Applications to Photochemistry

K. Kalyanasundaram and M. Grätzel, Lausanne

(EPFL Institute of Chemical Physics)

With the advent of lasers, there are hardly any areas in chemical physics that have not advanced considerably. Of particular interest is the ability to time-resolve molecular events in photochemistry and it is now possible to study the physical and chemical behaviour of light-induced transient species that last only a few nanoseconds. Laser applications to photochemistry are rather extensive, and we restrict ourselves here to the use of pulsed lasers in flash photolysis where short laser light pulses are used to initiate excited state processes. The events that follow are monitored both spectroscopically and kinetically on very short time scales - from a few picoseconds to several hundred nanoseconds.

The excited state species that are produced upon light (visible or UV) excitation are better understood in terms of the Jablonski diagram (Fig. 1). Consider the possibilities available for a "typical molecule" following absorption of a quantum of light of sufficient energy to place it in an excited vibrational level of a higher singlet excited state \( S_0 \) in the single manifold. The molecule will lose some of the excess energy rapidly in collisions - both by "vibrational relaxation" and "internal conversion" (on time scales \( 10^{-12} - 10^{-11} \) s) until it reaches the \( v = 0 \) level of the lowest singlet excited state \( S_1 \). It may then return to the ground state \( S_0 \) directly via either a radiative ("fluorescence") or a non-radiative process (time scales \( 10^{-9} - 10^{-10} \) s). Alternatively (or concurrently) the molecule in the excited state \( S_1 \) can cross over to some higher vibrational levels of the triplet sublevels (usually \( T_1 \)) by the process "intersystem crossing". From the triplet state it may eventually return to the ground state \( S_0 \) via either a radiative ("phosphorescence") or a non-radiative process (on time scales \( 10^{-6} - 10^{-3} \) s). In the presence of other non-excited molecules (of the same kind or another type: \( *S + Q \leftrightarrow S + Q^* \) (electron-transfer) \( \cdot S + Q \leftrightarrow S^* + Q^- \) (electron-transfer of excitation energy) the deactivation may lead to a transfer of excitation energy to the quencher or transfer of electrons (oxidation or reduction). Verification of the various energy transfer mechanisms (\( S \rightarrow S, S \rightarrow T, T \rightarrow T \), Forster-type, Dexter-type: dipole-induced or resonance-induced) as well as the distinction as to whether or not a given quenching process is an electron or energy-transfer requires direct monitoring of the possible transient species and this is easily done by the flash photolysis technique with pulsed lasers.

Excited State Characterization

Detailed studies can be made of the singlet, triplet excited states (their absorption spectra \( S_1 \rightarrow S_0, T_1 \rightarrow T_0 \) lifetimes and quantum yields of radiative processes such as fluorescence, phosphorescence) and their mutual cross-over processes such as inter-system crossing, internal conversion, vibrational relaxation and radiationless transfer. Laser photolysis has been applied extensively to small inorganic systems and large organic molecules such as condensed aromatic hydrocarbons and organic carbonyl compounds. As a result, it is now possible to construct an energy level diagram of the type shown in Fig. 1 with all the rate parameters known precisely for a wide variety of molecular systems. Fig. 2 presents, for example, the absorption spectrum of the transition metal-complex \( \text{Ru(bpy)}_3^2+ \) in water, recorded at the end of the 20 ns 530 nm Nd-3 laser pulse excitation:

\[ \text{Ru(bpy)}_3^2+ \xrightarrow{hv} \text{Ru(bpy)}_3^{2+} \]

The excited state which gives rise to this absorption spectrum has an emission lifetime of 650 ns in aqueous solution at room temperature. The phosphorescence emission can also be followed kinetically.

Excited State Interactions

In addition to the normal decay processes above, in the presence of other reactants (quenchers) the excited state species (singlets-triplets) can undergo a variety of reversible/irreversible chemical reactions. These can be broadly classified into three main categories.

(a) Quenching or more rapid deactivation of the excited state by interaction with ground state molecules of the same or another type:

\[ \cdot S + Q \rightarrow \cdot S + Q^- \] (energy-transfer) \[ \cdot S + Q \rightarrow \cdot S^- + Q^- \] (electron-transfer of excitation energy)

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Fig. 3 presents typical oscilloscope traces showing kinetic behaviour of the transients during the following photoredox reaction, (initiated with a 20 ns 530 nm Nd laser pulse):

\[ 3\text{Ru(bpy)}_3^2+ + \text{MV}^2+ \xrightarrow{k_4} \text{Ru(bpy)}_3^{2+} + 3\text{MV}^+ \]

Technique of Flash Photolysis

In a typical flash photolysis set-up, a Q-switched laser, which can be a Nd or ruby or even a dye laser, delivers pulses of 5-20 ns and the events that follow the excitation of the sample are monitored by fast absorption kinetic spectroscopy. Here, the analysing beam from a pulsed Xe lamp is focused onto the sample (perpendicular or collinear to the direction of the laser beam) and, after transmission, is monochromatised and then refocused onto a photomultiplier of a few ns response time. Picosecond spectroscopy, the exciting pulses are used as analysing source by converting a part of the incident beam into a continuum, and passing through an optical delay line. Picosecond trains of pulses from a mode-locked dye laser have also been used with time-correlated single photon counting, for time-resolved fluorescence studies.

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Fig. 1 - Energy level diagram showing inter-relationship of various excited states that are formed upon light excitation of a molecule ("Jablonski Diagram").
Isotope Separation

F.S. Becker and K.L. Kompa, Garching
(Max-Planck Institute for Quantum Optics)

Isotope separation is today one of the most actively pursued areas of laser application. The advent of laser excitation sources at many different wavelengths, with high spectral purity and high energy density has revolutionized concepts of photophysical or photochemical isotope separation, which were, in principle, known long ago but could never be put into practice because of the limited source quality of conventional lamps. Many isotopes have been separated successfully to date in laboratory experiments, but much still remains to be done to extend the results to an industrial scale, where the process is optimized for economy.

There are many problems in science which can be tackled if high quality pure isotopes are available, especially for the enrichment of uranium in the isotope 236U is of considerable importance to nuclear technology.

The most important differences between the isotopic constituents of an atomic or molecular mixture are spectral, which can be tackled if high quality pure isotopes are available. In any isotope separation scheme the following requirements must be satisfied:

1) The absorption spectrum must exhibit an isotope shift, sufficiently large in relation to the spectral line or band contours.
2) A laser light source or combination of sources must be available with appropriate wavelengths, monochromaticity and intensity.
3) The selective excitation of the desired species must lead to an irreversible separation process via a physical/chemical follow-up procedure.
4) The selectivity of the entire sequence of excitation and separation steps must not significantly be impaired by inter-isotope energy transfer and scrambling.

Spectral isotope shifts are found in both atomic and molecular spectra. We shall concentrate in the following on the latter and, in particular, on the use of infrared laser induced multiphoton absorption to dissociate the desired isotopic compound.

Basic Spectroscopic Prerequisites

In 1976 it was discovered by several groups that the incidence of high power infrared laser radiation on molecular gases,