LASERS IN PHOTOCHEMISTRY

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There is at present no wavelength in the visible and near-UV region between 200 and 800 nm which cannot be obtained from commercially available lasers. Although much more effort is needed to produce coherent radiation at wavelengths down to 100 nm, photochemists have now at their disposal tunable, narrow band and often intense sources over the wavelength range in which virtually all single-photon photochemistry can be initiated. Photochemical initiation with lasers is often accompanied by laser detection of the resultant products, and spectacular advances have been made in these areas of photochemistry over the past 12 years due to the development and application of four types of laser: powerful pulsed UV sources, tunable visible and UV lasers for detection, short (picosecond) pulsed lasers for studies of fast processes, and finally the application of standard IR lasers to a completely new branch of photochemistry, IR multiple-photon excitation.

Frequency mixing in non-linear crystals was the first method of generating high power UV radiation for photolysis, with the fundamental output of ruby and neodymium lasers (694.3 nm and 1064 nm respectively) converted with high efficiency to UV wavelengths of 347, 355 and 266 nm, resulting in high photon fluxes, short pulse lengths (nanosecond rather than the microsecond of conventional flash-lamps) and radiation which is spatially coherent and can thus be directed into the sample at high intensities and with little scattered light. In the mid-1970s the range of fixed wavelength sources was extended as rare gas halide excimer lasers were developed. Commercial availability of high (megawatt) powers at half a dozen wavelengths between 193 nm (ArF) and 351 nm (XeF), and operable down to 157 nm with F_2, has meant that these are now becoming the standard UV sources for laser photolysis. To single out a specific application of these lasers is hard and probably unfair, but a personal bias allows the choice of translational spectroscopy, developed by Wilson and coworkers [1] and subsequently used by a number of other groups [2]. Pulsed photolysis, generally in the UV but in some cases in the visible, is followed by time-of-flight detection of the photofragments, enabling their identities, translational energies and angular distributions with respect to the electric vector of the polarized laser beam to be measured, and thus revealing both the energetics and the dynamics of the dissociative states involved. Fixed frequency

in the UV can be overcome (albeit at lower pulse energies) by a variety of tunable UV sources based on the frequency doubling or four-wave mixing of tunable dye laser radiation, and photolysis as a function of wavelength can be carried out. A notable example is the measurement of the quantum yield of $O(^1D)$ production from the photolysis of O_3 in the 300 - 320 nm fall-off region near the $O(^1D)$ threshold, of importance in determining end products of atmospheric O_3 dissociation [3].

Tunable light (almost exclusively originating from liquid phase dye lasers) has generally made its photochemical impact not as a photolytic source but as a sensitive probe for photofragments or of reaction products following photodissociation, generally by laser-induced fluorescence, sometimes by absorption and increasingly by multiple-photon ionization. The range available from N_2, excimer, argon ion and Nd^{3+}–YAG pumped lasers ranges from 350 nm to the near IR (just above 1 μm), and frequency doubling can extend this range easily to 260 nm and less efficiently to 220 nm. Stimulated Raman scattering takes this to below 200 nm with usable powers for diagnostics, and recently gas phase frequency tripling has produced outputs down to about 100 nm with spectral brightness (photons per unit bandwidth per steradian per second) comparable with or higher than synchrotron sources at these wavelengths. No diatomic molecule is now immune to excitation by tunable laser light; the quantum state resolved detection of the nascent HD product from the $H + D_2$ reaction testifies to the healthy state of the art [4]. The type of information available from the application of tunable lasers to photochemistry is illustrated by recent experiments on HONO and NCNO. In HONO, laser-induced fluorescence detection of the ground state OH radical formed by photolysis at 369 nm shows that its internal energy is low (an approximately Boltzmann rotational distribution close to room temperature is found), that the rotational axis of the fragment is preferentially aligned with the electronic transition moment of the parent molecule, and that the OH velocity distribution (measured from Doppler profiles of the individual transitions) is sharply peaked, with almost 50% of the available energy appearing in OH translation [5]. NCNO has been dissociated throughout its visible absorption region, with internal states of the CN photofragment probed by laser-induced fluorescence [6]. One- and two-photon absorption processes in the parent molecule can be identified, not only from the dependence of product yield on laser intensity, but also because they produce vastly different CN internal distributions. In principle both diatomic products from these parent molecules can be observed by laser-induced fluorescence, and should allow full pictures of the dissociation dynamics to be generated. In passing we note that multiphoton dissociation processes (either with or without intermediate electronic states) are now providing a rich field for study with high powered lasers and will undoubtedly do so in the future. We also note that, despite the advantage of the availability of tunable narrow band laser sources, the photophysical and chemical behaviour of intensively investigated simple polyatomic molecules such as NO_2 and H_2CO still produces surprises and is incompletely understood.

