

TECHNIQUES IN PHOTOCHEMISTRY

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1. Introduction

Photochemistry has been, and is likely to remain, a subject which has benefitted from developments and applications of instrumentation. In recent times there has been a swing away from conventional photochemistry in favour of spectroscopy and laser photochemistry. The development of the laser, without doubt the most applicable excitation source, has enabled remarkable advances in many areas of spectroscopy. For example, in high resolution spectroscopy, IR diode lasers now offer spectral resolution of 10^{-4} cm^{-1} ; fast pulsed techniques employ tunable picosecond dye lasers, with laser amplifiers, for both transient absorption and emission measurements, and selective photochemistry enables high power tunable lasers to be employed effectively for isotope separation and preparative photochemistry.

2. Laser sources

Important advances in laser research and development have been accompanied by the relatively rapid introduction of suitable laser sources through commercial outlets. For example, the newly commercialized alexandrite laser can be tuned between 700 and 815 nm, with 20 ns Q-switched pulses of about 0.6 J. This laser has a similar efficiency to YAG but, unlike most solid state materials, it becomes more efficient at higher temperatures, reducing the need for special cooling. Tervalent rare earth ions in solid hosts (such as lanthanum, yttrium and lutetium) have the potential of being pumped by an excimer laser and this could lead to the development of lasers tunable from 156 to 322 nm.

The increasingly important excimer lasers have principal emission wavelengths (at 193, 249, 308 and 351 nm) which are obtained by changing the rare gas-halide gas filling. The high energy output at 249 nm is suitable for pumping many fluorescent dyes, including some which emit in the UV. Excimer lasers can generate both Stokes and anti-Stokes wavelengths with high Raman scattering in gases such as hydrogen with high efficiency giving coverage of the region 190 - 360 nm, the range 320 - 360 nm also being covered continuously by the KrF pumped *p*-terphenyl dye laser.

Frequency up-conversion using non-linear interactions has proved to be an important source of coherent radiation in the vacuum UV region. Examples of this technique have included seventh harmonic generation in helium to produce 38 nm radiation from laser pulses at 266 nm, four-wave mixing from dye lasers in producing coherent radiation in the 130 - 152 nm range and fifth harmonic conversion of XeCl laser radiation in argon and krypton to generate radiation at 61.6 nm. There would appear to be no difficulty in obtaining high power laser radiation at almost any wavelength in the UV and visible region. At the other end of the laser wavelength scale, far-IR lasers, which are useful for laser magnetic resonance experiments, have been reported out as far as 1.8 mm by optically pumping methanol, HCN etc. High efficiency tunable frequency shifting in pulsed IR lasers has many applications in pulsed and preparative photochemistry and four-wave mixing of carbon dioxide laser beams in germanium, for example, has been used to provide thousands of high power lines of discrete frequencies in the 8 - 13 μm region at a high conversion efficiency. Various devices can generate other wavelengths; the range 1 - 24 μm is covered by F centre, diode, spin flip and stimulated electronic Raman lasers, and by optical parametric oscillators although not continuously.

3. Laser spectroscopy

Very narrow bandwidth sources (often tunable dye lasers) are especially suitable for investigations of lifetimes of atomic and molecular states with analogue, photon counting or pulse sampling techniques. Laser-induced fluorescence, in particular, has proved to be an extremely sensitive technique for monitoring gas phase free radicals. Emission spectra are obtained by using a laser line tuned to a particular excitation wavelength and used to give information on the ground electronic state. Fluorescence excitation, however, can reveal information on vibrational and rotational structures.

Primary photoexcitation need not be confined to the vacuum UV or UV regions. IR lasers are being increasingly used as sources for multiphoton excitation, a technique with such promising applications as isotope separation and selective reactions. Although IR laser-induced fluorescence measurements have been mostly used to study collision-induced vibrational energy transfer in small polyatomic molecules, tunable optical parametric oscillators have been used in some experiments to excite specific vibrational modes.

Fluorescence measurements provide the simplest and most direct method of obtaining information on the rates of depopulation of excited electronic singlet states, intermolecular and intramolecular energy transfer and radiationless processes. Time-correlated photon counting is now accepted as being unsurpassed in terms of accuracy, sensitivity and the ability to resolve heterogeneous fluorescence emissions. The time resolution of the technique is about 0.5 ns or less with flash-lamp excitation but considerably greater accuracy and improved time resolution are found with laser sources.

Furthermore, the technique is readily adaptable for the measurement of time-resolved emission spectra or time-dependent fluorescence depolarization spectra.

Laser magnetic resonance has been used with considerable success at far-IR frequencies to study pure rotational spectra of chemically unstable species. IR and far-IR lasers provide fixed frequency sources which lie close to vibration-rotation and rotation transitions of free radicals. A magnetic field is used to bring Zeeman components into resonance with the laser. There is considerable gain in sensitivity with this technique over electron paramagnetic resonance.

Double resonance has rapidly become a powerful technique in high resolution spectroscopy and for studies of collisional relaxation. Until recently, pulsed and continuous studies were confined to the microwave region where frequency tunable sources of sufficient power and stability were available. The development of coherent sources has led to an extension in the optical portion of the spectrum with considerable advantages. Tunable IR lasers, for example, have the theoretical advantage over normal thermal reactions in that excitation of selected vibrational levels can be made without simultaneous excitation of all other degrees of freedom.

