Lasers for Chemical Applications

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Abstract. The characteristics of lamps and lasers are contrasted from the viewpoint of a photochemist. The number of potential photochemical applications of lasers is shown to be vastly greater than that using conventional lamps. Several examples are given, which are only made feasible by the special properties of laser light.

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When talking about chemical applications of lasers what first comes to one's mind is photochemistry, where lasers replace the time-honoured mercury-lamp of the photochemist. Perhaps this is why most chemists still think of a laser as an expensive lamp – and no more. I will later make a detailed comparison of lamps and lasers and actually demonstrate that laser photons can even be cheaper than lamp photons and one can use lasers in a multitude of sophisticated photochemical applications that one would never have dreamed to be possible with a lamp.

But, of course, there are many more chemical applications of lasers than just photochemical ones, e.g. analytical applications like trace analysis with infrared lasers, or coherent anti-Stokes Raman scattering and laser-induced fluorescence in combustion research, or laser mass spectroscopy. Then there are also kinetic or mechanistic investigations which have only become possible with ultrashort pulses from tunable lasers.

It is, of course, impossible to talk about all the different lasers that are useful in all these diverse applications, so I will only give a brief synopsis of the wavelength range covered by the different classes of lasers in the first figure and then concentrate on excimer lasers and dye lasers, which I believe cover more than 90% of all chemical applications.

The upper part of Fig. 1 contains the most important fixed-frequency lasers:

a) solid-state lasers, e.g. the ruby laser in the red end of the visible region and the Nd^{3+} glass or -YAG laser near 1 μm,

b) gas lasers, e.g. the He–Ne laser and the Ar^+- and Kr^+-ion lasers, with several lines throughout the visible,

c) excimer lasers, e.g. ArF (193 nm), KrF (248.5 nm), XeCl (308 nm), and F_2 (158 nm) in the near-UV and a so-called "X-ray laser" which was first operated in October 1984 at the Lawrence Livermore National Laboratory using a laser-generated Se-plasma emitting at 20 nm. At present, this XUV laser is still no more than a scientific curiosity but is listed here to remind one of the high hopes for future X-ray lasers which should operate down to wavelengths of a few Ångströms and will eventually open up a whole bonanza of important new applications.

In the infrared there are

d) the chemical lasers, e.g. the iodine-photo-dissociation laser at 1.35 μm and the HF laser with many vibronic lines near 2.5 μm,

e) the electrically excited molecular gas lasers, operating on many discrete vibronic lines, e.g. the CO laser around 5–6 μm and the CO_2 laser between 9 and 11 μm, and finally

f) the optically excited molecular gas lasers, e.g. water, formic acid, methanol and many others operating on thousands of pure rotational transitions in the far-infrared from about 30 μm extending into the millimetre region.

In the middle and lower part of Fig. 1 the wavelength range of the truly continuously tunable lasers is indicated. The low-power semiconductor lasers, which are important for analytical applications, operate from the red end of the visible to about 50 μm. Dye lasers
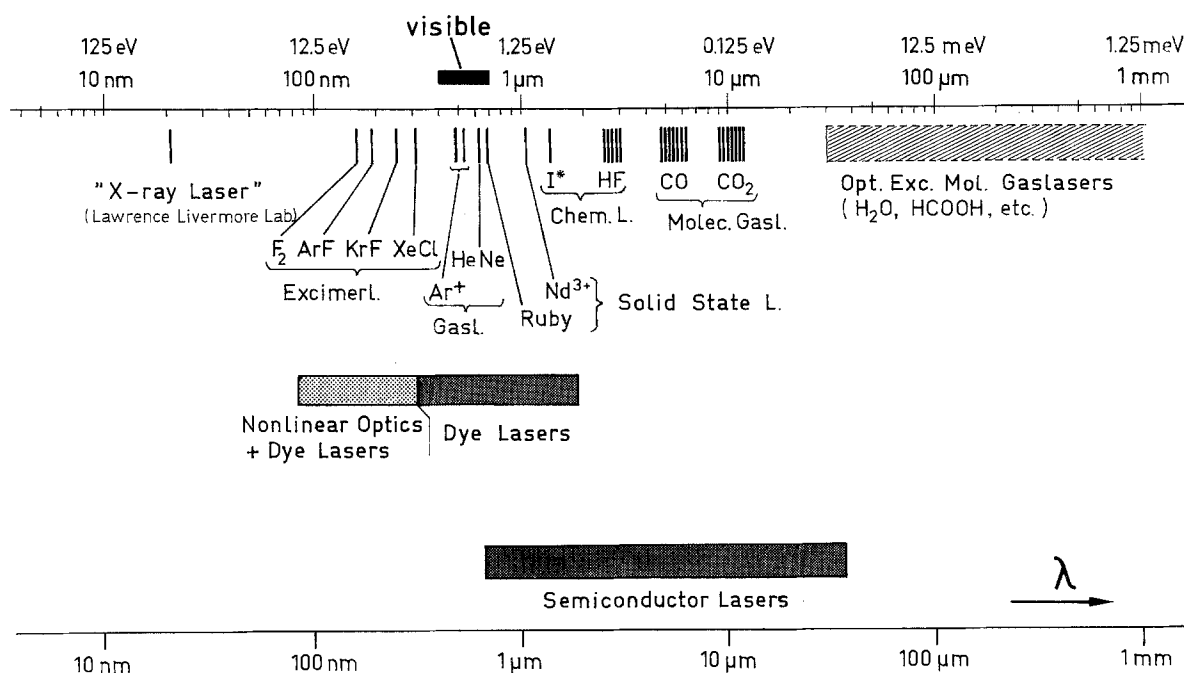
WAVELENGTH RANGE OF LASERS

Fig. 1. Wavelength range of the most important lasers

presently operate in the range from 308.5 nm to 1.85 μm. Using nonlinear optical methods, e.g. frequency multiplication in crystals or gases, extends this range down to about 80 nm.

