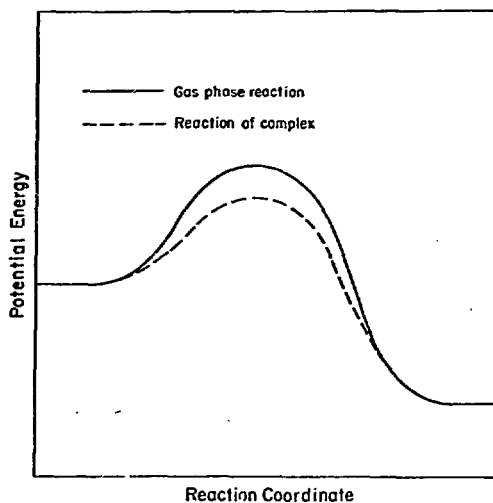


Fig. 6. Effect of complexation.

For bimolecular reactions, the most favorable situation would be a reaction between solute and solvent. Practically every solute molecule would be surrounded by potential reaction partners. As in the gas phase, bimolecular reactions would be less selective than unimolecular reactions. However, because of electrostatic attraction, molecules might be oriented more favorably for a reaction in the semistructure of a liquid than in the random collisions of a gas. If the solvent is a reactant, energy transfer to the solvent molecules surrounding the excited solute molecule may be less harmful to the reaction probability than energy transfer in a gas. Finally, because motion is much more constrained in a liquid than in a gas, the reactants will experience many collisions during an encounter, rather than flying apart after a single collision.

#### IV. NUMERICAL EXAMPLES

In the preceding sections we have been very qualitative in our descriptions and examples; we will now give specific numerical examples to emphasize these points. Because of the importance of collisional processes we shall first discuss collision rates in gases. We shall then discuss the population of the energy levels in gas molecules and show how this affects laser chemistry experiments and finally will give some numerical examples of rate constants.

Since we are emphasizing chemistry in this paper, we will express collision frequencies and collision rates in a form similar to that used for reaction rates, that of a rate constant multiplied by a concentration term. Concentrations will be given in number of particles per cubic centimeter. From the perfect gas law it can be shown that

$$N = 9.656 \times 10^{18} \left( \frac{P}{i} \right) \quad (1)$$

where  $N$  = number of particles/cm<sup>3</sup>

$T$  = temperature in °K

$P$  = gas pressure in torr.

Some numerical examples of concentrations at various pressures are given in Table I for 298 K.

To calculate collision frequencies and rates we will use a hard-sphere molecular model. The frequency  $Z_A$  with which a molecule of A is struck by a molecule of B is

TABLE I  
Gas Concentrations at Various Pressures (298 K)

$P$ (torr)	$N$ (number/cm <sup>3</sup> )
0.01	$3.24 \times 10^{14}$
0.10	$3.24 \times 10^{15}$
1.00	$3.24 \times 10^{16}$
10.00	$3.24 \times 10^{17}$
100.00	$3.24 \times 10^{18}$
760.00	$2.46 \times 10^{19}$

$$Z_A = \pi \left( \frac{d_A + d_B}{2} \right)^2 \left[ \frac{8 RT}{\pi} \left( \frac{1}{M_A} + \frac{1}{M_B} \right) \right]^{1/2} [N_B] \quad (2)$$

where  $d_A, d_B$  = molecular diameters (cm)

$R$  = gas constant (erg/mole-deg)

$M_A, M_B$  = molecular weights

$[N_B]$  = concentration of B (molecules/cm<sup>3</sup>)

In a gas containing only A molecules, the same expression applies with  $[N_A]$  replacing  $[N_B]$ . Some numerical examples of collision frequencies and time between collisions ( $1/Z_A$ ) for helium at 298 K are given in Table II.

The total rate of bimolecular collisions between A and B molecules is given by

$$Z_{AB} = Z_A [N_A], \quad (3)$$

the product of the collision frequency and the concentration of A molecules. The units of  $Z_{AB}$  are collisions/(cm<sup>3</sup>-s). In a pure gas containing only A, the expression is

$$Z_{AA} = \frac{1}{2} Z_A [N_A]. \quad (4)$$

From the data in Tables I and II the reader can calculate the bimolecular collision rate at the various pressures listed.

