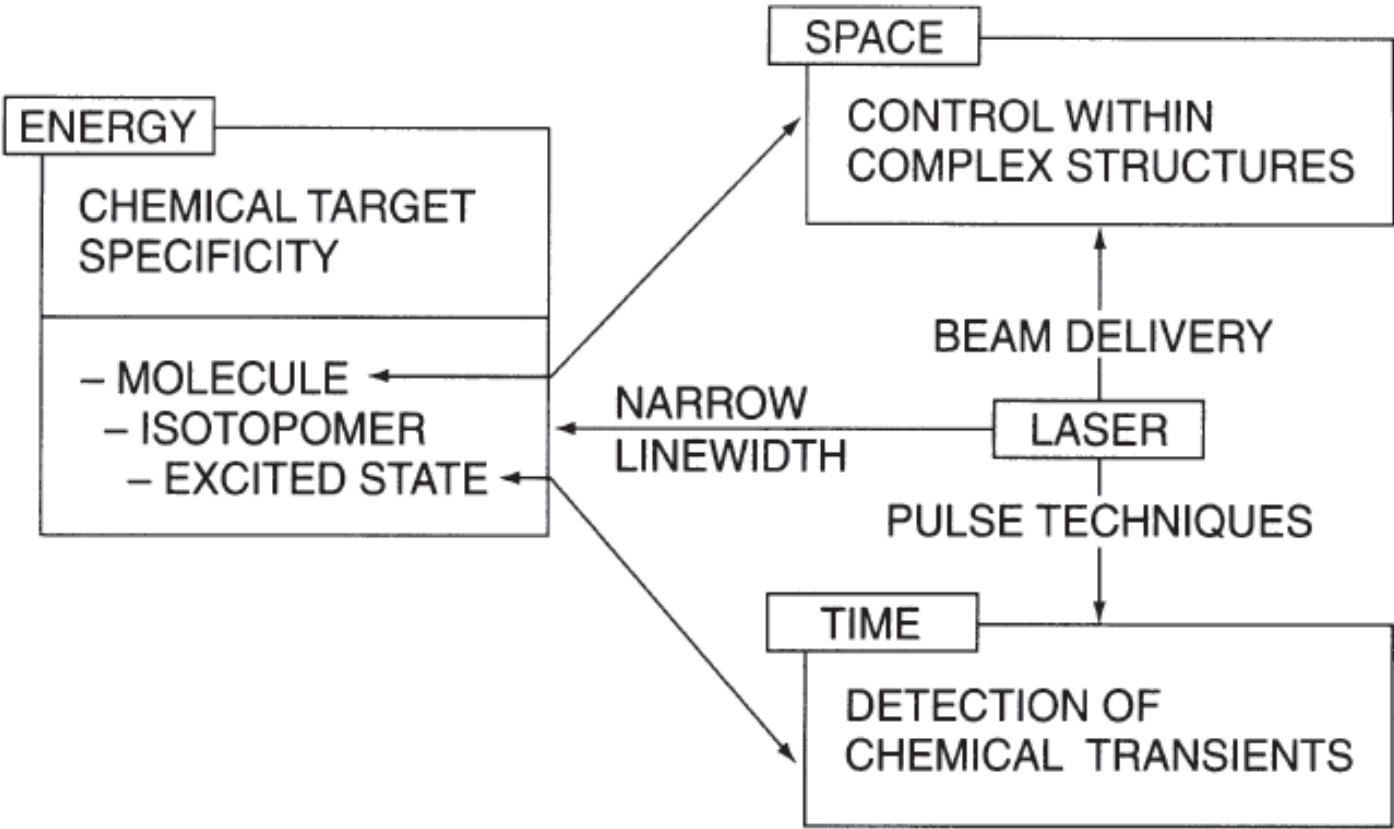


Applications of Laser in Chemistry

Laser-Induced Chemistry

- Chemistry induced by optical excitation is by definition *photochemistry*, and the whole of laser-induced chemistry can thus be regarded as one part of this much wider field.
- Although lasers can replace other light sources in any conventional photochemistry, there is a significant number of laser-induced reactions that are not practicable with conventional light sources.
- Laser monochromaticity naturally lends itself to applications requiring the selective excitation of particular sites within a heterogeneous system or of one specific chemical species in a mixture of reactants.
- The generally high intensity of laser sources is significant both for increasing excitation efficiency and also for thereby promoting multiphoton processes;
- Pulsed laser excitation offers a temporal selectivity that is now widely being exploited for inducing and monitoring fast and ultrafast chemical processes.