The enhancement of absorption when relatively weak and narrow band absorbers are placed inside the cavity of a tunable laser forms the basis of intracavity absorption techniques. These have the distinct advantage of making available 20 - 150 times higher circulating power inside the laser cavity compared with outside and tunability over the entire visible spectrum and beyond. For example, a novel excitation technique for the preparation of $O_2^*(b^1\Sigma_g^+)$ in order to study its reactions with various olefins used a dye laser tuned to the O_2 transition at 760.6775 nm and monitored the photoacoustic signal from an intracavity detector. More conventional intracavity spectroscopy measurements enabled extremely weak transitions (near 630 nm) in O and HCl to be measured and it has been estimated that band systems with oscillator strengths of 10^{-10} could be detected readily.

4. Multiphoton techniques

High power pulsed and continuous lasers enable non-linear interactions of light with matter to be studied in detail. The field of two-photon absorption (TPA) spectroscopy promises to open up a new classification of UV and visibly absorbing materials with obvious analytical and spectroscopic applications. Two-step sequential absorption processes are a natural extension to conventional TPA measurements where simultaneous excitation occurs and are closely related to conventional flash photolysis. For example, two independently tunable high resolution dye lasers, excited simultaneously by a pulsed dye laser, have been used to excite selective rotational band structures in iodine and to probe for absorptions to higher excited states.

In general, the recent availability of spectrally intense and continuously tunable lasers in the UV-visible region has opened up the possibility of time-

resolved detection and studies of high-lying states of simple atomic, molecular and radical species via a multiphoton excited and fluorescence scheme. By exciting a two-photon allowed transition, an upper electronic state in the vacuum UV region can be reached. In many cases the multiphoton excitation and fluorescence approach avoids the use of the more restrictive vacuum UV optics since both the excitation and fluorescence detection can all be done in the UV-visible or near-IR regions.

Multiphoton ionization (MPI) can be regarded as an extension of TPA spectroscopy except that ions rather than photons are detected. The signal-to-noise ratio in MPI is generally higher than that of a comparable laser-induced fluorescence experiment because of the relative efficiency of counting collected ions *versus* the relative inefficiency of collecting only a small fraction of the emitted fluorescence. Furthermore, states whose emission is quenched by internal mechanisms are still detectable. There is also no requirement for an atomic or molecular species to be luminescent. In laser-induced fluorescence, the ultimate sensitivity is set by scattered light levels, whereas in MPI, which is unaffected by scattered light, only the ion background (which can be suppressed) and fluctuations in the laser intensity determine this limit.

Detailed studies concerning product internal state distributions following photodissociation are currently of great interest. By making such measurements and studying energy disposal among fragments, it is possible to gain insight into the dissociative mechanism(s), lifetime and geometry of the dissociative state(s) of the parent molecule. Various techniques have been used to monitor photofragments including photofragment spectroscopy, laser-induced fluorescence, two-photon excitation and MPI.

5. Picosecond techniques

Despite the obvious practical difficulties of picosecond flash photolysis, there have been some ingenious arrangements to overcome detector limitations which have enabled both the kinetics and the spectroscopy of photochemically produced transients to be recorded in times as short as 10^{-10} s. The recording of real-time events using fast photodetectors and oscilloscopes is not feasible because of insufficient response time or low photometric signal-to-noise ratios (the streak camera is a notable exception). In practice, time resolution is achieved more conveniently in picosecond studies by using the finite velocity of light to generate short time delays, techniques used extensively in picosecond probe and light gate techniques.

Until recently, picosecond measurements were made with mode-locked solid state lasers and confined to wavelengths generated by the laser itself (*i.e.* harmonics). Broad band monitoring is now possible using the phenomenon of self-phase modulation to record complete absorption spectra of transient species in a few picoseconds.

Synchronously pumped dye lasers are used in complementary arrangements in which fluorescence techniques (time-correlated single-photon

counting and, to a lesser extent, up-conversion) have been widely applied to studies of subnanosecond events. The energy content of such pulses (a few nanojoules) is too low for some applications where a much higher energy is required. Furthermore it may be necessary to shift the excitation wavelength to regions of the spectrum where lasers do not operate. High peak power laser pulses, non-linear optical processes such as second harmonic generation or stimulated Raman scattering can be used to produce short pulses in new spectral regions.

Although passive mode-locked dye lasers can produce picosecond pulses, the use of a colliding pulse mode-locked scheme has further reduced pulse widths to tens of femtoseconds. Recent reports have described the production of 30 fs pulses which have been applied to study optically induced phase transitions in silicon, molecular rotation of CS_2 and transport in the one-dimensional semiconductor polyacetylene. Transient absorption spectroscopy should be possible following continuum generation with amplified femtosecond pulses.

The last decade in particular has witnessed how developments in fields far removed from chemistry, such as laser physics, computing, digital electronics and electro-optics, have been applied in order to obtain a better understanding of chemical and biological processes induced by light. It is certain that such instrumental applications will continue at a rate limited only by the ingenuity of photochemists.