Comparison of Lamps and Lasers

Now let us compare the photochemically relevant properties of three often-used lamps and three typical lasers, namely an excimer laser, a dye laser, and a CO_2 laser (Fig. 2).

The 60 kW TL-doped mercury lamp is the largest lamp used in industry for a photochemical step in the high-volume production of nylon 6; the 700 W medium-pressure mercury lamp is a type most popular in the organic photochemist's laboratory; the high-pressure short-arc mercury lamp, HBO 200, used with a filter for singling out a spectral line or spectral region and a collimator to create a "parallel" beam is most popular with physical chemists and physicists.

Of the multitude of lasers three are chosen from different classes, which are relevant for photochemistry: a popular commercial KrF laser of 100 W average optical output power, a typical dye laser of 10 W average or continuous optical power, and a 10 kW CO_2 laser, which can be used in multiphoton-infrared photochemistry, where molecules absorb on the aver-

age about 20 photons, which results in the same molecular energy content as by absorption of a photon in the green.

The first line gives the quantum flux of these lamps and lasers, which determines ceteris paribus the yield per unit time in a photochemical reaction. Even in this simplest aspect lasers are at least on par, but often better than lamps. When intensity is considered (2nd line), lasers are seen to be orders of magnitude superior to lamps. The same is true for spectral width (3rd line), where lasers emit only on a single spectral line without any continuum: also for divergence (4th line), since all lasers naturally emit a "parallel" beam, as well as for pulse duration (5th line), where lasers are seen to be able to emit extremely short pulses. Finally, lasers can very simply be made to emit polarized light by inclusion of a Brewster window in the resonator, which in most cases is used anyhow.

Figure 3 compares the spectra of a lamp and some lasers. The upper part of the figure shows the lines of the above-mentioned 700 W mercury lamp, which are all emitted simultaneously. Selecting a single line or line pair with filters results in high losses of usually over 70%. On the other hand, the lines shown for the excimer laser in the lower part of the figure are only emitted one at a time, depending on the gas mixture used in the laser. The dye laser output shown as a

	Lamp			Laser		
	60 kW Hg-Tl at 535 nm	700 W Hg Medium Pressure (Original Hanau TQ 718) at 254 nm	HBO 200 + Collimator + Filter at 336 nm	KrF-Laser (Lambda-Physik EMG 302MSC) at 248.5 nm	Dye Laser 10 W at 590 nm	CO_2-Laser 10 kW at 10.6 μm
Quantum Flux $\left(\dfrac{Einstein}{h}\right)$	211	0.14	$<5 \cdot 10^{-4}$	0.73	0.18	$3.2 \cdot 10^3$ (162)
Intensity $\left(\dfrac{W}{cm^2}\right)$	3.5	0.01	$2.5 \cdot 10^{-3}$	$1 \cdot 10^7$	140	10^4
Spectral Width [nm]	ca. 20 + Lines	ca. 2 + Lines	ca. 2 + Continuum	1	$<10^{-3}$	<0.1
Divergence [°]	360	360	2.5	0.1x0.2	0.1	<0.1
Pulse Duration [s]	CW	CW	$CW - >10^{-3}$	$2 \cdot 10^{-8}$	$CW - <10^{-10}$	<0.1
Polarization	unpolarized			Polarization >100:1 (with Brewster Window)		

Fig. 2. Comparison of some lamps with some lasers

shaded area is also emitting only one single line, which can be tuned over the range indicated. This single line emission of a laser vs. the multiline emission of a lamp is a great advantage of lasers applied to photochemistry.

E-beam-pumped excimer lasers that are capable of pulse energies of >15 kJ have been built in research institutions, and others are in the planning stage with MJ-pulse energies. However, the chemist is mostly interested in commercially available excimer lasers which are all discharge pumped. So Fig. 4 shows what one can expect from state-of-the-art excimer lasers.
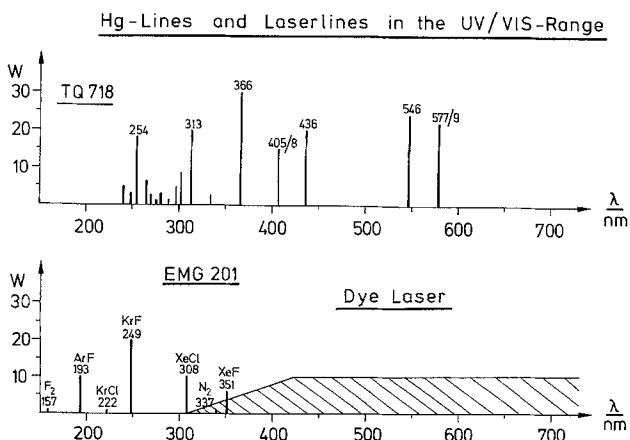
Only the four most efficient excimers are shown. One should notice that, of course, not all specified values apply simultaneously, e.g., there is usually only a certain fraction of the maximum pulse energy available at the maximum repetition rate.

