

LASERS IN PHOTOCHEMISTRY

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Photochemical reactions play a significant role in modern organic synthetic strategies. Some of the advantages photochemistry offers are – enhanced reaction rates, increased selectivity and synthesis of compounds hitherto impossible by traditional routes. Conventional photochemistry is somewhat hampered by the unavailability of high-intensity light sources – this is where lasers come in. The fast excitation possible by using lasers allows us to *manipulate* a reaction, to make it proceed *at our will*. The products of the reaction are now controllable; one of the advantages of this is increased selectivity.

Selectivity implies the tendency of the synthetic method or route, to *favour* the product which is required - this obviously also implies the lesser amounts of unwanted side-products generated. Apart from the economic benefit derived out of optimum use of reactant material, good selectivity also reduces generation of waste products, disposal of which could be harmful to the environment.

Of late, researchers are on the lookout for synthetic processes that are *inherently* selective, and thus obviate the need for extensive (and expensive) separation techniques. Laser-induced reactions show considerable promise to fulfill this need for selectivity, in the future.

Limitations of Conventional Methods

As we all know, chemical reactions involve bond-fission and re-formation. Every molecule has a number of bonds of varying strengths, which require different amount of energy for their fission. When the energy required for a reaction is supplied by conventional heating methods, this can be visualized as a 'brute force' approach - wherein the bond which is most unstable, thermodynamically, will be broken first.¹

For some time now, chemists have been looking for methods to break the bonds they *want* to, *choosing* the bond to be broken. This is possible to an extent using laser irradiation, which is tuned to the particular frequency of vibration of the bond that is to be broken. Thus, we can make reactions proceed in ways other than that dictated by the thermodynamics.

Most of the applications of tunable lasers in this field are due to their high monochromaticity and intensity, without which such manipulations are not possible. In most cases, the lasers used are CO₂ lasers, neodymium-YAG and neodymium-glass lasers, dye lasers, excimer lasers, etc.⁶

In this review, the focus is on photochemical processes using lasers in the ultraviolet and infrared range.

Infrared Laser Photochemistry

IR radiation falls in the same energy range as the vibrational energy of molecules, hence; IR radiation can only cause vibrational excitation. The interaction of IR radiation with a molecule is detailed below.

All chemical bonds are not static but in a state of vibration. When energy is supplied to the bond, the frequency of vibration remains constant but the amplitude increases. This continues, till the bond eventually breaks as shown in Fig. 1 below.

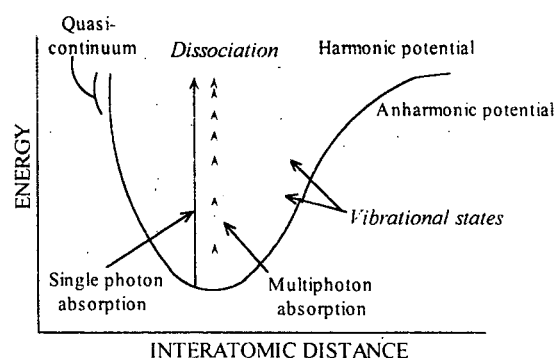


Fig. 1: Vibrational excitation of a bond.

A molecule has many degrees of freedom, corresponding to the many bonds in it. Usually these degrees of freedom are efficiently coupled (e.g. by *resonance* - electron cloud delocalisation) so that energy supplied to one of the bonds of the molecule, via irradiation, is dissipated over the other degrees of freedom. Hence more than one bond will be broken, *even if* monochromatic light is used for irradiation; thus giving rise to a number of reaction

pathways. The reactivity of the molecule when such low-intensity light sources are used, is described by the RRKM theory of statistical thermodynamics.^{2,3}

However, laser light is of high intensity – this means the *pulse duration* is very small. Use of lasers enables us to focus all the radiant energy on one bond, since it is supplied in such a small interval of time that no dissipation to the other degrees of freedom is possible. Thus, we can cleave a bond selectively, deviating from the RRKM theory.