Exploitation of laser characteristics for chemical selectivity in energy, space and time



General feature of Laser excitation:

- Since, the input radiation is commonly pulsed and so has time-variable intensity, and since both saturation and multiphoton absorption may further complicate the dynamics of photoabsorption, it is clearly no longer appropriate to employ the Beer-Lambert Law.
- The absorbance (optical density), defined through an obvious generalisation as.

$$A = -\log_{10}(1-F), \text{ F being the fraction of energy absorbed}$$

- One can then gauge the often complex dependence on a multitude of factors such as: laser wavelength, fluence (energy density of the radiation), pulse duration, optical path length, temperature, and the concentration or pressure of both absorbing and non-absorbing species.

LASER Initiated Processes

- In polyatomic molecules, the initial photo-induced transition to an electronically excited state is almost invariably followed by some degree of intramolecular relaxation before any real chemistry takes place.
- Such unimolecular relaxation processes generally involve redistribution of energy amongst vibrational states and take place typically over nanosecond or sub-nanosecond timescales,
- The state directly populated by photon absorption may therefore have little *chemical* significance. Relaxation may lead to ionisation, isomerisation or dissociation.

For a polyatomic molecule ABC



- While the previous considerations apply to unimolecular reactions, lasers can also be used to induce bimolecular reactions in which either one or both of the reactants are initially excited by the absorption of laser light.
- In principle, a wide range of reaction conditions can be obtained by promoting each reactant to various energy levels.
- Often IR lasers are used instead of UV/Vis lasers.

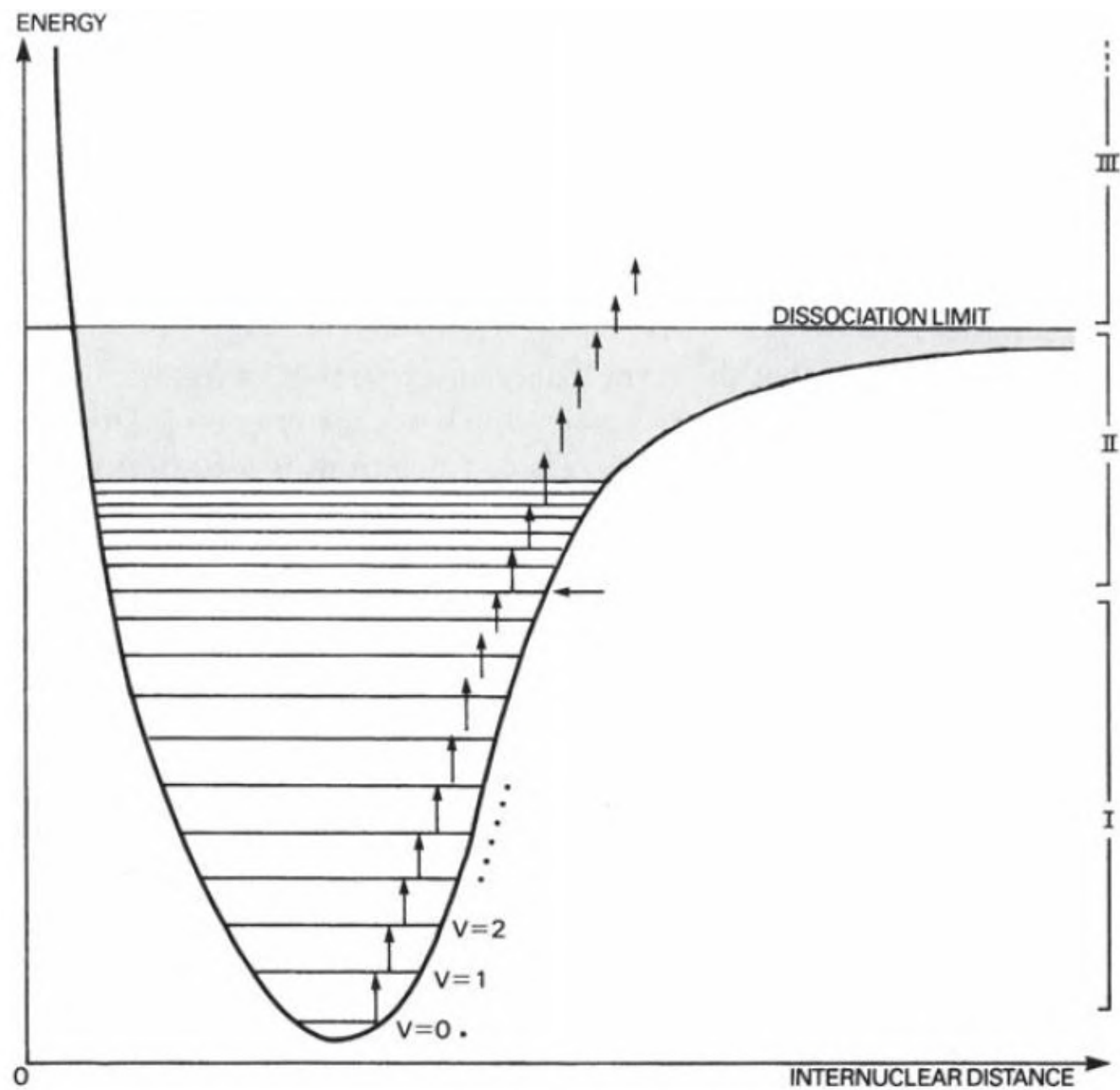
Multiphoton Infra-red Excitation

- A very distinctive kind of laser photochemistry can be induced by powerful infra-red sources, the carbon dioxide laser being by far the most widely used.
- The multiphoton processes which can be induced by intense radiation become particularly efficient if one or more resonance condition can be satisfied by the molecular energy levels.
- Vibrational energy levels are more or less equally spaced, at least for the lowest levels of excitation. Hence, with infra-red radiation of the appropriate wavelength, multiphoton absorption can become highly significant.