Let us have a look at the cost of one mole of photons from a XeCl laser to demonstrate that excimer lasers are by far cheaper than the high price of such an instrument seems to suggest. In Fig. 5 it is seen that the cost of photons is mainly determined by refurbishment costs at the present [1]. As the lifetime of energy storage capacitors, thyratrons (or other switches),

Hg-Lines and Laserlines in the UV/VIS-Range

Fig. 3. Spectra of a mercury lamp used for preparative photochemistry and some lasers

Excimer Lasers – Standard Discharge Pumped

Excimer	ArF	KrF	XeCl	XeF	
λ	193	248	308	351	nm
Max. avg. power	60	120	100	50	W
Max. pulse energy	0.6	1	2	0.5	J
Max. pulse width	20	25	250	25	ns
Max. rep. rate	400	500	500	250	Hz
Min. Divergence (50% of energy)	<0.2 2	<0.2 2	<0.2 2	<0.2 2	mrad (oscill.-ampl.) mrad

Fig. 4. Characteristics of standard discharge-pumped excimer lasers

COSTS OF UV-LASER LIGHT

① DEPRECIATION OF THE LASER , ANNUAL

② OPERATING COSTS (LASER-GAS , ELECTRICITY , H_2O)

③ REFURBISHMENT COSTS

② ≪ ③   ① ≲ ③ DEPENDING ON USAGE OF CAPACITY

③ TYPICALLY $2 \cdot 10^4$ DM / $2 \cdot 10^8$ LASER SHOTS

                    $\sim 10^{-4}$ DM / LASER SHOT

	XeCl 150mJ	XeCl 1J
COSTS / MOLE (UV) ($6 \cdot 10^{23}$ PHOTONS)	250 DM	37,50 DM
COSTS / kWh (UV)	2400 DM	360 DM

④ CREW COSTS

Fig. 5. Costs of UV laser light [1]

Dye Lasers – Standard Types

	Pulsed (Excimer- or Nd-l. pumped)	C.W. (Ar⁺- or Kr⁺- l. pumped)
λ-range	309 (189) – 1850 nm	≈ 400 – ≈1000 nm
Bandwidth	0.2 cm⁻¹	1 MHz (single freq.)
Peak power	> 20 MW (>1 GW w.ampl.)	> 1 kW (cavity dumped)
Average power	> 10 W (Rh.6G)	> 5 W (Rh.6 G)
Pulse width	< 1 ps – >100 ns	< 1 ps – ∞
Divergence	0.5 mrad	diffraction lim.

Fig. 6. Characteristics of typical dye lasers

windows, etc. will increase with further technical development, the cost of laser photons will also come down. Since a comparable calculation for the above-mentioned 700 W mercury lamp gives a cost of about 40 DM per mole UV [2], one sees that excimer lasers have already now reached break-even point with lamps as far as cost is concerned.

Figure 6 gives an overview of state-of-the-art dye lasers. The main division line here is between dye lasers for pulsed emission and those for continuous emission. As pulsed dye lasers only those pumped by excimer lasers or neodymium lasers are considered, since flashlamp-pumped dye lasers play only a minor rôle in some special applications. Cw-(continuous-wave) dye lasers are always pumped by either Ar⁺- or Kr⁺-ion lasers. (The recently reported first operation of a cw-dye laser with incoherent lamp pumping [3] at present cannot yet be assessed regarding its developmental potential as a photochemically interesting light source.) For special applications in laser isotope separation (v.i.) pulsed dye lasers of average power > 300 W pumped by copper-vapour lasers at a multi-kHz repetition rate have been developed.

Laser Applications in Chemistry

After these introductory remarks on the interesting properties of lasers in contrast to lamps, one might want to know what new and unique applications in chemistry are made possible by lasers. If we want to bring the multitude of new applications into a certain systematic order, we should apply the morphological method of the late Swiss astronomer Zwicky [4] and construct a morphological box, as shown in Fig. 7.

Here all possible combinations of the five properties of lasers, which are important for the chemist, namely intensity, monochromaticity, collimation, pulse length, and polarization, are listed. Coherence, another property of lasers, which is important for many physical applications is not considered in this context. Thus, all applications which make use of only one of these properties of lasers are listed in the first five fields in the box, those applications which make use of two of these properties simultaneously are filed in the next ten fields, and so on. One finds that a complete listing contains 31 classes of laser applications in chemistry, which could hardly be realized with lamps.

Morphological Box for Laser Applications

Types of Laser Applications	Important Properties of Lasers and Combinations Thereof
5	Intensity I Monochromaticity M Collimation C Pulselength T Polarization P
10	I+M I+C I+T I+P M+C M+T M+P C+T C+P T+P
10	I+M+C I+M+T I+M+P I+C+T I+C+P I+T+P M+C+T M+C+P M+T+P C+T+P
5	I+M+C+T I+M+C+P I+M+T+P I+C+T+P M+C+T+P
1	I+M+C+T+P

Fig. 7. Morphological box for laser applications
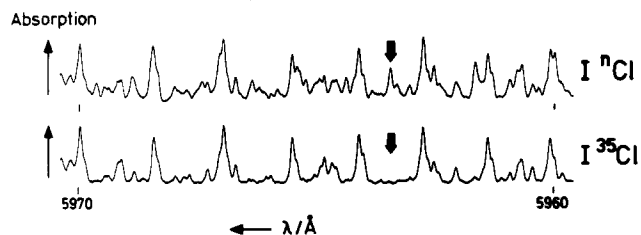
Absorption