Consider a *gaseous* system, containing many reactant species. On irradiation using monochromatic, high intensity lasers tuned to the vibrational frequency of a particular bond in one of the reactants, these molecules attain an excited state. The time for which the molecule remains in this state, as compared to the time required for various relaxation processes, will determine the future reaction pathway of the molecule, as described below.

We have,

$$T_{\text{stochastic}} < T^* < T$$

where,

$T_{\text{stochastic}}$ - the time required for intramolecular vibrational energy redistribution (IVR) between different vibrational modes of the molecule.

T^* - the time required for intermolecular transfer of vibrational energy by collisions between molecules of different kinds in a mixture (V-V relaxation).

T - the relaxation time for the vibrational energy of a molecule to be transferred to the translational degree of freedom (V-T relaxation) due to collisions.

Let W_{exc} be the rate of vibrational excitation of the reactant molecule, and T_{exc} the time for which the molecule is in the excited state, which depends upon the laser pulse duration.

There can be the following cases depending on the value of T_{exc} :

1. $T_{\text{exc}} < T_{\text{stochastic}}$, where $T_{\text{stochastic}}$ is approx. 10^{-13} - 10^{-11} s.

In this case, there is not enough time for redistribution of energy supplied to a bond, to the other bonds in the molecule, i.e. selective excitation occurs without vibrational equilibrium

of the molecule that interacts with the IR field. Here a certain mode or functional group of a polyatomic molecule has higher vibrational energy than the others. *Bond- or mode-selective chemistry is now possible.*

2. $T_{\text{stochastic}} < T_{\text{exc}} < T^*$, where T^* is approx. 10^{-9} - 10^{-6} s

Here, the energy is redistributed among the bonds in a molecule (IVR), but not to the other species in the system. There is vibrational equilibrium only for those molecules interacting with the IR field. These molecules have higher energy than the others, although the translational energy (temperature of the system) remains the same. *Molecule- selective chemistry becomes possible.* The applications include laser isotope separation, dissociation of molecules, etc.

3. $T^* < T_{\text{exc}} < T$, where T is approx. 10^{-6} - 10^{-3} s.

In this case a degree of vibrational equilibrium is established in the mixture, causing general activation and enhancement of reaction rates. However, there is no V-T relaxation to cause general heating. *Hence non-selective vibrational IR photochemistry is possible.*

4. $T < T_{\text{exc}}$ - here there is V-T relaxation, causing *heating of the gas*. Thus equilibrium thermal excitation of all the molecules in the system is established.

The 4 possibilities are represented in Fig. 2.

It is seen that, for a photochemical reaction to take place, the energy of the vibrationally excited molecule should be comparable to the activation energy of the reaction (E_a). Since the energy of a single quantum ($h\nu$) is much less than E_a , we would require a large number of IR quanta to effect a reaction. Hence we are usually dealing with *multiphoton* excitation processes.⁵

Applications of IR lasers: -

1. Bond- or mode-selective reactions: -
Bond-selective chemistry is a very exciting field, because it offers near infinite possibilities in the rearrangement of a molecule at will. Research in this area has become possible only of late, after the development of lasers having ultrashort pulse duration of the order of femtoseconds (10^{-15} s).

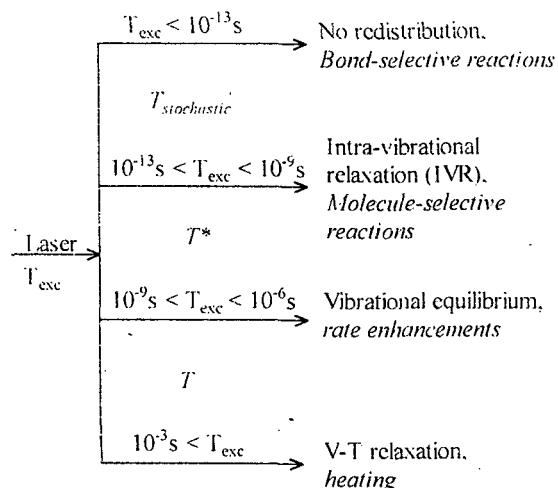


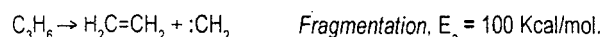
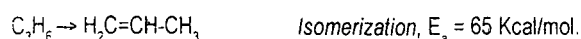
Fig. 2: The possible reaction pathways following IR laser excitation.