TABLE II  
Collision Frequencies and Time Between Collisions for Helium at 298 K

$P$ (torr)	$Z_A$ (s <sup>-1</sup> )	$1/Z_A$ (s)
0.01	$1.22 \times 10^5$	$8.20 \times 10^{-6}$
0.10	$1.22 \times 10^6$	$8.20 \times 10^{-7}$
1.00	$1.22 \times 10^7$	$8.20 \times 10^{-8}$
10.00	$1.22 \times 10^8$	$8.20 \times 10^{-9}$
100.00	$1.22 \times 10^9$	$8.20 \times 10^{-10}$
760.00	$9.29 \times 10^9$	$1.08 \times 10^{-10}$

Writing the full expression for  $Z_{AB}$  gives

$$Z_{AB} = \pi \left( \frac{d_A + d_B}{2} \right)^2 \left[ \frac{8 RT}{\pi} \left( \frac{1}{M_A} + \frac{1}{M_B} \right) \right]^{1/2} [N_A][N_B] \quad (5)$$

or

$$Z_{AB} = K_{\text{coll}} [N_A][N_B] \quad (6)$$

where

$$K_{\text{coll}} = \pi \left( \frac{d_A + d_B}{2} \right)^2 \left[ \frac{8 RT}{\pi} \left( \frac{1}{M_A} + \frac{1}{M_B} \right) \right]^{1/2} \quad (7)$$

We define  $K_{\text{coll}}$  as the rate constant for bimolecular collisions in analogy with the rate constant for a bimolecular reaction.

With the above discussion on gas densities and collision frequencies as background we can now give some numerical examples of numbers of molecules to be vibrationally excited by the incident laser radiation. We shall now put numbers on some of the quantities depicted in Figs. 1 and 2. For an example we will use the linear triatomic gas OCS (carbonyl sulfide). Figure 7 is a plot of the rotational distribution for OCS at 298 K. The maximum population is 2.68% at  $J = 22$ . Assuming a laser pulse length less than the time between collisions and assuming a frequency match for an absorption originating from  $J = 22$ , at saturation, the maximum percentage of

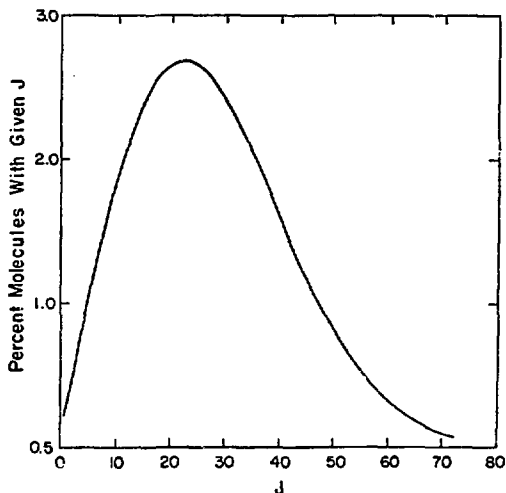


Fig. 7. Rotational distribution for OCS at 298 K.

molecules in the 00<sup>0</sup> state that can be vibrationally excited is 1.34. If a 0.5- $\mu$ s laser pulse were available, to satisfy the first assumption above, the maximum pressure one could use is 0.10 torr. At this pressure, 1.34% of the gas molecules corresponds to  $7.22 \times 10^{-11}$  moles/cm<sup>3</sup>. The reader can do similar calculations for various assumed laser pulse lengths.

Requiring the laser pulse length to be less than the time between collisions is severe, but may be necessary for isotope separation. If only one isotopic species is vibrationally excited, as soon as one collision occurs with another species, there is a high probability that vibrational energy will be transferred to the other isotopic species. As soon as this occurs, the isotopic selectivity of the process will be lost.

For laser chemistry experiments in which isotopic selectivity is not important the situation is different. Rotational relaxation is rapid and will occur in both the ground and excited state rotational distributions allowing more molecules to be vibrationally excited. Thus, laser pulses can be longer and pressures can be higher. The limiting factor in this case is the bulk heating effects due to the V-T relaxation.