Fig. 8. A 1 nm section of the spectrum of ICl; upper spectrum for a sample with natural isotopic composition, lower spectrum for a sample which is highly enriched in ^{37}Cl

Selective Photoaddition

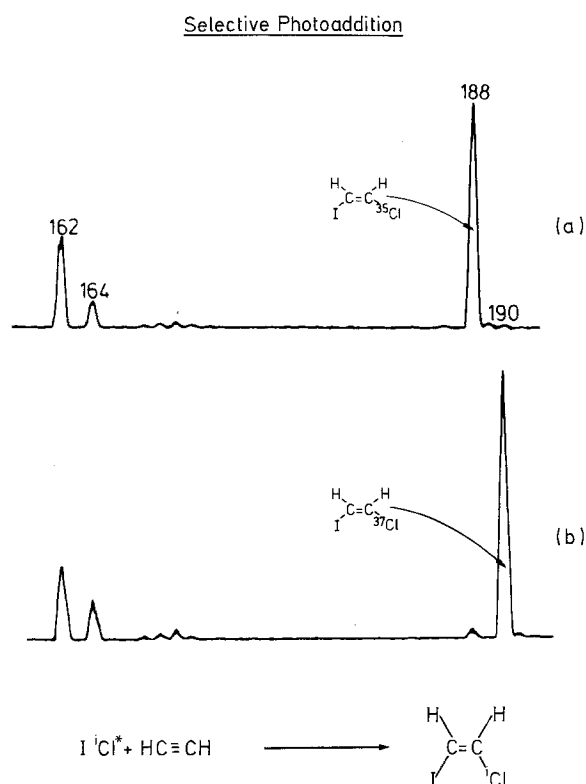$$I \; ^iCl^* + HC \equiv CH \longrightarrow \text{(product)}$$

Fig. 9. Mass spectra of the educts and products of the photoreaction shown on the bottom line, starting with a sample of natural isotopic composition. Upper spectrum: irradiation at a line of $I^{35}Cl$, lower spectrum: irradiation at a line of $I^{37}Cl$

Fig. 10. Schematic demonstration of the AVLIS principle [6]

The three fields into which the following examples belong, are underlined in the morphological box.

As the first example of an application, where only one property of the laser, namely the monochromaticity is used (together, in this case, with the tunability), let us consider the laser-isotope separation of the chlorine isotopes that we did several years ago [5]. In Fig. 8 a part of the spectra of ICl is shown, recorded with a dye laser. The upper spectrum is obtained with a sample of natural isotope abundance of chlorine, the lower one with a ^{35}Cl-enriched sample. The bands in the upper spectrum which are missing in the lower one, are
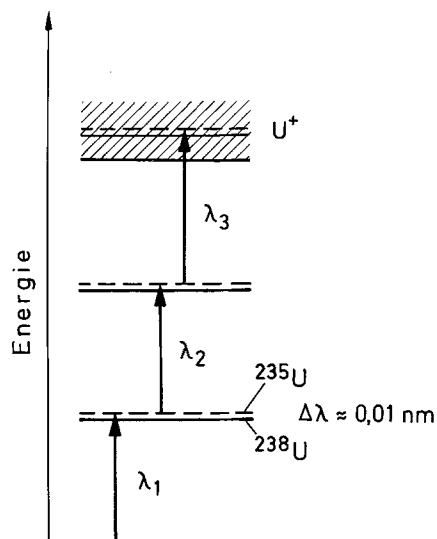
caused by the content of $I^{37}Cl$ in the sample. This is most clearly seen at the wavelength marked by an arrow, where $I^{35}Cl$ does not absorb at all. Irradiating a sample of natural isotope abundance at this wavelength with a properly tuned dye laser, will only excite $I^{37}Cl$ molecules. If we now add a reactant, which only reacts with molecules in the excited state, the reaction will be highly isotopically selective. The result of such a reaction, in this case a photoaddition of acetylene to iodine chloride, is shown in Fig. 9.

Two mass spectra of partly reacted mixtures are shown. The peaks at masses 162 and 164 belong to $I^{35}Cl$ and $I^{37}Cl$, respectively, those at 188 and 190 to the corresponding reaction products. For the upper trace an irradiation wavelength was chosen where only $I^{35}Cl$ absorbs, while for the lower trace the other isotopomer was chosen. As can be seen here, a high enrichment of the desired isotope is obtained. Depending on the reaction conditions we found enrichment factors of over 100 in a single step.