One of earliest studied examples is of the reaction between H and HOD molecules, with one quantum of excitation in either the OH or OD vibrations.^{7,8} It was found that the H atom reacts preferentially with that bond in HOD, which has been vibrationally excited.

Note: - A denotes radical form.



Another important reaction is the multiphoton IR laser excitation of either of two fundamental vibrational modes of cyclopropane (C_3H_6). In both cases, the products are the same as that of the thermal process, but the relative yields are vastly different.⁹



On excitation of the C-H asymmetric stretch at 3.22 microns, isomerization gives propylene ($\text{H}_2\text{C}=\text{CH}-\text{CH}_3$) with almost no fragmentation products; however, the excitation of the CH_2 wag at 9.5 microns produces roughly equal yields of propylene and fragmentation products.

The effect of intermolecular collisions cannot be responsible for the above observations. These results are thus consistent with an excitation that is initially non-statistical or mode-selective.

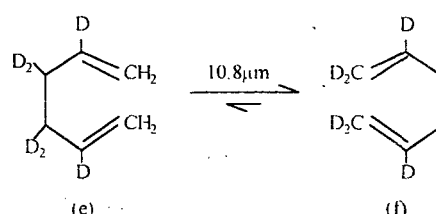
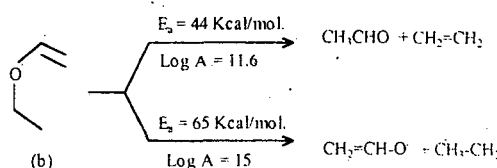
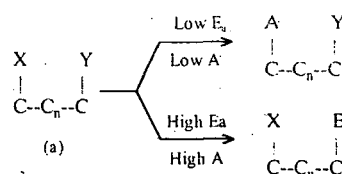
However, mode-selective reactions where the effects of different vibrational modes have been tested are still very few; one of the major problems being the intramolecular energy redistribution (IVR) which is quite difficult to avoid.

2. **Molecule-selective processes:** - Molecule-selective processes are the most widely studied in the field of laser chemistry. Three major applications are laser isotope separation, production of very pure substances, and laser-induced photo-biochemical processes.

a. **Selective reaction of one functional group in the presence of a more reactive group:** -

Consider a molecule (a) with groups X and Y undergoing the reaction shown in Scheme 1. By using conventional methods, when the functional groups react in a unimolecular fashion, the dominant product will be the one with the lower E_a . However, by using pulsed IR laser, the higher activation energy pathway is likely to be followed. This is due to the ability of the laser to heat the molecule, resulting in (a) being excited to a greater extent above the threshold.

An example¹⁰ which illustrates the above is also shown in Scheme 1.



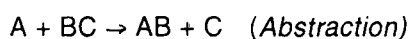
Scheme 1: Molecule-selective IR laser processes.

b. **The electrolytic isomerization of substituted cyclobutene (c) to give an open chain product (d):** - (See Scheme 1). This reaction also

illustrates how the stability parameters can be side-stepped using laser techniques.¹¹ The deactivation of the product by collisional V-T relaxations inhibits the reverse reaction to some extent.

An important feature of such reactions is that they are also economically feasible, and hence show great potential as substitutes for the currently used inefficient industrial processes.

- c. **Reversible Cope rearrangement of 1,5-hexadiene:** - (See Scheme 1). In this case, deuterium-labelled hexadiene (e) when irradiated by 10.8 μm CO_2 laser, results in complete conversion to (f), as opposed to the thermal process which has low yields due to its reversibility.¹²
3. **Enhancement of chemical reactions:** - The rates of many chemical reactions can be substantially enhanced by the excitation of the reactant molecules. This can be shown by the following simple bimolecular reaction



The dynamics of the reaction is based on the Arrhenius equation. Now if the major component of the reaction co-ordinate is a particular vibrational mode reactant, a molecule excited in that mode by a level $h\nu$, experiences a reduced barrier. This implies that the laser does not affect the reaction, but *channels* the energy into a selected reactant mode. Hence the conversion of the reactant is increased.