## V. LASER REQUIREMENTS

So far we have assumed that a laser of the proper wavelength, energy and pulse length is available for the experiment of interest. Since information on available lasers is compiled in many places, we will not include a general discussion of lasers here. Instead we will discuss intensity and power requirements and show how they can be affected by the experiment being performed. We will then briefly discuss wavelength requirements.

To parallel the mathematical expressions for chemical reaction rates, induced absorption rates will be expressed as the product of a rate constant and a concentration term. Designating the upper state with the subscript u and the lower state with the subscript l, the induced absorption rate is then

$$\frac{dN_l}{dt} = -K_{lu} N_l \quad (8)$$

where  $N_l$  is the concentration in the lower energy state and  $K_{lu}$  is the rate constant for the induced absorption. The rate constant is given by

$$K_{lu} = B_{lu} \rho_{\nu} \quad (9)$$

where  $B_{lu}$  is the Einstein coefficient for induced absorption and  $\rho_{\nu}$  is the radiation spectral density at the frequency  $\nu$  corresponding to the energy difference between the upper and lower states. The units of  $\rho_{\nu}$  are ergs-s/cm<sup>3</sup>, those of  $B_{lu}$  are cm<sup>3</sup>/(ergs-s<sup>2</sup>), so that the units of  $K_{lu}$  are s<sup>-1</sup>. The quantity  $B_{lu}$  can be calculated from the equations

$$A_{ul} = \frac{8\pi h \nu^3}{c^3} B_{ul} \quad (10)$$

and

$$g_l B_{lu} = g_u B_{ul} \quad (11)$$

where  $A_{ul}$  is the Einstein coefficient for spontaneous emission,  $B_{ul}$  is the Einstein coefficient for induced emission, and  $g$  is the degeneracy of the indicated level. The spontaneous emission coefficient,  $A_{ul}$ , is given by  $1/T$  where  $T$  is the lifetime of the upper state (units of  $A_{ul}$  are s<sup>-1</sup>). The radiation spectral density,  $\rho_{\nu}$ , can be expressed as

$$\rho_{\nu} = I / (c \cdot \Delta\nu) \quad (12)$$

where  $I$  is the radiation intensity expressed in ergs/(cm<sup>2</sup>-s) and  $\Delta\nu$  is the absorption linewidth. The rate constant for induced absorption,  $K_{lu}$ , can be expressed as

$$K_{lu} = B_{lu} \rho_{\nu} = \frac{c^2}{8\pi h \nu^3 \Delta\nu T} I \quad (13)$$

where all the terms are as defined above. The term  $I$  in the above equation is the laser radiation intensity required.

For the first example we assume that the laser pulse is shorter than the mean time between collisions in the gas phase. We also assume saturation of the vibration-rotation transition of interest. Using these assumptions and integrating Eq. 8 gives the requirement that

$$K_{lu} \Delta t = B_l \rho_{\nu} \Delta t = 1, \quad (14)$$

where  $\Delta t$  is the laser pulse length. Substituting into Eq. 12 gives

$$I = \frac{8\pi h \nu^3 \Delta\nu T}{c^2 \Delta t} \text{ ergs}/(\text{cm}^2\text{-s}). \quad (15)$$

Consider the 00<sup>0</sup> → 00<sup>1</sup> absorption band in OCS (carbonyl sulfide), one line of which is at 2051 cm<sup>-1</sup> with a  $\Delta\nu$  (Doppler half-width) of 0.0916 cm<sup>-1</sup>. Substituting the proper numbers into Eq. 15 gives

$$I = 0.209 \frac{T}{\Delta t}. \quad (16)$$

Converting the energy units from ergs to joules gives

$$I = 2.09 \times 10^{-6} \frac{T}{\Delta t} \text{ J}/(\text{cm}^2\text{-s}). \quad (17)$$

The intensity and power requirements for various pressures of OCS are listed in Table III. For the numbers in the table  $T$  is taken as 0.1 s. Note that the laser power goes as the square of the pressure. The intensity and power requirements listed in Table III are for the case where isotopic selectivity could be preserved because the laser excitation is done "between collisions".