A similar scheme for laser-isotope separation, which is much more important, however, than the one just discussed, is the Atomic Vapour Laser Isotope Separation scheme (AVLIS for short) for the enrichment of uranium. The schematic diagram of Fig. 10 shows only a few energy levels from the huge number actually found in uranium vapour. The isotope splitting between ^{235}U and ^{238}U, which is typically 0.01 nm for many transitions, are indicated [6]. Since dye lasers can easily be tuned to the ^{235}U line, selective excitation of this rare isotope is achieved. To enhance the selectivity, a second dye laser at a properly chosen second wavelength transfers the population of the first excited level to a second level, and finally a third dye laser at a third wavelength brings the atoms into the
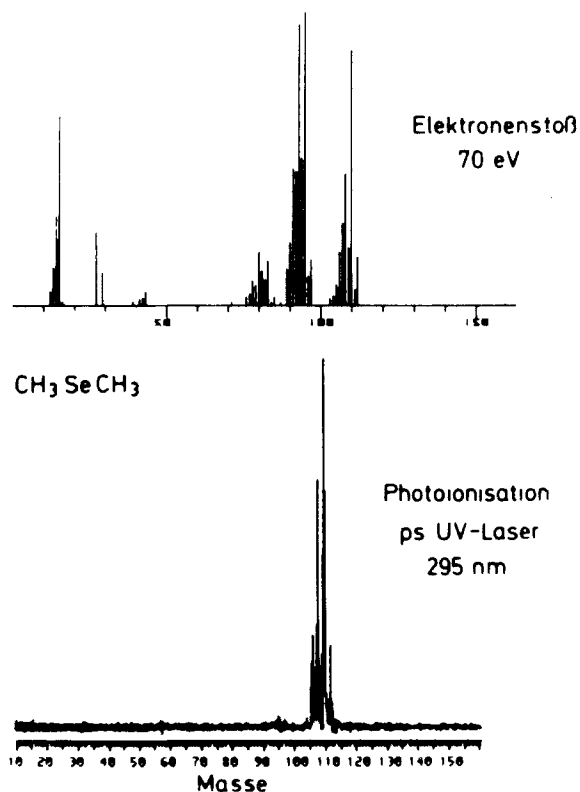
Fig. 11. Mass spectra of CH_3SeCH_3. Upper trace: ionization by electron beam; lower trace: ionization by a ps-UV laser [7]

make an optical absorption path length of several metres absolutely mandatory.

The next example is one from laser mass spectrometry and makes use, in addition to the properties just mentioned, also of the capability of the laser to produce ultrashort pulses. It is taken from [7] and is illustrated in Fig. 11. This example gives the two mass spectra of a metal-organic compound, CH_3SeCH_3, useful for laser-chemical vapour deposition (LCVD). The upper trace is taken in the conventional way, with an electron gun of 70 eV ionizing the molecules. One can notice the usual pattern of the many different fragments created by the electron collisions. A similar pattern is also obtained if one irradiates the molecules by a strongly focussed dye laser beam at a wavelength that is absorbed by the molecules. Multiphoton absorption first ionizes the molecules and further multiphoton absorption by the ions causes dissociation into many smaller fragments during the usual irradiation pulses of 10–20 ns pulse length. There is, however, one advantage of laser ionization over electron beam ionization in the case of mixtures of several molecular species: choosing a wavelength where only the species of interest absorbs, one selectively ionizes only this species without perturbation by the other species present.

A much more important advantage, however, is obtained when using a picosecond dye laser pulse, as shown in the lower trace of Fig. 11. Here only the mother peaks of CH_3SeCH_3 appear (6 peaks of the isotopomers with the known natural abundance ratios). This is so, because the ion created in the ps pulse cannot be dissociated any more since there are no more photons available, in contrast to ns pulse irradiation.

Of principal importance are all multi-photon processes, since the population density of some excited states is intensity dependent. The intensity which is necessary to keep one half of the molecules in some excited state is given in Fig. 12. From triplets in

ionization continuum. The $^{235}U^+$ ions are deflected by an electric field and collected at the electrode. More details of this AVLIS process and the huge demonstration plant under construction by the Lawrence Livermore National Laboratory will be reported in the paper by J. A. Paisner later in this issue.

This is an example where the monochromaticity, the intensity and the collimation of the laser are absolutely essential, since the population of the excited states is intensity dependent and the small absorption cross-sections and small densities of uranium vapour

Intensity $I_{1/2}$, to hold 1/2 of all molecules in the excited state (with lifetime τ):

$$I_{1/2} = \frac{N_L \cdot h \cdot \nu}{1000 \cdot \ln 10 \cdot \varepsilon \cdot \tau} \qquad \text{(optically thin solution)}$$

Numerical example for $\varepsilon = 10^4 \ 1 \cdot M^{-1} \cdot cm^{-1}$, $\lambda = 590$ nm

τ	Realization	$I_{1/2}$	Laser
10 μs	Triplet, degassed solution	880 W/cm^2	cw, weakly focussed
100 ns	Triplet, air saturated solution	88 kW/cm^2	cw, strongly focussed
1 ns	Singlet	8,8 MW/cm^2	Pulsed laser, 10-ns-pulse
1 ps	Vibrational level	8,8 GW/cm^2	Ultrashort laser pulse (10 ps)

Fig. 12. Tabulation of intensities needed to hold half of the irradiated molecules in the excited state with lifetime τ

short pulse:

$$\frac{1}{T_{pulse}} \gg k_f + k_{ic} + k_{isc} + k_{r1} + k_{rn}$$

Advantages of short pulses:

1. Higher ratio of products over by-products

2. Higher quantum yield

3. Higher chemical yield

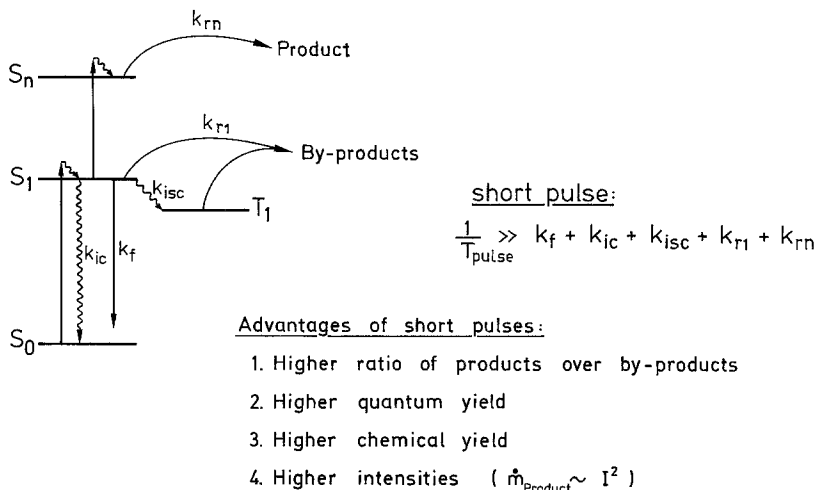4. Higher intensities $(\dot{m}_{Product} \sim I^2)$
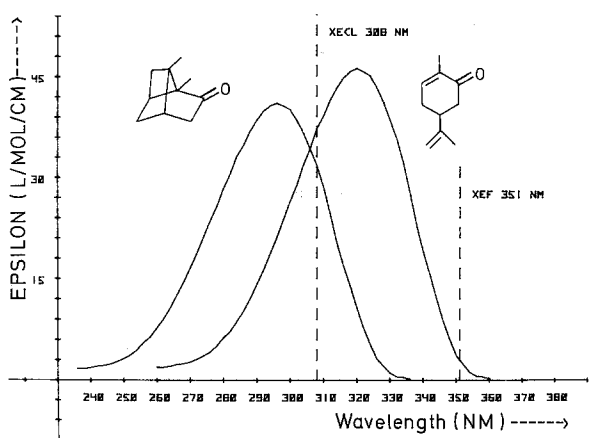
Fig. 13. Advantages of using short pulses in photochemistry

Fig. 14. Spectra of carvone and carvone camphor

degassed room temperature solutions with an intensity $I_{1/2} \approx 1 \text{ kW/cm}^2$ to vibrational level excitation the intensity rises to $I_{1/2} \approx 10 \text{ GW/cm}$ because of the shorter lifetime.

The higher the intensity which one needs to keep one half of the molecules in the excited states, the shorter the laser pulse must be for a given pulse energy. But short pulses actually have some advantages for reactions from higher excited states, as shown in Fig. 13. The relative importance of these advantages depends, of course, on the specific reaction and substances involved.

I would like to give two examples of reactions from higher excited states. The first is the famous example of the isomerization of carvone to carvone camphor [8] and the molecular formulae and the spectra are shown in Fig. 14. The dashed lines indicate the wavelengths of the two excimer lasers which can be used for this photoreaction. If XeF is used, only the educt absorbs and reacts, if, however, XeCl is used, also the product

absorbs, which results in a consecutive reaction leading to an (usually unwanted) ester in alcoholic solution at room temperature.

The result of the reaction executed 1) with a mercury lamp, 2) with a XeCl laser, 3) with a XeF laser is shown in Fig. 15. The fact that the quantum efficiency increases from near zero (in the case of the lamp with low intensity) to 7% at high laser intensity is a clear indication that this is a two-photon reaction involving higher excited states. The resulting products are practically pure, without any of the brown, tarry byproducts obtained with lamp irradiation [9].

The second example was studied earlier with mercury lamps and found to be a 2-photon process [10], as shown in Fig. 16. While at room temperature in liquid solution no reaction occurs with even the strongest lamp irradiation, in organic glass at 77 K the reaction only occurs when irradiation at both mercury lines, at 313 and 404 nm, is used simultaneously. It was assumed that the short wavelength first populates the lowest triplet state, while the longer wavelength transfers the molecules into a higher lying reactive triplet.

We have irradiated this molecule and two similar ones with a laser at room temperature and found that we could obtain a second product, as seen in Fig. 17. We supposed that the second reaction path was via a higher lying reactive singlet state, since the high-intensity laser can populate the lowest lying singlet state notwithstanding its short lifetime, as discussed above, so that a transition to the higher lying reactive singlet by the absorption of a second laser photon becomes highly probable, proportional to the laser intensity.

We investigated this in more detail [11] with a combination of one excimer laser plus one dye laser and found some interesting results, as shown in Fig. 18. Simultaneous irradiation at 308 and 650 nm led main-
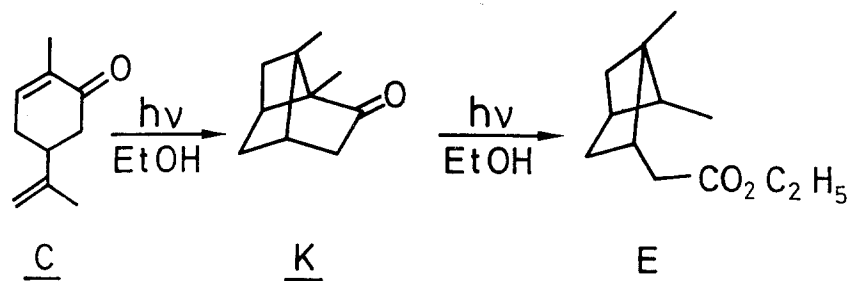
	Quantum Efficiency	Ratio E/K
Hg-Lamp (313 nm)	$<3 \cdot 10^{-3}$	0.54 + byproducts
Laser (XeCl, 308 nm)	increases with I_0 to 7 %	decreases with I_0 to 0.15
Laser (XeF, 351 nm)	increases with I_0 to 7 %	0.07