Diatomic Molecule

- To consider multiphoton infra-red absorption in more detail, we first take the simple case of a diatomic molecule, where there is only one vibrational frequency.
- The first thing to note is that as we move up the ladder of vibrational states, although the spacing between adjacent levels starts off fairly constant, it diminishes at an increasing rate.
- It also has to be borne in mind that each vibrational level has its own manifold of much more closely spaced rotational levels.
- An asymptotic limit is reached, at which point there is no longer any restoring force as the two atoms move apart, and dissociation occurs.
- The process of multiphoton absorption displays different characteristics over different regions of the energy scale, and it has become common to speak in terms of regions I, II and III, illustrated in figure..

Laser : Fundamentals and Applications



- In region I, vibrational levels are quite widely spaced, and the spacing is greater than the overall absorption bandwidth. Because the spacing is non-uniform, however, the photon energy soon gets out of step, and multiphoton processes occur.
- In the diagram, for example, the transitions $v = 0 \rightarrow 1$, $1 \rightarrow 2$, $2 \rightarrow 3$, $3 \rightarrow 4$ and $4 \rightarrow 5$ all require energies close to that of a single photon and lying within the overall bandwidth.
- These transitions therefore all take place by the process of single photon absorption. The energy required for the $5 \rightarrow 6$ transition, however, is sufficiently different that it lies outside the bandwidth and cannot take place by absorption of one photon.
- Nonetheless, excitation can proceed up to the $v = 10$ level, as indicated, by a direct $5 \rightarrow 10$ transition involving four-photon absorption.
- This necessitates a fairly intense flux of photons and, hence, a powerful source of radiation. Generally achievable by mode-locked pulsed LASERs

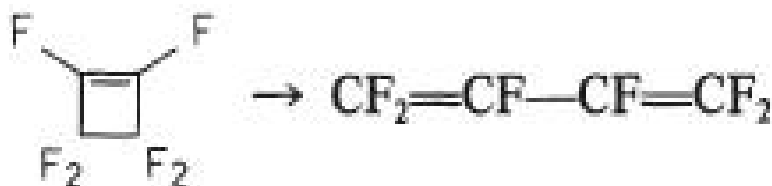
- Region II is characterised by quasi-continuum behaviour resulting from the fact that vibrational energy level spacing has become *less than* the bandwidth. Here successive photons can be absorbed in a series of energetically allowed single-photon transitions.
- Since energy conservation is satisfied at every step, the molecule can at each point exist for a finite lifetime before absorbing the next photon; hence, excitation through this region does not necessitate the enormously large photon flux which might at first appear necessary.
- Finally, once the level of excitation has reached the dissociation threshold, a true energy level continuum is encountered, and further photons can be absorbed in the short time before the atoms separate; this is known as region III behaviour.

Laser Photochemical Processes

Unimolecular Laser-Induced Reactions

- The largest number of laser-induced chemical reactions fall into the category of unimolecular reactions, and the carbon dioxide laser, producing powerful emission at numerous discrete wavelengths around 9.6 μm and 10.6 μm is the most commonly applied source.
- The simplest type of unimolecular reaction is isomerisation, and several studies have shown how laser-induced *photoisomerisation* can modify the relative proportions of different isomers in a mixture.
- The selective laser excitation of one isomer, using a wavelength which no other isomer appreciably absorbs, can substantially modify the relative proportions either towards or, indeed, in some cases away from equilibrium.

- 1,2-dichloroethene, where the cis-isomer is more stable than the trans-isomer by approximately 2 kJ mol^{-1} . Pulsed irradiation of a mixture containing an excess of the trans-compound at a frequency of 980.9 cm^{-1} results in conversion to a mixture in which the cis-isomer predominates.
- Pulsed irradiation of hexafluorocyclobutene at 949.5 cm^{-1} , however, results in up to 60% conversion to its isomer hexafluoro-1,3-butadiene, which is thermodynamically less stable by 50 kJ mol^{-1}



- A classic case of laser-induced chemistry involves the conversion of 7 – dehydrocholesterol (I) to previtamin D₃ (II), which is, once again, an isomerisation reaction.

The product (II) is reversibly convertible to vitamin D₃ (III)