For the second example we will assume that the laser pulse length is fifty times the mean time between collisions. We again use the requirement that  $B_{lu} \rho_{\nu} \Delta t$  be approximately unity. Again for these conditions, the intensity and power requirements for various pressures of OCS are listed in Table IV. These intensity and power requirements are for the case where vibrational excitation is required but isotopic selectivity is not required. For these conditions the power and intensity requirements are easier to meet experimentally.

In discussing laser intensity and power requirements we have assumed the existence of a laser of the proper frequency or wavelength. A brief discussion of laser wavelength requirements is in order here.

Ideally, the laser wavelength should exactly match the molecular frequency to be vibrationally excited. An example is using a CO<sub>2</sub> laser to vibrationally excite CO<sub>2</sub> for energy transfer measurements.

TABLE III  
Laser Intensity and Power Requirements for OCS

OCS Pressure (torr)	$(\Delta t = 1/2_{\Lambda})$		
	$1/2_{\Lambda}$ (s)	Intensity (J/cm <sup>2</sup> -s)	Power (W/cm <sup>2</sup> )
0.01	$1.256 \times 10^{-5}$	$1.66 \times 10^{-2}$	$1.324 \times 10^3$
0.10	$1.256 \times 10^{-6}$	$1.66 \times 10^{-1}$	$1.325 \times 10^5$
1.00	$1.256 \times 10^{-7}$	1.66	$1.325 \times 10^7$

TABLE IV

Laser Intensity and Power Requirements for OCS

$$(\Delta t = 50/Z_A)$$

OCS Pressure (torr)	$50/Z_A$ (s)	Intensity ( $J/cm^2-s$ )	Power ( $W/cm^2$ )
0.01	$6.28 \times 10^{-4}$	$3.328 \times 10^{-4}$	$5.30 \times 10^{-1}$
0.10	$6.28 \times 10^{-5}$	$3.328 \times 10^{-3}$	$5.30 \times 10^1$
1.00	$6.28 \times 10^{-6}$	$3.328 \times 10^{-2}$	$5.30 \times 10^3$
10.00	$6.28 \times 10^{-7}$	$3.328 \times 10^{-1}$	$5.30 \times 10^5$

However, for most laser chemistry experiments the energy levels are not as conveniently matched. Practically, the approach to use is as follows. The infrared spectrum of the compound of interest is obtained experimentally or from the literature. By comparing the spectrum to known laser line positions a candidate laser can be chosen. An experimental check is the most reliable way to see if the chosen laser will work. As tunable infrared lasers become more easily available, more and more laser chemistry experiments will become possible.

The discussion in this section is based on material in the books by Fenner (1959) and Pilar (1968) and the thesis by Wood (1969).

## VI. LITERATURE SURVEY

Gas Phase Experiments

Laser enhancement of chemical reactions has been approached from many different viewpoints. In addition, because of the newness of the field, experiments may not be clear-cut, and mechanisms of reaction are often not determined. These factors make a systematic breakdown of the literature impossible beyond gas and liquid phases. We have therefore chosen to consider the literature chronologically.

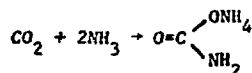
Selective photochemistry was proposed in the early 1950's (Billings *et al.*, 1953), but light sources with a sufficiently narrow wavelength spread were not available for most systems until the laser was developed. From the mid-1960's through the present, many experiments have been done in which lasers were used primarily as heat sources; chemical compounds or mixtures are irradiated with laser light. Yampol'skiĭ (1972) reviews this work comprehensively. Many effects have been observed, but it is difficult to separate effects produced by

selective excitation by the laser light from those produced by the bulk heating of the reactants. Many of these experiments, however, did produce results differing from those produced by simple heating.

Tiffany *et al.* (1967) and Tiffany (1968) reported the electronic excitation of bromine molecules by laser light to bound states near the dissociation continuum. Energy supplied by a few collisions caused the bromine to dissociate to free radicals, which reacted with unsaturated fluorocarbons. It was possible to excite a particular isotopic species of bromine, but the free-radical reactions that followed prevented any isotopic separation. The reaction rate was found to depend strongly on the match between the laser light and the bromine absorption frequency.