A study of the reaction rates shows that K_{laser} is *much* greater than K_{thermal} .¹³

There are numerous examples which illustrate this effect:

- $\text{HCl} (V=1) + \text{K} \rightarrow \text{KCl} + \text{H}$ $\text{HCl laser}, K_{\text{laser}}/K_{\text{thermal}} = 100$
 - $\text{HF} (V=1) + \text{Ca} \rightarrow \text{CaF} + \text{H}$ $\text{HF laser}, K_{\text{laser}}/K_{\text{thermal}} = 10^4$
 - $\text{HF} (V=1) + \text{Sr} \rightarrow \text{SrF} + \text{H}$ $\text{HF laser}, K_{\text{laser}}/K_{\text{thermal}} = 10^4$
3. Laser-induced matrix isolation reactions have been shown to exhibit isotopic, orientational and site selectivity.



Applications of UV lasers

In contrast with IR lasers, UV lasers provide a much wider range of operations, mostly due to their higher energy content. Hence many dissociation and ionization reactions are possible. These methods have found some limited application in industry till date.⁴

The theory of UV laser photochemistry is not presented here. However, some of the major applications are as below: -

- Synthesis of vitamin D:** The biomolecules vitamins D_2 and D_3 are quite important due to their use as animal feed additives. The photolytic ring opening of 7-Dehydrocholesterol (7-DHC) to give vitamin D_3 via previtamin D_3 (P_3), has long been employed for the large-scale synthesis of vitamin D_3 .¹⁴

The usual photochemical process using a Hg lamp has a low yield, due to the side reactions forming two isomers tachysterol (T_3) and lumisterol (L_3), other than P_3 . When the same process is catalysed by two-step irradiation with KrF laser light at 248 nm. and N_2 laser

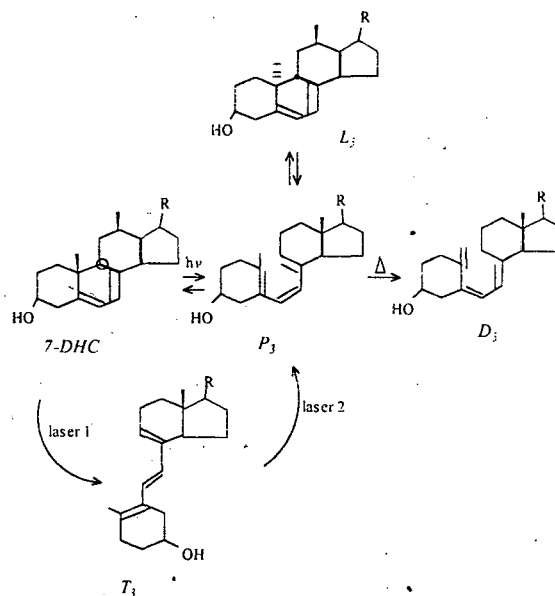


Fig. 3: - The production of vitamin D_3 using two-step laser irradiation.

light at 337 nm., interconversion between the 3 isomers increases the yield of the required product P_3 .^{15,16,17} This is shown in Fig. 3 above.

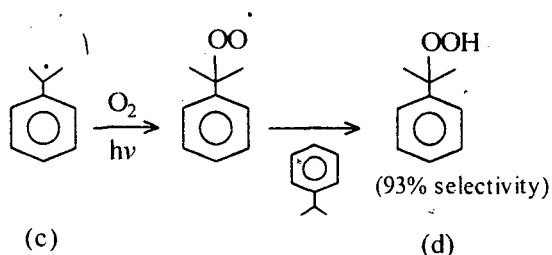
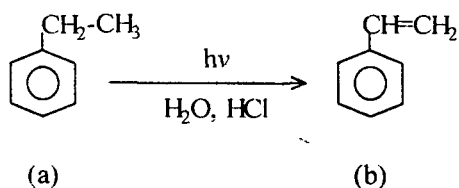
The following table shows the relative yields