Fig. 15. Results for the carvone-carvone camphor rearrangement done with lamp and lasers [8]
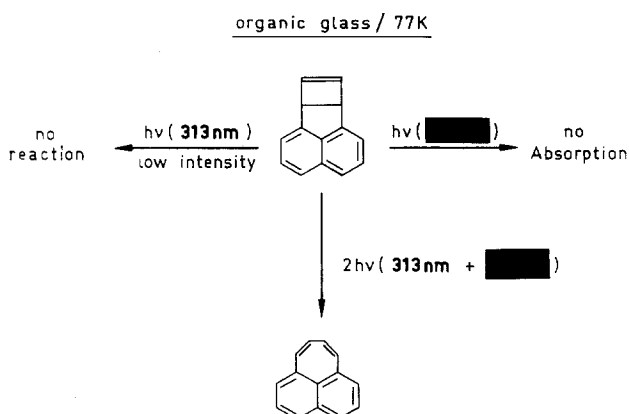
Fig. 16. Two-photon reaction with lamp irradiation in an organic glass at 77 K [10]
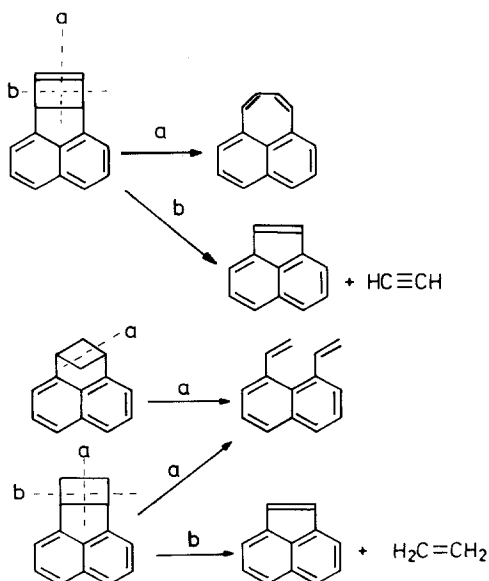

Fig. 17. Possible reaction pathways for some aromatic-substituted cyclobutanes and cyclobutene [11]

ly to compound 3, while at 308 nm plus a 160 ns delayed pulse at 440 nm led almost exclusively to compound 2, as in the organic glass with lamp irradiation. The ratio 2/3 was always intensity dependent. From these facts it is clear that the first reaction path is via a higher lying reactive singlet S_n, while the second one is via a higher lying reactive triplet T_n.

So far I have only shown photochemical reactions, which we followed with conventional techniques. But if one wants to learn about the mechanism of the reaction, one can often do so by studying the kinetics on a time scale that is adequate for the reaction under study. This usually means ps- or sub-ps pulses, if the primary steps are to be resolved.

Normally this means a very complex experimental set-up with several lasers and a lot of electronic and electrooptic equipment that needs at least one physicist to keep it running. We wanted to develop a much simpler device for pump-probe experiments, so simple, if possible, that any chemist or biologist can switch on the system in the morning and immediately start to work with it, not on it. Although we have already gone a long way in this direction, as will be seen immediately, we probably need one more year to reach this goal and probably another year until it becomes commercially available.

Figure 19 shows a block diagram of our hybrid excimer-laser/dye laser system for the generation of fs pulses in the UV and visible. It consists of an excimer laser with two discharge channels triggered simultaneously (Lambda Physik, EMG 150). One channel is surrounded by a standard laser resonator and its output at 308 nm is used to pump a number of dye cells forming a ps dye laser system and another set of dye cells arranged to form an amplifier chain for ultrashort pulses at 616 nm. The output of the fs dye laser system has a wavelength of about 380 nm and a pulse length of