A group in the USSR (Karlov *et al.*, 1970) dissociated  $BCl_3$  molecules by  $CO_2$  laser radiation. In this experiment, the investigators felt that heat effects were ruled out, so that the decomposition must have resulted from vibrational excitation. A group at Aerospace Corporation (Mayer *et al.*, 1970) reported separating  $H_3COH$  from  $D_3COD$  by vibrational excitation of the  $H_3COH$  with an HF laser and subsequent reaction with bromine. The results of both these experiments are now being questioned as being due to heat effects.

Karlov *et al.* (1971) continued their investigation of  $BCl_3$  by initiating its explosive reaction with hydrogen by means of a  $CO_2$  laser. They feel that these experiments point to the possibility of controlling chemical reactions with lasers. In similar work (Basov *et al.*, 1971a, 1971b),  $N_2F_4$ ,  $BCl_3$ ,  $SF_6$ ,  $SiH_4$ , and  $PF_5$  were irradiated by a  $CO_2$  laser in the presence of various other gases, both potential reaction partners and buffer gases. The mixtures were stable at the temperatures of the experiments, and irradiation of these compounds in a pure state did not produce dissociation. Thus, the reactions must have taken place as a result of vibrational excitation. The products of the laser-initiated reactions were also different from those of the corresponding thermal reactions. Similarly, Laurent and Kikindai (1972) report an increase in the rates of the reaction



and the reaction between  $\text{NH}_3$  and  $\text{NO}_2$  when the reactants are irradiated by a  $\text{CO}_2$  laser. They suggest that nitrogen isotopes can be separated in this way, but their experiments merely demonstrate an increase in reaction rate, and give little detail. In a molecular beam experiment, Odiorne *et al.* (1971) demonstrated that laser vibrational excitation of HCl increased the reaction rate with K atoms.

Lyman and Jensen (1972) demonstrated that  $\text{N}_2\text{F}_4$  could be dissociated by laser vibrational excitation. Ambartzumian and Letokhov (1972a, 1972b) proposed selective two-step laser reactions, in which an infrared laser vibrationally excites an atom or molecule, and then an ultraviolet photon causes ionization or dissociation. This extremely fast process probably offers the maximum selectivity possible in a laser photochemical reaction. Photoionization of rubidium vapor and photodissociation of HCl and  $\text{NH}_3$  by this method were reported. Two papers which present few details but discuss reactions potentially of interest are those by Tardieu de Maleissye *et al.* (1972) and Evans and Thonemann (1972). In the former, mixtures of acetylene,  $\text{SF}_6$ , and  $\text{N}_2$  are irradiated by laser light and found to follow different kinetics than a purely thermal reaction. In the latter, heavy hydrocarbon molecules are found to ionize more easily under the influence of laser light than they would be expected to by multiphoton ionization theory. Yeung and Moore (1972) report separation of hydrogen isotopes by laser predissociation of formaldehyde. Also published in 1972 was a paper on the reactions of limonene and isoprene (Vogev *et al.*), to which we devote a separate section in this report.

Recent papers on energy transfer in laser-irradiated  $\text{BCl}_3$  (Houston *et al.*, 1973) and laser-driven reactions of  $\text{N}_2\text{F}_4$  and  $\text{SF}_6$  with hydrogen (Lyman and Jensen, 1973) are extensions of earlier work.

#### Liquid Phase Experiments

Only two areas of investigation have been pursued in laser-induced reactions in the liquid phase: production of singlet oxygen and its subsequent reactions and energy transfer, and photoionization. The former is an electronic excitation rather than a vibrational one, but some of the considerations can be transferred to liquid-phase reactions induced by vibrational excitation.

LeRoux *et al.* (1968) studied the photo-oxidation of guanine photosensitized by methylene blue in conventional and laser light, and found no difference. In both cases, singlet molecular oxygen apparently added to guanine to form an unstable endoperoxide which then decomposed. Matheson and Lee (1970) produced singlet oxygen in solution by direct laser excitation of an electronic transition. Detailed studies have been made of the lifetime of singlet oxygen in solution and the modes of energy transfer (for example, Matheson and Lee, 1972a, 1972b; Merkel and Kearns, 1972).