obtained with different irradiating agents: -

Light source	% 7-DHC	% tachysterol	% lumisterol	% P ₃
Low-pressure Hg lamp	1.5	75	2.5	20
Medium pressure Hg lamp	3.4	26	17	53
KrF laser at 248 nm.	2.9	71	-	26
XeCl laser at 308 nm.	13	3.4	42	35
KrF + N ₂ laser at 334 nm.	0.1	11	9	80

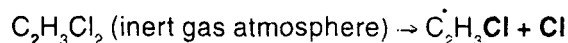
2. Laser-induced radical chain reactions: The high energy UV laser makes many homolytic dissociation reactions possible, which give a wide range of applications as below: -

- In the conversion of ethylbenzene (a) to styrene (b), the dehydration reaction is catalyzed by the OH initiator radicals. These are obtained by the photolysis of water vapour with an ArF laser at 1 atm: O₂ vapour is added to prevent premature styrene polymerization. Yields obtained are 10⁵ at 500°C and 10³ at 300°C (See Scheme 2).¹⁸
- Cumene (c) is photo-oxidized to cumene hydroperoxide (d), a precursor of methylstyrene, by using a laser as a catalyst. (See Scheme 2). A number of undesired side products are formed in the thermal oxidation using air. By using an XeF laser at 351 nm. the quantum yield obtained is about 500.¹⁹



Scheme 2: - Chain reactions catalyzed by UV lasers.

- Vinyl chloride (VC, C₂H₃Cl) is the monomer of PVC, which is a very industrially important polymer. VC is produced mainly from 1,1-dichloroethane (C₂H₃Cl₂) by the thermal cleavage of HCl. The photolytic reaction is a unimolecular process and hence has an advantage over thermal initiation of the chain reaction, because the former is rate-determining with a low energy barrier.



Hence, the reaction requires low activation energy. This leads to low reactor temperatures, higher conversions and fewer side products.

- Laser induced polymerization:** Polymerization reactions are the most important reactions, by sheer volume, in the chemical industry. Almost all fields require polymer-based substances, which have a dazzling variety of uses.

Conventional thermal processes (e.g. radical polymerization of ethylene) have a number of disadvantages including long induction periods for heating of the monomer-initiator mixture, necessity of multicomponent mixtures, initiation by heat transfer from the walls which is inhibited by formation of a polymer layer on the walls, etc. Explosive decomposition of the monomer can occur at a critical temperature in exothermic processes.

In contrast, a controlled and homogenous initiation is possible using lasers, which give a number of advantages. Quantum yields of about 10⁴ can be achieved and the rate constants for the intermediate reactions are very high.

- The laser-initiated copolymerization of cyclohexene oxide with maleic anhydride is two orders of magnitude more efficient than is the case for irradiation with conventional UV lamps.²⁰
- Very rapid crosslinking in epoxy acrylate can be obtained by irradiation with an N₂ laser at 337 nm. by using a suitable photo-initiator.²¹
- Laser-induced polymerization allows 3-D structures to be produced with high spatial resolution.^{22,23}

Conclusion:

The development of the laser has revolutionized most scientific pursuits ranging from physics to medicine - it now appears that the time of the laser in chemistry has come. Finally laser-induced photochemistry seems to be fulfilling part, if not all of the promise it showed in the very early stages. Indeed, the first research in this field had many proclaiming the arrival of *laser alchemy* - unfortunately, that medieval dream still remains just a dream.

Nevertheless, the laser shows tremendous potential in heralding inherently selective synthetic routes. At this point of time, neither has sufficient research gone into the industrial applicability of such novel systems; nor has the expense involved scaled down to a reasonable level. Only then will such techniques be applicable on the large-scale - and maybe then bring about the revolution chemists have always dreamed of. There is no doubt, however, that there is a light at the end of the tunnel - a laser light?

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