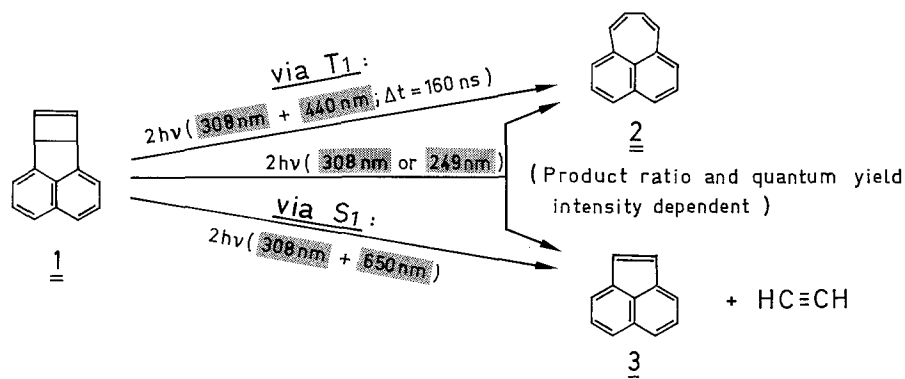## Liquid Solution at Room Temperature

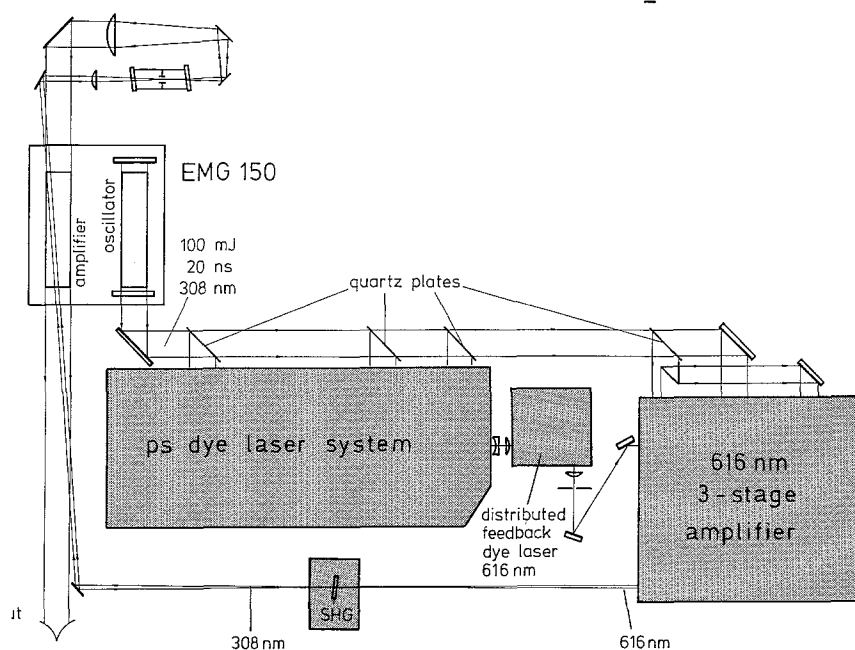Fig. 18. Reaction pathways with laser irradiation [11]

Fig. 19. Arrangement for the generation of ps excimer-laser pulses [12]

8 ps and is used to pump a special dye laser ("distributed feedback dye laser") which creates subpicosecond pulses at 616 nm. These pulses are amplified in the above-mentioned dye laser amplifier chain to high peak powers (several GW) and are then frequency-doubled in a potassium dihydrogen phosphate (KDP) crystal to give a few μJ at 308 nm. These pulses are then sent through the second amplifier channel of the EMG 150, where they are amplified to several mJ, while the pulse width is reduced below 300 fs [12].

One simple experiment, which demonstrates the temporal resolution of this system is shown in Fig. 20. The 308 nm pulse and a fraction of the 616 nm pulse are sent collinearly to a dichroic mirror, where they are separated and sent separately over two delay lines to a dye cell, which contains a bifluorophoric dye (v.i.). The blue absorbing moiety of the dye molecules is

excited by the 308 nm pulse and within a very short time transfers the excitation energy to the longer wavelength absorbing moiety. Since this latter moiety emits fluorescence peaking near 616 nm, the red pulse will experience amplification, when it arrives at the dye cell at or shortly after the time of the 308 nm pump pulse. By changing the delay of the red pulse from shot to shot, one can follow the rise and fall time of the gain. The difference between this time function and the one calculated for the case of direct excitation is the time needed for the energy transfer from the absorbing to the emitting dye moiety [13].

The result of the intramolecular energy-transfer measurements can be seen in Fig. 21. For the molecule shown in the inset the rise of the gain follows the curve connecting the measurement points which coincides with the curve calculated for a transfer time
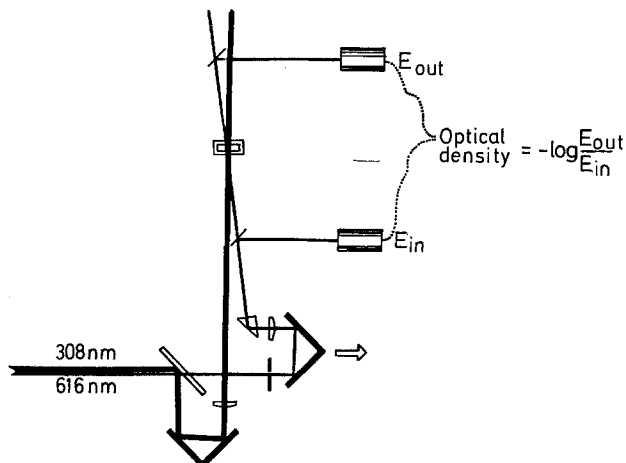
Fig. 20. Experimental pump-probe arrangement [13]

Fig. 21. Measurement of the intramolecular energy transfer in the bichromophoric molecule shown in the inset [13]

$\tau_{FT} = 300$ fs. The other solid line is the calculated curve for $\tau_{FT} = 500$ fs, while the dotted line is calculated for zero transfer time.

This brief description of a laser system for kinetic measurements, which is capable of following even the fastest primary processes in photochemical reactions, is the end of this review in which I endeavoured to give an overview of the state of the art in lasers for chemical applications and I hope to have outlined several perspectives on how to exploit the marvellous properties of lasers for chemical purposes.

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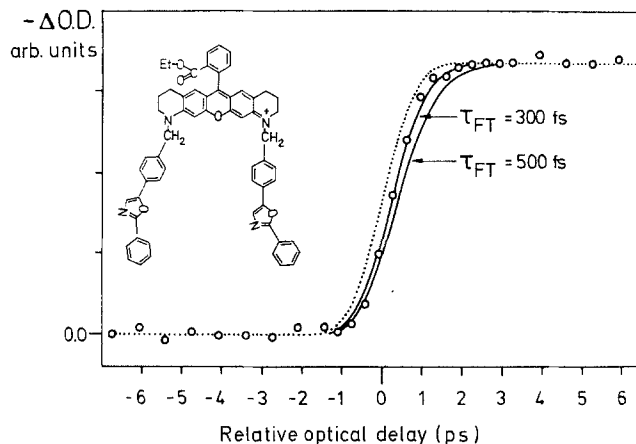1. Lambda Physik, Göttingen: Private communication
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