Goodall and Greenhow (1971) used a Nd:glass laser to ionize water by vibrational excitation. Under similar conditions  $\text{D}_2\text{O}$  was not ionized, removing the possibility of a heat effect. Water molecules, because of hydrogen bonding, form a network that should equilibrate an energy deposition faster than most other liquids. For longer relaxation times, reaction is more probable. Thus, the fact that water could be ionized in this way implies that laser-induced reactions are possible in other liquids, particularly where the excited frequency is not matched in the solvent molecule.

#### Patents

Several patents have been issued over the past few years on processes involving laser-enhanced chemistry. Not enough patents have been issued in this area to give a clear idea of trends; a search of further work done by the holders of the patents indicates no further expansion on the idea of laser-enhanced chemistry. In fact, the primary interests of some patent holders seem to lie in other areas.

The question of photon absorption vs heat effects will be much less clear in patents than in journal articles. As was mentioned earlier, heat effects may well be tolerable in industrial processes, even though they confuse the picture for research. Thus, patents are not very useful in the theoretical elucidation of laser chemistry, but they do show what processes have successfully been developed.

American Cyanamid (Freeman and Travis, 1972) has been issued a German patent for a process involving one or more gaseous reactants. With infrared laser radiation of a wavelength less than  $2 \mu\text{m}$  and power densities greater than  $40 \text{ W/cm}^2$ , reactions can be carried out at temperatures lower than normal.

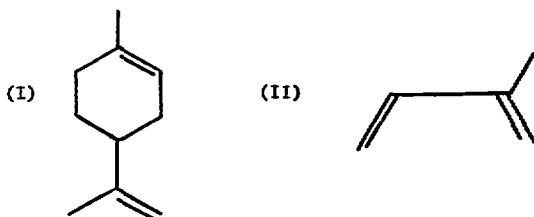
Three patents require laser light close to vibrational frequencies of the molecules involved in the reaction; they involve electrolytic production of chlorine (Farmakides, 1971) production of acetylene from methanol (Ishihashi, 1971), and polymerization (Hoskins, 1968).

Finally, German, British, and French patents have been issued on a uranium isotope separation process developed by Guers (1972a, 1972b) at the Battelle Institut e.V. (1972). They cover the decomposition of a gaseous uranium compound, such as  $UF_6$  or  $U(BH_4)_4$ , by laser light corresponding to a molecular vibration. Significant increases in the reaction rate of the irradiated isotopic species are said to take place.

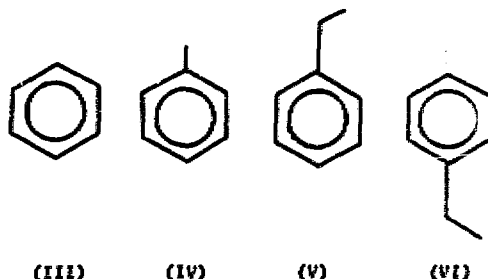
#### VII. PHOTOCHEMISTRY IN THE ELECTRONIC GROUND STATE

Yogev *et al.* (1972) have begun an investigation that is relevant to our area of interest. It is a careful study, directed explicitly at reactions enhanced by laser excitation of vibrational states. In addition, the molecules under study are polyatomic. Diatomic molecules are clearly simpler to understand, but only polyatomic molecules can give an answer to the question of whether energy can be localized in one bond of a molecule. In addition, many compounds of economic interest are organic. A paper dealing with these reactions in the liquid phase would be ideal for our purposes, but the gas phase offers some important simplifications at this stage of development. Hopefully, in the future, both liquid and gas studies will become available.

Limonene (I) and isoprene (II) were irradiated by a cw  $CO_2$  laser at various pressures.



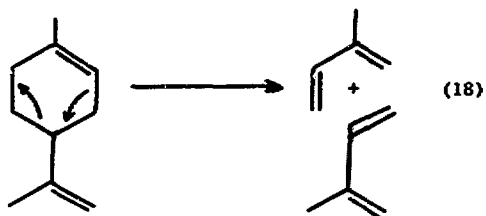
The  $10.6\text{-}\mu\text{m}$  ( $943\text{-cm}^{-1}$ ) wavelength of the  $CO_2$  laser corresponds to several vibrational modes in these molecules. Products from the irradiation of limonene at 2 torr were isoprene, benzene (III), toluene (IV), ethylbenzene (V), methylethylbenzene (VI),



isomers of dihydrolimonene and allocimene, and low molecular weight compounds that could have been formed by further cleavage of isoprene or by the cleavage of limonene to form aromatic compounds. The products obtained from the irradiation of isoprene at 1 torr were the same as from the irradiation of limonene, but no limonene was found. At pressures above 3 torr, no detectable amounts of products were found, and a maximum amount of products was formed at 0.05 torr.