The record for short pulse formation stands at about 30 fs [7], and subpicosecond pulses are now being used to measure photochemical processes directly, *e.g.* in a recent report of the lifetime of the $3R_g$ Rydberg level of benzene, measured as 70 ± 20 fs and thought to decay via rapid internal conversion to the vibrationally excited ground state levels [8]. Condensed phase photochemistry in particular has benefitted highly from the use of picosecond laser sources, both fixed frequency and tunable. A relatively early application of picosecond photochemistry was in studies of the geminate recombination rate of iodine atoms in liquids, known for many years to be a fast process but only measured directly 10 years ago [9]. Areas of current interest include measurements of dephasing and of energy and orientational relaxation of excited levels of solids and liquids, and studies of light conversion systems of biological importance [10].

Photochemistry received a jolt in the early 1970s with the then surprising discovery that gas phase molecules could be dissociated in an isotopically selective fashion with high power IR light from a pulsed CO_2 laser [11]. A great deal of experimental and theoretical effort in this area has now produced at least a qualitative understanding of how an isolated polyatomic molecule can absorb many tens of monochromatic IR photons, and the process has been applied to isotope separation, free-radical formation and chemical synthesis. Although the process is molecule selective, because the absorption of the first few IR photons depends crucially on the match between vibration–rotation energy levels and the IR laser frequency, it is not bond selective, *i.e.* the molecule does not remember the site of the initial excitation because intramolecular energy transfer (picoseconds) takes place faster than radiative up-pumping (nanoseconds). Virtually all studies have used standard multimode transversely excited atmospheric pressure CO_2 lasers, operating between 9 and 11 μm. Although other pulsed IR lasers have been used (HF laser near 3 μm, optical parametric oscillator at 3.3 μm and NH_3 laser at 12.8 μm) these are exceptions and this partially reflects the lack of convenient pulsed sources at wavelengths other than those produced by CO_2 lasers, particularly in the near IR. Undoubtedly development is possible if a pressing need exists. This was demonstrated when dissociation of UF_6 was being considered as a method for uranium isotope separation, either by multiple-photon dissociation or by selective single-photon IR excitation followed by UV photolysis of the vibrationally excited molecule. For this a pulsed IR laser near 16 μm was needed, and in the mid-1970s many schemes appeared in the literature (and others undoubtedly did not), *e.g.* optically pumped fixed frequency transition in CO_2, CF_4 or potassium vapour, tunable four-wave mixing in H_2 and tunable spin flip Raman lasers, testifying to the ingenuity of laser developers if commercial interests are at stake.

In the next decade, as well as seeing welcome improvements in reliability and performance of existing commercial laser systems (*e.g.* the lifetimes of gas fills in excimer systems have increased dramatically over the past 5 years), photochemists will perhaps be using some of the following newly

developing laser sources. Tunable radiation between 100 and 200 nm through frequency mixing in gases will become straightforward, at first with powers suitable for the probing of photoproducts, or the excitation of specific states in polyatomic molecules for which the subsequent behaviour can be sensitively monitored. High powers in the far UV on specific wavelengths will become available, possibly using up-conversion processes in which a chemical reaction or electrical discharge forms a highly excited species which is then pumped by a laser source to a higher level inverted on a 5 - 10 eV transition. More efficient dye laser pumping with new sources (*e.g.* copper vapour laser at 510 nm) will take place. Tunable pulsed IR lasers will be more commonly available, both for single-photon excitation in the mid-IR by fundamental or low overtone pumping and in multiple-photon excitation studies. Narrow bandwidths will hopefully become easier to generate in the IR at photochemically useful powers. Finally, perhaps the free-electron laser will really work and provide a fully tunable output over the whole wavelength range of photochemical interest.

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