The activation energies for these reactions far exceed the 2.7 kcal/Einstein supplied by the  $CO_2$  laser. Multiple-photon transitions and heating by the laser could be ruled out. Addition of helium and argon inhibited the formation of compounds with molecular weights larger than that of isoprene, but did not influence the formation of low molecular weight compounds. Nitrogen was much more effective in inhibiting product formation, the inverse of what would be expected from thermal conductivities. The most effective inhibitor of product formation was isoprene itself. Clearly, the inhibition was caused by vibrational de-excitation of the isoprene; nitrogen has a vibrational degree of freedom that helium does not, and the most effective inhibition occurred when the vibrational frequencies matched exactly.

Yogev *et al.* do not discuss possible reaction mechanisms in great detail, except to say that isoprene could be formed from limonene by a retro-Diels-Alder reaction:





and that higher molecular weight compounds may be formed from isoprene through a vibrationally excited dimer. A dimer with the configuration shown for the products in Eq. 18 is one possibility.

This work offers little insight into the question of selective excitation of a given bond within a molecule. Isoprene has a strong absorption near 10.6  $\mu\text{m}$ , and several modes are probably excited by this wavelength. Yegov *et al.* argue that energy stored in the absorbing mode is redistributed in the other modes, so that the absorbing mode acts as a window to let the energy into the whole molecule. They cite several experiments in which emission is observed not only from the band that was excited, but from other levels with much higher energies than those supplied by the exciting laser beams. These experiments, however, were done at pressures in the tens and hundreds of torr. At these pressures, collisions would quickly redistribute the excitation energy. Intramolecular distribution of energy before the collision may well be different.

In any case, excitation of limonene and isoprene by 10.6- $\mu\text{m}$  laser radiation cannot be a decisive test of the "window" idea, because too many bonds are likely to be excited by this wavelength. An experiment to test the "window" idea would have to make use of a molecule having several different types of bonds, which would absorb on very different wavelengths and react in different ways.

An important result in this paper is that above a few torr heat effects become predominant; thus, in most of the other papers dealing with laser-induced chemical reactions, what is being observed is a mixture of heat effects and nonequilibrium vibrational excitation. Heat effects may be tolerable in industrial processes, but investigations of laser-induced reactions will have to be carried out at very low pressures to provide definitive results.

This paper leaves many questions unanswered, but it is a firm beginning in the investigation of laser-enhanced chemistry.

#### VIII. CONCLUSIONS

Molecules can be excited to vibrational temperatures well above their translational temperatures by laser radiation of the appropriate wavelength. This excitation results in enhanced reactivity for both unimolecular and bimolecular reactions. No studies have been done with polyatomic molecules to

determine whether laser radiation in resonance with one part of the molecule excites only that part of the molecule or the entire molecule.

Resonant excitation can be done in liquids. Its effectiveness in producing commercially useful reactions has not yet been investigated in detail. Liquids seem to offer some advantages over gases for reactions of this sort, namely, prevention of vibrational energy transfer from one isotopic species to another, and availability of reaction partners if the solvent is one of the reactants. The area of laser-enhanced reactions in liquids has been almost completely ignored, but it seems promising.

Interest is being shown in the commercial potential of laser chemistry. A few patents have been issued on laser-enhanced chemical processes. However, these processes are simple ones. The area of organic chemistry is practically untouched by patents.

Laser-enhanced chemistry promises to be an aid in elucidating mechanisms of biological energy transfer. This area has only been suggested in recent publications, and experimental work seems to be difficult. Anything that can be learned about resonant energy transfer in relatively simple organic systems will contribute to at least proposals of experiments to investigate biological energy transfer. The implications of understanding biological energy transfer are vast: they could range from an efficient use of solar power to a cure for cancer. However, this field is now extremely speculative.

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